Catalytic Steam Reforming of Bio-Oil to Hydrogen Rich Gas

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Catalytic Steam Reforming of Bio-Oil to Hydrogen Rich Gas

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This thesis has been submitted as partial fulfillment of the requirements to obtain a Ph.D.-degree at the Technical University of Denmark. This Ph.D.-project is entitled "Catalytic Steam Reforming of Bio-Oil to Hydrogen Rich Gas" and the work has been carried out at the Combustion and Harmful Emissions Control (CHEC) research group at the Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU). Besides the experimental work presented in this thesis, the tasks of the project have been; supervision of students projects, work as a teaching assistant in the course "Introduction to Chemical and Biochemical Engineering", and participation in courses corresponding to 30 ECTS-points. An external research stay of 3 months at the School of Chemical, Biological, and Material Engineering at the University of Oklahoma (OU) has been included as well. The work was conducted in the biofuel research group under the supervision of Professor Daniel E. Resasco.

The Ph.D.-project is a part of Catalysis for Sustainable Energy (CASE) initiative and the European Graduate School for Sustainable Energy (EGSSE). CASE is a collaboration between several departments from DTU and industrial partners, while EGGSE is a collaboration between DTU, the Technical University of München (TUM), and Eindhoven University of Technology (TUE). Both of these organizations aim to increase collaboration between different departments at DTU and other technical universities in Europe.

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Rasmus Trane-Restrup, 13. September 2013
Bio-oil is a liquid produced by pyrolysis of biomass and its main advantage compared with biomass is an up to ten times higher energy density. This entails lower transportation costs associated with the utilization of biomass for production of energy and fuels. Nevertheless, the bio-oil has a low heating value and high content of oxygen, which makes it unsuited for direct utilization in engines. One prospective technology for upgrading of bio-oil is steam reforming (SR), which can be used to produce H\textsubscript{2} for upgrading of bio-oil through hydrodeoxygenation or synthesis gas for processes like the Fischer-Tropsch synthesis. In the SR of bio-oil or bio-oil model compounds high degrees of conversion and high yields of H\textsubscript{2} can be achieved, but stability with time-on-stream is rarely achieved. The deactivation is mainly due to carbon deposition and is one of the major hurdles in the SR of bio-oil.

There are two main pathways to minimize carbon deposition in steam reforming; either through optimization of catalyst formulation or through changes to the process parameters, like changes in temperature, steam to carbon ratio (S/C), or adding O\textsubscript{2} or H\textsubscript{2} to the feed. In this thesis both pathways have been explored.

Steam reforming of ethanol has been conducted over Ni-based catalysts in attempts to minimized carbon deposition through changes to the catalyst formulation. Furthermore the effect of temperature was investigated for Ni on MgAl\textsubscript{2}O\textsubscript{4}, CeZrO\textsubscript{4}/MgAl\textsubscript{2}O\textsubscript{4}, CeO\textsubscript{2}, and Ce\textsubscript{0.6}Zr\textsubscript{0.4}O\textsubscript{2} at a S/C-ratio of 6. The support material affected the conversion and carbon deposition while the product distributions as function of temperature were similar. The yield of CO and H\textsubscript{2} increased with increasing temperature while the yield of CO\textsubscript{2}, methane, and ethene decreased with temperature. The most abundant by-products were methane and ethene but acetic acid, acetone, and acetaldelyde were also produced in minor amounts. Ni/Ce\textsubscript{0.6}Zr\textsubscript{0.4}O\textsubscript{2} showed the highest activity, but also suffered from severe carbon deposition as carbon whiskers. Ni/CeZrO\textsubscript{4}/MgAl\textsubscript{2}O\textsubscript{4} had the second highest activity and showed lower carbon deposition compared with both Ni/Ce\textsubscript{0.6}Zr\textsubscript{0.4}O\textsubscript{2} and Ni/MgAl\textsubscript{2}O\textsubscript{4}. The carbon deposition over Ni/Ce\textsubscript{0.6}Zr\textsubscript{0.4}O\textsubscript{2} and Ni/MgAl\textsubscript{2}O\textsubscript{4} had a maximum at 500 °C, which coincided with the maximum in the ethene formation. This, along with estimations of the affinity for carbon deposition from the gas composition, showed that ethene is the main precursor to carbon deposition.

CeO\textsubscript{2}, ZrO\textsubscript{2}, K, or mixtures hereof were added to Ni/MgAl\textsubscript{2}O\textsubscript{4}, and all of them lowered the carbon deposition and increased the activity. The addition of CeO\textsubscript{2} gave the lowest carbon deposition probably due to an increased oxidation of carbon by CeO\textsubscript{2}. Stability tests over 24 h at 600 °C over Ni-K/MgAl\textsubscript{2}O\textsubscript{4} and Ni/K-CeO\textsubscript{2}/MgAl\textsubscript{2}O\textsubscript{4} both showed deactivation with time-on-stream mainly due to carbon deposition as carbon whiskers.

Sulfur was added as K\textsubscript{2}SO\textsubscript{4} to Ni-CeO\textsubscript{2}/MgAl\textsubscript{2}O\textsubscript{4} to selectively poison Ni-sites and inhibit carbon deposition. The sulfur poisoning induced a decrease in the carbon deposition and an increase in the yield of hydrocarbons indicating a lowering of the hydrocarbon SR activity. The optimal loading of sulfur was 0.03 wt\% S added as K\textsubscript{2}SO\textsubscript{4} and the lowest rate of carbon deposition of 1.2 mg C g\textsubscript{Cat}·h\textsuperscript{-1} was achieved with this catalyst.
The results from changes in the catalyst composition indicated that carbon free operation was not possible and so operational measures were investigated next. The effect of the S/C-ratio and addition of H\textsubscript{2} or O\textsubscript{2} to the feed on the product yields and carbon deposition in the SR of ethanol over Ni/MgAl\textsubscript{2}O\textsubscript{4}, Ni/\text{Ce}_{0.6}\text{Zr}_{0.4}O\textsubscript{2}, and Ni/CeO\textsubscript{2} at 600 °C was investigated. Increasing the S/C-ratio from 1.6 to 8.2 over Ni/MgAl\textsubscript{2}O\textsubscript{4} increased ethanol conversion from 53 % to 80 % as well as the yield of H\textsubscript{2}, while the carbon deposition and yield of hydrocarbons decreased. Oxygen addition increased conversion, decreased the yield of hydrocarbons and H\textsubscript{2} as well as the carbon deposition. Carbon deposition was almost eliminated at an O/C-ratio of approximately 0.8. The penalty of adding O\textsubscript{2} was a decrease in the yield of H\textsubscript{2} corresponding to loss of 1 mole of H\textsubscript{2} pr. mole of ethanol converted compared with SR without O\textsubscript{2}. H\textsubscript{2}-addition had little influence on the catalyst performance, only a slight deactivation was observed at high H\textsubscript{2}/ethanol-ratios probably due to a high surface coverage of H-species inhibiting the reforming reactions.

A 90 h test at O/C=1.1, S/C=6, and 600 °C over Ni/MgAl\textsubscript{2}O\textsubscript{4} showed stable behavior and a total carbon deposition of less than 0.1 mg (rate of carbon deposition was 7 \( \text{µg C g}^{-1} \text{Cat} \cdot h^{-1} \)). The results indicate that stable operation in the SR of ethanol is only possible under oxidative conditions.

Bio-oil contains a wide range of oxygenated species ranging from acetic acid to guaiacol and it would be of interest to obtain knowledge about their behavior in reforming. Therefore SR of ethanol, acetic acid, acetone, acetal, 1-propanol, and propional was investigated over Ni/MgAl\textsubscript{2}O\textsubscript{4} at temperatures between 400 and 700 °C and at S/C=6. The yield of H\textsubscript{2} and conversion increased with increasing temperature while the yield of by-products decreased with temperature in the SR of the investigated compounds. The yield of H\textsubscript{2} approached the thermodynamic limit at the highest temperatures investigated, where full conversion was achieved at the applied space velocity. No significant differences in conversion as function of temperature between the different model compounds were observed. However, the product distribution depended on the model compound and C\textsubscript{3}-oxygenates produced a larger fraction of by-products compared to C\textsubscript{2}-oxygenates. Temperatures of 600 °C or above were generally needed to minimize the fraction of by-products and obtain a syngas containing mainly CO, CO\textsubscript{2}, H\textsubscript{2}, and H\textsubscript{2}O with only traces of CH\textsubscript{4}.

Significant deactivation of the catalyst was observed for all of the compounds and was mainly due to carbon deposition. The carbon formation was highest for alcohols due to a higher formation of olefins, which are potent coke precursors.

Steam reforming of 2-methylfuran, furfural, and guaiacol as function of temperature and time was investigated over one of the most promising catalysts, Ni/CeO\textsubscript{2}-K/MgAl\textsubscript{2}O\textsubscript{4}. The major products were, at all temperatures, CO, CO\textsubscript{2}, and H\textsubscript{2}, but formation of by-products, such as small hydrocarbons or fragments of the parent model compounds, was observed and the yield of these compounds decreased with increasing temperature. A large formation of aromatic compounds, benzenediols and phenol, was observed in the SR of guaiacol even at 600 °C and temperatures as high as 780 °C were needed to eliminate the formation of these compounds. Temperatures of 600 °C were needed to eliminate the formation of by-products in the SR of 2-methylfuran and furfural.

Carbon deposition was apparent in the SR of the model compounds at 600 °C and S/C-ratio of 5 over Ni/CeO\textsubscript{2}-K/MgAl\textsubscript{2}O\textsubscript{4} and was most pronounced for guaiacol followed by furfural and 2-methylfuran. The carbon deposition could almost be eliminated by adding oxygen to feed at the expense of a lower yield of H\textsubscript{2}. However, stable operation over 24 h could not be achieved in the SR of guaiacol and furfural even under oxidative SR conditions.
DANSK RESUMÉ


I denne afhandling er forskellige redskaber til at mindske kuldannelse blevet undersøgt i dampreforming af ethanol over Ni-baserede katalysatorer. Bærermaterialet er blevet varieret mellem MgAl₂O₄, CeZrO₄/MgAl₂O₄, CeO₂ og Ce₀.₆Zr₀.₄O₂, hvilket ikke ændrede produktfordelingen væsentligt, mens både aktivitet og dannelse af kul varierede. Omdannelsen samt udbyttet af H₂ og CO steg med stigende temperaturer, mens udbyttet af CO₂, methan og ethen faldt i damp reformationen af ethanol ved et S/C-forhold på 6. CeZrO₄/MgAl₂O₄, som bærer, viste lovlige resultater, da den både havde en høj og stabilt aktivitet, samt en lav kuldannelse. Ce₀.₆Zr₀.₄O₂ havde den højeste aktivitet, men også den højeste kuldannelse, som whiskers. Kuldannelsen som funktion af temperaturen over Ni/MgAl₂O₄ og Ni/Ce₀.₆Zr₀.₄O₂ havde en maksimum ved 500 °C, hvor den maximale produktion af ethen også blev observeret. Dette viser, sammen med termodynamiske estimeringer af kuldannelsespotentialet af produktgassen, at ethen er den væsentligste kilde til kuldannelse i dampreformingen af ethanol over disse katalysatorer.

K, CeO₂ og ZrO₂ samt blandinger heraf blev tilsat Ni/MgAl₂O₄ og de bidrog alle til at mindske kuldannelsen og øge aktiviteten. Ni/CeO₂-K/MgAl₂O₄ viste sig, at være en interessant katalysator, da den både havde lav kuldannelse og høj aktivitet ved 600 °C. Førsøg over længere tid viste dog kuldannelse som whiskers.

Svovl tilsætning i små mængder (0.03-0.12 wt% S) gennem imprægnering med K₂SO₄ til Ni-CeO₂/MgAl₂O₄ viste, at man kunne mindske kuldannelsen yderligere, men den totale aktivitet blev også svagt sænket. Den laveste kuldannelseshastighed blev opnået over Ni-CeO₂/MgAl₂O₄ tilsat 0.03 wt% S som K₂SO₄ og den var 1.2 mg C g⁻¹ Cat h⁻¹.

Endringer i katalysatorformuleringen var ikke nok til at eliminere kuldannelse i dampreforming af ethanol og derfor blev ændringerne af procesparametre også undersøgt. Tilsætning af mere damp eller ilt til fødestrommen kunne mindske kuldannelse samt øge aktiviteten i dampreformationen af ethanol. Kuldannelsen blev sænket mest ved tilsætning af ilt, hvilket dog skete på bekostning af udbyttet af H₂, som faldt fra 75 % ved O/C=0 til 50 % ved O/C=0.8. Ilttilsætning med et O/C-forhold på 0.8 eller derover kunne stort set eliminere kuldannelse, og et forøg over 90 h ved O/C=1.1 og 600 °C over Ni/MgAl₂O₄ viste en total kuldannelse på mindre end 0.1 mg C (gennemsnitlig kuldaflejringshastighed var 7 mg C g⁻¹ Cat h⁻¹).
Brinttilsætningen til føden blev også undersøgt i dampreformering af ethanol, men dette gav en svag deaktivering ved høje forhold mellem H<sub>2</sub> og ethanol, sandsynligvis på grund af en høj dækningsrelation på katalysatoren, hvilket inhiberede reformeringsreaktionerne.


Deaktivering grundet kul dannelse blev observeret for alle komponenter og var ca. 30 % højere i dampreformeringen af ethanol, 1-propanol, og eddikesyre, sammenlignet med dampreformering af de resterende komponenter. I dampreformering af alkoholer skyldes dette en højere dannelse af olefiner, som er kilde til kulaflægning.

Dampreformering af cykliske modelkomponenter, som 2-methylfuran, furfural, og guaiacol, blev blev undersøgt som funktion af både temperatur og tid over en de mest løvende katalysatoren, Ni/CeO<sub>2</sub>-K/MgAl<sub>2</sub>O<sub>4</sub>. Producenter i disse reaktioner var hovedsagligt CO, CO<sub>2</sub>, og H<sub>2</sub> ved alle temperaturer, men der blev også observeret mindre kulbrinter samt forskellige fragmenter af modelkomponenterne. Udbyttet af CO<sub>2</sub> og biprodukter faldt med stigende temperaturer, mens omdannelsen, samt udbyttet af H<sub>2</sub> og CO steg. I dampreformering af furfural og 2-methylfuran var udbyttet af biprodukter lavt ved temperaturer omkring 600 °C, mens der krævedes temperaturer omkring 780 °C i dampreformering af guaiacol for at eliminere dannelsen af biprodukter. Biprodukterne var methane, ethanol, 1-propanol og acetone i dampreformeringen af furfural og 2-methylfuran, mens aromatiske forbindelser som phenol og benzenediooler blev observeret i dampreformeringen af guaiacol.

Kuldannelsen i dampreformering af de cykliske forbindelser ved S/C=5 og 600 °C var højere for guaiacol, efterfulgt af furfural og 2-methylfuran, hvilket sammen med det væsentligt højere udbytte af biprodukter viser, at dampreformering af aromatiske forbindelser er vanskelig.

Tilsætning af ilt til føden i dampreformering af de cykliske forbindelser mindske kuldannelsen og udbyttet af H<sub>2</sub>, samtidig med at aktiviteten blev øget. Hvilket O/C-forhold, der kræves for stabil drift over 4 h afhæng af modelkomponenten og var 0.4 i dampreformeringen af 2-methylfuran, mens det var 1.0 eller derover i dampreformeringen af furfural og guaiacol. Stabil dampreformering af furfural og guaiacol ved 600 °C over 24 h kunne dog ikke opnås selv ved tilsætning af ilt.
LIST OF PUBLICATIONS

*International peer-reviewed journals*


- Rasmus Trane-Restrup, Anker Degn Jensen: Steam reforming of bio-oil model compounds, Planned for submission to an international peer reviewed journal, (2013).

*Oral conference contributions*


*Poster conference contributions*

- Rasmus Trane, Søren Dahl, Anker Degn Jensen: Steam reforming of bio-oil model compounds, Presented at: The International Congress of Catalysis, München, Germany, 1st-6th of July 2012.


*Non-scientific publications*

- Peter Mølgård Mortensen, Rasmus Trane: Bulk Chemical Production with Bio-oil, Published online at http://www.case.dtu.dk, spring 2011.
• Peter Molgård Mortensen, Rasmus Trane: Affald fra marken bliver til CO₂-neutrale brændstoffer, Published online at http://www.case.dtu.dk, spring 2011.
INTRODUCTION

In present years the world is experiencing rising oil prices, partly due to a lack of oil. Furthermore, the climate debate has led to an increasing request for fuels for transportation with a lower carbon footprint. Thus, there is a need for alternative liquid fuels based on biomass, which is considered a CO$_2$ neutral fuel.

One interesting option is to pyrolyse the biomass to obtain char and pyrolysis oil, which could in principle be used as a fuel. This is particularly attractive for the use of biomass resources from remote areas, where the pyrolysis can be performed locally to obtain the oil with an energy density which is about 10 times higher than that of the loosely packed biomass (e.g. a straw bale). The resulting biomass char could be spread on the fields to improve soil properties and return most of the nutrients.

However, pyrolysis oil is a complex mixture containing hundreds of organic oxygen containing compounds, such as acids, alcohols, aldehydes, furans, phenols and esters, in which the oxygen content can be as high as 50%. These oxygenates leads to several problematic properties of the oil including high viscosity, thermal and chemical instability, corrosiveness, poor heating value, and immiscibility with hydrocarbon fuels. Therefore pyrolysis oils must be upgraded before use, by processes where the content of oxygen is decreased, i.e. involving de-oxygenation, hydro-deoxygenation and decarboxylation. This is most efficiently carried out by the action of suitable catalysts in the gas phase in the presence of hydrogen. The required hydrogen could be obtained by steam reforming a part of the oil. Hydrogen is also of interest in fuel cell applications and in many chemical processes such as synthesis of ammonia, synthetic natural gas etc. However, the mechanism and kinetics of steam reforming of oxygenates such as those present in pyrolysis oil is not yet well understood and so there is a lack of efficient and stable catalysts for this purpose.

The purpose of this Ph.D. project is to investigate the gas phase steam reforming (SR) of biomass pyrolysis oil. The study will be devoted to well-defined model compounds from the different classes of compounds present in pyrolysis oils, as mentioned above. The project includes a literature study of the current state-of-art for steam reforming of pyrolysis oil oxygenates. Furthermore an experimental setup as well as the necessary analytical techniques to analyze the product mixtures was established. The heterogeneous catalysts suitable for the steam reforming of selected oxygenates was identified based on literature studies. Characterization of the catalysts by different methods (BET, TEM, XRD etc.) was also conducted.

This Ph.D. thesis consists of seven chapters, which describes the experimental work conducted during the course of this project along with a review of literature on the steam reforming of hydrocarbons and oxygen containing hydrocarbons. The chapters are briefly described below.

- Chapter 1 reviews the SR of oxygen containing hydrocarbons with respect to reaction mechanisms, suitable catalysts, and their stability. Furthermore alternative strategies for SR of oxygen containing compounds like fluidized bed, oxidative SR, or aqueous
phase SR is discussed. This chapter has been published as a review of steam reforming of bio-oil in International Journal of Hydrogen Energy.

• Chapter 2 describes the experimental setups used at DTU and OU, how the catalysts were prepared, and how the characterization of the catalysts was conducted.

• Chapter 3 discusses the experimental work regarding the SR of ethanol and how changes to the catalyst formulation affected activity, carbon deposition, and product distribution. The main results from this chapter have been accepted for publication in International Journal of Hydrogen Energy.

• Chapter 4 contains the results from the SR of ethanol on the effect of the level of H₂, O₂, and H₂O in the feed on carbon deposition, conversion, and product distribution. The main results from this chapter have been submitted to Applied Catalysis A: General.

• Chapter 5 shows results from the SR of light water soluble oxygenates. The product distributions as function of temperature are used to elucidate steps in the reaction paths. Furthermore reactivity and deactivation of the different model compounds are compared. The results presented in this chapter have been submitted to Catalysis Science and Technology.

• Chapter 6 contains results from the SR of three cyclic model compounds of bio-oil, 2-methyl furan, furfural, and guaiacol, where the product distribution as function of temperature as well as function of time was investigated. Furthermore oxygen addition was investigated. The main results from this chapter will be submitted to an international peer reviewed journal.

• Chapter 7 summarizes the main findings from the literature and the experimental work. Furthermore, the prospect for SR of oxygen containing compounds as a source of hydrogen or synthesis gas in the future is discussed.

Supporting information used in the different chapters are found in appendix A and B.
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NOMENCLATURE

List of abbreviations

- CSTR : Continuous stirred tank reactor
- CT : Cold trap
- DS : Desulfurization
- FID : Flame ionization detector
- GC : Gas chromatograph
- GHSV : Gas hourly space velocity
- HDO : Hydrodeoxygenation
- ICP-OES : Inductively coupled plasma optimal emission spectroscopy
- LHSV : Liquid hourly space velocity
- LHV : Lower heating value
- MAR : Mass action ratio
- MFC : Mass flow controller
- MS : Mass spectrometer
- OSR : Oxidative steam reforming
- P : Pump
- PFR : Plug flow reactor
- POX : Partial oxidation
- SP : Syringe pump
- SR : Steam reforming
- SV : Space velocity
- TCD : Thermal conductivity detector
- TEM : Transmission electron microscopy
- TPO : Temperature programmed oxidation
- TPR : Temperature programmed reduction
• WGS : Water gas shift
• WHSV : Weight hourly space velocity
• XRD : X-ray diffraction

List of symbols
• $A$ : Area
• $C_i$ : Concentration
• $D_i$ : Diffusion coefficient
• $D_a$ : Effective dispersion coefficient
• $d_p$ : Particle diameter
• $F_{i,m}$ : Molar flow of $i$
• $F_v$ : Volumetric flow rate
• $h$ : Heat transfer coefficient
• $H$ : Height
• $k$ : Rate constant
• $k_c$ : Mass transfer coefficient
• $k_t$ : Thermal conductivity
• $L_b$ : Length of bed
• $M$ : Molar mass
• $m_i$ : Mass of $i$
• $n$ : Reaction order
• $n_{C,i}$ : Number of carbon atoms in $i$
• $n_i$ : Molar flow of $i$
• $Nu$ : Nusselt's number
• $p$ : Pressure
• $Pe$ : Peclet number
• $Pr$ : Prandtl's number
• $R$ : Gas constant
• $r_i$ : Reaction rate
• $Re$ : Reynolds number
• $Sc$ : Schmidts number
• $Sh$ : Sherwoods number
• $T$ : Temperature
• $U$ : Gas velocity
• $V_i$ : Volume of $i$
• $X$ : Conversion

List of greek symbols

• $\beta$ : Full width at half maximum
• $\epsilon$ : Characteristic energy
• $\eta$ : Viscosity
• $\theta$ : Bragg angle
• $\lambda$ : X-ray wavelength
• $\nu$ : Kinematic viscosity
• $\rho_b$ : Density of bed
• $\rho_c$ : Density of the catalyst
• $\sigma$ : Hard-sphere diameter
• $\sigma_c$ : Constriction factor
• $\tau$ : Tortuosity
• $\phi_p$ : Porosity
1. LITERATURE REVIEW

The purpose of this review is to present the state-of-the-art of SR of bio-oil for synthesis gas production. The main focus will be on SR of whole bio-oil and model compounds such as phenols, but results from the SR of ethanol and acetic acid will also be presented. Reaction mechanisms, kinetics, applied catalysts, and reforming concepts will be presented and suggestions to further investigations will be given.

1.1 Introduction

In the recent decades it has become evident that fossil fuels are a limited resource and that the emission of CO$_2$ could cause global warming with severe changes to the climate [1, 2]. To diminish the dependency on fossil fuels and to reduce CO$_2$ emissions much research is focused on new or alternative and sustainable fuels or energy sources. One of the possible alternative energy sources is biomass, which is a renewable and CO$_2$-neutral fuel and carbon source. The biomass energy potential has been estimated to be between 50 and 1100 EJ/year in 2050 [3-6] while the total global energy consumption is estimated to be between 600 and 1000 EJ/year in the same year [7]. Based on these numbers it appears that biomass can provide some of the energy needed in the future and thereby delay the depletion of the fossil resources.

Biomass can be converted by thermal and catalytic processes to several types of liquid or gaseous products. It can be gasified to produce synthesis gas, which subsequently can be used to produce power in gas turbines or to produce a wide range of fuels; methanol, DME, alcohols of various chain length by the higher alcohol synthesis, and high grade diesel by the Fischer-Tropsch synthesis [8-10]. Another interesting possibility is to flash pyrolyze the biomass, which produces liquids (bio-oil), gases, and solids (char) [8, 11-14]. The flash pyrolysis is conducted in an inert atmosphere at temperatures between 400 and 600 °C with high heating and cooling rates (1000-10,000 K/s) and low residence time in the reactor (1-2 s). Liquid yields up to 75 wt% can be achieved by a proper choice of operating conditions in the pyrolysis process [8, 11, 14, 15]. The gas and char yields typically range between 10-20 wt% and 10-15 wt%, respectively [13, 14]. Bio-oil can be produced in several different reactor types ranging from entrained flow to ablative and fluidized bed systems. Demonstration and industrial pyrolysis reactors with capacities between 1 and 50 t/h have been or are in operation [13].

The bio-oil can have a volumetric energy density up to ten times higher than biomass and is therefore more suitable for transport as the transportation cost will be much lower compared with biomass [15]. One of the problems with utilizing biomass in the energy sector can therefore be partly solved by the flash pyrolysis process.

The by-products from the flash pyrolysis can be utilized as the gases can be used to dry the biomass and be combusted to provide energy for the pyrolysis process [8, 11]. The char can be combusted as well. However this might be troublesome as the char contains high amounts of inorganics, which can vaporize and condense again on the heat transfer surfaces causing corrosion and reduced heat transfer. Therefore an attractive possibility could be to spread the char on agricultural lands as fertilizer and soil improver, which also would sequest CO$_2$ to
1. Literature review

Tab. 1.1: The average composition of bio-oil produced through flash pyrolysis of two different types of biomass, a mix of pine and spruce or a softwood mixture. Results are from a round robin laboratory analysis of the same bio-oils [20]. *Others* include ketones, aldehydes, and alcohols. PAH: Poly aromatic hydrocarbons. Pine and spruce bio-oil was produced in a fluidized bed reactor at 460 °C and the bio-oil from softwood was produced in a rotating cone reactor at 500 °C.

<table>
<thead>
<tr>
<th></th>
<th>85 % pine and Softwood mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 % spruce</td>
</tr>
<tr>
<td>Water [wt%]</td>
<td>20-23</td>
</tr>
<tr>
<td>Acids [wt%]</td>
<td>3-22</td>
</tr>
<tr>
<td>Others [wt%]</td>
<td>2-21</td>
</tr>
<tr>
<td>Sugars [wt%]</td>
<td>4-9</td>
</tr>
<tr>
<td>Phenols [wt%]</td>
<td>3-4</td>
</tr>
<tr>
<td>Lignin [wt%]</td>
<td>2-18</td>
</tr>
<tr>
<td>PAH [ppm]</td>
<td>8</td>
</tr>
</tbody>
</table>

some extent [16, 17]. According to Lehman and Joseph [17] if 1 % of annual plant uptake is converted into char it could mitigate 10 % of the anthropogenic CO$_2$ emissions. The carbon in the char is believed to be released over a period of 1000 years [16]. However, the char could contain PAH's or trace metals which could cause pollution of the soil.

The bio-oil consists of many different oxygenated compounds like acids, ketones, alcohols, phenols, guaiacols etc. The bio-oil and the biomass have similar heating values per mass and the energy efficiency of the pyrolysis is therefore close to the liquid yield in the flash pyrolysis, which means that values around 60-75 % can be achieved [18, 19]. However, energy should also be supplied to dry, downsize, and pyrolyze the biomass and since the energy from the pyrolysis gases may not be sufficient the energy efficiency for the entire biomass to bio-oil process might be lower.

The distribution among the different types of oxygenates in the bio-oil varies depending on the feedstock and under which conditions the bio-oil was produced. The average oxygenate composition for two bio-oils produced in different reactors and from different feedstock is shown in table 1.1. Acids and lignin constitutes the largest organic fraction in the bio-oil, while significant amounts of water also are present. Acetic acid, hydroxyacetalddehyde, acetol, and levoglucosan constitute some of the most abundant molecules [20].

The physical properties and elemental composition of bio-oil are compared to the composition of fossil fuel oil in table 1.2. The fuel oil used for comparison is equivalent to fuel oil no. 4, which is a heavy diesel blend sometimes referred to as residual fuel oil. The most important differences between bio-oil and fuel oil are the oxygen content, sulfur content, and pH. The high oxygen content in the bio-oil induces the low heating value, high acidity, and also instability of the bio-oil as the oxygenates can polymerize under storage. The polymerization causes an increase in viscosity and average molar weight with time [20-22]. A doubling or even tripling of the viscosity of bio-oil due to ageing might occur over a year [20]. This polymerization might make upgrading of the bio-oil more difficult as complex molecules, which are more difficult to convert, could be formed. Ageing of the bio-oil can also decrease the volatility, cause phase separation, and gum formation in the bio-oil as well [21]. Thus long-term storage of the bio-oil could cause severe changes to the bio-oil and should be avoided. The acidity of bio-oil is another problem as corrosive resistant materials are needed for piping and process
equipment, which often are more expensive. The sulfur content in bio-oil is much lower than in crude oil which, in general, is advantageous, but even the low levels might be a problem for catalytic processing of the oil as sulfur might deactivate the catalysts. This is especially a problem if Ni or noble metals are used as catalysts.

**Tab. 1.2:** The composition and other characteristics of an average bio-oil and fuel oil equivalent to fuel oil no. 4 [22, 23].

<table>
<thead>
<tr>
<th></th>
<th>Bio-oil</th>
<th>Fuel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content [wt%]</td>
<td>15-30</td>
<td>0.02</td>
</tr>
<tr>
<td>pH</td>
<td>2.0-3.7</td>
<td>-</td>
</tr>
<tr>
<td>Density [kg/m³]</td>
<td>1.1-1.3</td>
<td>0.9</td>
</tr>
<tr>
<td>C [wt%]</td>
<td>32-49</td>
<td>85</td>
</tr>
<tr>
<td>H [wt%]</td>
<td>6.9-8.6</td>
<td>11</td>
</tr>
<tr>
<td>O [wt%]</td>
<td>44-60</td>
<td>1</td>
</tr>
<tr>
<td>N [wt%]</td>
<td>0-0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>S [wt%]</td>
<td>0-0.05</td>
<td>0.2</td>
</tr>
<tr>
<td>Solids [wt%]</td>
<td>0.2-1</td>
<td>1</td>
</tr>
<tr>
<td>Lower heating value [MJ/kg]</td>
<td>13-18</td>
<td>40.3</td>
</tr>
</tbody>
</table>

The bio-oil can be converted to different products and might therefore constitute a platform feedstock in a bio-refinery. It can be converted to a gasoline like product by partial hydrodeoxygenation (HDO) or to synthesis gas by steam reforming (SR) [8, 9, 24]. The H₂ from the SR can be used as a fuel or a reactant in either the HDO of the bio-oil or in other chemical processes like hydrotreating or ammonia synthesis which uses H₂ or in the Fischer-Tropsch production of synthetic natural gas, which uses synthesis gas.

Steam reforming of bio-oil has the potential to be CO₂-neutral and is therefore a sustainable route to hydrogen or synthesis gas. Steam reforming of fossil fuels is used frequently in the chemical industry to produce reactants and the shift to SR of bio-oil would decrease the CO₂-emission. A lifecycle analysis has shown the SR of bio-oil is more energy demanding compared to SR of fossil fuels, which is partly due to addition of methanol as a stabilizer for the bio-oil and also a lower H/C-ratio is the feed. However, the decrease in greenhouse gas emissions would be around 50 % for the SR of bio-oil compared with SR of natural gas [25]. Another life cycle analysis based on an entire biorefinery with pyrolysis and bio-oil upgrading has shown that the concept could be economically viable and lead to decreased emissions of CO₂ [26]. In the analysis performed by Gebreslassie et al. [26] the H₂ used for hydrotreating of the bio-oil was produced by SR of CH₄ and therefore a further decrease in greenhouse gas emissions might be achievable if SR of bio-oil was used for H₂ production instead. Similar results was reported in a LCA study by Han et al. [27]. Furthermore it has been estimated that the production costs of bio-oil through flash pyrolysis enables a selling price of bio-oil at values lower than the cost of fuel oil [28]. A simple flow diagram for the process from biomass to synthesis gas can be seen in figure 1.1. Another process for converting biomass into synthesis gas or H₂ is through gasification and subsequent shift conversion. However, the yield of H₂ is lower compared with the flash pyrolysis and SR of bio-oil [12]. Furthermore, gasification will often require an air separating unit to produce pure oxygen and this is expensive and energy intensive.
1. Literature review

Fig. 1.1: Simple flow diagram for the complete path from biomass to synthesis gas via bio-oil SR.

1.2 Conventional steam reforming

Steam reforming is a process where hydrocarbons react with steam at high temperatures and are converted to carbon oxides and H₂. Steam reforming is normally accompanied by the water gas shift (WGS) and the methanation reaction, where the extents of these reactions depend on the operating conditions. The reforming, WGS, and methanation reactions are shown below [29–31].

Reforming: \[ C_n H_m + n H_2 O \rightleftharpoons n CO + (n + m \gamma 2) H_2 \] (1.1)

WGS: \[ CO + H_2 O \rightleftharpoons CO_2 + H_2 \] (1.2)

Methanation: \[ CO + 3H_2 \rightleftharpoons CH_4 + H_2 O \] (1.3)

The reforming reaction is endothermic reaction while the methanation and WGS are exothermic reactions. The reforming equilibrium is favored by high temperatures and low pressures, while the WGS is shifted toward CO and H₂O at high temperatures [29–31]. The reforming reaction (reaction 1.1) is not reversible over most SR catalysts at the reaction conditions usually employed.

Fig. 1.2: Simple flowsheet for an industrial steam reforming unit with a prereformer.

The SR process has been investigated thoroughly with natural gas and other fossil fuels as reactants and is also used industrially to produce synthesis gas or hydrogen for processes like the Haber-Bosch (NH₃) or the Fischer-Tropsch (diesel) synthesis [30–33]. An industrial plant for SR of natural gas generally consist of three units as shown in figure 1.2. First a desulfurization unit with two reactors to reduce the sulfur content to ppb-levels by hydrogenating the sulfur compounds in the first reactor (hydrogenator) and then absorbing the formed H₂S in
the second reactor (sulfur absorber). Secondly a prereformer, which operates at temperatures between 350 and 550 °C, converts the C₂⁺ hydrocarbons to mainly methane and carbon oxides. The third unit is the primary reformer, where the methane is converted to synthesis gas at temperatures from 450 to 1050 °C[29–31, 34, 35]. The desulfurization is needed because the Ni-catalysts typically used in the reformers are deactivated by H₂S in trace amounts [29–31, 36]. The prereformer allows feedstock flexibility and a higher inlet temperature to the reformer, because the higher hydrocarbons, which can cause carbon deposition at high temperatures, are converted to CH₄ before they reach zones with high temperatures [35]. The synthesis gas can be shifted catalytically downstream the reformer to achieve a ratio between H₂ and CO suitable for the downstream processing [29–31]. The SR of natural gas is generally conducted at pressures around 30 bar as the natural gas is delivered at this pressure and the downstream processing is pressurized as well. Furthermore the equipment will be smaller when the gas is pressurized and the process is operated at elevated pressures.

The SR of hydrocarbons occurs through adsorbed species on the catalyst (adsorbed species will be denoted with *). The hydrocarbons dissociatively adsorb on the metal forming CₓHᵧ* and the steam dissociatively adsorbs on the support or on the metal particles forming OH-species. The OH* and CₓHᵧ* can then react at the interface between the metal and the support or on the metal particles forming CO and H₂ [30, 37]. CO₂ is formed from CO and H₂O through the WGS (reaction 1.2). Bengaard et al. [38] have shown that the reaction mechanism for SR of CH₄ proceeds through the adsorbed species, as described above. The surface reactions in the SR of CH₄ are generally assumed to be [30, 38, 39]:

\[
\begin{align*}
    \text{CH}_4(g) + 2* & \rightleftharpoons \text{CH}_3* + \text{H} * & (1.4) \\
    \text{CH}_3* + * & \rightleftharpoons \text{CH}_2* + \text{H} * & (1.5) \\
    \text{CH}_2* + * & \rightleftharpoons \text{CH}* + \text{H} * & (1.6) \\
    \text{CH} * + * & \rightleftharpoons \text{C} * + \text{H} * & (1.7) \\
    \text{H}_2\text{O}(g) + 2* & \rightleftharpoons \text{HO}* + \text{H} * & (1.8) \\
    \text{OH}* + * & \rightleftharpoons \text{O}* + \text{H} * & (1.9) \\
    \text{C}* + \text{O}* & \rightleftharpoons \text{CO}* + * & (1.10) \\
    \text{CO}* & \rightleftharpoons \text{CO}(g) + * & (1.11) \\
    2\text{H}* & \rightleftharpoons \text{H}_2(g) + 2* & (1.12) \\
    \text{Overall:} & \text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons 3\text{H}_2 + \text{CO} & (1.13)
\end{align*}
\]

Carbon formation in conventional SR can occur both in the gas phase and through surface reactions. The gas phase reactions include cracking of hydrocarbons and free radical reactions, which induces condensation of tars [40–42]. On the surface of the catalyst and under SR-conditions free reactive surface carbon atoms, called Cᵦ, can be formed and these can easily be gasified to carbon oxides. If Cᵦ is not converted to gaseous species (carbon oxides or CH₄) it may accumulate on the surface and polymerize to the less reactive carbon type, Cᵦ, which can lead to formation of encapsulating carbon or carbon whiskers. Accumulation and polymerization of Cᵦ to Cᵦ will require a larger ensemble of Ni-atoms. Therefore, small Ni-particles reduce the carbon formation tendency. Another strategy is to decorate the most active carbon forming sites by sulfur. This has been used in SPARG process from Haldor Topsoe A/S, which enables SR units to operate at low S/C-ratios and with no carbon formation [43, 44].
The deposited carbon can have three different forms; pyrolytic coke, whiskers, and gum. The formation of pyrolytic coke and whiskers occurs mainly at high temperatures while gum formation is a problem at low temperatures [30, 36, 38]. The actual limit where carbon free operation is possible depends on feedstock, pressure, and S/C-ratio. The potential for forming whiskers and pyrolytic coke can be estimated as described by Rostrup-Nielsen and Christiansen [42]. The carbon formation is generally reduced at high steam-to-carbon (S/C) ratios meaning that the temperature window between the high and low temperature carbon formation increases with S/C [30, 31]. The different carbon formation reactions are shown below [30, 32, 36]:

\[
\text{Boudouard: } \quad 2\text{CO} \rightleftharpoons \text{C} \text{s} + \text{CO}_2 \quad (1.14)
\]

\[
\text{CO decomposition: } \quad \text{CO} + \text{H}_2 \rightleftharpoons \text{C} \text{s} + \text{H}_2\text{O} \quad (1.15)
\]

\[
\text{CH}_4 \text{ decomposition: } \quad \text{CH}_4 \rightleftharpoons \text{C} \text{s} + 2\text{H}_2 \quad (1.16)
\]

\[
\text{CH decomposition: } \quad \text{C}_n\text{H}_m \rightarrow \text{nC} \text{s} + \frac{m-2}{2}\text{H}_2 \quad (1.17)
\]

\[
\text{Gum: } \quad \text{C}_n\text{H}_m \rightarrow (\text{CH}_2)_n \rightarrow \text{Gum} \quad (1.18)
\]

\[
\text{Pyrolytic coke: } \quad \text{C}_n\text{H}_m \rightarrow \text{Olefins} \rightarrow \text{Coke} \quad (1.19)
\]

Reactions 1.14 to 1.18 are catalytic reactions and dependent on the type of catalyst while reaction 1.19 mainly depends on temperature. However, CO decomposition and the Boudouard reaction are mainly thermodynamical favorable at low temperature, while \(\text{CH}_4\) decomposition or other decomposition reactions mainly will occur at high temperatures. Carbon whiskers are produced through reactions 1.14 to 1.17 and is a major problem for Ni-catalysts [30, 31]. The whiskers are graphene tubes, which grow from the nickel particles and they are mainly initiated at the most active step sites on the metal (Ni) particles. The whiskers will leave most of the Ni surface free to catalyze reactions and the main problem is that they will cause disintegration of the support material [42]. Addition of small amounts of alkali metals or other metals, which can adsorb on the step sites, to the catalyst can significantly reduce the formation of whiskers [30, 38]. They block, completely or partially, the most active sites (step sites) and the nucleation of the graphene cannot occur. The addition of alkali metals, which blocks the step sites, will also decrease the activity of catalyst, because the step sites are the most active sites for the SR as well [30, 38]. Furthermore the addition of alkali can cause an increased risk of sintering. A smaller metal particle size can also decrease the whisker formation, because the formation of the graphene tubes is not energetically favorable before the carbon island exceeds a critical size. This value has been estimated by DFT calculations to be 25 Å and experimental results suggest that metal particles less than 50 Å in diameter should show low whisker formation [30].

Sintering of the catalyst can also be a problem especially at high temperatures, high metal loadings, or high steam partial pressures [30, 45]. In this process fewer and larger metal particles are formed, either by Ostwald ripening or cluster migration and coalescence. Sintering will usually occur above the Tamman temperature of metals, which is half the melting temperature in Kelvin, because the metal atoms become mobile above this point. The Tamman temperature for pure nickel is 863 K [46].

Poisoning of the SR catalysts by sulfur can also be problem, which will be discussed further in section 1.4.

The conventional SR process is usually catalyzed by group VIII metals and nickel is preferred due to its lower price and good activity, even though noble metal catalysts can be more active and less prone to coke formation [29, 30, 47]. The support material used are MgO, other basic oxides, \(\text{Al}_2\text{O}_3\), calcium or magnesium aluminates [32].
1.3 Steam reforming of oxygenates

In this section results from SR of several different model compounds and bio-oil will be presented. The first subsection will be general considerations regarding the SR of oxygenates. The term yield of $\text{H}_2$ will be used in the following sections as descriptor for how well equilibrated a gas is produced. The maximum achievable production of $\text{H}_2$ will be determined by the temperature and the approach to equilibrium in the WGS and methanation reactions.

1.3.1 General considerations

The general reaction scheme for the SR of oxygenates is:

$$C_nH_mO_p + (n-p) \text{H}_2\text{O} \rightarrow n\text{CO} + (n-p + \frac{m}{2}) \text{H}_2$$  \hspace{1cm} (1.20)  

Reaction 1.20 in combination with WGS (reaction 1.2) fully shifted toward the right is:

$$C_nH_mO_p + (2n-p) \text{H}_2\text{O} \rightarrow n\text{CO}_2 + (2n-p + \frac{m}{2}) \text{H}_2$$  \hspace{1cm} (1.21)  

Steam reforming of oxygenates is often described by reaction 1.21 although at high temperatures WGS is shifted to the left and CO will also be present in significant amounts. The methanation of CO (reaction 1.3) will also influence the product distribution at equilibrium especially at low temperatures and/or high pressures as these conditions favor this reaction [30]. Thermal decomposition can also occur as the oxygenates often are thermally unstable and this reaction should be minimized due to the coke formation [48–51]. The decomposition can be described by:

$$C_nH_mO_p \rightarrow C_xH_yO_z + \text{gases} + \text{coke}$$  \hspace{1cm} (1.22)  

Steam reforming of oxygenates is, like the conventional SR, endothermic and therefore it is favored by high temperatures. Low pressures will also favor the SR as predicted by Le Châteliers principle. Thermodynamics predicts full conversion of oxygenates and the composition of the final product will be governed by the equilibrium prescribed by WGS and methanation. High yields of $\text{H}_2$ in SR requires a shift catalyst downstream the reformer operated at a lower temperature, which can convert the CO to $\text{CO}_2$ and $\text{H}_2$ by WGS [12]. If SR of oxygenates should provide synthesis gas to a process, a shift catalyst might be needed to adjust the $\text{CO}/\text{H}_2$-ratio. The $\text{CO}/\text{H}_2$-ratio depends on the temperature and S/C-ratio; high temperatures will increase the $\text{CO}/\text{H}_2$ while increasing the S/C will lower the $\text{CO}/\text{H}_2$-ratio at a given temperature.

The possible yields of $\text{H}_2$, both stoichiometric and at equilibrium, in the SR of different model compounds and a bio-oil, at 750 °C, S/C-ratio of 5, and atmospheric pressure, are shown in table 1.3. The stoichiometric yield is defined as the number of moles of $\text{H}_2$ produced pr. mole of carbon based on reaction 1.21. The equilibrium yield + WGS assumes that the CO present in the offgas can be shifted to $\text{H}_2$ and $\text{CO}_2$ in a downstream shift reactor at 200 °C [12, 51]. The WGS equilibrium is, at this temperature, shifted completely toward $\text{H}_2$ and $\text{CO}_2$. In table 1.3 it can be seen that possible equilibrium yields are around 85 % of the stoichiometric. Values close to 100 % should be possible if a shift catalyst at 200 °C is employed downstream the reformer as indicated by the last column in table 1.3 [12, 51].

The use of high temperatures in the SR process has two effects; one is that WGS is shifted toward CO and $\text{H}_2\text{O}$, which decreases the $\text{H}_2$-concentration, and the other one is that the methane is steam reformed. Therefore high temperatures are needed for full conversion of the
Tab. 1.3: Thermodynamical equilibrium hydrogen yield from the steam reforming of different bio-oil model compounds or whole bio-oil [12, 51]. Values from Aspen Plus simulations at 750 °C, atmospheric pressure, and S/C-ratio of 5. st: stoichiometric. + WGS indicates the offgas is shifted at 200 °C.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Stoichiometric</th>
<th>Equilibrium</th>
<th>+ WGS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mole H₂/mole C</td>
<td>[% of st.]</td>
<td>[% of st.]</td>
</tr>
<tr>
<td>Ethanol</td>
<td>3.0</td>
<td>85.9</td>
<td>96.2</td>
</tr>
<tr>
<td>Phenol</td>
<td>2.33</td>
<td>84.3</td>
<td>96.3</td>
</tr>
<tr>
<td>Glucose</td>
<td>2.0</td>
<td>86.3</td>
<td>97.5</td>
</tr>
<tr>
<td>Poplar bio-oil</td>
<td>2.14</td>
<td>85.2</td>
<td>96.9</td>
</tr>
</tbody>
</table>

a Average molar composition C₆H₈.₈₂O₄.₀₂.

Fig. 1.3: The equilibrium H₂ concentration on a water free basis as function of the temperature for S/C-ratios 1 and 1.5 at 1 bar and S/C-ratio of 1 at 10 bar for ethanol. + WGS indicates that the CO present is shifted to H₂ and CO₂ by a low temperature shift catalyst at 200 °C. The thermodynamic calculations are conducted in FactSage 6.0.

The ratio between steam and carbon is an important parameter because increasing this ratio will increase the conversion and also reduce carbon formation. This occurs because steam gasification of the deposited carbon might be possible due to a higher partial pressure of water and because the thermal decomposition of the oxygenates is suppressed [52]. The effects of the S/C-ratio and the pressure are illustrated in figure 1.3, where the equilibrium H₂ concentration as function of the temperature is shown for different S/C-ratios and pressures. In figure 1.3 it can be seen that the equilibrium H₂ concentration on a H₂O free basis increases with increasing S/C-ratio or decreasing pressure. The effect of shifting the offgas by the WGS catalyst at 200 °C can also be seen in figure 1.3.

The equilibrium offgas composition as function of the temperature in the SR of ethanol is shown in figure 1.4 to illustrate the trends in the product distribution in the SR of oxygenates. The conversion is at low temperatures, below 400 °C, mainly to CH₄ and CO₂ and as the
temperature increases the CH\textsubscript{4}, CO\textsubscript{2}, and H\textsubscript{2}O fractions decrease and the H\textsubscript{2} and CO fractions increase. The WGS reaction shifts toward CO and H\textsubscript{2}O above 700 °C, which lowers the H\textsubscript{2} and CO\textsubscript{2} concentration. The effects of S/C-ratio, pressure, and temperature has been shown by thermodynamic calculations [53–56] and verified by several experimental studies [48, 57–63]. However, the conversion predicted by thermodynamics cannot be reproduced below 400 °C as full conversion rarely is achieved at low temperatures.

The deactivation mechanisms in the SR of oxygenates are similar to those encountered in the conventional SR, namely; carbon deposition, sintering, and sulfur poisoning.

The SR of oxygenates have mainly focused on the SR of ethanol, due to the general large interest in bio-ethanol, but SR of acetic acid, as model compound for bio-oil, have also been investigated. There have also been conducted studies on larger model compounds of bio-oil, like phenols, cresols, or whole bio-oil, but not to the same extent as for acetic acid and especially ethanol.

The motivation for testing model compounds instead of whole bio-oil is that it is possible to get a better understanding of the reactions, influence of experimental conditions, deactivation etc. because it is known exactly what enters the reactor. Therefore it is possible to recreate similar conditions and concentrations when testing different catalysts and hereby allow better comparison between them. Furthermore, the separation and analysis of the reactor effluent is easier due to the limited number of products.

1.3.2 SR of acetic acid

Carboxylic acids are present in large amounts in bio-oil (see table 1.1) and acetic acid is reported as the most abundant [20]. Therefore acetic acid has been used as model compound of bio-oil in many studies. The SR of acetic acid is accompanied by many possible side reactions. The most relevant of these can be seen in table 1.4. The unwanted reactions are dehydration to ketene (reaction 6 in table 1.4) and the ketonization (reaction 2 in table 1.4) to acetone. Ketene can combine to form ethene by reaction 8, which is a known coke precursor [48, 52, 64], while acetone can polymerize by aldol condensation and form coke through reactions 9 to 11.
Tab. 1.4: Possible reactions in the steam reforming of acetic acid [48, 52, 64, 67, 68].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Name</th>
<th>Reaction scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SR</td>
<td>$\text{CH}_3\text{COOH} + 2 \text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 4\text{H}_2$</td>
</tr>
<tr>
<td>2</td>
<td>Ketonization</td>
<td>$2\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COCH}_3 + \text{CO}_2 + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>3</td>
<td>SR acetone</td>
<td>$\text{CH}_3\text{COCH}_3 + 3 \text{H}_2\text{O} \rightarrow 3\text{CO} + 6\text{H}_2$</td>
</tr>
<tr>
<td>4</td>
<td>Decomposition 1</td>
<td>$\text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2$</td>
</tr>
<tr>
<td>5</td>
<td>Decomposition 2</td>
<td>$\text{CH}_3\text{COOH} \rightarrow 2\text{H}_2 + \text{CO}_2 + \text{C}$</td>
</tr>
<tr>
<td>6</td>
<td>Dehydration</td>
<td>$\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{CO} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>7</td>
<td>SR ketene</td>
<td>$\text{CH}_2\text{CO} + \text{H}_2\text{O} \rightarrow 2\text{CO} + 2\text{H}_2$</td>
</tr>
<tr>
<td>8</td>
<td>Ketene coupling</td>
<td>$2\text{CH}_2\text{CO} \rightarrow \text{C}_2\text{H}_4 + 2\text{CO}$</td>
</tr>
<tr>
<td>9</td>
<td>Acetone 1</td>
<td>$2\text{CH}_3\text{COCH}_3 \rightarrow \text{H}_2\text{O} + (\text{CH}_3)_2\text{CCHCOCH}_3$</td>
</tr>
<tr>
<td>10</td>
<td>Acetone 2</td>
<td>$(\text{CH}_3)_2\text{CCHCOCH}_3 + \text{CH}_3\text{COCH}_3 \rightarrow \text{C}<em>9\text{H}</em>{12} + 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>11</td>
<td>Acetone 3</td>
<td>$\text{C}<em>9\text{H}</em>{12} \rightarrow \text{Coke}$</td>
</tr>
</tbody>
</table>

[65]. The dehydration and ketonization are mainly observed at medium conversions, or in experiments, where support materials are used without an active phase [48, 52]. Rhodium and some support materials, especially ZrO$_2$, catalyze the ketonization and larger amounts of acetone can be formed [48, 65]. Takanabe et al. [66] reported that ZrO$_2$ without metal had a conversion around 85% mainly to acetone at weight hourly space velocity (WHSV) of 9 h$^{-1}$ and 450 °C. The addition of metal to the support material will generally reduce the extent of the ketonization [52, 66].

The most desired reactions in table 1.4 are the SR reactions or the decomposition to CH$_4$ and CO$_2$, which can be reformed to the desired products.

The complete conversion of acetic acid is reported to occur at temperatures between 400 and 800 °C depending on the catalyst and operating conditions [48, 48, 59, 60, 66, 69-74]. The conversion over support material, like Al$_2$O$_3$, without a catalytic active metal exceeds 10% at WHSV of 36 h$^{-1}$ and temperatures above 850 °C and is mainly by thermal decomposition to CH$_4$ and CO$_2$ [48]. At higher temperatures (900 °C or above) hydrogen production can also occur over Al$_2$O$_3$ [48]. The conversion over quartz particles is higher compared with support materials and full conversion can be achieved at 950 °C and WHSV of 36 h$^{-1}$ [48, 70]. However, homogenous reactions affect the process and full conversion to CH$_4$, CO$_2$, H$_2$, and CO have been reported to occur in the empty reactor at 950 °C at the same flow rate and same reactor as used by Basagiannis and Verykios [48]. At 750-800 °C the conversion is 10% or below [48, 74].

**Mechanism and kinetics**

Takanabe et al. [75] used IR-measurements, pulse experiments, and flow reactor experiments to arrive at a mechanism for SR of acetic acid over a Pt/ZrO$_2$-catalyst, where the first step is a dissociative adsorption of the acid to form acetate or acyl species on the Pt-surface by the reactions:

\[
\text{CH}_3\text{COOH} + 2 * \rightleftharpoons \text{CH}_3\text{COO}* + \text{H}* \quad (1.23)
\]

\[
\text{CH}_3\text{COOH} + 2 * \rightleftharpoons \text{CH}_3\text{CO*} + \text{OH*} \quad (1.24)
\]

DFT-calculations and experiments have shown that these species are formed on Pt-surfaces [76, 77]. In the DFT-calculations direct conversion of acetic acid to CH$_4$, CO, and CO$_2$ is
assumed to occur through acyl species [76, 78]. The decomposition reactions of acyl species was proposed by Gursahani et al. [76] to be:

\[
\begin{align*}
\text{CH}_3\text{CO}^* & \rightleftharpoons \text{CH}_4 + \text{CO}^* - \frac{1}{2}\text{H}_2 \quad (1.25) \\
\text{CH}_2\text{CO}^* + * & \rightleftharpoons \text{CH}_2\text{CO}^* + \text{H}^* \quad (1.26) \\
\text{CH}_2\text{CO}^* + * & \rightleftharpoons \text{CHCO}^* + \text{H}^* \quad (1.27) \\
\text{CHCO}^* + * & \rightleftharpoons \text{CH}^* + \text{CO}^* \quad (1.28) \\
\text{CH}^* + 2\text{H}^* & \rightleftharpoons \text{CH}_4 + 3^* - \frac{1}{2}\text{H}_2 \quad (1.29)
\end{align*}
\]

The acyl and acetate species formed in reactions 1.23 and 1.24 can decompose to CO, CO$_2$, and CH$_x$* where $x \leq 3$ according to Takanabe et al. [75]. However, no specific surface reactions were proposed for the decomposition reaction but it could be:

\[
\text{CH}_3\text{CO}^* \rightleftharpoons \text{CH}_3^* + \text{CO}^* \quad (1.30)
\]

In combination with with reactions 1.5-1.12, which is supported by Wang et al. [78].

Takanabe et al. [75] proposed that the CH$_x$-species either could polymerize to form a carbon layer on the catalyst or react with OH-species from the support and form carbon oxides and H$_2$. The OH-species are formed by dissociative adsorption of steam, reaction 1.8. The operating conditions will probably determine whether the carbon formed in this mechanism is pyrolytic carbon, gum, or whiskers. Takanabe et al. [75] proposed that the reaction between OH-species and CH$_x$ or graphite species occurs at the boundary between the Pt and ZrO$_2$ [75]. In a mechanism similar to the one described above, decomposition of the oxygenate on the metal and reaction with OH-species at the metal-surface interface, could occur for all oxygenates according to Takanabe et al. [75].

To substantiate the bifunctional mechanism it was shown that the hydrogen production from the SR of acetic acid over Pt-catalysts could be related to the number of Pt-atoms at the periphery of the metal particles rather than number of Pt-sites in total [79]. Furthermore, a study with deuterated acetic acid (CH$_3$COOD) on Pt-ZrO$_2$ by Güell et al. [77] showed that the acetic acid indeed decomposed to CH$_3$* and CO$_2$ as proposed by Takanabe et al. [75].

**Fig. 1.5:** The bifunctional reaction mechanism proposed by Takanabe et al. [75], where possible side reactions are indicated as well. Figure adapted from ref. [75].

A schematic of the mechanism proposed by Takanabe et al. [75] for the SR of acetic acid is shown in figure 1.5. This mechanism is, in some aspects, similar to the bifunctional mechanism
proposed for conventional SR \([30, 39]\). However, this mechanism is not very specific and do not describe the actual surface reactions, which might occur.

Wang et al. \([51]\) have proposed the following surface reactions to occur in the SR of acetic acid:

\[
\begin{align*}
\text{CH}_3\text{COOH} + 2 * & \rightleftharpoons \text{CH}_3\text{COO}^* + \text{H}^* \\
\text{CH}_3\text{COO}^* & \rightleftharpoons \text{CH}_3^* + \text{CO}_2 \\
\text{CH}_3^* + 3* & \rightleftharpoons \text{C}^* + 3\text{H}^* \\
\text{C}^* + \text{H}_2\text{O} & \rightleftharpoons \text{CO}^* + \text{H}_2
\end{align*}
\]

Reactions 1.33 and 1.34 are not elementary steps and must occur through several reactions, which could be similar to steps in the mechanism for SR of methane, which is described by reactions 1.4 to 1.12. At low temperatures the reverse of reaction 1.4 will also be important as \(\text{CH}_4\) can be formed from \(\text{CH}_3^*\). The main difference between these two mechanisms is how the \(\text{CH}_3^*\)-species is formed. The above sequence of reactions corresponds well with the general mechanism proposed by Takanabe et al. \([75]\). It should also be noted that elemental carbon is involved in the process and gasification of this species should occur fast to minimize the carbon formation \([51, 80]\).

A kinetic study of the SR of acetic acid has been conducted by Galdamez et al. \([81]\), where first order kinetics were proposed and based on this assumption it was shown that the hydrogen production rate could be related to the difference between the actual and the equilibrium concentrations. The expression used by Galdamez et al. \([81]\) was:

\[
r_i = k_i \cdot \left( \frac{m_i}{m_a} \right)_{\text{Eq}} - \frac{m_i}{m_a}
\]

where \(r_i\) is the production rate of component \(i\), \(m_i\) is the mass flow of component \(i\), \(m_a\) is the mass flow of acetic acid in the feed, \(m_i/m_a\) is the yield of component \(i\) in \(g/(g(\text{acetic acid}))\), and the subscript \(\text{Eq}\) refers to the equilibrium. The term \(\left( \frac{m_i}{m_a} \right)_{\text{Eq}}\) is zero for \(\text{CH}_4\) and \(\text{C}_2\)-species and equation 1.35 is reduced to:

\[
r_i = -k_i \cdot \left( \frac{m_i}{m_a} \right)
\]

The rate constants based on eq. 1.35 and 1.36 are shown in table 1.5 along with the \(R^2\)-values which indicates a good correspondence between the experiments and eq. 1.35 and 1.36. The model by Galdamez et al. \([81]\) might fit the data quite well, but it is highly empirical and extrapolation based on eq. 1.35 seems questionable.

**Catalysts**

Several different transition metals have been tested in the SR of acetic acid. These are the base metals Co, Ni, Fe, and Cu \([48, 57, 59, 60, 64, 69-74, 80-83]\) and the noble metals Pt, Pd, Rh, and Ru \([48, 52, 66, 68, 75]\). The reaction rate over base metals is highest for Co and Ni, while the rate over Fe and Cu is significantly lower \([70]\). At 450 °C and LHSV of 8.3 \(h^{-1}\) full conversion can be achieved over Co or Ni while the conversion over Fe or Cu are roughly 25 \(wt\%\). The order of decreasing activity for the base metals is \([70]\):
Tab. 1.5: The rate constant based on the kinetic expression proposed by Galdamez et al. [81] and shown in eq. 1.35. $C_2$ includes $C_2H_2$, $C_2H_4$, and $C_2H_6$.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Rate constant $R_2$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>0.3802</td>
<td>0.9985</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>0.5655</td>
<td>0.9816</td>
</tr>
<tr>
<td>$CH_4$</td>
<td>0.1705</td>
<td>0.9687</td>
</tr>
<tr>
<td>$C_2$</td>
<td>0.4534</td>
<td>0.9809</td>
</tr>
</tbody>
</table>

Ni > Co > Fe > Cu

The metals were all supported on alumina and had a metal loading of 20 wt%.

The Co and Ni-catalysts have the ability to both break C-C and C-H-bonds, which is needed for converting acetic acid, and this explains the better performance of these metals compared to Fe, which mainly can break C-C bonds and Cu which mainly can break C-H bonds [70]. The long-term stability is higher for Ni compared with Co and in some cases also the activity [70, 84]. This is due to an increased carbon formation on the Co catalysts. Another drawback of Co is that it cannot be kept reduced under industrial conditions, where there is plug flow [85]. In laboratory scale experiments back mixing and diffusion of $H_2$ can keep Co reduced.

A mixture of Ni and Co in a molar ratio of 1 to 4 without any support have shown better performances compared to pure Ni or Co [69]. Full conversion and no CO formation could be achieved at temperatures down to 400 °C and LHSV of 5.1 $h^{-1}$.

A study by Basagiannis and Verykios [48] has shown that the most active noble metals were Rh and Ru, while Pd and Pt showed much lower activity. In this study it was reported that Ni catalysts were even more active compared with the noble metals [48]. The order of activity in terms of conversion and TOF, with 1 wt% metal content for all the noble metals except for Rh with 0.5 wt%, was [48]:

$$Ni > Rh > Ru > Pd > Pt$$

The Ni catalysts used in the comparison above had a metal loading of 17 wt% and was like the other metals supported on Al$_2$O$_3$. In general it is reported that Ni catalysts can obtain activities similar to the noble metals, but the noble metals are less prone to carbon formation and therefore more stable over time [48, 86].

A study by Hu and Lu [82] investigated the influence of different promoter metals on the performance of a Ni/Al$_2$O$_3$-catalyst in the SR of acetic acid. They tested Li, Na, K, Mg, Fe, Co, Zn, Zr, La, and Ce and found that the addition of K gave the largest improvement in the catalytic performance both in the terms of activity and stability. The addition of Co, Fe, or Zn decreased the conversion over the catalyst, while the addition of the other promoters increased the conversion, but only K, Li, and Na decreased the yield of CH$_4$ as well [82]. The performances of some of the promoted Ni-catalysts are listed in table 1.6, where the aforementioned trends can be seen. $Y_{CH_4}$ describes how many moles of carbon in carbon containing products and similar $Y_{H_2}$ describes how many moles of $H_2$ is produced compared with total number of moles of $H_2$ in the $H_2$ containing products.
Tab. 1.6: The conversion and yield of CH₄ and H₂ for different promoted Ni-catalysts in the SR of acetic acid [82]. T: 400 °C, p: 1 bar, S/C: 7.5, LHSV: 12.1 h⁻¹.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>X_AA [%]</th>
<th>Y_CH₄ [%]</th>
<th>Y_H₂ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Al₂O₃</td>
<td>67.8</td>
<td>14.7</td>
<td>66.2</td>
</tr>
<tr>
<td>Ni-Na/Al₂O₃</td>
<td>93.8</td>
<td>4.0</td>
<td>89.6</td>
</tr>
<tr>
<td>Ni-K/Al₂O₃</td>
<td>100</td>
<td>1.4</td>
<td>93.5</td>
</tr>
<tr>
<td>Ni-Mg/Al₂O₃</td>
<td>47.8</td>
<td>12.3</td>
<td>57.6</td>
</tr>
</tbody>
</table>

The optimal amount of promoter was 8 wt% for K, which could increase activity, decrease the yield of CH₄, and increase the long-term stability. These effects were ascribed to a decrease in the activity for methanation, because CO dissociation, which is most likely to occur at step sites, was inhibited by K. The addition of K decreased the reduction temperature, resulting in more metallic Ni-particles on the catalyst at the applied reduction temperature of 600 °C, which also could be responsible for the improved performance [82]. It was also suggested that K-promotion decreased sintering of Ni on the catalysts [82]. The addition of K is known from the SR of hydrocarbons to decrease the carbon whisker formation because the active step sites are covered by K [38, 87], and it is also reported to increase the steam adsorption [32, 37]. This could explain the increased long-term stability for the K promoted Ni-catalysts.

The promoting effect of K, increased activity and stability, and perhaps also decreased sintering, in the SR of oxygenates is contrary to what is observed in the SR of CH₄ where K promotion decreases the overall activity of the catalyst and increase the risk of sintering [30, 42].

The support material in the catalyst is important and can be optimized to induce a more stable and active catalyst. Al₂O₃ is an acidic support and is known to catalyze cracking reactions and hereby form coke on the catalyst [88]. The coke formation can be suppressed and the catalytic activity improved, if the Al₂O₃ is mixed with a basic oxide like MgO, CeO₂, or La₂O₃ [48, 52, 89]. The structure of the mixed oxides is probably a spinel type structure, at least for the mixture of MgO and Al₂O₃ [52]. Of the basic oxides it seems that MgO is the best promoter [48, 52]. The increased activity by the addition of basic oxides can be ascribed to a higher amount of OH-species from water dissociation on the support, which can diffuse onto the metal particles and participate in reactions and also a smaller size of the metal particles [48, 52]. The improved stability is due to less coke deposition, because less cracking occurs as the number of acid sites is decreased and also because steam gasification of the coke might be facilitated by spillover of O- or OH-species from the support to the metal particles [52].

Apparent activation energies for the SR of acetic acid over different active metals on different support materials have shown that surface reactions on the support or at the support metal interface are important as the activation energies changes most with a change in support and not with a change in the type of active metal [48].

Support materials, like ZrO₂ and CeO₂, have also been tested with Ni as the active material; severe coking occurs on the acidic ZrO₂-catalyst and much less on CeO₂-catalyst [68]. ZrO₂ is an acidic support, which leads to significant cracking and also coke deposition, and furthermore it catalyzes the formation of acetone which can condense and form coke [65, 68]. CeO₂ showed a better performance compared with ZrO₂ which was ascribed to a higher activity in the SR of acetone or lower production of acetone [90]. It was also suggested that Ce has the ability to supply oxygen to oxidize the coke on the catalyst and being reoxidized by steam, which
Tab. 1.7: The conversion, yield of H\textsubscript{2}, and carbon deposition at 750 °C for five different catalysts in the steam reforming of acetic acid [48]. Carbon deposition was estimated based on a 4 h experiment and defined as the percentage of carbon fed to reactor, which deposits on the catalyst. Atmospheric pressure, S/C-ratio=1.5, GHSV= 13050 cm\textsuperscript{3}/(g·h).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion [%]</th>
<th>Y\textsubscript{H\textsubscript{2}} [%]</th>
<th>Carbon deposition [% of carbon feed]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>5</td>
<td>0</td>
<td>4.65</td>
</tr>
<tr>
<td>1 wt% Pt/Al\textsubscript{2}O\textsubscript{3}</td>
<td>8</td>
<td>20</td>
<td>0.37</td>
</tr>
<tr>
<td>0.5 wt% Rh/Al\textsubscript{2}O\textsubscript{3}</td>
<td>55</td>
<td>95</td>
<td>0.39</td>
</tr>
<tr>
<td>17 wt% Ni/Al\textsubscript{2}O\textsubscript{3}</td>
<td>80</td>
<td>99</td>
<td>0.24</td>
</tr>
<tr>
<td>17 wt% Ni/(MgO/Al\textsubscript{2}O\textsubscript{3})</td>
<td>100</td>
<td>100</td>
<td>0.10</td>
</tr>
</tbody>
</table>

also was shown by TPR experiments [68]. Another explanation could be that the CeO\textsubscript{2} can activate H\textsubscript{2}O through dissociative adsorption and the formed OH* or O* can diffuse on to the metal particles and react with the carbon. Mixtures of CeO\textsubscript{2} and ZrO\textsubscript{2} have also been used as support and better performance than with Al\textsubscript{2}O\textsubscript{3} or MgAl\textsubscript{2}O\textsubscript{4} could be achieved [67, 91]. Ni or Rh supported on Ce\textsubscript{0.63}Zr\textsubscript{0.37}O\textsubscript{2} had a higher yield of H\textsubscript{2} compared with Ni or Rh on CeO\textsubscript{2} in the SR of ethanol [92]. Pt/Ce\textsubscript{0.63}Zr\textsubscript{1-x}O\textsubscript{2} catalysts with a ratio between Ce and Zr of 1:3, on the other hand, showed a lower conversion and yield of H\textsubscript{2} compared with Pt/CeO\textsubscript{2} [90].

The influence of the carrier and active metal in the catalyst for SR of acetic acid is illustrated in table 1.7, where the conversion, yield of H\textsubscript{2}, and carbon deposition for four different catalysts and two support materials are shown. When adding metal to the support material conversion increases and the carbon deposition decreases, and when the metal changes from Pt to Rh to Ni the conversion and yield of H\textsubscript{2} increases and the carbon deposition decreases. However, the much higher metal loading on the Ni catalyst will contribute to the increased conversion. Finally table 1.7 shows that adding MgO to an acidic support like Al\textsubscript{2}O\textsubscript{3} increases the conversion and yield of H\textsubscript{2} and diminishes the carbon deposition even further [48].

The metal content in the Ni catalysts is generally around 5-30 wt% [49, 60, 61, 74, 89, 93] and for the noble metals it is often around 1 wt%, although values up to 10 wt% have been reported [48, 58, 63, 84, 94, 95]. The conversion generally increases with increasing metal content [48, 84, 95] and for a Ni-Al co-precipitated catalyst it was found that the optimal Ni loading was 28 wt% [60, 61]. However a Ni content between 10 and 20 wt% is more common as higher loading can cause severe problems with sintering [45]. A recent study by An et al. [80] have shown that the optimal Ni loading on γ-Al\textsubscript{2}O\textsubscript{3} was 12 wt% as the highest conversion and H\textsubscript{2}-yield in combination with lower carbon deposition could be achieved with this catalyst. The different values for Ni loading indicate that the optimal loading depends on the carrier material.

Some of the most promising catalysts for the SR of acetic acid are highlighted in table 1.8 along with their performances. The stability is the time taken for the conversion to decrease 10 % from its initial value. If the conversion has not decreased 10 % within the time shown in the article the stability is indicated as larger than that time. This definition of stability will be used throughout this review. However, the stability of the catalyst is difficult to tabulate
Tab. 1.8: Selected catalysts and their performance in the SR of acetic acid.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>17 wt% Ni</td>
<td>MgO/Al₂O₃</td>
<td>650</td>
<td>1.5</td>
<td>36 (W)</td>
<td>95</td>
<td>-</td>
<td>&gt;45 (1 %)</td>
<td>[48]</td>
</tr>
<tr>
<td>5 wt% Ru</td>
<td>MgO/Al₂O₃</td>
<td>650</td>
<td>1.5</td>
<td>36 (W) d</td>
<td>99</td>
<td>-</td>
<td>75</td>
<td>[48]</td>
</tr>
<tr>
<td>30 wt% Ni</td>
<td>Al₂O₃</td>
<td>600</td>
<td>1.5</td>
<td>12.1</td>
<td>95</td>
<td>75</td>
<td>&gt;30 (6 %)</td>
<td>[82]</td>
</tr>
<tr>
<td>with 8 wt% K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18 wt% Ni</td>
<td>Al₂O₃</td>
<td>600</td>
<td>5.8</td>
<td>16</td>
<td>82</td>
<td>74</td>
<td>-</td>
<td>[96]</td>
</tr>
<tr>
<td>18 wt% Co</td>
<td>La/Al₂O₃</td>
<td>400</td>
<td>1</td>
<td>10.1</td>
<td>85</td>
<td>75</td>
<td>&gt;20 (2 %)</td>
<td>[83]</td>
</tr>
<tr>
<td>0.5 wt% Rh</td>
<td>CeZrO₄</td>
<td>650</td>
<td>3</td>
<td>47</td>
<td>90</td>
<td>80</td>
<td>15</td>
<td>[86]</td>
</tr>
</tbody>
</table>

a (W) indicates that the SV is stated as WHSV.

b Yield of hydrogen defined as moles produced divided by the maximum theoretical yield.

c Time for the conversion or Y_H₂ to decrease 10 % from its initial value. > X indicates that data in the article are shown for X hours, but the conversion have not decreased 10 %. The number in parenthesis is the decrease in conversion in percent.

d WHSV increased to 58 after 40 h.

as it might depend on the space velocity (SV). If the catalyst bed is much larger than required for full conversion then a deactivation front would move down the bed and full conversion might be possible despite that a large part of the catalyst bed has been deactivated. Ideally stability experiments should be conducted at experimental conditions which do not provide full conversion in order to make a good estimate of the deactivation rate and stability. A problem with this might be that under these conditions the carbon deposition potential might be larger as well and therefore not give a suitable estimate of the possible time of operation.

It can be seen that none of the catalysts in table 1.8 have stability over longer periods of time, which is primarily due to carbon formation. It is possible to achieve full conversion and high yields of H₂, but the catalysts are not stable over time, which is the main concern if the SR of bio-oil should have industrial potential.

1.3.3 SR of ethanol

The equilibrium composition in the SR of ethanol is shown in fig. 1.4, but in practice a number of by-products can be formed through the reactions shown in table 1.9. The most common ones are acetaldehyde, acetic acid, acetone, ethene, and methane [49, 50, 57, 93, 97-99]. Reaction 1 and 1a are the overall SR reactions with and without WGS, while reactions 2-9 in table 1.9 constitutes the possible side reactions for the SR of ethanol. Acetone can be converted to coke by the same reactions as in the SR of acetic acid (reactions 9-11 in table 1.4). The dehydration reaction (reaction 3 in table 1.9) should be minimized as ethene is as precursor for carbon formation as indicated by reaction 3a in table 1.9, which is the decomposition of ethene. Ethene has the highest potential for carbon formation of all hydrocarbons [32, 100].

Barattini et al. [57] reported that the main products from the SR of ethanol over an inert material like quartz at temperatures between 400 and 800 °C were acetic acid from oxidation (reaction 5 in table 1.9) and ethene from dehydration (reaction 3 in table 1.9). In the presence of a catalyst and at low degrees of conversion, oxidation to acetic acid and the formation of acetaldehyde were the dominating reactions [57]. At higher conversions the products were CO₂, CO, H₂, and CH₄, which can be formed by combinations of many of the reactions shown in table 1.9. Barattini et al. [57] also reported that acetate or acetic acid were the
key intermediates in the SR of ethanol over NiZnAl-catalysts. These intermediates would correspond well to the mechanism proposed by Takanabe et al. [75], where acetate species participated in surface reactions in the SR of acetic acid.

Acetone and acetaldehyde were reported as the main by-products at low conversions and temperatures below 500 °C over Ni, Ir, and Co supported on ceria by Zhang et al. [93]. Benito et al. [101] concluded, based on a temperature-programmed desorption (TPD) study, that the SR of ethanol proceeded through acetaldehyde species adsorbed on the surface. The surface species could either decompose, be steam reformed, or react with surface species like \( \text{CH}_3^* \) and form acetone, which could undergo SR as well.

Fatsikostas and Verykios [89] and others [95, 102] found acetaldehyde as a by-product along with \( \text{CH}_4 \) and \( \text{C}_2\text{H}_4 \). It therefore seems that the main by-products in the SR of ethanol are acetaldehyde and small hydrocarbons. Acetaldehyde might be an intermediate in the process as it is present in most studies of SR of ethanol. The formation of by-products is generally low at high conversion and the main problem is not the yield of desired products nor activity, but rather catalyst deactivation due to carbon deposition [89, 95].

Based on the literature regarding SR of hydrocarbons and ethanol it seems likely that the most important reactions are the SR of ethanol combined with WGS and SR of methane as these will determine the product distribution. Thermal decomposition is probably also an important reaction, especially at high temperatures. The main deactivation path would probably be through dehydration and subsequent ethene decomposition due the high carbon formation potential of this compound. A reaction network similar to the reactions described above have been proposed by Subramani and Song [99] and can be seen in figure 1.6. In this network it is indicated the acetaldehyde is one of the intermediates, which is in accordance with the literature.

Experimental studies on the SR of ethanol are generally conducted at temperatures between 300 and 800 °C and full conversion can be achieved at 400 °C although mainly to \( \text{CH}_4 \). At higher temperatures the yield of \( \text{CH}_4 \) decreases, because the methanation equilibrium is shifted toward CO and \( \text{H}_2 \), and the yield of \( \text{H}_2 \) increases [57, 93, 97]. This is in accordance with the thermodynamic equilibrium shown in figure 1.4.

---

**Tab. 1.9: Possible reactions in the steam reforming of ethanol [49, 50, 57, 93, 97].**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Name</th>
<th>Reaction scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SR ethanol</td>
<td>( \text{CH}_3\text{CH}_2\text{OH} + 3\ \text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 6\text{H}_2 )</td>
</tr>
<tr>
<td>1a</td>
<td>SR ethanol without WGS</td>
<td>( \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow 2\text{CO} + 4\text{H}_2 )</td>
</tr>
<tr>
<td>2</td>
<td>Dehydrogenation</td>
<td>( \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2 )</td>
</tr>
<tr>
<td>3</td>
<td>Dehydration</td>
<td>( \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2 + \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>3a</td>
<td>Ethene decomposition</td>
<td>( \text{CH}_2\text{CH}_2 \rightarrow 2\text{C}_2 + 2\text{H}_2 )</td>
</tr>
<tr>
<td>4</td>
<td>Decarboxylation</td>
<td>( \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO} )</td>
</tr>
<tr>
<td>5</td>
<td>Oxidation</td>
<td>( \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{H}_2 )</td>
</tr>
<tr>
<td>6</td>
<td>Decomposition</td>
<td>( \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_4 + \text{CO} + \text{H}_2 )</td>
</tr>
<tr>
<td>7</td>
<td>Recombination</td>
<td>( 2\text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{COCH}_3 + \text{CO} + \text{H}_2 )</td>
</tr>
<tr>
<td>8</td>
<td>SR acetone</td>
<td>( \text{CH}_3\text{COCH}_3 + 3\ \text{H}_2\text{O} \rightarrow 3\text{CO} + 6\text{H}_2 )</td>
</tr>
<tr>
<td>9</td>
<td>SR acetic acid</td>
<td>( \text{CH}_3\text{COOH} + 2\ \text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 4\text{H}_2 )</td>
</tr>
</tbody>
</table>
Mechanism and kinetics

The reaction mechanism for SR of ethanol is not completely clear and no general consensus has been reached. However, similarities between the mechanisms proposed for the SR of acetic acid and ethanol do exist.

The surface species involved in the SR of ethanol has been reported as ethoxy, acetate, acetaldehyde, and formic acid [103–105]. One of the mechanisms that have been proposed is based on three main reactions, namely SR of ethanol (reaction 1 in table 1.9), WGS (reaction 1.2), and ethanol decomposition (reaction 6 in table 1.9) [104]. It involves both formic acid and acetaldehyde as intermediates and was proposed by Sahoo et al. [104]. Both the SR and decomposition might occur through acetaldehyde intermediates. In the SR mechanism, the ethanol adsorbs on the surface and undergoes dehydrogenation to acetaldehyde and the steam undergoes dissociative adsorption to OH- and H-species. Acetaldehyde will then decompose to methyl and formaldehyde and both of them are transformed into formic acid, which decomposes to CO$_2$ and H. The reactions involved in this mechanism for the SR of ethanol are [104]:

\[
\begin{align*}
CH_3CH_2OH(g) + 2* & \rightleftharpoons CH_3CH_2O* + H* \\
CH_3CH_2O* + * & \rightleftharpoons CH_3CHO* + H* \\
2* + H_2O(g) & \rightleftharpoons OH* + H* \\
CH_3CHO* + H* & \rightleftharpoons CH_3* + HCHO* \\
CH_3* + OH* & \rightleftharpoons CH_3OH* + * \\
CH_3OH* + * & \rightleftharpoons CH_3O* + H* \\
CH_3O* + * & \rightleftharpoons HCHO* + H* \\
HCHO* + OH* & \rightleftharpoons HCOOH* + H* \\
HCOOH* + 2* & \rightleftharpoons CO_2* + 2H* \\
CO_2* + & \rightleftharpoons CO_2(g) + * \\
2H* & \rightleftharpoons H_2(g) + 2* 
\end{align*}
\]

The ethanol decomposition is suggested to occur through reactions 1.37 and 1.38 combined with the two following reactions [104]:

\[
\begin{align*}
CH_3CHO* + * & \rightleftharpoons CH_4* + CO* \\
CH_4* & \rightleftharpoons CH_4(g) + *
\end{align*}
\]

where the CO* can desorb as shown in reaction 1.52.

In reaction 1.40 there is formed CH$_3$*, which also is an intermediate in the SR of hydrocarbons, and an alternative or parallel path could therefore be reactions 1.5 to 1.12. The path...
might be more probable as it is energetically favorable in the SR of methane. DFT-calculations by Mavrikakis et al. [106] have shown that the C-C bond breaking in reaction 1.40 could be energetically favorable, but the study also indicated that CH₂CO ∗ might be an important intermediate in C-C bond breaking.

The WGS was included in the mechanism by Sahoo et al. [104] and it was assumed to occur through formate species. Usually the WGS is assumed to proceed through CO ∗, CO₂ ∗, H ∗, and O ∗ [107]. Sahoo et al. [104] described the WGS by the following reactions along with the dissociative adsorption of water (reaction 1.39), dissociation of formic acid (reaction 1.45), and dissociative adsorption of H₂ (reaction 1.47) [104].

\[ \text{HCOOH} + + \rightleftharpoons \text{HCOO} + \text{H} + \] (1.50)
\[ \text{HCOO} + + \rightleftharpoons \text{CO} + \text{OH} + \] (1.51)
\[ \text{CO} + \rightleftharpoons \text{CO(g)} + + \] (1.52)
\[ \text{HCOO} + + \rightleftharpoons \text{CO₂} + \text{H} + \] (1.53)

CO₂ and H₂ can desorb from the catalyst through reactions 1.46 and 1.47, respectively. The rate determining steps were proposed to be reactions 1.38, 1.48, and 1.51 for the ethanol SR, ethanol decomposition, and the WGS, respectively, but no reason for this choice was given [104]. A further refinement of this mechanism could be to include the carbon formation, e.g. by reaction 3 and 3a in table 1.9 and also an alternative reaction path for the dissociation of CH₃ ∗.

Rate expressions were deduced based on the three rate determining steps mentioned above and a Langmuir-Hinshelwood approach and showed good agreement with experimental data [104].

The mechanism proposed by Sahoo et al. [104] is more detailed compared to the mechanism proposed by Takanabe et al. [75] for the SR of acetic acid as detailed surface reactions are included. The overall scheme in both mechanisms have similarities: adsorption through the oxygen functionality followed by decomposition to CHₓ and COₓ. However, the mechanism proposed by Sahoo et al. [104] does not use two different adsorption sites for steam and ethanol as proposed by Takanabe et al. [75]. Mechanisms similar to one described above have also been proposed in refs. [101, 108–110].

Another mechanism has been proposed by Busca et al. [105], where the acetaldehyde reacts with O²⁺-species from the surface and forms acetate. Acetate can then react with OH⁻ forming CH₄, CO, and O²⁻ and the CH₄ can then be reformed. Another proposal is that the acetate can decompose to CH₄ and CO₂ [111]. Similar mechanisms have been reported by others [103, 112, 113].

The kinetics of the SR of ethanol have been investigated by Akande et al. [114], who proposed four different models, with different rate limiting steps. The models were based on three basic steps. Step one is the adsorption of ethanol (reaction 1.54); step two is the dissociation of adsorbed ethanol (reaction 1.55); step three is the reaction between gaseous steam and the absorbed species (an Eley-Rideal mechanism as shown in reactions 1.56 and 1.57):

\[ \text{CH₃CH₂OH} + + \rightleftharpoons \text{CH₃CH₂OH} + \] (1.54)
\[ \text{CH₃CH₂OH} + + \rightleftharpoons \text{CH₃OH} + \text{CH₂} + + \] (1.55)
\[ \text{CH₃OH} + + \text{H₂O} \rightleftharpoons \text{CO₂} + 3\text{H₂} + + \] (1.56)
\[ \text{CH₂} + 2\text{H₂O} \rightleftharpoons \text{CO₂} + 3\text{H₂} + + \] (1.57)

Akande et al. [114] concluded that the dissociation of ethanol on the catalyst surface (reaction 1.55) was the rate determining step.
The assumption of an Eley-Rideal type mechanism (reaction 1.56 and 1.57) is questionable as steam-species on the surface of the catalyst is reported to participate in the SR reactions [30, 38, 75, 104]. Furthermore, reactions 1.55 and 1.57 appear unlikely as they would require breaking and rearrangement of several bonds in one step. Therefore this mechanism and derived kinetics seems questionable.

Kinetic models based on simple power law expressions have also shown good agreement with experimental results [114–116]. The reaction order of water has been reported to be slightly negative or zero, while the reaction order of ethanol has been reported to be between 0.43 and 1 [114–116]. The dependence of total pressure has not been investigated.

Catalysts

The SR of ethanol is, like the SR of acetic acid, catalyzed by both base and noble metals. Within the group of noble metals there is disagreement on which metal is most active. Liguras et al. [95] have found that the order of activity for 1 wt% metal on Al$_2$O$_3$ was:

$$\text{Rh} > \text{Pt} > \text{Pd} > \text{Ru}$$

A similar order was reported by Aupretre et al. [92], with the small difference that Pd and Pt switched places. The metal loadings were approx. 1 wt% in this study as well. Basagiannis et al. [97] on the other hand reported that the activity based on conversion decreased in the following order:

$$\text{Pd} > \text{Pt} > \text{Ru} > \text{Rh}$$

The support was also Al$_2$O$_3$ in this study, but the metal loadings were 1 wt%, 0.5 wt%, 5 wt%, and 2 wt%, respectively. Based on TOF, Pt showed a higher activity compared with Pd. The metal crystallites size and dispersion were similar in the studies by Basagiannis et al. [97] and Liguras et al. [95]. The exact reason for the differences in activity is not known, but it might be ascribed to differences in the examined temperature interval, as Basagiannis et al. [97] investigated temperatures between 300 and 400 °C while Liguras et al. [95] investigated the SR of ethanol at temperatures between 600 and 850 °C. Both of the orders of activity for the noble metals in the SR of ethanol are different from what is observed in the SR of acetic acid. This might indicate that different reaction steps are important in the conversion of the two compounds.

Ni is the most used base metal and shows better performance compared with Co [49, 117]. The typical Ni-catalysts used in the SR of ethanol can achieve full conversion at temperatures between 300 and 800 °C depending on the type of support, S/C-ratio, and space velocity [89, 102, 118, 119], while noble metal catalysts showed full conversion at temperatures between 500 and 800 °C [94, 95, 97, 118, 120]. High yields of H$_2$ were achieved at full conversion for both types of catalysts. Similar temperature ranges were employed in the SR of acetic acid and similar performances have been achieved [48, 58, 59].

The activity of the noble metals and Ni are comparable, while the carbon formation is reported to be lower for noble metal catalysts, similar to what is observed in conventional SR and in the SR of acetic acid [30, 92, 121, 122].

Mixtures of different metals were tested by Le Valant et al. [123] in the SR of ethanol. It was shown that Rh-Ni/Al$_2$O$_3$ had an increased stability, conversion, and yield of H$_2$ compared to the Rh/Al$_2$O$_3$ catalyst [123]. The Rh-Ni had 10 wt% Ni and 1 wt% Rh and was compared to a catalyst with 1 wt% Rh so the increased conversion and yield of H$_2$ is expected as more metal sites are available for catalysis. The improved performance was ascribed to an increased activity for SR of CH$_4$ and the WGS due to the presence of Ni on the catalyst [123].
The addition of K to the catalyst in the SR of ethanol has been reported to lower the carbon formation, like in the SR of acetic acid [121, 122].

The influence of the support material is similar to the influence in the SR of acetic acid, namely that the addition of basic oxides to Al₂O₃ improves the performance and stability of the catalyst [89, 124, 125]. Other supports have been tested for SR of ethanol compared with the SR of acetic acid and these are MgO, TiO₂, ZnO, and Y₂O₃. MgO and TiO₂ have been used as support materials for Ru-catalysts. They showed lower activity compared with Al₂O₃, which probably can be ascribed to the much lower surface areas and poorer metal dispersion on the MgO and TiO₂-supported catalysts compared to the Al₂O₃-catalysts [95]. Y₂O₃ has been used as support for Ni catalysts where high conversion and yield of H₂ could be achieved at low temperatures [124]. Y₂O₃ was also found to be the best support for Ru in the SR of glycerin [126].

ZnO as a support material for Ni have shown high activity and good long term stability [127, 128].

Some of the promising catalysts for the SR of ethanol are shown in table 1.10 along with their performances. The yield of H₂ is based on equation 1 in table 1.9 thus 100 % yield corresponds to 6 moles of H₂ pr. mole of ethanol converted. In table 1.10 it can be seen that deactivation is a general problem in the SR of ethanol and the main source for this is carbon deposition.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Support</th>
<th>T [°C]</th>
<th>S/C [mole]</th>
<th>WHSV [h⁻¹]</th>
<th>X [%]</th>
<th>Y_{H₂} [%]</th>
<th>Stabilitya</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 wt% Pt</td>
<td>γ-Al₂O₃</td>
<td>340</td>
<td>1.5</td>
<td>17</td>
<td>98</td>
<td>40</td>
<td>55</td>
<td>[97]</td>
</tr>
<tr>
<td>1 wt% Rh</td>
<td>γ-Al₂O₃</td>
<td>675</td>
<td>2</td>
<td>18.5</td>
<td>99</td>
<td>63</td>
<td>24</td>
<td>[123]</td>
</tr>
<tr>
<td>+ 10 wt% Ni</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 wt% Ir</td>
<td>CeO₂</td>
<td>650</td>
<td>1.5</td>
<td>12.6</td>
<td>99</td>
<td>75</td>
<td>300</td>
<td>[93]</td>
</tr>
<tr>
<td>15 wt% Co</td>
<td>CeO₂</td>
<td>700</td>
<td>1.5</td>
<td>12.6</td>
<td>99</td>
<td>75</td>
<td>70</td>
<td>[93]</td>
</tr>
<tr>
<td>15.3 wt% Ni</td>
<td>La₂O₃</td>
<td>320</td>
<td>1.5</td>
<td>0.6</td>
<td>99</td>
<td>60</td>
<td>60</td>
<td>[124]</td>
</tr>
</tbody>
</table>

a Time for the conversion or Y_{H₂} to decrease 10 % from its initial value.

1.3.4 SR of oxygenated compounds

Several other oxygenated compounds than ethanol and acetic acid have also been tested in SR as model compounds for bio-oil. These include aromatic compounds like phenol and m-cresol, or smaller compounds, like ethyl acetate and butanol. The temperature needed for full conversion of oxygenates depends on the size and type of compound. The larger and more aromatic compounds require higher temperatures to reach full conversion [59], as is shown in table 1.11.

The carbon formation in the SR of fossil oil derived products is largest for olefins and aromatics and also larger for large molecules compared with smaller ones [32]. Therefore benzene will deposit more coke than cyclohexane, which would deposit more than butane [32]. A similar pattern seems to fit the SR of oxygenates as carbon deposition from aromatic molecules, like m-cresol, or large molecules, like sugars, is hard to avoid [59, 129, 130]. The carbon deposition in the SR of m-xylene and glucose has also been reported to be larger than
Tab. 1.11: The temperature needed for full conversion of different model compounds using a fixed bed reactor and a Ni/Al$_2$O$_3$-catalyst [59]. Operating conditions: LHSV: 10.1 h$^{-1}$, S/C: 6, pressure: 1 atm.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>CH$_3$COOH</td>
<td>450</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>HOCH$_2$CH$_2$OH</td>
<td>500</td>
</tr>
<tr>
<td>Acetone</td>
<td>CH$_3$COCH$_3$</td>
<td>500</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>C$_2$H$_5$COOCH$_3$</td>
<td>550</td>
</tr>
<tr>
<td>m-xylene</td>
<td>C$_6$H$_4$(CH$_3$)$_2$</td>
<td>650</td>
</tr>
<tr>
<td>Glucose</td>
<td>C$_6$H$_12$O$_6$</td>
<td>750</td>
</tr>
</tbody>
</table>

from SR of acetone and acetic acid under similar conditions and using the same catalyst [59]. It has also been shown that the carbon deposition increases with the chain length of both alcohols and ketones over Ni-catalysts [131]. The order of carbon deposition on same catalyst and under similar condition for several oxygenates is [59]:

Glucose > m-xylene > Ethyl acetate > Acetone > Ethylene glycol > Acetic acid

One type of compound that has proved difficult to reform is sugars, which can be present in amounts up to 10 wt% of the bio-oil. Sugars are non-volatile and thermal decomposition before the reactor bed is therefore possible. This can form char in the freeboard of the reactor which will deposit on the catalyst particles and in the reactor, thus high S/C-ratios (above 10) are needed if char formation should be diminished [132]. The steam is used to gasify the char, which otherwise would deposit on the catalyst causing deactivation. The char deposition is larger for disaccharides compared with monosaccharides, as char deposition is unavoidable in the SR of sucrose even at very high S/C-ratios (>30) [132]. SR of glucose and xylose with low carbon deposition could be achieved at high S/C-ratios (>10). The temperatures used in the SR of sugars are around 800°C and H$_2$-yields between 70 and 90 % at full conversion has been achieved [59, 132]. Due to the issues with volatility of sugars it has been proposed to process them in aqueous phase reforming (APR), which will be described in section 1.6.2.

Another compound, which has been reported to be present in large amounts in bio-oil is m-cresol (C$_7$H$_8$O). This compound has also proven difficult to reform over Ni-catalysts. High temperatures (up to 900°C) and S/C-ratios (up to 6) were needed for full conversion [129, 130, 132]. At these conditions there was still some carbon formation. This problem could be solved by recycling the liquid effluent from the reactor and hereby significantly increase the S/C, which caused the carbon formation to decrease to an acceptable level [129].

Some of the side reactions, which are reported to occur in the SR of m-cresol, are demethylation, isomerization, methylation, and polymerization [129, 130].

Steam reforming of ethylene glycol is proposed to occur through dioxy adsorbed species [133]. This compound will decompose mainly by breaking of C-H and C-C bonds forming CO and H$_2$. The breaking of the C-O bond could result in carbon deposition [133]. The mechanism is similar to ones proposed for ethanol with the difference that ethanol only have one oxy-bond to the surface.
<table>
<thead>
<tr>
<th>Feed</th>
<th>Metal</th>
<th>Content [wt%]</th>
<th>Support</th>
<th>Temp. [°C]</th>
<th>S/C</th>
<th>GHSV&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$Y_{H_2}$</th>
<th>Stability&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m$-Cresol</td>
<td>Ni</td>
<td>&gt; 6</td>
<td>MgO-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>800-900</td>
<td>5-5</td>
<td>0.5 (W)</td>
<td>82</td>
<td>6</td>
<td>[129]</td>
</tr>
<tr>
<td>$m$-Cresol</td>
<td>Ni</td>
<td>-</td>
<td>UC G-90C</td>
<td>625-875</td>
<td>3-6</td>
<td>8650</td>
<td>77</td>
<td>129</td>
<td></td>
</tr>
<tr>
<td>Dibenzyl Ether</td>
<td>Ni</td>
<td>-</td>
<td>UC G-90C</td>
<td>625-875</td>
<td>3-6</td>
<td>11790</td>
<td>85</td>
<td>129</td>
<td></td>
</tr>
<tr>
<td>Glucose</td>
<td>Ni</td>
<td>U C G-90C</td>
<td>-</td>
<td>7-47</td>
<td>538-717</td>
<td>89</td>
<td>2</td>
<td>129</td>
<td></td>
</tr>
<tr>
<td>Sucrose</td>
<td>Ni</td>
<td>UC G-90C</td>
<td>-</td>
<td>34</td>
<td>562</td>
<td>72</td>
<td>2</td>
<td>2</td>
<td>132</td>
</tr>
<tr>
<td>Phenol</td>
<td>Rh</td>
<td>0.5</td>
<td>MgO</td>
<td>575-725</td>
<td>13</td>
<td>32,400</td>
<td>92</td>
<td>134</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>Rh</td>
<td>0.5</td>
<td>CeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>575-725</td>
<td>13</td>
<td>32,400</td>
<td>78</td>
<td>134</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>Rh</td>
<td>0.5</td>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>575-725</td>
<td>13</td>
<td>32,400</td>
<td>78</td>
<td>134</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>Rh</td>
<td>0.5</td>
<td>MgZrCeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>575-725</td>
<td>13</td>
<td>32,400</td>
<td>71</td>
<td>134</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>Rh</td>
<td>0.5</td>
<td>MgZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>575-725</td>
<td>13</td>
<td>32,400</td>
<td>84</td>
<td>134</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>Rh</td>
<td>1.5</td>
<td>CeZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>575-725</td>
<td>7-13</td>
<td>80,000</td>
<td>80</td>
<td>24</td>
<td>135</td>
</tr>
<tr>
<td>Phenol</td>
<td>-</td>
<td>-</td>
<td>Calcite</td>
<td>650-800</td>
<td>11-13</td>
<td>22,000</td>
<td>15&lt;sup&gt;c&lt;/sup&gt;</td>
<td>136</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>-</td>
<td>-</td>
<td>Dolomite</td>
<td>650-800</td>
<td>11</td>
<td>22,000</td>
<td>17&lt;sup&gt;c&lt;/sup&gt;</td>
<td>137</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>Pt</td>
<td>1</td>
<td>CeZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>686-778</td>
<td>17</td>
<td>43</td>
<td>93</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>Rh</td>
<td>1</td>
<td>CeZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>675-771</td>
<td>17</td>
<td>43</td>
<td>97</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>Pd</td>
<td>1</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>672-766</td>
<td>17</td>
<td>43</td>
<td>58</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>Pd</td>
<td>1</td>
<td>CeZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>687-781</td>
<td>17</td>
<td>43</td>
<td>99</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>Glucose</td>
<td>Ni</td>
<td>30</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>300-800</td>
<td>1-9</td>
<td>10.1(W)</td>
<td>87</td>
<td>3</td>
<td>59</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>Ni</td>
<td>30</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>300-800</td>
<td>1-9</td>
<td>10.1(W)</td>
<td>90</td>
<td>11</td>
<td>59</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>Ni</td>
<td>30</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>300-800</td>
<td>1-9</td>
<td>10.1(W)</td>
<td>92.5</td>
<td>15</td>
<td>59</td>
</tr>
<tr>
<td>Acetol</td>
<td>Ni</td>
<td>23-33</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>550-750</td>
<td>5.6</td>
<td>30,000-60,000</td>
<td></td>
<td></td>
<td>61</td>
</tr>
<tr>
<td>$n$-butanol</td>
<td>Ni</td>
<td>23-33</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>550-750</td>
<td>14.7</td>
<td>30,000-60,000</td>
<td></td>
<td></td>
<td>61</td>
</tr>
</tbody>
</table>

<sup>a</sup> (W) indicates that the SV is stated as WHSV.

<sup>b</sup> Time for the conversion or $Y_{H_2}$ to decrease 10% from its initial value. > X indicates that data in the article are shown for X hours, but the conversion have not decreased 10%.

<sup>c</sup> At conversion around 30%.
Steam reforming of phenol has also been investigated with various metals and support materials [67, 134–138]. In these studies high S/C-ratios are often employed and despite this full conversion is rarely achieved. One of exception is catalysts with Rh supported on mixed metal oxides consisting of Ce, Mg, and Zr, which have been tested in the SR of phenol at temperatures between 350 and 550 °C and showed high degrees of conversion and high yields of H$_2$ [139]. Reaction mechanisms have not been proposed for the SR of phenol but studies have indicated phenol needs two different adsorption sites adjacent to each other for bonding to the surface and that some of the involved surfaces species are carbonates and formates [136, 139]. Based on a study by Rioche et al. [67] it appears that the Rh followed by Pt and Pd is the most active metal for the SR of phenol (see table 1.12).

Suggested reaction mechanisms for compounds larger than ethanol and acetic acid are few and not very specific as indicated above. This is probably due to the large number of possible products and surfaces species, which can react in many different ways. This is similar to what is observed in the SR of hydrocarbons, where an exact mechanism only has been elucidated for methane and paraffins.

The catalyst and operational conditions used in the SR of other model compounds than acetic acid and ethanol are shown in table 1.12 along with the performance of the catalysts. Specifically the SR of phenol requires very high S/C-ratios and despite the high S/C and use of noble metals, the catalyst is not stable for more than 24 h [135].

An interesting point observed in the SR of phenol is that CeZrO$_2$ appears to be a more interesting support as the hydrogen yield, in two of the cases, is improved when shifting from Al$_2$O$_3$ to CeZrO$_2$ [67]. This in accordance with results from SR of ethanol and acetic acid.

From table 1.12 it can be seen that high yields of H$_2$ is possible, but also that most of the catalysts suffer from rapid deactivation, despite high S/C-ratios.

### 1.3.5 SR of bio-oil

The SR of whole bio-oil and the aqueous fraction of the bio-oil (formed by fractionation due to water addition) has been tested over different catalysts and using different experimental setups. The aqueous phase contains water soluble oxygenates, like acetic acid, hydroxyacetone, furans, and phenols [140]. The organic fraction contains lignin-like compounds and other oxygenated compounds, like sugars, and can be a substitute for phenol in the production of phenol-formaldehyde resins after extraction with ethyl acetate [12, 141]. The aqueous fraction has a S/C ratio around 4 on weight basis or 6 to 8 on a molar basis, which corresponds well to the desired composition for SR and additional water is not needed (see table 1.13) [12, 141–144]. A slurry of bio-oil and char has also been processed in a fluidized bed reactor, but the char content only enhanced the problems with coke and ash formation, which entailed a lowered overall conversion and a shorter lifetime of the catalyst [145].

The reactions, which occur in the SR of bio-oil, are a combination of all the reactions, mentioned in section 1.3.2 and 1.3.3, and the reaction network is therefore large and complicated. The thermal decomposition and SR are, like for the model compounds, probably the most important reactions. Due to the large number of compounds in the bio-oil it might be hard to develop a detailed kinetic model for SR of bio-oil and it has not been attempted so far. However, a lumped kinetic model based on the different functional groups, chain length, or other subdivisions might be used to describe the reaction.

The metals used as catalysts in SR of bio-oil are similar to the ones used in the studies of model compounds and ranges from base to noble metal catalysts, although Ni catalysts are
favored [58, 144, 146-148]. The order of activity for the different metals might be similar to what is observed with model compounds and in the SR of hydrocarbons.

Garcia et al. [148] showed that the adding Cr or Co to a Ni catalyst could increase H\textsubscript{2} and decrease the yield of methane and benzene. Adding La\textsubscript{2}O\textsubscript{3} or MgO to alumina had a similar effect on the product distribution, which was ascribed to an increased steam gasification [148].

Sorbents for CO\textsubscript{2}, like dolomite or CaO, have also been tested as catalysts in SR of bio-oil and simultaneous CO\textsubscript{2} capture [149]. The degree of conversion is not stated but high yields of H\textsubscript{2} and a low production of CO\textsubscript{2} initially can be achieved at 600 °C. However, the sorbents deactivate fast and lose activity when regenerated [149].

The catalysts used to convert bio-oil might be deactivated by sintering and carbon formation, like for the model compounds. However, there is another problem when processing biomass derived products, which is the content of inorganics. Alkali or phosphor containing salts from the biomass might be present in the bio-oil and deposit on the catalysts during SR and may also cause deactivation [22, 23]. Sulfur containing hydrocarbons might be present in the bio-oil as well and these are known poisons to Ni and noble metal catalysts [29-31, 36]. A more thorough discussion of this problem is presented in section 1.4.

Conversion of bio-oil around 100 % and H\textsubscript{2}-yields between 60 and 100 % can be achieved [12, 58, 141]. The temperature needed for full conversion is between 600 and 800 °C depending on the other operating conditions. The type of reactors used in the SR of bio-oil ranges from fixed bed with trickle flow or liquid spray injection to fluidized beds. These configurations will be discussed further in section 1.5. The catalysts examined in SR of bio-oil and the operation conditions are shown in table 1.13. The stability of the catalyst is also shown and it can be seen that in most cases the catalyst deactivates rather fast, typically within 10 h mainly due to be carbon deposition by formation of gum or pyrolytic coke.

Based on table 1.13 it might be concluded that fluidized beds are more suited for the SR of bio-oil as the stability is higher for these reactors probably because the catalyst particles experience changing conditions as they move around in the bed, including those where coke can be gasified. However, the time of stable of operation is still far from what would be required for an industrial process at least for single stage operation with no regeneration of the catalyst.

In table 1.13 it can be seen that the temperature interval investigated is similar to the temperatures used in the SR of acetic acid and ethanol. The S/C-ratios are higher compared to SR of acetic acid and ethanol, but lower compared with SR of phenol.

### 1.4 Sulfur poisoning

Sulfur containing hydrocarbons and especially H\textsubscript{2}S are known poisons to both Ni and noble metals. The deactivation occurs because the sulfur binds strongly to the metal and so even very small amounts lead to severe deactivation [29-31, 36]. The sulfur blocks the active sites and reduces the activity of the catalysts. The S-bonding is reversible by treatment with H\textsubscript{2}, but the driving force for the sulfur desorption is small [30]. The sulfur poisoning can be used beneficially as in the SPARG-process from Haldor Topsoe A/S, where H\textsubscript{2}S in ppm levels is used to block the most active step sites on a Ni-catalyst [43, 44]. This decreases the coke formation, as step sites are very active in the whisker formation, which allows for operation at low S/C-ratios [30, 31].
<table>
<thead>
<tr>
<th>Type of oil</th>
<th>Metal</th>
<th>Metal Content [wt%]</th>
<th>Support</th>
<th>Temp. [°C]</th>
<th>S/C [mole/mole]</th>
<th>GC_HSV(^a) [h(^{-1})]</th>
<th>Y(_{H_2}) [% of st.]</th>
<th>Bed type</th>
<th>Stability(^b) [h]</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aq. poplar</td>
<td>Ni</td>
<td>15</td>
<td>Al(_2)O(_3)</td>
<td>825-875</td>
<td>5-11</td>
<td>62,300-126,000</td>
<td>87</td>
<td>Fixed</td>
<td>0.5</td>
<td>[148]</td>
</tr>
<tr>
<td>Aq. pine</td>
<td>Ni</td>
<td></td>
<td>C11-NK</td>
<td>800-850</td>
<td>7-9</td>
<td>770-1000</td>
<td>89</td>
<td>Fluid</td>
<td>90</td>
<td>[150]</td>
</tr>
<tr>
<td>Hemiceleolose</td>
<td>Ni</td>
<td></td>
<td>C11-NK</td>
<td>850</td>
<td>7-14.1</td>
<td>800-1000</td>
<td>77</td>
<td>Fluid</td>
<td>2.5</td>
<td>[150]</td>
</tr>
<tr>
<td>Glycerin</td>
<td>Ni</td>
<td></td>
<td>C11-NK</td>
<td>850</td>
<td>2.1-2.7</td>
<td>1400</td>
<td>74</td>
<td>Fluid</td>
<td>-</td>
<td>[150]</td>
</tr>
<tr>
<td>Grease</td>
<td>Ni</td>
<td></td>
<td>C11-NK</td>
<td>600-850</td>
<td>2.7-5</td>
<td>950-1100</td>
<td>82</td>
<td>Fluid</td>
<td>16</td>
<td>[150]</td>
</tr>
<tr>
<td>Hardwood</td>
<td>Ni</td>
<td></td>
<td>C11-NK</td>
<td>850</td>
<td>5.8</td>
<td></td>
<td>80</td>
<td>Fluid</td>
<td>16</td>
<td>[146]</td>
</tr>
<tr>
<td>Hardwood</td>
<td>Ni</td>
<td></td>
<td>NREL catalyst</td>
<td>850</td>
<td>5.8</td>
<td></td>
<td>-</td>
<td>Fluid</td>
<td>4</td>
<td>[146]</td>
</tr>
<tr>
<td>Aq. saw dust</td>
<td>Ni</td>
<td>20</td>
<td>Dolomite</td>
<td>600-800</td>
<td>6.5</td>
<td>1.5 (W)</td>
<td>74</td>
<td>Fluid</td>
<td>5</td>
<td>[142]</td>
</tr>
<tr>
<td>Aq. beech wood</td>
<td>Ni</td>
<td></td>
<td>NREL catalyst</td>
<td>300-1000</td>
<td>8.2</td>
<td>300-600</td>
<td>90</td>
<td>Fixed</td>
<td>5</td>
<td>[143]</td>
</tr>
<tr>
<td>Aq. pine wood</td>
<td>Ni</td>
<td>28.5</td>
<td>Ca/MgAl</td>
<td>650</td>
<td>7.6</td>
<td>5,400-11,800</td>
<td>-</td>
<td>Fluid</td>
<td>2</td>
<td>[144]</td>
</tr>
<tr>
<td>Saw dust</td>
<td>Ni</td>
<td>7.2</td>
<td>MgO</td>
<td>700-900</td>
<td>1-16</td>
<td>1.5 (W)</td>
<td>80</td>
<td>Fixed(^c)</td>
<td></td>
<td>[147]</td>
</tr>
<tr>
<td>Saw dust</td>
<td>Ni</td>
<td>15</td>
<td>γ-Al(_2)O(_3)</td>
<td>350-550</td>
<td>6.1</td>
<td>12,000</td>
<td>50</td>
<td>Fixed</td>
<td></td>
<td>[151]</td>
</tr>
<tr>
<td>Saw dust</td>
<td>Ni</td>
<td>15</td>
<td>CNT</td>
<td>350-550</td>
<td>2-6.1</td>
<td>12,000</td>
<td>92.5</td>
<td>Fixed</td>
<td>6</td>
<td>[151]</td>
</tr>
<tr>
<td>Beech wood</td>
<td>Pt</td>
<td>1</td>
<td>Ce(<em>{0.5})Zr(</em>{0.5})O(_2)</td>
<td>700-780</td>
<td>2.5-10</td>
<td>0.6-2.5 (W)</td>
<td>70</td>
<td>Monolith</td>
<td></td>
<td>[152]</td>
</tr>
<tr>
<td>Beech wood</td>
<td>Rh</td>
<td>1</td>
<td>Ce(<em>{0.5})Zr(</em>{0.5})O(_2)</td>
<td>700-780</td>
<td>2.5-10</td>
<td></td>
<td>52</td>
<td>Monolith</td>
<td></td>
<td>[152]</td>
</tr>
<tr>
<td>Aq. beech wood</td>
<td>Ru</td>
<td>5</td>
<td>MgAl(_2)O(_4)</td>
<td>550-800</td>
<td>7.2</td>
<td>3000-17000</td>
<td>60</td>
<td>Fixed</td>
<td>&gt; 45</td>
<td>[58]</td>
</tr>
<tr>
<td>Beech wood</td>
<td>Pt</td>
<td>1</td>
<td>CeZrO(_2)</td>
<td>740-860</td>
<td>10.8</td>
<td>3090</td>
<td>70</td>
<td>Fixed</td>
<td>&gt; 9(^d)</td>
<td>[67]</td>
</tr>
<tr>
<td>Beech wood</td>
<td>Rh</td>
<td>1</td>
<td>CeZrO(_2)</td>
<td>860</td>
<td>10.8</td>
<td>3090</td>
<td>75</td>
<td>Fixed</td>
<td></td>
<td>[67]</td>
</tr>
<tr>
<td>Model oil 1(^e)</td>
<td>Ni</td>
<td>7.2</td>
<td>MgO</td>
<td>450-850</td>
<td>1-10</td>
<td>0.8 (W)</td>
<td>85</td>
<td>Fixed</td>
<td>8</td>
<td>[147]</td>
</tr>
<tr>
<td>Model oil 2(^f)</td>
<td>Ni</td>
<td>7.2</td>
<td>MgO</td>
<td>450-850</td>
<td>1-10</td>
<td>0.8 (W)</td>
<td>85</td>
<td>Fixed</td>
<td>10</td>
<td>[147]</td>
</tr>
<tr>
<td>Aq. rice hull</td>
<td>Ni</td>
<td>5-12</td>
<td>CeO(_2)-ZrO</td>
<td>450-800</td>
<td>3.2-5.8</td>
<td>-</td>
<td>70</td>
<td>Fixed</td>
<td>0.5</td>
<td>[91]</td>
</tr>
</tbody>
</table>

\(^a\) (W) indicates that the SV is WHSV

\(^b\) Time for the conversion or Y\(_{H_2}\) to decrease 10 % from its initial value. > X indicates that data in the article are shown for X hours, but the conversion have not decreased 10 %.

\(^c\) 2-stage reactor with a guard bed

\(^d\) Autothermal conditions

\(^e\) Consisting of equal amounts of methanol, ethanol, acetic acid, and acetone on a weight basis

\(^f\) Consisting of equal amounts of furfural, phenol, catechol, and m-cresol on a weight basis
1. Literature review

The sulfur content in bio-oil can be up to 500 ppmw and for the aqueous fraction sulfur contents up to 370 ppmw have been reported [13, 23, 91], which is significant amounts as the H₂S to the conventional steam reformers are kept in the ppb-range [29]. Thus, this might be a problem for the metal catalysts shown in table 1.13, although it has not been addressed in the literature.

In the literature on the SR of hydrocarbons some information on sulfur resistant catalytic systems can be found [153–156]. One of the techniques used to avoid sulfur poisoning is to add a compound which binds sulfur stronger than the active metal, e.g. adding CuO to noble metal based catalysts [153, 154]. The binding of sulfur to the CuO is more thermodynamically stable and will act as a sacrificial barrier until a certain sulfur level is reached [153, 154]. A NiW catalyst on dolomite has also shown good performance for reforming of naphthalene with sulfur present as H₂S in concentrations up to 500 ppmw [155]. The sulfur tolerance was ascribed to an increased sulfur dissociation because of WO₃, which accelerates the sulfur release as H₂S from the catalyst [155]. Another possibility is to use a support material like Ce₀.₈Gd₀.₂O₁₉, where a redox reaction can occur and hereby remove the sulfur on the catalyst as H₂S [156]. However, both explanations for the S-resistance may be debated as H₂S released from the catalyst would be expected to bind to the Ni or the noble metal again forming adsorbed sulfide species. Further investigations of the mechanisms for the sulfur resistance are therefore needed.

1.5 Reactors and reforming concepts

The most widely used type of reactor in the literature is a fixed bed reactor with both liquid and gas feeds. Light model compounds like acetic acid and ethanol are typically vaporized upstream the reactor and transported to the reactor through heated lines. The bio-oil or larger model compounds cannot be vaporized without leaving a significant amount of residue and vaporization prior to the reactor is therefore not suitable. Furthermore rapid heating can cause thermal decomposition and coke formation. In studies where heavier compounds, like sugars or bio-oil, are converted other feeding techniques have been used to avoid or minimize these problems. One of them is to spray the liquid on to the catalyst through a spray nozzle in order to minimize the thermal decomposition and char formation before the reactor bed [141, 146, 150, 157, 158]. Other techniques like using droplets, where the bio-oil is encapsulated in a water droplet and dropped onto the catalyst bed [67], or only adding bio-oil drop wise [147], have also been used to minimize the thermal decomposition prior to the catalyst bed. Apart from the spray nozzle these techniques are mainly suitable for laboratory scale experiments.

In order to minimize the carbon deposition, related with the SR of bio-oil, different experimental setups have been investigated. These are two bed setups, in analogy to the prereformer concept, and a fluidized bed reactor [82, 124, 147, 150, 159, 160] as discussed below. Changes to the reaction conditions like co-feeding with O₂ has also been investigated and will be discussed along with other variations to the SR process.

Relatively high S/C-ratios are used in the SR of oxygenates as indicated in tables 1.12 and 1.13. From an industrial point-of-view this is a problem as high S/C-ratios are expensive, because more steam is needed. This will lead to high expenses for superheating of water and the size of piping and reactors will have to be increased [30]. Therefore it is important to optimize the catalyst and reactor conditions to achieve low carbon deposition at low S/C-ratios.
1. Literature review

1.5.1 Prereforming

A two reactor plant is an analogy to a conventional SR plant, with a prereformer and a reformer (see figure 1.2). The first reactor is used to convert the reactants into CH\textsubscript{4}, CO, CO\textsubscript{2}, and H\textsubscript{2}, while the second reactor is used to reform the CH\textsubscript{4} at higher temperatures [147]. The first reactor in a two reactor plant could be an inexpensive material like dolomite, which can be replaced when it is deactivated by carbon deposition. Vaporization, decomposition, and carbon deposition will mainly occur in the first reactor. The second bed would consist of a metal catalyst, which only process gaseous compounds and therefore the coke formation should be much smaller and the catalysts life time longer [147].

Another two-bed setup has been proposed for the SR of ethanol. Here the first bed was a Cu-catalyst operated at 370 °C, which converted the ethanol into acetaldehyde by dehydrogenation (see reaction 2 in table 1.9). The second bed was a Ni-catalyst operated at 650 °C, which could steam reform acetaldehyde and avoid the formation of coke and only have a small production of other by-products [159].

A similar setup with two Ni-catalysts operated at different temperature, like in the conventional SR process, could also be used. For this concept it is mainly interesting to examine the low temperature SR of oxygenates as commercial catalysts for CH\textsubscript{4} conversion exist. Experiments have been conducted on the low temperature SR of both acetic acid and ethanol and full conversion could be achieved between 350 and 450 °C [82, 97, 124]. The products mainly consisted of CH\textsubscript{4}, H\textsubscript{2}, CO\textsubscript{2}, and CO and the major part was CH\textsubscript{4}. The yield of CH\textsubscript{4} decreases with increasing temperature because the SR of CH\textsubscript{4} is favored at higher temperatures. The operating temperatures of 350-450 °C correspond well to the conventional prereformer conditions. Carbon formation might still be a problem at low temperatures as the carbon formation in the SR of oxygenates is found to decrease with increasing temperature [53, 54, 74]. However, a study by Rabenstein and Hacker [161] have shown that the carbon formation in the SR of ethanol have a maximum around 500-600 °C and thermodynamic calculations on the SR of acetic acid, acetone, and ethylene glycol indicate that if a S/C ratio of 3 or above is used then the carbon formation should be minimal [53]. However thermodynamics is perhaps not the most suitable way to evaluate carbon formation as it is mainly controlled by kinetics. The carbon formation might be avoided in the low temperature range (300-500 °C) and the prereformer concept could be beneficial. This is also seen in the low temperature experiments where stable operation over 50 to 60 h could be achieved [97, 124]. The yield of CH\textsubscript{4} is high at low temperatures and an additional reforming step is needed if high amounts of H\textsubscript{2} should be produced. A beneficial feature of the prereformer concept could be that the initial coke formation from heating the bio-oil could be decreased as the reactor inlet temperature would be much lower compared with a single step reformer, where temperatures between 600 and 800 °C are needed for full conversion of bio-oil to synthesis gas.

1.5.2 Fluidized bed reforming

Fluidized beds have also been examined as reactors for the SR of oxygenates [144, 145, 150, 160, 162], as it is believed that the thermal decomposition can be controlled better in this type of reactor [150]. This might be substantiated by table 1.13 where it can be seen that the stability is generally higher for the fluidized beds. Thermal decomposition can cause coke deposition which in a fixed bed reactor would form a layer of coke in the top and freeboard of the reactor. When using a fluidized bed reactor all of the catalyst particles are in contact with the fresh bio-oil, the carbon deposition on each particle will be smaller and because of the circulation of particles there is also a larger chance of gasifying the carbon on the particles. The time of stable operation has been shown to increase when using a fluidized bed and
the regeneration time by steam gasification for the catalyst was also decreased [150]. This might substantiate less carbon deposition as the lifetime is longer and the regeneration time is shorter. A study by Lan et al. [163] have also shown that the coke deposition at similar conditions and with the same catalyst is lower in a fluidized bed compared to a fixed bed.

The fluidized bed could also be made as a dual bed, where the catalyst circulates between the beds. It is used as a SR catalyst in one of the beds and regenerated by gasification or carbon oxidation in the other bed. However, the catalyst might need to be reduced again after the oxidation process which would require a third bed. This concept has, to the author’s knowledge, not been tested for this process although it is well known from catalytic cracking.

High yields of H$_2$ and full conversion could achieved in fluidized beds, but deactivation by carbon deposition and also attrition of the catalyst is still a problem [145, 150, 162]. The conventional support materials, like Al$_2$O$_3$ used in the SR are rather soft and unsuited for fluidization due to attrition [160]. Therefore more durable support materials are needed and mixing Al with Ca or Mg have improved the mechanical strength of the support making it more suitable for fluidization [144, 160]. Mixing of Mg and Al resulted in the best catalyst with a high conversion and yield of H$_2$ similar to what is observed when using mixed MgO and Al$_2$O$_3$ supports in fixed bed reactors. A recent study by Xu et al. [164] indicates that the main source of deactivation is sintering of catalyst and not carbon deposition. Therefore there might be three significant deactivation mechanisms, namely sintering, attrition, and carbon deposition, associated with utilizing fluidized bed reactors.

A fluidized bed can be combined with a fixed bed reactor in a staged reactor concept where the bio-oil is first passed through a fluidized bed of low activity materials, like sand, and then through a fixed bed consisting of a SR catalyst [162, 165]. The idea is that the evaporation of bio-oil occurs in a fluidized bed and the resulting vapors are steam reformed in a catalytic fixed bed [162, 165]. The temperatures in the two bed can be varied, but generally a high temperature (above 700 °C) is needed for complete conversion of the hydrocarbons in the fixed bed. The fraction of CH$_4$ and other small hydrocarbons are minimized resulting in an easy reformable off-gas from the fluidized bed. High yields of H$_2$ could achieved, but the carbon yield was below 100 % indicating that carbon deposition still occurred [165].

1.5.3 Autothermal reforming

The formation of carbon deposition is, as mentioned earlier, a major problem with the SR of oxygenates, as up to 15 % of the carbon might be deposited in the reactor [132, 150]. This might be reduced by co-feeding O$_2$ to the system, which could gasify or combust some of the deposited carbon and also provide energy for the endothermic reforming reactions. Experiments and also thermodynamics have shown that the H$_2$-yield decreases and the CO$_2$-yield increases compared with SR without O$_2$, while the coke formation is suppressed [54, 67, 166–168]. Laosiripojana et al. [169], on the other hand, investigated the oxidative SR of ethanol at S/C of 1.5 over Ni/CeO$_2$ and found that the addition of 0.4–0.6 mole of oxygen pr. mole of carbon (O/C-ratio) increased the yield of H$_2$ and lowered the carbon deposition. Over a Ni/Al$_2$O$_3$-catalyst at S/C-ratio of 1.5 oxygen addition, in general, increased the H$_2$-yield [169]. Medrano et al. [168] reported that an O/C-ratio of 0.04 increased the stability of the catalyst in the SR of acetic acid at 650 °C, WHSV of 9.3 h$^{-1}$, and S/C-ratio of 5.6 with only a minor influence on the H$_2$ yield. Similar results were found in the SR of bio-oil where the addition of oxygen in an O/C ratio of 0.04 decreased the carbon deposition by 50 % in a fluidized bed [144]. The above described effects are functions of the amount of O$_2$ fed to the reactor as increasing amounts of oxygen will decrease the carbon deposition and H$_2$-yield [124]. The amount of O$_2$ needed for autothermal conditions is dependent on the type
of biomass that is converted. It will increase with temperature and does not change much with increasing S/C-ratios [54]. An increased risk of catalyst sintering has been reported with oxygen present which might counterbalance the advantage of the decrease in carbon deposition [67, 166]. It should be noted that the process equipment for producing pure O\textsubscript{2} is expensive and is only economically viable for large industrial autothermal reformers [31].

In the autothermal reforming heat for the endothermic reforming reactions is supplied by combustion of some of the bio-oil. Thus, no external heat must be supplied to the reactor at autothermal conditions. However, heat should be supplied to preheat the reactants, because the H\textsubscript{2} yield would decrease significantly when heat supplied by the oxidation of bio-oil should preheat the feed as well [54]. The oxygen could also be supplied in amounts less than needed for autothermal conditions, which could decrease the coke formation and only affect the H\textsubscript{2} yield slightly. A hybrid reactor with both external (furnace) and internal heat supply (oxygen) could be used for this purpose.

### 1.5.4 Catalytic partial oxidation

Oxygen can be supplied as a reactant without H\textsubscript{2}O, which is referred to as catalytic partial oxidation (CPO), because the amount of air supplied is substoichiometric for combustion. Schmidt et al. [158] has tested the CPO and autothermal SR (reaction with both H\textsubscript{2}O and O\textsubscript{2}) in two different types of setups. A staged system with a large freeboard over a catalytic bed of Rh-Ce-Al\textsubscript{2}O\textsubscript{3}, where the bio-oil is introduced as a mist through a spray nozzle, and a similar setup where the spray is just above the catalyst bed. The staged setup provides better protection of the catalyst and a higher yield of H\textsubscript{2}, which could be due to a more efficient mixing of the gases prior to the reactor [158]. The two setups were tested both in the CPO and autothermal SR with bio-oil as feed. Both of these systems showed relatively high yields of H\textsubscript{2} and almost full conversion of carbon to gas, but deactivation was still a problem. The highest yield of H\textsubscript{2} was achieved with autothermal SR [158]. The staged setup was tested in the autothermal reforming of ethanol, where homogeneous decomposition of ethanol occurred prior to the catalysts bed. Promising results, with relatively long catalyst lifetime and short residence times (below 10 ms) were achieved with the configuration [157].

A thermodynamic analysis by Rabenstein and Hacker [161] of SR, CPO, and autothermal reforming of ethanol have shown that SR is the least energy demanding process at temperatures above 600 °C while below 600 °C autothermal reforming is favorable. CPO is less favorable at all the temperatures investigated. The CPO/SR has not been investigated thoroughly, but as mentioned above it might be a way to achieve relatively long catalytic lifetimes and relatively high hydrogen yield.

### 1.5.5 Other concepts

Current assisted SR, membrane reactors, and other alterations to the SR process have also been tested in the SR of different oxygenated compounds. Results from these studies are discussed below.

In the current assisted SR a wire runs through the catalytic bed and when current is passed through the wire it becomes hot and delivers energy to the bed and thermal electrons may also be formed [96]. The thermal electrons can reduce the metal species in the catalyst and also cause dissociation of water or oxygenate. The current assisted SR of acetic acid decreases the temperature needed for full conversion and increases the yield of H\textsubscript{2} [96]. These effects are functions of applied current and increases with increasing current. Similar results have been obtained by Hou et al. [151] in the SR of bio-oil and around 90 wt\% conversion could
be achieved at 400 °C. Another feature of the current assisted SR is that the energy efficiency is higher due to a more efficient heating by the wires inside the catalyst bed [96]. However on an industrial scale heating by use of electricity might be more expensive compared to heat generated at the plant and this method could therefore be less feasible in large scale.

The current assisted SR has been tested in a dual reactor with bio-oil as a feed as well. In this setup the bio-oil is first passed through a bed of inert materials and then through a catalytic bed where current could be applied [170]. Similar effects as described above were found in this study and Kan et al. [170] claims that the highest $H_2$ yield from biomass can be achieved through this process. However, full conversion was not achieved and deactivation still a problem.

The motivation for using a membrane reactor instead of the conventional fixed bed setup is that SR and gas separation can be combined in one unit, and produce high purity $H_2$ in a one-step process [171, 172]. This process is only suitable for $H_2$ production as $H_2$ permeable membranes are used. The membrane SR of acetic acid can at relatively low temperature of 400 °C be used with none or little carbon formation. The $H_2$ yield and CO-free $H_2$ recovery was low, around 50 % and 70 %, respectively [171, 172]. This indicates that the process is not efficient as the overall yield of CO free $H_2$ is only 35 %.

The co-feeding of $H_2$ and $H_2O$ has been tested, because it might hydrogenate coke precursors and decrease the coke formation. On an industrial scale $H_2$-addition might be done by recycling some of the reactor effluent. A study by Laosiripojana et al. [169] on the SR of ethanol have shown that the formation of hydrocarbons and coke was decreased by $H_2$ co-feeding. At high ratios between ethanol and $H_2$ (above 3) these effects became less pronounced and the $CH_4$ formation increased [169]. Jacobs et al. [111] tested the addition of $H_2$ to low temperature SR of ethanol, and found increased conversion and yield of $CH_4$.

A Y-shaped reactor with two catalytic beds has also been tested as possible reactor configuration. The idea behind this concept is that bio-oil can be fed both to the first and the second bed and the $CO_2$ produced in the first bed can used to reform the bio-oil in the second bed and hereby produce a gas which mainly consists of CO and $H_2$ [173]. The concept has been tested in SR, CPO, and oxidative SR coupled with $CO_2$ reforming and full conversion and a product gas of mainly $H_2$ and CO can be produced in all the cases at temperatures above 700 °C [173]. The main problem with the dry reforming is that the coke formation is larger compared to both SR, CPO, and oxidative SR alone and higher temperatures are also needed for full conversion [173].

1.5.6 Industrial plant

In the industry the reactor for the SR of bio-oil would probably be a fixed bed reactor as conventional SR is conducted in this type of reactor and knowledge from process design of conventional steam reformers can be used. This would require a catalyst with a low deactivation rate because regeneration or catalyst reloading is expensive. Large scale fixed bed reactors are easier to design and operate than fluidized beds; therefore fixed bed might be chosen despite a higher carbon deposition and shorter catalyst lifetime. If a coke resistant SR catalyst is found, it would also drive the reactor choice toward the fixed bed.

The steam reformer unit for converting bio-oil could have one or two reactors. However the two-reactor setup probably would be better suited as it has a lower potential for carbon formation, is better suited for variations in the feed, and have a better energy efficiency [174].
1. Literature review

**Fig. 1.7:** Simple flowsheet for a two-reactor industrial plant for the SR of bio-oil. (1) indicates possible location for the desulfurization of bio-oil or product gases.

The size of the main reformer would be smaller which could be favorable for an economic point-of-view. This is the case for the conventional SR-units [42, 174]. However, it would require a catalyst that could fully convert the bio-oil to C\textsubscript{1}-species at temperatures around 500 °C and be resistant toward carbon formation and catalyst poisons in the bio-oil. Downstream the reformer there would probably be a low temperature shift reactor to increase the H\textsubscript{2}-yield or achieve a specific H\textsubscript{2}/CO-ratio. A simple flow diagram for an industrial two reactor setup is shown in figure 1.7.

A desulfurization (DS) unit might be included prior to the reforming section as sulfur poisoning could be a problem as indicated in section 1.4. However, this might be difficult as carbon deposition could be a problem due to the thermally unstable oxygenates in the bio-oil. If the prereformer principle is used, the DS could be conducted after the prereformer to avoid coke formation in the DS-unit, if a sulfur resistant catalyst is used in the prereformer. DS is needed at some point in the process as the downstream processes require virtually sulfur-free gas. The DS between the reformers would probably entail lowering the temperature for the DS and then increasing it again after the DS unit, which is uneconomical but necessary if traditional SR catalysts are used in the reformer.

1.6 Other conversion techniques

In the following subsections alternative methods, like cracking of bio-oil or aqueous phase reforming of oxygenates, for converting the bio-oil to synthesis gas or hydrogen will be reviewed to provide a full picture of the possibilities.

1.6.1 Catalytic cracking

Catalytic cracking is to pass the bio-oil through a reactor with a catalytic bed and hereby crack or decompose the bio-oil to gaseous products. The theoretical H\textsubscript{2}-yield will be lower compared to SR because extra H\textsubscript{2} from H\textsubscript{2}O cannot be incorporated into the product gas. Catalytic cracking of the bio-oil has been investigated, because it does not require steam and therefore no energy for superheating the water is needed. The drawbacks of the process are a low H\textsubscript{2}-yield and increased formation of coke, because the carbonaceous residues cannot be gasified by steam. The catalyst will therefore have to be regenerated frequently by combustion using oxygen [87, 175]. The catalysts tested for cracking of bio-oil are monoliths with Pt or Rh on CeO\textsubscript{2}-ZrO\textsubscript{2} [175], Ni/Al\textsubscript{2}O\textsubscript{3} or Ni-K on La\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} [87].
Davidian et al. [87] proposed that the bio-oil is thermally decomposed in the gas phase to small hydrocarbons, carbon oxides and steam. The formed hydrocarbons can react with steam or CO$_2$ on the catalyst and form CO and H$_2$, but the carbon formation would be rather large due to the low steam content [87].

Cracking of acetic acid has also been investigated using a Ni-K/La$_2$O$_3$-Al$_2$O$_3$ catalyst, where full conversion and yield of H$_2$ close to the thermodynamic equilibrium could be achieved from 550 °C at LHSV of 4.1 h$^{-1}$ [176]. It should be noted that despite high yield of H$_2$, the production of H$_2$ will still be lower compared to SR. A dual reactor setup was also tested, where the feed or oxygen could be directed to the catalyst beds. Regeneration of the catalyst occurred under O$_2$-flow and was conducted in one of the beds, while the other one was used for hydrogen production. Using this configuration stable operation over 48 h could be achieved [176, 177].

### 1.6.2 Aqueous phase reforming

Aqueous phase reforming is, as the name implies, reforming of oxygenates in an aqueous solution by the use of a heterogeneous catalyst. The benefits of this process are the low temperatures, which reduces the thermal decomposition and ensures that the WGS (reaction 1.2) is shifted toward H$_2$ and CO$_2$. Furthermore, vaporization of feed and water is not needed, which reduces the energy consumption [178]. Aqueous phase reforming have been conducted at temperatures up to 265 °C and pressures up to 60 bar with WHSV between 3 and 30 h$^{-1}$ [179–182]. It has mainly been examined as a way to produce H$_2$ from sugars produced by acid or enzymatic hydrolysis of biomass [178, 179]. Ethylene glycol, other biomass related components like cellulose, and ethanol have also been tested as feed in APR [180, 181, 183–185], but not other model compounds of bio-oil. However, it could be an interesting way to process the aqueous phase of the bio-oil due to the lower energy requirements.

The main products in APR are CO, CO$_2$, H$_2$, or small hydrocarbons and it has been shown that the yield of H$_2$ decreases with increasing size of the feed molecule, while the hydrocarbon yield increases [178]. Furthermore feed molecules can undergo homogeneous reactions to produce other smaller oxygenated compounds e.g. in the APR of sorbitol the products included acids, ketones, alcohols, and paraffins of various length [186]. A problem with the process is that low concentrations of oxygenates is used (typically less than 10 wt%) and full conversion to gaseous compounds is rarely achieved [180–182]. The production rate of H$_2$ in APR of ethylene glycol is roughly 100-1000 times less than what can be achieved in SR of ethanol [57, 81, 187]. Shabaker et al. [187] reports a production rate of 188 µg/(g$_{\text{Cat}}$·min) in the APR of ethylene glycol while Galdamez et al. [81] and Barattini et al. [57] reports values between 0.06 and 0.19 g/(g$_{\text{Cat}}$·min) in the SR of acetic acid and ethanol, respectively. Another problem with APR is that low temperatures are used, which entails that the methanation equilibrium is shifted toward CH$_4$, and methane must therefore be converted in another step along with other gaseous hydrocarbons. The low degrees of conversion and low production rate for APR will entail large reactors and large recycle loops. Deactivation can also be a problem in APR, when processing heavier compounds, but stable operation over 250 h with ethylene glycol as feed has been achieved [187].

The reaction mechanism suggested for APR of ethylene glycol consists of two pathways, either C-O and C-C bond breaking and these pathways are shown in figure 1.8. The desired pathways is C-C-bond breaking leading to the formation of CH$_3$O-species on the catalyst, which can decompose to CO and H$_2$. The CO reacts with either water by the WGS or H$_2$ through the methanation forming CO$_2$ or CH$_4$, respectively. The C-O bond can also be
Fig. 1.8: The reaction mechanism for C-C and C-O breaking in the APR of ethylene glycol over a metal catalyst. The horizontal lines represent a metal surface. Figure adapted from [178].

cleaved, which would lead to the formation of small hydrocarbons like CH$_4$ or C$_2$H$_6$. A suitable catalyst should have a high activity in the WGS and the C-C-bond breaking and a low activity for the C-O cleaving to ensure that the products are mainly CO, CO$_2$, and H$_2$.

In ethylene glycol and sugars all the C-atoms are bound to O-atoms and CO-species can be formed almost exclusively, corresponding to the desired reaction path (C-C-bond breaking) and leading to high yields of H$_2$. Breaking of the C-C-bond in acetic acid or ethanol would lead to CO and CH$_x$-species on the catalyst. These species cannot be converted by the APR reforming and would lead to the formation of CH$_4$, other small hydrocarbons, or coke. The APR could be used as a prereforming step with subsequent SR of the small hydrocarbons, if it should be used to fully convert the bio-oil into H$_2$ and carbon oxides. A problem with processing bio-oil in an aqueous solution might be phase separation, which could cause transport problems and poor contact between reactants and catalyst as bio-oil is known to phase separate when mixed with water. A more drastic pretreatment step could be gasification in supercritical water without a catalyst to break down the molecules and possibly get a product which is more readily steam reformed.

The catalytic metals used in the APR are similar to the ones used in the SR of bio-oil and ranges from Ni to different noble metals. The order of decreasing activity based on TOF for CO$_2$-production over the different metals tested in the APR of ethylene glycol is [178, 183]:

$$\text{Pt} \approx \text{Ni} > \text{Ru} > \text{Rh} \approx \text{Pd} > \text{Ir}$$

The Pt-catalyst can be improved by alloying with Ni, Fe, or Co, which could be due to a lowering of the d-band center, which would cause a lowering of the heat of adsorption for H$_2$ and CO [179]. This would lead to more free surface sites on the catalyst and a higher probability for reaction.

The best support materials for the APR of ethylene glycol is TiO$_2$, carbon, or Al$_2$O$_3$ [178].

1.7 Discussion

In the previous sections different reactors and concepts, which can or have been used for SR of bio-oil, have been presented. It has been shown that SR of bio-oil is thermodynamically favorable and that highly active catalysts do exist, but carbon formation is a major concern.
as it causes fast deactivation. This problem can be attacked from two different angles either by changing the catalyst or by changing the reactor type and operating conditions. Another major concern is the sulfur content of the bio-oil as it can cause deactivation as well and it should either be removed prior to the reactor(s) or a sulfur resistant catalyst should be used and the sulfur could be removed downstream the reactor. The process gas should be virtually free of H$_2$S (sub ppb-level) if it should be used for Fischer-Tropsch or in fuel cells so sulfur removal must be employed at some point.

Sulfur resistant catalytic systems are known from the literature on SR of hydrocarbons and might be suited in SR of oxygenates, but these systems still need testing. Other changes to both support and metal in the catalyst might also enhance the performance of the catalyst. Alloying of different metals, new support materials, or new promoters could be possible changes to the SR catalysts.

Most of the conversion techniques, discussed above, have drawbacks and are far from industrial application. A one-step SR will have problems with carbon formation both in fixed and fluidized bed reactors with the current catalysts. However, slightly autothermal conditions might significantly improve the performance at the expense of lower H$_2$-yield. A two step process will probably improve the process both for fluidized and fixed beds. A prereformer-reformer concept therefore seems promising. These have not been investigated thoroughly, yet, and proof of concepts is still missing. The prereformer-reformer concept is known from the conventional SR, and the coke formation can probably be reduced because of a lower reactor inlet temperature and therefore also lower degree of thermal decomposition in the prereformer. Another possibility could be an APR reactor as a prereformer, but the APR still need further development as the products for the process ranges from C$_1$ to C$_6$-molecules and these might still be soluble in water. Therefore a separation and two additional steam reforming steps might be needed to produce synthesis gas or hydrogen from bio-oil through APR.

1.8 Conclusion

The SR of bio-oil is an environmentally friendly route to produce H$_2$ or synthesis gas and therefore could become an important process in the future. Many different catalytic systems have been investigated and the most promising metals seem to be Ni, Rh, or Ru. Ni is preferred if the catalyst should be used industrially as it is the cheapest and most abundant of the metals. The most promising support materials are mixtures of basic oxides and Al$_2$O$_3$ as these show higher activity and lower carbon formation compared to alumina. Potassium can be used as a promoter as it can increase the activity and reduce the coke formation. Nevertheless, one of the main concerns with the tested catalysts is the low stability with typical operating hours for acceptable rates being less than 100 h.

The SR of bio-oil is still in an early phase of its development. Some aspects of the SR of bio-oil which need further investigation and optimization if the SR should be used industrially are:

- Kinetics and reaction mechanisms for other compounds than ethanol are scarce but bio-oil consists of many other compounds. It could be interesting to test additional model compounds as well as whole bio-oil in order to gain further insights into the SR reactions.

- The influence of sulfur should be investigated as it is a known poison for the conventional SR process. Development of sulfur resistant catalysts could be interesting as desulfurization of the bio-oil might be troublesome.
• Proof of concept for the prereformer concept with a two step reactor, where the bio-oil is first converted to $C_1$-species at low temperature followed by a high temperature reformer, which converts the $CH_4$ into $H_2$, CO, and CO$_2$.

• Further studies of different catalysts or operating conditions to allow extended periods of operation.
2. EXPERIMENTAL

This chapter describes the production of catalysts, the used experimental setups, and the different characterization techniques. Two different experimental setups have been used, one at the Technical University of Denmark (DTU) and one at the University of Oklahoma (OU), and furthermore, the setup at DTU has been modified during the course of the Ph.D.-project to accommodate feeding of the different model compounds.

2.1 Catalyst preparation

The catalysts investigated in this project were prepared by incipient wetness impregnation. Five different carriers for NiO were impregnated with a Ni(NO$_3$)$_2$-solution; CeO$_2$ (AMR Ltd., 141 m$^2$/g), Ce$_{0.6}$Zr$_{0.4}$O$_2$ (AMR Ltd., 137 m$^2$/g), MgAl$_2$O$_4$ (Puralox MG30/150, SASOL Germany, 143 m$^2$/g), MgAl$_2$O$_4$, and CeZrO$_4$/MgAl$_2$O$_4$. The two latter supports were prepared in-house according to the procedure described below. Ni was added to the supports by dissolving Ni(NO$_3$)$_2$·6H$_2$O (Sigma-Aldrich, > 97 % pure) in a volume of water corresponding to the pore volume of the dry support material. The solution was mixed with the dry carrier material and stirred. The wet particles were dried at 110 °C overnight and calcined at 800 °C (heating rate 10 °C/min) for 2 h.

Magnesium aluminate was prepared by incipient wetness impregnation of a high surface area alumina (Puralox TH 150, SASOL Germany, 150 m$^2$/g) with Mg(NO$_3$)$_2$ as precursor for MgO. The alumina was mixed with a solution containing stoichiometric amounts of Mg(NO$_3$)$_2$ (Fluka, 99 % pure) followed by drying at 110 °C and calcination at 900 °C (heating rate 10 °C/min) for 8 h.

The synthesized MgAl$_2$O$_4$ was co-impregnated with Ni, K, CeO$_2$, ZrO$_2$. Maximum two species were impregnated at a time, so when naming the catalysts / denotes separate impregnation steps while - denotes co-impregnation. After each impregnation step the catalyst was dried and after the final impregnation it was calcined at 800 °C (heating rate 10 °C/min) for 2 h. Ce(NO$_3$)$_3$·6H$_2$O, ZrO(NO$_3$)$_2$·H$_2$O, and KNO$_3$ were used as precursors for CeO$_2$, ZrO$_2$, and K, respectively. The precursors were acquired from Sigma-Aldrich Ltd. and were ≥ 99 % pure.

Sulfur addition to the catalysts was done by impregnating the calcined catalyst with a solution of K$_2$SO$_4$ or H$_2$SO$_4$ followed by drying at 110 °C overnight. The impregnation liquids had concentrations corresponding to a nominal sulfur coverage of roughly 6, 13, and 26 %, which corresponded to a sulfur content of 0.03-0.12 wt%. Sulfur coverage was calculated by assuming that all the sulfur from the liquid adsorbs on the Ni-particles. The number of Ni surface sites was estimated based on the particle size determined by XRD and assuming spherical particles and a Ni-atom area of 6.2·10$^{-20}$ m$^2$ (calculated based on a face-centered cubic nickel atom in the (100) plane).

MgAl$_2$O$_4$ prepared in-house was used for the experiments presented in chapter 3, while the commercial MgAl$_2$O$_4$ from SASOL was used as support in the remaining experiments described in the chapters 4-6.
2.2 Experimental setup at DTU

The flowsheets for the different configurations of the experimental setup at DTU can be seen in fig. 2.1. The setup used for SR of ethanol, fig. 2.1(a), consisted of a gas supply section where up to eight different gases could be connected, a liquid supply section where two bubble columns were used to supply water and ethanol. Nitrogen flows were saturated with ethanol or water at 60 °C and 79 °C, respectively, in the bubble columns and led to the reactor. The gases and liquids were mixed in lines heated to 110 °C prior to entering a quartz reactor placed in a three zone furnace. After the reactor there was a condenser operated at 6-7 °C, which collected liquid samples. After the condenser the gases passed the analysis section, which consisted of a Varian MicroGC CP-4900 and a 5-channel Rosemount NGA 2000 on-line gas analyzer. The MicroGC had two parallel lines; a molecular sieve 5A column and a PoraPlot Q column connected to a thermal conductivity detector (TCD). The GC measured the concentrations of CO, CO₂, H₂, CH₄, C₂H₄, and C₂H₆ in the dry gas. Samples were injected to the GC every 10 min. The on-line gas analyzer measured the CO, CO₂, and O₂ concentrations continuously and data points were collected every 30-60 s. Data from the GC was used to determine the product distribution and representative measurements every approx. 30-60 min were used to show trends and deactivation.

![flowsheet](image1)

(a) Evaporator for H₂O and ethanol

![flowsheet](image2)

(b) Evaporator and pump

**Fig. 2.1:** Flowsheets of the experimental setups used at the Technical University of Denmark.

The feeding system was altered for long term experiments (≥ 24 h) with ethanol as well as experiments with 2-methylfuran, furfural, and guaiacol, as shown in fig. 2.1(b). The desired
Tab. 2.1: Comparison of conversion and yield of H₂, CO, CO₂, CH₄, and C₂H₄ with the feed delivered by a pump or evaporators over Ni/CeO₂-K/MgAl₂O₄. Experimental conditions: S/C: 5.5-6.0; Temp.: 586 °C; m_Cat = 0.50 g, Ni loading: 8.2 wt%, \( F_T = 1600 \text{ NmL/min}, y_{\text{Eth}} = 3.1 - 3.3 \text{ vol%}, y_{\text{H₂O}} = 36.3 - 37.2 \text{ vol%}, N_2 \text{ as balance.}

<table>
<thead>
<tr>
<th>Feed system</th>
<th>X [%]</th>
<th>( Y_{\text{H₂}} ) [%]</th>
<th>( Y_{\text{CO₂}} ) [%]</th>
<th>( Y_{\text{CO}} ) [%]</th>
<th>( Y_{\text{CH₄}} ) [%]</th>
<th>( Y_{\text{C₂H₄}} ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump</td>
<td>99.5</td>
<td>76.3</td>
<td>82.5</td>
<td>14.4</td>
<td>3.0</td>
<td>0</td>
</tr>
<tr>
<td>Evaporator</td>
<td>99.6</td>
<td>78.2</td>
<td>82.9</td>
<td>12.4</td>
<td>4.8</td>
<td>0</td>
</tr>
</tbody>
</table>

mixture of water and ethanol was pumped through an evaporator operated at 250 °C and then fed to the reactor through the feeding tube along with \( N_2 \) for dilution in the long term SR of ethanol experiments. The pump was a Knauer Smartline 100 pump and the evaporator was 3.175 mm stainless steel tube wrapped around a copper core heated by a heating cartridge. Similar results were obtained with the two feeding systems as shown table 2.1.

2-methylfuran, furfural, and guaiacol are immiscible with water and a third option was used for feeding oxygenate and water. Water was fed to the reactor by saturating a flow of nitrogen in a bubble column, while the oxygenate was pumped and mixed with a flow of nitrogen then sent to the top of the reactor and mixed with the steam/\( N_2 \)-stream before entering the reactor. Plugging of the evaporator occurred, when heating the 2-methyl furan and furfural in \( N_2 \), and therefore it was chosen to pump the oxygenate directly to the reactor without preheating to avoid polymerization of the oxygenates and subsequent plugging of the evaporator. The flow rate used in the SR of the different model compounds, as well as flow of nitrogen and steam can be seen in table 2.2.

Analysis of the liquid from the condenser was conducted by a Shimadzu GCMS/FID-QP2010 UltraEi fitted with a Supelco Equity-5 column. Identification was made on the mass spectrometer (MS) and quantification was done on the flame ionization detector (FID).

Tab. 2.2: Flow of oxygenate, steam, and water in the SR of the different model compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ethanol [NmL/min]</th>
<th>2-methyl furan [NmL/min]</th>
<th>Furfural [NmL/min]</th>
<th>Guaiacol [NmL/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_{\text{N}_2} )</td>
<td>960</td>
<td>1016</td>
<td>1015</td>
<td>1022</td>
</tr>
<tr>
<td>( F_{\text{Model compound}} )</td>
<td>0.1</td>
<td>0.082</td>
<td>0.097</td>
<td>0.089</td>
</tr>
<tr>
<td>( F_{\text{Model compound}} )</td>
<td>49</td>
<td>22.5</td>
<td>22.5</td>
<td>16.1</td>
</tr>
<tr>
<td>( F_{\text{H}_2\text{O}} )</td>
<td>588</td>
<td>562</td>
<td>562</td>
<td>563</td>
</tr>
<tr>
<td>( S/\text{C} )</td>
<td>6</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

In all the different experiments the catalyst was placed between two pieces of quartz wool resting on a quartz frit inside a quartz tube with an inner diameter of 17 mm placed in the furnace. The steam and oxygenate mixture was fed from the top of the reactor through an inlet tube with an outer diameter of 6 mm and perforated with 12 holes in the end to distribute the gas over catalyst bed. The outlet of the inlet/feeding tube was approx. 50 mm above
the catalyst bed allowing time for mixing while minimizing homogeneous gas phase reactions before reaching the catalyst. The temperature was measured by a thermocouple placed in a pocket just below the quartz frit. The schematics of the quartz reactor system, which consists of a main tube, reactor top and bottom as well as a sample tube, where the catalyst is placed, can be seen in fig. 2.2. Furthermore the assembled reactor is shown in this figure.

**Fig. 2.2:** Quartz reactor system developed at the Technical University of Denmark.
2. Experimental

**Tab. 2.3: General reaction conditions in the SR of ethanol. N₂ as balance gas in all experiments.**

<table>
<thead>
<tr>
<th>Flow [NmL/min]</th>
<th>Ethanol [vol%]</th>
<th>H₂O [vol%]</th>
<th>O₂ [vol%]</th>
<th>H₂ [vol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500-1600</td>
<td>3.0-3.5</td>
<td>10-50</td>
<td>0-6.3</td>
<td>0-3.6</td>
</tr>
</tbody>
</table>

2.2.1 Catalytic test

0.5 g of catalyst with \( d_p = 410 - 725 \ \mu m \) or \( d_p = 250 - 410 \ \mu m \) was loaded into the reactor and then heated to 600 °C in a flow of N₂. At 600 °C the flow was changed to a 50/50 flow of N₂ and H₂ of roughly 500 NmL/min for 1 hour to reduce the NiO to Ni. After reduction the reactor was purged with N₂ for 10 min and then the reactants were directed to the reactor. The general flow rates and gas composition investigated in the SR of ethanol can be seen in table 2.3. The overall flow rates were similar in the SR of cyclic compounds, but the feed gas consisted of 1.0-1.5 vol% of oxygenate, roughly 35 vol% H₂O, various amounts of O₂ (0-4.8 vol%), and N₂ as balance. The pressure was in all cases atmospheric and temperatures between 400 and 800 °C were investigated. The number of carbon atoms fed to the system was similar in the SR of 2-methylfuran, furfural, guaiacol, and ethanol.

Estimations based on Weisz-Prater and Mears criteria for internal and external diffusion showed that diffusion was not limiting for the overall reaction with the applied particle sizes and experimental conditions. Furthermore experiments with \( d_p = 410 - 725 \ \mu m \) and \( d_p = 250 - 410 \ \mu m \) showed similar results with respect to conversion and carbon deposition. Estimation of diffusion and other aspects of the reactor design are evaluated in Appendix A. The main conclusions are that external diffusion is not limiting and neither is internal diffusion as least for particles below 425 \( \mu m \). Furthermore, a criterion for achieving plug flow is not met, but it appears that modeling as plug flow reactor gives the best description of conversion. There should not be large temperature gradients between catalyst particles and the surrounding gas, based on a criterion by Mear and a simple energy balance over a particle.

2.2.2 Determination of the amount of carbon deposited

The amount of carbon deposited during an experiment was determined by temperature programmed oxidation (TPO) of the entire catalyst bed and sample tube. The procedure was, cooling of the reactor to 200 °C followed by heating to 700 °C (10 °C/min) in a 1 NL/min flow of 2-3 vol% O₂ in N₂. The evolution of CO and CO₂ was monitored by the online gas analyzer (data points every 5 s) and the amount of carbon was determined by integration of these signals.

Temperature programmed oxidation was also performed in another flow reactor setup, when the spent catalyst should be characterized by others techniques as well. The setup used only 10-15 mg of spent catalysts. The samples were oxidized in 1000 NmL/min flow of 10 % O₂ in N₂ between room temperature and 700 °C, with an average heating rate of 12 °C/min. The offgas composition was monitored by an ABB AO2000 gas analyzer with two channels and concentration of CO and CO₂ were logged every 15 s. No significant differences in the temperature of oxidation, CO and CO₂ release, or the amount of carbon deposited were observed between the two options for determination of the amount of carbon deposited.
2.3 Experimental setup at OU

The schematics of the setup used at OU are shown in Fig. 2.3. The setup consisted of four gas lines with corresponding mass flow controller (MFC) connected to a vaporizer where injection of a liquid was possible. The vaporizer was a 6.35 mm stainless steel tube heated to 300 °C by heating tape and the feed mixture of water and oxygenate was delivered by a syringe pump and injected into the vaporizer through a septum. In the vaporizer the feed was mixed with the carrier gas. The reactant mixture then entered a quartz reactor placed in a furnace. The temperature was measured by a thermocouple on the outside of the reactor tube. The reactor effluent was connected to a Varian 3800 gas chromatograph (GC) equipped with a Restek Rxi-5Sil mass spectrometry (MS) column, a flame ionization detector (FID), and a thermal conductivity detector (TCD) by a heated line kept at 300 °C. This GC was used to determine the concentrations of oxygenates and C₃-hydrocarbons. After the GC, there was a cold-trap with ice, to condense water, products, and unconverted oxygenates. The gases from the cold trap were collected in a gas bag and analyzed by a GC/TCD (Carle AGC 400) to determine the concentration of CO, CO₂, H₂, CH₄, C₂H₄, C₂H₆, and N₂. The online GC did measurements every 25 min, while gas samples were taken to the GC/TCD every 30 to 45 min.

2.3.1 Catalytic test at OU

The catalyst with a particle size of \( d_p = 250 - 425 \mu m \) was loaded in a quartz tube with an outer diameter of 6.35 mm and a length of 343 mm. The catalyst was placed on a constriction in the middle of the quartz tube between two layers of quartz wool. The catalyst was heated to 600 °C in a flow of N₂ of 40 NmL/min. At 600 °C the flow was changed to 50/50 mixture of N₂ and H₂ for 1 h to reduce the NiO on the catalyst to Ni. After the reduction the catalyst was flushed with N₂ for 5 min. The experiment was started hereafter by adjusting the N₂ flow, starting the syringe pump, and inserting the needle through the septum in the vaporizer. The feed gas had a S/C-ratio of 6 and the mole fractions of oxygenates and H₂O were 2-3 % and 36 %, respectively, with N₂ as balance.
2.3.2 Temperature programmed oxidation at OU

The amount of carbon on the spent catalysts was determined by TPO. 2-5 mg of spent catalyst was placed between two layers of quartz wool in a quartz reactor with outer diameter of 6.35 mm and a length of 394 mm. The sample was heated from room temperature to 800 °C (heating rate of 10 °C/min) in a flow of 5 % O₂ in He. The released carbon oxides were converted to CH₄ over a methanation catalyst operated at 400 °C and the amount of CH₄ formed was measured by FID.

2.4 Catalyst characterization

The BET surface area of all the prepared catalysts was measured by N₂ adsorption at its boiling point using multipoint BET theory with seven points in the \( p/p_0 = 0.05 - 0.3 \) range using a Quantachrome iQ2.

XRD-patterns were recorded for spent and fresh catalyst powders by a PANalytical X'Pert PRO Diffractometer, which had a rotating sample holder, a rotating copper anode X-ray source, nickel filter, and automatic anti-scatter and divergence slits. The particle size of Ni, NiO, and CeO₂ were determined from the XRD patterns and the line broadening of peaks using the Scherrer equation, eq. 2.1, [188]:

\[
d_p = \frac{K \cdot \lambda}{\beta \cdot \cos(\theta)}
\]

Where \( K \) is shape factor set to 0.9 [188], \( \lambda \) is the X-ray wavelength, \( \beta \) is full width at half maximum corrected for the instrumental line broadening, while \( \theta \) is the Bragg angle.

Temperature programmed reduction (TPR) of the catalysts were conducted in a flow of 10 % H₂ in He and the temperature was raised from room temperature to 900 °C with a temperature ramp of 5 K/min. The concentrations of H₂O, H₂, and He were followed by a mass spectrometer.

Bright field transmission electron microscopy of fresh and spent catalysts were conducted on a Tecnai T20 G2 microscope with a thermionic-lanthanum hexaboride, LaB₆, as electron source. The fresh catalysts were reduced, cooled down, and removed from the reactor and then transported to TEM investigations. The TEM samples were crushed, slurried with ethanol and deposited on a copper grid covered with a lacey carbon film.

Elemental analysis of the catalysts was conducted by dissolving the catalyst and then using inductively coupled plasma optimal emission spectroscopy (ICP-OES).

2.4.1 Calculations

\( W/F \) is defined as mass of catalyst pr. molar flow of oxygenates, \( F_{\text{Oxy}, \, m} \):

\[
W/F = \frac{m_{\text{Cat}}}{F_{\text{Eth}, \, m}} \left[ \frac{g \cdot h}{\text{mole}} \right]
\]

(2.2)

WHSV is defined as mass flow of ethanol, \( F_{\text{Eth}, \, m} \) pr. mass of catalyst:

\[
\text{WHSV} = \frac{F_{\text{Eth}, \, m}}{m_{\text{Cat}}} \left[ h^{-1} \right]
\]

(2.3)

Conversion, \( X \), is calculated on a carbon basis as:

\[
X = \sum_{n_{\text{C}, \, i} \cdot n_{\text{Oxy}, \, in}} \frac{n_{\text{C}, \, i} \cdot n_{\text{Oxy}, \, in}}{n_{\text{C}, \, i} \cdot n_{\text{Oxy}, \, in}} \cdot 100\%
\]

(2.4)
Table 2.4: \( n_{H_2, \text{Max}} \) used in calculations of the yield of \( H_2 \).

<table>
<thead>
<tr>
<th>Model compound</th>
<th>( n_{H_2, \text{Max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>4</td>
</tr>
<tr>
<td>Acetol</td>
<td>7</td>
</tr>
<tr>
<td>Acetone</td>
<td>8</td>
</tr>
<tr>
<td>Ethanol</td>
<td>6</td>
</tr>
<tr>
<td>Furfural</td>
<td>10</td>
</tr>
<tr>
<td>Guaiacol</td>
<td>16</td>
</tr>
<tr>
<td>2-methylfuran</td>
<td>12</td>
</tr>
<tr>
<td>Propanal</td>
<td>8</td>
</tr>
<tr>
<td>1-propanol</td>
<td>9</td>
</tr>
</tbody>
</table>

Where \( n_{C, i} \) is the number of carbon atom in component \( i \) and \( n_i \) is the number of moles of compound \( i \) produced.

The yield of products, \( Y_i \), is based on the definition by Fogler [189] and calculated as:

\[
Y_i = \frac{n_{C, i} \cdot n_i}{\sum n_{C, i} \cdot n_i} \cdot 100\% \tag{2.5}
\]

The yield of \( H_2 \) is defined as:

\[
Y_{H_2} = \frac{n_{H_2}}{n_{H_2, \text{Max}} \cdot X \cdot n_{Oxy, \text{in}}} \cdot 100\% \tag{2.6}
\]

The factor of \( n_{H_2, \text{Max}} \) is the maximum number of \( H_2 \) moles, which can be produced from 1 mole of oxygenates including full shift of CO to CO\(_2\) and \( H_2 \) (reaction 1.21). \( n_{H_2, \text{Max}} \) for all the investigated compounds is shown table 2.4.

Carbon deposition is reported as the amount of carbon deposited pr. amount carbon in the feed, \( \frac{\text{mole } C}{\text{mole } C_{\text{Feed}}} \), and in mass of carbon deposited pr. mass of catalyst and time, \( \frac{\text{mg } C}{\text{g Catalyst h}} \).
High degrees of conversion and high yield of H\textsubscript{2} can be achieved in the SR of bio-oil and other oxygenates, but deactivation due to carbon deposition is also observed and is one of the major hurdles for industrial application. In the following it is attempted to minimize the carbon deposition in the SR of ethanol over Ni-based catalysts. Ethanol was chosen as model compound of bio-oil because it has a functionality which is found in bio-oil and is prone to carbon deposition as shown by several studies [49, 50, 63, 122, 190]. Furthermore SR of ethanol is interesting on its own as it can be used to provide H\textsubscript{2} for fuel cells in mobile applications [49].

Steam reforming of ethanol can be described by the following reactions:

\[
\begin{align*}
C_2H_6O + H_2O &\rightleftharpoons 2 \text{CO} + 4 \text{H}_2 \quad (3.1) \\
C_2H_6O + 3 \text{H}_2O &\rightleftharpoons 2 \text{CO}_2 + 6 \text{H}_2 \quad (3.2)
\end{align*}
\]

Reaction 3.1 is the general SR-reaction, while reaction 3.2 assumes full shift of CO to CO\textsubscript{2} by reaction with H\textsubscript{2}O (reaction 1.2), which yields two additional moles of H\textsubscript{2}. Beside the water-gas shift (WGS), reaction 1.2, methanation, reaction 3.4, might also influence the product distribution:

\[
\begin{align*}
\text{CO} + \text{H}_2O &\rightleftharpoons \text{CO}_2 + \text{H}_2 \quad (3.3) \\
\text{CO} + 3\text{H}_2 &\rightleftharpoons \text{CH}_4 + \text{H}_2O \quad (3.4)
\end{align*}
\]

The offgas composition in the SR of ethanol is governed by the equilibrium between the reactions shown above e.g. reactions 3.1, 3.3, and 3.4. High temperatures will favor the reforming reactions and produce H\textsubscript{2} and CO as reaction 3.1 is shifted toward the right, while reaction 3.4 will be shifted to the left. The WGS, reaction 3.3, will be shifted toward CO and H\textsubscript{2}O at temperatures above 800 °C and therefore the maximum H\textsubscript{2} production is achieved at intermediate temperatures, 600-800 °C [85].

Side reactions observed in SR of ethanol are dehydration, reaction 3.5, or dehydrogenation, reaction 3.6, yielding ethene and acetaldehyde, respectively [49, 50, 89, 99, 191].

\[
\begin{align*}
\text{C}_2\text{H}_6\text{O} &\rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \quad (3.5) \\
\text{C}_2\text{H}_6\text{O} &\rightarrow \text{C}_2\text{H}_4\text{O} + \text{H}_2 \quad (3.6)
\end{align*}
\]

Especially, formation of ethene is troublesome as it has a high potential for forming carbon deposits [32, 99, 100, 192]. Carbon formation from ethene could occur through decomposition followed by accumulation and polymerization [100, 191, 192]:

\[
\text{C}_2\text{H}_4 \rightarrow 2\text{C} + 2\text{H}_2 \rightarrow \text{Carbon} \quad (3.7)
\]

Alternatively, carbon deposits can be formed through direct polymerization of ethene [49, 50, 89]:

\[
n\text{C}_2\text{H}_4 \rightarrow \text{Carbon} \quad (3.8)
\]
There are two routes to minimize carbon deposition, either the catalyst formulation can be optimized or the reaction conditions can be changed, e.g. changing the temperature, the water content, or adding oxygen to feed. In this chapter a systematic investigation of different options for lowering the rate of carbon deposition in SR of ethanol and hereby enhancing catalyst lifetime through changes in the catalyst formulation is carried out, including changing support material, adding promoters, and doping with sulfur. Furthermore the effect of temperature on conversion, product distribution, and carbon deposition will be investigated.

Several catalysts have been investigated in the SR of ethanol including Ni, Cu, Co, Ir, Au, Pt, Pd, Ru, and Rh on Al$_2$O$_3$ [63, 89, 95, 97, 131, 166, 193, 194]; Ni, Ag, Rh, and Ru on MgAl$_2$O$_4$ [121-123, 195]; Pt, Rh, Co, Pt, and Ir on Ce$_x$Zr$_{1-x}$O$_2$ [62, 90, 93, 94, 119, 120, 196-199], and several other systems like perovskites or hydrotalcites based catalysts [57, 200]. For a complete overview the reader is referred to the following reviews [49, 50, 98, 99]. As indicated above, many metals can be used in SR but Ni is one of few active metals used in conventional SR catalysts, due to the low price and good activity compared with the more expensive noble metals [42].

Magnesium or calcium aluminates are used as supports for industrial SR catalysts and have a low number of acid sites, which reduces the risk of decomposition of the oxygenates and therefore also the risk of carbon deposition [52]. Furthermore a more stable and higher activity for MgAl$_2$O$_4$ compared with Al$_2$O$_3$ has been reported [48, 52, 58]. The increased activity has been ascribed to an increased water dissociation on the support and formation of smaller metal particles [48, 52]. Furthermore steam gasification of the coke might be facilitated by spillover of O- or OH-species from the support to the metal particles [52]. CeO$_2$ and Ce$_x$Zr$_{1-x}$O$_2$ have been reported to facilitate water dissociation and thereby supply O for oxidation of carbon on the surface due to their redox properties [68, 90, 94, 201, 202].

Potassium is known from conventional SR to bind to step sites on Ni-particles and hereby reduce the rate of reaction but also the risk of carbon formation as carbon islands cannot grow large enough to nucleate carbon whiskers [30, 42]. Results from the SR of acetic acid over K-promoted Ni/Al$_2$O$_3$ catalysts showed reduced CH$_4$ formation, increased activity, and lower carbon deposition [82]. An optimal loading of K was reported to be 8 wt% [82]. Results from the SR of ethanol over Ni/MgAl$_2$O$_4$ showed a decrease in the carbon deposition by a factor of 3 when doping with 1 wt% of K [122].

Based on the results presented above it is chosen to investigate four support materials for Ni; MgAl$_2$O$_4$, CeZrO$_4$/MgAl$_2$O$_4$, CeO$_2$, and Ce$_{0.6}$Zr$_{0.4}$O$_2$. Furthermore addition of K, CeO$_2$, ZrO$_2$, or mixtures hereof to Ni/MgAl$_2$O$_4$ to promote stable activity will be investigated.

### 3.1 Characterization

The nickel particle size based on XRD measurements and surface area of all the tested catalysts are shown in table 3.1. The surface areas and nickel particle sizes are in the same range for all the MgAl$_2$O$_4$ based catalyst with values of 52-69 m$^2$/g and 6-9 nm, respectively. Ni/Al$_2$O$_3$ and Ni/Co$_{0.6}$Zr$_{0.4}$O$_2$ both have higher surface areas and larger Ni particles with values around 90-113 m$^2$/g and 10-20 nm, respectively. Therefore Ni seems to be better dispersed on MgAl$_2$O$_4$ and CeZrO$_4$/MgAl$_2$O$_4$ compared with CeO$_2$ and Ce$_{0.6}$Zr$_{0.4}$O$_2$.

TEM-images of reduced Ni/MgAl$_2$O$_4$ and Ni/Co$_{0.6}$Zr$_{0.4}$O$_2$ as well as the particle size distribution determined from TEM-images can be seen in fig. 3.1. For Ni/Co$_{0.6}$Zr$_{0.4}$O$_2$ (fig. 3.1(a)) it is difficult to distinguish between Ni and the support, but it can be seen that the particles in general had a size of 13 nm ± 3 nm, which is slightly below the results obtained with XRD.
Tab. 3.1: Nominal metal loading, surface area, and NiO particle size of the fresh catalysts prior to reduction. XRD reflection peak from NiO peak at \(2\theta = 62.8^\circ\) used for determination of particle size.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Promoter</th>
<th>Metal loading ([\text{wt}%])</th>
<th>Surface area ([m^2/g])</th>
<th>(d_{p, \text{NiO}}) ([\text{nm}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Ce(<em>{0.6})Zr(</em>{0.4})O(_2)</td>
<td>-</td>
<td>8.2</td>
<td>90</td>
<td>15-20</td>
</tr>
<tr>
<td>Ni/CeO(_2)</td>
<td>-</td>
<td>8.2</td>
<td>113</td>
<td>10</td>
</tr>
<tr>
<td>Ni/MgAl(_2)O(_4)</td>
<td>-</td>
<td>8.1</td>
<td>69</td>
<td>7</td>
</tr>
<tr>
<td>Ni/CeZrO(_4)/MgAl(_2)O(_4)</td>
<td>10 \text{wt}% CeO(_2) and ZrO(_2)</td>
<td>8.0</td>
<td>63</td>
<td>6</td>
</tr>
<tr>
<td>Ni-K/CeZrO(_4)/MgAl(_2)O(_4)</td>
<td>9 \text{wt}% CeO(_2) and ZrO(_2), 5 \text{wt}% K</td>
<td>8.2</td>
<td>47</td>
<td>8</td>
</tr>
<tr>
<td>Ni-K/MgAl(_2)O(_4)</td>
<td>5 \text{wt}% CeO(_2) and ZrO(_2)</td>
<td>8.2</td>
<td>55</td>
<td>7</td>
</tr>
<tr>
<td>Ni-CeO(_2)/MgAl(_2)O(_4)</td>
<td>11 \text{wt}% CeO(_2)</td>
<td>8.3</td>
<td>59</td>
<td>9</td>
</tr>
<tr>
<td>Ni/CeO(_2)-K/MgAl(_2)O(_4)</td>
<td>5 \text{wt}% CeO(_2) and K</td>
<td>8.2</td>
<td>54</td>
<td>6</td>
</tr>
</tbody>
</table>

The size distribution from the TEM-images is used to calculate the mean volume diameter, which is used for comparison. XRD was conducted on unreduced samples while the TEM was conducted on reduced samples, which could explain the difference in particle size. For Ni/MgAl\(_2\)O\(_4\) (fig. 3.1(b)) Ni and the support can be distinguished as the Ni particles are the dark/black particles. The particle size determined from the TEM analysis was \(8 \text{ nm} \pm 2 \text{ nm}\), which is similar to the XRD results. The trends in Ni particle sizes obtained by XRD are confirmed by TEM.

![TEM images](image1.png)

Fig. 3.1: TEM images of reduced catalysts prior to SR experiments.

The XRD-patterns for NiO on CeO\(_2\), Ce\(_{0.6}\)Zr\(_{0.4}\)O\(_2\), MgAl\(_2\)O\(_4\), and CeZrO\(_4\)/MgAl\(_2\)O\(_4\) can be seen in fig. 3.2(a), 3.2(b), 3.2(c), and 3.2(d), respectively. XRD-analysis of the different catalysts confirmed that the mixed oxide of Ce and Zr was Ce\(_{0.6}\)Zr\(_{0.4}\)O\(_2\) and that the MgAl\(_2\)O\(_4\) indeed had spinel structure and was not a mixture of MgO and Al\(_2\)O\(_3\). On the
Ni/MgAl\textsubscript{2}O\textsubscript{4}-catalysts, some formation of NiAl\textsubscript{2}O\textsubscript{4} phase was observed. Addition of K and CeO\textsubscript{2} to Ni/MgAl\textsubscript{2}O\textsubscript{4} could not be detected by the XRD-analysis, probably due to a small particle size or because they were present as layers or amorphous species. The loading of CeO\textsubscript{2} corresponded to roughly one monolayer, while the potassium loading was chosen based on the optimal value of 8 wt\% K found by Hu and Lu [82]. Their catalyst however had a surface area of 125 m\textsuperscript{2}/g, roughly twice the value of our catalyst, and thus we used about 4 wt\% K to provide the same surface coverage of K. It corresponded to about two monolayers of K.

The addition of CeZrO\textsubscript{4} to Ni/MgAl\textsubscript{2}O\textsubscript{4} was detected by XRD and confirmed the presence of CeZrO\textsubscript{4} and not single oxides like CeO\textsubscript{2} and ZrO\textsubscript{2}. No formation of mixed oxides with Ce or Zr incorporated in to the MgAl\textsubscript{2}O\textsubscript{4}-phase was observed showing that these species were present as true promoters on the surface of MgAl\textsubscript{2}O\textsubscript{4}.

The H\textsubscript{2}O evolution as function of temperature for TPR of Ni on CeO\textsubscript{2}, Ce\textsubscript{0.6}Zr\textsubscript{0.4}O\textsubscript{2}, MgAl\textsubscript{2}O\textsubscript{4}, and CeZrO\textsubscript{4}/MgAl\textsubscript{2}O\textsubscript{4} can be seen in fig. 3.3. All the supports had reduction peaks around 200-400 °C, which could correspond to the reduction of NiO with low interaction with the support. For Ni/MgAl\textsubscript{2}O\textsubscript{4} and Ni/CeZrO\textsubscript{4}/MgAl\textsubscript{2}O\textsubscript{4}, there is an additional broad reduction peak between 500 and 900 °C. This could correspond to reduction of NiO closely bound to the support material as high dispersion and strong interaction are known to shift the reduction peaks toward higher temperature [203–205]. However, the high temperature reduction
peak could also arise from the reduction of NiAl$_2$O$_4$ [204, 205]. An increased reducibility for Ni/CeZrO$_4$/MgAl$_2$O$_4$ compared with Ni/MgAl$_2$O$_4$ have been reported by Eltejai et al. [204]. This could also be the case here as the water evolution was higher for Ni/CeZrO$_4$/MgAl$_2$O$_4$ compared with Ni/MgAl$_2$O$_4$.

![Graph](image)

(a) Ni/Ce$_{0.6}$Zr$_{0.4}$O$_2$ and Ni/MgAl$_2$O$_4$

(b) Ni/CeO$_2$ and Ni/CeZrO$_4$/MgAl$_2$O$_4$

**Fig. 3.3:** Water evolution during TPR of for Ni/MgAl$_2$O$_4$, Ni/CeO$_2$, Ni/Ce$_{0.6}$Zr$_{0.4}$O$_2$, and Ni/CeZrO$_4$/MgAl$_2$O$_4$. Gas: 10 % H$_2$ in He, heating rate 10 °C/min.

In the TPR of Ni/CeO$_2$ there are a couple of small reduction peaks at 100-275 °C, which can be ascribed to reduction of oxygen in the CeO$_2$-lattice [206]. At 330 °C there is large reduction peak partly from the reduction of NiO [207, 208]. The significantly larger size of this peak could be explained by reduction of CeO$_2$ to Ce$_2$O$_3$ by spillover of H$_2$ from the metal particles, which has been observed for noble metal catalysts [208]. At 800 °C there is a reduction peak which could correspond to reduction of Ce$_2$O$_3$ to Ce$_2$O$_3$ [206, 209].

Temperature programmed reduction of Ni/Ce$_{0.6}$Zr$_{0.4}$O$_2$ showed two reduction peaks, one at 330 °C and one at 500 °C. The peak at 330 °C is probably due to the reduction of NiO, while the peak at 500 °C could be reduction of Ce$^{3+}$ to Ce$^{2+}$ or reduction of NiO with strong interaction with Ce$_{0.6}$Zr$_{0.4}$O$_2$ [207].

Reductions, which occurs higher than 600 °C, might still occur at 600 °C if exposed to H$_2$ in a much higher concentration [203]. Therefore, full reduction of at least the active Ni should be possible in the activity tests even though the catalysts are reduced at 600 °C.

### 3.2 Effect of temperature and W/F

The effect of temperature on conversion and product distribution in the SR of ethanol was investigated for several Ni-based catalysts at temperatures between 400-700 °C and a S/C-ratio of 6. The conversion of ethanol over all of the catalysts at each temperature level initially decreased with time and then reached a relatively stable conversion after approximately 1.5 h. The decrease in conversion was largest at 400 °C and 500 °C, which shows that severe deactivation due to carbon deposition or oxidation of Ni occurred at the lowest temperatures. The conversion as function of time at the four temperature levels during SR of ethanol over Ni/CeZrO$_4$/MgAl$_2$O$_4$ can be seen in fig. 3.4, while the initial and pseudo steady state conversion for the other catalysts can be seen in table 3.3. The conversion reported in the following is the pseudo steady state conversion, unless otherwise stated.

The temperature dependence experiments were conducted from high to low temperatures to minimize the influence of carbon deposition and subsequent deactivation of catalysts which
3. Steam reforming of ethanol: Effects of support and additives on Ni-based catalysts

Fig. 3.4: The conversion as function of time during SR of ethanol at different temperatures over Ni/CeZrO$_4$/MgAl$_2$O$_4$. Experimental conditions: S/C: 5.8, $m_{\text{Cat}} = 0.50$ g, Ni loading: 8.2 wt%, $F_T = 1.6$ NL/min, $y_{\text{Eth}} = 3.4$ vol%, $y_{\text{H}_2\text{O}} = 38.8$ vol%, $N_2$ as balance.

is reported to occur at a larger extent at temperatures between 400 and 550 °C [210]. To check for deactivation, the experiment at 600 °C over Ni/MgAl$_2$O$_4$ was repeated after operation at 500 °C and 400 °C. The conversion and yield of CH$_4$ and C$_2$H$_4$ from the last point at 600 °C during the first cycle and first point of the second cycle can be seen in table 3.2. There was a slight decrease in conversion after being at 400 °C and 500 °C, which could be due to carbon deposition.

Tab. 3.2: Comparison of conversion and yield of CH$_4$ and C$_2$H$_4$ after SR at 600 and 700 °C and after SR at 700, 600, 500, 400 °C.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Conversion [%]</th>
<th>$Y_{\text{CH}_4}$ [%]</th>
<th>$Y_{\text{C}_2\text{H}_4}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>84</td>
<td>3.3</td>
<td>2.4</td>
</tr>
<tr>
<td>2</td>
<td>82</td>
<td>3.8</td>
<td>1.8</td>
</tr>
</tbody>
</table>

The trends in product distribution as function of temperature were similar over all of tested catalysts and the results from SR of ethanol over Ni/CeZrO$_4$/MgAl$_2$O$_4$ are used to highlight these trends. The offgas concentrations on H$_2$O and N$_2$-free basis as function of the temperature over Ni/CeZrO$_4$/MgAl$_2$O$_4$ at S/C=6 can be seen in fig. 3.5. The fractions of CH$_4$ and CO$_2$ in the offgas decreased with increasing temperature, while the fractions of H$_2$ and CO increased. This corresponds to an increase in the activity for the SR reactions and a shift in the WGS toward CO and H$_2$ with temperature as predicted by thermodynamics. The fraction of ethene, decreased with temperature and approached zero at 600 °C and above.

A comparison between the thermodynamic equilibrium and the actual product distribution over Ni/CeZrO$_4$/MgAl$_2$O$_4$ can be seen in figure 3.6. The figure shows that the product distribution approached equilibrium with increasing temperature. At the highest temperature the actual offgas composition and thermodynamic equilibrium were quite close.
The yield of H$_2$ was 3% at 400 °C over Ni/CeZrO$_4$/MgAl$_2$O$_4$ and then increased with temperature to 75% or 4.5 moles of H$_2$ produced pr. mole of ethanol converted at 700 °C. There was no significant difference in maximum yield of H$_2$ between the different catalysts, which was achieved at 700 °C and varied between 72% and 75%.
The liquid effluent from the condenser contained mainly ethanol and water, but small amounts of acetaldehyde, acetic acid, and acetone were also identified. In addition condensation at dry ice temperature revealed di-ethyl ether as well. The conversions to these species decreased with increasing temperatures and were below 1% at 400 °C. The reactions responsible for formation of these compounds are dehydrogenation, oxidation, recombination, and dehydration as shown in reactions 3.9 to 3.12. Similar by-products have been reported by others [52, 57, 89].

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} & \rightleftharpoons \text{CH}_3\text{CHO} + \text{H}_2 & (3.9) \\
\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} & \rightleftharpoons \text{CH}_3\text{COOH} + \text{H}_2 & (3.10) \\
2\text{CH}_3\text{CHO} & \rightleftharpoons \text{CH}_3\text{COCH}_3 + \text{CO} + \text{H}_2 & (3.11) \\
2\text{CH}_3\text{CH}_2\text{OH} & \rightleftharpoons \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{H}_2\text{O} & (3.12)
\end{align*}
\]

The effect of W/F over Ni/MgAl\(_2\)O\(_4\) at 600 °C and a S/C-ratio of 6 is shown in fig. 3.7. The conversion and yield of H\(_2\) decreased with decreasing W/F, while the yield of CH\(_4\) and C\(_2\)H\(_4\) increased. This showed that as W/F became smaller the offgas composition moved away from the thermodynamical equilibrium as expected.

![Fig. 3.7: Conversion, yield of hydrocarbons, and yield of H\(_2\) as function of space velocity in the SR of ethanol over Ni/MgAl\(_2\)O\(_4\) at 600 °C. Experimental conditions: S/C: 6, Temp.: 563-583 °C, m\(_{\text{Cat}}\) = 0.50 g, Ni loading: 8.2 wt\%, \(F_T\) = 0.8 - 2.8 NL/min, \(x_{\text{Eth}}\) = 3.9 %, \(x_{\text{H}_2\text{O}}\) = 47%, \(N_2\) as balance.](image)

### 3.3 Influence of carrier material

The conversion as function of temperature over four different Ni-based catalysts is shown in fig. 3.8. The conversion was highest for Ni/Ce\(_{0.6}\)Zr\(_{0.4}\)O\(_2\) and Ni/CeZrO\(_4\)/MgAl\(_2\)O\(_4\) while Ni/MgAl\(_2\)O\(_4\) and Ni/CeO\(_2\) had lower degrees of conversion. Similar differences were observed in initial activities (see table 3.3).

The nickel particle size for the different catalysts ranged from 6 to 15 nm and it is generally assumed that smaller particles will be more active due to the higher dispersion and a higher
number of active step sites [38]. However, the nickel particle size did not seem to be determining for the conversion as the Ni/\text{CeZrO}_4/MgAl_2O_4 and Ni/MgAl_2O_4, which had similar \( d_p \) (see table 3.1), gave different conversions. Furthermore, Ni/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 with the largest nickel particles showed the highest conversion. Therefore it seems that the type of support is more important than the size of the nickel particles at least as long as the Ni particles do not differ much in size.

The high activity of Ni/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 could be ascribed to increased water dissociation for this support [66, 67]. This will lead to more OH-species on the surface of the catalysts, which can react with C-species forming carbon oxides and H\textsubscript{2}. Reactions with lattice oxygen on these types of support have also been proposed and might contribute as well [68]. It can be seen from fig. 3.8 that the addition of CeO\textsubscript{2} and ZrO\textsubscript{2} to MgAl\textsubscript{2}O\textsubscript{4} increased the conversion, which could be ascribed to a similar effect.

![Fig. 3.8: Comparison of conversion as function of temperature over the tested Ni-based catalysts. TOS: 50-70 h. Experimental conditions: S/C: 5.3-6.0, \( m_{\text{Cat}} = 0.50 \text{ g} \), Ni loading: 8.0-8.2 wt\%, \( F_T = 1.5 - 1.6 \text{ NL/min} \), \( y_{\text{Eth}} = 3.2 - 3.5 \text{ vol\%} \), \( y_{\text{H}_2\text{O}} = 38.6 - 39.2 \text{ vol\%} \), \( N_2 \) as balance.](image)
3. Steam reforming of ethanol: Effects of support and additives on Ni-based catalysts

3.3.1 Deactivation

It was chosen to test the different catalysts at 600 °C for 4 h in order to determine differences in carbon deposition and activity during SR of ethanol. At this temperature full conversion was not achieved, which leads to higher potential for forming carbon deposits and therefore it is easier to distinguish differences in catalytic performances.

The conversion as function of time over four different catalysts tested at 600 °C can be seen in fig. 3.9. All the tested catalysts showed a more or less pronounced decrease in conversion with time. The deactivation was most pronounced for Ni/CeO\(_2\) and Ni/MgAl\(_2\)O\(_4\) while especially Ni/Ce\(_{0.6}\)Zr\(_{0.4}\)O\(_2\) had a low drop in conversion with time.

![Graph showing conversion as function of time](image)

**Fig. 3.9:** Conversion as function of time at 580 °C for Ni on four different supports. Experimental conditions: S/C: 5.3-6.0, Temp.: 579-585 °C, m\(_{\text{Cat}}\) = 0.50 g, Ni loading: 8.0-8.2 wt%, \(F_\text{T} = 1.5 - 1.6\) NL/min, \(x_{\text{Eth}} = 3.2 - 3.5\) vol%, \(y_{\text{H}_2\text{O}} = 38.6 - 39.2\)vol%, \(N_2\) as balance.

Deactivation in the SR can be ascribed to sintering and carbon deposition [49, 50]. Temperature programmed oxidation of the spent catalysts as well as measurement of surface area and nickel particle size of the spent catalysts were performed to elucidate what caused the deactivation.

The release of carbon oxides during TPO of the spent catalysts is shown in fig. 3.10. It can be seen that the carbon oxides release occurred at different temperatures depending on the support material. Ni/Ce\(_{0.6}\)Zr\(_{0.4}\)O\(_2\) showed carbon oxide release in a broad peak at temperatures between 350 and 580 °C while Ni/MgAl\(_2\)O\(_4\) had a single broad peak with a maximum at 560 °C. Ni/CeO\(_2\) had two peaks; one around 475 °C and a broad one from 550 °C to 650 °C. Ni/CeZr\(_4\)/MgAl\(_2\)O\(_4\) showed carbon release at three different peak temperatures, 475 °C, 515 °C, and 545 °C. The first coincide with the first peak from Ni/CeO\(_2\), while the last peak coincide with the oxidation from Ni/MgAl\(_2\)O\(_4\). The results indicate that the carbon was oxidized at different temperatures depending on whether it is located on a redox-active support or on the Ni particles. CeO\(_2\) and CeZr\(_4\) are known as soot oxidation catalysts [202] and therefore these might catalyze the oxidation of carbon at lower temperature compared with MgAl\(_2\)O\(_4\) or Ni and be responsible for the carbon release at temperatures below 550 °C.

The results from the TPO experiments can give an indication of which type of carbon was deposited on the catalysts. It has been reported that carbon oxides released below 500
3. Steam reforming of ethanol: Effects of support and additives on Ni-based catalysts

Fig. 3.10: Carbon oxides release as function of temperature over Ni-based catalysts after 4 h on stream. Experimental conditions: $F_T = 0.9-1$ NL/min, $O_2 = 2-3\%$, $N_2$ as balance, heating rate: 10 K/min.

°C arises from monoatomic carbon or filamentous carbon like single walled carbon nanotubes, while carbon oxides released above 500 °C arises from amorphous carbon with different degrees of graphitization or bulkier forms of carbon nanotubes [119, 211, 212]. The oxidation agent in these studies was $O_2$. This could indicate that carbon formed on Ni/Ce$_{0.6}$Zr$_{0.4}$O$_2$ mainly was monoatomic carbon or single walled nanotubes, while the carbon formed on Ni/MgAl$_2$O$_4$ was amorphous carbon. On Ni/CeO$_2$ it appears that both types of carbon are formed as two peaks are observed. However due to the catalytic properties of CeO$_2$ and CeZrO$_4$ in carbon oxidation the above limits might not apply.

TEM-images of the spent catalysts were acquired to investigate this further. Figure 3.11(a) and 3.11(b) shows TEM images of spent Ni/Ce$_{0.6}$Zr$_{0.4}$O$_2$ particles and carbon whiskers can clearly be observed. This can, to some extent, explain the stable activity of this catalyst as the Ni particles will be able to catalyze the SR reactions despite carbon deposition [40, 41]. A TEM image of a spent Ni/MgAl$_2$O$_4$ catalyst can be seen in fig. 3.11(c). Analysis of this image and other images did not reveal carbon whiskers, which could indicate that the carbon was mainly present as amorphous or encapsulating carbon.

Tab. 3.4: Conversion and carbon deposition during a 4 h experiment at approx. 600 °C over Ni/Ce$_{0.6}$Zr$_{0.4}$O$_2$ and Ni/MgAl$_2$O$_4$. Experimental conditions: S/C: 5.3-6.0, Temp.: 579-585 °C, $m_{Cat} = 0.50$ g, Ni loading: 8.0-8.2 wt%, $F_T = 1.5 - 1.6$ NL/min, $x_{Eth} = 3.2-3.5\%$, $x_{H_2O} = 38.6-39.2\%$, $N_2$ as balance.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion</th>
<th>Carbon deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>After 4 h</td>
</tr>
<tr>
<td>Ni/Ce$<em>{0.6}$Zr$</em>{0.4}$O$_2$</td>
<td>98</td>
<td>95</td>
</tr>
<tr>
<td>Ni/CeO$_2$</td>
<td>89</td>
<td>67</td>
</tr>
<tr>
<td>Ni/MgAl$_2$O$_4$</td>
<td>89</td>
<td>78</td>
</tr>
<tr>
<td>Ni/CeZrO$_4$/MgAl$_2$O$_4$</td>
<td>95</td>
<td>90</td>
</tr>
</tbody>
</table>
The amount of carbon deposited on each of the catalysts is shown in table 3.4. The highest carbon deposition was observed over Ni/Ce\(_{0.6}\)Zr\(_{0.4}\)O\(_2\), 15.2 \(\text{mmole C} / \text{mole C}_{\text{Feed}}\) or 96 \(\text{mg C} / \text{gCat} \cdot \text{h}\), which may seem contradictory to the fact that it remained stable and active over time. However, as discussed above carbon was present as whiskers on this catalyst, which is known not to decrease the catalytic activity \([40, 41]\). The other catalysts had much lower levels of carbon deposition in the range of 2-4 \(\text{mmole C} / \text{mole C}_{\text{Feed}}\) or 15-26 \(\text{mg C} / \text{gCat} \cdot \text{h}\). The results show that adding CeZrO\(_4\) to Ni/MgAl\(_2\)O\(_4\) decreased carbon deposition from 26 to 15 \(\text{mg C} / \text{gCat} \cdot \text{h}\). This decrease could be due to reaction of coke with lattice oxygen from CeZrO\(_4\) \([202]\) or due to an increased amount of OH-species on the support. The carbon on Ni/CeZrO\(_4\)/MgAl\(_2\)O\(_4\) was oxidized at a lower temperature compared with Ni/MgAl\(_2\)O\(_4\), see fig. 3.10, which shows that CeZrO\(_4\) catalyzes carbon oxidation in the TPO experiments and will probably also do this under reaction conditions.

Ni/CeO\(_2\), Ni/MgAl\(_2\)O\(_4\), and Ni/CeZrO\(_4\)/MgAl\(_2\)O\(_4\) had nickel particles with a size of 6-10
nm while Ni/Ce_{0.6}Zr_{0.4}O_2 had nickel particles with \( d_p \) of 15-20 nm (see table 3.1). Therefore the lower amount of carbon on Ni/CeO_2, Ni/MgAl_2O_4, and Ni/CeZrO_4/MgAl_2O_4 compared with Ni/Ce_{0.6}Zr_{0.4}O_2 could be due to smaller Ni particles, which lowers the risk of formation of carbon whiskers [30].

The surface area and NiO-particle size before and after a temperature dependence experiment are shown in table 3.4. The surface area for Ni/CeO_2 and Ni/Ce_{0.6}Zr_{0.4}O_2 decreased by a factor of roughly 3 and 2, respectively, and the Ni particle size increased by similar factors. For Ni/MgAl_2O_4 and Ni/CeZrO_4/MgAl_2O_4 the surface area did not decrease significantly, while the Ni particle size increased by a factor of 1.5 for both catalysts. The change in Ni particle size for all the catalysts showed that sintering did occur. However, the two spinel based catalysts seemed more stable as the BET surface areas and Ni particle size did not change much over a 60-70 \( h \) experiment.

The results show that all the tested Ni-based catalysts suffer from sintering and carbon deposition to some extent, which led to deactivation. Therefore other changes to the catalyst formulation or process based optimization is needed in order to minimize these problems.

**Tab. 3.5:** Comparison between BET surface area and XRD Ni particle size before and after a temperature dependence experiment with 60-70 \( h \) on stream.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area</th>
<th>NiO particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh [m^2/g]</td>
<td>Spent [m^2/g]</td>
</tr>
<tr>
<td>Ni/Ce_{0.6}Zr_{0.4}O_2</td>
<td>90</td>
<td>42</td>
</tr>
<tr>
<td>Ni/CeO_2</td>
<td>113</td>
<td>35</td>
</tr>
<tr>
<td>Ni/MgAl_2O_4</td>
<td>69</td>
<td>66</td>
</tr>
<tr>
<td>Ni/CeZrO_4/MgAl_2O_4</td>
<td>63</td>
<td>53</td>
</tr>
</tbody>
</table>

**3.4 Effect of temperature on carbon deposition**

The carbon deposition and ethene formation as function of temperature in the SR of ethanol at S/C=6 for experiments with 4 \( h \) on stream over Ni/MgAl_2O_4 and Ni/Ce_{0.6}Zr_{0.4}O_2 can be seen in fig. 3.12. The experiments for Ni/Ce_{0.6}Zr_{0.4}O_2 at 400 °C and 500 °C were stopped after 2 \( h \) on stream due to excessive carbon build up causing a large pressure drop over the reactor.

The carbon deposition on both Ni/MgAl_2O_4 and Ni/Ce_{0.6}Zr_{0.4}O_2 had a maximum at 500 °C. For Ni/MgAl_2O_4 it decreased with temperature from 15 \( \frac{\text{mmol C}}{\text{mol C}_{\text{Pool}}} \) to 0.03 \( \frac{\text{mmol C}}{\text{mol C}_{\text{Pool}}} \) (94 to 0.2 \( \frac{\text{mg C}}{\text{g Cat} \cdot \text{h}} \) ) when increasing the temperature from 506 to 741 °C. For Ni/Ce_{0.6}Zr_{0.4}O_2 a decrease from 88 \( \frac{\text{mmol C}}{\text{mol C}_{\text{Pool}}} \) to 0.06 \( \frac{\text{mmol C}}{\text{mol C}_{\text{Pool}}} \) (552 to 0.4 \( \frac{\text{mg C}}{\text{g Cat} \cdot \text{h}} \) ) in carbon deposition was observed when increasing the temperature from 495 to 755 °C. The peak release of carbon oxides over Ni/MgAl_2O_4 during TPO occurred at 520 °C after operating at 400 °C while carbon oxides release after operating at 700 °C occurred at 600 °C. For Ni/Ce_{0.6}Zr_{0.4}O_2 an additional carbon oxides release peak at 630 °C was observed after operation at 700 °C and 750 °C. The shift in carbon oxide release toward higher temperatures during TPO indicated that the carbon deposited at low temperatures had a lower degree of graphitization and was more reactive. Furthermore, other routes to carbon deposition like thermal decomposition of ethanol may become important with increasing temperatures and led to other types of carbon deposition causing the observed shift.
3. Steam reforming of ethanol: Effects of support and additives on Ni-based catalysts

![Graph: Carbon deposition and ethene formation as function of temperature](image)

**Fig. 3.12:** Carbon deposition and ethene formation after 4 h on stream as function of temperature over Ni/MgAl₂O₄ and Ni/Co₆Zr₄O₂. Full lines: Carbon deposition; Dashed lines: Ethene formation. The experiments at 400 and 500 °C for Ni/Co₆Zr₄O₂ were stopped after 2 h due to risk of blockage. Experimental conditions: S/C: 5.5-6.2, Temp: 408-755 °C, m_cat = 0.50 g, Ni loading: 8.1-8.2 wt%, F_T = 1.5 NL/min, \( y_{Eth} = 3.2 - 3.6 \) vol%, \( y_{H_2O} = 38.8 - 39.0 \) vol%, \( N_2 \) as balance.

The formation of ethene as function of temperature had a maximum at 500 °C and at low temperatures were significantly higher for Ni/Co₆Zr₄O₂ compared to Ni/MgAl₂O₄, see fig. 3.12. The maximum in carbon deposition over both catalysts coincide with the maximum of formation of ethene, which is a very potent coke precursor [43, 192]. This could explain the high deposition of carbon at 500 °C. Thermodynamic analysis using the measured and thermodynamic equilibrium offgas composition (Rostrup-Nielsen and Christiansen [42]) did not show potential for carbon formation from methane decomposition, Boudouard reaction, or CO decomposition at 500 °C. However, at 400 °C there is affinity for carbon formation through methane decomposition. The affinity for carbon formation through the different reactions as function of temperature is described in Appendix B.

The decrease in carbon deposition with increasing temperature could also be explained by an increased reaction rate for the SR reactions leading to fewer carbon-species on the surface of the catalysts. Furthermore the gasification of deposited carbon by either steam or CO₂ will increase with temperature as well. At the lowest temperature of 400 °C ethanol may not be activated and therefore conversion and carbon deposition are lower. In fig. 3.4, there was observed a large drop in conversion at 400 °C over time, even larger than at 500 °C, where carbon deposition was more severe. An explanation could be partial oxidation of the catalyst at 400 °C caused by the high concentration of steam and low concentration of H₂.

Results from thermodynamic and experimental studies of the SR of ethanol predict a decrease in carbon deposition with temperature [53, 64, 74, 213, 214]. Similar to this study, Wang et al. [210] found a maximum in carbon deposition at 500 °C for SR of ethanol over a Co/Co₂O₃ catalyst. Wang et al. [210] ascribed the high carbon formation to disproportionation of CO and CH₄ and a slow reaction rate for steam and dry reforming. Another and perhaps more likely explanation could be a formation of carbon from ethene, as indicated in fig. 3.12.
An interesting difference between Ni/MgAl2O4 and Ni/Ce0.6Zr0.4O2 was found in the product distribution at 750 °C where Ni/MgAl2O4 completely converted ethanol to carbon oxides while Ni/ Ce0.6Zr0.4O2 still had small amounts of methane in the offgas. Furthermore, a slight loss in both methane SR and WGS activity with time over Ni/Ce0.6Zr0.4O2 was observed at 755 °C, whereas Ni/MgAl2O4 was stable over time (the experiment had a run time of 4 h).

A drawback of running at high temperatures is that sintering is more likely to occur. Therefore the surface area of the spent catalysts was measured to investigate how severe the sintering was and the results are shown in table 3.6. It can be seen that no sintering of the catalysts took place at temperatures between 500 °C and 700 °C, while at roughly 750 °C sintering increased and the surface area decreased.

Table 3.6: Surface area of Ni/Ce0.6Zr0.4O2 and Ni/MgAl2O4 after 4 h on stream at different temperatures. Experimental conditions: S/C: 5.5-6.2, Temp: 408-755 °C, mCat = 0.50 g, Ni loading: 8.1-8.2 wt%, FT = 1.5 NL/min, yEth = 3.2 - 3.6 vol%, yH2O = 38.8 - 39.0 vol%, N2 as balance.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Fresh</th>
<th>400 °C</th>
<th>500 °C</th>
<th>600 °C</th>
<th>700 °C</th>
<th>750 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/ Ce0.6Zr0.4O2</td>
<td>88</td>
<td>-</td>
<td>-</td>
<td>67</td>
<td>67</td>
<td>53</td>
</tr>
<tr>
<td>Ni/MgAl2O4</td>
<td>69</td>
<td>66</td>
<td>61</td>
<td>61</td>
<td>60</td>
<td>53</td>
</tr>
</tbody>
</table>

3.5 Effect of additives

Steam reforming of ethanol at 600 °C and S/C-ratio of 6 for 4 h and subsequent determination of carbon deposition was conducted for Ni/MgAl2O4 promoted with K, CeO2, ZrO2, or mixtures hereof to evaluate whether these additives could have a beneficial effect on the catalyst performance. The surface area, NiO particle size, additive- and Ni-loading for the promoted catalysts can be seen in table 3.1. The additives did not significantly influence Ni-particle size or surface area and therefore the changes in catalytic performance can be ascribed to the properties of the additives.

The conversion as function of time for the different Ni/MgAl2O4 catalysts can be seen in fig. 3.13. The conversion was high and relatively stable for the catalysts promoted with K, CeO2, CeZrO4, and K/CeZrO4. The base catalyst, Ni/MgAl2O4, behaved as shown previously with a decrease in conversion over the entire 4 h while the catalyst with CeO2 had an induction period of 1 h before reaching a stable conversion in the range of 85 %. In conclusion adding CeO2, K, or CeZrO4 seem to promote a more stable performance of the catalyst.

The product distributions were similar for the base and promoted Ni/MgAl2O4 and above 95 % of converted ethanol was converted to carbon oxides and H2, and less than 5 % to methane and ethene. However, a slight increase in the yield of CH4 was observed for the promoted catalysts compared with Ni/MgAl2O4. The yield of ethene can be seen in fig. 3.14 and was similar for the base case and most of the promoted catalysts. Two exceptions were for Ni/K-CeO2/MgAl2O4, which had no ethene in the offgas, and Ni/CeO2/MgAl2O4, which had a higher yield of ethene.

The effect of tested additives on conversion, yield of ethene, and carbon deposition are shown in fig. 3.14. All of the additives improved the catalyst performance either with respect to conversion, carbon deposition, or in most of the cases both. Promotion with CeO2 led to the lowest carbon deposition of 0.9 \( \text{mmol C} / \text{mol C}_{\text{Feed}} \) or 6 \( \text{mg C} / \text{gCat·h} \) while the conversion was similar.
3. Steam reforming of ethanol: Effects of support and additives on Ni-based catalysts

**Fig. 3.13:** Conversion as function of time on stream for Ni/MgAl₂O₄ and Ni/MgAl₂O₄ promoted with CeO₂, CeO₂-K, CeZrO₄, K, and K-CeZrO₄. Experimental conditions: S/C: 5.6-6.1, Temp.: 579-592 °C, mCat = 0.50 g, Ni loading: 8.0-8.3 wt%, F_T = 1.5 NL/min, yEth = 3.2 – 3.6 vol%, yH₂O = 38.8 – 39.0 vol%, N₂ as balance.

**Fig. 3.14:** Comparison of conversion, carbon deposition, and yield of ethene after 4 h on stream for Ni/MgAl₂O₄-catalysts with different additives. Experimental conditions: S/C: 5.6-6.1, Temp.: 579-592 °C, mCat = 0.50 g, Ni loading: 8.0-8.3 wt%, F_T = 1.5 NL/min, yEth = 3.2 – 3.6 vol%, yH₂O = 38.8 – 39.0 vol%, N₂ as balance.

to the base case. Ni/CeO₂ had the lowest activity of the four tested support materials and sintered quite significantly, however it did show low carbon deposition. The higher conversion of ethanol over Ni-CeO₂/MgAl₂O₄ compared to Ni/CeO₂, as well as an improved stability could be explained by a stabilization of the CeO₂ on MgAl₂O₄ so sintering decreased (see fig.
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The decrease in carbon deposition might be explained by ceria monomers or small CeO$_2$ particles on MgAl$_2$O$_4$, which facilitated oxidation of surface carbon during SR.

Ni-K/MgAl$_2$O$_4$ also showed a decrease in carbon deposition and as well as an increased conversion compared with the base case. Therefore K and CeO$_2$ both seem to influence the catalyst by enhancing oxidation/gasification or decreasing deposition of solid carbon while K also induces a higher activity. Similar trends have been reported by others [82, 122]. Adding both CeO$_2$ and K to the base catalyst improved the conversion while carbon deposition was on a level between adding either only K or only CeO$_2$. The promotion with CeZrO$_4$ also increased conversion, but carbon deposition was the highest among the promoted catalysts, albeit still significantly lower than the base Ni/MgAl$_2$O$_4$ catalyst. The increase in conversion when adding CeZrO$_4$ could be due to increased water dissociation or spill-over effects, as mentioned earlier. The Ni/K-CeO$_2$/MgAl$_2$O$_4$ seems to be the most interesting catalyst as it combined a high conversion with a low rate of carbon deposition.

The decrease in carbon deposition was not due to changes in ethene formation and therefore it appears the role of the additives is to increase the rate of SR reactions and hereby minimize the carbon deposition.

**Tab. 3.7:** Conversion and carbon deposition in SR of ethanol after 4 h on stream over Ni/K-CeO$_2$/MgAl$_2$O$_4$ and Ni-K/CeZrO$_4$/MgAl$_2$O$_4$ at different space velocities. Experimental conditions: S/C: 5.6-6.1, Temp.: 579-592 °C, $m_{Cat}$ = 0.264 – 0.50 g, Ni loading: 8.2 wt%, $F_T$ = 1.5 NL/min, $y_{Eth}$ = 3.2 – 3.5 vol%, $y_{H_2O}$ = 38.8 – 39.0 vol%, $N_2$ as balance.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>WHSV $[h^{-1}]$</th>
<th>Conversion [%]</th>
<th>Carbon deposition $Y_{C,H_4}$</th>
<th>$Y_{C,H_4}$ [mmole C/mole C$_{Feed}$]</th>
<th>Carbon deposition [%]</th>
<th>Carbon deposition [mg C/h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/K-CeO$_2$</td>
<td>13</td>
<td>98</td>
<td>1.2</td>
<td>4</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Ni/K-CeO$_2$</td>
<td>25</td>
<td>81</td>
<td>1.3</td>
<td>4</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>Ni-K/CeZrO$_4$</td>
<td>12</td>
<td>100</td>
<td>1.8</td>
<td>5</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>Ni-K/CeZrO$_4$</td>
<td>25</td>
<td>81</td>
<td>1.5</td>
<td>5</td>
<td>0.59</td>
<td></td>
</tr>
</tbody>
</table>

Ni/K-CeO$_2$/MgAl$_2$O$_4$ and Ni-K/CeZrO$_4$/MgAl$_2$O$_4$ both showed almost full conversion and to ensure that the low carbon deposition was due to the additives and not full conversion the experiments were repeated at a higher space velocity. The results from the experiments at different space velocities are shown in table 3.7. The results show interestingly that the same amount of carbon was deposited at the higher space velocity with conversion around 80 % and this shows that the additives do decrease the carbon deposition in the case of Ni/K-CeO$_2$/MgAl$_2$O$_4$ and Ni-K/CeZrO$_4$/MgAl$_2$O$_4$ also under more demanding conditions. The yield of ethene increased slightly with increasing space velocity, however it did not seem to influence the carbon deposition significantly. The carbon deposition seemed to be more dependent on temperature compared to space velocity as the increasing the space velocity did not influence the total amount of carbon deposition.

Carbon burn-off experiments were also carried for the Ni/MgAl$_2$O$_4$ catalysts with the different additives. The carbon oxides release as function of temperature over the promoted catalysts are shown in fig. 3.15. The carbon oxides release for the promoted catalysts shifted toward lower temperatures, which indicates that combustion and also gasification is catalyzed by K as well as ZrO$_2$ and CeO$_2$. However, the difference could also be due to different types
of carbon on the catalysts. The catalyzing effects of K, CeO₂, and ZrO₂ on combustion and gasification is known from the combustion and gasification literature [202, 215, 216]. This is also a contributing factor to the lowering of carbon deposition as well as the increase in activity observed in this study.

3.5.1 Effect of TOS

Two of the catalysts with additives, Ni-K/MgAl₂O₄ and Ni/CeO₂-K/MgAl₂O₄, which showed a rather stable conversion with time and a low rate of carbon deposition, were tested for an extended period of time (24 h) to further investigate stability and carbon deposition. The conversion and yield of hydrocarbons as function of time for Ni-K/MgAl₂O₄ and Ni/CeO₂-K/MgAl₂O₄ can be seen in fig. 3.16. The conversion over both catalysts decreased slowly with time with a rate of roughly 0.1 %-point pr. h. Furthermore the yield of hydrocarbons increased with time and a more pronounced increase was observed after 20 h on stream. No ethene was detected in the effluent from SR of ethanol over Ni/CeO₂-K/MgAl₂O₄, while the yield of ethene increased from 0.10 % to 0.16 % over Ni-K/MgAl₂O₄. Therefore deactivation was apparent even though the first four h on stream appeared stable. However the decrease in conversion with time was more pronounced for Ni/MgAl₂O₄ and therefore the additives still provided a marked improvement.

The amount of carbon formed after 24 h on stream was determined and the total carbon deposition and the average rate of carbon formation at different times can be seen in table 3.8. The carbon deposition over Ni-K/MgAl₂O₄ and Ni/CeO₂-K/MgAl₂O₄ was quite similar after 4 h, however the buildup of carbon after 24 h was lower for Ni/CeO₂-K/MgAl₂O₄. This could indicate that CeO₂ has a positive effect on the carbon deposition even during longer periods of operation. The TPO profiles moved towards higher temperatures after 24 h on stream and for Ni/CeO₂-K/MgAl₂O₄ a shoulder at 475 °C increased with time, which could indicate that the type of carbon deposition changes with time.

TEM-images of spent Ni-K/MgAl₂O₄ and Ni/CeO₂-K/MgAl₂O₄ can be seen in fig. 3.17. These images show that carbon whiskers were formed on both catalysts. Carbon whiskers can,
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Fig. 3.16: Conversion and yield of hydrocarbons as function of time for Ni-K/MgAl₂O₄ and Ni/CeO₂-K/MgAl₂O₄. Experimental conditions: S/C: 6, Temp.: 576 °C, mCat = 0.50 g, Ni loading: 8.0-8.3 wt%, FT = 1.5 NL/min, yEth = 3.3 vol%, yH₂O = 40.1 vol%, N₂ as balance.

Tab. 3.8: Total carbon deposition and average rate of formation on Ni-K/MgAl₂O₄ and Ni/CeO₂-K/MgAl₂O₄ as function of time at 600 °C. Average values are from intervals from 0-4 h and 4-24 h. Experimental conditions: S/C: 6.0, Temp: 579-586 °C, mCat = 0.50 g, Ni loading: 8.2 wt%, FT = 1.5−1.6 NL/min, yEth = 3.7−3.9 vol%, yH₂O = 38.9 vol%, N₂ as balance.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time [h]</th>
<th>Total C Dep [mg C]</th>
<th>Carbon deposition [mg C g⁻¹ Cat·h]</th>
<th>mmole C mole⁻¹ C Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-K/MgAl₂O₄</td>
<td>4</td>
<td>20</td>
<td>8.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Ni-K/MgAl₂O₄</td>
<td>24</td>
<td>44</td>
<td>2.7</td>
<td>0.4</td>
</tr>
<tr>
<td>Ni/CeO₂-K/MgAl₂O₄</td>
<td>4</td>
<td>17</td>
<td>9.8</td>
<td>1.5</td>
</tr>
<tr>
<td>Ni/CeO₂-K/MgAl₂O₄</td>
<td>24</td>
<td>33</td>
<td>3.7</td>
<td>0.6</td>
</tr>
</tbody>
</table>

with time, break the catalyst pellets causing pressure drop over the catalyst bed, which can be detrimental for industrial units, due to mal distribution of the gas causing local hot spots [42].

The surface area and nickel particle size before and after a 24 h experiment at 600 °C can be seen in table 3.9. The surface area of the catalysts did not change during 24 h operation at 600 °C. However, the NiO particle size increased from 7 to 12 nm for Ni-K/MgAl₂O₄ and from 6 to 9 nm for Ni/CeO₂-K/MgAl₂O₄, which indicate sintering of the Ni-particles for both of the catalysts. Sintering due to the TPO might also account for some of the observed sintering as O₂ is known to promote sintering [217].

3.6 Sulfur addition

Sulfur addition was investigated on Ni-CeO₂/MgAl₂O₄ to test if coverage of part of the Ni particles by sulfur could decrease the carbon deposition. Sulfur might lower the carbon depo-
3. Steam reforming of ethanol: Effects of support and additives on Ni-based catalysts

(a) Ni-K/MgAl₂O₄ at 9900 times magnification
(b) Ni-K/MgAl₂O₄ at 95000 times magnification
(c) Ni/CeO₂-K/MgAl₂O₄ at 9900 times magnification
(d) Ni/CeO₂-K/MgAl₂O₄ at 29000 times magnification

Fig. 3.17: TEM images of spent Ni-K/MgAl₂O₄ and Ni/CeO₂-K/MgAl₂O₄ after 24 h on stream in the SR of ethanol at 600 °C and a S/C-ratio of roughly 6.

Tab. 3.9: Comparison between BET surface area and XRD Ni particle size for Ni-K/MgAl₂O₄ and Ni/CeO₂-K/MgAl₂O₄ before and after a stability experiment with 24 h on stream at 600 °C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area</th>
<th>NiO particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
<td>Spent</td>
</tr>
<tr>
<td>Ni-K/MgAl₂O₄</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>Ni/CeO₂-K/MgAl₂O₄</td>
<td>54</td>
<td>54</td>
</tr>
</tbody>
</table>

Transition by covering the step sites which are active in carbon deposition and hereby decrease the formation of solid carbon or the presence of sulfur might limit the size of carbon islands and
inhibit the formation of carbon whiskers [41, 42]. A sulfur coverage of roughly 13 % (0.06 wt% S) on Ni-CeO$_2$/MgAl$_2$O$_4$ was achieved by impregnation with an aqueous solution of K$_2$SO$_4$ or H$_2$SO$_4$ to test if a decrease in carbon deposition could be achieved and how the conversion and product distribution would be influenced by sulfur, or sulfur and potassium. The sulfur and potassium content of fresh and spent catalysts was determined by ICP-OES. The sulfur content of a Ni/MgAl$_2$O$_4$-catalyst impregnated with K$_2$SO$_4$, nominal content: 0.03 wt% S (300 ppmw S), before and after an experiment was 245 ppmw S before and 260 ppmw S after an experiment. Therefore the sulfur impregnated on catalysts remained there after heating, reduction, steam reforming, and oxidation.

The sulfur content was determined for a spent catalyst impregnated with H$_2$SO$_4$ and it was 690 ppmw S, compared with the calculated amount of 600 ppmw S. The sulfur and potassium content of the spent catalyst with 300 ppmw and and 700 ppmw K was determined to be 530 ppmw S and 920 ppmw K, so a bit higher than expected. Thus neither sulfur nor potassium were lost from the catalyst during calcination or reduction.

**Tab. 3.10:** Conversion, yield of hydrocarbons, and carbon deposition for Ni/CeO$_2$/MgAl$_2$O$_4$ with different S-sources and without sulfur addition. The nominal sulfur coverage was 13 % or 0.06 wt% S. TOS: 4 h. Experimental conditions: S/C: 5.7-6.0, Temp: 586-588 °C, $m_{\text{cat}}$ = 0.50 g, Ni loading: 8.2 wt%, $F_T$ = 1.5 NL/min, $y_{\text{Eth}}$ = 3.3 – 3.4 vol%, $y_{\text{H}_2}$ = 38.8 – 39.0 vol%, $N_2$ as balance.

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>Conversion (%)</th>
<th>$Y_{C_yH_x}$ (%)</th>
<th>Carbon deposition $[mg\ C/y_{\text{cat}}h]$</th>
<th>$[\text{mmole} C/\text{mole} \text{C}_{\text{fuel}}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/CeO$_2$/MgAl$_2$O$_4$</td>
<td>85</td>
<td>2.9</td>
<td>6.0</td>
<td>9.3</td>
</tr>
<tr>
<td>Ni/CeO$_2$/MgAl$_2$O$_4$ K$_2$SO$_4$</td>
<td>89</td>
<td>9.5</td>
<td>2.2</td>
<td>3.4</td>
</tr>
<tr>
<td>Ni/CeO$_2$/MgAl$_2$O$_4$ H$_2$SO$_4$</td>
<td>85</td>
<td>11.6</td>
<td>3.3</td>
<td>5.1</td>
</tr>
</tbody>
</table>

The conversion, yield of hydrocarbons, and carbon deposition with and without sulfur are presented in table 3.11. An increase in conversion and yield of hydrocarbons, and a decrease in carbon deposition upon sulfur addition by K$_2$SO$_4$ was observed. The increase in conversion was unexpected as sulfur is known to inhibit SR due to blockage of surface sites on the Ni particles. Therefore the effect of K was investigated by adding the sulfur in the form of H$_2$SO$_4$. Potassium can influence the catalytic performance and increase conversion as shown in section 3.5 as well as by others [82, 122]. Table 3.11 shows that impregnation with H$_2$SO$_4$ induced a decrease in carbon deposition and a larger increase in yield of hydrocarbons compared with K$_2$SO$_4$, but the conversion was similar to the base case. Therefore, the increased conversion might be ascribed to the presence of potassium and it also appears that K induces a lower yield of hydrocarbon. This was also reported by Hu and Lu [82], who investigated the effect of potassium on Ni/Al$_2$O$_3$ in the SR of acetic acid. The increase in the yield of hydrocarbons compared with the base catalyst can be interpreted as a decrease in activity as the hydrocarbons were not converted to the same extent. The hydrocarbons were 95 % CH$_4$ and 5 % C$_2$H$_4$. Interestingly, the amount of ethene formed was highest with sulfur present so the decrease in carbon deposition cannot be ascribed to a decrease in the ethene formation.

The product yields and conversion as function of time over Ni-CeO$_2$/MgAl$_2$O$_4$ impregnated with 0.06 wt% S by either H$_2$SO$_4$ or K$_2$SO$_4$ as impregnation agent can be seen in fig. 3.18(a) and 3.18(b). The catalysts impregnated with either H$_2$SO$_4$ or K$_2$SO$_4$ showed quite stable conversion and product distribution with time on stream. A slight increase in the yield of ethene with time was observed Ni-CeO$_2$/MgAl$_2$O$_4$ impregnated with H$_2$SO$_4$. 

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**Steam reforming of ethanol: Effects of support and additives on Ni-based catalysts** 81
Catalysts with a sulfur loading of 0.03 wt%, 0.06 wt%, and 0.12 wt% were synthesized by impregnation with K$_2$SO$_4$ to investigate the influence of the amount of sulfur on the catalytic performance and the results of these tests are shown in table 3.11. It was found that the yield of hydrocarbons increased while the yield of H$_2$ decreased with increasing amounts of sulfur on the catalysts. All of the sulfur treated catalysts showed a relatively stable conversion during the 4-hour experiments. This shows that sulfur does inhibit especially conversion of methane and ethene to carbon oxides and H$_2$. The carbon deposition is lower with sulfur than without in the three cases investigated with a minimum at 0.03 wt% S. These results indicate that addition of small amounts of sulfur can be used to block sites on the catalyst and hereby inhibit carbon deposition. The loss in activity due to sulfur can mainly be seen.
as an increase in the yield of hydrocarbons. Bengaard et al. [38] have shown that the SR of CH\textsubscript{4} has a lower energy barrier on step sites and blockage of these sites will lead to a lower conversion of methane. This entails a lower amount of carbon species on the surface and a lower risk of carbon deposition due to slower nucleation of carbon whiskers or agglomeration of carbon deposits. Similar to the observations in this study.

**Tab. 3.11:** Conversion, yield of H\textsubscript{2}, yield of hydrocarbons, and carbon deposition in SR of ethanol over Ni/CeO\textsubscript{2}/MgAl\textsubscript{2}O\textsubscript{4} with different degrees of sulfur coverage. Sulfur added as K\textsubscript{2}SO\textsubscript{4}. TOS: 4 h. Experimental conditions: S/C: 5.7-6.0, Temp: 586-588 °C, \( m_{\text{cat}} = 0.50 \) g, Ni loading: 8.1-8.2 wt\%, \( F_T = 1.5 \) NL/min, \( y_{\text{Eth}} = 3.3 - 3.4 \) vol\%, \( y_{\text{H}_2\text{O}} = 38.8 - 39.0 \) vol\%, \( N_2 \) as balance.

<table>
<thead>
<tr>
<th>Sulfur [wt% S]</th>
<th>S-coverage [%]</th>
<th>Conversion [%]</th>
<th>Carbon deposition ( [mg \text{ C}/g_{\text{cat}} \cdot h] )</th>
<th>( \text{mmole C/mole C}_{\text{feed}} )</th>
<th>( Y_{\text{H}_2} ) [%]</th>
<th>( Y_{C,H_x} ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>85</td>
<td>6.0</td>
<td>9.3</td>
<td>80</td>
<td>3.5</td>
</tr>
<tr>
<td>0.03</td>
<td>6</td>
<td>90</td>
<td>1.2</td>
<td>1.5</td>
<td>74</td>
<td>6.2</td>
</tr>
<tr>
<td>0.06</td>
<td>13</td>
<td>89</td>
<td>2.2</td>
<td>3.4</td>
<td>73</td>
<td>9.5</td>
</tr>
<tr>
<td>0.12</td>
<td>26</td>
<td>89</td>
<td>2.4</td>
<td>3.4</td>
<td>64</td>
<td>12.7</td>
</tr>
</tbody>
</table>

### 3.7 Conclusions

In this work the SR of ethanol was investigated over Ni-based catalysts and several strategies for minimizing carbon deposition by changing the catalyst formulation were explored. The main conclusions are:

- Carbon deposition and sintering leading to loss of activity was apparent in SR of ethanol for Ni supported on different carriers including CeO\textsubscript{2}, Ce\textsubscript{0.6}Zr\textsubscript{0.4}O\textsubscript{2}, MgAl\textsubscript{2}O\textsubscript{4}, and CeZrO\textsubscript{4}/MgAl\textsubscript{2}O\textsubscript{4}.

- Carbon deposition was most severe at 500 °C most likely due to a high fraction of ethene in the product gas which is known as a severe carbon precursor. Increasing the temperature to 700 °C or above significantly decreased the carbon deposition.

- Promotion of Ni/MgAl\textsubscript{2}O\textsubscript{4} with K, CeO\textsubscript{2}, and ZrO\textsubscript{2} increased the conversion and lowered the carbon deposition by factors of 2-4. These catalysts appeared very stable over 4 hours of operation. Potassium most likely partly blocks the sites of carbon formation, while the redox-active promoters increase the OH availability on the catalyst and/or provide lattice oxygen for reaction with carbon precursors.

- Experiment over 24 h with Ni/CeO\textsubscript{2}-K/MgAl\textsubscript{2}O\textsubscript{4} and Ni-K/MgAl\textsubscript{2}O\textsubscript{4} catalysts, however, did showed a slow decrease in activity with time accompanied with carbon deposition with a rate of 0.8-1.2 mg C/h. The carbon formed after 24 h was partly as carbon whiskers, which can be detrimental for SR reactors.

- Selective poisoning with sulfur in the form of SO\textsubscript{4} to Ni-CeO\textsubscript{2}/MgAl\textsubscript{2}O\textsubscript{4} led to a decrease in carbon deposition as well as the overall activity of the catalyst, probably due to blockage of step sites on the Ni-particles. The lowest carbon deposition rate over 4 hours of operation of all the tested catalysts was obtained for the Ni-CeO\textsubscript{2}/MgAl\textsubscript{2}O\textsubscript{4} catalyst with 0.03 wt\% S added in the form of K\textsubscript{2}SO\textsubscript{4}.
The results show that it is possible to improve the stability and activity of Ni-based catalysts in steam reforming of oxygenated species by suitable promoters. Nevertheless, carbon formation still takes place which indicates that other, process related means are needed as well for long term operation.
4. STEAM REFORMING OF ETHANOL: EFFECT OF FEED COMPOSITION ON CATALYST STABILITY

Carbon deposition, leading to catalyst deactivation, is major hurdle for the SR of bio-oil and oxygenates, as mentioned above. The previous chapter dealt with optimization of catalyst formulation in order to minimize the carbon deposition, but this could not completely eliminate carbon deposition. Therefore other options for minimizing carbon deposition and inducing a stable performance of the catalyst, like changing the feed composition, is investigated. In this chapter, the addition of H$_2$, O$_2$, and H$_2$O to the feed gas in SR of ethanol has been tested systematically to elucidate the effects on carbon deposition, conversion, and product yields.

Oxidative SR can be used to decrease carbon deposition as oxygen may react with carbon or carbon precursors on the surface of the catalysts. However, oxidative conditions will increase the formation of CO$_2$ and decrease the H$_2$-production [54, 67, 157, 158, 166–168, 197, 200, 218]. Among others Cavallaro et al. [63] reported a decrease in carbon deposition from 0.28 mg/(g$_{cat}$·h) to 0.01 mg/(g$_{cat}$·h) at 650 °C and S/C-ratio of 4.2 over Rh/Al$_2$O$_3$ when adding O$_2$ to the feed gas at a O/C-ratio of 0.4. No carbon was deposited on a La$_{0.9}$Ce$_{0.1}$NiO$_3$-perovskite catalyst operated at 300-800 °C, S/C=1.5, and O/C=0.5 [200]. Furthermore it was shown that O/C-levels lower than 0.5 led to carbon deposition over La$_{0.9}$Ce$_{0.1}$NiO$_3$ at S/C=1.5 and 500 °C [200]. The yield of H$_2$ depends on both S/C-ratio and O/C-ratio and Salge et al. [218] reported a maximum yield of H$_2$ in SR of ethanol under oxidative conditions of 57.5 %, according to the definition of yield used in this work, at 600 °C, S/C=4.5, and O/C=0.66 over a Rh-Ce monolith catalyst [218]. Peea et al. [197] reported a drop in the yield of H$_2$ at 550 °C and S/C=3 from 65 % at O/C=0 to 43 % at O/C=1.5. These results show that addition of oxygen to the feed may solve the carbon deposition problem, but at the cost of a lower yield of H$_2$.

Another strategy to minimize the carbon deposition problem would be to add hydrogen to the feed. Hydrogen might hydrogenate unsaturated compounds like ethene and therefore decrease the deposition of carbon. Furthermore the additional H$_2$ will ensure that the catalyst is reduced under the reaction conditions. Laosiripojana et al. [169] investigated addition of H$_2$ at H/C-ratios between 0 and 5 at S/C-ratio of 1.5 and found a decrease in the yield of hydrocarbons and carbon deposition on Ni/Al$_2$O$_3$ at 900 °C in the SR of ethanol. The yield of CH$_4$ decreased from 10.6 % at H/C=0 to 7.1 % at H/C=5, while the carbon deposition decreased from 1.08 monolayers at H/C=0 to 0.13 monolayers at H/C=5 over Ni/Al$_2$O$_3$. Jacobs et al. [111] reported an increased conversion and methane formation over Pt/Al$_2$O$_3$ at 300 °C, S/C-ratio of 16.7, and H/C-ratio between 0-26.7 in SR of acetic acid. The conversion increased from 5.4 % at H/C=0 to 35.6 % at H/C=26.7, while the yield of CH$_4$ increased from 28 % at H/C=0 to 49.4 % at H/C=26.7. The opposite effect of H$_2$ on the methane formation between Laosiripojana et al. [169] and Jacobs et al. [111] might be ascribed to the effect of temperature on the equilibrium. At temperatures below 500 °C methanation of CO and CO$_2$ is thermodynamically favorable while at temperatures above 500 °C the equilibrium will be shifted toward carbon oxides. Therefore the effect of H$_2$ might be
Table 4.1: Nominal metal loading, surface area, and NiO particle size of the fresh catalysts prior to reduction. XRD reflection peak from NiO peak at $\theta = 62.8^\circ$ used for determination of particle size.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal loading [wt%]</th>
<th>Surface area [$m^2/g$]</th>
<th>NiO particle size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Ce$<em>{0.6}$Zr$</em>{0.4}$O$_2$</td>
<td>8.2</td>
<td>90</td>
<td>28</td>
</tr>
<tr>
<td>Ni/CeO$_2$</td>
<td>8.2</td>
<td>113</td>
<td>10</td>
</tr>
<tr>
<td>Ni/MgAl$_2$O$_4$</td>
<td>8.2</td>
<td>98</td>
<td>4</td>
</tr>
</tbody>
</table>

an increased rate of reaction, which brings the product gas closer to equilibrium i.e. methane at temperatures below 500 °C and carbon oxides above 600 °C.

Ni/MgAl$_2$O$_4$ has been used as test catalyst in most of the experiments presented in this work. It was chosen as the main catalyst, because it is a thermally very stable catalyst, which has proven effective in SR of hydrocarbons. It is often the choice for industrial SR units due to a good compromise between price and activity [30, 42]. Results from SR over Ni/Ce$_{0.6}$Zr$_{0.4}$O$_2$ and Ni/CeO$_2$ catalysts are presented to show that the trends observed in the SR over Ni/MgAl$_2$O$_4$ can be transferred to other catalytic systems.

4.1 Characterization

The surface area, metal loading, and NiO particle size for the investigated catalysts are shown in table 4.1. The three support materials, CeO$_2$, Ce$_{0.6}$Zr$_{0.4}$O$_2$, and MgAl$_2$O$_4$, all yielded catalysts with surface areas in the range of 90-113 $m^2/g$, while the NiO particles were between 4 and 28 nm in diameter. The quite large difference in particle size might influence catalyst performance as well as carbon deposition [196, 200]. Generally, smaller particles increase activity and decrease carbon deposition. The XRD patterns for the three catalysts in table 3.1 can be seen in fig. 4.1(a)-4.1(c) and confirmed that the structure of both of the mixed oxides were Ce$_{0.6}$Zr$_{0.4}$O$_2$ and MgAl$_2$O$_4$.

4.2 Effect of S/C-ratio

The effect of temperature and space velocity (W/F) on the SR of ethanol over different Ni-based catalysts were investigated in the previous chapter. Based on these results the temperature 600 °C was chosen to investigate the effect of $H_2$, $O_2$, $H_2O$. The conversion was around 75 % over Ni/MgAl$_2$O$_4$ at this temperature, a S/C-ratio of 6, and the applied space velocity, which allows evaluation of changes in activity and product distribution with time on stream. In addition the propensity to carbon deposition of the reaction mixture is more clearly revealed when the conversion is kept well below 1. The products obtained in the SR of ethanol over Ni/Ce$_{0.6}$Zr$_{0.4}$O$_2$, Ni/MgAl$_2$O$_4$, and Ni/CeO$_2$ were CO, CO$_2$, CH$_4$, C$_2$H$_4$ as well as acetone, acetic acid and acetaldehyde. The three latter compounds were only formed in minor amounts at 600 °C with a combined yield of 0.1 %.

The S/C-ratio is important in SR as it can influence product distribution, conversion, and deactivation. The conversion as function of time at 600 °C over Ni/MgAl$_2$O$_4$ at four different S/C-ratios ranging from 1.6 to 8.2 is shown in fig. 4.2. Deactivation was apparent in all the
cases and was most pronounced at the lowest S/C-ratios. A decrease in conversion of 4-5 %-point over 4 h operation was observed for S/C-ratios between 1.6 and 6.0. At an S/C-ratio of 8.2 the decrease in conversion was significantly smaller, roughly 1 %-point.

The conversion and carbon deposition after 4 h on stream as function of S/C-ratio is shown in fig. 4.3. The conversion increased from 53 % to 80 % when the S/C ratio increased from 1.6 to 8.2. The effect of increasing the S/C-ratio was most pronounced at low values, where an increase in conversion from 53 % to 69 % was observed when increasing S/C-ratio from 1.6 to 2.9. The carbon deposition decreased almost linearly with increasing S/C-ratio from 10.5 mmole C/mole C_feed or 70 mg C/g Cat·h at S/C=1.6 to 1.8 mmole C/mole C_feed or 11 mg C/g Cat·h at S/C=8.2. Both of these trends could be due to increased rate of steam gasification/reforming due to increased amount of oxygen containing species on the catalyst.

The almost linearly decreasing carbon deposition suggests that further increments of the S/C-ratio could decrease the carbon deposition further. Linear extrapolation of the carbon deposition as function of S/C-ratio indicates that a S/C-ratio of 9.7 is required for carbon free operation at the applied reaction conditions.

The yield of H₂, CH₄, and C₂H₄ as function of S/C-ratio can be seen in fig. 4.5. The yield of H₂ increased with S/C-ratio from 45 % at S/C=1.6 to 76 % at S/C=8.2. Furthermore, the approach to equilibrium became closer with increasing S/C-ratio and the yield of H₂ in % of equilibrium increased from 64 to 90 % when increasing the S/C-ratio from 1.6 to 8.2. Increasing the amount of steam was expected to increase the yield of H₂ as the WGS will
Fig. 4.2: Conversion as function of time over Ni/MgAl₂O₄ during SR of ethanol at different S/C-ratios. Experimental conditions: Temp.: 585-590 °C; m_{Cat} = 0.50 g, Ni loading: 8.2 wt%, F_T = 1.6 NL/min, y_{Eth} = 3.0 – 3.3 vol%, y_{H_2O} = 10.2 – 50.4 vol%, N_2 as balance.

shift toward CO₂ and H₂. This was also seen on the CO₂/CO-ratio, which increased from about 1 at S/C=1.6 to 4.7 at S/C=8.2. The mass action ratio (MAR) for the WGS and methanation reactions as functions of S/C-ratio can be seen in fig. 4.4. The MAR for WGS increased with increasing S/C-ratio showing that the product gas approached equilibrium for WGS with increasing S/C-ratio. Similar trends were observed in ref. [57, 63, 169, 219]. The
MAR for methanation varied slightly with S/C-ratio and no clear trend was observed.

**Fig. 4.4:** Mass action ratios for water gas shift and methanation as function of S/C-ratio over Ni/MgAl₂O₄. Experimental conditions: Temp.: 585-590 °C; m_Cat = 0.50 g, Ni loading: 8.2 wt%, F_T = 1.6 NL/min, y_Eth = 3.0 - 3.3 vol%, y_H₂O = 10.2 - 50.4 vol%, N₂ as balance.

The yield of C₂H₄ was 26% at S/C=1.6 and decreased to 3.1% at S/C=8.2 and combined with the increase in conversion with S/C-ratio this could indicate that the first step in the SR of ethanol over Ni/MgAl₂O₄ is dehydration. This indicates that the effect of increasing the S/C-ratio was to increase the overall rate of reaction, which increases the total conversion and decreases the yield of intermediates. The decrease in carbon deposition correlated well with the C₂H₄ in the offgas (see fig. 4.3 and 4.5) and therefore a contributing factor to the decrease in carbon deposition could be a faster SR of C₂H₄, converting it before it is turned into solid carbon. Thermodynamical equilibrium calculations for the dehydration of ethanol shows that it should be shifted toward ethene and water regardless of the water content at 600 °C. This indicates that the formation of C₂H₄ should not be limited by the higher water concentration at increasing S/C-ratios and the lower C₂H₄ concentration is therefore likely due to faster conversion.

The yield of CH₄ was stable at S/C-ratios from 1.6 to 8.2, indicating little influence of steam concentration on the conversion of CH₄ at 600 °C. A decrease in the yield of hydrocarbons with increasing S/C-ratios was observed in refs. [169, 219]. The MAR for methanation (see fig. 4.4) varied slightly with S/C-ratio and a very small decrease in the MAR was observed. This again shows that the S/C-ratio have little influence on the methanation equilibrium at 600 °C in the SR of ethanol.

The effect of S/C-ratio on the product yields was highest, when increasing from 3 to 6, which indicates that relatively high S/C-ratios are needed to suppress carbon deposition and increase conversion of ethanol over Ni/MgAl₂O₄.

The principle of equilibrated and actual gas is described in Appendix B and was used to estimate the potential for carbon formation through methane decomposition, the Boudouard reaction, and CO decomposition [42]. There was no potential for forming carbon from an equilibrated gas, but affinity to form carbon deposits was found for the actual product gas through methane decomposition at a S/C-ratio of 1.6. This shows that carbon formation is...
mainly from ethene, although there might be positions in the catalyst bed with a gas composition, which could have the potential to form carbon deposits through methane decomposition especially at low S/C-ratios.

Overall, the results show that increasing the S/C-ratio increased the conversion of ethanol and yield of H$_2$ while decreasing the yield of hydrocarbons and carbon deposition. Operation at high S/C-ratios seems beneficial from a stability point-of-view, but it might be uneconomical in industrial units due to a high cost for superheating the steam. Furthermore it would lead to a larger reactor, pipelines, and general equipment as the gas flow rate would be high.

### 4.3 Oxidative steam reforming

An alternative to increasing the S/C-ratio is to co-feed oxygen, so called oxidative SR (OSR) in order to minimize the carbon deposition during SR of ethanol. The O$_2$ might influence the homogeneous reactions and therefore the effect of O$_2$ was investigated at 600 °C, S/C=6, O/C=0.26, and $y_{O_2}=0.8$ vol% in an empty reactor. The results can be seen in table 4.2. At 600 °C and without O$_2$ equal amounts of CO, CH$_4$, and C$_2$H$_4$ were produced and the conversion was 3%. Therefore the most important homogenous reactions were dehydration, reaction 3.5, and decomposition of ethanol, reaction 4.1:

$$\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_4 + \text{CO} + \text{H}_2 \quad (4.1)$$

With O$_2$ present the product distribution was similar but the conversion was 15%. This indicates that the presence of O$_2$ increased the rate of homogenous dehydration and decomposition of ethanol.

The conversion of O$_2$ was 81% in the blank experiment with O$_2$ in the feed, which indicated that O$_2$ would reach and react on the catalysts as no O$_2$ was detected in the product gas in OSR experiments regardless of the inlet concentration of O$_2.$
4. Steam reforming of ethanol: Effect of feed composition on catalyst stability

Tab. 4.2: Conversion and offgas concentration from blank experiment with and without O_2 present. Experimental conditions: S/C: 6.1; O/C: 0.26; Temp.: 600-611 °C; \( F_T = 1450 \text{ NmL/min} \), \( y_{\text{Eth}} = 3.3 \text{ vol}\% \), \( y_{\text{H}_2\text{O}} = 39.6 \text{ vol}\% \), \( y_{\text{O}_2} = 0.1 \text{ vol}\% \), \( N_2 \) as balance.

<table>
<thead>
<tr>
<th>Type</th>
<th>Conversion [%]</th>
<th>CO [vol%]</th>
<th>CO(_2) [vol%]</th>
<th>CH(_4) [vol%]</th>
<th>C(_2)H(_4) [vol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SR</td>
<td>3</td>
<td>0.07</td>
<td>0</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>OSR</td>
<td>15</td>
<td>0.31</td>
<td>0.01</td>
<td>0.45</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Oxygen co-feeding at an O/C ratio of 0.2-0.3 was tested over three different catalysts; Ni/\( \text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 \), Ni/MgAl\(_2\text{O}_4\), and Ni/\( \text{CeO}_2 \). The O/C-ratios in these experiments were below what is needed for autothermal conditions which would require an O/C-ratio about 0.36 or above. Autothermal conditions are obtained when the energy from combustion of part of the ethanol equals the energy required for SR of the remaining part of the ethanol. The calculations are based on the assumption that all the energy from combustion is used for steam reforming, not heating of gas to 600 °C.

A comparison of conversion, carbon deposition, and yield of H\(_2\) after 4 h on stream for Ni/\( \text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 \), Ni/MgAl\(_2\text{O}_4\), and Ni/\( \text{CeO}_2 \) at SR and OSR conditions can be seen in table 4.3. The conversion increased for all the catalysts when adding O\(_2\) to the feed and full conversion was achieved for Ni/\( \text{CeO}_2 \). The increase in conversion could partly be due to an increase in homogeneous reactions as an increased conversion was observed with O\(_2\) present in an empty reactor. More importantly, O\(_2\) might facilitate surface reactions and increase conversion hereby. The conversion was stable with time at OSR conditions over all the catalysts.

The carbon deposition was lower at OSR conditions for all the catalysts indicating that the O\(_2\) present under OSR will react with carbon on the catalyst and hereby remove it and/or limit its formation by oxidizing precursor species.

In table 4.3 it can also be seen that the yield of H\(_2\) decreased at OSR-conditions with 3 to 12 %-point, which is due to oxidation to CO\(_2\) and H\(_2\)O instead SR to H\(_2\) and CO.

Tab. 4.3: Conversion, carbon deposition, and yield of H\(_2\) at SR and OSR conditions after 4 h on stream over Ni/\( \text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 \), Ni/MgAl\(_2\text{O}_4\), and Ni/\( \text{CeO}_2 \). Experimental conditions: S/C: 5.8-6.0; O/C: 0.19-0.28; Temp.: 579-592 °C; \( m_{\text{Cat}} = 0.50 \text{ g} \), Ni loading: 8.2 wt\%, \( F_T = 1.6 \text{ NL/min} \), \( y_{\text{Eth}} = 3.2 - 3.5 \text{ vol}\% \), \( y_{\text{H}_2\text{O}} = 38.4 - 38.6 \text{ vol}\% \), \( y_{\text{O}_2} = 0.6 - 1.0 \text{ vol}\% \), \( N_2 \) as balance.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>O/C</th>
<th>S/C</th>
<th>Conversion [%]</th>
<th>Carbon deposition [\text{mmole C/mole C}_{\text{Feed}}]</th>
<th>[\text{mg C/gCat-h}]</th>
<th>( Y_{\text{H}_2}) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/( \text{Ce}<em>{0.6}\text{Zr}</em>{0.4}\text{O}_2 )</td>
<td>-</td>
<td>6.0</td>
<td>84</td>
<td>8.6</td>
<td>54.9</td>
<td>75</td>
</tr>
<tr>
<td>Ni/( \text{Ce}<em>{0.6}\text{Zr}</em>{0.4}\text{O}_2 )</td>
<td>0.19</td>
<td>5.8</td>
<td>87</td>
<td>1.4</td>
<td>9.3</td>
<td>65</td>
</tr>
<tr>
<td>Ni/MgAl(_2\text{O}_4)</td>
<td>-</td>
<td>6.2</td>
<td>73</td>
<td>4.4</td>
<td>28.0</td>
<td>70</td>
</tr>
<tr>
<td>Ni/MgAl(_2\text{O}_4)</td>
<td>0.25</td>
<td>6.0</td>
<td>95</td>
<td>1.7</td>
<td>11.0</td>
<td>67</td>
</tr>
<tr>
<td>Ni/( \text{CeO}_2 )</td>
<td>-</td>
<td>5.8</td>
<td>67</td>
<td>2.7</td>
<td>18.8</td>
<td>68</td>
</tr>
<tr>
<td>Ni/( \text{CeO}_2 )</td>
<td>0.28</td>
<td>5.9</td>
<td>99</td>
<td>1.6</td>
<td>10.7</td>
<td>66</td>
</tr>
</tbody>
</table>

The effect of the O/C-ratio on conversion, carbon deposition, and product distribution was investigated over Ni/MgAl\(_2\text{O}_4\) and Ni/\( \text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 \). The conversion and carbon deposition
after 4 h on stream as function of O/C-ratio over these catalysts are shown in fig. 4.6. For Ni/Ce\textsubscript{0.6}Zr\textsubscript{0.4}O\textsubscript{2} the conversion increased with increasing O/C-ratio and reached nearly full conversion at an O/C-ratio of 0.5. A similar trend was observed with Ni/MgAl\textsubscript{2}O\textsubscript{4}, however the conversion increased more rapidly with addition of low amounts of oxygen and reached full conversion at O/C-ratio of 0.84.

The carbon deposition on Ni/Ce\textsubscript{0.6}Zr\textsubscript{0.4}O\textsubscript{2} decreased significantly with increasing O/C-ratio and at an O/C-ratio of 0.5 around 0.2 \( \frac{\text{mmole C}}{\text{mmole C}} \) Feed or 1.5 \( \frac{\text{mg C}}{\text{g Cat} \cdot \text{h}} \) ended up on the catalyst. Increasing the O/C-ratio to 1 decreased the carbon deposition further by approximately a factor of 10 to 0.02 \( \frac{\text{mmole C}}{\text{mmole C}} \) Feed or 0.16 \( \frac{\text{mg C}}{\text{g Cat} \cdot \text{h}} \). A large decrease in carbon deposition with increasing O/C-ratio was also observed over Ni/MgAl\textsubscript{2}O\textsubscript{4}. The carbon deposition at an O/C-ratio of 0.84 was 0.03 \( \frac{\text{mmole C}}{\text{mmole C}} \) Feed or 0.20 \( \frac{\text{mg C}}{\text{g Cat} \cdot \text{h}} \), which was similar to the results from OSR over Ni/Ce\textsubscript{0.6}Zr\textsubscript{0.4}O\textsubscript{2} at a similar O/C-ratio. The results indicate that O/C-ratios of roughly 1 is needed for almost carbon free operation at 600 °C over both Ni/Ce\textsubscript{0.6}Zr\textsubscript{0.4}O\textsubscript{2} and Ni/MgAl\textsubscript{2}O\textsubscript{4}.

When adding oxygen to the system the overall reaction changed from being endothermic at an O/C-ratio below 0.36 to exothermic at O/C-ratios above this value. This was also observed during the experiments as the reactor was almost isothermal at an O/C-ratio of 0.5, while the temperature decreased by 10 °C or increased by 10-15 °C over the reactor at O/C-ratios of 0.2 and 0.8-1.0, respectively.

**Fig. 4.6:** Conversion and carbon deposition after 4 h on stream as function of O/C-ratio over Ni/MgAl\textsubscript{2}O\textsubscript{4} and Ni/Ce\textsubscript{0.6}Zr\textsubscript{0.4}O\textsubscript{2}. Full lines are carbon deposition and dashed lines are conversion. Experimental conditions: S/C: 5.5-6.0; Temp.: 586-615 °C; \( m_{\text{Cat}} = 0.50 \text{ g} \), Ni loading: 8.2 wt%, \( F_{\text{T}} = 1.6 \text{ NL/min} \), \( y_{\text{Eth}} = 3.1 - 3.3 \text{ vol\%} \), \( y_{\text{H}_2\text{O}} = 36.3 - 37.2 \text{ vol\%} \), \( y_{\text{O}_2} = 0 - 3.2 \text{ vol\%} \), \( N_2 \) as balance.

The yield of H\textsubscript{2}, CH\textsubscript{4}, and C\textsubscript{2}H\textsubscript{4} as functions of the O/C-ratio over Ni/Ce\textsubscript{0.6}Zr\textsubscript{0.4}O\textsubscript{2} and Ni/MgAl\textsubscript{2}O\textsubscript{4} can be seen in fig. 4.8. The yield of H\textsubscript{2} dropped from 77 % to 50 % for Ni/Ce\textsubscript{0.6}Zr\textsubscript{0.4}O\textsubscript{2} and from 70 % to 51 % for Ni/MgAl\textsubscript{2}O\textsubscript{4} by increasing the O/C-ratio from 0 to 1. This corresponds to a loss of 1 mole of H\textsubscript{2} pr. mole of ethanol converted. A low temperature shift catalyst bed downstream the reactor might recover part of the H\textsubscript{2} as CO is present in the off gas. Furthermore additional H\textsubscript{2} can be obtained by converting the remaining hydrocarbons to carbon oxides.
The MAR for WGS and methanation as function of O/C-ratio over Ni/Ce$_{0.6}$Zr$_{0.4}$O$_2$ and Ni/MgAl$_2$O$_4$ can be seen in fig. 4.7. The MAR for WGS decreased slightly with increasing O/C-ratio, while the MAR for methanation increased with increasing O/C-ratio over both catalysts. This shows that oxygen is capable of converting methane under the applied conditions.

![Fig. 4.7](http://example.com/fig4.7.png)

**Fig. 4.7:** Mass action ratios for water gas shift and methanation as function of O/C-ratio over Ni/MgAl$_2$O$_4$ and Ni/Ce$_{0.6}$Zr$_{0.4}$O$_2$. Experimental conditions: S/C: 5.5-6.0; Temp.: 586-615 °C; $m_{Cat} = 0.50$ g, Ni loading: 8.2 wt%, $F_T = 1.6$ NL/min, $y_{Eth} = 3.1 - 3.3$ vol%, $y_{H_2O} = 36.3 - 37.2$ vol%, $y_{O_2} = 0 - 3.2$ vol%, $N_2$ as balance.

The yield of hydrocarbons over both catalysts decreased with increasing O/C-ratio. The yield of C$_2$H$_4$ decreased from 3-5 % at O/C=0 to zero at O/C-ratios above 0.8 for both catalysts indicating a higher rate of conversion of ethene with increasing concentration of O$_2$. Similarly the methane yield decreased from 5 % at O/C=0 to 1-2 % at O/C-ratios above 0.8. Carbon deposition in OSR is also mainly from ethene as the principle of equilibrated and actual gas do not predict carbon formation through methane decomposition, the Boudouard reaction, and CO decomposition.

The results show that oxidative SR is an efficient way of limiting carbon deposition but at a cost of decreasing the yield of H$_2$.

### 4.4 Hydrogen addition

Hydrogen addition to the feed was tested during SR of ethanol over a Ni/MgAl$_2$O$_4$ catalyst at 600 °C, S/C-ratio of roughly 6, and H$_2$/EtOH-ratio (H/C-ratio) between 0 and 2.5 (on molar basis). The conversion and carbon deposition as function of the H/C-ratio can be seen in fig. 4.9. The conversion increased from 73 % at H/C=0 to 81 % at H/C=1.1 and then decreased to 62 % at H/C=2.4. This indicated that additional H$_2$ in the feed improved the performance of the catalysts when adding H$_2$ in a H/C-ratio of 1 and below. However, adding higher amounts of H$_2$ decreased conversion probably due to a shift in the WGS, reaction 1.2, leading to fewer oxygen-species to oxidize the carbon intermediates. This is discussed further in section 4.6. The carbon deposition as function of H/C-ratio can be seen in fig. 4.9. There was a slight decrease in carbon deposition with increasing H/C-ratio. The decrease in carbon deposition might be due to increasing hydrogenation of C or CH$_x$-species or due to competitive adsorption between H$_2$ and ethanol derivatives leading to lower amounts of C on the surface.
4. Steam reforming of ethanol: Effect of feed composition on catalyst stability

Fig. 4.8: Yield of $H_2$, $CH_4$, and $C_2H_4$ as function of $O/C$-ratio over $Ni/MgAl_2O_4$ and $Ni/Co_0.6Zr_0.4O_2$. Full lines are $H_2$ yield, dashed lines are $C_2H_4$ yield, and dotted lines are $CH_4$ yield. Experimental conditions: $S/C$: 5.5-6.0; Temp.: 586-615 °C; $m_{Cat} = 0.50 \, g$, Ni loading: 8.2 wt%, $F_T = 1.6 \, NL/min$, $y_{Eth} = 3.1 - 3.3 \, vol\%$, $y_{H_2O} = 36.3 - 37.2 \, vol\%$, $y_{O_2} = 0 - 3.2 \, vol\%$, $N_2$ as balance.

Fig. 4.9: Conversion and carbon deposition after 4 h on stream as function of $O/C$-ratio over $Ni/MgAl_2O_4$. Full lines are carbon deposition and dashed lines are conversion. Experimental conditions: $S/C$: 5.9-6.0; Temp.: 586-592 °C; $m_{Cat} = 0.50 \, g$, Ni loading: 8.2 wt%, $F_T = 1.6 \, NL/min$, $y_{Eth} = 3.0 - 3.3 \, vol\%$, $y_{H_2O} = 36.0 - 37.2 \, vol\%$, $y_{H_2} = 0 - 7.4 \, vol\%$, $N_2$ as balance.

The yield of $H_2$, $CH_4$, $C_2H_4$, and $C_2H_6$ as function of $H/C$-ratio is shown in fig. 4.11. The yield of $H_2$ was not influenced at $H/C$-ratios between 0 and 1.1, but decreased at $H/C$-ratios higher than 1.1. This is expected as a higher concentration of $H_2$ will shift the WGS toward CO and $H_2O$ (see reaction 1.2). This can also be seen on the $CO_2/CO$-ratio, which decreased
from 4.1 at H/C=0 to 2.5 at H/C=2.4.

The yield of methane increased from 5.9 % at H/C=0 to 6.7 % at H/C=2.4, which corresponded to an increase of 15 %. The increase was expected as an increase in the concentration of H\(_2\) will shift the methanation reaction toward CH\(_4\).

The MAR for WGS and methanation as function of H/C-ratio can be seen in fig. 4.10. The MAR for methanation increased with H/C-ratio indicating that the equilibrium was approached with increasing H/C-ratio. The MAR for WGS decreased with increasing H/C-ratio, showing that the WGS moves further away from equilibrium with increasing H/C-ratio. The coverage of catalysts with H-species with increasing H/C-ratio could account for the decrease in the WGS activity.

The yield of ethene was 4.9 % at H/C=0 then decreased to a minimum of 2.6 % at H/C=1.1 and increased to 6.2 at H/C=2.4. The decrease in yield of ethene at between H/C-ratios of 0 to 1.1 was probably due to increased rate of SR reactions as the conversion of ethanol also increased at H/C-ratios between 0 and 1.1. The increase in yield of ethene at H/C above 1.1 indicate a lower conversion of ethene, which could be due to a high coverage of hydrogen species on surface of the catalysts, H \(\ast\), which limits the adsorption of ethene.

The yield of ethane increased from 0.52 % at H/C=0 to 1.9 % at H/C=2.4. This shows that the hydrogenation of ethene to ethane increased with increasing H/C-ratio as expected. Thermodynamics of the hydrogenation of ethene to ethane predicts full hydrogenation, so this reaction, like the methanation approaches equilibrium with increasing H/C-ratio.

The principle of equilibrated and actual gas did not show potential for carbon formation, again indicating ethene as the primary source of carbon deposition.

### 4.5 Stability tests

Oxidative SR and SR at a high S/C-ratio both seemed interesting as they showed low carbon deposition and stable performance for 4 h during SR of ethanol at 600 °C. Therefore it was
chosen to conduct SR of ethanol at these reaction conditions for 24 hours to get a deeper understanding of the stability and rate of carbon deposition. The conversion and yield of hydrocarbons as function of time on stream for SR of ethanol at S/C-ratio of 6, 8, and at S/C=6 and O/C=0.8 can be seen in fig. 4.12. The yield of hydrocarbons is the combined yield of CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{4}. The conversion remained stable around 100% during the entire experiment for SR with oxygen present, while the two conditions without O\textsubscript{2} present showed deactivation. It was most pronounced for SR at S/C=6, where the conversion decreased from 80% to 72% over 24 h, while the conversion at S/C=8 decreased from 81% to 78%.

The total yield of hydrocarbons under OSR was stable around 3.5-4%, however an increase in the yield of C\textsubscript{2}H\textsubscript{4} with time on stream from 0.2% after 1 h to 0.7% after 24 h was observed. The total yield of hydrocarbons was stable around 7% at S/C=8 and the yield of C\textsubscript{2}H\textsubscript{4} increased from 1.9% to 3.5% during the experiment. The yield of hydrocarbons in the SR of ethanol at S/C=6 increased from 10% to 12% over 24 h, mainly due to an increase in the yield of C\textsubscript{2}H\textsubscript{4} from 4.4% to 7.7%. Both conversion and yield of hydrocarbons as functions of time showed that more stable behavior was achieved by adding either additional water or O\textsubscript{2}.

The conversion with oxygen present was 100% for the entire 24 h experiment and therefore the experiment was repeated with a lower mass of catalyst to attempt to obtain less than full conversion. A comparison of conversion, yield of C\textsubscript{2}H\textsubscript{4}, CH\textsubscript{4}, and H\textsubscript{2} both initially and after 24 h at the two different space velocities (SV) can be seen in table 4.4. As expected the conversion decreased while the yield of hydrocarbons increased with increasing SV. A slight deactivation at the higher SV over 24 h could be observed as conversion and yield of H\textsubscript{2} decreased with time, while the yield of both CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{4} increased with time.

The carbon deposition after 4 h and 24 h during SR at S/C=6, SR at S/C=6 with O/C=0.8, and SR at S/C=8 can be seen in table 4.5. In general, the rate of carbon deposition decreased with time for the three cases. At S/C=6 the total amount of carbon on the catalyst decreased from 4 to 24 h on stream, which could indicate that the carbon deposition had reached a
4. Steam reforming of ethanol: Effect of feed composition on catalyst stability

![Conversion and yield of hydrocarbons as function of time on stream.](image)

- **Fig. 4.12:** Conversion and yield of hydrocarbons as function of time of OSR at O/C=1 and S/C=6, SR at S/C=8, and SR at S/C=6. Experimental conditions: Temp.: 590-606 °C, \( m_{\text{Cat}} = 0.50 \text{ g} \), Ni loading: 8.2 wt\%, \( F_T = 1.6 \text{ NL/min} \), \( y_{\text{Eth}} = 3.2 \% \), \( y_{\text{H}_2\text{O}} = 40.1 - 51.5 \text{ vol\%} \), \( y_{\text{O}_2} = 0 - 2.5 \text{ vol\%} \), \( N_2 \) as balance. Hydrocarbons are CH\(_4\) and C\(_2\)H\(_4\).

steady state and would remain at this level. However, an additional experiment with 100 h on stream had a total carbon deposition of 106 mg compared to 54 mg after 24 h, so the carbon deposition did still increase with time on stream. The conversion also decreased with time on stream during the entire 100 h. The conversion, yield of hydrocarbons, and yield of H\(_2\) as function of time on stream for the 100 h experiment can be seen in fig. 4.13.

Steam reforming with oxygen present seems to be most promising as the lowest carbon deposition and highest conversion can be achieved with this feed. Furthermore, at the more severe conditions (higher SV), where the ethene fraction in the offgas was higher, the carbon deposition was still low.
4. Steam reforming of ethanol: Effect of feed composition on catalyst stability

Tab. 4.4: Conversion, yield of $H_2$, $CH_4$, and $C_2H_4$ in oxidative SR at S/C of 6 and O/C of 0.7-0.8 after 1 and 24 h on stream at different space velocities. Y: yield. Experimental conditions: Temp.: 606-608 °C, $m_{Cat} = 0.27 - 0.50$ g, Ni loading: 8.2 wt%, $F_T = 1.6$ NL/min, $y_{Eth} = 3.2 - 3.8$ %, $y_{H_2O} = 38.7 - 38.9$ vol%, $y_{O_2} = 2.5 - 2.8$ vol%, $N_2$ as balance.

<table>
<thead>
<tr>
<th>WHSV [h⁻¹]</th>
<th>Conversion</th>
<th>$Y_{H_2}$</th>
<th>$Y_{CH_4}$</th>
<th>$Y_{C_2H_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 h</td>
<td>100</td>
<td>56</td>
<td>3.4</td>
<td>0.2</td>
</tr>
<tr>
<td>24 h</td>
<td>100</td>
<td>54</td>
<td>3.1</td>
<td>0.7</td>
</tr>
<tr>
<td>1 h</td>
<td>28.3</td>
<td>50</td>
<td>6.3</td>
<td>2.7</td>
</tr>
<tr>
<td>24 h</td>
<td>99</td>
<td>48</td>
<td>6.8</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Tab. 4.5: Carbon deposition after 4 and 24 h for SR at S/C=6, SR at S/C=6 with O/C=0.7-0.8, and SR at S/C=8. Experimental conditions: Temp.: 576 °C, $m_{Cat} = 0.50$ g, Ni loading: 8.2 wt%, $F_T = 1.6$ NL/min, WHSV= 12.9-28.3 h⁻¹, $y_{Eth} = 3.3$ %, $y_{H_2O} = 39.5 - 51.5$ vol%, $y_{O_2} = 0 - 3.2$ vol%, $N_2$ as balance.

<table>
<thead>
<tr>
<th>Type</th>
<th>TOS [h]</th>
<th>Carbon deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\frac{mmole \ C}{mole \ C_{Feed}}$</td>
</tr>
<tr>
<td>SR at S/C=6</td>
<td>4</td>
<td>4.4</td>
</tr>
<tr>
<td>SR at S/C=6</td>
<td>24</td>
<td>0.7</td>
</tr>
<tr>
<td>SR at S/C=8</td>
<td>4</td>
<td>1.8</td>
</tr>
<tr>
<td>SR at S/C=8</td>
<td>24</td>
<td>0.7</td>
</tr>
<tr>
<td>SR at O/C=0.8</td>
<td>4</td>
<td>0.03</td>
</tr>
<tr>
<td>SR at O/C=0.8</td>
<td>24</td>
<td>0.02</td>
</tr>
<tr>
<td>SR at O/C=0.7</td>
<td>24</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The surface area and NiO particle size for fresh and spent Ni/MgAl₂O₄ after 24 h on stream in the SR of ethanol at S/C=6, S/C=8, and O/C=0.8 and after oxidation of the carbon deposits can be seen in table 4.6. The NiO particle size increased and surface area decreased with time-on-stream indicating that sintering of the Ni particles and support material occurred at all of the conditions investigated. The sintering was most pronounced with oxygen present and could account for the deactivation seen in OSR despite the low carbon deposition.

Tab. 4.6: BET surface area and Ni particle size for Ni/MgAl₂O₄ before and after operation at S/C=6, S/C=8, and O/C=1 and 600 °C for 24 h. XRD analysis were used to determine the particle size and the NiO reflection peak at $2\theta = 62.8$° were used.

<table>
<thead>
<tr>
<th></th>
<th>Surface area [m²/g]</th>
<th>NiO particle size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>98</td>
<td>4</td>
</tr>
<tr>
<td>SR at S/C=6</td>
<td>84</td>
<td>6</td>
</tr>
<tr>
<td>SR at S/C=8</td>
<td>79</td>
<td>7</td>
</tr>
<tr>
<td>SR at O/C=0.8</td>
<td>69</td>
<td>9</td>
</tr>
</tbody>
</table>

Carbon deposition was not completely inhibited during SR at O/C below 1 and therefore a long term stability test was conducted at an even higher O/C-ratio. The yield of hydrocarbons
4. Steam reforming of ethanol: Effect of feed composition on catalyst stability

4.1 Effect of feed composition on catalyst stability

Fig. 4.13: Conversion and yield of hydrocarbons and $\text{H}_2$ as function of time at $S/C=6$. Experimental conditions: Temp.: 590 °C, $m_{\text{Cat}} = 0.50$ g, Ni loading: 8.2 wt%, $F_T = 1.6$ NL/min, $y_{\text{Eth}} = 3.2 \%$, $y_{\text{H}_2\text{O}} = 40.1$ vol%, $N_2$ as balance.

and $\text{H}_2$ as well as conversion and $\text{CO}_2/\text{CO}$-ratio as function time on stream during SR at $O/C=1.1$ can be seen in fig. 4.14. The $\text{CO}_2/\text{CO}$-ratio decreased while the yield of methane and ethene both increased during the first 30 hours on stream and hereafter remained stable for the next 60 h. The increase in yield of hydrocarbons and drop in yield of $\text{H}_2$ after 24 h on stream was due to a short malfunction of the feeding system, which caused the feed of $\text{H}_2\text{O}$ and ethanol to stop for a short period of time (5-10 s). A slight oxidation of the catalyst might have occurred at this point.

The total carbon deposition after 90 hours on stream was 0.1 mg, corresponding to 0.2 $\mu$mol C/mole C$_{\text{Feed}}$. The stable behavior with time-on-stream and low amount of carbon on catalyst shows that oxidative SR of ethanol at O/C-ratio above 1 are needed for stable operation with very low rate of carbon deposition ($7$ $\mu$g C/g$_{\text{Cat}}$·h) over Ni/MgAl$_2$O$_4$. Due to the high content of $\text{O}_2$ in the feed it might be possible to lower the S/C-ratio as the main purpose of the steam might be to shift the gas and not to keep the catalysts free of coke.

The penalty of the more stable performance of the catalysts is a loss in the $\text{H}_2$ production of respectively 1 or 2 mole of $\text{H}_2$ pr. mole ethanol converted at $O/C=0.8$ and at $O/C=1.1$ compared with SR at $S/C=6$ without $\text{O}_2$ addition. As mentioned above additional $\text{H}_2$ may be obtained by a low temperature shift of the remaining CO and conversion of hydrocarbons. In this way a total hydrogen yield of 59 % or 3.6 moles of $\text{H}_2$ pr. mole of ethanol (shift at 300 °C) may optimally be obtained at O/C-ratio of 1.1.

That oxidative SR of ethanol is required for stable operation was also concluded by the work of Deluga et al. [157] and others [194, 196, 197, 218] using noble metal catalysts.

4.6 Discussion of reaction mechanism in SR of ethanol

Reactions 3.1-3.6 are the overall reactions for the SR of ethanol and based on results from the literature the overall mechanism for SR of ethanol appears to be: adsorption of ethanol followed by removal of hydrogen, breaking of the C-C-bonds, and subsequent breaking of C-
4. Steam reforming of ethanol: Effect of feed composition on catalyst stability

Fig. 4.14: Conversion, CO\textsubscript{2}/CO-ratio, yield of hydrocarbons, and yield of H\textsubscript{2} as function of time at O/C=1.1 and S/C=6 over Ni/MgAl\textsubscript{2}O\textsubscript{4}. Experimental conditions: Temp.: 617 °C, m\textsubscript{Cat} = 0.36 g, Ni loading: 8.2 wt\%, F\textsubscript{T} = 1.6 NL/min, y\textsubscript{Eth} = 3.6 %, y\textsubscript{H\textsubscript{2}O} = 37.8 vol\%, y\textsubscript{O\textsubscript{2}} = 4 vol\%, N\textsubscript{2} as balance.

H and C-O-bonds [101, 104, 108–110, 114]. Carbon deposition in the SR of ethanol can be caused by slow removal of reactive carbon species, C\textalpha, which causes it to polymerize and form the less active carbon species C\textbeta [40–42]. Carbon deposits may also be formed from thermal decomposition in the gas phase above the catalysts. However, no carbon deposition was visible on the reactor tube indicating that at this temperature thermal decomposition is not significant. A third pathway to carbon deposition is through ethene as shown in reactions 3.7 and 3.8. Based on the results presented above this path appears to dominate in the carbon formation, at least with the catalysts and at the conditions applied in this study. The surface reactions for WGS, SR of ethanol, and possible carbon depositing reactions can be seen below [101, 104, 108–110, 114]. * denotes a surface species or a vacant surface site.

Water gas shift [101, 104, 108–110, 114]:

\[
\begin{align*}
H_2O(g) + 2* & \rightleftharpoons OH* + H* \\
OH* + * & \rightleftharpoons O* + H* \\
CO* & \rightleftharpoons CO(g) + * \\
CO* + O* & \rightleftharpoons CO_2* + * \\
CO_2* & \rightleftharpoons CO_2(g) + * \\
2H* & \rightleftharpoons H_2(g) + 2*
\end{align*}
\]

Steam reforming of ethanol [101, 104, 108–110, 114]:

\[
\begin{align*}
CH_3CH_2OH(g) + 2* & \rightleftharpoons CH_3CH_2O* + H* \\
CH_3CH_2O* + * & \rightleftharpoons CH_3CHO* + H* \\
CH_3CHO* + * & \rightleftharpoons CH_2CH_2* + O*
\end{align*}
\]
\[
\begin{align*}
\text{CH}_2\text{CH}_2^* & \rightleftharpoons \text{CH}_2\text{CH}_2(g) + * & (4.11) \\
\text{CH}_2\text{CH}_2^* + * & \rightleftharpoons 2\text{CH}_2* & (4.12) \\
\text{CH}_2\text{CHO}^* & \rightleftharpoons \text{CH}_3\text{CHO}(g) + * & (4.13) \\
\text{CH}_3\text{CHO}^* + * & \rightleftharpoons \text{CH}_3^* + \text{CHO} * & (4.14) \\
\text{CH}_3\text{CHO}^* + * & \rightleftharpoons \text{CH}_3\text{CO}^* + \text{H} * & (4.15) \\
\text{CH}_3\text{CO}^* + * & \rightleftharpoons \text{CH}_3^* + \text{CO} * & (4.16) \\
\text{CH}_3^* + \text{H} * & \rightleftharpoons \text{CH}_4* & (4.17) \\
\text{CH}_4* & \rightleftharpoons \text{CH}_4(g) + * & (4.18) \\
\text{CH}_3^* + * & \rightleftharpoons \text{CH}_2^* + \text{H} * & (4.19) \\
\text{CH}_2^* + * & \rightleftharpoons \text{CH}^* + \text{H} * & (4.20) \\
\text{CH}^* + * & \rightleftharpoons C^* + \text{H} * & (4.21) \\
\text{CHO}^* + * & \rightleftharpoons \text{CO}^* + \text{H} * & (4.22) \\
C^* + \text{O}^* & \rightleftharpoons \text{CO}^* + * & (4.23)
\end{align*}
\]

Carbon deposition:
\[
\begin{align*}
C^* & \rightarrow C_\alpha^* \rightarrow C_\beta^* \rightarrow \text{Carbon deposits} & (4.24) \\
\text{CH}_2\text{CH}_2^* & \rightarrow \text{Carbon deposits} & (4.25)
\end{align*}
\]

An alternative mechanism for SR of ethanol over Pt/Al\textsubscript{2}O\textsubscript{3} at 300-400 °C was presented by Sutton et al. [110]. In this mechanism, the initial step was dehydrogenation of α-C-H in ethanol followed by dehydrogenation to ketenyl (CHCO \(^*\)) and C-C bond scission of ketenyl. However, ethoxy species has been observed by diffuse infrared Fourier transform spectroscopy on Ni/MgAl\textsubscript{2}O\textsubscript{4} catalyst in SR of ethanol [220], which indicates that the presented mechanism could be valid. The differences in the mechanisms could be due to the active metal as well as temperature interval investigated.

Acetaldehyde has been reported as an intermediate in several studies and is therefore included in the mechanisms [89, 97, 110, 200]. However, the results from this study suggest that the ethene is a more significant intermediate.

Increasing the amount of steam in the SR of ethanol over Ni/MgAl\textsubscript{2}O\textsubscript{4} increased the conversion and yield of H\textsubscript{2} and decreased the carbon deposition and yield of hydrocarbons. These effects are consistent with the mechanism shown in reactions 4.2-4.25. Reaction 4.2 and subsequent reaction 4.3 will shift toward the right with increasing steam concentration leading to higher amounts of H\(^*\) and O\(^*\). The O-species will increase the partial and full oxidation of C\(^*\), reactions 4.5, 4.6, and 4.23, which in turn will decrease the accumulation of carbon on the surface. The increased amount of H\(^*\) on the surface will shift reaction 4.7 toward the right leading to a higher production of H\textsubscript{2}.

Addition of O\textsubscript{2} to the feed increased conversion and decreased yield of H\textsubscript{2} as well as the carbon deposition. This can be understood because addition of O\textsubscript{2} increased the amount of O\(^*\) on the surface of the catalyst through dissociative adsorption of O\textsubscript{2}:
\[
\text{O}_2(g) + 2^* \rightleftharpoons 2\text{O}^* & (4.26)
\]

This will, like for the addition of steam, lead to increased oxidation of C\(^*\) to carbon oxides. Furthermore it will inhibit the dissociation of OH\(^*\), reaction 4.3, and of H\textsubscript{2}O, reaction 4.2, leading to lower amounts of H\(^*\) and subsequently lower yields of H\textsubscript{2}. 

Addition of H₂ to the feed in high concentration led to a decrease in conversion and increase in the yield of CH₄. The amount of H⁺ will increase with increasing concentration of H₂ in the feed through reaction 4.7, which will shift reactions 4.19-4.21 toward the left and lead to a higher formation of CH₄ in reaction 4.18. Furthermore, the presence of H⁺ might inhibit the WGS leading to less O⁺ and lower degree of oxidation of carbon.

The proposed rate determining step in SR of ethanol differs between different studies of SR of ethanol. Sahoo et al. [104] used dehydrogenation of adsorbed ethoxy, reaction 4.9, in the development of a microkinetic model for SR of ethanol over Co/Al₂O₃. Sutton et al. [110] found by kinetic analysis and DFT calculations for SR of ethanol on Pt/Al₂O₃ that either dehydrogenation of α-C-H or C-C bond scission of ketenyl. Graschinsky et al. [109] reported that the surface reactions of C₁-species, reactions 4.19-4.23, were rate limiting in the SR of ethanol over Rh(1%)MgAl₂O₄/Al₂O₃. Furthermore, a parallel can be drawn to SR of CH₄, where Jones et al. [221] concluded that either C-oxidation, reaction 4.23, or CH₄ activation was the rate limiting step in SR of CH₄ depending on the applied temperature. CH₄ activation is less relevant in SR of ethanol and therefore the assumption of reaction 4.23 being rate limiting could be valid. This is supported by the experimental observation that increasing S/C- or O/C-ratio increased the conversion. In that case, increasing the amount of O⁺ on the catalyst leads to higher rates of reactions 4.8-4.22 and a higher degree of conversion and lower yield of hydrocarbons. This is in line with observations by Graschinsky et al. [109] and Llerca et al. [108].

### 4.7 Conclusions

The influence of feed gas composition in terms of O₂, H₂ and H₂O concentrations on SR of ethanol over Ni-based catalysts has been investigated in this chapter. Most experiments were made using a Ni/MgAl₂O₄ catalyst but also Ni/CeO₂ and Ni/Co₀.₆Zr₀.₄O₂ were investigated. Increasing the S/C-ratio from the stoichiometric value of 1.5 to 8.2 improved the performance of the catalyst significantly as the conversion of ethanol and yield of H₂ increased while the yield of hydrocarbons and carbon deposition decreased. At S/C-ratio of 8.2 and 600 °C the conversion was 80 %, the yield of H₂ was 73 %, and the rate of carbon deposition was 1.8 mmole C/mole CFeed or 11.4 mg C/gCat·h in a 4 h experiment at the applied space velocity. The decrease in carbon deposition with increasing S/C-ratio was mainly ascribed to a faster conversion of ethene, which is a main intermediate species in the conversion of ethanol, and a severe coke precursor.

The addition of O₂ was particularly beneficial as conversion of ethanol increased while the yield of hydrocarbons and carbon deposition decreased with increasing O/C-ratio. Oxygen addition at an O/C-ratio of 0.8 to 1.0 decreased the carbon deposition to less than 0.02 mmole C/mole CFeed or 0.2 mg C/gCat·h over both Ni/MgAl₂O₄ and Ni/Co₀.₆Zr₀.₄O₂. The penalty of adding oxygen was a loss in the yield of H₂ from 70 % to 50 % when increasing the O/C-ratio from 0 to 0.8-1.0. The decrease in carbon deposition was probably due to oxidation of carbon, while the lower yield of H₂ was due to oxidation of H₂, CO and hydrocarbons to CO₂ and H₂O. The beneficial effects of adding O₂ to the feed over Ni/MgAl₂O₄ catalysts, decreased carbon deposition and increased conversion, was also found on Ni/CeO₂ and Ni/Co₀.₆Zr₀.₄O₂ catalysts.

Addition of H₂ to the feed did not improve the SR of ethanol significantly with respect to conversion, carbon deposition, or yield of hydrocarbons. High amounts of H₂ in the feed led
to lower conversion of ethanol, probably due to a high coverage of H\textsubscript{2} preventing ethanol to react or a decrease in surface O-species on the catalysts.

A long term test over 90 h showed that stable operation and high conversion with very low rate of carbon deposition, \(7 \\frac{\mu g \cdot C}{g \cdot Cat \cdot h}\), could be achieved over Ni/MgAl\textsubscript{2}O\textsubscript{4} with O\textsubscript{2} in the feed at an O/C-ratio of 1.1. The results showed that oxidative SR of ethanol is the most promising method for enhancing the performance of Ni-based catalysts in the SR of ethanol.
Steam reforming of light water soluble oxygenates

Steam reforming of oxygen containing hydrocarbons other than acetic acid and ethanol has not been investigated to a great extent and little is known of reaction mechanisms and how they depend on the oxygen functionality and chain length. Therefore this chapter will investigate the SR of different light oxygenates, ethanol, acetic acid, acetone, acetal, 1-propanol, and propanal to elucidate differences in reactivity, reaction mechanisms, and side reactions. Furthermore will deactivation and carbon deposition during SR of these light oxygenates be investigated. Acetic acid and acetol were chosen because they are present in bio-oil and the aqueous fraction of bio-oil [19, 20], while the remaining model compounds were chosen to elucidate general trends in the SR of oxygenates.

Studies of SR of bio-oil have been conducted with the entire oil fraction, the aqueous fraction, or with single model compounds like ethanol or acetic acid [66, 67, 74, 104, 122, 141-144, 200, 222]. Other model compounds, which have been investigated to a lesser extent compared with bio-oil, ethanol, and acetic acid are; acetol [61, 131, 223, 224], propanol [131, 224-226], butanol [61, 131], ethylene glycol [59, 143, 182, 183, 187], acetone [59, 64, 75, 131, 224], ethyl acetate [59, 224], phenol [134, 136-138, 201], and sugars like glucose and sorbitol [59, 186, 227].

In the SR of hydrocarbons the main products are CH$_4$, CO$_2$, CO, and H$_2$, but small amounts of hydrocarbons larger than C$_1$ can also be formed [219, 228-232]. The suggested reaction mechanism is that the hydrocarbon adsorbs on surface followed by sequential cleaving of the C-C-bonds [219, 229]. This leads to C$_1$-fragments which can desorb as CH$_4$ or react further forming CO, CO$_2$, and H$_2$ by breaking the C-H bonds and reacting with O-species on the surface of the catalyst. The conversion at a given temperature is lowest for CH$_4$ and in the same range for hydrocarbons with longer chains [228].

Reaction mechanisms for ethanol and acetic acid suggest that the first step is adsorption through the oxygen followed by breaking of the C-C-bonds, which mainly produces C$_1$-species [75, 78, 104, 109, 110, 233].

The main products reported in the SR of oxygen containing hydrocarbons are carbon oxides, hydrogen, and hydrocarbons of equal or shorter chain length than the original compounds [61, 64, 131, 234]. Side reactions like dehydrogenation, condensation, and ketonization, which lead to oxygen containing products, have also been observed [226].

One of the few studies comparing the SR of different oxygenates at similar conditions was conducted by Palmeri et al. [131]. A similar conversion was observed in the SR of C$_2$-C$_4$ alcohols while a decrease in conversion with increasing carbon number was observed in the SR of C$_2$-C$_4$ ketones and aldehydes in this study [131]. Furthermore it was found that the CH$_4$ selectivity increased with increasing chain length while the H$_2$ selectivity decreased for both alcohols, ketones, and aldehydes [131]. A decrease in reactivity and an increase in carbon deposition with increasing chain length has also been reported by Hu and Lu [224] in the SR of both ketones and alcohols.

Ni/MgAl$_2$O$_4$ was chosen as catalyst in this study, as it was mainly focused on differences in reactivity, reaction pathways, and deactivation between the different model compounds.
and these trends should be similar for more active catalyst with less carbon deposition like Ni/CeO₂-K/MgAl₂O₄.

5.1 Characterization

The surface area and NiO particle size were determined for the Ni/MgAl₂O₄ catalyst used for these experiments. The characteristics of the support and catalyst can be seen in table 5.1.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni loading [wt%]</th>
<th>Surface area [m²/g]</th>
<th>dₚ,NiO [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgAl₂O₄</td>
<td>-</td>
<td>143</td>
<td>-</td>
</tr>
<tr>
<td>Ni/MgAl₂O₄</td>
<td>8.2</td>
<td>115</td>
<td>5</td>
</tr>
</tbody>
</table>

The catalyst, Ni/MgAl₂O₄, had a surface area of roughly 115 m²/g, which was lower compared to the support, indicating sintering during the calcination of the catalysts. The NiO particles were quite and roughly 5 nm in diameter. XRD analysis of the catalyst showed a MgAl₂O₄ and NiO phase and did not indicate that Ni was incorporated into the spinel structure, see fig. 5.1.

![XRD pattern for fresh Ni/MgAl₂O₄](image)

**Fig. 5.1:** XRD pattern for fresh Ni/MgAl₂O₄.

5.2 General trends

The effect of temperature and time-on-stream in the SR of several light oxygenates has been investigated at S/C of 6 and a mole fraction of oxygenates and H₂O of 2-3 % and 36 %, respectively. The total flow rate and molar flow of C were similar in each experiment.

In the SR of different model compounds it was found that the trends in the yield of CO and CO₂ with temperature were in accordance with the equilibrium of the WGS at temperatures of 500 °C or above. This means that the yield of CO increased with temperature while the yield of CO₂ decreased. The yield of H₂ increased with temperature in all the cases and a
maximum yield of \( \text{H}_2 \) of roughly 70-80 % was observed at 700 °C, showing that \( \text{H}_2 \)-production was not significant at 400 and 500 °C. The conversion of the model compounds increased with temperature from roughly 10 % at 400 °C to full conversion at 700 °C.

Blank experiments in the SR of ethanol showed conversion of less than 15 % at 700 °C and less than 2 % at 500 °C, so the contribution from homogeneous reactions is considered to be insignificant. Similar degrees of conversion have been reported in the SR of ethanol [57, 61, 89, 235] and SR of acetic acid [48, 68] in a blank reactor. Higher degrees of conversion have been reported in blank experiments in the literature [81, 125, 236] but it is usually over quartz or SiC particles and therefore not comparable to our experiments as we do not dilute our catalyst.

The effect of the support material, \( \text{MgAl}_2\text{O}_4 \), has been tested in the SR of ethanol at 600 °C and only showed dehydration activity with a conversion of 30 %, so the production of carbon oxides and \( \text{H}_2 \) is mainly related to metal particles. A conversion of 40 % has been reported in the SR of acetic acid over \( \text{CaAl}_2\text{O}_4 \) at 750 °C mainly to decomposition products, \( \text{CH}_4 \) and \( \text{CO}_2 \), and similar products were reported in the SR of acetone over the same support material, although the conversion was 80 % [64]. Basagiannis and Verykios [48] reported almost zero % conversion of acetic acid over \( \text{Al}_2\text{O}_3 \) and \( \text{La}_2\text{O}_3 \) at 700 °C. Therefore \( \text{MgAl}_2\text{O}_4 \) may induce dehydration but formation of \( \text{CH}_4 \) as well as \( \text{CO}, \text{CO}_2 \), and \( \text{H}_2 \) is mainly related to \( \text{Ni} \) and interactions between \( \text{Ni} \) and \( \text{MgAl}_2\text{O}_4 \). Ketonization and other coupling reaction may also be catalyzed by \( \text{MgAl}_2\text{O}_4 \) as oxides have shown activity for these reactions [237–239].

### 5.3 Steam reforming of ethanol

The conversion of ethanol and the product yields of \( \text{CO}, \text{CO}_2, \text{H}_2, \text{CH}_4, \) and \( \text{C}_2\text{H}_4 \) as functions of temperature in the SR of ethanol are summarized in fig. 5.2. The yield of \( \text{CO}_2 \) had a maximum at 600 °C, while the yield of \( \text{CO} \) increased with temperature from 500 to 700 °C. This is consistent with an increased activity for the SR reactions and shift in the WGS with temperature as predicted by thermodynamic equilibrium. The yield of \( \text{H}_2 \) increased with temperature from 6 % at 400 °C to 74 % at 700 °C. The yield of \( \text{CH}_4 \) was high at low temperatures (29 % at 400 °C), but decreased with temperature and ended at 0 % at 700 °C, while the yield of \( \text{C}_2\text{H}_4 \) had a maximum of 3 % at 500 °C, although only slightly higher compared with yield at 400 °C, and decreased to 0 % at 600 °C. Ethene is most likely formed through dehydration of ethanol and is known as a severe carbon precursor [32, 100]. Note that with the chosen definition of yield it is possible to have a high yield even if the conversion is low.

These results suggest that ethanol adsorbs on the surface and then either dehydrate to ethene or break the C-C-bond leading to the formation of two \( \text{C}_1 \)-species, which can, depending on the temperature, react and form either \( \text{CH}_4 \) or \( \text{CO}_3 \). Ethene might also react further to \( \text{CH}_2^* \) by breaking the C-C-bond. Further information on the SR of ethanol can be found in chapters 1, 3, and 4 and in refs. [49, 50, 99, 104, 240].

### 5.4 Steam reforming of acetic acid

The conversion of acetic acid and the product yields of \( \text{CO}, \text{CO}_2, \text{H}_2, \text{CH}_4, \) and acetone as functions of temperature in the SR of acetic acid is summarized in fig. 5.3. Here it can be seen that the main products were \( \text{CO}_2 \) and \( \text{CO} \) at all temperatures, while at low temperatures \( \text{CH}_4 \) and acetone were formed as well. From 500 to 700 °C the yield of \( \text{CO}_2 \) slightly decreased.
while the yield of CO increased indicating that the WGS shifted towards CO and H$_2$O. The yield of H$_2$ increased with temperature from 5% at 400°C to 80% at 700°C.

Ketonization of acetic acid to acetone occurred at 400 and 500°C and the yield of acetone was roughly 8%. The yield of CH$_4$ was less than 1% for all the temperatures and decreased with temperature and was thus much lower in the SR of acetic acid compared to the SR of ethanol. It might have been expected that the yield would be similar to yield of CH$_4$ in SR of ethanol as breaking the C-C bond in both cases would form a CH$_3$ and CH$_3$O$_x$-species, where especially the CH$_3$-species are likely to react with H forming CH$_4$ at low temperatures. Ketonization of acetic acid is shown by DFT and experiments to occur through the β-keto
5. Steam reforming of light water soluble oxygenates

5.5 Steam reforming of acetone

The conversion of acetone and the product yields of CO, CO\textsubscript{2}, H\textsubscript{2}, and CH\textsubscript{4} as functions of temperature in the SR of acetone can be seen in fig. 5.4. There was mainly observed CO, CO\textsubscript{2}, and CH\textsubscript{4} as the carbon containing products. However, small amounts of self-condensation products like 4-methyl 4-penten-2-one were observed at 400 °C. The yield of CO increased with temperature, while the yield of CO\textsubscript{2} and CH\textsubscript{4} decreased with temperature. The formation of methane and carbon oxides as the only products suggests that the acetone adsorbs through the carbonyl and then cleaves both of the C-C bonds. C\textsubscript{2}-compounds like ethanol, acetaldehyde, or ethene might be expected in the product gas, but these compounds were not observed. This indicates that CH\textsubscript{3}CO * formed when removing one of the methyl groups undergoes rapid transformation into CO * and CH\textsubscript{3} *.

5.6 Steam reforming of propanal

The conversion of propanal and the product yields of CO, CO\textsubscript{2}, H\textsubscript{2}, CH\textsubscript{4}, and C\textsubscript{2}-species as functions of temperature in the SR of propanal can be seen in fig. 5.5. There was observed
Fig. 5.5: Conversion and yield of CO, CO$_2$, H$_2$, CH$_4$, and C$_2$H$_4$ as functions of temperature in SR of propanal. 8.0 wt% Ni/MgAl$_2$O$_4$, $S/C=6.0$, $m_{Cat}=50$ mg, Flow=210 NmL/min, $y_{PA}=2$ vol%, $y_{H2O}=36$ vol%, N$_2$ as balance.

ethene, ethane, methane, and carbon oxides as products. The C$_2$-fraction consisted of roughly 2/3 ethene and 1/3 ethane and the relative amounts of these species were not significantly influenced by temperature. At 400 °C there was a high yield of C$_2$-species and no formation of CH$_4$. Methane was observed in the SR of acetone, ethanol, and acetic acid at 400 °C and the difference could be that more C-C-bonds needs to be broken to convert propanal to methane compared with the model compounds discussed so far. The yield of C$_2$-species decreased with temperature while the yield of CH$_4$ increased with temperature until 600 °C and decreased hereafter. The formation of C$_2$-compounds could come from breaking the C-C bond closest to the carbonyl group in propanal and methane might be produced from breaking the C-C-bond in the C$_2$-species on the surface. This would also explain the increasing level of methane in the offgas, while the yield of C$_2$-species decreased.

The results suggest that the propanal is converted by sequential breaking of carbon backbone from the carbonyl end as no oxygen containing by-products were formed.

5.7 Steam reforming of 1-propanol

The conversion of 1-propanol and the product yields of CO, CO$_2$, H$_2$, CH$_4$, C$_2$-species, propene, and propanal as functions of temperature in the SR of 1-propanol are summarized in fig. 5.6. There was observed the same products as in SR of propanal with the addition of propene and propanal, which can be formed through dehydration and dehydrogenation of 1-propanol. The C$_2$ product fraction consisted of 75-85 % ethene and 15-25 % ethane. The major products were propene, CO$_2$, propanal, and C$_2$-species at 400 °C. The yield of propene, C$_2$-species, and propanal all decreased with temperature and reached 0 % at 600 °C. The yield of CH$_4$ increased with temperature until 600 °C and then decreased. This behavior was similar to what was observed in the SR of propanal and suggest that methane might be formed from further reaction of C$_3$- and C$_2$-species and is not a primary product.

The reaction path for conversion of 1-propanol appears to be a sequential scission of the carbon backbone similarly to what was observed in the SR of propanal. No methanol and ethanol was observed in SR of 1-propanol, indicating that the C-C-bond scission starts from the
5.8 Steam reforming of acetol

The conversion of acetol and the product yields of CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, and other products as functions of temperature in the SR of acetol can be seen in fig. 5.7. The products from SR of acetol were different from the other oxygenates investigated, especially at 400 and 500 °C. Here a large fraction of products were formed through different condensation reactions forming butanediol, 2,5-hexanediol, substituted cyclopentanedione, furandiones, and furanones (Others in fig. 5.7) and constituted the major product group at both 400 and 500 °C. Furthermore, there was observed small amounts of ethanol and acetaldehyde as products as well, which can be formed by breaking of one of the C-C-bonds in acetol. The yield of CH<sub>4</sub> had a maximum at 500 °C and then decreased to 0 % at 700 °C, while the yield of H<sub>2</sub> increased from 0 at 400 °C to 76 % at 700 °C. Acetol has two oxygen functionalities and this seems to induce a high formation of condensation products especially at low temperatures. This might be explained by a free oxygen end, when acetol is adsorbed on the catalyst, which can react with other compounds on the surface and oligomerize.

Two main types of reaction pathways can take place in the SR of acetol, either condensation reactions leading to larger compounds or C-C-bond breaking leading to smaller compounds like CO<sub>x</sub>, H<sub>2</sub>, and CH<sub>4</sub>.

5.9 Comparison

The conversion of the investigated model compounds as function of temperature is summarized in fig. 5.8. There was mainly a difference in conversion at 500 °C, while the conversions were similar at all other temperatures. The higher conversion of acetol at 400 °C and 500 °C
compared with the other compounds was mainly as condensation products and included a wide range of different oxygenates, as discussed above. The conversion of ethanol was similar to the conversion of 1-propanol at all temperatures, which indicates that the chain length of oxygenate did not influence the total conversion in the SR of alcohols. Similar results were obtained by Palmeri et al. [131] for SR of alcohols. Furthermore the conversion of acetone was higher compared to the conversion of propanal indicating that the position of the oxygen functionality in the molecule influences the reactivity. In this case, it might be explained by a more favorable conversion of CH₃CO * formed when breaking the first C-C-bond in acetone. These species are probably more readily converted compared with ethene or C₂-species formed by breaking the first C-C-bond in propanal. DFT-calculations on the conversion of acetic acid shows that conversion of CH₃CO * to CH₃ * and CO * is favorable with a decrease in energy of 38 kJ/mole and an activation energy of 78 kJ/mole [78].

Many by-products were produced at 400 and 500 °C and a comparison of the yield of oxygenates as function of temperature can be seen in fig. 5.9(a), while a comparison of yield of hydrocarbons as function of temperature can be seen in fig. 5.9(b). The yield of both types of by-products decreased with temperature and were close to zero above 600 °C. For the alcohols it can be seen that relatively high amounts of hydrocarbons were formed and a fraction of those were olefins, ethene and propene, which might cause problems with carbon deposition as indicated in the previous chapters as well in refs. [30, 32, 100]. The yield of hydrocarbons and oxygenates were higher for 1-propanol compared ethanol, which indicates that the reactivity decreased slightly with increasing chain length. Similar results has been reported by Palmeri et al. [131]. Acetic acid, 1-propanol, and acetol produced oxygen containing compounds as well as hydrocarbons. Acetol had the highest yield of oxygenates of all the compounds.

From fig. 5.9 it appears that temperatures above 600 °C are needed to avoid by-products in the offgas. However this might be due to either a higher degree of conversion or a changed reaction path at higher temperature. To investigate this, an experiment at a higher space velocity at 600 °C was carried out while keeping the overall conversion close to that at 500 °C and the lower space velocity. A comparison of the yield of by-products at the two conditions
5. Steam reforming of light water soluble oxygenates

**Fig. 5.8:** Conversion as function of temperature in SR of ethanol, acetic acid, acetone, 1-propanol, and propanal. 8.0 wt% Ni/MgAl₂O₄, S/C = 6.0, m_Cat = 50 mg, Flow = 210 NmL/min, \( y_{O_{2}} = 2-3 \text{ vol\%} \), \( y_{H_{2}O} = 37 \text{ vol\%} \), \( N_{2} \) as balance.

**Fig. 5.9:** Yield of by-products as function of temperature in SR of light oxygenates. 8.0 wt% Ni/MgAl₂O₄, S/C = 6.0, m_Cat = 50 mg, Flow = 230 NmL/min, \( y_{O_{2}} = 2-3 \text{ vol\%} \), \( y_{H_{2}O} = 36 \text{ vol\%} \), \( N_{2} \) as balance.

can be seen in table 5.2. For most of the experiments at 600 °C the yield of hydrocarbons and oxygenates were lower compared to the experiment at 500 °C. It was especially pronounced for acetol, where a decrease in yield of oxygenates from 51 to 5 % was observed at similar conversion but different temperatures. Furthermore the by-products were mainly acetone, ethanol, and acetaldehyde at 600 °C and not condensation products as observed at 500 °C. Therefore it appears that operation at 600 °C or higher minimized the formation of by-products and especially condensation products.

The desired compounds in SR are carbon oxides and \( H_{2} \) and the conversion to carbon oxides (\( CO_{x} \)) can be seen in fig. 5.10. Here it can be seen that the conversion of \( C_{2} \) oxygenates was slightly higher compared with \( C_{3} \) oxygenates. This indicates that the reactivity decreased with chain length. The one exception was acetone, which might be because breaking of the C-C
Tab. 5.2: Comparison of conversion, yield of hydrocarbons, and yield of oxygenates at different temperatures and similar conversions. 8.0 wt% Ni/MgAl$_2$O$_4$, S/C = 6.0, $m_{\text{Cat}} = 25-50$ mg, Flow = 210 NmL/min, $y_{\text{Oxy}} = 2-3$ vol%, $y_{\text{H}_2\text{O}} = 36$ vol%, $N_2$ as balance.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp [°C]</th>
<th>X [%]</th>
<th>$Y_{\text{C}_x\text{H}_y}$ [%]</th>
<th>$Y_{\text{C}_x\text{H}_y\text{O}_z}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>500</td>
<td>57</td>
<td>27</td>
<td>0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>600</td>
<td>68</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td>Acetone</td>
<td>500</td>
<td>49</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>Acetone</td>
<td>600</td>
<td>60</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>500</td>
<td>51</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>600</td>
<td>62</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>Acetol</td>
<td>500</td>
<td>65</td>
<td>3</td>
<td>51</td>
</tr>
<tr>
<td>Acetol</td>
<td>600</td>
<td>58</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>500</td>
<td>59</td>
<td>33</td>
<td>13</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>600</td>
<td>65</td>
<td>27</td>
<td>5</td>
</tr>
<tr>
<td>Propanal</td>
<td>500</td>
<td>43</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>Propanal</td>
<td>600</td>
<td>61</td>
<td>6</td>
<td>0</td>
</tr>
</tbody>
</table>

The bond closest to the carbonyl group would lead to CH$_3$-species, which might be easier to convert as discussed previously.

Fig. 5.10: Conversion to carbon oxides as function of temperature in SR of light oxygenates. 8.0 wt% Ni/MgAl$_2$O$_4$, S/C = 6.0, $m_{\text{Cat}} = 50$ mg, Flow = 210 NmL/min, $y_{\text{Oxy}} = 2-3$ vol%, $y_{\text{H}_2\text{O}} = 37$ vol%, $N_2$ as balance.

5.9.1 Reaction pathway

Steam reforming of light oxygenates over Ni/MgAl$_2$O$_4$ at low temperatures produced a large fraction of byproducts with similar or shorter chain length than the parent model compounds. For alcohols dehydrogenation to olefins or dehydration to aldehydes with the same chain length were observed, while for the carboxyls only decarboxylation products were observed.
5. Steam reforming of light water soluble oxygenates

This indicates that the first step in the reaction is adsorption to the catalyst site through the oxygen functionality. Adsorption through oxygen is shown to be preferred by DFT-studies on adsorption of oxygenates on transition metal surfaces [78, 233, 241, 242]. The products shifted from C$_3$ and C$_2$-species towards C$_1$-species with increasing conversion and temperature and furthermore a build-up of CH$_4$ was observed as C$_3$ and C$_2$-species was converted. This indicates that the conversion occurs through sequential breaking of the C-C-bonds in the oxygenate. Furthermore, in the SR of acetone, only C$_1$-products were formed, which also fits the proposed pathway of adsorption through the oxygen and breaking of the C-C-bonds closest to the oxygen. The proposed reaction pathway is shown for SR of 1-propanol in Fig. 5.11.

The formation of condensation products at 500 °C was significantly higher for acetol which has two oxygen containing functional groups. This could be due to a free oxygen functionality, which can react with other surface species forming larger chains.

Carbon deposits can be formed through the Boudouard reaction, CO decomposition, polymerization of acetone, methane decomposition, as well as through polymerization of ethene and propene depending on the temperature and S/C-ratio.

5.9.2 Deactivation

Steam reforming of the different model compounds was investigated for 4 hours at 600 °C, S/C-ratio of 6, and with a conversion between 60-80 %. The influence of time-on-stream on the conversion can be seen in Fig. 5.12. The conversion for all of the compounds decreased with time and the decrease was most pronounced for acetol and acetic acid, where the conversion decreased by 15-20 %-points, while for ethanol, 1-propanol, and propanal the decrease in conversion was roughly 10 %-points. The conversion of acetone was most stable with a 7 %-points decrease in conversion over time.

The final conversion (initial conversion can be seen in Fig. 5.12), yield of by-products, and carbon deposition for a 4 hour experiment can be seen in Table 5.3. The two model compounds which led to the highest carbon deposition were the two alcohols, ethanol and 1-propanol. This was due to the relatively high formation of ethene and propene, which are likely to polymerize as carbon deposits on the catalyst [31, 32, 100]. Acetic acid also had a high carbon deposition, while the other three model compound showed a 25 % lower carbon deposition. A higher carbon deposition in SR of alcohols compared to ketones and aldehydes over Ni/Al$_2$O$_3$ at 700 °C and S/C-ratio of 4 was also reported by Palmeri et al. [131]. However, the differences was more pronounced in the study by Palmeri et al. [131] as SR of ethanol resulted in 33 % higher carbon deposition compared with SR of acetaldehyde, while SR of 2-butanol produced 6 times

Fig. 5.11: Proposed reaction pathway in SR of 1-propanol.
5. Steam reforming of light water soluble oxygenates

**Fig. 5.12:** Conversion as function of time in SR of light oxygenates at 600 °C. 8.0 wt% Ni/MgAl₂O₄, S/C = 6.0, m_Cat = 25 mg, Flow = 210 NmL/min, y_O₂ = 2-3 vol%, y_H₂O = 37 vol%, N₂ as balance.

**Tab. 5.3:** Conversion, product yields, and carbon depositions in SR of light oxygenates at 600 °C after 4 h on stream. 8.0 wt% Ni/MgAl₂O₄, S/C = 6.0, m_Cat = 25 mg, Flow = 210 NmL/min, y_O₂ = 2-3 vol%, y_H₂O = 37 vol%, N₂ as balance.

<table>
<thead>
<tr>
<th>Compound</th>
<th>X</th>
<th>Y_C₆H₁₂</th>
<th>Y_C₅H₄O₆</th>
<th>Carbon deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[%]</td>
<td>[%]</td>
<td>[%]</td>
<td>mg g_Cat⁻¹ h⁻¹</td>
</tr>
<tr>
<td>Ethanol</td>
<td>68</td>
<td>12</td>
<td>0</td>
<td>41</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>62</td>
<td>0.4</td>
<td>8</td>
<td>40</td>
</tr>
<tr>
<td>Acetone</td>
<td>60</td>
<td>2</td>
<td>0</td>
<td>32</td>
</tr>
<tr>
<td>Acetol</td>
<td>58</td>
<td>7</td>
<td>2</td>
<td>33</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>65</td>
<td>28</td>
<td>5</td>
<td>42</td>
</tr>
<tr>
<td>Propanal</td>
<td>61</td>
<td>6</td>
<td>0</td>
<td>29</td>
</tr>
</tbody>
</table>

as much carbon as SR of 2-butanone. Hu and Lu [59] reported a higher carbon deposition in SR of acetone compared with acetic acid over Ni/Al₂O₃ at 600 °C and stoichiometric S/C-ratio. However, the opposite trend was observed in this study.

The carbon release during TPO of the spent catalysts is shown in Fig. 5.13. Ethanol, 1-propanol, and acetone all show carbon oxidation in a single peak with a maximum at roughly 600-615 °C. Acetol, acetic acid, and propanal had two carbon oxidation peaks, a main peak at roughly the same temperatures as the other model compounds, and a smaller peak at lower temperatures, 500-525 °C. The low-temperature peak might indicate that encapsulating carbon was formed with these oxygen containing model compounds, as it would have close contact with Ni and therefore oxidize at a lower temperature. Furthermore acetol, acetic acid, and propanal also showed a rather steep deactivation with time on stream, which also could point to coverage of the Ni-particles by carbon, while whisker formation would not significantly deactivate the catalyst [30, 42].
5. Steam reforming of light water soluble oxygenates

5.10 Conclusions

Steam reforming of ethanol, acetic acid, acetone, acetol, 1-propanol, and propanal has been investigated on Ni/MgAl$_2$O$_4$ at temperatures between 400 and 700 °C at S/C-ratio of 6. In all the cases full conversion were achieved at 700 °C at the applied space velocity and the yield of H$_2$ varied between 70 and 80 %. The conversion as function of temperature did not vary significantly between the different model compounds. However, the yield of by-products was higher for C$_3$-oxygenates compared to C$_2$-oxygenates, which shows a decrease in reactivity with chain length.

The product gas consisted mainly of H$_2$, CO, CO$_2$, and CH$_4$ in various proportions and a fraction of by-products, which was most pronounced at temperature of 500 °C and below. Olefins and aldehydes were by-products in the SR of alcohols, while SR of propanal and acetone led to olefins and hydrocarbons as byproducts. Ketonization to acetone was observed in the SR of acetic acid at 500 °C and below. These results indicate that the SR of oxygenates proceeds through adsorption by the oxygen containing part followed by sequential breakage of the C-C-bonds.

Deactivation with time-on-stream was observed for all of model compounds and was most pronounced for acetol and acetic acid. However, the carbon deposition was roughly 30 % higher in the SR of alcohols and acetic acid compared with the SR of the remaining model compounds. The carbon deposition in the SR of alcohols was due to a high formation of olefins which are severe precursors for carbon deposition. The results further indicate that stable operation would require high S/C-ratios or oxidative reforming.

*Fig. 5.13:* Formation of methane as function temperature during TPO of spent catalysts. $m_{\text{Sample}} = 2 - 5 \text{ mg}$, $\Delta T$: 10 °C/min, $y_{O_2} = 5 \text{ vol\%}$, He as balance. Methanation catalyst operated at 400 °C.
6. STEAM REFORMING OF CYCLIC OXYGENATES

Bio-oil contains many different compounds of varying size and little is known on the SR of other oxygen containing compounds other than ethanol and acetic acid. Furthermore are cyclic and aromatic compounds known to cause problems in SR and therefore the aim of this chapter is to investigate the SR of furfural, guaiacol, and 2-methyl furan. The focus will be on the product distribution as function temperature as well as function of time to investigate catalyst deactivation. Furthermore oxidative conditions will be investigated to clarify what levels of O$_2$ are needed for stable operation.

Steam reforming of bio-oil has been investigated with the entire oil fraction [67, 141, 146, 148, 150, 158, 163, 164, 243, 244] or the aqueous fraction of bio-oil, formed by water addition to the bio-oil [58, 142-144, 245, 246]. However there is a lack of studies with cyclic oxygenates as model compounds of bio-oil, which are present in the bio-oil and may be responsible for a high fraction of the carbon deposition. Recently Xu et al. [247] studied the SR of several model compounds of bio-oil, including furfural and $m$-cresol, over Ni/MgO at 600 °C, S/C-ratio of 6, and liquid hourly space velocity (LHSV) of 5 h$^{-1}$. This study focused on the type of by-products formed, however the stability of system as well as the effect of temperature on product distribution was not investigated. Another study of SR of cyclic oxygenates was conducted Lan et al. [243], who investigated the SR of furfural and $m$-cresol at a S/C-ratio of 5 as function of temperature over several Ni/Al$_2$O$_3$ based catalysts and found that CO and CO$_2$ were the main products in the SR of furfural. Conversions above 90 % was achieved at temperatures above 700 °C and LHSV of 2.5 h$^{-1}$. A stability test over 10 h showed a slight deactivation, but the source of deactivation was not investigated [243]. To the authors knowledge, there are no other results on SR of furfural, guaiacol, and 2-methyl furan, which are all present in the bio-oil and may lead to severe deactivation.

Ni/CeO$_2$-K/MgAl$_2$O$_4$ have in chapter 3 showed high activity and low rate of carbon deposition in the SR of ethanol and therefore was it chosen as catalyst in this chapter.

6.1 Characterization

The surface areas and particle sizes of NiO and CeO$_2$ for the fresh catalysts used in this study can be seen in table 6.1. The surface area of Ni/CeO$_2$-K/MgAl$_2$O$_4$ was 78 m$^2$/g, while the NiO and CeO$_2$ particles had diameters of 7 nm and 6 nm, respectively. This was slightly higher compared with the NiO-particles on MgAl$_2$O$_4$, which was 5 nm in diameter. EDX-analysis of the catalyst showed that the loading of K, Ni, and CeO$_2$ was 3.2 wt%, 7.8 wt%, and 4.7 wt%, respectively, which was closed to the nominal loading.

The XRD patterns of Ni/CeO$_2$-K/MgAl$_2$O$_4$ and Ni/MgAl$_2$O$_4$ are compared with the standard peaks for NiO, MgAl$_2$O$_4$, and CeO$_2$ in fig. 6.1. Here it can be seen that NiO and MgAl$_2$O$_4$ accounts for the peaks in the XRD pattern of Ni/MgAl$_2$O$_4$, while the additional peaks in the XRD pattern of Ni/CeO$_2$-K/MgAl$_2$O$_4$ corresponds to CeO$_2$. K was not observed on the XRD-pattern indicating that K is present as a layer, small crystallites, or amorphous K.
6. Steam reforming of cyclic oxygenates

Tab. 6.1: Characterization results of the fresh catalysts (Ni as NiO) prepared by calcination in stagnant air at 800 °C. Particles size of NiO and CeO$_2$ are determined based on the XRD patterns.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Promoter</th>
<th>Ni loading [wt%]</th>
<th>Surface area [m$^2$/g]</th>
<th>$d_{p, \text{NiO}}$ [nm]</th>
<th>$d_{p, \text{CeO}_2}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgAl$_2$O$_4$</td>
<td>-</td>
<td>143</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni/MgAl$_2$O$_4$</td>
<td>-</td>
<td>8.2</td>
<td>104</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>Ni/CeO$_2$-K/MgAl$_2$O$_4$</td>
<td>5 wt% CeO$_2$</td>
<td>8.2</td>
<td>78</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>MgAl$_2$O$_4$</td>
<td>5 wt% K</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 6.1: XRD patterns for unreduced catalysts, NiO/MgAl$_2$O$_4$ and Ni/CeO$_2$-K/MgAl$_2$O$_4$.

6.2 Steam reforming of 2-methylfuran

Steam reforming of 2-methylfuran at S/C-ratio of 5 was carried out in an empty reactor to examine the extent of the homogenous decomposition of 2-methylfuran. The conversion to gaseous products, CO, CO$_2$, CH$_4$, C$_2$- and C$_3$-hydrocarbons, was 3 % at 700 °C and increased to 66 % at 860 °C. Therefore homogeneous reactions seem to be insignificant at the investigated temperatures. It should be noted that carbon deposition was observed in reactor indicating that the thermal decomposition of 2-methylfuran also occurred.

Steam reforming of 2-methylfuran was investigated at temperatures between 400 and 700 °C over Ni/CeO$_2$-K/MgAl$_2$O$_4$ at a S/C-ratio of 5. The product yields and conversion of 2-methylfuran as function of temperature can be seen in fig. 6.2. The main products at all temperatures were CO, CO$_2$, CH$_4$, and H$_2$ and as expected from thermodynamics, the yield of CO increased with increasing temperature, while the yield of CO$_2$ and CH$_4$ decreased with temperature. The yield of H$_2$ had a maximum of 76 % at 600 °C (note our definition of yield, which is based on the fraction of converted reactant, eq. 2.6), while the conversion increased with increasing temperature, reaching full conversion at 700 °C. The product fraction called Others in fig. 6.2 covers various compounds like ethanol, acetone, acetaldehyde, 2-butanol, hydrofuran, and furanes, which all are fragments of 2-methylfuran. This fraction decreased
with temperature from 7% at 400 °C to 0% at 600 °C. Ethanol and acetone were the major constituents of this fraction and reached maximum yields of 0.8 and 1.5% respectively at 400 °C. However, the conversion was 20% at 400 °C and therefore the production of these compounds were quite low.

The conversion of 2-methylfuran and the product yields of CO, CO$_2$, CH$_4$, and H$_2$ as function of time at 600 °C and S/C=5 can be seen in fig. 6.3. The yield of H$_2$ was 77%, while the conversion was 86% and both the product yields and conversion remained quite stable with time-on-stream. Nevertheless, carbon deposition at a rate of $8 \frac{mg \ C}{g \cdot cat \cdot h}$ was observed (see table 6.2). The low degree of deactivation indicates that the carbon may be deposited as whiskers [40–42].

Steam reforming of 2-methylfuran was conducted for 24 h to further investigate the stability with time. A comparison of final conversion and carbon deposition at 600 °C and S/C=5 for different times on stream and over both Ni/MgAl$_2$O$_4$ or Ni/CeO$_2$-K/MgAl$_2$O$_4$ can be seen in table 6.2. The conversion of 2-methylfuran was 12% points lower and the carbon deposition was 7 times higher over Ni/MgAl$_2$O$_4$ compared with Ni/CeO$_2$-K/MgAl$_2$O$_4$, which shows the beneficial effect of adding both CeO$_2$ and K to the catalyst. This was also shown in chapter 4 for the SR of ethanol [240].

A comparison of the conversion over Ni/CeO$_2$-K/MgAl$_2$O$_4$ after 4 h and 24 h on stream shows that the catalyst deactivated with time, see table 6.2. This was probably due to carbon deposition which increased with a constant rate. This was different from the SR of ethanol over the same and similar Ni-based catalysts, where the rate of carbon deposition decreased with time on stream, see table 3.8 in chapter 3.

The release of carbon oxides as function of temperature during TPO of spent Ni/CeO$_2$-K/MgAl$_2$O$_4$-catalysts used in the SR of 2-methylfuran at SR- and oxidative SR-conditions can be seen in fig. 6.4. The carbon oxides release over a catalyst used in the SR at S/C=5 had a maximum at 410–420 °C, which was similar to the observations from the TPO of spent catalyst used in the SR of ethanol, see fig. 3.15 in chapter 3 [240]. A much smaller carbon

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**Fig. 6.2:** Yield of CO, CO$_2$, CH$_4$, H$_2$, Others, and conversion as function of temperature over Ni/CeO$_2$-K/MgAl$_2$O$_4$ in the SR of 2-methylfuran. Experimental conditions: S/C: 5, $m_{cat}$ = 0.50 g, Ni loading: 8.2 wt%, $F_T$ = 1.6 NL/min, $y_{2MF}$ = 1.4 vol%, $y_{H_2O}$ = 38.0 vol%, $N_2$ as balance.
6. Steam reforming of cyclic oxygenates

**Fig. 6.3:** Yield of CO, CO₂, CH₄, H₂, and conversion as function of time in SR of 2-methylfuran over Ni/CeO₂-K/MgAl₂O₄. Experimental conditions: S/C: 5.1, m_Cat = 0.50 g, Ni loading: 8.2 wt%, Temp.: 584 °C, F_T = 1.6 NL/min, y_2MF = 1.4 vol%, y_H₂O = 38.0 vol%, N₂ as balance.

**Fig. 6.4:** Carbon oxides release as function of temperature over Ni/CeO₂-K/MgAl₂O₄ after 4 h at SR and OSR conditions with 2-methylfuran as reactant. Experimental conditions: Δ T= 10 °C/min, F_T = 1 NL/min, y_O₂ = 2 – 3 vol%, N₂ as balance.

Carbon oxides release was observed at 650 °C, which was not seen in the SR of ethanol and could correspond to carbon deposition on the reactor walls. This was observed visually on the reactor used in the SR of 2-methylfuran, but not in the SR of ethanol. Carbon whiskers was observed in the SR of ethanol over Ni/CeO₂-K/MgAl₂O₄ [240] and together with the stable behavior with time and the similar TPO-profiles this suggests that the carbon deposition was as carbon whiskers in the SR of 2-methylfuran.
**Tab. 6.2:** Final conversion and carbon deposition over Ni/MgAl$_2$O$_4$ and Ni/CoO$_2$-K/MgAl$_2$O$_4$ in the SR of 2-methylfuran. Experimental conditions: $S/C$: 5.1, $m_{\text{cat}}$ = 0.50 g, Ni loading: 8.2 wt%, Temp.: 584 °C, $F_T$ = 1.6 NL/min, $y_{2MF}$ = 1.4 vol%, $y_{H_2O}$ = 38.0 vol%, $N_2$ as balance.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOS</th>
<th>X [%]</th>
<th>mmole C/mole C$_{\text{Feed}}$</th>
<th>mg C/g$_{\text{cat}}$·h</th>
<th>mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/MgAl$_2$O$_4$</td>
<td>4</td>
<td>74</td>
<td>7.7</td>
<td>60</td>
<td>121</td>
</tr>
<tr>
<td>Ni/CoO$_2$-K/MgAl$_2$O$_4$</td>
<td>4</td>
<td>86</td>
<td>1.1</td>
<td>8</td>
<td>16</td>
</tr>
<tr>
<td>Ni/CoO$_2$-K/MgAl$_2$O$_4$</td>
<td>24</td>
<td>80</td>
<td>1.1</td>
<td>8</td>
<td>99</td>
</tr>
</tbody>
</table>

Oxidative SR of ethanol can minimize carbon deposition [248] and therefore the SR of 2-methylfuran was investigated under oxidative conditions at $O/C$-ratio of 0.2. The conversion of 2-methylfuran and the products yields of CO, CO$_2$, CH$_4$, and H$_2$ as function of time in the SR of 2-methylfuran at 600 °C, $S/C$=5, and $O/C$=0.2 can be seen in fig. 6.5. The conversion remained at 100 % during the 4 h experiment, while the yield of CH$_4$ and H$_2$ was stable at roughly 0.4 % and 68 %, respectively, which was lowered compared with yields at SR-conditions. The product yields of CO and CO$_2$ were also stable with time. No formation of other compounds was observed.

**Fig. 6.5:** Yield of CO, CO$_2$, CH$_4$, H$_2$, and conversion as function of time in OSR of 2-methylfuran over Ni/CoO$_2$-K/MgAl$_2$O$_4$. Experimental conditions: $S/C$: 5.1, $m_{\text{cat}}$ = 0.50 g, Ni loading: 8.2 wt%, Temp.: 600 °C, $F_T$ = 1.6 NL/min, $y_{2MF}$ = 1.5 vol%, $y_{H_2O}$ = 37.5 vol%, $y_{O_2}$ = 1.5 vol%, $N_2$ as balance.

A comparison of conversion, carbon deposition, yield of H$_2$ and CH$_4$ after 4 h and 24 h on stream in the OSR and 24 h in the SR can be seen in table 6.3. The addition of O$_2$ to the feed increased the conversion and therefore the mass of catalyst was lowered from 0.5 g to 0.39 g in the 24 h OSR experiment to see if less than full conversion could be achieved. However, full conversion was still reached, while the carbon deposition and yield of H$_2$ still were lower compared with SR at $S/C$=5. The fraction of feed being converted to carbon
deposits decreased by a factor of 18 from 1.1 \( \frac{\text{mmole C}}{\text{mole C}_{\text{Feed}}} \) to 0.06 \( \frac{\text{mmole C}}{\text{mole C}_{\text{Feed}}} \), showing that oxygen addition is effective in minimizing carbon deposition in SR of oxygenates.

The product yields were stable in the 24 h experiment, but the yield of CH\(_4\) was slightly higher compared with the 4 h experiment. This was probably due to the lower mass of catalysts, which did not allow for the same degree of conversion of CH\(_4\). The rate of carbon deposition was similar after 4 h and 24 h, when comparing the fraction of the feed converted to carbon deposition, \( \frac{\text{mmole C}}{\text{mole C}_{\text{Feed}}} \).

**Tab. 6.3:** Final conversion, yield of H\(_2\) and CH\(_4\), and carbon deposition after 24 h on stream in SR of 2-methylfuran and after 4 and 24 h in the OSR of 2-methylfuran over Ni/\(\text{CeO}_2\)-K/\(\text{MgAl}_2\text{O}_4\). Experimental conditions: S/C: 5.1, \( n_{\text{Cat}} \) = 0.39 − 0.50 g, Ni loading: 8.2 wt\%, Temp.: 584 °C, \( F_T \) = 1.6 NL/min, \( y_{\text{MF}} \) = 1.4 − 1.5 vol\%, \( y_{\text{H}_2\text{O}} \) = 37.5 − 38.0 vol\%, \( y_{\text{O}_2} \) = 0 − 1.5 vol\%, \( N_2 \) as balance.

<table>
<thead>
<tr>
<th>Type</th>
<th>TOS</th>
<th>X</th>
<th>( Y_{\text{H}_2} )</th>
<th>( Y_{\text{CH}_4} )</th>
<th>Carbon deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[h]</td>
<td>[%]</td>
<td>[%]</td>
<td>[%]</td>
<td>( \frac{\text{mmole C}}{\text{mole C}_{\text{Feed}}} )</td>
</tr>
<tr>
<td>SR</td>
<td>24</td>
<td>82</td>
<td>81</td>
<td>0.7</td>
<td>1.1</td>
</tr>
<tr>
<td>OSR</td>
<td>4</td>
<td>100</td>
<td>68</td>
<td>0.4</td>
<td>0.05</td>
</tr>
<tr>
<td>OSR (High SV)</td>
<td>24</td>
<td>100</td>
<td>66</td>
<td>0.7</td>
<td>0.06</td>
</tr>
</tbody>
</table>

The release of carbon oxides during TPO of the catalysts used in the oxidative SR of 2-methylfuran for 4 and 24 h are shown in fig. 6.4. The rate of carbon oxidation had a maximum at roughly 610 °C after 4 h on stream, indicating that the carbon was not deposited on CeO\(_2\), K, or Ni which catalyzes the oxidation leading to oxidation at lower temperatures [202, 215, 216, 240]. The carbon oxides release over 500 °C in SR was roughly 4 times as high as the carbon oxides release observed in OSR of 2-methylfuran after 4 h. This indicates that the oxygen addition decreases both the carbon deposition on the catalyst and on the reactor wall.

After 24 h the carbon oxidation occurred over a broader temperature range and with several peaks at 430 °C, 480 °C, 520 °C, and 620 °C, which indicates that carbon was deposited on the catalytic particles as well as surfaces with little or no catalytic activity. This shows that it is not only the amount of carbon deposits which changes with time; it is also the type and/or placement of the carbon.

### 6.3 Steam reforming of furfural

The product yields of CO, CO\(_2\), CH\(_4\), H\(_2\), Others, and conversion of furfural as function of temperature in the SR of furfural at S/C=5 are summarized in fig. 6.6. The conversion increased with temperature and reached 96 % at 700 °C. The yield of CO increased with temperature while the yield of CO\(_2\) had a maximum at 500 °C. The trends in the yield of CO and CO\(_2\) at 500 °C and above are as expected based on thermodynamics. The yield of H\(_2\) had a maximum of 85 % at 600 °C, however only slightly higher compared to yields at 500 and 700 °C. The yield of Others was 19 % at 400 °C and decreased to less 0.1 % at 500 °C. The fraction called Others contained 90 % of ethanol and 2-propanol in a ratio of 10:1, but small amounts of acetic acid, butanoic acid, furanes, and hydrofuranes were also detected in the effluent. Similar products were observed by Xu et al. [247]. Hydrofuranes are formed by oxidation of the furan-ring, while ethanol and 2-propanol are fragments of furfural. The yield of CH\(_4\) had a maximum of 0.2 % at 500 °C, which was significantly lower compared with the
yield of CH\textsubscript{4} in the SR of 2-methylfuran. 2-methylfuran has a methyl group in the 2-position on the furan ring, where furfural has a carbonyl group. The higher yield of CH\textsubscript{4} in the SR of 2-methylfuran is probably related to the methyl-group, which easily can be converted to methane by reaction with H\textsuperscript{*}.

The conversion of furfural and the product yields of CO, CO\textsubscript{2}, CH\textsubscript{4}, and H\textsubscript{2} as function of time in the SR of furfural at 600 °C and S/C=5 can be seen in fig. 6.3. The product distribution was quite stable with time-on-stream although a slight decrease in the yield of H\textsubscript{2} from 61 % to 57 % was observed. However, the conversion decreased significantly from 82 % to 53 % during 4 h on stream. The much faster rate of deactivation compared with SR of 2-methylfuran was apparent in the rate of carbon deposition, which was 66 \text{mg C g\textsuperscript{-1} Cat h\textsuperscript{-1}} compared to 8 \text{mg C g\textsuperscript{-1} Cat h\textsuperscript{-1}} in the SR of 2-methylfuran at similar conditions.

Oxidative SR of furfural was investigated at two different O/C-ratios. The O/C-ratio of 0.4 used in the SR of 2-methylfuran was not high enough to induce a high and stable conversion and therefore a higher O/C-ratio of 1.2 was investigated as well. The conversion as function of time-on-stream at the different O/C-ratios can be seen in fig. 6.8. The conversion increased and became stable at the high O/C-ratio. Full conversion was achieved at O/C-ratio of 1.2 and it remained stable for 4 h.

The yield of H\textsubscript{2} and hydrocarbons as well as conversion and carbon deposition after 4 h on stream as function of O/C-ratio can be seen in fig. 6.9. Similar to the observations in the SR of 2-methylfuran under oxidative conditions the yield of H\textsubscript{2} and carbon deposition decreased while the conversion increased. The yield of hydrocarbons shown in fig. 6.8 includes methane, ethene, ethane, and propene, and increased with increasing O/C-ratio, which is unexpected. Generally a higher conversion leads to lower yields of hydrocarbons, as they are intermediates in the SR reactions. This trend could be due to partial oxidation of the Ni-particles as high amounts of H\textsubscript{2}O and O\textsubscript{2} are fed to the reactor along with a low production of H\textsubscript{2}, which may not be enough to keep the catalyst reduced. An unreduced Ni/CeO\textsubscript{2}-K/MgAl\textsubscript{2}O\textsubscript{4} produced a
6. Steam reforming of cyclic oxygenates

Fig. 6.7: Yield of CO, CO₂, CH₄, H₂, and conversion as function of time in SR of furfural over Ni/CeO₂-K/MgAl₂O₄. Experimental conditions: S/C: 5.1, m_cat = 0.50 g, Ni loading: 8.2 wt%, Temp.: 584 °C, F_I = 1.6 NL/min, y_FF = 1.4 vol%, y_H₂O = 38.0 vol%, N₂ as balance.

Fig. 6.8: Conversion as function of time in SR of furfural over Ni/CeO₂-K/MgAl₂O₄ at different O/C-ratios. Experimental conditions: S/C: 5.0-5.3, m_cat = 0.50 g, Ni loading: 8.2 wt%, Temp.: 584-616 °C, F_I = 1.6 NL/min, y_FF = 1.4 – 1.5 vol%, y_H₂O = 38.0 – 38.4 vol%, y_O₂ = 0 – 4.8 vol%, N₂ as balance.

A high fraction of decomposition products like hydrocarbons. This can be seen in fig. 6.10, which shows the product yields and conversion as function of time on stream in the SR of furfural over an unreduced Ni/CeO₂-K/MgAl₂O₄. The total yield of hydrocarbons was initially 20 % and then decreased to zero % after 1 h. This decrease is likely due to reduction of NiO leading to an increase in the SR activity. It may be noticed that an unreduced Ni/MgAl₂O₄ is not able to catalyzes any reactions, which shows that K and CeO₂ either increases the reducibility of NiO or has enough SR activity to produce H₂ to initiate the reduction of NiO.
Fig. 6.9: Conversion, carbon deposition, yield of $H_2$ and hydrocarbons as function of O/C-ratio in the SR of furfural over Ni/CeO$_2$-K/MgAl$_2$O$_4$. Experimental conditions: S/C: 5.0-5.3, $m_{Cat} = 0.50$ g, Ni loading: 8.2 wt%, Temp.: 584-616 °C, $F_T = 1.6$ NL/min, $y_{2MF} = 1.4-1.5$ vol%, $y_{H_2O} = 38.0-38.4$ vol%, $y_{O_2} = 0-4.8$ vol%, $N_2$ as balance.

Steam reforming of furfural at O/C=1.2, S/C=5.2, and 600 °C was conducted for 24 h and a comparison of product yields, conversion, and carbon deposition after 4 h and 24 h on stream can be seen in table 6.4. The conversion was 100 % both after 4 and 24 h, but the yield of hydrocarbons increased, while the yield of $H_2$ decreased showing deactivation of the catalyst. Furthermore, the $CO_2/CO$-ratio decreased with time indicating a loss in WGS activity. The deactivation was also apparent in the rate of carbon deposition, which increased drastically from 0.11 $\frac{mmole\ C}{mole\ C_{Food}}$ after 4 h to 18.9 $\frac{mmole\ C}{mole\ C_{Food}}$ after 24 h, which almost was a factor of 200.
Tab. 6.4: Product yields, conversion, and carbon deposition after 4 and 24 h in OSR of furfural. Experimental conditions: S/C: 5.0-5.3, m_{Cat} = 0.50 g, Ni loading: 8.2 wt%, Temp.: 584-616 °C, F_T = 1.6 NL/min, y_{FF} = 1.4 - 1.5 vol%, y_{H_2O} = 38.0 - 38.4 vol%, y_{O_2} = 0 - 4.8 vol%, N_2 as balance.

<table>
<thead>
<tr>
<th>TOS [h]</th>
<th>CO [%]</th>
<th>CO_2 [%]</th>
<th>CH_4 [%]</th>
<th>C_2H_4 [%]</th>
<th>C_3H_7 [%]</th>
<th>H_2 [%]</th>
<th>X [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>23</td>
<td>67</td>
<td>5</td>
<td>4</td>
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<td>24</td>
<td>34</td>
<td>56</td>
<td>2</td>
<td>7</td>
<td>1</td>
<td>14</td>
<td>100</td>
</tr>
</tbody>
</table>

| C_{Dep} [mmole C/mole C_{Fed}] | 0.3 | 18.9 |
| C_{Dep} [mg C/g_{Cat}·h] | 0.1 | 6.2 |

The release of carbon oxides as function of temperature during TPO of the catalyst after 4 h at SR conditions and after 4 and 24 h at OSR conditions can be seen in fig. 6.11. The carbon release after 4 h at SR conditions showed one distinct oxidation peak at 410 °C, which probably is due to oxidation of carbon in contact with K, Ni, or CeO_2. Carbon oxidation was also observed in the range of 600-700 °C, which could be due to oxidation of carbon deposits on material with little or no catalytic activity like the reactor walls, MgAl_2O_4, and on top of the catalyst bed [249]. The release of carbon oxides in TPO of two empty reactors used in the SR of furfural are shown in fig. 6.12. This figure shows carbon oxidation at 400-450 °C and at 500-650 °C, where the oxidation at high temperatures could correspond to carbon on reactor wall, while the oxidation at the low temperatures indicates that a more reactive carbon form also was deposited. However, it could also be catalyst particles or catalytic material deposited on the reactor walls. It should be noted that the majority of the carbon deposition is on the catalysts as carbon oxides release from the empty reactors only corresponds to 1 % of the total carbon deposition on the catalyst and reactor.

The carbon oxides release at 600-700 °C were observed in the SR and OSR after 4 hours, but was lower in OSR indicating that the oxygen decreases carbon deposition on both catalytic and uncatalytic materials. Similar to the observations in the SR and OSR of 2-methylfuran. The carbon oxides release after 24 h at OSR conditions showed one broad peak from 300 to 750 °C with a maximum at 415 °C, indicating carbon deposits on both materials with and without catalytic activity. The large increase in rate of carbon deposition from 4 to 24 h as well as the change in oxidation profile could indicate an induction period and hereafter the rate of carbon deposition might reach a constant rate, similar to the observations in SR of 2-methylfuran.

6.4 Steam reforming of guaiacol

Steam reforming of guaiacol was investigated at S/C=5 and the conversion and product yields as function of temperature are summarized in fig. 6.13. The conversion, yield of H_2, and yield of CO all increased with increasing temperature, while the yield of CO_2 remained at a value
6. Steam reforming of cyclic oxygenates

Fig. 6.11: Carbon oxides release as function of temperature over Ni/CeO$_2$-K/MgAl$_2$O$_4$ after 4 h at SR and OSR conditions and 24 h at OSR conditions. Experimental conditions: $\Delta T = 10 \, ^\circ\text{C}/\text{min}$, $F_T = 1 \, \text{NL/min}$, $y_{O_2} = 2 - 3 \, \text{vol}\%$, $N_2$ as balance.

Fig. 6.12: Carbon oxides release as function of temperature over empty reactors after 4 h at SR conditions with furfural as reactant. Experimental conditions: $\Delta T = 10 \, ^\circ\text{C}/\text{min}$, $F_T = 1 \, \text{NL/min}$, $y_{O_2} = 2 - 3 \, \text{vol}\%$, $N_2$ as balance.

of 60-70 % at all temperatures. The yield of H$_2$ had a maximum of 88 % at 780 °C, while full conversion was reached at 700 °C and above. Besides the expected products, CO, CO$_2$, CH$_4$, and H$_2$, ethene and ethane was produced in a ratio of 1:10 at all temperatures. The high formation of ethane was unlike any of the other compounds investigated. Benzene-diols and phenol were produced in quite high yields and constituted the major part (70-80 %) of the product fraction Others shown in fig. 6.13. The high yield of benzene-diols and phenols indicates that the removal of the methyl group from guaiacol is facile. The yield of Others, methane, ethane, and ethene all decreased with increasing temperature. The yield of Others was quite high even at 700 °C, which indicates that the activation and conversion of aromatic
compounds requires high temperature. Full conversion with yield of Others below 0.5% was achieved at 780 °C, which was significantly higher compared with furfural and 2-methylfuran.

**Fig. 6.13:** Yield of CO, CO$_2$, CH$_4$, C$_2$H$_4$, C$_2$H$_6$, H$_2$, Others, and conversion as function of temperature in the SR of guaiacol over Ni/CoO$_2$-K/MgAl$_2$O$_4$. Experimental conditions: S/C: 5.2, $m_{\text{Cat}}=0.50$ g, Ni loading: 8.2 wt%, $F_T=1.6$ NL/min, $y_{\text{GUA}}=1.1$ vol%, $y_{\text{H}_2\text{O}}=38.1$ vol%, $N_2$ as balance.

The conversion and product yields as function of time-on-stream in the SR of guaiacol at 600 °C and S/C=5 can be seen in fig. 6.14. The yield of H$_2$ and conversion remained stable at 61% and 90%, respectively, for the entire experiment. Despite the stable behavior, there was still observed significant carbon deposition at a rate of 73.5 $\frac{mg\ C}{g_{\text{Cat}}\cdot h}$. This indicates that the carbon deposition was as whiskers.

Oxidative SR of guaiacol at S/C=5 and O/C=0.8 was tested for 4 h and 24 h, and the conversion and the products yields at the end of each experiment can be seen in table 6.5. The beneficial effect of adding O$_2$ is seen for SR of guaiacol as the conversion increased, while the carbon deposition was decreased significantly, again at the expense of the yield of H$_2$.

Full conversion was achieved both after 4 and 24 h on stream at OSR. However, the catalyst showed signs of deactivation in the product distribution as the yield of H$_2$ decreased while the yield of by-products increased. Furthermore the rate of carbon deposition increased with time.

The carbon oxides release as function of temperature after 4 h at SR conditions and 4 h and 24 h at OSR conditions can be seen in fig. 6.16. The carbon oxides release after 4 h at SR-conditions occurred in single peak at 410 °C with a shoulder at 580 °C similar to the other investigated compounds. The carbon oxides release during TPO of an empty reactor used in the SR of guaiacol is compared with the TPO-profile from a reactor with catalysts in fig. 6.15. The empty reactor showed carbon oxides release at 560 °C indicating that the shoulder is related to carbon deposited on the reactor walls. Furthermore the amount carbon deposited in the empty reactor was 10% of total carbon deposition. This was higher compared to the SR of furfural, which indicates that the thermal decomposition of guaiacol is higher.

The TPO profiles of the spent catalysts used in OSR of guaiacol suggest that the main part of carbon deposition was on the reactor walls or other materials with little or no catalytic
activity as the carbon oxides release was mainly at 600 °C and above and not at 410-420 °C as expected for catalyzed carbon oxidation. The carbon oxides release after 24 h in OSR was higher and moved toward lower temperatures indicating covering of catalytic particles by carbon with time-on-stream, which also could explain the increase in the rate of carbon deposition.

Further increments of the O/C-ratio is probably needed to obtain a stable product distribution and suppress carbon deposition in the SR of guaiacol and furfural at 600 °C.
**Tab. 6.5**: Product yields, conversion, and carbon deposition after 4 and 24 h in OSR of furfural. Experimental conditions: S/C: 5.2-5.4, O/C: 0.80-0.83, \( m_{\text{Cat}} \) = 0.50 g, Ni loading: 8.2 wt\%, Temp.: 584-616 °C, \( F_T \) = 1.6 NL/min, \( y_{\text{GU}} \) = 1.0 - 1.1 vol\%, \( y_{\text{H}_2\text{O}} \) = 38.2 - 39 vol\%, \( y_{\text{O}_2} \) = 0 - 3.1 vol\%, \( \text{N}_2 \) as balance.

<table>
<thead>
<tr>
<th>Type</th>
<th>SR</th>
<th>OSR</th>
<th>OSR</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOS [h]</td>
<td>4</td>
<td>4</td>
<td>24</td>
</tr>
<tr>
<td>Yield</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO [%]</td>
<td>12.2</td>
<td>16.1</td>
<td>19.6</td>
</tr>
<tr>
<td>( \text{CO}_2 ) [%]</td>
<td>80.4</td>
<td>80.5</td>
<td>76.3</td>
</tr>
<tr>
<td>( \text{CH}_4 ) [%]</td>
<td>4.2</td>
<td>2.2</td>
<td>1.9</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 ) [%]</td>
<td>0.3</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_6 ) [%]</td>
<td>3.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Others [%]</td>
<td>13.7</td>
<td>0.9</td>
<td>5.1</td>
</tr>
<tr>
<td>( \text{H}_2 ) [%]</td>
<td>64</td>
<td>54</td>
<td>48</td>
</tr>
<tr>
<td>( \text{X} ) [%]</td>
<td>86</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>( \text{C}<em>{\text{Dep}} \left[ \text{mmole C/mole } C</em>{\text{Feed}} \right] )</td>
<td>9.9</td>
<td>0.2</td>
<td>0.6</td>
</tr>
<tr>
<td>( \text{C}_{\text{Dep}} \left[ \text{mg C/g Cat·h} \right] )</td>
<td>73.5</td>
<td>1.3</td>
<td>4.5</td>
</tr>
</tbody>
</table>

**Fig. 6.16**: Carbon oxides release as function of temperature over \( \text{Ni/CeO}_2\text{-K/MgAl}_2\text{O}_4 \) after 4 h at SR and OSR conditions and 24 h at OSR conditions with guaiacol as reactant. Experimental conditions: \( \Delta T = 10 \, ^\circ \text{C/min}, \ F_T = 1 \, \text{NL/min}, \ y_{\text{O}_2} = 2 - 3 \, \text{vol}\%, \ \text{N}_2 \) as balance.

### 6.5 Postreaction characterization

Catalysts, which have been used in the SR of furfural at S/C=5, SR of guaiacol at S/C=5, or SR of guaiacol at S/C=5 and O/C=1.2 for 4 h, were characterized by XRD and TEM. The XRD patterns of the spent catalysts used in the SR of furfural and guaiacol at S/C=5 can be seen in fig. 6.17. XRD analysis of the spent catalysts from SR of furfural and guaiacol showed an additional peak at 52° compared with the XRD pattern of the fresh catalyst. The peak is
Table 6.6: Particle size of NiO and CeO$_2$ crystals on fresh and spent Ni/\textit{CeO}_2-K/MgAl$_2$O$_4$ catalysts used in the SR of furfural and guaiacol at SR and oxidative SR conditions for 4 h and 24 h.

<table>
<thead>
<tr>
<th></th>
<th>NiO [nm]</th>
<th>CeO$_2$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>SR of furfural, S/C=5</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>SR of guaiacol, S/C=5</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>SR of guaiacol, S/C=5, O/C=1.2</td>
<td>17</td>
<td>6</td>
</tr>
<tr>
<td>SR of guaiacol, S/C=5, O/C=0.8, 24 h</td>
<td>17</td>
<td>6</td>
</tr>
</tbody>
</table>

Figure 6.17: XRD patterns for spent Ni/\textit{CeO}_2-K/MgAl$_2$O$_4$ catalysts used in the SR of furfural and guaiacol.

probably from metallic Ni.

The NiO and CeO$_2$ particle size of the fresh and spent catalyst, estimated by XRD, can be seen in table 6.6. Sintering was not significant in SR at S/C=5 as the Ni particles were estimated to be 6 nm in diameter.

The XRD patterns of spent catalyst used in the SR of guaiacol at S/C=5 and O/C=1.2 for 4 h and 24 h are shown in fig. 6.18. The peaks from NiO were higher for these catalysts, which indicate that the NiO particles sintered and the particle sizes were estimated to be roughly 17 nm. Sintering was more pronounced in oxidative SR, which also has been shown in the SR and oxidative SR of ethanol, see chapter 4. The sintering of the particles in oxidative SR did not significantly increase with time-on-stream as XRD analysis of spent catalysts, which had been operated for 24 h in the SR of guaiacol had a similar NiO particle diameter, see table 6.6.

Sintering of the CeO$_2$ was not observed neither under SR conditions nor oxidative SR conditions, as shown in table 6.6.

The sintering observed in OSR may explain the accelerated rate of carbon deposition with time, as the larger particles may be more susceptible to carbon deposition compared with smaller particles. Therefore the carbon deposition might accelerate, once the particles reach a critical size.
TEM images of the spent catalysts can be seen in fig. 3.17. Carbon whiskers were formed in quite large amounts in the SR of furfural and guaiacol at S/C=5 as shown in fig. 3.17(a) and 3.17(c). This implies that the carbon oxidation at 400-430 °C is related to the carbon whisker. Carbon deposition as encapsulating gum was observed in the SR of guaiacol, which can be seen in fig. 3.17(d) as a layer on the surface of the metal particles, and in fig. 3.17(c) as large dark areas [122]. The encapsulating carbon was present in lower amounts and it could correspond to the carbon oxidized at temperatures above 500 °C.

No formation of carbon whiskers was observed on the catalyst, which had been used in the oxidative SR of guaiacol, as indicated in fig. 3.17(e) and 3.17(f). However, indications of carbon deposition as encapsulation gum were still observed in fig. 3.17(f). This also implies that the high temperature carbon oxidation is encapsulating carbon as carbon oxidation was mainly observed at temperatures above 550 °C in oxidative SR of guaiacol after 4 h on stream.
Fig. 6.19: TEM images of spent Ni/CeO$_2$-K/MgAl$_2$O$_4$-catalysts used in the SR of furfural and guaiacol at SR- and oxidative conditions.
6. Steam reforming of cyclic oxygenates

6.6 Comparison of SR of different oxygenates

Steam reforming of different cyclic model compounds of bio-oil has been investigated in this study and a comparison of conversion, carbon deposition, yield of $H_2$, by-products, and hydrocarbons after 4 h on stream for the SR of ethanol (data from chapter 4), 2-methylfuran, furfural, and guaiacol at 600 °C and S/C-ratio of 5-6 can be seen in fig. 6.20. The conversion was lower for all the cyclic compounds compared to ethanol. The carbon deposition was highest for guaiacol followed by furfural, while 2-methylfuran and ethanol had similar rates of carbon deposition. The larger cyclic compounds were less reactive and had a higher tendency to form carbon deposits compared with the SR of ethanol. Similar results have been reported by Hu and Lu [59] for the SR of glucose, $m$-xylene, ethyl acetate, acetone, ethylene glycol, acetic acid.

The only structural difference between furfural and 2-methylfuran is that furfural has a carbonyl group in the 2-position on the furan-ring, while 2-methylfuran has a methyl group. This indicates that the increased rate of carbon deposition in the SR of furfural compared to the SR of 2-methylfuran is related to the carbonyl group. A possible explanation could be self-condensation reactions by furfural leading to carbon deposition and catalyst deactivation. Another explanation for the differences in carbon deposition could be differences in the formation of olefins, like ethene or propene, but this was not observed.

The aromatic nature of guaiacol is probably responsible for the high rate of carbon deposition observed in the SR of guaiacol compared to furfural and especially ethanol and 2-methylfuran. The yield of $H_2$ was similar in the SR of ethanol and 2-methylfuran and higher compared to the yield obtained in the SR of guaiacol and furfural. Significant amounts of by-products were mainly observed in the SR of guaiacol and ethanol, and was mainly methane in the SR of ethanol and large fractions of both $CH_4$, $C_2H_6$, and aromatic compounds in the SR of guaiacol.
The conversion and total yield of byproducts as function of temperature for the cyclic model compounds can be seen in fig. 6.21. The conversion as function of temperature was similar for 2-methylfuran and furfural which is expected as the two model compounds have similar structure. The conversion of guaiacol was lower compared to the other model compounds at 400 and 500 °C indicating that high temperatures are needed to activate the aromatic ring. At 600 °C the conversion was higher for guaiacol, but the yield of by-products was still high (24%), so the conversion to the desired produced was lower compared with furfural and 2-methylfuran. Overall the results show that the conversion of guaiacol requires higher temperature and furthermore the carbon deposition in the SR of guaiacol is the highest of all showing that guaiacol is more difficult to steam reform.

![Conversion and yield of byproducts as function of temperature in the SR of 2-methylfuran, furfural, and guaiacol in SR over Ni/CeO$_2$-K/MgAl$_2$O$_4$ at S/C-ratio of 5. Solid lines are conversion while dotted lines are yield of by-products. Experimental conditions: S/C: 5.0-5.2, m$_{\text{Cat}}$ = 0.50 g, Ni loading: 8.2 wt%, $F_T$ = 1.6 NL/min, $y_{\text{Oxy}}$ = 1.1 – 1.5 vol%, $y_{\text{H}_2\text{O}}$ = 38.1 vol%, $N_2$ as balance.](image)

### 6.7 Conclusions

Steam reforming of three different model compounds of the cyclic oxygenates in bio-oil, 2-methylfuran, furfural, and guaiacol, have been investigated at S/C-ratio of 5 and temperatures between 400-800 °C over Ni/CeO$_2$-K/MgAl$_2$O$_4$. The conversion, yield of H$_2$, and CO increased with increasing temperature, while the yield of CO$_2$ and by-products decreased with increasing temperature for all the model compounds. The major products at all temperatures were carbon oxides (CO and CO$_2$) and H$_2$, but small hydrocarbons, like methane and ethene, as well as fragments of the model compounds, like acetone, ethanol, phenol, were also observed in the effluent. This was most pronounced for guaiacol, where a yield of aromatic by-products of 17% at 97% conversion was observed at 600 °C. Temperatures of 700 °C were needed to fully convert 2-methylfuran and furfural to carbon oxides and H$_2$, while temperatures above 780 °C were required in the SR of guaiacol.

Significant carbon deposition was observed for all the model compounds and it was highest for guaiacol followed by furfural and 2-methylfuran. TEM-images showed that the carbon
deposited as carbon whiskers at SR conditions. Sintering of Ni or CeO$_2$ was not observed at SR-conditions.

The carbon deposition could be significantly decreased by adding oxygen to feed at a O/C-ratio between 0.4 and 1.2. The oxygen addition increased the conversion and full conversion, with low yields of by-products, could be achieved at 600 °C. The beneficial effects of oxygen addition were at the expense of significant decrease in the yield of H$_2$. The actual decrease in the yield of H$_2$ depended on the model compound and the applied O/C-ratio. Furthermore significant sintering of the Ni-particles was observed in oxidative SR as well as an increase in the rate of carbon deposition with time on stream. Stable behavior was not achieved over 24 h in the oxidative SR of furfural and guaiacol.

Overall, the results indicate that the SR of oxygenates is very challenging and is even more so for aromatic compounds. The results indicate that the only path to stable operation with no carbon deposition is through oxidative SR although here sintering may be a challenge.
7. CONCLUSIONS

Flash pyrolysis of biomass can be used to produce bio-oil, which has the key feature that the energy density is higher compared with untreated biomass making the transportation less expensive. Conversion of biomass to bio-oil is expected to improve the economics in the energy production from biomass but the oil is not well suited for direct use. Therefore upgrading of bio-oil through steam reforming is an interesting and sustainable route to hydrogen and synthesis gas and can be incorporated into existing processes or it can be used as part of biorefinery, which upgrades bio-oil to transportation fuels. However, several problems arise from SR of bio-oil, with carbon deposition and catalysts deactivation as the most severe. Furthermore there is a lack of understanding of the surface reactions and the influence of process parameters, like O/C-, H/C-, and S/C-ratios, on product distribution, activity, and deactivation. Steam reforming of model compounds other than ethanol and acetone has not been investigated thoroughly. These points have been addressed in this thesis to get a deeper understanding of the SR of oxygen containing hydrocarbons.

Steam reforming of ethanol was investigated on Ni-based catalysts at a S/C-ratio of roughly 6 to elucidate the effect of support, additives, and selective poisoning as well the influence of process parameters. The product distribution as function of temperature did not vary much depending on the support and resembled the thermodynamic equilibrium at temperatures of 500 °C and above. CO, CO\(_2\), and H\(_2\) were the major products, while methane, ethene, acetaldehyde, acetone, and acetic acid were formed in low yields, which decreased with increasing temperature. The production of ethene was highest at 500 °C, which coincided with the highest carbon deposition rate, showing that ethene is one of the main sources of carbon deposition in the SR of ethanol.

Ni/Ce\(_{0.6}\)Zr\(_{0.4}\)O\(_2\) was the most active catalyst, but also suffered from severe carbon deposition as whiskers. Ni/CeZrO\(_4\)/MgAl\(_2\)O\(_4\) showed both high conversion and low carbon deposition and therefore was more interesting. The high activity of both Ni/Ce\(_{0.6}\)Zr\(_{0.4}\)O\(_2\) and Ni/CeZrO\(_4\)/MgAl\(_2\)O\(_4\) is probably related to the CeZrO\(_4\), which can decrease the water dissociation and supply oxygen to surface reactions.

Additives to Ni/MgAl\(_2\)O\(_4\) could decrease the carbon deposition and increase the activity, but did not influence the product distribution significantly. CeO\(_2\) induced the lowest carbon deposition and, in combination with K, increased the activity significantly as well. The effect of CeO\(_2\) and K is probably due to an increased rate of carbon oxidation and facilitation of surface reactions with OH- or O-species. Despite stable activity over the first hours on stream, both Ni-K/MgAl\(_2\)O\(_4\) and Ni/CeO\(_2\)-K/MgAl\(_2\)O\(_4\), showed deactivation over longer periods on stream and detrimental carbon deposition as whiskers was observed.

Sulfur addition in small amounts to the catalyst had a beneficial effect on carbon deposition but a slight deactivating effect on the overall rate of reaction. The lowest rate carbon deposition in the SR of ethanol, without oxygen addition, was achieved with a sulfur poisoned Ni-CeO\(_2\)/MgAl\(_2\)O\(_4\) catalyst and it was 1.2 mg C g\(_{\text{Cat}}\) h\(^{-1}\).
Hydrogen addition to the feed in the SR of ethanol had little effect on the carbon deposition and conversion, while increasing the S/C-ratio from 1.6 to 8.2 or the O/C-ratio from 0 to 1.1 increased conversion and decreased carbon deposition. The yield of H2 increased with increasing S/C-ratio, while it decreased with increasing O/C-ratio. Oxidative SR at O/C-rations of 0.8 or above over Ni/MgAl2O4 could inhibit the carbon deposition and long term experiments did not show deactivation. However the yield of H2 decreased by 1-2 moles of H2 pr. mole of ethanol converted. Therefore oxidative SR seems as the most promising process for conversion of oxygen containing compounds.

Steam reforming of acetol, acetic acid, acetone, ethanol, 1-propanol, and propional was investigated to elucidate differences in reactivity and catalysts deactivation between the different model compounds. The product distribution approached the thermodynamical equilibrium with increasing temperature. Meaning that the yield of H2 and CO increased, while the yield of CO2 and byproducts decreased with temperature. The conversion of the model compounds increased with increasing temperature, but did not vary significant between the model compounds. The formation of by-products was most pronounced at 500 °C and below. Dehydration and dehydrogenation as well as coupling reactions, e.g. ketonization of acetic acid or condensation reactions, could account for the observed by-products. Based on the product distribution as function of temperature it was found that the reaction pathway is a sequential breaking of C-C-bonds in the carbon backbone of the molecule initiated from the oxygen containing part of the molecule.

Deactivation occurred for all of the tested model compounds and the carbon deposition was most severe for alcohols, which can be related to the higher fraction of olefins in the offgas.

Steam reforming of 2-methylfuran, furfural, and guaiacol was investigated as function of temperature and time at S/C-ratio of 5 over Ni/K-CeO2/MgAl2O4. The product distributions as function of temperature all showed an increase in the yield of H2 and CO and a decrease in the yield of CO2 and by-products with increasing temperature. The by-products were both small hydrocarbons, like methane, ethene, and propene, as well as fragments of the model compounds. Guaiacol was the most difficult compound to convert as the aromatic ring required high temperatures to open and convert and furthermore the carbon deposition was highest in the SR of guaiacol compared to the SR of furfural, 2-methylfuran, and ethanol. This shows that the reactivity decreases and the carbon deposition increases with increasing size of the model compounds.

Oxygen addition could increase conversion and significantly lower the carbon deposition, but also the yield of H2. The level of O2 needed to stabilize the conversion with time-on-stream depended on which compound was converted. Stable behavior over 24 h could not be achieved in the SR of furfural and guaiacol despite high levels of O2 in the feed. Under these conditions catalyst sintering appeared to be more significant than carbon deposition.

7.1 Outlook

The results from this thesis shows that the SR of oxygen containing hydrocarbons is a difficult process as deactivation due to carbon deposition occurs. However, there are several approaches which can minimize the carbon deposition. Additives, like CeO2 or K, which catalyzes oxidation reactions can increase the activity and lower the carbon deposition. Further lowering of the carbon deposition can be achieved by increasing the temperature or adding O2 to the feed. However, the oxygen addition will lower the yield of the most interesting product, H2,
and should therefore be kept at minimum level. A possible scheme could be to run the SR at 700 °C compared to 600 °C used in this study, where the carbon deposition is lower and the level of oxygen addition needed to minimize the carbon deposition probably would be lower and subsequently the yield of H₂ higher.

The catalysts used in this thesis have not been fully optimized and improvements of catalyst performance could be achieved. The levels of additives have not been varied and more optimal loadings of CeO₂ and K may be found. Furthermore, the preparation of the catalysts may also be optimized, as studies have shown that it is possible to lower the metal particle size by doing a combined calcination and reduction, where the catalyst is heated in a flow of H₂ in N₂. Smaller metal particles will probably give a higher activity and lower carbon deposition. Another route to small particles could be flame spray pyrolysis synthesis of the catalysts, which further has the advantage of being a one-step production method.

The active metal could also be changed to a noble metal, which are less prone to carbon deposition and have high activity. Another possibility is a La₀.₉Ce₀.₁NiO₄-perovskite catalyst, which have shown promising results in OSR of ethanol and could be interesting to investigate further. However, both types of catalysts are expensive and may only be interesting in smaller scale.

Scaling up of the SR of bio-oil to pilot or industrial scale might give additional problems besides catalyst deactivation and carbon deposition. Bio-oil is thermally unstable, and conventional heating of the feed through heat exchangers may lead to clogging of pipes as the bio-oil can polymerize forming gum or carbon deposits. A possible solution could be to spray the cold bio-oil into the reactor, however, this require a high input of energy to the reactor as the bio-oil needs to be heated and energy for the endothermic SR reactions should be provided. Oxygen addition could lower the energy demand as the reaction would be exothermic and deliver energy to the system. The addition of oxygen in industrial scale is quite expensive, due to the air separation unit, and mainly economical feasible in large scale.

There are still areas in the SR of bio-oil, which can be investigated further. The reaction mechanisms as well reaction kinetics for many compounds or compound groups are still undetermined and these are needed for sizing of industrial reactors and plants. The bio-oil can also contain S, P, and other inorganic elements, which can lead to deactivation, and the effects of these compounds should be elucidated as cleaning of the bio-oil may be expensive and difficult.

The investigated catalysts could also be characterized by other techniques e.g. it could be interesting to use in-situ XRD or EXAFS to determine if the Ni is partially oxidized under oxidative conditions. Furthermore, elemental mapping of Ni and additives on MgAl₂O₄ could be conducted as it may provide clues to the exact reason for the increased conversion and decreased carbon deposition.
BIBLIOGRAPHY


Appendices
Appendix A

DIFFUSION LIMITATIONS

In experimental work it is important to know as much as possible about the system, which is being studied. For example, the transport of reactants or products to and from the active site might be hindered and therefore slow down the entire reaction. The data from such experiments cannot be used for measurements of intrinsic kinetics and might give a wrong picture of the product distribution and conversion. In the following it will therefore be examined if diffusion from the bulk gas to the catalyst particles or diffusion of reactants within the particles is rate limiting for the overall reaction. This will be estimated by using Mears and Wéisz-Prater criteria, which can be used to examine if internal or external diffusion is rate limiting based on the physical parameters of the system. The reactor is a gas phase reactor operated at atmospheric pressure and diffusion limitations can cause concentrations gradients across the boundary layer between gas and pellets or inside the catalyst pellets. The overall SR of ethanol reaction is:

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow 2\text{CO} + 4\text{H}_2
\]  

(A.1)

However the water gas shift, reaction A.2, and the methanation reaction, reaction A.3, will influence the off gas composition as well:

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2
\]  

(A.2)

\[
\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}
\]  

(A.3)

A.1 Mears criterion

To evaluate the effect of the external diffusion Mears criterion for external diffusion will be used. This criterion states that external diffusion can be neglected if [189]:

\[
\frac{-r'_a (\text{obs}) \cdot \rho_b \cdot d_p \cdot n}{2 \cdot k_c \cdot C_{Ab}} < 0.15
\]  

(A.4)

Where \(-r'_a\) is the measured reaction rate in mol/(kg·s), \(\rho_b\) is the bulk density of the catalyst bed in kg/m\(^3\), \(d_p\) is the diameter of the catalyst particles in m, \(n\) is the reaction order, \(k_c\) is the mass transfer coefficient in m/s, and \(C_{Ab}\) is the concentration of reactant \(A\) in the bulk in mol/m\(^3\).

Mears criterion is an evaluation of the external diffusion of one compound and this investigation will focus on the diffusion of ethanol or water in N\(_2\).

In order to calculate Mears criterion (eq. A.4) many parameters have to be determined and how this is done will be explained in the following.
The observed reaction rate is calculated based on experimental data as the number of moles of ethanol converted to gaseous species per time divided by the mass of catalyst:

\[-r'_a^{\text{obs}} \frac{F_{\text{Eth, m}} \cdot X}{m_{\text{cat}}}(A.5)\]

Where \( F_{\text{Eth, m}} \) is the molar flow of ethanol to the reactor and \( m_{\text{cat}} \) is the mass catalyst used in the experiment. The observed rate is taken as the maximum rate observed in the experiments, which at temperatures above 600 °C, where full conversion is observed:

\[-r'_a^{\text{obs}} = 1.19 \cdot 10^{-5} \text{ mol/s} = 0.024 \text{ mole/kg} \cdot \text{s} (A.6)\]

The bed density, \( \rho_b \), is calculated as the mass of the catalyst used in the given experiment divided by the volume of the bed:

\[\rho_b = \frac{m_{\text{cat}}}{V_{\text{bed}}} = 2.1 \text{ g/4.4 mL} = 482 \frac{\text{kg}}{\text{m}^3} (A.7)\]

Where \( V_{\text{bed}} \) is the volume of the catalyst, which is measured by pouring \( m_{\text{cat}} \) of catalyst into a measuring glass and measure the volume, \( V_{\text{bed}} \).

To determine the mass transfer coefficient, \( k_c \), the Frössling correlation will be used, which is valid for laminar flows [189]:

\[Sh = 2 + 0.6 \cdot Re^{1/2} \cdot Sc^{1/3} (A.8)\]

Where \( Sh \) is Sherwood's number, \( Re \) is Reynolds number, and \( Sc \) is Schmidts number. The three dimensionless numbers are defined as:

\[Sh = \frac{k_c \cdot d_p}{D_{AB}} \quad Sc = \frac{\nu}{D_{AB}} \quad Re = \frac{U \cdot d_p}{\nu} (A.9)\]

Where \( U \) is the free-stream velocity, \( D_{AB} \) is the diffusion coefficient and \( \nu \) is the kinematic viscosity. There is no data available on neither \( D_{AB} \) nor \( \nu \). These two parameters therefore have to be estimated, which can be done by using the Lennard-Jones potentials for the relevant compounds and these are given in table A.1.

**Tab. A.1:** The Lennard-Jones potentials for the relevant compounds, where \( \sigma \) is the hard-sphere diameter and \( \frac{\epsilon}{k} \) is the characteristic energy divided by Boltzmann’s constant. The data are obtained from [250]

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \sigma ) [Å]</th>
<th>( \frac{\epsilon}{k} ) [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>3.789</td>
<td>71.4</td>
</tr>
<tr>
<td>Ethanol</td>
<td>4.53</td>
<td>362.6</td>
</tr>
<tr>
<td>Water</td>
<td>2.641</td>
<td>809.1</td>
</tr>
</tbody>
</table>

It is difficult to calculate \( D_{AB} \), because the gas which surrounds the catalyst is a mixture of different compounds. To simplify the system, it is assumed that the surrounding gas is nitrogen, as it constitutes 58 vol% of the feed gas. To estimate the value of the diffusion
coefficient of one of the products (A) into the surrounding gas (B) the Chapman and Enskog equation is used [250]:

\[ D_{AB} = \frac{0.00266 \cdot T^{3/2}}{P \cdot M_{AB}^{1/2} \cdot \sigma_{AB}^2 \cdot \Omega_D} \quad \text{[cm}^2/\text{s]} \tag{A.10} \]

Where \( T \) is the temperature, \( P \) is the pressure, and \( M_{AB} \), \( \sigma_{AB} \), and \( \Omega_D \) are given by:

\[ M_{AB} = 2 \cdot \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{-1} \tag{A.11} \]
\[ \sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \tag{A.12} \]
\[ \Omega_D = \frac{kT}{\epsilon_{AB}}^{0.156} + \frac{0.193}{\exp \left( \frac{0.4764kT}{\epsilon_{AB}} \right)} + \frac{1.03587}{\exp \left( \frac{1.530kT}{\epsilon_{AB}} \right)} + \frac{1.76474}{\exp \left( \frac{3.8941kT}{\epsilon_{AB}} \right)} \tag{A.13} \]
\[ \epsilon_{AB} = \left( \frac{\epsilon_A \cdot \epsilon_B}{k} \right)^{1/2} \tag{A.14} \]

Where \( M \) is the molar mass. Equation A.10 is valid for binary gas systems at low pressure.

To estimate the kinematic viscosity, \( \nu \), of the gas in the reactor, it is assumed that the stream consist of nitrogen. \( \nu \) can be calculated as:

\[ \nu = \frac{\eta}{\rho} \tag{A.15} \]

The viscosity can, in analogy to the diffusion coefficient, be determined by the Chapman-Enskog equation [250]:

\[ \eta = \frac{26.69 \cdot M_A \cdot T}{\sigma_{AB}^2 \cdot \Omega_v} \tag{A.16} \]

Where \( \Omega_v \) is:

\[ \Omega_v = \frac{1.16145}{\left( \frac{kT}{\epsilon_A} \right)^{0.1561}} + \frac{0.14874}{\exp \left( \frac{0.7732kT}{\epsilon_A} \right)} + \frac{2.16178}{\exp \left( \frac{2.43787kT}{\epsilon_A} \right)} \tag{A.17} \]

This equation is only valid for low pressures.

The density of nitrogen is calculated by the ideal gas law:

\[ \rho = \frac{P \cdot M_{Avg}}{R \cdot T} = \frac{101325 \text{ Pa} \cdot 0.024 \text{ kg/mol}}{8.314 \text{ m}^3/\text{Pa} \cdot \text{K} \cdot 873 \text{ K}} = 0.34 \text{ kg/m}^3 \tag{A.18} \]

A viscosity for nitrogen of 0.036 cP at 600 °C and a kinematic viscosity of 0.0011 m²/s has been estimated based on eq. A.15 to A.18.

The velocity, \( U \), is calculated from the flow measurements conducted during the experiment through the following equation:

\[ U = \frac{F_v \cdot T_0 \cdot P_0}{A_{tube} \cdot P} = \frac{1600 \text{ Nml/min} \cdot \frac{873 \text{ K}}{873 \text{ K}} \cdot 101325 \text{ Pa}}{(8.5 \text{ mm})^2 \cdot \pi} = 0.375 \text{ m/s} \tag{A.19} \]

Where \( F_v \) is the volumetric inlet flow.

\( Re \) can now be determined:

\[ Re = \frac{U \cdot d_p}{\nu} = \frac{0.375 \text{ m/s} \cdot 710 \times 10^{-6} \text{ m}}{0.0011 \text{ m}^2/\text{s}} = 2.5 \tag{A.20} \]
It is hereby seen, that the flow is laminar, because $Re$ is below 20 [251] and therefore is the Frössling correlation valid. Equation A.8 can then be used to find $k_c$ from $Sh$ as:

$$k_c = \frac{Sh \cdot D_{AB}}{d_p} = \frac{2.80 \cdot 8.14 \cdot 10^{-5}}{710 \, \mu m} = 0.35 \, m/s$$  \hfill (A.21)

The last parameter we have to determine is the concentration of A in the bulk. This is determined as the concentration of ethanol or $H_2O$ in the feed, which can be calculated by the ideal gas law using a molar fraction of 0.030 for ethanol and 0.36 for $H_2O$:

$$C_{Eth} = \frac{y_{Eth} \cdot P}{R \cdot T} = \frac{0.03 \cdot 101325 \, Pa}{8.314 \, \frac{J}{mol \cdot K} \cdot 873 \, K} = 0.42 \, mol/m^3$$  \hfill (A.22)

$$C_{H_2O} = \frac{y_{H_2O} \cdot P}{R \cdot T} = \frac{0.36 \cdot 101325 \, Pa}{8.314 \, \frac{J}{mol \cdot K} \cdot 873 \, K} = 5.0 \, mol/m^3$$  \hfill (A.23)

In table A.2 all the values for each of the calculations steps can be seen, and also the value of the left hand side of eq. A.4. It can here be seen that the criterion is met for the investigated compounds, which means that there is probably not exterior diffusion limitations.

**Tab. A.2:** Different values calculated to estimate Mears criterion

<table>
<thead>
<tr>
<th></th>
<th>Ethanol</th>
<th>$H_2O$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y_i$</td>
<td>0.030</td>
<td>0.36</td>
</tr>
<tr>
<td>$d_p$ [μm]</td>
<td>710</td>
<td>710</td>
</tr>
<tr>
<td>$M_{ab}$ [g/mol]</td>
<td>34.81</td>
<td>21.92</td>
</tr>
<tr>
<td>$F_i$ [mol/s]</td>
<td>$8 \cdot 10^{-5}$</td>
<td>$1 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>$-r_a'(obs)$ [mol/(kg·s)]</td>
<td>0.022</td>
<td>0.27</td>
</tr>
<tr>
<td>$n$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$c_{AB}$ [K]</td>
<td>160.9</td>
<td>240.4</td>
</tr>
<tr>
<td>$\sigma_{AB}$</td>
<td>4.16</td>
<td>3.22</td>
</tr>
<tr>
<td>$\Omega_D$</td>
<td>0.81</td>
<td>0.87</td>
</tr>
<tr>
<td>$D_{AB}$ [m²/s]</td>
<td>$8 \cdot 10^{-5}$</td>
<td>$1 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>$S_c$</td>
<td>1.33</td>
<td>0.67</td>
</tr>
<tr>
<td>$Sh$</td>
<td>3.03</td>
<td>2.82</td>
</tr>
<tr>
<td>$k_c$ [m/s]</td>
<td>0.35</td>
<td>0.64</td>
</tr>
<tr>
<td>Mears</td>
<td>0.03</td>
<td>0.01</td>
</tr>
</tbody>
</table>

### A.2 Weisz-Prater criterion

The reaction is not limited by external diffusion, but it can still be limited by diffusion within the pore structure of the catalyst, also called internal diffusion. In order to investigate if this is the case the Weisz-Prater criterion [189] is used. The Weisz-Prater criterion is:

$$C_{wp} = \frac{-r_a'(obs) \cdot \rho_c \cdot (d_p/2)^2}{D_e \cdot C_{As}}$$  \hfill (A.24)

Where $\rho_c$ is the density of the catalyst in $kg/m^3$, $D_e$ is the pore diffusion coefficient, and $C_{As}$ is the concentration of the investigated compound upon the surface of the catalyst. The Weisz-Prater criterion says, that if $C_{wp} \gg 1$ there is interior diffusion problems, and if $C_{wp} \ll 1$
there is not interior diffusion problems. To evaluate eq. A.24 the different parameters has to be determined like it was done for Mears criterion. 

$-r'_a(obs)$ is determined analogously eq. A.5, and $d_p$ is the catalyst particle diameter. These parameters have been determined already in the previous calculations. $C_{As}$ can be assumed to be equal to the concentration in the bulk, because it was concluded that there was not any external diffusion limitation. $C_{As}$ is therefore found from eq. A.22 or A.23.

$\rho_c$ is the density of the solid catalyst and it is calculated by:

$$\rho_c = \frac{m_{Cat}}{V_{Bed} - \phi_{bed} \cdot V_{Bed}} = 778 \text{ kg/m}^3$$

(A.25)

Where $\phi_{Bed}$ is the porosity of the bed which is assumed to be 0.38, which an average value for spheres poured into bed [252].

To determine the pore volume diffusion, the procedures described in [253] will be used, where it is calculated on the basis of two diffusion coefficients: $D_K$ and $D_{AB}$. Where $D_{AB}$ is the same diffusion coefficient as the one calculated from eq. A.10 and listed in table A.2.

The Knudsen diffusivity, $D_K$, is an estimation of how large the resistance the molecules meet inside the catalyst pores, and it is given by:

$$D_K = 3.068 \cdot a \cdot \left(\frac{T}{M}\right)^{1/2} \text{ [m/s]}$$

(A.26)

Where $a$ [m] is the radius of the pores inside the catalyst. The exact pore size have not been determined but it is assumed to 44 nm, which is estimated based on a pore volume (1.0 mL/g), surface area (90 m$^2$/g), and assuming that the pores are tubes.

The effective diffusion coefficient can now be calculated as:

$$D_{ABe} = \left(\frac{1}{D_K} + \frac{1}{D_{AB}}\right)^{-1}$$

(A.27)

$$D_e = \frac{D_{ABe} \cdot \phi_p \cdot \sigma_c}{\tau}$$

(A.28)

Where $\phi_p$ is the porosity of the catalyst, $\sigma_c$ is the constriction factor, and $\tau$ is the tortuosity. Equation A.28 is introduced to correct the diffusion coefficient calculated from eq. A.27, because the diffusion is taking place inside a pellet. This is done with $\phi_p$, $\sigma_c$ and $\tau$, which have the respective values of 0.77, 0.8, and 2.5. The porosity is calculated as:

$$\phi_p = \frac{V_{Pore}}{V_{Cat}} = \frac{V_{Pore}}{V_{Bed} - V_{Void}} = - \frac{2.1 \text{ cm}^3}{4.4 - 1.73 \text{ cm}^3} = 0.77$$

(A.29)

All the parameters needed to calculate $C_{wp}$ from eq. A.24 are now determined. In table A.3 all the calculated coefficients needed for the calculations can be seen. The Weisz-Prater criterion is around one for ethanol and particles between 425 and 710 $\mu$m indicated that there might not be internal diffusion problems for ethanol, while for water $C_{wp}$ is well below one and diffusion of water should not cause problems.

The particle diameter can be decreased in order to minimize diffusion problems and in table A.4 $C_{wp}$ can be seen for several different particle diameters. As expected the Weisz-Prater decreases with decreasing particle sizes. A catalyst fraction consisting of 125-250 $\mu$m or 250-425 $\mu$m particles should have little or no internal diffusion limitations.

---

1 Equation A.27 is obtained from [253] and A.28 is obtained from [189]
Appendix A. Diffusion limitations

Tab. A.3: Different values calculated to estimate the Weisz-Prater criterion.

<table>
<thead>
<tr>
<th></th>
<th>Ethanol</th>
<th>H_2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>D_k ([m^2/s])</td>
<td>3.9 \cdot 10^{-5}</td>
<td>4.9 \cdot 10^{-5}</td>
</tr>
<tr>
<td>D_e ([m^2/s])</td>
<td>6.5 \cdot 10^{-6}</td>
<td>9.3 \cdot 10^{-6}</td>
</tr>
<tr>
<td>C_{wp} (710 , \mu m)</td>
<td>1.25</td>
<td>0.15</td>
</tr>
<tr>
<td>C_{wp} (425 , \mu m)</td>
<td>0.45</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Tab. A.4: Values of Weisz-Prater criterion at different particle sizes.

<table>
<thead>
<tr>
<th>Particle diameter ([\mu m])</th>
<th>C_{wp}</th>
</tr>
</thead>
<tbody>
<tr>
<td>710</td>
<td>1.25</td>
</tr>
<tr>
<td>425</td>
<td>0.45</td>
</tr>
<tr>
<td>250</td>
<td>0.16</td>
</tr>
<tr>
<td>125</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Two size fractions, 250-425 \(\mu m\) and 425-710 \(\mu m\), were tested in a standard experiment at 600 °C for 4 h to determine if diffusion was limiting for performance of the catalyst. The average conversion, yield of methane, and carbon deposition are shown in table A.5. Here it can be seen that there only are small differences between the different fractions and therefore diffusion do not seem to be limiting.

A.3 Temperature gradients

Steam reforming reactions are highly endothermic and temperature gradients between the surrounding gas and the particles might occur. Mear has also proposed a criterion for whether or not there is a significant temperature difference particle and gas [189]. The criterion is:

\[
\left| \frac{-r'_a(obr) \cdot \rho_b \cdot d_p \cdot (-\Delta H_R)}{h \cdot T^2 \cdot R} \right| < 0.15
\]  
(A.30)

Where \(-\Delta H_r\) is the reaction enthalpy, which is 210 kJ/mole, \(E\) is the activation energy, which is assumed to be 82.7 kJ/mole, and \(h\) is the heat transfer coefficient. \(-\Delta H_r\) is calculated for reaction 1.4 from the formation enthalpies found in ref. [254]. The activation energy is found in ref. [104].

Tab. A.5: Conversion, yield of methane, and carbon deposition in SR of ethanol at 600 °C for two size fractions of Ni/MgAl_2O_4.

<table>
<thead>
<tr>
<th>Fraction ([\mu m])</th>
<th>Conversion [%]</th>
<th>CH_4-sel. [%]</th>
<th>Carbon deposition [mole% of feed]</th>
</tr>
</thead>
<tbody>
<tr>
<td>250-425</td>
<td>79.5</td>
<td>5.2</td>
<td>0.44</td>
</tr>
<tr>
<td>425-710</td>
<td>79.1</td>
<td>6.3</td>
<td>0.53</td>
</tr>
</tbody>
</table>
The heat transfer coefficient, $h$, can be estimated from Nusselt number, which is given by:

$$Nu = \frac{h \cdot d_p}{k_t}$$  \hspace{1cm} (A.31)

Where $k_t$ is the thermal conductivity of the gas, which is estimated to be 0.061 $W/(K \cdot m)$.

Nusselt number, $Nu$, can be estimated by the following correlation [189]:

$$Nu = 2 + 0.6 \cdot Re^{1/2} \cdot Pr^{1/3}$$ \hspace{1cm} (A.32)

Prandtl number, $Pr$, is defined as:

$$Pr = \frac{\nu \cdot C_p}{k_t}$$ \hspace{1cm} (A.33)

The kinematic viscosity, $\nu$, is estimated by eq. A.16.

The values for Mears criteria for temperature gradients along with selected calculated values are shown in table A.6. Here it can be that temperature difference is negligible as the values are well below 0.15.

**Tab. A.6: Different values calculated to estimate Mears criterion for temperature gradients.**

<table>
<thead>
<tr>
<th></th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Pr$</td>
<td>0.062</td>
</tr>
<tr>
<td>$Nu$</td>
<td>2.56</td>
</tr>
<tr>
<td>$h$</td>
<td>$[kJ/(m^2 \cdot s \cdot K)]$ 0.20</td>
</tr>
<tr>
<td>Mears</td>
<td>$1.9 \cdot 10^{-4}$</td>
</tr>
</tbody>
</table>

Another way to estimate the temperature gradients between particles and the surrounding gas is by a simple energy balance:

$$q = h \cdot A \cdot \Delta T$$ \hspace{1cm} (A.34)

Where $A$ is the surface area of the particle. The energy needed can be calculated as:

$$q = \Delta H_r \cdot r_a' \cdot V_p$$ \hspace{1cm} (A.35)

Where $V_p$ is the particle volume. Eq. A.34 and A.35 can be combined to:

$$\Delta T = \frac{\Delta H_r \cdot r_a' \cdot V_p}{A \cdot h}$$ \hspace{1cm} (A.36)

$$= \frac{210 \text{ $kJ/mole$} \cdot 9.70 \text{ $mole/(m^3 \cdot s)$} \cdot 1.87 \cdot 10^{-10} \text{ $m^3$}}{1.58 \cdot 10^{-6} \text{ $m^2 \cdot 0.222 \text{ $kJ/(m^2 \cdot s \cdot K)$}} = 1.08 \text{ $K$}}$$

Based on the energy balance is also appears the temperature differences between gas and particles should be small. A drop of up to 5-15 $K$ in temperature is observed when the SR reactions is initiated, depending on catalyst and temperature. However, the temperature remains constant after the initial temperature drop and it is this value which is reported.
### Tab. A.7: Right hand side of eq. A.37 at different degrees of conversion for particles with a diameter of 425 µm. First order reaction assumed.

<table>
<thead>
<tr>
<th>Conversion [%]</th>
<th>0.1</th>
<th>0.5</th>
<th>0.9</th>
<th>0.95</th>
<th>0.99</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\frac{8n}{P_e} \cdot \ln \left(\frac{1}{1-X}\right))</td>
<td>4</td>
<td>26</td>
<td>87</td>
<td>113</td>
<td>173</td>
</tr>
</tbody>
</table>

### A.4 Reactor geometry

The reactor was a quartz tube with an inner diameter of 17 mm and the bed was roughly 4 mm high. The catalysts were crushed to 425-710 µm or 250-425 µm fractions. The ratio of bed diameter to particle diameter is recommended to be over 10 to achieve plug flow and it is 24 for 710 µm particles and 40 for 425 µm particles [255]. The ratio between height of the bed and particle diameter (\(H/d_p\)) is also determining for the possibility to obtain plug flow. It has been shown that [255]:

\[
\frac{H}{d_p} > \frac{8 \cdot n}{P_e} \cdot \ln \left(\frac{1}{1-X}\right)
\]

in order to obtain plug flow. Where \(H\) is the height of the bed, \(n\) is the reaction order, and \(P_e\) is the particle Peclet number, defined as:

\[
P_e = \frac{d_p \cdot P_c}{L_b}
\]

Where \(d_p\) is the particle size and \(L_b\) is the bed length. \(Pe\) is assumed be 2 (see further below). The right hand side of eq. A.37 at different degrees of conversion can be seen in table A.7. \(\frac{H}{d_p}\) is 7.0 for a particle size of 567 µm (average of 710 and 425 µm) and 11.8 for 338 µm particles (average of 250 and 425 µm). It can be seen that the criteria for plug flow is not met. Therefore it appears that plug flow is not fully achieved for this reactor geometry.

### A.5 Dispersion

The effective dispersion coefficient, \(D_a\), can estimated from figure 14-12 in Fogler [189]. This figure shows \(\frac{D_a}{U \cdot d_p}\) as function of Reynolds number. \(\frac{D_a}{U \cdot d_p}\) at \(Re = 1.5\) is approx. 0.5 and based on this \(D_a = 1 \cdot 10^{-4} m^2/s\). The Peclet number, which describes the ratio between transport by convection and transport by diffusion or dispersion, can then be calculated by:

\[
P_e = \frac{U \cdot d_p}{\epsilon \cdot D_a} = 2
\]

This shows transport by convection is more important than transport by diffusion or dispersion.

The dispersion model, first published by Danckwerts, can be used to predict the rate constant, \(k\), if the Peclet number is known. The conversion as function of \(Pe_r\) for the dispersion is:

\[
X = \frac{4 \cdot q \cdot \exp(Pe_r/2)}{(1 + q)^2 \cdot \exp(Pe_r \cdot q/2) - (1 - q)^2 \cdot \exp(-Pe_r \cdot q/2)}
\]

where \(q = \sqrt{1 + 4 \cdot Da/Pe_r}\) and \(Da = \tau \cdot k\).
**Tab. A.8:** Rate constants calculated from the dispersion model (eq. A.40) at different temperatures and degrees of conversion.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Conversion [%]</th>
<th>Rate constant [s(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>398</td>
<td>9</td>
<td>4.7</td>
</tr>
<tr>
<td>500</td>
<td>35</td>
<td>22.0</td>
</tr>
<tr>
<td>593</td>
<td>85</td>
<td>120.1</td>
</tr>
<tr>
<td>697</td>
<td>95</td>
<td>230.4</td>
</tr>
</tbody>
</table>

The Peclet number, \(Pe_r\), used in eq. A.40 is calculated by:

\[
Pe_r = \frac{U \cdot L}{D_a} = 14.5
\]  

(A.42)

Where \(L\) is the height of catalytic bed. The inverse of \(Pe_r\) can be used to predict the amount of dispersion in the reactor and based on fig. 14-13 in ref. [189], it seems that the dispersion in the reactor is low.

Based on eq. A.40 values for of \(k\) were calculated using the measured conversion in the temperature dependence experiment. The values of \(k\), \(X\), and the corresponding temperature are shown in tab. A.8.

The reaction rate for steam reforming of ethanol can be calculated by:

\[
-r_{Eth} = k \cdot C_{eth} \left[ \frac{mole}{m^3 \cdot s} \right]
\]

(A.43)

It is assumed that the reaction is first order with respect to ethanol.

It is possible to calculate the conversion based on a CSTR or a PFR design equation and the rate constants estimated from eq. A.40 and then compared these values with the measured values to see if the reactor behaves either as a PFR or a CSTR. The design equations used are:

CSTR:

\[
V = \frac{F_{A0} \cdot X}{-r_A}
\]

(A.44)

PFR:

\[
\frac{dX}{dW} = -\frac{r_A'}{F_{A0}}
\]

(A.45)

The conversion for a CSTR can be calculated from:

\[
X_{CSTR} = \frac{\tau \cdot k}{1 + \tau \cdot k}
\]

(A.46)

For a PFR, the conversion is calculated by:

\[
X_{PFR} = 1 - \exp(-\tau \cdot k)
\]

(A.47)

A constant volume is assumed in the derivation of eq. A.47. The conversion has also been calculated assuming an increase in volume as more molecules are formed than consumed and it is denoted \(X_{PFRm}\). The general design equation for a PFR has been used along with the following expression for the reaction rate:

\[
r = k \cdot C \cdot \frac{1 - X}{1 + X}
\]

(A.48)
The design equation is solved numerically using Maple 17.

The conversion as function of temperature for the measured and the calculated conversion are shown in fig. A.1. Here it can be seen that both a CSTR and PFR model describes the measured conversion quite well. However, it appears that PFR model has a better fit as the deviation from the measured values is quite low at all temperatures.

A.6 Conclusions

The calculations of Mears and Weisz-Prater criteria shown that external and internal diffusion were negligible and that temperature gradients between gas and particles are negligible as well. The reactor geometry did not meet the criteria for achieving plug flow but, based on dispersion, but it appears that the reactor can be modeled as plug flow reactor.
Appendix B

ESTIMATION OF AFFINITY FOR CARBON DEPOSITION

Carbon deposition in the SR of CH$_4$ can occur through methane decomposition, CO decomposition, or the Boudouard reaction and the two latter are mainly a problem at low temperatures, while the former occurs at high temperatures. Based on the equilibrium constants for these reactions as well as a gas composition it is possible to estimate if there is a risk of forming carbon deposits from any of three reactions. The theory behind the estimation is described in ref. [42] and it is called the principle of equilibrated gas or the principle of actual gas, depending on whether it is the equilibrium or the actual gas phase composition, which is used in the calculations. The affinity, $\Delta G_C$, is calculated and if $\Delta G_C$ is negative then there is no affinity for carbon formation through the investigated reaction. The method is developed for SR of methane, and not well suited for the SR of higher hydrocarbons as the decomposition of these compounds are irreversible and not taken into account. The affinity calculations will be used to estimate the affinity for carbon formation through methane decomposition, CO decomposition, or the Boudouard reaction, and determine if these can contribute to the observed carbon formation.

The three carbon forming reactions are:

- **Boudouard:** $2\text{CO}\rightleftharpoons \text{C}_s + \text{CO}_2$ (B.1)
- **CO decomposition:** $\text{CO} + \text{H}_2\rightleftharpoons \text{C}_s + \text{H}_2\text{O}$ (B.2)
- **CH$_4$ decomposition:** $\text{CH}_4\rightleftharpoons \text{C}_s + 2\text{H}_2$ (B.3)

$\Delta G_C$ for methane decomposition is calculated by:

$$\Delta G_C = R \cdot T \ln \left[ \frac{K_{eq}}{Q} \right]$$ (B.5)

Where $K$ is the equilibrium constant and $Q$ is reaction quotient, which can be calculated from the actual or equilibrated gas. For the methane decomposition eq. B.5 translates to:

$$\Delta G_C = R \cdot T \ln \left[ K_{eq} \cdot \frac{p_{\text{CH}_4}}{p_{\text{H}_2}^2} \right]$$ (B.6)

The equilibrium constants for methane decomposition, CO decomposition, and the Boudouard reaction used for estimations of affinity for carbon formation is calculated by:

$$\ln(K_{eq}) = C_1 \cdot \ln(T) + \frac{C_2}{T} + C_3 + C_4 \cdot T + C_5 \cdot T^2 + C_6 \cdot T^3$$ (B.7)

The coefficients, $C_1 - C_6$, for the different reactions are listed in table B.1. The are two equilibrium constants for methane decomposition, where one reaction assumes carbon formation as graphite and one assuming carbon formation as whisker, $C_W$. The equilibrium constant for carbon formation as whiskers compared to graphite is higher, because it is more energy demanding to form whiskers compared with graphite [42].
Appendix B. Estimation of affinity for carbon deposition

(a) SR of ethanol over Ni/MgAl$_2$O$_4$

(b) SR of ethanol over Ni/Ni/Ce$_{0.6}$Zr$_{0.4}$O$_2$

**Fig. B.1:** Affinity to form carbon from a actual gas composition in SR of ethanol at S/C-ratio of 6.

**Tab. B.1:** Coefficients used in the calculations of equilibrium constant by eq. B.7 [42]. $C_W$ refers carbon deposition as whiskers.

<table>
<thead>
<tr>
<th></th>
<th>CH$_4$ ↔ C + 2H$_2$</th>
<th>CH$_4$ ↔ C$_W$ + 2H$_2$</th>
<th>2CO ↔ C + CO$_2$</th>
<th>CO + H$_2$ ↔ C + H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$</td>
<td>5.291666</td>
<td>0</td>
<td>-3.635623</td>
<td>-3.319458</td>
</tr>
<tr>
<td>$C_2$</td>
<td>-7610.846</td>
<td>-10779</td>
<td>20053.61</td>
<td>15037.16</td>
</tr>
<tr>
<td>$C_3$</td>
<td>-24.48443</td>
<td>12.68</td>
<td>0.3674049</td>
<td>4.471772</td>
</tr>
<tr>
<td>$C_4$</td>
<td>-0.002023153</td>
<td></td>
<td>0.005096533</td>
<td>0.00295691</td>
</tr>
<tr>
<td>$C_5$</td>
<td>-1.59352·$10^{-7}$</td>
<td></td>
<td>-1.16153·$10^{-6}$</td>
<td>-5.57093·$10^{-7}$</td>
</tr>
<tr>
<td>$C_6$</td>
<td>7.79721·$10^{-11}$</td>
<td></td>
<td>1.33663·$10^{-10}$</td>
<td>5.78377·$10^{-11}$</td>
</tr>
</tbody>
</table>

The affinity to form carbon as function of temperature is estimated for a real and equilibrium gas in the SR of ethanol at S/C-ratio of 6. The equilibrium gas does not show affinity for forming carbon through the investigated reactions, but as indicated in fig. B.1 the actual gas composition does show affinity to form carbon through methane decomposition and the Boudouard reaction at 400 °C.

There was no affinity to form carbon from an equilibrium gas phase composition in SR of ethanol at S/C-ratios between 1.5 and 8, O/C-ratios between 0 and 1.2 at S/C=6, or H/C-ratios between 0 and 2.4 at S/C=6 by methane decomposition, CO decomposition, or the Boudouard reaction. The carbon affinity for the actual gas phase composition in the experiments where the S/C-, O/C-, and H/C-ratios are varied can be seen in fig. B.2. There is only an affinity to form carbon through methane decomposition at a S/C-ratio of 1.6.
Fig. B.2: Affinity to form carbon from the actual gas compositions in SR of ethanol over Ni/MgAl₂O₄ at 600 °C.