

Production of 1,3-butadiene from ethanol using zeolite-based catalysts

Gao, Kai

Publication date: 2022

Document Version Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA): Gao, K. (2022). *Production of 1,3-butadiene from ethanol using zeolite-based catalysts.* DTU Chemistry.

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.

- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Production of 1,3-butadiene from ethanol

using zeolite-based catalysts

Ph.D. dissertation 2022 Kai Gao (高凯)



Supervisors:

Professor Søren Kegnæs Senior Researcher Jerrik Mielby

Department of Chemistry, Technical University of Denmark

Preface

This dissertation is submitted to the Technical University of Denmark (DTU) in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the discipline of Chemistry.

The research was carried out at the Centre for Catalysis and Sustainable Chemistry (CSC) in DTU Chemistry from September 1st, 2018 to February 28th, 2022 including a 6-month extension due to the pandemic of COVID-19. This work was performed under the supervision of Professor Søren Kegnæs and co-supervision Senior Researcher Dr. Jerrik Mielby. The project aimed to investigate the application of zeolite materials in the conversion of biomass-derived substrates such as ethanol and acetaldehyde to high-value-added bulk chemicals like 1,3-butadiene.

This dissertation consists of three projects described in six chapters, where Chapter 1 gives the background knowledge about catalysis and zeolite materials that are relevant for the dissertation. Chapter 2 provides the characterization techniques used for the physical and chemical properties of the related zeolite catalysts. Chapter 3 presents the project about ethanol dehydrogenation to acetaldehyde over Zn-containing zeolites. Chapter 4 describes the preparation of Zn and Y containing zeolites investigated in the direct conversion of ethanol to 1,3-butadiene tandem process. Chapter 5 demonstrates the preparation of Y supported on ZSM-5 zeolites as catalysts for the production of 1,3-butadiene from ethanol-acetaldehyde mixtures. Chapter 6 offers the conclusions of major research outputs and prospects.

Acknowledgment

First of all, I would like to express my sincere gratitude to my supervisor Professor Søren Kegnæs and co-supervisor Senior Researcher Dr. Jerrik Mielby for their countless supervision and immense knowledge in chemistry. I want to thank Professor Søren Kegnæs for letting me join his research group as a Ph.D. student. He showed great consideration to me when I came to Denmark as a freshman. Søren's friendly attitude, fruitful guidance, and endless optimism made it a pleasure to work in this delightful group. I was so lucky to be a Ph.D. student under his kind supervision. Søren always showed his encouragement to me when my research was stuck at the bottleneck. I never forgot that he helped me to figure out the problem of my experimental apparatus at night when I started the research project in November 2018. I am greatly thankful to my co-supervisor Senior Researcher Dr. Jerrik Mielby for his super-smart help both in chemistry and engineering work. He has been a mentor to give me strong support with various and challenging tasks during my entire Ph.D. studies. I really appreciate the time and knowledge he has put into my research. The smile he always had on his face was often a silent reminder to me to be enthusiastic about chemistry and optimistic about life.

I am grateful to my group members David Benjamin Christensen, Simone Louise Zacho, Kristoffer Hauberg Møller, Mikkel Burggraaf Buendia, Farnoosh Goodarzi, and Rouzana Pulikkal Thumbayil that they created a friendly working atmosphere. We had discussions about research results, also life in general both in the laboratories and office. A special thanks to Dr. Benjamin B. Christensen for his useful suggestions and comments on my research project. I also want to thank my officemates Mikkel Kock Larsen, Dimitra Iltsiou, Rasmus Lykke Mortensen, Kachaporn Saenluang, and Qi Gao for their help with electron microscopy and pleasant time in the office. Mikkel K. Larsen is extra appreciated for translating English abstract to Danish language, which is out of my ability. Their enthusiasm for science and life cut a deep impression in my memory, and I learned from it the strength of an optimistic role model. Wenting Fang and Junjie Kang are also acknowledged for their kindly help with TPD measurements and ultrapure water. My good friends Ping Zhu, Runtian Qie, Faliu Yang, Yulong Miao deserve special thanks for their continuous support not only in the research discussion but also in life support during my entire Ph.D. study time.

I would like to thank the CSC group in DTU Chemistry for the friendly working environment and help with all instruments, especially Dr. Leonard Schill and Dr. Mariusz Kubus for their help with plenty of tasks of the apparatus. The people from DTU Chemistry give me a great deal of assistance to make my research work convenient and efficiently such as the Reception, Buildingcenter, and Workshop teams.

Finally, I would like to thank my parents for their endless support for my study in Denmark, and they are always confident absolutely in me. China Scholarship Council is greatly appreciated for the financial support during my stay in Denmark.

Kai Gao (高凯), 2800 Kgs. Lyngby, Copenhagen, Denmark, February 2022

Abstract

The strategy of Carbon Neutrality was widely accepted by many countries around the world due to contemporary climate change issues including global warming. It is urgent to switch traditional fossil fuels to clean energy as alternatives like wind, solar, and biomass to make the world sustainable. Biomass-derived low carbon resources have a wide range of applications in the production of basic chemicals like ethanol, which can be generated from sugarcane through fermentation. However, the utilization of ethanol to produce downstream value-added chemicals need to develop novel technologies. Therefore, the aim of this thesis focuses on the development of heterogeneous catalysts in the application of ethanol conversion.

Zeolite-supported metal materials were investigated as heterogeneous catalysts in the process of ethanol conversion process due to their high catalytic activity and thermal stability of the structures. The thesis described the research about the conversion of ethanol and the formation of 1,3-butadiene. There are four key consecutive steps in the process of ethanol conversion to 1,3-butadiene: (1) ethanol dehydrogenation to acetaldehyde; (2) aldol condensation to acetaldol, and further dehydration to crotonaldehyde; (3) crotonaldehyde to crotyl alcohol through Meerwein–Ponndorf–Verley (MPV) reaction; (4) crotyl alcohol dehydration to 1,3-butadiene. The zeolite catalysts involved in this thesis were MFI and BEA topologies, in which Zn and/or Y acted as the metallic active sites for the process of the tandem reaction.

Chapter 1 provides fundamental knowledge about catalysis, especially the concept of heterogeneous catalysis. Zeolites are of great importance in the field of heterogeneous catalysis and metal-containing zeolites are described as well.

Chapter 2 introduces characterization techniques related to the zeolite catalysts analysis in this thesis such as N₂ physisorption and X-ray analysis to explore the chemical and physical properties of the synthesized zeolite catalysts.

Chapter 3 demonstrates the process of ethanol dehydrogenation to acetaldehyde over Zncontaining zeolites over Zn-containing MFI zeolites such as Zn/Silicalite-1, Zn/Na-ZSM-5, Zn/H-ZSM-5, and Zn incorporation framework MFI zeolite. The catalytic activity and selectivity of acetaldehyde depend on the chemical composition of the Zn metallic sites. The optimum catalyst comprises 5 wt.% Zn supported on the Silicalite-1 zeolite and results in conversion of 65.2% and selectivity of 94.5%. Chapter 4 investigates the direct conversion of ethanol to 1,3-butadiene over Zn and Y containing zeolite catalysts. The monometallic Zn or Y exhibited very little catalytic activity towards the selectivity of 1,3-butadiene. Several Zn-containing catalysts like Zn/Na-ZSM-5 and Zn/Silicalite-1 demonstrated excellent production of acetaldehyde but terrible selectivity of 1,3-butadiene due to the absence of active sites for aldol condensation reaction. However, the Y containing zeolite catalysts did not show a sufficient yield of 1,3-butadiene due to the lack of acetaldehyde as an intermediate. The bimetallic ZnY/Na-ZSM-5 zeolite catalyst facilitated the production of 1,3-butadiene with a selectivity of 12.4%. The layer by layer arrangement of Zn/Na-ZSM-5 and Y/Na-ZSM-5 zeolites improved the production of 1,3-butadiene with the optimum selectivity of 39%, which indicated the critical role of the distance between Zn and Y active sites.

Chapter 5 describes the conversion of ethanol and acetaldehyde mixtures into the 1,3butadiene process over Y-supported on ZSM-5 zeolite catalysts. The effects of counter ions in the zeolite on the production of 1,3-butadiene are also investigated. The Y/K-ZSM-5 zeolite was the most effective catalyst and resulted in the production of 1,3-butadiene with the maximum selectivity of 65% at 450°C using a volume ratio of ethanol to acetaldehyde to be 1.5:1. The selectivity of the other catalysts decreased in the order Y/K-ZSM-5 > Y/Na-ZSM-5 \approx Y/Li-ZSM-5 >> Y/H-ZSM-5. The acidity of zeolite catalyst plays a critical role in the 1,3butadiene production from ethanol and acetaldehyde mixtures. Furthermore, we show that the ethanol to acetaldehyde ratio has a significant effect on the conversion and selectivity.

Chapter 6 summarizes the major conclusions about all aforementioned projects and gives prospective suggestions to improve the catalytic activity and selectivity regards the 1,3-butadiene production from ethanol and acetaldehyde conversion.

Resumé

Strategien for kulstofneutralitet er accepteret vidt og bredt af mange_lande i verdenen grundet klimaforandringer, heriblandt global opvarmning. Det haster at skifte fra fossile brændstoffer til vedvarende energiformer, heriblandt vindenergi, solenergi og biomasse, for at sikre en bæredygtig verden. Biomasse-deriverede ressourcer med lavt kulstoftal har en bred række applikationer i produktionen af basale kemikalier såsom ætanol, som kan opnås fra sukkerrør via gæring. Ætanol kan herefter bruges til at lave værdifulde downstream kemikalier, dog skal nyskabende teknologier udvikles til formålet. Målet for denne afhandling fokuserer derfor på udviklingen af heterogene katalysatorer til omdannelse af ætanol.

Zeolit-båret metal materialer har været undersøgt som heterogene katalysatorer i ætanolkonversionsprocessen grundet deres høje katalytiske aktivitet og termiske stabile strukturer. Denne afhandling beskriver forskningen omhandlende omdannelsen af ætanol og formationen af 1,3-butadiene. For at omdanne ætanol til 1,3-butadiene skal ætanol gennemgå fire nøglereaktioner: (1) ætanol dehydrogenering til ethanal; (2) aldolkondensation 3-hydroxybutanal og yderligere dehydrering til crotonaldehyd; (3) crotonaldehyd til crotonylalkohol gennem Meerwein-Ponndorf-Verley (MPV) reaction; (4) dehydrering af crotonylalkohol til 1,3-butadiene. Zeolitkatalysatorerne involveret i denne afhandling var MFI og BEA topologier, hvor Zn og/eller Y er de metallisk aktive positioner i omdannelsen af ætanol til 1,3-butadiene.

Kapitel et omhandler fundamental viden om katalyse, specielt omhandlende konceptet om heterogen katalyse. Zeolitter er vigtige indenfor heterogen katalyse, og zeolitterne indeholdende metaller er ydermere beskrevet heri.

Kapitel to introducerer de forskellige karakteriseringsteknikker som relaterer sig til zeolitkatalysatorers analyse i denne afhandling. Disse teknikker inkluderer N₂-physisiorption og røntgenanalyse til at undersøge de kemiske såvel som fysiske egenskaber af de syntetiserede zeolit-baseret katalysatorer.

Kapitel tre demonstrerer processen af ætanol dehydrogenering til ethanal over en Znindeholdene zeolitter, såsom Zn/silicalite-1, Zn/Na-ZSM-5, Zn/H-ZSM-5 og Zn inkorporeret i strukturen af MFI-zeolitter. Den katalytiske aktivitet og selektivitet af ethanal afhænger af den kemiske komposition af Zn-metalsiderne. Den optimale katalysator består af 5 vægtprocent Zn båret på Silicalite-1 zeolitten og resulterer i en konversion på 65,2% med en selektivitet på 94,5%. Kapitel fire undersøger den direkte konversion af ætanol til 1,3-butadiene over Zn og Y indeholdende zeolit katalysatorer. Den monometalliske Zn eller Y viste lav katalytisk aktivitet og lav selektivitet af 1,3-butadiene. Flere Zn-indeholdende katalysatorer såsom Zn/Na-ZSM-5 og Zn/Silicalite-1 demonstrerede fortræffelige egenskaber i produktionen af ethanal, dog ringe selektivitet af 1,3-butadiene grundet fraværet af aktive sider for aldolkondesationreaktionen. Zeolitten som indeholder Y viste ikke et tilstrækkeligt udbytte af 1,3-butadiene grundet manglen på ethanal som intermediat. Den bimetalliske ZnY/Na-ZSM-5 zeolitkatalysator faciliterede produktionen af 1,3-butadiene med en selektivitet på 12,4%. Lag-på-lag sammensætningen af Zn/Na-ZSM-5 og Y/Na-ZSM-5 zeolitterne forbedrede produktionen af 1,3-butadiene og opnåede selektivitet op til 39%, hvilket var en indikerede at, distancerne mellem de aktive placeringer af Zn og Y er kritisk.

Kapitel fem beskriver omdannelse af ætanol og ethanal blandinger til 1,3-butadiene over Ybåret på ZSM-5 zeolit katalysatorer. Effekterne af modioner i zeolitten i produktionen af 1,3butadiene er også undersøgt. Y/K-ZSM-5 zeolitten var den mest effektive katalysator som resulterede i 65% selektivitet af 1,3-butadiene, ved 450°C og et rumfangsforhold af 1,5:1 ætanol til ethanal. Selektiviteten af de andre katalysatorer faldt i rangeringen af Y/K-ZSM- $5>Y/Na-ZSM-5 \approx Y/Li-ZSM-5 >> Y/H-ZSM-5$. Surheden af zeolitkatalysatoren spiller en kritisk rolle i 1,3-butadiene produktionen fra ætanol og ethanal blandingen. Ydermere viser vi at ætanol til ethanal forholdet har en signifikant effekt på konversionen og selektiviteten..

Kapitel seks opsummerer hovedkonklusionerne om alle førnævnte projekter og giver fremadrettede forslag til at forbedre den katalytiske aktivitet og selektivitet vedrørende 1,3butadiene produktionen fra ætanol og ethanal konversionen.

Preface	i
Acknowledgmenti	iii
Abstract	.v
Resumév	/ii
1 Introduction	.1
1.1 Background of catalysis	.2
1.1.1 Homogeneous catalysts	.4
1.1.2 Heterogeneous catalysts	.6
1.2 Zeolites	.8
1.2.1 Zeolites structure	.9
1.2.2 Zeolite synthesis1	10
1.2.3 Zeolite shape selectivity1	12
1.2.4 Mesoporous zeolite and zeolite modifications1	13
1.2.5 Metal species in zeolites1	14
1.3 Summary1	16
1.4 Aim and outline of the dissertation1	16
1.5 References 1	18
2 Characterization techniques2	23
2.1 Physisorption measurement2	24
2.2 Scanning electron microscopy (SEM)2	28
2.3 Transmission electron microscopy (TEM)	30
2.4 X-ray diffraction (XRD)	32
2.5 X-ray photoelectron spectroscopy (XPS)	33
2.6 Temperature programmed desorption (TPD)	34
2.7 Thermal gravimetric analysis (TGA)	35
2.8 References	36
3 Ethanol conversion to acetaldehyde	39

Contents

3.1 Introduction	40
3.1.1 Ethylene oxidation	40
3.1.2 Acetylene hydration	40
3.1.3 Acetic acid reduction	41
3.1.4 Ethane oxidation	42
3.1.5 Ethanol oxidation	42
3.1.6 Ethanol dehydrogenation	
3.1.7 Support	
3.2 Experimental	50
3.2.1 Materials	50
3.2.2 Zeolite synthesis	50
3.2.3 Zn-containing zeolite catalyst synthesis	52
3.2.4 Catalyst characterization	52
3.2.5 Catalyst test	52
3.3 Results and discussion	55
3.3.1 Characterisation	55
3.3.2 Catalytic performance	59
3.3.3 Zeolite support modification via dealumination	62
3.4 Conclusions	63
3.5 References	
4 Ethanol conversion into 1,3-butadiene	71
4.1 Introduction	72
4.1.1 Metal oxides composite catalysts	74
4.1.2 Zeolite-support materials	75
4.2 Experimental section	
4.3 Results and discussions	79
4.3.1 Zn-containing catalysts in the Lebedev process	79
4.3.2 Y-containing catalysts in the Lebedev process	

4.3.3 Zn and Y-containing zeolite catalytic systems	84
4.4 Conclusions	87
4.5 References	
5 Ethanol/acetaldehyde conversion into 1,3-butadiene	95
5.1 Introduction	96
5.2 Materials and methods	98
5.2.1 Materials	98
5.2.2 Catalyst synthesis	98
5.2.3 Catalysts characterization	99
5.2.4 Catalytic activity measurements	100
5.3 Results and discussion	100
5.3.1 Characterisation results	100
5.3.2 Catalyst evaluation	
5.3.3 TGA of coke deposition on the spent Y/K-ZSM-5 zeolite catalyst.	
5.3.4 Stability and regeneration test	112
5.4 Conclusions	113
5.5 References	114
6 Conclusions and perspective	117
Appendix A Supporting information of Chapter 5	
Appendix B Phenol hydrogenation to cyclohexanol	120
Appendix C Disseminations	122
Appendix D Co-author statement	123

Chapter 1 Introduction

This chapter focuses on the general background on catalysis and its applications in chemical reactions. A brief introduction on both homogeneous and heterogeneous catalysts is described in this chapter. Furthermore, the use of zeolites as supporting materials is worth investigating owing to their excellent property of selective adsorption-desorption and thermal stability. The active metal sites are equally important for chemical reactions. Hence, the combination of zeolite support and active metal sites has also been introduced in this chapter.

1.1 Background of catalysis

Chemistry is the field of science where existing molecules can be converted into new molecules via electrons migration. Some chemical reactions take place under harsh conditions, such as high temperature, toxic to the environment, and high pressure, which are unsustainable and need to be urgently altered for a green and environmentally harmonious society.

In 1998, Paul Anastas and John Warner proposed the concept of 'The Twelve Principles of Green Chemistry' as shown in Figure 1-1,¹ which can be used as a guideline for the design of a reaction process to meet the requirements of sustainability and environmentally friendliness.



Figure 1-1. Twelve principles of green chemistry. Adapted from the literature.¹

The twelve principles of green chemistry and their detailed explanations are described as shown below:

- It is difficult and energy-consuming to remove the waste and purify the co-products formed during a reaction. Therefore, the reaction should be designed to reduce or eliminate the production of waste.
- 2. The optimum reaction route with the highest atom efficiency is always preferred and all the reactants are converted into the final target product(s).
- 3. Toxic reactants and products should be avoided as much as possible when designing the reaction process. It is important to decrease the damage to human health and the environment.
- 4. Products should be designed as less toxic compounds and maintain their desired function(s).

- 5. The utilization of assistant chemicals should be limited and preferably non-toxic.
- 6. Harsh reaction conditions, such as high temperature, and pressure should be considered as a negative factor in the design of the reaction process. Short reaction times are an advantage for a synthetic method.
- 7. The regeneration of raw materials is regarded as a recyclable and renewable process in a cascade reaction process.
- 8. Temporary modification of an intermediate, such as protection/deprotection, should be avoided since it requires extra reagents and produces waste products.
- 9. The utilization of a catalyst has priority over reactants because the catalyst decreases the activation energy of the reaction process.
- 10. Co-products should be designed as degradable in the environment after the reaction.
- 11. Real-time monitoring of the reaction process should be developed and applied to terminate the reaction and prevent the formation of unnecessary hazardous co-products.
- 12. All relevant chemicals used in the reaction, including reactants, intermediates, and products, should be safe for researchers rather than associated with potential risks such as explosions and fire.

The pivotal point to overcome the drawbacks of the aforementioned chemical reactions using harsh conditions is to reduce the energy barrier, which is a huge challenge for the ongoing reaction process. Therefore, catalysis, which possesses the ability to decrease the activation energy and speed up the chemical reaction rate, has attracted significant research attention. Low activation energy makes the reaction less energy-consuming and environmentally benign. Catalyst can also change the reaction mechanism to proceed via a faster pathway.² Furthermore, high atom efficiency is another non-negligible advantage for catalytic reactions. According to a rough estimate, catalysts have been utilized in >75% of all existing chemical processes and 90% of the most recently developed synthesis reactions.³

Catalysts are necessary for most chemical reactions to improve the reaction kinetics even though the final products are not changed. Unlike reactants, the catalyst is not consumed before and after the chemical reaction but still participates in the reaction to generate the intermediate(s) or transition state(s). Subsequently, they can be regenerated when the reaction is complete. Therefore, only a small amount of catalyst(s) is required to decrease the activation energy, as shown in Figure 1-2.⁴ Catalysts are often classified into three categories: heterogeneous, homogeneous, and biocatalysts. Biocatalysts, such as enzymes and proteins,

are generally applied in biological processes for metabolism. This dissertation will not discuss this category since they are not related to the project.





Figure 1-2. Diagrammatic sketch of the potential energy in the reaction with and without a catalyst. Adapted from the literature.⁴

Figure 1-2 clearly shows the initial and final potential energies are not affected in the existence or absence of the catalyst. Therefore, the catalyst cannot change the thermodynamic equilibrium of the reaction. The catalyst only reduces the activation energy when compared to that without the catalyst. There is no adsorption of the reactant molecules in the reaction system when the catalyst is not involved, which results in the existence of a large intermolecular distance between reactants A and B. Therefore, the reactant molecules should have enough energy to collide with each other to overcome the energy barrier. However, the situation changes in the presence of a catalyst because it leads to lower energy required for effective collision and electron transfer.

1.1.1 Homogeneous catalysts

Homogeneous catalysts are soluble catalysts that dissolve in the reactant(s) and then form a single phase, normally a liquid. In other words, the homogeneous phase reaction indicates there is no pressure drop during the reaction, which is an inevitable issue of heterogeneous catalytic reactions, especially for reactions performed in a fixed-bed reactor. Another obvious advantage of homogeneous reactions is the uniform contact between the active sites and reactants.⁵

The most commonly used homogeneous catalysts are acids or bases (e.g., nitric acid, hydrochloric acid, sulphuric acid, potassium hydroxide, and sodium hydroxide) and soluble transition metal complexes.^{5,6} Many of them are commercially available for the synthesis of fine chemicals, polymers, and pharmaceutical intermediates. These successful industrial applications validate the great potential of homogeneous catalysis. The remarkable advantage of homogeneous catalysts is their high catalytic efficiency due to the complete contact formed between the active sites and reactant species.

Apart from the aforementioned acid or base catalysts, other conventional homogeneous catalysts include organometallic catalysts, which consist of a central metal atom and organic ligands, as shown in Figure 1-3 in the application of hydrocyanation.³



Figure 1-3. The coordination geometry of organometallic Ni-based.

One of the tremendous challenges of homogeneous catalysis is the separation and recycling of the catalyst from the reactant and substrate mixture, which is the major restriction for industrial scale-up and production. The general method used to recycle homogeneous catalysts is distillation.^{3,7,8} However, the high energy consumption of distillation and potential damage to the thermal stability of the catalyst should be considered when researchers attempt to reuse a homogeneous catalyst. Another challenge for homogeneous catalysts is the issue of their intrinsic thermal stability. These catalysts do not tolerate fairly high reaction temperatures. In general, the lifetime of a homogeneous catalyst is shorter than its heterogeneous analogue on account of the difficult recovery and restocking issue of its metal sites.³

With the development of scientific research, a new concept of 'heterogenizing homogeneous catalysts' has been proposed, in which homogeneous catalysts can be converted into their heterogeneous derivatives and utilized in fine chemical synthesis, such as pharmaceuticals.⁹ It includes the advantages of both homogeneous and heterogeneous catalysts, such as high activity and easy recovery, respectively. However, heterogenized homogeneous catalysts are related to polymer science and complicated to make, which limits their applications in bulk chemical synthesis. It includes the benefits of both homogeneous and heterogeneous catalysts, such as excellent activity and easy recyclability, respectively. However, heterogenized

homogeneous catalysts are related to polymer science and complicated to make, which limits their applications in bulk chemical synthesis.¹⁰

1.1.2 Heterogeneous catalysts

The heterogeneous catalysts mean the catalysts and reactants are in different phases in the reaction system, generally the catalyst is the solid phase and the reactants are liquid or gas phase. Heterogeneous catalysts have a wider range of applications when compared to homogeneous catalysis in the bulk chemical industry owing to their excellent thermal stability and easy recovery.

Heterogeneous catalytic processes generally involve three consecutive steps. First, the reactants are absorbed on the surface of the catalyst to form a new interaction between the active sites and reactants. Subsequently, the cleavage of the chemical bond takes place inside or between reactant molecules, and new products are formed on the catalyst surface. Finally, the absorbed reactants or species are allowed to leave the solid catalyst surface to the surroundings. The diffusions of reactants from the bulk phase to the interface and the desorption of products from the interface to the bulk phase are also necessary steps for heterogeneous catalytic reactions. However, these three procedures do not have clear boundaries. In other words, desorption is simultaneous with the previous absorption and reaction steps at different catalytically active sites.¹¹

Although the detailed mechanisms of the reaction processes within heterogeneous catalysts are difficult to explore. There are two generally accepted mechanisms for reactant(s) absorbing on the surface of a heterogeneous catalyst, as shown in Scheme 1-1.



Langmuir-Hinshelwood mechanism

Eley-Rideal mechanism

Scheme 1-1. Two common reaction mechanisms of heterogeneous catalysis. (1) Langmuir-Hinshelwood, and (2) Eley-Rideal mechanisms. Adapted from literature.¹²

In the Langmuir-Hinshelwood mechanism, reactant molecules A and B are both absorbed on the surface of the catalyst and they then collide with sufficient energy to overcome the energy barrier to form product C; C disassociates later from the catalyst surface. However, the Eley-Rideal mechanism is only involved in the reactant molecule A absorbing on the catalyst surface. Subsequently, reactant molecule B diffuses from the bulk phase to the neighbouring of adsorbed A molecule and the reaction takes place to form product C without the adsorption of B molecule.

The rate constant of the reaction (*k*) is a correlation to the instant concentrations of reactants and reaction time as shown in Equation 1-1 for the reaction of $mA + nB \rightarrow C$.

$$r = \frac{d[C]}{dt} = k[A]^m[B]^n$$
 (Equation 1-1)

where the brackets [] represent the instantaneous concentrations of reactants and product, separately. Here we assume that partial orders of reaction are equal to the stoichiometric coefficients. The unit of k is useful to determine the reaction orders. And r and t are the reaction rate and reaction time at a particular temperature. The rate constant of the reaction (k) is related to the Arrhenius equation as shown in Equation 1-2.

$$k = Ae^{-\frac{La}{RT}}$$
 (Equation 1-2)

where A means the pre-exponential factor, R indicates the gas constant, T is the temperature, and E_a is the activation energy. In general, the Arrhenius equation should be taken in the natural logarithm and rearranged as shown in Equation 1-3 to get a linear relationship between $\ln k$ and $\frac{1}{r}$.

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \ln A \qquad (\text{Equation 1-3})$$

The slope $-\frac{E_a}{R}$ of the linear curve can be used to determine the apparent activation energy. The activation energy can be decreased by the utilization of catalysts as described in Figure 1-2. To evaluate the catalytic activity of the catalyst, the turn-over number (TON) and turn-over frequency (TOF) are major parameters. The definitions of TON and TOF are shown in Equation 1- 4 and Equation 1- 5.

$$TON = \frac{mol \ of \ converted \ substrate}{number \ of \ active \ sites}$$
(Equation 1-4)

$$TOF = \frac{mol \ of \ converted \ substrate}{number \ of \ active \ sites \ \times \ reaction \ time}$$
(Equation 1-5)

The TON value represents the stability of the catalyst or whole-life evaluation until it is completely deactivated regardless of its lifetime. Therefore, it is obviously deceptive and misleading when compared to real reaction conditions, especially in industrial applications, because we cannot wait for an extremely long period of time for obtaining the maximum yield of product. Therefore, the TOF value is a more valuable parameter to estimate the catalytic performance since the reaction time is taken into consideration.

Material diffusion and heat transfer are restrictions for the application of heterogeneous catalysts when compared to homogeneous catalysts. Hence, many studies have been conducted to improve the aforementioned issues, such as tuning channel size to shorten the transport pathway and facilitate the diffusion of reactants and products.¹³ Heterogeneous catalysts are typically metal or metal oxide nanoparticles. In addition, the metal or metal oxide nanoparticles supported on the material are one of the categories of heterogeneous catalysts and they are one of the major members of the heterogeneous catalyst family because they not only have metal active sites but also possess the characteristic functions of the supporting material. As one of the most significant support materials, zeolite-based catalysts play a critical role in the catalysis processes due to their unique characteristics like high surface area, thermal stability, and tunable acidity. The synergistic properties between zeolite support and metal active sites are of significant importance to improve the activity and selectivity in metal-supported catalysis. Moreover, the zeolite itself can be used as the catalyst in the chemical industrial process like trimerization of isobutene over beta zeolite.¹⁴ Therefore, zeolites are excellent candidates for heterogeneous catalysis not only as support material but also as catalyst without extra metal addition.15-19

1.2 Zeolites

Zeolites are a family of different crystalline and well-organized inorganic materials, which were first named in 1756 by Swedish scientist Axel Fredrik Cronstedt.²⁰ The most important properties of these three-dimensional (3D) materials are their high surface area, specific cavity, and regular pore size distribution. Zeolites are composed of a large number of primary building blocks, which consist of tetrahedral TO_4 (T = Si, Al, P, and Ti, among others) units. These repeating tetrahedral units combine with each other through shared oxygen atoms to form secondary building units that comprise different amounts of tetrahedral units. The secondary building unit has a ring structure with different amounts of tetrahedral units (n-member ring, two-dimensional (2D)) and this ring structure constitutes the main skeleton of the zeolite structure. The ring structures expand through the shared oxygen atoms into 3D space, and

channels, pores, and cavities are then formed in the 3D structure of the zeolite, as shown in Scheme 1-2. The typical pore size in zeolites is in the range of 3 - 20 Å.²¹



Scheme 1-2. Construction of zeolite frameworks from tetrahedral TO₄ units. Adapted from literature.²²

Zeolites are categorized into four types according to the number of tetrahedral units in the secondary building units. Small-, medium-, large- and extra-large-pore zeolites have up to 8, 10, 12, and more than 12 tetrahedral units, respectively.²³ Recently, more than 200 types of zeolite topologies have been recorded and the International Union of Pure and Applied Chemistry (IUPAC) has distributed a code to represent each zeolite topology.²⁴

1.2.1 Zeolites structure

As described above, the composition of a zeolite is made up of repeating tetrahedral TO₄ (T=Si, Al, P, Ti...) units. The slight acidic characteristics of an Al-free framework zeolite have been confirmed by Xing *et al.*²⁵ Their results indicate that a trace amount of isolated silanol (=Si–OH) groups exist in the Silicalite-1 zeolite. The silanol group may result from the defects originating from the Si atoms formed during the synthesis of Silicalite-1 zeolite.²⁶

The partial Si atoms can be substituted for Al atoms in the TO₄ units leads to the increasing acidity of the zeolite when compared to Silicalite-1 zeolite. The different electron pairs between tetravalent Si and trivalent Al result in the charge deficiency in the framework and therefore, a compensation counter ion (organic or inorganic alkaline cation). The Brønsted acidity of the zeolite can be increased via ion exchange of the alkaline cation with a proton using NH_4^+ as a precursor. The ion-exchanged protons are connected to the shared oxygen atom between the

adjacent Si and Al atoms, as shown in Figure 1-4, which then exhibit Brønsted acidic characteristics in the zeolite.



Figure 1-4. Schematic representation of Brønsted acidic sites in the Al-containing zeolite.

The Si/Al ratio is decided by the amount of Al in zeolite's framework. However, there is a generally accepted rule that the composition of the Al-O bridge linked structure, in which no Al-O-Al bond exists in the adjacent two Al atoms, is in accordance with Löwenstein's rule.²⁷ Some researchers claim that contravention of Löwenstein's rule exists in a few zeolites, such as H-SSZ-13 and H-MOR, and the reasons were deduced from theoretical calculations.²⁸ Nevertheless, obvious experimental evidence has still not been provided via direct synthesis and characterization. Zheng *et al.* have investigated the in-depth -Al-O- bond distribution using density functional theory to confirm the validation of Löwenstein's rule via hydrothermal synthesis.²⁹

Zeolites can be categorized using different Si/Al ratios as follows:

- Low silica zeolites: Si/Al < 2, such as analcime (ANA), cancrinite (CAN), natrolite (NAT), philipsite (PHI), and sodalite (SOD).
- Intermediate silica zeolites: 2 < Si/Al < 5, such as chabazite (CHA), faujasite (FAU), mordenite (MOR), and Na-Y (FAU).
- High silica zeolites: Si/Al > 5, such as ZSM-5 (MFI), and zeolite-Beta (BEA).³⁰

The Al atoms in the high silica zeolites exhibit a random distribution rather than assemble in a small region. Silicalite-1 (MFI) zeolite has the highest Si/Al ratio (∞) since it does not contain any Al sites.

1.2.2 Zeolite synthesis

In general, the tetrahedral TO_4 units of zeolites comprise SiO₄ and AlO₄ units. Therefore, the synthesis of zeolites involves the rearrangement of Si and Al precursor mixtures to form a particular topological structure. The crystallization process is the critical step in the synthesis of zeolites and higher temperature accelerates the crystallization step because of the shortened nucleation and crystal growth processes. However, the excess temperature can result in the

formation of different zeolite structures, for instance, metastable NaX zeolite (70–90 °C) switches to a more thermodynamically stable hydroxylsodalite phase (130 °C).³¹ The synthesis of zeolite not only relates to the temperature but also involves the structuring directing agent (SDA) used to manufacture a particular molecular structure. There are three types of SDA used for the synthesis of zeolites: inorganic cations, organic ammonium, and zeolite seeds.³² Although alkaline cations, such as Na⁺ and K⁺, are effective for the synthesis of Al-rich zeolites and can be regarded as the first type of SDA, they are not suitable for the synthesis of Si-rich zeolite because of their high positive charge density over-balance the negative framework with few Al sites.^{31,33} To obtain the Si-rich zeolites, organic structuring directing agents (OSDAs) have attracted research attention, such as quaternary ammonium ions, as shown in Figure 1-5 and can be regarded as the second type of SDA.^{34–38} The tetrapropylammonium (TPA⁺) and tetraethylammonium (TEA⁺) assist the synthesis of zeolites with MFI and BEA topologies, respectively.



Figure 1-5. The quaternary ammonium ions as OSDA.

OSDAs assist the arrangement of counter ions in the ordered manner during the assembly and filling of the pores. Therefore, the structure of the OSDA has a significant impact on the zeolite topology, such as the MFI and BEA zeolite structures obtained from TPA⁺ and TEA⁺ cations, respectively.^{35,37} The OSDA can be easily removed through calcination after the termination of the crystallization process and the zeolite crystals are obtained.

The nucleation and crystallization processes used in zeolite synthesis are regarded as the rate-determination steps, especially at the very beginning of the nucleation step. This is one of the reasons that zeolite synthesis is a time-consuming process, as shown in Figure 1-6. Therefore, it is necessary to investigate new SDAs to decrease the nucleation and crystallization time for the efficient synthesis of zeolites.



Figure 1-6. Crystallization curve for the formation of zeolite X (FAU). Adapted from literature.³⁹

In the aforementioned two types of SDA used during the synthesis of zeolites, the first batch of crystal nuclei are formed via the slow arrangement of tetrahedral TO₄ units. This has shown scientists that a trace amount of crystal nucleus can be provided in the initial precursor mixture to skip the time-consuming process of crystal nucleus formation. Zeolite seeds are excellent options as the first batch crystal nucleus and can be regarded as the third type of SDA.³² The seed-induced synthesis of zeolites has some advantages, such as eliminating the utilization of expensive organic templates and their subsequent calcination. However, it is only suitable for aluminosilicate zeolites synthesis and has great challenges in the synthesis of aluminophosphate-based zeolites.³²

1.2.3 Zeolite shape selectivity

Zeolite is also referred to as 'molecular sieve' and possesses the function for molecules screening. The sizes of the zeolite pores are in the range of 3–20 Å.²¹ Therefore, only the special size of the reactant and product molecules can be permitted to pass through the channels as shown in Scheme 1-3. If metal sites are inside the channel, the pore size can act as a 'gate guard' for the particular size of reactant' molecules passing through the channel to have the interaction with metal sites, which results in high selectivity of the products.⁴⁰ The product shape selectivity takes place in several co-products and the pore size plays a critical role for the desired product escaping from zeolite materials.





Scheme 1-3. Illustration of reactants and products selectivities in the zeolite. Adapted from the literature.⁴¹

The zeolites synthesized in this thesis are microporous or mesoporous structures depending on their pore-size distribution. Microporous zeolites exhibit narrow pore diameters, which means they have the unique property of shape selectivity for both the reactants and products. However, their small and narrow pore size exhibits an obstacle in terms of the catalysis rate resulting from the difficult diffusion of reactant into zeolite channels and cavities. Therefore, microporous zeolites are only limited to small-sized molecules and exhibit a great challenge to large molecules. The pore size should be expanded or the channel length decreased to avoid this issue. Mesoporous zeolites have attracted the attention of researchers to achieve favorable diffusion efficiency.

1.2.4 Mesoporous zeolite and zeolite modifications

The synthesis of mesoporous structure zeolites involves the utilization of hard or soft templates. The hard templating method is related to the utilization of templates like carbon black and the soft template approach is associated with the use of templates like a surfactant. In this thesis, the hard template method was applied to the synthesis of mesoporous zeolites and the procedures adopted from those reported in the literature by our group.^{40,42} In brief, the Si and Al precursor solution was distributed in carbon black powder, and the zeolite crystals grown in the presence of carbon black. The mesoporous zeolites are obtained after the removal of the hard template via calcination. The microporous structure still exists in the zeolite and the additional mesoporous structures are created with the utilization of the carbon black template.

As mentioned in Section 1.2.1, different ratios of Si/Al have an important impact on the Brønsted acidity of zeolite. However, Si/Al ratio can also be adjusted during a post-synthesis modification step, such as dealumination and desilication. In the dealumination step, the zeolites are stirred in concentrated nitric acid solution at moderate temperature.^{43–45} The desilication modification step involves treatment with a dilute base, such as NaOH (aq) under elevated temperature.^{46,47} These methods are relatively convenient and pore size may be

controlled through adjusting alkalinity, time, and temperature. Exposed metal vacancies and silanol nests are formed in the resulting zeolites, as shown in Scheme 1-4. It can be seen from the zeolite structure formed after modification that the Brønsted acidity is significantly increased due to the newly formed silanol nests in the framework when compared to its original proton counter ions.



Scheme 1-4. Post-treatment of Al-containing zeolites. Adapted from the literature.⁴⁶

1.2.5 Metal species in zeolites

Catalytic reactions normally occur in the presence of metal particles and particle size plays a significant role in their catalytic activity. Metal sites can be on the outer surface of zeolite support or incorporated inside of the zeolite framework.

(1) The metal particles on the surface of zeolite are normally formed via impregnation using both incipient wetness- and wetness-impregnation. The difference between these two metal impregnation methods is the water content in the metal precursor solutions. The water content in the incipient wetness impregnation is based on the pore volume of zeolite. However, water content is much larger in the wetness impregnation process to prepare the zeolite suspension and metal precursor solution. The metal sites can be three types, as shown in Figure 1-7: (a) isolated metal atoms, (b) small-size metal clusters, and (c) large metal particles, which are confined in the pores of the zeolite.⁴⁸ Isolated metal atoms exist in the inner pores and channels of zeolite resulting in high catalytic efficiency since every single metal atom can participate in the catalytic process as long as the reactant molecules have access to collide with the metal atom. Isolated metal atoms can be formed in the very low metal loading catalysts such as 0.07 wt.% Pd supported on the ZnO through the incipient wetness impregnation method.⁴⁹ Metal atoms are easier to form small-size metal clusters to receive a bigger surface area for the increasing collision frequency between reactant molecules and metal active sites.⁵⁰ If the metal

particles severely agglomerate from these nanoparticle clusters, the size of the newly formed large metal particles may inevitably exceed the pore size of zeolite. It causes the confining of large particles into the small pores of the zeolite without moving into the channels and avoids further agglomeration.



Figure 1-7. Three types of metal sites in zeolite structure. Adapted from reference.⁴⁸

(2) The metal particles fabricated and incorporated on the inside of the zeolite framework can avoid metal leaching and agglomeration because these metal active sites are anchored in the framework rather than attached on the surface. There are two approaches for metal incorporation that are categorized as pre-synthesis and post-synthesis methods.

The pre-synthesis method means that the metal precursor is introduced along with the Si and Al precursor solutions and the crystallization process occurs including the metal active sites in the gel, as shown in Figure 1-8 (left).⁵¹ A mechanochemical treatment such as ball milling has also been carried out in the preparation of metal incorporated zincosilicate zeolites.⁵² However, there is an obvious disadvantage in the pre-synthesis method that the metal precursor salt can easily precipitate as M(OH)_m due to the presence of high pH in the precursor mixture solution.

The post-synthesis method indicates metal sites are introduced into the zeolite framework after modification of the prepared zeolite. The modifications include desilication or dealumination to create a vacancy inside of the zeolite framework. The newly generated silanol nest is ready for active metal site anchoring via impregnation and calcination, as shown in Figure 1-8 (right).⁵³ Desilication or dealumination process is highly influenced by silicon or aluminum content in the zeolite. In addition, the modified zeolite exhibits strong Brønsted acidity due to the abundant number of hydroxy groups in the silanol nest, which facilitates the dehydration process.





Figure 1-8. Two different methods for Zn incorporation in the zeolite framework: Pre-synthesis (left) and post-synthesis (right). Adapted from the literature.^{52,53}

1.3 Summary

Catalysis is of great importance in the current chemical industry to decrease the energyconsuming and accelerate the reaction rate, and heterogeneous catalysis plays a critical role in the production of bulk chemicals like acetaldehyde and 1,3-butadiene.

Zeolites and zeolite-encapsulated active metal sites, which act as heterogeneous catalysts, are significant materials in the field of catalysis. The pore size of the zeolite offers excellent selectivity toward both reactants and products. Zeolites used as supporting materials for active metal sites provide stability to the catalyst in the reaction to avoid metal agglomeration. There are many different methods for the encapsulation of metal species in zeolites in the aforementioned sections and some of them have been applied in the projects described in this dissertation.

1.4 Aim and outline of the dissertation

Ethanol is regarded as a sustainable biomass-derived chemical, which can be used as the starting material to produce 1,3-butadiene, a significant monomer in the styrene rubber industry. This thesis aims to investigate the synthesis and characterization of different zeolites and their applications in the conversion of ethanol and the formation of 1,3-butadiene. Zn and Y have been applied as the active metal sites to facilitate the conversion of the substrate and improve the selectivity of the desired product(s).

Chapter 3 investigates the conversion of ethanol into acetaldehyde over different Zncontaining zeolite catalysts. The catalytic activity correlation to different catalyst preparation methods was discussed. Furthermore, the chemical compositions of the Zn active sites through different incorporation methods were studied in this reaction process.

Chapter 4 aims to study the 1,3-butadiene production process from the direct conversion of ethanol via different Zn and Y containing zeolites as catalysts. The impregnation and encapsulation of Zn and Y active sites in different zeolite materials were fully investigated towards the production of 1,3-butadiene.

Chapter 5 describes the ethanol/acetaldehyde mixture as the substrate to produce 1,3butadiene via Y/ZSM-5 zeolite catalysts bearing different counter ions. The influences of the different cations and the various substrate ratios on the selectivity of 1,3-butadiene were discussed. The catalyst deactivation and stability of the optimum catalyst were studied as well.

1.5 References

- Anastas, Paul T.; Warner, J. C. Green Chemistry: Theory and Practice. Oxford Univ. Press New York, 1998.
- (2) Twigg, M. V. Catalyst Handbook-Fundamental Principles. *Routledge* 2018, 17–84.
- (3) Bhaduri, S.; Mukeshi, D. Homogeneous Catalysis: Mechanisms and Industrial Applications. *John Wiley Sons. Inc.-Second Ed.* **2014**.
- Hussein, L. Decorated Nanostructured Carbon Materials for Abiotic and Enzymatic Biofuel Cell Applications. *Dr. Diss.* 2012.
- (5) Leeuwen, P. W. N. M. van. Homogeneous Catalysis-Understanding the Art. *Kluwer Acad. Publ.* **2004**.
- (6) Cornils, B.; Herrmann, W. A. Concepts in Homogeneous Catalysis: The Industrial View.
 J. Catal. 2003, 216 (1–2), 23–31.
- (7) Shende, V. S.; Saptal, V. B.; Bhanage, B. M. Recent Advances Utilized in the Recycling of Homogeneous Catalysis. *Chem.Rec.* 2019, *19*, 2022–2043.
- Sordakis, K.; Tang, C.; Vogt, L. K.; Junge, H.; Dyson, P. J.; Beller, M.; Laurenczy, G. Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols. *Chem. Rev.* 2018, *118* (2), 372–433.
- (9) Bailar, J. C. "Heterogenizing" Homogeneous Catalysts. *Catal. Rev. Sci. Eng.* 1974, 10 (1), 17–36.
- Barbaro, P.; Liguori, F. Heterogenized Homogeneous Catalysts for Fine Chemicals Production: Materials and Processes. *Springer*, **2010**.
- (11) Schlögl, R. Heterogeneous Catalysis. Angew. Chem. Int. Ed. 2015, 54 (11), 3465–3520.
- (12) Misono, M. Heterogeneous Catalysis of Mixed Oxides: Perovskite and Heteropoly Catalysts; Newnes, 2013.
- (13) Chen, S.; Fu, H.; Zhang, L.; Wan, Y. Nanospherical Mesoporous Carbon-Supported Gold as an Efficient Heterogeneous Catalyst in the Elimination of Mass Transport Limitations. *Appl. Catal. B Environ.* **2019**, 248, 22–30.
- (14) Jhung, J. W. Y. J.-S. C. H.-D. L. T.-J. K. S. H. Trimerization of Isobutene over a Zeolite

Beta Catalyst. J. Catal. 2007, 245, 253-256.

- (15) Xu, Y.; Ma, G.; Bai, J.; Du, Y.; Qin, C.; Ding, M. Yolk @ Shell FeMn @ Hollow HZSM
 5 Nanoreactor for Directly Converting Syngas to Aromatics. ACS Catal. 2021, 11, 4478–4485.
- (16) Pinilla-Herrero, I.; Borfecchia, E.; Holzinger, J.; Mentzel, U. V.; Joensen, F.; Lomachenko, K. A.; Bordiga, S.; Lamberti, C.; Berlier, G.; Olsbye, U.; Svelle, S.; Skibsted, J.; Beato, P. High Zn/Al Ratios Enhance Dehydrogenation vs Hydrogen Transfer Reactions of Zn-ZSM-5 Catalytic Systems in Methanol Conversion to Aromatics. J. Catal. 2018, 362, 146–163.
- (17) Poursaeidesfahani, A.; de Lange, M. F.; Khodadadian, F.; Dubbeldam, D.; Rigutto, M.; Nair, N.; Vlugt, T. J. H. Product Shape Selectivity of MFI-Type, MEL-Type, and BEA-Type Zeolites in the Catalytic Hydroconversion of Heptane. *J. Catal.* **2017**, *353*, 54–62.
- (18) Wen, C.; Jiang, J.; Chiliu, C.; Tian, Z.; Xu, X.; Wu, J.; Wang, C.; Ma, L. Single-Step Selective Conversion of Carbon Dioxide to Aromatics over Na-Fe3O4/Hierarchical HZSM-5 Zeolite Catalyst. *Energy Fuels* **2020**, *34* (9), 11282–11289.
- Wu, J. F.; Yu, S. M.; Wang, W. D.; Fan, Y. X.; Bai, S.; Zhang, C. W.; Gao, Q.; Huang, J.; Wang, W. Mechanistic Insight into the Formation of Acetic Acid from the Direct Conversion of Methane and Carbon Dioxide on Zinc-Modified H-ZSM-5 Zeolite. *J. Am. Chem. Soc.* 2013, *135* (36), 13567–13573.
- (20) Kianfar, E.; Mahler, A. Zeolites: Properties, Applications, Modification and Selectivity. *Zeolites: Advances in Research and Applications*, **2020**.
- Koohsaryan, E.; Anbia, M. Nanosized and Hierarchical Zeolites: A Short Review. *Chin. J. Catal.* 2016, *37* (4), 447–467.
- (22) Rani, P.; Srivastava, R. Comprehensive Understanding of the Eco-Friendly Synthesis of Zeolites: Needs of 21st Century Sustainable Chemical Industries. *Chem. Rec.* 2020, 20 (9), 968–988.
- Blakeman, P. G.; Burkholder, E. M.; Chen, H. Y.; Collier, J. E.; Fedeyko, J. M.; Jobson, H.; Rajaram, R. R. The Role of Pore Size on the Thermal Stability of Zeolite Supported Cu SCR Catalysts. *Catal. Today* 2014, *231*, 56–63.
- (24) Database of Zeolite Structures. Struct. Comm. Int. Zeolite Assiciation (IZA-SC).

https://europe.iza-structure.org/IZA-SC/ftc_table.php Accessed 20th Jan. 2022.

- (25) Javed, M.; Cheng, S.; Zhang, G.; Cyril, C.; Wang, J. A Facile Solvent-Free Synthesis Strategy for Co-Imbedded Zeolite-Based Fischer-Tropsch Catalysts for Direct Gasoline Production. *Chin. J. Catal.* **2020**, *41* (4), 604–612.
- (26) Zhang, J.; Zhu, X.; Wang, G.; Wang, P.; Meng, Z.; Li, C. The Origin of the Activity and Selectivity of Silicalite-1 Zeolite for Toluene Methylation to Para-Xylene. *Chem. Eng. J.* 2017, *327*, 278–285.
- (27) Loewenstein, W. The Distribution of Aluminum in the Tetrahedra of Silicates and Aluminates. *Am. Mineral. J. Earth Planet. Mater.* **1954**, *39* (1–2), 92–96.
- (28) Fletcher, R. E.; Ling, S.; Slater, B. Violations of Löwenstein's Rule in Zeolites. *Chem. Sci.* 2017, 8 (11), 7483–7491.
- (29) Tang, X.; Liu, Z.; Huang, L.; Chen, W.; Li, C.; Wang, G.; Li, G.; Yi, X.; Zheng, A. Violation or Abidance of Löwenstein's Rule in Zeolites under Synthesis Conditions? *ACS Catal.* 2019, 9 (12), 10618–10625.
- (30) Yoldi, M.; Fuentes-Ordoñez, E. G.; Korili, S. A.; Gil, A. Zeolite Synthesis from Industrial Wastes. *Microporous Mesoporous Mater.* 2019, 287, 183–191.
- (31) Dimitrijevic, R.; Lutz, W.; Ritzmann, A. Hydrothermal Stability of Zeolites: Determination of Extra-Framework Species of H-Y Faujasite-Type Steamed Zeolite. J. Phys. Chem. Solids 2006, 67 (8), 1741–1748.
- (32) Ji, Y.; Wang, Y.; Xie, B.; Xiao, F. S. Zeolite Seeds: Third Type of Structure Directing Agents in the Synthesis of Zeolites. *Comments Inorg. Chem.* **2016**, *36* (1), 1–16.
- (33) Itakura, M.; Goto, I.; Takahashi, A.; Fujitani, T.; Ide, Y.; Sadakane, M.; Sano, T. Synthesis of High-Silica CHA Type Zeolite by Interzeolite Conversion of FAU Type Zeolite in the Presence of Seed Crystals. *Microporous Mesoporous Mater.* 2011, 144 (1–3), 91–96.
- (34) Hamidzadeh, M.; Komeili, S.; Saeidi, M. Seed-Induced Synthesis of ZSM-5 Aggregates Using the Silicate-1 as a Seed: Characterization and Effect of the Silicate-1 Composition. *Microporous Mesoporous Mater.* 2018, 268, 153–161.
- (35) Persson, A. E.; Schoeman, B. J.; Sterte, J.; Otterstedt, J. E. Synthesis of Stable

Suspensions of Discrete Colloidal Zeolite (Na, TPA)ZSM-5 Crystals. *Zeolites* **1995**, *15* (7), 611–619.

- (36) Li, T. Y.; Chang, C. Y.; Wan, B. Z. Effect of Concentration of Tetrapropylammonium Hydroxide on Silica Suspensions for Making Spin-on Porous Low Dielectric Constant Films. *Thin Solid Films* **2014**, *562*, 513–518.
- (37) Takewaki, T.; Beck, L. W.; Davis, M. E. Synthesis of CIT-6, a Zincosilicate with the *BEA Topology. *Top. Catal.* 1999, 9 (1–2), 35–42.
- (38) Takewaki, T.; Beck, L. W.; Davis, M. E. Zincosilicate CIT-6: A Precursor to a Family of *BEA-Type Molecular Sieves. *J. Phys. Chem. B* **1999**, *103* (14), 2674–2679.
- (39) Prodinger, S.; Derewinski, M. A. Synthetic Zeolites and Their Characterization; INC, 2020.
- (40) Rasmussen, K. H.; Goodarzi, F.; Christensen, D. B.; Mielby, J.; Kegnæs, S. Stabilization of Metal Nanoparticle Catalysts via Encapsulation in Mesoporous Zeolites by Steam-Assisted Recrystallization. ACS Appl. Nano Mater. 2019, 2 (12), 8083–8091.
- (41) Degnan, T. F. The Implications of the Fundamentals of Shape Selectivity for the Development of Catalysts for the Petroleum and Petrochemical Industries. J. Catal. 2003, 216 (1–2), 32–46.
- (42) Goodarzi, F.; Kang, L.; Wang, F. R.; Joensen, F.; Kegnæs, S.; Mielby, J. Methanation of Carbon Dioxide over Zeolite-Encapsulated Nickel Nanoparticles. *ChemCatChem* 2018, *10* (7), 1566–1570.
- (43) Sushkevich, V. L.; Ivanova, I. I. Ag-Promoted ZrBEA Zeolites Obtained by Post-Synthetic Modification for Conversion of Ethanol to Butadiene. *ChemSusChem* 2016, 9 (16), 2216–2225.
- (44) Yu, D.; Dai, W.; Wu, G.; Guan, N.; Li, L. Stabilizing Copper Species Using Zeolite for Ethanol Catalytic Dehydrogenation to Acetaldehyde. *Chin. J. Catal.* 2019, 40 (9), 1375– 1384.
- (45) Dai, W.; Sun, X.; Tang, B.; Wu, G.; Li, L.; Guan, N.; Hunger, M. Verifying the Mechanism of the Ethene-to-Propene Conversion on Zeolite H-SSZ-13. J. Catal. 2014, 314, 10–20.
- (46) Groen, J. C.; Peffer, L. A. A.; Moulijn, J. A.; Pérez-Ramírez, J. Mechanism of Hierarchical Porosity Development in MFI Zeolites by Desilication: The Role of Aluminium as a Pore-Directing Agent. *Chem. Eur. J.* 2005, *11* (17), 4983–4994.
- (47) Verboekend, D.; Mitchell, S.; Milina, M.; Groen, J. C.; Pérez-Ramírez, J. Full Compositional Flexibility in the Preparation of Mesoporous MFI Zeolites by Desilication. J. Phys. Chem. C 2011, 115 (29), 14193–14203.
- (48) Wang, L.; Xu, S.; He, S.; Xiao, F. S. Rational Construction of Metal Nanoparticles Fixed in Zeolite Crystals as Highly Efficient Heterogeneous Catalysts. *Nano Today* 2018, 20, 74–83.
- (49) Ouyang, M.; Cao, S.; Yang, S.; Li, M.; Flytzani-Stephanopoulos, M. Atomically Dispersed Pd Supported on Zinc Oxide for Selective Nonoxidative Ethanol Dehydrogenation. *Ind. Eng. Chem. Res.* **2020**, *59* (6), 2648–2656.
- (50) Nørskov, J. K.; Bligaard, T.; Hvolbæk, B.; Abild-Pedersen, F.; Chorkendorff, I.; Christensen, C. H. The Nature of the Active Site in Heterogeneous Metal Catalysis. *Chem. Soc. Rev.* 2008, 37 (10), 2163–2171.
- (51) Orazov, M.; Davis, M. E. Catalysis by Framework Zinc in Silica-Based Molecular Sieves. *Chem. Sci.* **2016**, *7* (3), 2264–2274.
- (52) Hu, P.; Iyoki, K.; Yamada, H.; Yanaba, Y.; Ohara, K.; Katada, N.; Wakihara, T. Synthesis and Characterization of MFI-Type Zincosilicate Zeolites with High Zinc Content Using Mechanochemically Treated Si–Zn Oxide Composite. *Microporous Mesoporous Mater.* 2019, 288, 109594.
- (53) Qi, L.; Zhang, Y.; Conrad, M. A.; Russell, C. K.; Miller, J.; Bell, A. T. Ethanol Conversion to Butadiene over Isolated Zinc and Yttrium Sites Grafted onto Dealuminated Beta Zeolite. *J. Am. Chem. Soc.* **2020**, *142* (34), 14674–14687.

Chapter 2 Characterization techniques

In this chapter, different characterization methods were described including the mechanism of the characterization instruments. X-ray powder diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Nitrogen physisorption, Chemisorption about Temperature Programmed Desorption (NH₃-TPD and CO₂-TPD), Scanning Electron Microscopy(SEM), Transmission Electron Microscopy (TEM), Thermogravimetric Analysis (TGA). It should be noted that all scientific principles of characterization techniques and instruments are adapted and concluded from different kinds of literature.

2.1 Physisorption measurement

The physical texture properties are examined through physisorption analysis using the instrument of Micromeritrics 3 FLEX at liquid nitrogen temperature. In general, the purpose of physisorption measurement is to study the pore characteristics of solid material such as nitrogen adsorption and desorption isothermal curves, surface area, and porosity. The mechanism of nitrogen physisorption is the adsorption and desorption of nitrogen molecules at liquid nitrogen temperature at different relative pressures. The adsorption process can be divided into three consecutive steps: monolayer adsorption, bilayer adsorption, and finally multilayer filling in the pore structure of the material. The physisorption analysis can also apply Ar as the adsorbent at the liquid Ar temperature of 84 K. All the physisorption analysis were conducted with nitrogen as the adsorbent in my project.

In general, the pores are categorized based on their size distribution:

- (i) Macropores mean that the pores widths excess 50 nm;
- (ii) Mesopores mean that the pores widths are in the range between 2 nm and 50 nm;
- (iii) Micropores mean that the pores widths are lower than 2 nm;

The adsorption-desorption isotherms are classified as six types following guidelines by the IUPAC as shown in Figure 2-1.¹



Figure 2-1. Categories of physisorption isotherms. Adapted from literature.¹

Type I isotherm normally occurs at the solid material with a small surface area like the flat cubic block but still with micropores. The adsorption of nitrogen reaches its limitation at very low relative pressure p/p^0 . The difference between Type I(a) and Type I(b) is that the latter material has higher relative pressure than Type I(a). The reason can be ascribed as the width of micropores size of Type I(b) is around 1-2 nm. By contrast, the pore width of Type I(a) material is normally lower than 1 nm.

Type II material has an obvious infinite amount of adsorbed nitrogen gas at the relative pressure p/p^0 of 1, which is different from Type I material. That means the material could be nonporous. Point B means the finish of monolayer adsorption. And then turn to the multilayer adsorption but without the maximum adsorption amount because the thickness of multilayer nitrogen molecules keeps increasing on the surface of the nonporous or macroporous material.

Type III shows the isotherm without the monolayer adsorption in micropores. This isotherm is rare to obtain and normally comes from macroporous material. The final amount of adsorbed nitrogen is finite at the saturation pressure.

Type IV(a) isotherm has an obvious hysteresis loop, which means the micropores and mesopores both exist in the material. In general, the material is only referred to as a mesoporous structure because micropores are usually formed during the mesopores formation. The sharp knee in the low relative pressure means the nitrogen adsorption of a monolayer in the micropores and mesopores. Then the multilayer of nitrogen molecules formed in the mesopores and follows the pore condensation. The pore condensation means that the gas phase nitrogen condenses to a liquid-like phase at the real pressure lower than the corresponding liquid saturation evaporation pressure. The final amount of nitrogen adsorption does not change along with the increase of relative pressure at a high range because the mesopores are filled with liquid-like phase nitrogen, and no more nitrogen molecules will be further adsorbed even increasing nitrogen gas pressure. However, the relative pressure p/p^0 value of the pore condensation finishing depends on the mesopores' volume. The final pore condensation point may reach the point that the real pressure equals bulk liquid nitrogen saturation pressure and the relative pressure p/p^0 of 1. Therefore, the final saturation plateau disappears in this circumstance. The capillary condensation occurs when the pore width is more than 4 nm at the nitrogen physisorption in cylindrical pores. It is inclined to form a concave meniscus of liquidlike phase nitrogen in big mesopores. The vapor pressure on the concave meniscus surface is smaller compared to saturated vapor pressure on a horizontal plane of liquid-like phase nitrogen. Therefore, the capillary condensation takes place in the mesopores at the concave meniscus surface of liquid-like phase nitrogen. However, in the desorption branch, the relative pressure at the desorption process is lower than the adsorption branch at the same amount of adsorbed

nitrogen just like to draw a horizontal line to explain the different relative pressure at the same adsorption amount of nitrogen.

Type IV(b) isotherm generally occurs at the material with pores width smaller than 4 nm of cylindrical mesopores, and the mesopores are closed in the tapered end.

Type V isotherm means the mesopores material like hydrophobic property. The low relative pressure p/p^0 means the weak interaction between the nitrogen molecule and material surface just like Type III in the same relative pressure region. However, the high relative pressure region has the same tendency as Type IV(a) isotherm indicating the pore filling.

Type VI isotherm indicates the layered adsorption of nitrogen molecules on the pore-free substance. The different amounts of nitrogen adsorption in each layer can be obtained in the isotherm.

Types of the hysteresis loop

There are six kinds of classical hysteresis loop as mentioned in the above Type IV(a) isotherm as shown in Figure 2-2.¹ They are the characteristic symbols to identify the mesoporous structure material.



Figure 2-2. Different types of the hysteresis loop. Adapted from literature.¹

Type H1 loop is obtained from the ordered mesopores materials. The narrow and vertical hysteresis loop is a typical sign compared to other type loops. And the loop at the adsorption branch is different from the H2(a) type isotherm because of a delayed condensation. The H1 hysteresis loop can also be obtained in the network of ink-bottle pores material.

Type H2(a) loop has an obvious difference at the adsorption branch compared to the H1 loop, and the desorption branch is the same shape as the H1 loop. The broad adsorption branch of isotherm means the complex pore structure compare to the simple ordered mesopores material of the H1 loop. The sharp desorption branch indicates that there is a pore-blocking in the narrow pores that the desorption of nitrogen forms a concave meniscus surface and leads to the real condensing pressure lower than the real saturation pressure of liquid-like phase nitrogen. This loop can be found in silica gel porous glasses and ordered mesoporous substances.

Type H2(b) isotherm can be assigned to the pore-blocking phenomenon as well. The size of the pore has a wider range than the Type H2(a) material. Mesocellular foams are the typical material to form this wide range of relative pressure in adsorption-desorption branches.

Type H3 isotherm has the same adsorption branch as H2 isotherms but the amount of adsorbed nitrogen is infinite at the relative pressure of 1, which means the surface of the material may contain the macropores.

Type H4 isotherm at the low relative pressure has a large amount of nitrogen adsorption and the sharp knee means the existence of micropores. The H4 isotherm is normally obtained from the aggregates that composes of micropores and mesopores zeolites.

Type H5 isotherm is unusual and normally obtained from open and partially blocked mesopores material.

Assessment of surface and porosity

The surface area is generally determined through the Brunauer–Emmett–Teller (BET) theory as shown in Equation 2-1. The surface area can be regarded as the active area that is used for nitrogen molecules adsorbing. The amount of adsorbed monolayer nitrogen molecules can be obtained through the calculation derived from the isotherm with the assistance of the Avogadro constant. And then the single nitrogen molecule can be equivalent to a sphere. The sphere area of the projection on the material surface is equal to the circle with the same diameter.

$$\frac{p/p^0}{n(1-p/p^0)} = \frac{1}{n_m} + \frac{C-1}{n_m C} (p/p^0)$$
(Equation 2-1)

where n is the adsorption capacity at relative pressure p/p^0 , coefficient C has a bearing on the energy absorbed by monolayer, and n_m is specific monolayer capacity.

The surface area calculation is based on the hypothesis model that all the nitrogen molecules are arranged next to each other to form the monolayer adsorption on the material surface and without any gap between each other. This hypothesis has a big deviation from the real circumstance that it can not form the strict monolayer adsorption of nitrogen molecules with a specific border of two layers of nitrogen molecules. Another drawback is the projection area of a single nitrogen molecule on the material surface. It is difficult to simulate a nitrogen molecule as a sphere. However, the BET method is still regarded as the most conceived method to calculate the surface area of materials, especially with Type II and Type IV isotherms.

Special attention should be paid to the materials with Type I isotherm that belongs to microporous material or some materials contain microporous structure. Because it is hard to identify the microporous adsorption from the BET plot.

The micropore volume is easy to calculate when the isotherm belongs to Type I. Then it can be simply measured as the adsorbed amount of nitrogen. Many methods are proposed to measure the micropore volume from the physisorption isotherm like DFT calculation. The tplot is recognized as an effective method for measuring micropore volume.

Pore volume consists of micropore and mesopore volumes if the material has the Type IV isotherm. Then the pore volume can be measured in the high range p/p^0 of 0.95-0.99 by assuming both micropores and mesopores are filled with the nitrogen molecules.

The measurement of pore size distribution is according to the Kelvin equation for a long time, and it is modified along with the improvement of the technique and theory development. The generally accepted method to measure the pore diameter is proposed by Barrett, Joyner, and Halenda (BJH) when assuming that pores are cylindrical. It is worth noting that the Kelvin equation method and the BJH method can inevitably underrate the pore size for small mesopores. The BJH method can be trusted when the argon is used as the adsorbent at the temperature of 87 K rather than the nitrogen adsorbent at 77 K, especially in the case of the micropores size analysis.

2.2 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is an efficient and direct technology to detect the morphology of the specimens including zeolites. The resolution of SEM can be 0.5-1 nm and the magnification ratio can reach 10 to 1 million times. The schematic showing of the SEM apparatus is shown in Figure 2-3.

Emitted electrons from a tungsten filament or a field emission gun (FEG) are accelerated to a high-energy incident electron beam like 20-40 keV through a high voltage. The high-energy divergent electron flow is concentrated on the spot size of 1-5 nm by one or two condenser lenses. The aperture is used to control the fraction of the electron beam to hit the sample. The position of the incident electron beam can be controlled by adjusting the current of scan coils. The objective lens can make the focus of the incident beam located on the surface of the specimen.²



Figure 2-3. Schematic showing of the SEM apparatus. Adapted from literature.³

The high-energy electron beam only penetrates a thin surface layer of the sample normally 10 nm to 1 μ m according to different secondary electrons (SE) and backscattered electrons (BSE), separately. The interaction volume is referred to the region of the sample where the beam interacts with. The interaction volume exhibits pear-shaped as shown in Figure 2-4. The secondary electrons mean the orbital electron is knocked out from the atoms of the specimen by the primary electron (PE) of the incident beam. And it can escape from the scope of the nucleus constraint then be captured by the detector.

The secondary electron only emits from a few nm depths of the surface of the specimen that is very close to the specimen surface. Therefore, the secondary electron detector can provide good topographical information about the specimen. The backscattered electrons escape from a larger depth to µm range of the surface range because they are scattered back from the nucleus with higher energy than secondary electrons. Since the backscattered electrons have an interaction with the nucleus, the image from the backscattered electrons detector can provide useful information about the atomic number contrast. The energy from the inelastic interaction of incident beams and electrons could also emit as X-ray form. The X-ray contains information about the mapping of the elements from the energy dispersive spectroscopy (EDS) detector.



Figure 2-4. SEM interaction volume of the primary electron (PE) inside the specimen (left), and the formation of secondary electrons (SE) and backscattered electrons (BSE). Adapted from literature.⁴

As it can be obtained from Figure 2-4 the spot size strongly depended on the secondary electron. Therefore, the resolution of secondary electrons emitted is close to the spot size of the incident beam. It should be noted that the interaction volume is greatly affected by the energy of the incident beam and the atomic number of the material due to strong interaction and constraints between the nucleus and electrons. In general, the higher atomic number z means the larger constraints of electrons and lower energy of scattered electrons. In this dissertation, the SEM was used to determine the morphology of the zeolite samples about the crystal size, sharp and the size distribution of the particles.

2.3 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a useful technology to detect the internal structure of the specimen such as the size, shape, and composition. The biggest difference between TEM and SEM is the position of the specimen. The specimen is located at the bottom of the SEM apparatus and the incident electrons only scan the surface of the specimen. However, the specimen is in the middle position of the TEM apparatus and the high-energy incident electron beam penetrates the specimen. Therefore, the specimen must be thin enough

(around 20 nm and maximum 100 nm) to allow the high-energy electrons beam to pass through. The schematic diagram of a TEM is shown in Figure 2-5.



Figure 2-5. Schematic diagram of TEM apparatus. Adapted from literature.⁵

The electron beam before contacting the specimen in the TEM apparatus is the same as in the SEM but the electron beam with higher energy compared to SEM accelerating voltage. The electron source is typically a field emission gun (FEG) and the accelerating voltage is in the range of 100-400 kV. The high-energy incident beam is focused through two or three condenser lenses. The first condenser lens is used for changing the spot size of the beam for the following analysis. The second condenser lens is used for controlling the illuminated area. Then the transmission electrons that penetrate the thin specimen are collected for further image formation or diffraction pattern. The objective lens is located underneath the specimen and the first magnification of the specimen takes place at the objective lens. Therefore, the quality of the objective lens plays a key role in the microscope resolution because the following magnifications relate to the first magnification. Subsequently, the objective aperture is important to form the image or diffraction pattern. The sample image mode is formed by inserting the objective aperture to focus the transmission beam in the image plane.⁶ To obtain the diffraction pattern, the objective aperture is removed and the beam is focused on the back focal plane as shown in Figure 2-6.



Figure 2-6. Illustration of the diffraction pattern and the final image mode. Adapted from literature.⁷

The projector lens is placed below the objective aperture to magnify the image or diffraction pattern and finally displayed on the fluorescent screen. The image and diffraction pattern are recorded by a Charge Coupled Device (CCD) array camera. The image acquired from the transmitted electrons is a bright-field (BF) image and the image acquired from diffracted electrons is a dark-field (DF) image. It should be noted that the white-black contrast has a relationship to the atomic mass and it can be used to rough identify different atoms. In general, the atoms with high atomic numbers exhibit a relative black area than the atoms with small atomic numbers.

2.4 X-ray diffraction (XRD)

X-ray diffraction (XRD) is a useful technique to determine crystalline structure materials. The organized sample atoms can form the lattice planes with a specific distance *d*. The X-ray beam has a constant wavelength λ to scatter the atom with a glancing angle θ and then reflect with the same glancing angle as shown in Figure 2-7.

$$n\lambda = 2d \times \sin\theta \qquad (\text{Equation 2-2})$$



Figure 2-7. Illustration of Bragg diffraction.

The diffraction intensity will change along with the glancing angle increasing and the distance of lattice planes follows the rule of Bragg's law as shown in Equation 2-2. The crystalline phases can be obtained from the XRD pattern through the comparison of the standard material database. The crystallinity and particles sizes can be obtained by rough calculation with different physical equations like crystalline peak area ratio and the Sherrer equation, separately.⁸

2.5 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technology that can be utilized to detect the oxidation state of different atoms according to the detection of different kinetic energy ($E_{kinetic}$). The incident x-ray beam with a particular wavelength λ transforms the energy to the orbital electron of the atoms. The energy-absorbed orbital electron will emit as the photoelectron and then be detected by a detector as shown in Figure 2-8. Ultrahigh vacuum is necessary for detecting the energy of emitted electrons to avoid the interaction between electrons and air. And the operating pressure is about 10⁻⁹ mbar.⁹ The kinetic energy of the photoelectron can be calculated using the photoelectric effect equation as shown in Equation 2-3.

$$E_{\text{binding}} = E_{\text{photon}} - E_{\text{kinetic}} - \varphi \qquad (Equation 2-3)$$

where $E_{binding}$ is the binding energy of the emitted photoelectron that is related to the chemical potential, E_{photon} is the energy of the incident X-ray beam that can be obtained from the Planck's constant due to a particular wavelength λ , and φ is the work function-like term for the specific surface of the material which can be thought as the correlation factor of the instrument.



Figure 2-8. Schematic illustration of the photoelectron emission. Adapted from literature.¹⁰

In principle, the survey spectrum of the material should be recorded with a wide binding energy range from several eV to 1400 eV to identify all potential elements. The spectrum of C 1s is also necessary to record as the correction binding energy for all other spectrums, and the standard C 1s spectrum has binding energy at 284.8 eV.^{11–13} A high-resolution spectrum of a specific element at electrons located in a particular orbital should be recorded for analyzing more details of the element like oxidation state.

2.6 Temperature programmed desorption (TPD)

The temperature-programmed desorption (TPD) is an effective technique to study the surface active sites.¹⁴ In this thesis, two kinds of TPD measurements are applied: CO_2 -TPD and NH₃-TPD that NH₃ or CO₂ are utilized as the probe molecules. The CO₂-TPD and NH₃-TPD are used to determine and quantify the basic sites and acidic sites of zeolite samples, respectively. The mechanism of TPD measurement is according to the pressure change recording during the heating of the sample. The pressure change is monitored through a thermal conductivity detector (TCD). In general, the sample is placed in a U-shape tube with a thermocouple inside of the sample. The inert gas is used to purge the remained gas in the sample and then the reaction gas (NH₃ or CO₂) is adsorbed on the sample surface. Subsequently, the sample is heating at a linear heating ramp versus time, and the adsorbed reaction gas is desorbed from the surface of the sample. The sample analysis chamber is shown in Figure 2-9.



Figure 2-9. The sample chamber and adsorption-desorption process analysis.¹⁵

2.7 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) is a technique of thermal analysis of a sample to obtain information about coke deposition, which is the main reason for the deactivation of zeolite catalysts. The instantaneous mass of the sample is recorded through a fine balance along with the temperature increase.

2.8 References

- Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem.* 2015, 87 (9–10), 1051–1069.
- (2) Akhtar, K.; Khan, S. A.; Khan, S. B.; Asiri, A. M. Scanning Electron Microscopy: Principle and Applications in Nanomaterials Characterization. *Handb. Mater. Charact. Springer, Cham.* 2018, 113–145.
- (3) Shah, F. A.; Ruscsák, K.; Palmquist, A. 50 Years of Scanning Electron Microscopy of Bone—a Comprehensive Overview of the Important Discoveries Made and Insights Gained Into Bone Material Properties in Health, Disease, and Taphonomy. *Bone Res.* 2019, 7 (1), 1–15.
- Goodhew, P. J.; Humphreys, J.; Beanland, R. Electron Microscopy and Analysis. *CRC Press* 2000.
- (5) Inkson, B. J. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) for Materials Characterization. *Mater. Charact. Using Nondestruct. Eval. Methods* 2016, 17–43.
- Kohjiya, S.; Kato, A.; Ikeda, Y. Principle and Practice of Three-Dimensional Transmission Electron Microscopy (3D-TEM). *Springer* 2020, 49–56.
- Williams, D. B.; Carter, C. B. Transmission Electron Microscopy: Lenses, Apertures, and Resolution. *Springer* 1996.
- (8) Epp, J. X-Ray Diffraction (XRD) Techniques for Materials Characterization; Elsevier Ltd, 2016.
- (9) Heide, P. Van Der. X-Ray Photoelectron Spectroscopy-An Introduction to Principles and Practices. *John Wiley Sons.* 2012.
- (10) Zatsepin, D. A. Familirization with XPS The Scope : 2 . Why X Ray Photoelectron Method Features). 2014.
- Wang, C.; Garbarino, G.; Allard, L. F.; Wilson, F.; Busca, G.; Flytzani-Stephanopoulos,
 M. Low-Temperature Dehydrogenation of Ethanol on Atomically Dispersed Gold
 Supported on ZnZrOx. ACS Catal. 2016, 6 (1), 210–218.

- (12) Yan, T.; Yang, L.; Dai, W.; Wang, C.; Wu, G.; Guan, N.; Hunger, M.; Li, L. On the Deactivation Mechanism of Zeolite Catalyst in Ethanol to Butadiene Conversion. J. *Catal.* 2018, 367, 7–15.
- (13) Yang, F.; Libretto, N. J.; Komarneni, M.; Zhou, W.; Miller, J. T.; Zhu, X.; Resasco, D.
 E. Enhancement of M-Cresol Hydrodeoxygenation Selectivity on Ni Catalysts by Surface-Decoration of MoOx-Species. ACS Catal. 2019, 7791–7800.
- (14) Ishii, T.; Kyotani, T. Temperature Programmed Desorption (Chapter 14). *Mater. Sci. Eng. Carbon* 2016, 287–305.
- (15) Rakić, V.; Damjanović, L. Temperature-Programmed Desorption (TPD) Methods. *Springer Ser. Mater. Sci.* **2013**, *154*, 131–174.

Chapter 3 Ethanol conversion to acetaldehyde

This chapter focuses on the dehydrogenation of ethanol used to prepare acetaldehyde over different Zn-containing MFI zeolite catalysts, including Zn/Silicalite-1, Zn/H-ZSM-5, Zn/Na-ZSM-5, and Zn-MFI. The as-synthesized catalysts were characterized and tested in a fix-bed apparatus at different reaction temperatures. The main part has been used as the manuscript entitled *Catalytic dehydrogenation of ethanol over zinc-containing zeolites* submitted to the international journal, *Catalysis Today*. The reprint permission is obtained from publisher Elsevier and this thesis is not to be published commercially.

This project was conducted by Kai Gao (Ph.D. student), supervisor Søren Kegnæs (Professor), and supervisor Dr. Jerrik Mielby (Senior researcher).



Graphical abstract

MFI zeolite

Figure 3-1. Ethanol conversion to acetaldehyde over Zn-containing zeolites. This is the graphical abstract from the article with permission from publisher Elsevier.

3.1Introduction

Acetaldehyde has many applications in chemistry as a building block for many downstream products, such as acetic acid, pyridines, and ethyl acetate. It is also applied in high value-added products, such as in food and beverage additives as a preservative and flavouring agent, as well as pharmaceuticals and cosmetics. The annual value of production was valued at 1.26 billion US dollars in 2017 and will increase to 1.80 billion US dollars by 2023 exceeding 1.4 million tonnes.¹ Therefore, the large-scale and efficient production of acetaldehyde has become imperative and an extensive market prospect. The reaction routes of acetaldehyde production can be described as follows: 1) ethylene oxidation; 2) acetylene hydration; 3) acetic acid reduction; 4) ethane oxidation; 5) ethanol oxidation; and 6) ethanol dehydrogenation.

3.1.1 Ethylene oxidation

Most acetaldehyde is manufactured from ethylene oxidation, also called the Wacker process, in the presence of oxidizing agent (air or oxygen) over palladium chloride (PdCl₂) as shown in Scheme 3-1.² However, the substrate ethylene comes from fossil fuels by steam-cracking which is disharmony with the current renewable world target. Another drawback of this process is the toxic damage to the natural environment from the utilization of chloride-containing chemicals. Hence, the ethylene oxidation process should be improved to be environmentally friendly.

$$H_2C = CH_2 \xrightarrow{PdCl_2} H_3C \xrightarrow{O} H_3C$$

Scheme 3-1. Wacker process used to produce acetaldehyde via ethylene oxidation.

3.1.2 Acetylene hydration

In addition to the Wacker process, acetaldehyde can be produced from acetylene via a hydration reaction performed in the presence of a mercury complex (HgX_n) as the catalyst.³ The post-treatment of mercury complex is extremely difficult and dangerous to comply with environmental regulations. Even though many efforts have been devoted to discovering non-mercury processes like those using Cu-Zn catalysts,⁴ there remain some challenges, such as the short lifetime of the catalyst and low conversion of acetylene.

3.1.3 Acetic acid reduction

The reduction of acetic acid using hydrogen is another alternative method used to produce acetaldehyde. Vannice et al. investigated the catalytic performance of Fe in the acetic acid reduction process.⁵ The optimum acetaldehyde selectivity was ~80% with an acetic acid conversion of 40%. A very interesting result was that the acetaldehyde selectivity is only related to the H₂ pressure and independent of the acetic acid pressure. The mechanism of acetic acid reduction is explained by the L-H model (Chapter 1), which involves reactant adsorption and activation. Specifically, the H₂ atoms are adsorbed on the surface of the metallic Fe atoms and then form the activation intermediate, Fe:H. Meanwhile, acetic acid is adsorbed on the surface of the Fe oxide to form acetate-Fe oxidic species. The CH₃COO-FeO_x will further transform into an CH₃COO-FeO_x-H intermediate and then react with Fe:H to form CH₃CHO-FeO_x-OH and the initial Fe metallic phase. CH₃CHO-FeO_x-OH reacts with another Fe:H to produce CH₃CHO-FeO_x and H₂O (g). CH₃CHO-FeO_x will decompose into the target product, CH₃CHO, and initial Fe oxide.⁵ Several chemical equilibriums are involved in the aforementioned mechanism. They also investigated the reduction of acetic acid over Pt supported on a TiO₂ catalyst, which confirmed the major route for acetaldehyde production.⁶ The reaction takes place between the H atoms adsorbed on Pt and the acyl species on the TiO₂ support. It is similar to the abovementioned Fe-FeOx catalysts except for the different CH₃COOH related transition states. CH₃COOH is activated with the TiO₂ support to form a transition state acyl species (Figure 3-2).



Figure 3-2. Structure of the acyl species and acetate-FeO_x species.

The adsorbed H atoms on Pt are transferred to the acyl carbon and hydroxyl group to form $CH_3CH=O$ and generate H_2O , respectively. However, the generated acetaldehyde can be further hydrogenated to ethanol by the activated H atoms adsorbed on Pt.⁶ Acetic acid reduction is not widely used for acetaldehyde production because of the corrosive effects on the apparatus. The catalyst deactivation by the acetic acid vapour is the main restriction for the industrial-scale production of acetaldehyde via acetic acid reduction.

3.1.4 Ethane oxidation

Natural gas is a co-product of fossil fuel exploitation. The comprehensive and efficient utilization of both fossil fuel and natural gas are of significant interest for minimizing the use of these non-renewable resources. Natural gas is mainly composed of methane and ethane. Hence, acetaldehyde synthesis via ethane oxidation is one of the methodologies used. Kobayashi *et al.* have indicated that low loading bismuth (Bi) with isolated or well-dispersed species is critical for acetaldehyde production in the presence of caesium (Cs). Nevertheless, high loading Bi catalysts facilitate the deep oxidation of ethane. This can be ascribed to the addition of Cs improving the basicity that benefits the interactions formed between ethane and the catalyst.⁷ Wang *et al.* demonstrated the particle size distribution of molybdenum oxide has a significant impact on product selectivity.⁸ The MoO_x nanoparticles are found at a high loading Mo content and they improve the ethane conversion due to the sufficient amount of Mo active sites and higher reducibility, whereas the selectivity of acetaldehyde is much lower than those using highly dispersed MoO_x species catalysts. The cause for different catalytic performances should be assigned to the silica wall of SBA-15 collapse when the Mo loading increased, subsequently altering the selectivity of the acetaldehyde and formaldehyde products.⁸

3.1.5 Ethanol oxidation

As mentioned above, the drawbacks of the ethylene oxidation and acetylene hydration processes limit their industrial applications. Therefore, it becomes an urgent issue to discover a renewable starting material and non-toxic process for acetaldehyde production to achieve a sustainable society. Inspired by its chemical structure, scientists have come up with a novel method to produce acetaldehyde via ethanol dehydrogenation^{9–15} or partial oxidation.^{16–19} Moreover, ethanol is an environmentally friendly and economically feasible bio-derived substrate due to the fermentation approach using sugarcane and starch as starting materials. It can be regarded as the most promising chemical alternative to petroleum for producing acetaldehyde. Ethanol dehydrogenation and oxidation reactions have different catalytic mechanisms despite them both being assigned as gas-phase heterogeneous reaction processes. The major difference in these two reaction processes is with or without oxygen or air participation as the reactant.

In addition, utilizing oxygen in the ethanol conversion process can suppress the formation of carbon-material deposition, which is a major reason resulting in catalyst deactivation due to the decreasing of available metal sites. Moreover, the major issue to be addressed in ethanol oxidation is that excessive oxidation of ethanol will inevitably produce acetic acid, which corrodes the metal active sites in the catalysts even in trace amounts. The excess air or oxygen will lead to the complete oxidation of ethanol (Scheme 3-2), and thus, it has attracted attention.

 $C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O \quad \Delta H_R \cong -1280 \text{ KJ/mol}$

Scheme 3-2. Complete oxidation of ethanol.

Unlike the Wacker process that belongs to a homogeneous catalytic system, the reactions involving ethanol use heterogeneous catalysts, including metal-doped activated carbon,²⁰ Au supported on $ZnZrO_x^{10}$, and Ni-Cu alloys.¹⁴ Cu and Ag catalysts are widely used to produce acetaldehyde via ethanol dehydrogenation or oxidation.^{11,17,21,22} The abovementioned reaction mechanisms are described separately in the following parts.

Clarizia *et al.* have proposed that the oxidation process can be achieved in an aqueous ethanol solution in a photocatalytic system using a UV/Vis lamp.²³ However, the ethanol oxidation process normally takes place in a fixed-bed reactor rather than the batch reactor to obtain continuous acetaldehyde production. The ethanol substrate is preheated to the vapour phase, mixed with air/oxygen, and passed through the heterogeneous catalyst bed.

Cu catalysts have been extensively investigated in the ethanol oxidation process.^{16,18,23–26} Liu et al. investigated different M-Cu synergistic effects during ethanol oxidation to produce acetaldehyde (M = Ag, Pd, Pt, and Au). They found that Pt and Pd were active for C–C bond cleavage to produce undesired CO₂ because of their strong ability toward dehydrogenation, which results in low acetaldehyde selectivity at reaction temperatures higher than 200 °C. Cu⁰ and Ag⁰ are easier to oxidize and exhibit low activity toward the conversion of ethanol. Au shows the optimal catalytic performance among the aforementioned catalysts for both ethanol conversion and acetaldehyde selectivity due to the stable Au⁰–Cu⁺ synergy.²⁵ They speculated the mechanism of the Cu-Au catalyzed ethanol oxidation reaction.¹⁸ Cu⁺ species play a critical role during the ethanol oxidation process for oxygen activation, and Au also demonstrates a synergistic effect. The oxygen molecule is firstly activated to form O⁻ as Lewis base sites by Cu^+ sites. The newly generated O⁻ basic sites connect with Cu^+ to create a $Cu^{2+} \cdots O^-$ transition state, whereas it forms $O^- \cdots H$ with the hydroxy group of the ethanol molecule. Subsequently, the cleavage of original O-H bonds takes place to produce two intermediate species: Cu²⁺-OH and Au–O–CH₂–CH₃. Afterward, a C–H bond breaks in the –CH₂– generates an active H atom, and the separation of Au-alcoholate creates active Au. A new intermediate Au-H hydride is generated by their combination. Meanwhile, CH₃-CH=O is produced along with an Au-H hydride breaking away from Au–O–CH₂–CH₃. Finally, the previously formed Cu²⁺–OH can be reduced to Cu⁺ and H₂O by the H-Au hydride, which results in the regeneration of Cu⁺ and Au.¹⁸ Unlike the excellent catalytic performance of isolated Cu²⁺ to form acetaldehyde, Pavel *et al.* discovered that oligomeric vanadate complexes [VO_x]_n play a critical role in terms of ethanol oxidation. The reasons for the low catalytic activities of the mono-complex VO_x and multilayer VO_x results from the slow re-oxidation of VO_x and the collision of vanadium atoms inside the clusters with the reactants being difficult, respectively.²⁷ Silver is also a good candidate for ethanol oxidation due to the redox properties between the Ag_n^{δ+} cluster and Ag,¹⁰ which is similar to the aforementioned Cu²⁺–Au synergistic effect.¹⁸ However, the high cost of Ag catalysts is a limitation for its utilization on an industrial scale. More investigations are necessary to explore the use of non-noble metal catalysts to substitute Ag in order to meet industrial requirements.

3.1.6 Ethanol dehydrogenation

Ethanol dehydrogenation is a promising pathway to produce acetaldehyde and the coproduct hydrogen. Hydrogen gas is also produced simultaneously as a by-product of the ethanol dehydrogenation reaction used to form acetaldehyde. This has spurred researchers to produce hydrogen, which is a clean energy resource for fuel cells or vehicles that can reduce greenhouse gas emissions to obtain the target of being 'carbon neutralization'. Hydrogen can be produced via the partial oxidation of ethanol over Ru and Ni (Scheme 3-3).²⁸

$$2C_2H_5OH + O_2 \longrightarrow 4CO + 3H_2 \quad \Delta H_R \cong +20 \text{ KJ/mol}$$

Ethanol dehydration to ethylene/diethyl ether and dehydrogenation to acetaldehyde processes are competitive with each other via the catalyzation with Brønsted and Lewis acid. Some non-metallic materials possess both above acid sites, which means their utilization for the ethanol dehydrogenation process. The mechanism of ethanol dehydrogenation on the γ -Al₂O₃ surface proposed by Bhan *et al.* shows hydrogen transfer from the ethoxy species to the γ -Al₂O₃ surface. Ethanol is adsorbed on the γ -Al₂O₃ to form CH₃–CH₂–O: ethoxy and Al–O:H species. Subsequently, the adsorbed ethoxy species undergo cleavage of the C_a–H bond and the disconnected H associates with the γ -Al₂O₃ surface to form another Al–O:H species. Afterward, CH₃–CH=O is produced via separation from the γ -Al₂O₃ surface and H₂ is formed via rapid hydride transfer between two Al–O:H species. C_a–H bond cleavage has been identified as the rate-limitation step for acetaldehyde production.²⁹ In addition to non-metallic

material used as an ethanol dehydrogenation catalyst, a series of metal or metal oxides catalysts is applied to ethanol dehydrogenation, such as Mg,³⁰ Cu,^{11–13,21,22,31} Au,^{9,32} Zn,^{13,33,34} Ni,^{31,35} and V.³⁶ Meanwhile, metal alloys or bimetallic compounds are introduced into the ethanol dehydrogenation process to overcome the defects of mono-metal/metal oxide catalysts, such as their rapid deactivation.^{10,14,15,37}

Monometallic catalysts are attractive due to their simple preparation. Cu-based monometallic catalysts have been extensively investigated because they exhibit outstanding activity and acetaldehyde selectivity. The high selectivity can be attributed to the efficient C_{α} -H bond cleavage by Cu, which is the key factor for acetaldehyde production. In addition, Cu is incapable of C–C bond or C–O bond cleavage that will produce undesired by-products. A big challenge for monometallic Cu-based catalysts is their rapid deactivation after several hours due to the sintering of the Cu particles. A trace amount of Ni (from 0.1 to 1 wt.%) dispersed around the Cu particles can mitigate the deactivation issue and improve the catalyst stability. The reason for the low Ni loading is due to the atomic dispersion of Ni atoms rather than the formation of Ni clusters at high Ni loadings, in which the latter species will result in ethanol decomposition. The highly dispersed Ni atoms facilitate catalyst stability against Cu sintering.¹⁴ However, the intrinsic reason for Ni atom facilitation has still to be revealed and needs further research. Besides the addition of a trace amount of Ni to form Ni-Cu alloys to avoid Cu sintering, SiO₂ is also helpful toward suppressing Cu sintering via the formation of a Cu phyllosilicate phase, which is formed between the Cu crystallites and SiO₂. Another important cause of catalyst deactivation is coke formation, which leads to fewer Cu active sites being exposed to the substrate. A high Cu loading (10 wt.%) will weaken coke formation rather than a low Cu loading because the higher Cu loading catalyst still provides an abundant number of Cu particle sites for the reaction after coke deposition.¹² The high dispersion of Cu particles relies on an appropriate impregnation method or calcination temperature, but the stability is unsatisfactory based on the various reaction conditions because the Cu species are attached to the support via weak physical interactions or intermediates. Li et al. improved the Cu catalyst stability upon the insertion of Cu species into a zeolite framework to form a chemical bond interaction.²¹ The confined Cu is stabilized in the silanol defects created from the dealumination of zeolite (Figure 3-3) to suppress the agglomeration of Cu species. The chemical valence of various Cu species such as Cu²⁺, Cu⁺, and Cu⁰ arise due to the different number of silanol groups. They found that Cu²⁺ and Cu⁺ species worked well in the ethanol dehydrogenation process, whereas Cu⁰ was the main reason for catalyst deactivation. Cu²⁺ and Cu^+ increase the acetaldehyde selectivity and are reduced to Cu^0 nanoparticles in the presence

of the H_2 co-product. Cu⁰ nanoparticles are prone to agglomerate by sintering under high-temperature reaction conditions.²¹



Figure 3-3. Silanol defect in the dealumination of zeolite structure.

As described in the above work, the chemical state of Cu also plays a critical role in acetaldehyde production and there are diverse opinions on the active Cu sites, such as metallic Cu particles,^{12,38} Cu⁺ species,^{25,39} and Cu²⁺ species.²¹ Supported Au catalyst is also active in the process of ethanol dehydrogenation, and the DFT studies have provided theoretical insight into the ethanol dehydrogenation process from the viewpoint of the electron orbital overlap among the different chemical valences of Au-based catalysts. Limtrakul et al. investigated the orbital overlap geometries of Au and Au-O supported on ZSM-5 zeolites and found that the sorbital of Au and sp-orbital of the framework oxygen atoms overlap in Au/ZSM-5 to form an O···Au···O bond bridge, but the sp-orbital of surface O overlapped with Au orbital in Au-O/ZSM-5 zeolite.³² Electronegativity of the surface O atom is higher than the Au atom, which means the surface O atom can capture hydrogen (proton) from the ethanol O-H group to produce acetaldehyde. Therefore, the presence of surface O atoms in the Au-O/ZSM-5 improves ethanol conversion into CH₃-CH₂-O: ethoxide species, which subsequently dissociate to form acetaldehyde.³² We should be aware that the H dissociation process with the Au–O/ZSM-5 zeolite is completely different from the aforementioned C_a–H bond cleavage observed using Cu-based and γ -Al₂O₃ catalysts.



Figure 3-4. Optimised geometries and orbital overlap of Au/ZSM-5 and Au–O/ZSM-5. Adapted with permission from literature.³²

Theoretical calculations should agree with the experimental results to guide the synthesis of efficient catalysts. Flytzani-Stephanopoulos investigated the activity of an Au–O_x/ZnZrO_x catalyst during ethanol dehydrogenation at low temperatures. The atomic dispersed single Au cation boosts the conversion of ethanol,⁹ which confirmed the above theoretical calculations. Au-based catalysts have the same issue of sintering as Cu despite their high activity for acetaldehyde production. Inspired by Shan's work,¹⁴ Giannakakis *et al.* proposed the introduction of a small amount of Ni into Au catalysts to form NiAu alloys to resist Au sintering and improve the catalytic performance.⁴⁰ The Ni atoms are atomically dispersed on the Au surface to decrease the apparent activation energy, which facilitates the production of acetaldehyde. However, Ni clusters are formed at high Ni loadings and the catalytic performance is in agreement with Ni-Cu catalyst,¹⁴ leading to complete ethanol decomposition. The H₂ co-product pushes the Ni species (Ni²⁺ and Ni⁰) into the sub-surface region, but ethanol exhibits the ability to abstract sub-surface Ni to the Au surface and protects the NiAu alloy structure from Au sintering.⁴⁰

The high price of Au limits its large-scale utilization. Therefore, a relatively cheaper metal, Zn, has attracted increasing attention for use in the ethanol dehydrogenation process. Zn-based catalysts used for ethanol dehydrogenation are normally divided into two categories, the support^{9,11,15} or active site.^{13,33,34,37,41–44}

(1) ZnO as a support

Ouyang *et al.* have proposed that ZnO powder and alkali-treated ZnO nanoparticles affect the distribution of other active metal sites like Pd when ZnO is applied as the support. As described above, high loading of Pd (5 wt.%) is prone to form Pd cluster. Nevertheless, this situation changes with low loading of Pd (0.07 wt.%), which has two different sizes distributions. Isolated Pd atoms and Pd clusters are found on the ZnO nanoparticles and ZnO powder support, respectively.¹⁵ The reason for low loading Pd still forming Pd clusters is that there are fewer defects in conventional ZnO powder than alkali-treated ZnO nanoparticles. The abundant defects in alkali-treated ZnO nanoparticles force the Pd atoms to be isolated from each other. The distribution of the Pd species has a significant effect on the ethanol conversion pathway. Isolated Pd atoms facilitate acetaldehyde production, while contiguous Pd sites lead to C–C bond scission to form CO and CH₄. This gives guidance for isolated active metal site formation due to the highly defective support. The defects in the support not only anchor the metal active sites to the isolated form but also keep the active sites from agglomeration or sintering.

In general, the Brønsted acidic sites should be passivated to improve the ethanol dehydrogenation process to form acetaldehyde. Otherwise, the strong Brønsted sites lead to ethanol dehydration to ethylene and diethyl ether. The special complex composite ZnZrOx acts as excellent support for the Au impregnated catalyst to give high selectivity for acetaldehyde production. ZnO can not only incorporate ZrO₂ to modulate the acidity but can also form a composite with Al₂O₃ to form ZnAl₂O₄ as the catalyst³⁴ or act as a support for the Cu-based catalyst¹¹ during the ethanol dehydrogenation process. The Lewis acidity of ZnAl₂O₄ composite without any other metals can also convert ethanol into acetaldehyde but lacks selectivity.³⁴ It should be noted that ZnAl₂O₄ also possesses dehydration ability that results in undesired by-products, such as ethylene and diethyl ether, and Cu is necessary to passivate the acidity of the ZnAl₂O₄ support to improve the selectivity toward acetaldehyde. The Zn species are not uniformly distributed in the ZnAl₂O₄ support. Therefore, the ZnAl₂O₄ support is composed of a poor-Zn region $[Zn_x O \cdot Al_2 O_3]^-$ (x <1) and rich-Zn region $[Zn_x O \cdot Al_2 O_3]^+$ (x >1). The poor-Zn region has a higher electron density than the rich-Zn region, and the poor-Zn area can reduce the CuO to form Cu metal particles. The Cu metal species can suppress the formation of coke and the coke is then prone to deposit next to the normal ZnO·Al₂O₃ and $[Zn_xO \cdot Al_2O_3]^+$ (x >1) regions with highly dispersed CuO.¹¹ As described previously, the Lewis acidity of single ZnAl₂O₄ can convert ethanol into acetaldehyde at the Al₂O₃ sites and the Zn_xO

sites can dehydrate ethanol to form ethylene. These dehydration and dehydrogenation processes occur simultaneously and compete with each other at different reaction temperatures. (2) Zn(O) as the active sites

Pure ZnO can also be used as a catalyst for ethanol dehydrogenation,⁴⁵ but the produced acetaldehyde will easily be over-converted to acetone because of the Zn–O–Zn structure in the ZnO crystal, which shows low catalytic activity below 400 °C.^{34,46} Therefore, ZnO should be modified by impregnating on a support⁴¹ or coupling with other metal compositions 9,34,44 to improve the selectivity toward acetaldehyde. Miyake et al. studied the reaction pathway for ethanol dehydrogenation to form acetaldehyde over a ZnO/SiO₂ catalyst and found that the α-H and H atom in the hydroxy group interact with the two adjacent O atoms in the O-Zn-O-Zn–O catalyst to form a new C_{α} –O–H···O–Zn–O···H– C_{α} transition state and the ratedetermination step was the dissociation of the O–H and H– C_{α} bonds. Then, CH₃–CH=O and H₂ derived from H···O-Zn-O···H are generated and desorbed from the O-Zn-O catalyst surface.¹³ Seker investigated sol-gel prepared SiO₂-supported ZnO-catalysts with different ZnO loadings (up to 50 wt.%) used for bio-ethanol reforming. The crystallite size of ZnO has an impact on the ethanol reforming activity rather than the basic site density, and the overconverted acetone product was only formed with ZnO crystallite sizes larger than 5 nm. The highly dispersed ZnO crystallite preferred to produce acetaldehyde via ethanol dehydrogenation.46

Taylor *et al.* investigated mordenite (MOR) as a support for a ZnO impregnated catalyst and found that alkali cation-exchanged mordenite showed high activity for acetaldehyde production. ZnO/Rb-MOR exhibited the optimum catalytic activity with an acetaldehyde selectivity of >90% and an ethanol conversion of 40% among the different counter cations (Na, K, Rb, and Cs) zeolite catalysts studied. The high activity was attributed to the low level of carbon deposition formed during the reaction.⁴⁷ However, the intrinsic synergistic effect between the counter cations and ethanol molecules is still unclear and needs further research. ZnMO_x composites (M = Al, Zr, Cu, Pt, Co, and Ag) not only work as supports^{9,11} for other transition metal impregnated catalysts but also act as active sites^{44,48,49} for ethanol conversion to form acetaldehyde. Most research focuses on the catalytic activity of ZnMO_x composites rather than monometallic Zn-containing catalysts during the ethanol dehydrogenation to acetaldehyde process.

3.1.7 Support

The support is of great importance to maintain the catalyst structure and suppress the active sites from sintering or agglomeration. Moreover, the Lewis-Brønsted acidity equilibrium, pore size distribution, and porous structure of the support also play critical roles in the selectivity toward acetaldehyde by suppressing the polymerization products and coke formation that result in rapid inactivation of the catalyst. Many supports have been investigated in the ethanol dehydrogenation process, such as SiO₂,^{13,30,41} zeolite,^{42,50} metal oxide,¹⁵ and their composites.^{11,34} Matsumura *et al.* found that Silicalite-1 can be utilized as the catalyst for ethanol dehydrogenation to form acetaldehyde. The active sites are regarded as the active oxygen bridge in the -Si-O-CH₂-CH₃ structure, which is responsible for the dissociative adsorption of ethanol. Ethanol can be adsorbed by the silanol group (–Si-OH) that is located in the defect center of the zeolite framework to form the -Si-O-CH₂-CH₃ active oxygen bridge. However, the trace amount of isolated silanol groups in the zeolite framework means the zeolite contains strong acid sites where the dehydration process occurs.⁵¹ Therefore, it is worthwhile to investigate the different Zn-containing MFI zeolites catalysts in the ethanol dehydrogenation process.

Herein, we report several monometallic Zn-supported catalysts using different MFI structured zeolites used for ethanol dehydrogenation to form acetaldehyde, such as Zn/ZSM-5, Zn/Silicalite-1, Zn-MFI, and Zn/DeAlZSM-5. The influence of the zeolite support and Zn active sites in different positions have been investigated.

3.2 Experimental

3.2.1 Materials

Tetrapropylammonium hydroxide solution (TPAOH, 1.0 M in H₂O), tetraethyl orthosilicate (TEOS, \geq 99.0% (GC)), sodium aluminate (NaAlO₂), Ludox AS40 (40 wt.% suspension in H₂O), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 98%), zinc sulfate heptahydrate (ZnSO₄·7H₂O, \geq 98%), lithium hydroxide monohydrate (LiOH·H₂O, \geq 98%), ethylene (\geq 99.5%), and acetaldehyde (\geq 99.5%) were obtained from Sigma-Aldrich. Ethanol (\geq 99.6%) was obtained from VWR. The commercial zeolite NH₄-ZSM-5 (CBV 28014, SiO₂/Al₂O₃ = 280 and Si/Al = 140) was purchased from Zeolyst in its ammonium form.

3.2.2 Zeolite synthesis

MFI-type zeolites, including Silicalite-1, ZSM-5, and Zn-MFI, have been applied as the support (Silicalite-1 and ZSM-5) or Zn-containing catalyst (Zn-MFI) during the evaluation of

the ethanol dehydrogenation process to form acetaldehyde. Zn was impregnated on the zeolites as active sites except for Zn-MFI zeolite, and the bare zeolite supports used as reference catalysts.

Silicalite-1 zeolite was synthesized according to previously-reported methods.^{52,53} In brief, TEOS (4.47 mL) was added into TPAOH solution (7.24 mL) in a small Teflon beaker. The small Teflon beaker was transferred into a big Teflon-lined autoclave and deionized water (15 mL) was filled in the gap between the small Teflon beaker and big Teflon-lining for steam-assisted synthesis. Subsequently, the temperature of the sealed autoclave was kept at 180 °C for crystallization. The autoclave was subsequently quenched in water after 72 h and solid matter was collected through the Büchner funnel. The solid matter was cleaned with deionized water until the filtrate was neutral. The residue was dried at 80 °C overnight to get rid of the remaining moisture. Finally, the Silicalite-1 zeolite was obtained via calcination of the asobtained solid at 550 °C for 20 h with 4 h of temperature ramping.

ZSM-5 zeolites are divided into two types based on their different counter ions: Na-ZSM-5 and H-ZSM-5 zeolites.

The Na-ZSM-5 zeolite was synthesized using our group's previously-reported procedure.⁵⁴ It is similar to the Silicatlite-1 synthesis with the exception of the addition of NaAlO₂ (0.016 g) into TPAOH solution with stirring until completely dissolved. The subsequent procedure was the same as that used in the Silicalite-1 synthesis. The obtained white powder was denoted as Na-ZSM-5 zeolite with a molar ratio of SiO₂/Al₂O₃ = 280.

H-ZSM-5 zeolite was synthesized from commercially available NH₄-ZSM-5 calcined at 550 °C for 4 h under a static air atmosphere and the molar ratio of SiO_2/Al_2O_3 was 280.

The Zn-MFI zeolite was prepared according to a patent of British Petroleum (BP).^{55,56} In brief, ZnSO₄·7H₂O (1.93 g) was added into deionized water (5.0 g), followed by the dropwise addition of an ammonia solution with stirring. The resulting precipitate was washed and mixed with NaOH (0.85 g) and H₂O (18.0 g). Thereafter, TPAOH (10.5 mL) and Ludox AS40 (15.02 g) were introduced into the above mixture to form a gel. The formed gel was transferred in an autoclave and kept at 175 °C for 4 d. The solid substance was washed with deionized water via the Büchner funnel and dried at 80 °C for 12 h. Finally, the Zn-MFI zeolite was achieved after calcination at 550 °C for 18 h.

3.2.3 Zn-containing zeolite catalyst synthesis

Zn/Silicalite-1 zeolite was obtained using an incipient wetness impregnation method using Silicalite-1 as the support. In brief, Silicalite-1 (0.95 g) was placed in the vacuuming oven overnight to remove the remaining moisture prior to the impregnation step. $Zn(NO_3)_2 \cdot 6H_2O$ (0.232 g) was dissolved in a specific volume of water (based on the pore volume obtained from nitrogen physisorption) to form a colorless Zn precursor solution, and it was added to Silicalite-1 zeolite with fierce stirring. The Zn-impregnated zeolite was dried at 80 °C overnight prior to the calcination at 550 °C for 4 h with 4 h temperature ramping to decompose the $Zn(NO_3)_2$, and final 5 wt.% Zn/Silicalite-1 was obtained.

The Zn/ZSM-5 zeolite has two forms in this chapter with different counter ions: Zn/Na-ZSM-5 and Zn/H-ZSM-5. Both of them were obtained using the same incipient wetness impregnation method as Zn/Silicalite-1 zeolite.

3.2.4 Catalyst characterization

XRD patterns of as-synthesized zeolite catalysts were recorded employing the Cu-K α irradiation from a focused quartz monochromator in the 2 θ range of 3–55°.

 N_2 physisorption measurements were performed at 77 K on Micromeritics 3 FLEX equipment. The zeolites were outgassed at 400 °C before measurement. The total surface area was calculated according to the BET method. The micropore volume was determined using the *t*-plot method. The total pore volume was determined using single-point adsorption at $p/p^\circ = 0.95$. The pore size distribution was obtained using the BJH method (desorption branch).

X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fischer Scientific K-AlphaTM equipped with a monochromated Al K α X-ray source. The analysis was performed at ~2 × 10⁻⁹ mbar. The spectra were recorded in 0.1 eV steps with a pass energy of 50 eV and a spot size of 400 mm. Then, 50 scans were performed for elemental analysis.

SEM was performed on a Quanta 200 ESEM FEG instrument operated at 10 kV with the calcined zeolite samples placed on a carbon film. The samples were coated with gold for 5 s.

3.2.5 Catalyst test

All zeolite catalysts were fractionated into a particle size range of $180-355 \ \mu m$ prior to packing into the quartz tube reactor (Figure 3-5). The length of the quartz tube reactor was 36 mm with inner and external of 4 and 6 mm, respectively. Further, 150 mg of catalyst was mounted in the quartz reactor and two layers of silica wool were before and after the catalyst

bed. The carrier gas of the fixed-bed setup was selected as N_2 at a gas flow of 50 mL/min. The system was purged with N_2 for 30 min prior to the addition of ethanol to remove the remaining air. Subsequently, ethanol was introduced into the reactor using a micropump at a liquid flow of 0.05 mL/min. Furthermore, the aqueous ethanol should be preheated to the vapor phase in a vaporizer at 190 °C together with N_2 prior to passing through the quartz reactor with the catalyst. The initial ethanol peak area was determined through a bypass route and directly injected into the GC without any reaction.



Figure 3-5. Block schematic of the fixed-bed apparatus used for catalyst evaluation.

All products were quantified using an online continuous auto-injection gas chromatography instrument. The response signal of different chemicals was recorded via a flame ionization detector. The chromatography column used for the separation of the products was a DB-1 non-polar column. The temperature ramping programme was kept at 80 °C for 2 min from the beginning, following a 10 °C/min temperature ramping to 200 °C for 5 min. The retention time of the different products was determined using individual standard chemicals. Online GC analysis was started after 30 mins of ethanol pumping and passing through the catalyst to obtain a steady-state and the reaction temperature was maintained at the desired temperature until three GC analyses were completed to eliminate the accidental error and airflow disturbance. The conversion of ethanol was calculated using Equation 3-1.

$$Conversion_{EtOH}(\%) = \frac{Peak area_{initial} - Peak area_{remained}}{Peak area_{initial}} \times 100$$
(Equation 3-1)

where Peak area_{initial} and Peak area_{remained} represent the ethanol peak areas before and after the reaction.

The products involved in the ethanol dehydrogenation reaction were selected from the literature, including acetaldehyde, ethylene, diethyl ether, acetone, and hydrogen. Since ethylene is always produced as the co-product in the ethanol dehydrogenation reaction, it is

difficult to use different molar concentrations of standard ethylene gas to obtain the calibration curve. There is only a pure standard ethylene gas sample commercially available from Sigma-Aldrich and other suppliers. Therefore, it is reasonable to use the carbon number of each product to calculate the selectivity instead of the direct molar amount obtained from the calibration curve. Special attention should be paid to the carbon atom selectivity and molar selectivity because they are not always equal.

The FID response of the hydrocarbon compound is related to the number of carbon atoms $(N_{C \text{ atoms}})$, which means the peak area divided by $N_{C \text{ atoms}}$ is proportional to the molar amount. If a mixture gas sample has the same molar amount of pentane (C_5H_{12}) , hexene (C_6H_{12}) , and octyne (C_8H_{14}), then the relative peak area will be 5:6:8. However, the peak area from the GC-FID detector is not proportional to the carbon number of each compound, if it is in the presence of heteroatoms such as S, O, and N, and carbonyl groups. Therefore, it is inaccurate to count all the carbon atoms contributing to the peak area. The concept of effective carbon number (ECN) was first invented by Sternberg et al. in the 1960s to investigate the relationship between peak area and the number of carbon atoms.⁵⁷ The ECN describes how many carbon atoms per molecule participate in the detector response and can be calculated if the structure is known. As mentioned above, for pure hydrocarbons, the relative response of the FID only depends on the number of carbon atoms. Carbonyl and aldehyde groups do not contribute to the FID detector response and the ECN is one less than the total carbon number. During the conversion of ethanol into acetaldehyde, the oxygen atom connects with carbon via a single bond (σ bond) to form diethyl ether and the ECN was then calculated as the total carbon number minus 0.5; if the oxygen atom connects with carbon via a double bond (σ and π bond) to form acetaldehyde, the ECN was calculated as the total carbon number minus 1. Table 3-1 shows the different ECN of each compound related to the conversion of ethanol into acetaldehyde according to the aforementioned rules.

Table 3-1 The effect of the	carbon number	of related	compounds in	this project

00

Compound	Ethanol	Acetaldehyde	Ethylene	1,3-Butadiene	Acetic acid	Diethyl ether	
ECN	1.5	1	2	4	1	3	

Therefore, the carbon-atom-based selectivity value was different from the molar concentration-based selectivity because of the different $N_{C \ atoms}$ in each compound at the same molar concentration. The peak area of each compound was proportional to the $N_{C \ atoms}$ in its structure.

Selectivity_{product i} (C atom%) =
$$\frac{\frac{\frac{Peak \, area_{product i}}{ECN} \times Carbon \, atoms_{product i}}}{\sum_{i=1}^{n} \left(\frac{\frac{Peak \, area_{product i}}{ECN} \times Carbon \, atoms_{product i}}{ECN}\right) \times 100\%$$
(Equation 3-2)

where the $\frac{Peak \, area_{product \, i}}{ECN}$ means the peak area contributed from each effective carbon atom of product i.

$$Peak \ area_{product \ i} = k \times ECN_{product \ i} \times n_{product \ i}$$
(Equation 3-3)

where $n_{\text{product i}}$ is the molar amount of product i, and *k* is the coefficient of peak area, molar amount, and ECN. The coefficient *k* is a fixed constant for all products from the above example of pentane to octyne (C₅-C₈).

3.3 Results and discussion

3.3.1 Characterizations

Nitrogen physisorption



Figure 3-6. N₂ absorption–desorption isotherms of Silicalite-1 (top left), Na-ZSM-5 (top right), H-ZSM-5 (bottom left), and Zn-MFI (bottom right).

The physisorption isotherms shown in Figure 3-6 exhibit typical Type-I (top right) and Type-IV (top left, bottom left, and right) isotherms. While Na-ZSM-5 mainly contains

micropores, the significant hysteresis loops in the Silicalite-1, H-ZSM-5, and Zn-MFI isotherms also reveal a mesoporous structure. We can ascribe the small hysteresis loop at p/p^0 = 0.17 in the H-ZSM-5 zeolite isotherm to a fluid-to-crystal-like phase transition typically observed in MFI zeolites.⁵²





Figure 3-7. XRD patterns obtained for the as-prepared Zn-contained zeolites.

Figure 3-7 shows the XRD patterns obtained for the Zn-impregnated and Zn-incorporated zeolites. As expected, the four XRD patterns are consistent with the MFI structure with peaks at 20 degrees of 7.8, 8.9, 23.1, and 23.9° .^{58,59} The XRD pattern of Zn-MFI shows a significant decrease in intensity, indicating that the incorporation of Zn in the zeolite framework decreases the crystallinity. In contrast, the impregnation of zinc species has little effect on MFI zeolites. In general, we only observed a small peak from bulk ZnO at $2\theta = 36.3^{\circ}$ in the 5%Zn/Na-ZSM-5 sample (JCPDS Card No. 65-3411). We speculate that this peak may originate from the relatively small amount of ZnO crystalline particles present in the mesopores or on the surface of Na-ZSM-5. In general, the relatively weak peak from ZnO indicates the high dispersion of Zn species. The peak attributed to ZnO crystal is observed in the XRD pattern of 5%Zn/Silicalite-1 as well.



Figure 3-8. XPS spectra obtained for the as-prepared Zn-containing zeolites at the Zn2p level.

Figure 3-8 shows the XPS analysis of the Zn-modified zeolites at the Zn2p level. In general, the intensity of the Zn-MFI was significantly lower than that of the Zn-impregnated catalysts. We can attribute this observation to the successful embedding of Zn in the zeolite skeleton and resulting in a low Zn amount on the external surface. The fitting curve of the Zn XPS spectra at ~1045 eV and the satellite peak at 1049.2 eV (which only exists in 5%Zn/H-ZSM-5) belong to Zn 2p_{1/2}. Meanwhile, the two fitting peaks of Zn 2p_{3/2} spectra with binding energies at 1022.6 and 1025.8 eV were assigned to the ZnO (Zn-O bond) and [ZnOZn]²⁺ species, respectively.^{60,61} The presence of [ZnOZn]²⁺ species in 5%Zn/H-ZSM-5 was attributed to the tighter interactions formed with the parent zeolite framework. The [ZnOZn]²⁺ species were generated via the dehydration of two [ZnOH]⁺ species and the [ZnOH]⁺ species were generated from the combination of ZnO and protons at the Brønsted acid sites.⁶⁰ The fitting peaks with binding energies at 1021.1 (5%Zn/Silicalite-1) and 1021.3 eV (5%Zn/Na-ZSM-5) were assigned to the ZnO clusters, which are dispersed outside of the zeolites. Furthermore, the Zn 2p_{1/2} peak at a binding energy of ~1044.5 eV observed in all of the catalysts suggest the presence of [ZnOH]⁺ species.⁴³

SEM


Figure 3-9. SEM images of the as-synthesized zeolite catalysts.

Figure 3-9 shows the morphologies of various MFI-type zeolites. SEM analysis shows that the as-prepared zeolites are highly crystalline. The well-defined terraces of Zn-MFI have a polycrystalline spherical morphology and hierarchical structure, which was different from Silicalite-1 and ZSM-5 zeolites. The hierarchical flakes of Zn-MFI demonstrate the Zn component in the zeolite system affects the crystal growth process, which favors the formation of nanocrystals.⁴³ The coffin-shaped Silicalite-1 and ZSM-5 zeolites exhibit cuboid morphologies, which is the typical shape for MFI synthesized using TPAOH as the structure-directing agent.^{53,62}

3.3.2 Catalytic performance



Figure 3-10. Conversion and selectivity observed for the catalytic dehydrogenation of ethanol over pure ZnO, 5%Zn/Silicalite-1, Zn, and Silicalite-1.

Figure 3-10 gives the conversion and selectivity observed for the catalytic dehydrogenation of ethanol over pure ZnO and Zn (upper left and bottom left). While pure Zn was completely inactive even at high temperature (Figure 3-10, bottom left), pure ZnO results in some catalytic conversion and selectivity toward acetaldehyde. When compared to pure ZnO, the zeolite-supported ZnO-catalysts result in significantly higher selectivity toward either ethylene or acetaldehyde. While pure Silicalite-1 exhibits no catalytic activity and mainly resulted in small amounts of ethylene, 5%Zn/Silicalite-1 results in a conversion of 11–55% and selectivity of >95% between 300 and 400 °C. In general, the selectivity slightly decreased at temperatures above 360 °C, although the competing selectivity toward ethylene remained at all temperatures studied. When compared to the poor catalytic properties of pure Silicalite-1, the data confirmed

that Zn was responsible for the high catalytic activity. Furthermore, we noted that the weakly acidic silanol groups in Silicalite-1 may be responsible for the dehydration of ethanol, which results in the formation of the main by-products ethylene and diethyl ether. In general, we observed more diethyl ether at lower temperatures and more ethylene at higher temperatures. The equilibrium between intermolecular and intramolecular dehydration at different temperatures was also in good agreement with the previous thermodynamic calculations.¹¹



Figure 3-11. Conversion and selectivity observed for the catalytic dehydrogenation of ethanol over Zn/H-ZSM-5, Zn/Na-ZSM5, H-ZSM-5, and Na-ZSM-5.

To investigate the catalytic effect of the acidity of ZSM-5 zeolite support bearing different counter ions, which differ in the aforementioned Silicalite-1 zeolite catalyst, we also prepared a series of Zn-containing catalysts supported on a highly acidic MFI zeolite (H-ZSM-5). Figure 3-11 shows the catalytic conversion and selectivity observed for Zn/H-ZSM-5 and H-ZSM-5, respectively. As expected, this catalyst results in the high conversion of ethanol, but a complete

change in the selectivity toward the dehydration products, particularly ethylene. Ethylene was the main product observed in pure H-ZSM-5 and Zn/H-ZSM-5 catalysts. These results may be explained by the high acidity of ZSM-5 in its proton form, which easily facilitates the acidcatalyzed dehydration of ethanol into ethylene. When compared to pure H-ZSM-5, the 5%Zn/H-ZSM-5 results in slightly lower conversion and slightly higher selectivity toward acetaldehyde. We speculate that this observation can be explained by the formation of $[ZnOH]^+$ species, which decrease the acidity and have some catalytic activity toward dehydrogenation. The formation of [ZnOH]⁺ was consistent with the higher binding energy peak observed in our XPS analysis shown in Figure 3-8. However, ZnO was the main Zn component in the Na-form of ZSM-5 and has an entirely different product distribution when compared to the proton form of ZSM-5. For comparison, pure Na-ZSM-5 only results in the limited conversion of ethanol and primarily dehydration products, including both diethyl ether and ethylene. Over 5% Zn/Na-ZSM-5, the conversion increases and product selectivity shifts toward acetaldehyde. This confirmed that the ZnO particles play a critical role in ethanol dehydrogenation. When compared to 5%Zn/Silicalite-1, we observed a slightly lower selectivity due to an increased formation of 1,3-butadiene. Interestingly, this indicates that the Zn-loaded and Na-exchanged zeolite has multiple active sites that can catalyze the direct production of 1,3-butadiene from ethanol. This process is believed to involve several consecutive steps, including: 1) the dehydrogenation of ethanol, 2) an aldol condensation of generated acetaldehyde to acetaldol, 3) dehydration of produced acetaldol to crotonaldehyde, 4) Meerwein-Ponndorf-Verley (MPV) reduction into crotyl alcohol, and 5) dehydration into 1,3-butadiene.



Figure 3-12 The conversion and selectivity observed for the catalytic dehydrogenation of ethanol over 5%Zn-MFI.

To further investigate the catalytic activity of intrinsical property of Zn sites, we also prepared a Zn-based zeolite, in which Zn was incorporated in the MFI framework during the hydrothermal synthesis as previously disclosed by BP.⁵⁶ Although the as-prepared Zn-MFI catalyst only results in <15% conversion, the selectivity toward acetaldehyde was almost 100%. At 400 °C, we started to observe small amounts of ethylene. When compared to 5%Zn/Silicalite-1, the 5%Zn-MFI catalyst results in significantly lower conversion, indicating that the framework Zn has lower catalytic activity than the supported ZnO. In contrast, the high selectivity indicates that the direct incorporation of Zn may result in fewer acidic silanol groups that cause the formation of dehydration products.

3.3.3 Zeolite support modification via dealumination

Another method for the post-synthesis of Zn-containing zeolite catalysts is the incorporation of Zn in the silanol nest of dealuminated Na-ZSM-5 zeolite. The details of the dealumination and Zn incorporation processes can be found in the literature.^{42,63,64} The Zn site was confined in the framework of the zeolite structure within the four silanol groups, as shown in Figure 3-13 (left).



Figure 3-13. Zn single site in the zeolite framework (left) and conversion and selectivity observed for the catalytic dehydrogenation of ethanol over 5% Zn/DeAlNaZSM-5 (right).

The results obtained for Zn/DeAlNaZSM-5 are shown in Figure 3-13 and the distribution of the products was significantly different when compared to the Zn-MFI zeolite catalyst shown in Figure 3-12. The selectivity toward ethylene reaches 98% and only a small amount of acetaldehyde (~1%) was produced. This is the reverse situation when compared to Zn-MFI zeolite catalysts, in which acetaldehyde is the dominant product. The conversion of Zn/DeAlNaZSM-5 reaches 100% except at 300 °C. Therefore, the dealumination of Na-ZSM-5 zeolite provides zeolite with much stronger Brønsted acidity, which facilitates the ethanol

dehydration process and inhibits the dehydrogenation process. The H⁺ inside of the ZSM-5 zeolite originates from the ionic exchange of concentrated HNO₃ solution during the dealumination process. In addition, the strong Brønsted acidity of ZSM-5 zeolite results in the low activity of the active framework Zn sites. The very low selectivity of acetaldehyde also confirmed that the active framework Zn sites were not as active as ZnO particles. This was in good agreement with the catalytic activity observed for the Zn-MFI zeolite catalyst. The dehydration process has the priority for the parallel reactions of ethanol dehydration and dehydrogenation.

3.4 Conclusions

We have demonstrated that ZnO supported on Silicalite-1 and Na-ZSM-5 are effective catalysts for the dehydration of ethanol at temperatures between 300 and 400 °C. In contrast, ZnO supported on the acidic proton form of H-ZSM-5 catalyzes the dehydration of ethanol, which results in the formation of ethylene. This reaction is not only catalyzed by the strongly acidic Al sites but also by the less acidic silanol groups. Therefore, 5% Zn/Silicalite-1 resulted in the highest productivity, reaching 65% conversion and 95% selectivity at 400 °C. Finally, we compared the catalytic performance of pure Na-ZSM-5 and Zn/ZSM-5 zeolite catalysts, which demonstrate entirely different reaction processes of dehydration and dehydrogenation, respectively. The different preparation procedures used for Zn-containing zeolites show that several Zn species may be active for the catalytic reaction, although ZnO appears to be the most active component.

3.5 References

- Acetaldehyde Market Trends, Global Industry Analysts Inc., Strategy.Com/ MarketResearch/Acetaldehyde-Ethanal-Market-Trends.Asp.; 2016. Accessed on 21st January 2022
- (2) Barthos, R.; Drotár, E.; Szegedi, Á.; Valyon, J. Wacker Oxidation of Ethylene over Vanadia Nanotube Supported Pd Catalysts. *Mater. Res. Bull.* 2012, 47 (12), 4452–4456.
- Ponomarev, D. A.; Shevchenko, S. M. Hydration of Acetylene: A 125th Anniversary. J. Chem. Educ. 2007, 84 (10), 1725.
- (4) Yang, L.; Xiao, F.; Zhang, Q.; Xu, C.; Dai, B. Non-Mercury Catalytic Acetylene Hydration over Bimetallic Cu–Zn Catalysts for Acetaldehyde Production in Gas-Liquid System. *ChemistrySelect* 2019, *4* (24), 7096–7101.
- (5) Rachmady, W.; Vannice, M. A. Acetic Acid Reduction to Acetaldehyde over Iron Catalysts. I. Kinetic Behavior. J. Catal. 2002, 208 (1), 158–169.
- (6) Rachmady, W.; Vannice, M. A. Acetic Acid Reduction by H2 over Supported Pt Catalysts: A DRIFTS and TPD/TPR Study. J. Catal. 2002, 207 (2), 317–330.
- (7) Zhao, Z.; Kobayashi, T. Partial Oxidation of Ethane into Acetaldehyde and Acrolein by Oxygen over Silica-Supported Bismuth Catalysts. *Appl. Catal. A Gen.* 2001, 207 (1–2), 139–149.
- (8) Lou, Y.; Wang, H.; Zhang, Q.; Wang, Y. SBA-15-Supported Molybdenum Oxides as Efficient Catalysts for Selective Oxidation of Ethane to Formaldehyde and Acetaldehyde by Oxygen. J. Catal. 2007, 247 (2), 245–255.
- Wang, C.; Garbarino, G.; Allard, L. F.; Wilson, F.; Busca, G.; Flytzani-Stephanopoulos,
 M. Low-Temperature Dehydrogenation of Ethanol on Atomically Dispersed Gold
 Supported on ZnZrOx. ACS Catal. 2016, 6 (1), 210–218.
- (10) Mukda, N.; Autthanit, C.; Praserthdam, P.; Jongsomjit, B. Production of Acetaldehyde via Oxidative Dehydrogenation of Ethanol over AgLi/SiO2 Catalysts. *Bull. Chem. React. Eng. Catal.* **2020**, *15* (3), 714–725.
- (11) Garbarino, G.; Riani, P.; Villa García, M.; Finocchio, E.; Sanchez Escribano, V.; Busca,
 G. A Study of Ethanol Dehydrogenation to Acetaldehyde over Copper/Zinc Aluminate
 Catalysts. *Catal. Today* 2020, *354*, 167–175.

- (12) Zhang, H.; Tan, H. R.; Jaenicke, S.; Chuah, G. K. Highly Efficient and Robust Cu Catalyst for Non-Oxidative Dehydrogenation of Ethanol to Acetaldehyde and Hydrogen. *J. Catal.* 2020, *389*, 19–28.
- (13) Ohira, M.; Liu, H.; He, D.; Hirata, Y.; Sano, M.; Suzuki, T.; Miyake, T. Catalytic Performance and Reaction Pathways of Cu/SiO2 and ZnO/SiO2 for Dehydrogenation of Ethanol to Acetaldehyde. *J. Jpn. Pet. Inst.* **2018**, *61* (4), 205–212.
- (14) Shan, J.; Janvelyan, N.; Li, H.; Liu, J.; Egle, T. M.; Ye, J.; Biener, M. M.; Biener, J.; Friend, C. M.; Flytzani-Stephanopoulos, M. Selective Non-Oxidative Dehydrogenation of Ethanol to Acetaldehyde and Hydrogen on Highly Dilute NiCu Alloys. *Appl. Catal. B Environ.* 2017, 205, 541–550.
- (15) Ouyang, M.; Cao, S.; Yang, S.; Li, M.; Flytzani-Stephanopoulos, M. Atomically Dispersed Pd Supported on Zinc Oxide for Selective Nonoxidative Ethanol Dehydrogenation. *Ind. Eng. Chem. Res.* **2020**, *59* (6), 2648–2656.
- (16) Redina, E. A.; Greish, A. A.; Mishin, I. V.; Kapustin, G. I.; Tkachenko, O. P.; Kirichenko, O. A.; Kustov, L. M. Selective Oxidation of Ethanol to Acetaldehyde over Au-Cu Catalysts Prepared by a Redox Method. *Catal. Today* **2015**, *241*, 246–254.
- (17) Xu, J.; Xu, X. C.; Yang, X. J.; Han, Y. F. Silver/Hydroxyapatite Foam as a Highly Selective Catalyst for Acetaldehyde Production via Ethanol Oxidation. *Catal. Today* 2016, 276, 19–27.
- Liu, P.; Hensen, E. J. M. Highly Efficient and Robust Au/MgCuCr2O4 Catalyst for Gas-Phase Oxidation of Ethanol to Acetaldehyde. *J. Am. Chem. Soc.* 2013, *135* (38), 14032– 14035.
- (19) Guan, Y.; Hensen, E. J. M. Selective Oxidation of Ethanol to Acetaldehyde by Au-Ir Catalysts. J. Catal. 2013, 305, 135–145.
- (20) Ob-Eye, J.; Praserthdam, P.; Jongsomjit, B. Dehydrogenation of Ethanol to Acetaldehyde over Different Metals Supported on Carbon Catalysts. *Catalysts* 2019, 9 (1).
- Yu, D.; Dai, W.; Wu, G.; Guan, N.; Li, L. Stabilizing Copper Species Using Zeolite for Ethanol Catalytic Dehydrogenation to Acetaldehyde. *Chin. J. Catal.* 2019, 40 (9), 1375– 1384.
- (22) Hanukovich, S.; Dang, A.; Christopher, P. Influence of Metal Oxide Support Acid Sites

on Cu-Catalyzed Nonoxidative Dehydrogenation of Ethanol to Acetaldehyde. *ACS Catal.* **2019**, *9* (4), 3537–3550.

- (23) Clarizia, L.; Andreozzi, R.; Apuzzo, J.; Di Somma, I.; Marotta, R. Efficient Acetaldehyde Production and Recovery upon Selective Cu/TiO2-Photocatalytic Oxidation of Ethanol in Aqueous Solution. *Chem. Eng. J.* **2020**, *393*, 123425.
- (24) Liu, P.; Li, T.; Chen, H.; Hensen, E. J. M. Optimization of Au0–Cu+ Synergy in Au/MgCuCr2O4 Catalysts for Aerobic Oxidation of Ethanol to Acetaldehyde. *J. Catal.* 2017, 347, 45–56.
- (25) Liu, P.; Zhu, X.; Yang, S.; Li, T.; Hensen, E. J. M. On the Metal–Support Synergy for Selective Gas-Phase Ethanol Oxidation over MgCuCr2O4 Supported Metal Nanoparticle Catalysts. J. Catal. 2015, 331, 138–146.
- Mukherjee, P.; Roy, P. S.; Mandal, K.; Bhattacharjee, D.; Dasgupta, S.; Bhattacharya,
 S. K. Improved Catalysis of Room Temperature Synthesized Pd-Cu Alloy Nanoparticles for Anodic Oxidation of Ethanol in Alkaline Media. *Electrochim. Acta* 2015, *154*, 447–455.
- (27) Čičmanec, P.; Ganjkhanlou, Y.; Kotera, J.; Hidalgo, J. M.; Tišler, Z.; Bulánek, R. The Effect of Vanadium Content and Speciation on the Activity of VOx/ZrO2 Catalysts in the Conversion of Ethanol to Acetaldehyde. *Appl. Catal. A Gen.* **2018**, *564*, 208–217.
- (28) Deluga, G. A.; Salge, J. R.; Schmidt, L. D.; Verykios, X. E. Renewable Hydrogen from Ethanol by Autothermal Reforming. *Science*. 2004, *303* (5660), 993–997.
- (29) DeWilde, J. F.; Czopinski, C. J.; Bhan, A. Ethanol Dehydration and Dehydrogenation on γ-Al2O3: Mechanism of Acetaldehyde Formation. *ACS Catal.* 2014, *4* (12), 4425–4433.
- (30) Abdulrazzaq, H. T.; Rahmani Chokanlu, A.; Frederick, B. G.; Schwartz, T. J. Reaction Kinetics Analysis of Ethanol Dehydrogenation Catalyzed by MgO-SiO2. *ACS Catal.* 2020, *10* (11), 6318–6331.
- (31) Luo, S.; Song, H.; Philo, D.; Oshikiri, M.; Kako, T.; Ye, J. Solar-Driven Production of Hydrogen and Acetaldehyde from Ethanol on Ni-Cu Bimetallic Catalysts with Solar-to-Fuels Conversion Efficiency up to 3.8 %. *Appl. Catal. B Environ.* **2020**, 272, 118965.
- (32) Maihom, T.; Probst, M.; Limtrakul, J. Density Functional Theory Study of the Dehydrogenation of Ethanol to Acetaldehyde over the Au-Exchanged ZSM-5 Zeolite:

Effect of Surface Oxygen. J. Phys. Chem. C 2014, 118 (32), 18564–18572.

- (33) Raynes, S. J.; Taylor, R. A. Zinc Oxide-Modified Mordenite as an Effective Catalyst for the Dehydrogenation of (Bio)Ethanol to Acetaldehyde. *Sustain. Energy Fuels* 2021.
- (34) Garbarino, G.; Riani, P.; Villa García, M.; Finocchio, E.; Sánchez Escribano, V.; Busca, G. A Study of Ethanol Conversion over Zinc Aluminate Catalyst. *Reac. Kinet. Mech. Cat.* 2018, *124* (2), 503–522.
- (35) Neramittagapong, A.; Attaphaiboon, W.; Neramittagapong, S. Acetaldehyde Production from Ethanol over Ni-Based Catalysts. *Chiang Mai J. Sci.* **2008**, *35* (1), 171–177.
- (36) Autthanit, C.; Praserthdam, P.; Jongsomjit, B. Oxidative and Non-Oxidative Dehydrogenation of Ethanol to Acetaldehyde over Different VOx/SBA-15 Catalysts. J. *Environ. Chem. Eng.* 2018, 6 (5), 6516–6529.
- (37) De Waele, J.; Galvita, V. V.; Poelman, H.; Detavernier, C.; Thybaut, J. W. PdZn Nanoparticle Catalyst Formation for Ethanol Dehydrogenation: Active Metal Impregnation vs Incorporation. *Appl. Catal. A Gen.* **2018**, 555, 12–19.
- Wang, F.; Shi, R.; Liu, Z. Q.; Shang, P. J.; Pang, X.; Shen, S.; Feng, Z.; Li, C.; Shen, W.
 Highly Efficient Dehydrogenation of Primary Aliphatic Alcohols Catalyzed by Cu
 Nanoparticles Dispersed on Rod-Shaped La2O2CO 3. ACS Catal. 2013, 3 (5), 890–894.
- (39) Cassinelli, W. H.; Martins, L.; Passos, A. R.; Pulcinelli, S. H.; Rochet, A.; Briois, V.;
 Santilli, C. V. Correlation between Structural and Catalytic Properties of Copper
 Supported on Porous Alumina for the Ethanol Dehydrogenation Reaction.
 ChemCatChem 2015, 7 (11), 1668–1677.
- (40) Giannakakis, G.; Trimpalis, A.; Shan, J.; Qi, Z.; Cao, S.; Liu, J.; Ye, J.; Biener, J.; Flytzani-Stephanopoulos, M. NiAu Single Atom Alloys for the Non-Oxidative Dehydrogenation of Ethanol to Acetaldehyde and Hydrogen. *Top. Catal.* 2018, *61* (5–6), 475–486.
- (41) Mušič, A.; Batista, J.; Levec, J. Gas-Phase Catalytic Dehydrogenation of Methanol to Formaldehyde over ZnO/SiO2 Based Catalysts, Zeolites, and Phosphates. *Appl. Catal. A Gen.* 1997, *165* (1–2), 115–131.
- (42) Zhang, X.; Li, Y.; Huo, Y.; Guo, L.; Wu, C.; Wu, Z. Synthesis of Pyridine Bases from Ethanol, Methanol and Ammonia over Micro-Mesoporous Zn–OH/HZSM-5 Catalyst. *Microporous Mesoporous Mater.* 2020, *306*, 1–8.

- (43) Niu, X.; Gao, J.; Miao, Q.; Dong, M.; Wang, G.; Fan, W.; Qin, Z.; Wang, J. Influence of Preparation Method on the Performance of Zn-Containing HZSM-5 Catalysts in Methanol-to-Aromatics. *Microporous Mesoporous Mater.* 2014, 197, 252–261.
- (44) Sun, J.; Zhu, K.; Gao, F.; Wang, C.; Liu, J.; Peden, C. H. F.; Wang, Y. Direct Conversion of Bio-Ethanol to Isobutene on Nanosized ZnxZryOz Mixed Oxides with Balanced Acid-Base Sites. J. Am. Chem. Soc. 2011, 133, 11096–11099.
- (45) Gao, J.; Teplyakov, A. V. Surface Species Formed during Thermal Transformation of Ethanol on ZnO Powder. J. Catal. 2013, 300, 163–173.
- (46) Seker, E. The Catalytic Reforming of Bio-Ethanol over SiO2 Supported ZnO Catalysts: The Role of ZnO Loading and the Steam Reforming of Acetaldehyde. *Int. J. Hydrog. Energy* 2008, *33* (8), 2044–2052.
- (47) Campa, M. C.; Doyle, A. M.; Fierro, G.; Pietrogiacomi, D. Simultaneous Abatement of NO and N2O with CH4 over Modified Al2O3 Supported Pt, Pd, Rh. *Catal. Today* 2022, 384–386 (2), 76–87.
- (48) Liu, C.; Sun, J.; Smith, C.; Wang, Y. A Study of ZnxZryOz Mixed Oxides for Direct Conversion of Ethanol to Isobutene. *Appl. Catal. A Gen.* 2013, 467, 91–97.
- (49) Hu, P.; Iyoki, K.; Yamada, H.; Yanaba, Y.; Ohara, K.; Katada, N.; Wakihara, T. Synthesis and Characterization of MFI-Type Zincosilicate Zeolites with High Zinc Content Using Mechanochemically Treated Si–Zn Oxide Composite. *Microporous Mesoporous Mater.* 2019, 288, 109594.
- (50) Ni, Y.; Sun, A.; Wu, X.; Hai, G.; Hu, J.; Li, T.; Li, G. The Preparation of Nano-Sized H[Zn, Al]ZSM-5 Zeolite and Its Application in the Aromatization of Methanol. *Microporous Mesoporous Mater.* 2011, 143 (2), 435–442.
- (51) Matsumura, Y.; Hashimoto, K.; Yoshida, S. Selective Dehydrogenation of Ethanol to Acetaldehyde over Silicalite-1. J. Catal. 1990, 122 (2), 352–361.
- (52) Goodarzi, F.; Kang, L.; Wang, F. R.; Joensen, F.; Kegnæs, S.; Mielby, J. Methanation of Carbon Dioxide over Zeolite-Encapsulated Nickel Nanoparticles. *ChemCatChem* 2018, 10 (7), 1566–1570.
- (53) Rasmussen, K. H.; Goodarzi, F.; Christensen, D. B.; Mielby, J.; Kegnæs, S. Stabilization of Metal Nanoparticle Catalysts via Encapsulation in Mesoporous Zeolites by Steam-Assisted Recrystallization. ACS Appl. Nano Mater. 2019, 2 (12), 8083–8091.

- (54) Goodarzi, F.; Thumbayil, R. P.; Enemark-Rasmussen, K.; Mielby, J.; Nguyen, T. T. M.;
 Beato, P.; Joensen, F.; Kegnæs, S. Enhanced Catalytic Performance of Zn-Containing HZSM-5 upon Selective Desilication in Ethane Dehydroaromatization Process. *ChemCatChem* 2020, *12* (5), 1519–1526.
- (55) Orazov, M.; Davis, M. E. Catalysis by Framework Zinc in Silica-Based Molecular Sieves. *Chem. Sci.* 2016, 7 (3), 2264–2274.
- (56) US5208201 A. The British Petroleum Company P.L.C. **1993**, pp 1–8.
- (57) Scanlon, J. T.; Willis, D. E. Calculation of Flame Ionization Detector Relative Response Factors Using the Effective Carbon Number Concept. *J. Chromatogr. Sci.* 1985, *23* (8), 333–340.
- Mielby, J.; Abildstrøm, J. O.; Wang, F.; Kasama, T.; Weidenthaler, C.; Kegnæs, S.
 Oxidation of Bioethanol Using Zeolite-Encapsulated Gold Nanoparticles. *Angew. Chem. Int. Ed.* 2014, No. 126, 12721–12724.
- (59) Hamidzadeh, M.; Komeili, S.; Saeidi, M. Seed-Induced Synthesis of ZSM-5 Aggregates Using the Silicate-1 as a Seed: Characterization and Effect of the Silicate-1 Composition. *Microporous Mesoporous Mater.* 2018, 268, 153–161.
- (60) Su, X.; Zan, W.; Bai, X.; Wang, G.; Wu, W. Synthesis of Microscale and Nanoscale ZSM-5 Zeolites: Effect of Particle Size and Acidity of Zn Modified ZSM-5 Zeolites on Aromatization Performance. *Catal. Sci. Technol.* **2017**, *7* (9), 1943–1952.
- (61) Cheng, S.; Wei, L.; Julson, J.; Muthukumarappan, K.; Kharel, P. R.; Cao, Y.; Boakye, E.; Raynie, D.; Gu, Z. Hydrodeoxygenation Upgrading of Pine Sawdust Bio-Oil Using Zinc Metal with Zero Valency. *J. Taiwan Inst. Chem. Eng.* 2017, 74, 146–153.
- (62) Egeblad, K.; Kustova, M.; Klitgaard, S. K.; Zhu, K.; Christensen, C. H. Mesoporous Zeolite and Zeotype Single Crystals Synthesized in Fluoride Media. *Microporous Mesoporous Mater.* 2007, 101 (1-2), 214–223.
- (63) Wang, J.; Zhong, Z.; Ding, K.; Zhang, B.; Deng, A.; Min, M.; Chen, P.; Ruan, R. Successive Desilication and Dealumination of HZSM-5 in Catalytic Conversion of Waste Cooking Oil to Produce Aromatics. *Energy Convers. Manag.* 2017, *147*, 100–107.
- (64) Qi, L.; Zhang, Y.; Conrad, M. A.; Russell, C. K.; Miller, J.; Bell, A. T. Ethanol Conversion to Butadiene over Isolated Zinc and Yttrium Sites Grafted onto

Dealuminated Beta Zeolite. J. Am. Chem. Soc. 2020, 142 (34), 14674–14687.

Chapter 4 Ethanol conversion into 1,3-butadiene

This chapter aims to study the process of 1,3-butadiene production from the direct conversion of ethanol *via* different Zn and Y containing zeolites as catalysts such as Zn/ZSM-5, Y/ZSM-5, Zn-Y/ZSM-5, and Zn/Beta, Y/Beta, Zn-Y/Beta. The impregnation and encapsulation of Zn and Y active sites in different zeolite materials were fully investigated towards the production of 1,3-butadiene.

Graphical abstract



Figure 4-1. The production of 1,3-butadiene from ethanol over zeolite catalysts.

4.1 Introduction

The global market of tyres will increase from 1.9 trillion units in the year 2020 to an estimated 2.5 trillion units by 2026 along with the booming of the automobile according to Cision PR Newswire.¹ The tyre is made up of natural rubber and/or synthetic rubber with various kinds of reinforcing additives. The natural rubber is produced in specific geographical locations like equatorial regions (Southeast Asia, central and western Africa, and Central and South America). The limited amount of natural rubber can not meet the requirement of the prosperous automobile industry. Therefore, synthetic rubber takes a more important role in the tyre industry to fill in the gap and attract great interest among the giant tyre manufacturing enterprises. Styrene-butadiene rubber (SBR) is the largest general synthetic rubber variety and one of the earliest rubber to achieve industrial production. 1,3-Butadiene is a fundamental monomer for SBR synthesis. Besides SBR, 1,3-butadiene is also the starting material for nylon and acrylonitrile butadiene styrene (ABS) resins production. Furthermore, 1,3-butadiene is also used in the famous Diels-Alder (DA) reaction to form cyclohexene derivatives.^{2,3} Scheme 4-1 is a typical six-member ring cycloaddition reaction for the synthesis of a natural product like paclitaxel.



Scheme 4-1. Diels-Alder reaction pathway.

The wide applications of 1,3-butadiene make a tremendous demand to meet the industrial development. The 1,3-butadiene market will reach an estimated valuation of 19.6 Million Tons by 2027 while registering this growth at a rate of 4.50% for the forecast period of 2020 to 2027 according to Data Bridge Market Research (DBMR).⁴ Currently, most 1,3-butadiene is produced as a co-product from the naphtha steam cracking to light olefins like ethylene.^{5–8} However, the limited storage amount of petroleum leads to the producing cost of 1,3-butadiene increasing along with the increasing fossil fuel consumption. The strategy of "Carbon Balance and Carbon Neutrality" in many countries around the world urges industries to cut down the consumption of fossil fuels for sustainable social development. Another challenge of 1,3-butadiene industrial production is that the ethylene production shifted from naphtha cracking to shale gas utilization, which inturns decrease the co-product 1,3-butadiene production as mentioned above method. Therefore, it is necessary to invent a low-cost and "green" method

to produce 1,3-butadiene. Biomass is regarded as an unlimited renewable carbon resource that not only for CO₂ capture and utilization (CCU) but also is used as an alternative to petroleum for producing some bulk chemicals and fuels. Ethanol is one of the most investigated biomassderived chemicals through biomass refining and fermentation processes. A large number of scientists have paid attention to the conversion of ethanol to the 1,3-butadiene sustainable process. It has a long history of ethanol conversion into 1,3-butadiene that was first discovered in the 1920s by Lebedev as shown in Scheme 4-2,⁹ and was applied into the industrial production of 1,3-butadiene for synthetic rubbers during the Second World War.^{10–12} In general, the Lebedev process includes four consecutive steps: (1) ethanol dehydrogenation to acetaldehyde; (2) aldol condensation of acetaldehydes to form acetaldol subsequently dehydrated to crotonaldehyde; (3) Meerwein–Ponndorf–Verley (MPV) reaction of crotonaldehyde with ethanol to form crotyl alcohol and acetaldehyde; (4) dehydration of crotyl alcohol to 1,3-butadiene.

The first reaction of the Lebedev process is the ethanol dehydrogenation to acetaldehyde, and hydrogen is produced as the co-product. Acetaldehyde is a critical intermediate for the production of 1,3-butadiene through the Lebedev process. The ethanol dehydrogenation process was investigated in Chapter 3 with different Zn-containing zeolite catalysts. The second step of the Lebedev process is established in the extension of the carbon chain through aldol condensation among two acetaldehyde molecules. However, the C-C bond formation reaction is still in debate and the main reason is the absence of direct existing evidence of acetaldol during the experiment. The acetaldol dehydrated rapidly to crotonaldehyde and the lifetime is too short to detect.¹³ The following MPV reaction occurs between the crotonaldehyde and ethanol to produce crotyl alcohol and acetaldehyde. Ethanol plays a critical role in the MPV reaction not merely as the substrate to produce acetaldehyde. Meanwhile, acetaldehyde can be produced through the MPV reaction that can be reused in the aldol condensation reaction. The final dehydration step of crotyl alcohol occurred in the presence of acidic sites.

The real catalyst compositions are not disclosed due to the patent but many researchers tried to explore the main components of the catalyst. The mixture of various contents of SiO_2 and MgO materials may be the catalyst in the Lebedev process.¹⁴ Many catalysts have been investigated in the Lebedev process such as metal oxides supported on silica ^{13,15–19}, and the cascade reaction pathway desires the application of multi-functional catalysts for each step like

acidic, basic, and redox sites. It is critically important to make a balance of different sites to achieve the optimum 1,3-butadiene selectivity.



Scheme 4-2. Conversion pathways of ethanol to 1,3-butadiene through the Lebedev method

The dehydrogenation of ethanol requires the metal oxides species like ZnO.^{20–22} The Lewis acid sites facilitate the aldol condensation and MPV reaction processes.^{7,23} The dehydration reactions require the existence of Brønsted acidic sites. Nevertheless, the strong Brønsted acidity results in the dehydration of ethanol to ethylene and diethyl ether.⁷ Therefore, the overall Brønsted acidity should be adjusted to decrease the side-reaction of ethanol dehydration. The application of weak Brønsted acidic material like SiO₂^{17,18} and zeolites with silanol groups^{5,24} is a general method. Another option is the addition of other basic sites to passivate the strong acidic support material such as $ZnO_xZrO_y^{25}$ composite and zeolite material²⁶. Therefore, the catalyst can be categorized into metal oxides composites and zeolite-supported materials according to their composing forms.

4.1.1 Metal oxides composite catalysts

The MgO-SiO₂ catalyst system is extensively investigated including the preparation methods such as wet kneading^{14,18}, impregnation²⁷, mechanical mixing¹⁷, sol-gel method²⁸, and coprecipitation²⁷. However, the preparation methods of MgO-SiO₂ catalysts have a remarkable influence on the yield of 1,3-butadiene. The wet-kneading method shows the optimum catalytic activity towards the production of 1,3-butadiene due to the formation of a limited amount of strong basic sites and a moderate amount of acidic sites.¹⁴ Tan et al. proposed that the calcination temperature in the catalyst synthesis process is of great importance to the structure of catalyst compositions.²⁹ For instance, the low calcination temperature (350 and 400 °C) results in the incomplete decomposition of $Mg(NO_3)_2$ precursor, and the residual $Mg(NO_3)_2$ facilitates the formation of 1-butanol. Nevertheless, the high calcination temperature at 700 °C leads to the formation of forsterite Mg₂SiO₄ and it favors the ethanol dehydration to ethylene and diethyl ether. The MgO-SiO₂ catalyst synthesized through an intermediate calcination temperature at 500 °C has a positive effect on the production of 1,3-butadiene. The reason is ascribed to the formation of a large number of amorphous magnesium silicates accompanied by a few crystalline magnesium silicates at a moderate calcination temperature of 500 °C.²⁹ The various preparation methods of MgO-SiO₂ catalysts synthesis make it difficult to tune the

intrinsic balance of acidic-basic active sites, which is of pivotal importance to the catalyst activity and selectivity. Therefore, the addition of a third component to the MgO-SiO₂ catalyst as the promoter to improve the catalytic activity and stability is extensively researched such as $Zn^{15,30}$, Ta^{31} , and $Cu^{30,32}$. Jiang *et al.* explored the doping of Ta into MgO-SiO₂ material to form Ta-O-Si bonds, thus generating strong Lewis acid sites to promote the aldol condensation and MPV reduction. The strong Lewis acid sites come from the mononuclear Ta(V) in the $\equiv Ta$ - $O-Si \equiv$ structure.³¹ Bruijnincx *et al.* investigated that 1 wt.% CuO boosted the production of 1,3-butadiene because the small cluster-like CuO species facilitate ethanol dehydrogenation to acetaldehyde and further shift the aldol condensation to be the rate-determination step in the Lebedev process.³² They also found the oxidation state of Cuⁿ⁺ species has a different effect on the ethanol conversion process that Cu^{2+} species was reduced to Cu^{0} and Cu^{+} species. The Cu^{0} species were the main promoter of the Cu/MgO-SiO₂ catalyst for the Lebedev process because of the increased dehydrogenation activity.²⁷ Coke deposition and sintering of metallic sites are leading causes of catalyst deactivation due to the insufficient exposure of active sites. Therefore, the MgO-SiO₂ catalyst system should be improved and further research is necessary to overcome the obstacles such as the utilization of zeolite supported materials as the catalysts in the Lebedev process. Sekiguchi et al. studied the simple Zn-containing talc catalyst in the Lebedev process from the aspect of the crystal structure³³ because the Mg-Si related catalysts do not have specific crystal structures, and found the crucial role of talc structure in the production of 1,3-butadiene. The ZnO-supported MgO-SiO₂ catalyst owns two types of Lewis acid sites in the connected regions of MgO-SiO₂ and ZnO-SiO₂ phases, which improves the 1,3-butadiene synthesis from ethanol.¹⁵

4.1.2 Zeolite-support materials

The thermal stability and pore-structure make zeolites to be the excellent support material for the design of the catalysts to achieve high efficiency of mass transfer and tolerance of coke deposition.^{34–36} Zeolites with silanol groups are suitable catalyst candidates for dehydration processes and exhibit great potential as support material for the aforementioned metal oxides and Lewis acid sites.^{7,37–39} Massive zeolite-supported bimetallic active sites catalysts were investigated in the ethanol to 1,3-butadiene process, for instance, ZnZr/Silicalite-1,⁴⁰ ZnZr/TUD-1,²⁴ ZnMg/SBA-15,⁷ ZnCe/SBA-15,⁵ and trimetallic composite zeolite material LiZnHf/MFI zeolite catalyst.⁴¹ All catalysts are focusing on the equilibrium of acid-base properties to achieve the synergistic effect among different active sites such as basic sites, Lewis acid sites, and weak Brønsted acid sites. There is not a fixed value of acidity to acquire

the optimum catalytic activity and selectivity because the pore structure of the support material also influences the tandem reaction results.

Tsubaki *et al.* investigated the ZnMg/SBA-15 zeolite catalyst in the Lebedev process and identified the active site of each step as shown in Figure 4-2. The Zn addition not only plays a key role in the high efficiency of ethanol dehydrogenation but also tunes the acid-base properties of the catalyst for a synergistic effect in the Lebedev process.⁷ The MgO act as Lewis acid site for the aldol condensation and MPV reaction. Silanol groups in the SBA-15 zeolite provide mild Brønsted acidic properties for the dehydration processes.



Figure 4-2. The identification of active sites for each step in the Lebedev process. Adapted from literature.⁷

They also reported a nanosized ZnZr/Silicalite-1 zeolite catalyst in the Lebedev process because the hierarchical nanosized structure zeolite support exhibited excellent performance on the mass transfer efficiency and resistance of coke deposition.⁴⁰ The acid-base properties were investigated to discover the relationship with the catalytic activity in the tandem reaction. It should be noted that the higher total acid amount does not mean the stronger Lewis acidity. The Lewis acid sites came from the Zn and Zr species interaction with silanol groups in the Silicalite-1 zeolite. The Zr-(OH)-Si = species has weaker Lewis acidity than the Zn-(OH)-Si = species due to the weaker electronegativity of the Zr (7.5) than Zn (15.9).⁴² But the synergistic effect of Zn and Zr exhibits the optimum Lewis acid properties towards the aldol condensation and MPV reduction in the Lebedev process compared to the sole metallic active center. Zn species plays a critical role in the ethanol dehydrogenation to acetaldehyde, which is extremely important for the production of 1,3-butadiene. Nevertheless, Zr species exhibited a stronger dehydration ability of ethanol rather than dehydrogenation.⁴⁰ It gives the hint for the catalyst synthesis that Zn active centers are responsible for ethanol dehydrogenation, and Zr species dominate the aldol condensation and MPV reduction process. The ZnO nanoparticles were easy

to be reduced to Zn in the presence of H_2 , which was derived from ethanol dehydrogenation, and the newly generated Zn⁰ nanoparticles suppress the ethanol dehydrogenation process.¹⁰ The sintering of metal particles and reduced Zn were the main reasons for the catalyst deactivation as well as the blockage by coke deposition.¹¹ Therefore, the confining of metallic active centers is of great importance to improve the catalyst activity and stability.

Dealuminated zeolite is a suitable support material for metal active site anchoring to suppress the sintering and oxidation state-changing issues like ZnY/DeAlBEA zeolite catalyst as shown in Figure 4-3.³⁹ The newly formed \equiv Si-O-Zn-O-Si-O \equiv groups exhibit high activity for the ethanol dehydrogenation. Meanwhile, the \equiv Si-O-Y(OH)-O-Si \equiv groups are found to facilitate the aldol condensation and MPV reduction. The dehydration processes are achieved through the remained silanol groups or the silanol nest.



Figure 4-3. The anchoring of Zn and Y single sites in the dealuminated BEA structure. Adapted from reference.³⁹

The metallic active center of Y in the dealuminated BEA (DeAlBEA) zeolite exhibited much high activity than Y sites supported on the silica due to the latter catalyst lack of –OH groups. Bell *et al.* also proposed a new mechanism about the carbon-carbon bond coupling mechanism that the reaction occurs among the coadsorbed ethanol and acetaldehyde from crotyl alcohol.³⁹ The inactive of Y/DeAlBEA and Zn/DeAlBEA catalysts in the aldol condensation process of pure acetaldehyde reactant are the evidence of the proposed mechanism of carbon-carbon coupling. The previous literature claimed the carbon chain expansion took place in two acetaldehyde molecules.^{7,23,43–45} Li *et al.* also investigated the ZnY/DeAlBEA in the Lebedev process but they insisted the aldol condensation occurred among two acetaldehyde molecules, and Lewis acidic Y species facilitated the aldol condensation and MPV reactions.⁴⁵ They elucidated that the Lewis acidic Zn species has higher activity in ethanol dehydrogenation but inadequate activity in acetaldehyde aldol condensation and MPV reduction.

The corporation of dehydrogenation sites, Lewis acidic sites, and moderate acid sites in the catalyst jointly promoted the catalytic activity and production of 1,3-butadiene. In addition to

this, the chemical environment of the active centers also affects the catalytic activity such as different positions of metallic active sites on the surface of support material or the encapsulation into the framework of the support material. Therefore, the key point for the catalyst design is to obtain the synergistic effect among all active sites.

4.2 Experimental section

Materials

Tetraethylammonium hydroxide solution (TEAOH, 35 wt.% in H₂O), concentrated nitric acid (HNO₃, ACS reagent, 70%) solution, lithium hydroxide monohydrate (LiOH·H₂O, ACS reagent, \geq 98.0%), zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, ACS reagent, \geq 98%), Ludox[®] AS-40 colloidal silica (40 wt. % suspension in H₂O), 1,3-butadiene (16 wt.% in hexane), and Yttrium(III) nitrate hexahydrate (99.8% trace metals basis) were received from Sigma-Aldrich.

Zeolite synthesis

M/Zeolite catalysts (M refers to Zn or Y, Zeolite refers to Na-ZSM-5, H-ZSM-5, H-Beta, or Silicalite-1) were synthesized the same as in Chapter 3. The Y(NO₃)·6H₂O was used as the precursor for the Y-containing zeolite catalysts. Zn-MFI zeolite was synthesized as described in Chapter 3.

CIT-6 zeolite was synthesized according to the published literature.^{46,47} Briefly, TEAOH (8.9 mL), LiOH·H₂O (0.07 g), Zn(CH₃COO)₂·2H₂O (0.22 g), Ludox[®] AS-40 (3.9 mL), and H₂O (9.05 mL) were mixed in the Teflon beaker and stirring for 2 h. Afterward, the mixture was transferred to a stainless autoclave and sealed for crystallization at 140 °C for 7.5 days. The solid residue was collected washed, dried, and calcined at 540 °C for 6 hours with 4 h heating ramp.

Na-Beta zeolite ($n_{Si}/n_{Al}=140$) was synthesized according to the literature^{48,49} with the modification of utilization of Ludox[®] AS-40 as the silica source instead of fumed silica. Briefly, TEAOH (8.9 mL), Ludox[®] AS-40 (3.9 mL), NaAlO₂ (0.019 g), and H₂O (5.7 mL) were mixed in the Teflon beaker and stirred for 2 h. Afterward, the mixture was transferred to a stainless autoclave and sealed for crystallization at 150 °C for 6 days. The solid residue was collected washed, dried, and calcined at 540 °C for 6 h with 4 h heating ramp.

Dealuminated zeolite synthesis was referred to the literature with the utilization of concentrated nitric acid solution (13 mol/L).³⁹ In brief, parent zeolite (3 g) was suspended in 100 ml HNO₃ solution of 13 mol/L with stirring at 100 °C for 20 hours equipped with a vertical condenser tube for water reflux. The obtained powder was washed with deionized water through centrifugation until the pH of the liquid phase was around 6-7. Subsequently, the solid powder was dried in an oven at 80 °C overnight. The prepared dealuminated zeolites were designated as DeAlBEA or DeAlZSM-5 according to their parent zeolites.

Zn/DeAlZeolite and Y/DeAlZeolite were synthesized through the incipient wetness impregnation method same as the aforementioned Zn/Na-ZSM-5 in Chapter 3. ZnY/DeAlZeolite was prepared through mixed Zn and Y precursor solutions then followed the impregnation process as described above. The Zn and Y loading in the zeolite catalysts were 5 wt.% and 2 wt.%, respectively.

Catalyst evaluations

The synthesized catalysts were evaluated in the fixed-bed that was described in Chapter 3. As described in Chapter 3, we continue to use the ECN method to calculate the selectivity of different products due to the difficult issue of ethylene calibration determination. And the ECN of each compound related to the project can be found in Table 4-1.

CN	Compound	ECN
5	Acetic acid	1
	Crotonaldehyde	3
	Crotyl alcohol	3.5
	Diethyl ether	3
5	N	N Compound Acetic acid Crotonaldehyde Crotyl alcohol Diethyl ether

Table 4-1. The effect carbon number of related compounds in this project

4.3 Results and discussions

4.3.1 Zn-containing catalysts in the Lebedev process

A series of Zn-containing zeolite catalysts are synthesized and evaluated in ethanol conversion into the 1,3-butadiene process, and their conversions of ethanol and selectivities of co-products are shown in Table 4-2. The bare Na-ZSM-5, HZSM-5, DeAlZSM-5, and Silicalite-1 zeolites without Zn impregnation are investigated as well to exclude the influence of the zeolite support.

Entry	Catalyst	EtOH .	Selectivity (%)						
			Ethylene	Acetald-	1,3-	Diethyl-	Cronton-	Crotyl	
		COIIV. (70)		ehyde	Butadiene	ether	aldehyde	alcohol	
1	Silicalite-1	2.3	86.3	13.7	0	0	0	0	
2	Zn/Silicalite-1	64.7	2.6	91.5	1.4	1.5	0	0	
3	Na-ZSM-5	34.3	84.8	2.1	0	13.1	0	0	
4	Zn/Na-ZSM-5	54.9	3.0	91.5	4.2	1.3	0	0	
5	H-ZSM-5	99.9	99.9	0	0	0.1	0	0	
6	Zn/H-ZSM-5	99.8	96.3	3.6	0.1	0	0	0	
7	DeAlZSM-5	99.8	99.6	0.2	0.2	0	0	0	
8	Zn/DeAlZSM-5	99.5	97.8	2.0	0.2	0	0	0	
9	Na-Beta	1.6	43.5	56.5	0	0	0	0	
10	Zn/Na-Beta	37.8	24.5	53.7	0.4	21.4	0	0	
11	DeAlBeta	98.8	95.7	4.3	0.4	0	0	0	
12	Zn/DeAlBeta	96.1	63.0	20.2	7.5	5.9	2.0	0.6	
13	CIT-6	29.7	2.5	84.6	6.8	2.7	1.6	0.4	
14	Zn-MFI	8.4	0.6	99.4	0	0	0	0	

Table 4-2. The conversion and selectivities of ethanol conversion into 1,3-butadiene over different Zn-containing zeolite catalysts.^[a]

[a]The conversion of ethanol and selectivity of all products are based on the reaction temperature that the highest selectivity of 1,3-butadiene obtained. If there is no 1,3-butadiene produced, then the conversion and selectivity are selected based on the highest ethanol conversion.

As it shows in Table 4-2 that all the Zn-containing zeolites did not exhibit high selectivity of 1,3-butadiene. The conversion of ethanol over zeolites without Zn-containing was generally lower than their counterpart Zn-containing zeolites such as Na-ZSM-5, Silicalite-1, and Na-Beta zeolites. However, the high ethanol conversion of H-ZSM-5, DeAlZSM-5, and DeAlBEA zeolites with or without Zn-containing should be ascribed to the abundant Brønsted acid sites in the framework, which facilitates the dehydration of ethanol to obtain the high selectivity of ethylene. The high selectivity of acetaldehyde obtained over the Zn/Na-ZSM-5 and Zn/Silicalite-1 catalysts indicates that monometallic Zn-containing zeolite catalysts are unable to promote the effective aldol condensation of acetaldehydes.

The main products were acetaldehyde and ethylene among all monometallic Zn-containing zeolite catalysts. As it can be seen from Figure 3-10 in Chapter 3, no 1,3-butadiene is produced both over the Zn and ZnO catalysts without any zeolite support. The conversion of ethanol over pure Zn catalyst is less than 3% which means Zn is inactivity towards the ethanol conversion either dehydrogenation or dehydration. On the contrary, the ZnO catalyst exhibits a much higher ethanol conversion of 40% compared to the Zn catalyst. The overall comparison between Zn and ZnO gives a conclusion that ZnO has a better catalytic activity than metallic Zn to facilitate the ethanol conversion with the highest conversion of 40% but inactive towards the production of 1,3-butadiene. That means the ZnO catalyst only possesses the dehydrogenation sites without the ability to promote the aldol condensation process. It is necessary to improve the catalytic activity through the modification of the metallic active sites incorporation with zeolite support materials towards the production of 1,3-butadiene. Na-ZSM-5 and Silicalite-1 zeolites were selected as the support materials for Zn impregnation and formed the metal-supported zeolite catalysts (Zn/Na-ZSM-5 and Zn/Silicalite-1) in the Lebedev process. They exhibit higher conversion of ethanol and selectivity of acetaldehyde compared to Zn/Na-Beta zeolite.



Figure 4-4. Conversion and selectivities of ethanol direct conversion into the 1,3-butadiene process over Zn/Silicalite-1 (left) and Zn/NaZSM-5 catalysts (right) (Adapted from Chapter 3)

The catalytic results of Zn/Silicalite-1 and Zn/Na-ZSM-5 zeolite catalysts are shown in Figure 4-4 that very little 1,3-butadiene was produced with the selectivity less than 5%. The conversions of ethanol over both two catalysts improved a lot compared to the pure ZnO catalyst. Acetaldehyde is the dominant product with selectivity above 90% over both catalysts. The decreasing selectivities of ethylene over Zn/Silicalite-1 and Zn/Na-ZSM-5 indicate the acidity of Zn/Silicalite-1 and Zn/Na-ZSM-5 decreased compared to ZnO. Very little 1,3-

butadiene was produced over Zn/Silicalite-1 and Zn/Na-ZSM-5 zeolite catalysts, and the high selectivity of acetaldehyde indicates the generated acetaldehyde is remained without participating in the following aldol condensation reaction. CIT-6 zeolite shows a bit higher selectivity than Zn/Na-ZSM-5 and Zn/Silicalite-1 zeolites but the conversion of ethanol was quite low. The Zn/DeAlBEA zeolite exhibits very low selectivity of acetaldehyde, which is unfavorable for the following aldol condensation. Therefore, Zn/Na-ZSM-5 and Zn/Silicalite-1 zeolites are promising catalysts for the first step of the Lebedev process.

4.3.2 Y-containing catalysts in the Lebedev process

The selectivity of 1,3-butadiene over monometallic Zn-containing zeolite catalyst is not high enough to compare the catalysts in the previous literature.^{15,50} The main reason is that the Zn can not catalyze the carbon-carbon coupling reaction to expand the carbon chain. Therefore, it is reasonable to switch to another metal to facilitate the carbon-carbon coupling reaction. Yttrium is selected as the promising active site to this aldol condensation process. But it is necessary to investigate the role of monometallic Y in the ethanol direct conversion to 1,3butadiene process. The Y₂O₃ was evaluated in the ethanol conversion process without the zeolite support, and the result was shown in Figure 4-5.



Figure 4-5. The conversion and selectivity of ethanol conversion into the 1,3-butadiene process over Y₂O₃.

The pure Y_2O_3 catalyst exhibits neither effective dehydrogenation nor aldol condensation reactions and the maximum conversion of ethanol of 11.7%. Ethylene is the main product with a selectivity of more than 90% except for reaction temperature at 300 °C which is ascribed to the strong acidity of Y_2O_3 . A fraction of acetaldehyde is produced that may be in the presence of a few dehydrogenation sites but the little ethanol conversion should also be taken into consideration. The naked Y_2O_3 catalyst is not suitable for the 1,3-butadiene production through the Lebedev process. Therefore, the zeolite should be applied as the support for the Y active sites and investigated in the process of 1,3-butadiene production.

Several zeolite catalysts were synthesized and investigated in the process of ethanol conversion into the 1,3-butadiene according to the hints from above Zn-containing zeolite. The list of the catalytic activity over different zeolite catalysts is shown in Table 4-3.

Table 4-3. The conversion and selectivities of ethanol direct conversion into the 1,3-butadiene process over different Y-containing zeolite catalysts.^[a]

			Selectivity (%)					
Entry	Catalyst	EtOH	Ethylene	Acetald-	1,3-	Diethyl	Cronton-	Crotyl
		Conv. (%)		ehyde	Butadiene	ether	aldehyde	alcohol
1	Y2O3+quartz sand	11.7	92.8	7.2	0	0	0	0
2	Y/Silicalite-1	14.6	75.6	23.4	0	1.0	0	0
3	Y/Na-ZSM-5	14.0	79.4	18.8	0	1.8	0	0
4	Y/DeAlZSM-5	99.6	99.4	0.3	0.3	0	0	0

[a]The conversion of ethanol and selectivity of all products are based on the reaction temperature that the highest selectivity of 1,3-butadiene obtained. If there is no 1,3-butadiene produced, then the conversion and selectivity are selected based on the highest ethanol conversion.

The Y/Silicalite-1 and Y/Na-ZSM-5 zeolite catalysts have a maximum conversion of 14.6%, which is significantly lower than Zn/Silicalite-1 and Zn/Na-ZSM-5 zeolite catalysts that have an ethanol conversion of around 60% as shown in Figure 4-4. It can be concluded that Y was much less active than Zn in the ethanol conversion because bare dehydrogenation sites exist in the Y-containing zeolite catalysts. The conversions of ethanol over Y/Zeolite and Y₂O₃ catalyst have no significant difference, which indicates the zeolite does not play a good synergistic catalytic effect to improve the ethanol conversion. However, the selectivity of the products has an obvious difference even though the main products are acetaldehyde and ethylene. The decreased selectivity of ethylene over Y/Zeolite catalyst can be assigned to the lower acidity when Y active sites are supported on the Na-ZSM-5 and Silicalite-1. The extremely high conversion of ethanol and selectivity of ethylene over Y/DeAIZSM-5 zeolite catalyst should be attributed to the abundant silanol groups in the zeolite framework, which provide strong Brønsted active sites.

4.3.3 Zn and Y-containing zeolite catalytic systems

Since the monometallic active sites of Zn or Y containing zeolite catalysts are incapable of producing high selectivity of 1,3-butadiene. The Zn/Na-ZSM-5 zeolite catalyst has the superior ability to facilitate the ethanol dehydrogenation process and the Y active sites can promote the aldol condensation process.^{39,45,51} Therefore, the combination of Zn and Y active sites supported on the zeolite materials seems promising catalysts to the Lebedev process. A series of ZnY catalysts were synthesized and evaluated in the ethanol conversion to 1,3-butadiene process as shown in Table 4-4.

Table 4-4. The conversion and selectivities of ethanol direct conversion into the 1,3-butadiene process over different bimetallic ZnY-containing zeolite catalysts.^[a]

			Selectivity (%)					
Entry	Catalyst	EtOH	Ethylene	Acetald-	1,3-	Diethyl	Cronton-	Crotyl
		Conv. (%)		ehyde	Butadiene	ether	aldehyde	alcohol
1	ZnY/Silicalite-1	65.2	3.2	90.6	3.0	1.3	0	2.0
2	ZnY/NaZSM-5	61.8	4.1	75.4	12.4	1.5	3.5	1.4
3	ZnY/DeAlZSM-5	94.3	91.8	6.2	0.8	1.1	0	0.1

[a]The conversion of ethanol and selectivities of all products are based on the temperature that the highest selectivity of 1,3-butadiene obtained. If there is no 1,3-butadiene produced, then the conversion and selectivities are selected based on the highest ethanol conversion.

The progress of 1,3-butadiene production was obtained through ZnY/Na-ZSM-5 zeolite catalyst with the maximum selectivity of 1,3-butadiene of 12.4%. The ZnY/Na-ZSM-5 zeolite shows a higher selectivity of 1,3-butadiene than ZnY/Silicalite-1 zeolite that can be assigned to the formation of [ZnOZn]⁺ species in the ZnY/Na-ZSM-5, which provides stronger Lewis acid sites.⁵² Nevertheless, the ZnY/DeAlZSM-5 zeolite catalyst exhibits high selectivity towards ethylene that can be ascribed to the strong Brønsted acidic sites after dealumination.



Figure 4-6. The conversion and selectivities of ethanol direct conversion into the 1,3-butadiene process over ZnY/Na-ZSM-5 zeolite catalyst.

The Zn and Y active sites in the bimetallic zeolite catalysts may exist in the adjacent positions during the synthesis since the Zn and Y are impregnated simultaneously onto the zeolite materials. The ethanol was dehydrogenated to acetaldehyde on the Zn active sites, and in principle, the acetaldehyde should start the aldol condensation reaction on the Y active sites. Nevertheless, the carrier gas flow may take the generated acetaldehyde away from the adjacent Y active sites. It results in a very limited opportunity for the interaction between acetaldehyde and Y active sites. Therefore, the distance of Zn and Y active sites should be taken into consideration to achieve a possible longer contact time between generated acetaldehyde and Y active sites. The physical mixing and core-shell structure of Zn/Na-ZSM-5 and Y/Na-ZSM-5 zeolite catalysts are investigated in the Lebedev process as shown in Figure 4-7. The conversion and selectivities of ethanol conversion into the 1,3-butadiene process over different locations of Zn and Y active sites are shown in Figure 4-7 as well.





The selectivity of 1,3-butadiene over the combination of Zn/Na-ZSM and Y/Na-ZSM-5 zeolite catalysts is higher than bimetallic ZnY/Na-ZSM-5 zeolite catalysts as shown in Figure 4-6 and Figure 4-7. The 1,3-butadiene has a maximum selectivity of 39.2% in the case of layer by layer structure that has an upper layer of Zn/Na-ZSM-5 and a bottom layer of Y/Na-ZSM-5 zeolite catalysts. It should be noted that the physical mixtures of Zn/Na-ZSM and Y/Na-ZSM-5 zeolite catalysts exhibited a selectivity of 1,3-butadiene to be 37.2% at the reaction temperature of 340 °C, which is close to the layer by layer catalysts structure. However, the selectivity of 1,3-butadiene is lower than the state-of-the-art results that have the maximum selectivity of 65%⁵³ and 61.4%⁴⁰ over Ag/ZrO₂/SiO₂ and ZnZr/Silicalite-1 catalysts, respectively.

4.4 Conclusions

The Zn-containing and Y-containing zeolites were synthesized and evaluated in the Lebedev process to produce 1,3-butadiene from ethanol. The Zn-containing zeolite catalysts exhibited high selectivity of acetaldehyde, while they were inactive for the production of 1,3-butadiene because the Zn active sites show the basic properties and only facilitate the dehydrogenation process.⁴⁰ However, the Zn-containing zeolites were in the shortage of Lewis acid sites, which is the critical factor for the aldol condensation reactions. The Y-containing zeolite catalysts show little activation in ethanol conversion due to the deficiency of dehydrogenation sites. Nevertheless, the acidity of Y species resulted in the high selectivity of ethylene from the ethanol dehydration process. The bimetallic ZnY/Na-ZSM-5 zeolite catalyst exhibited a promising 1,3-butadiene selectivity of 12.4% due to the synergistic effect between dehydrogenation sites and Lewis acid sites. However, acetaldehyde was still the main product with a selectivity of exceeding 75%, which indicated the tough aldol condensation to expand the carbon-carbon chain. The arrangements of monometallic Zn/Na-ZSM-5 and Y/Na-ZSM-5 zeolites demonstrated the superior activity of 1,3-butadiene production with the maximum selectivity of 39.2% in the case of layer by layer structure. The physical mixture of Zn/Na-ZSM-5 and Y/Na-ZSM-5 zeolites catalyst has a very close selectivity of 37.2% that indicating the critical role of the distance between Zn and Y active species when compared to the 1,3butadiene selectivity of 12.4% over ZnY/Na-ZSM-5 zeolite catalyst.

4.5 References

- Prnewswire.Com/News-Releases/Global-Tires-Market-to-Reach-2-5-Trillion-Unitsby-2026--301299008. Accessed on 23rd January 2022.
- (2) Angelici, C.; Weckhuysen, B. M.; Bruijnincx, P. C. A. Chemocatalytic Conversion of Ethanol into Butadiene and Other Bulk Chemicals. *ChemSusChem* 2013, 6 (9), 1595– 1614.
- Li, S.; Abdelrahman, O. A.; Kumar, G.; Tsapatsis, M.; Vlachos, D. G.; Caratzoulas, S.;
 Dauenhauer, P. J. Dehydra-Decyclization of Tetrahydrofuran on H ZSM5: Mechanisms, Pathways, and Transition State Entropy. ACS Catal. 2019, 9, 10279– 10293.
- (4) Global 1, 3 Butadiene Market Industry Trends and Forecast to 2027. Https://Www.Databridgemarketresearch.Com/Reports/Global-1-3-Butadiene-Market. Accessed on 23rd January, 2022.
- (5) Zhao, Y.; Li, S.; Wang, Z.; Wang, S.; Wang, S.; Ma, X. New ZnCe Catalyst Encapsulated in SBA-15 in the Production of 1, 3-Butadiene from Ethanol. *Chin. Chem. Lett.* 2020, *31* (2), 535–538.
- Pomalaza, G.; Arango, P.; Capron, M.; Dumeignil, F. Y. Ethanol-to-Butadiene: The Reaction and Its Catalysts. *Catal. Sci. Technol.* 2020, *10* (15), 4860–4911.
- Wang, K.; Peng, X.; Gao, X.; Araki, Y.; Zhao, H.; Liang, J.; Xiao, L.; Chen, J.; Liu, G.;
 Wu, J.; Yang, G.; Tsubaki, N. Insights into the Synergistic Effect of Active Centers over ZnMg/SBA-15 Catalysts in Direct Synthesis of Butadiene from Ethanol. *React. Chem. Eng.* 2021, 6 (3), 548–558.
- (8) Sushkevich, V. L.; Ivanova, I. I.; Ordomsky, V. V.; Taarning, E. Design of a Metal-Promoted Oxide Catalyst for the Selective Synthesis of Butadiene from Ethanol. *ChemSusChem* 2014, 7 (9), 2527–2536.
- (9) Kyriienko, P. I.; Larina, O. V.; Soloviev, S. O.; Orlyk, S. M.; Calers, C.; Dzwigaj, S. Ethanol Conversion into 1,3-Butadiene by the Lebedev Method over MTaSiBEA Zeolites (M = Ag, Cu, Zn). ACS Sustain. Chem. Eng. 2017, 5 (3), 2075–2083.
- (10) Cabello González, G. M.; Murciano, R.; Villanueva Perales, A. L.; Martínez, A.; Vidal-

Barrero, F.; Campoy, M. Ethanol Conversion into 1,3-Butadiene over a Mixed Hf-Zn Catalyst: A Study of the Reaction Pathway and Catalyst Deactivation. *Appl. Catal. A Gen.* **2019**, *570*, 96–106.

- (11) Pomalaza, G.; Arango Ponton, P.; Capron, M.; Dumeignil, F. Ethanol-to-Butadiene: The Reaction and Its Catalysts. *Catal. Sci. Technol.* **2020**, *10* (15), 4860–4911.
- (12) Pomalaza, G.; Capron, M.; Ordomsky, V.; Dumeignil, F. Recent Breakthroughs in the Conversion of Ethanol to Butadiene. *Catalysts* **2016**, *6* (203), 1–35.
- (13) Lewandowski, M.; Babu, G. S.; Vezzoli, M.; Jones, M. D.; Owen, R. E.; Mattia, D.; Plucinski, P.; Mikolajska, E.; Ochenduszko, A.; Apperley, D. C. Investigations into the Conversion of Ethanol to 1,3-Butadiene Using MgO:SiO2 Supported Catalysts. *Catal. Commun.* 2014, 49, 25–28.
- (14) Angelici, C.; Velthoen, M. E. Z.; Weckhuysen, B. M.; Bruijnincx, P. C. A. Influence of Acid-Base Properties on the Lebedev Ethanol-to-Butadiene Process Catalyzed by SiO2-MgO Materials. *Catal. Sci. Technol.* **2015**, *5* (5), 2869–2879.
- (15) Larina, O. V.; Kyriienko, P. I.; Soloviev, S. O. Ethanol Conversion to 1,3-Butadiene on ZnO/MgO-SiO2 Catalysts: Effect of ZnO Content and MgO:SiO2 Ratio. *Catal. Lett.* 2015, *145* (5), 1162–1168.
- (16) Taifan, W. E.; Baltrusaitis, J. In Situ Spectroscopic Insights on the Molecular Structure of the MgO/SiO2 Catalytic Active Sites during Ethanol Conversion to 1,3-Butadiene. *J. Phys. Chem. C* 2018, *122* (36), 20894–20906.
- (17) Reschetilowski, W.; Hauser, M.; Alscher, F.; Klauck, M.; Kalies, G. Studies on the Binary MgO/SiO2 Mixed Oxide Catalysts for the Conversion of Ethanol to 1,3-Butadiene. *Catalysts* 2020, 10 (8), 1–17.
- (18) Chung, S. H.; Ramirez, A.; Shoinkhorova, T.; Mukhambetov, I.; Abou-Hamad, E.; Telalovic, S.; Gascon, J.; Ruiz-Martínez, J. The Importance of Thermal Treatment on Wet-Kneaded Silica–Magnesia Catalyst and Lebedev Ethanol-to-Butadiene Process. *Nanomaterials* 2021, *11* (3), 1–17.
- (19) Chung, S. H.; Angelici, C.; Hinterding, S. O. M.; Weingarth, M.; Baldus, M.; Houben,
 K.; Weckhuysen, B. M.; Bruijnincx, P. C. A. Role of Magnesium Silicates in Wet-Kneaded Silica-Magnesia Catalysts for the Lebedev Ethanol-to-Butadiene Process. ACS

Catal. **2016**, *6* (6), 4034–4045.

- (20) Ohira, M.; Liu, H.; He, D.; Hirata, Y.; Sano, M.; Suzuki, T.; Miyake, T. Catalytic Performance and Reaction Pathways of Cu/SiO2 and ZnO/SiO2 for Dehydrogenation of Ethanol to Acetaldehyde. *J. Jpn. Pet. Inst.* **2018**, *61* (4), 205–212.
- (21) Ouyang, M.; Cao, S.; Yang, S.; Li, M.; Flytzani-Stephanopoulos, M. Atomically Dispersed Pd Supported on Zinc Oxide for Selective Nonoxidative Ethanol Dehydrogenation. *Ind. Eng. Chem. Res.* **2020**, *59* (6), 2648–2656.
- (22) Raynes, S. J.; Taylor, R. A. Zinc Oxide-Modified Mordenite as an Effective Catalyst for the Dehydrogenation of (Bio)Ethanol to Acetaldehyde. *Sustain. Energy Fuels* 2021.
- (23) Li, X.; Pang, J.; Wang, C.; Li, L.; Pan, X.; Zheng, M.; Zhang, T. Conversion of Ethanol to 1,3-Butadiene over High-Performance Mg-ZrO: X/MFI Nanosheet Catalysts via the Two-Step Method. *Green Chem.* **2020**, *22* (9), 2852–2861.
- Wang, K.; Guo, L.; Gao, W.; Zhang, B.; Zhao, H.; Liang, J.; Liu, N.; He, Y.; Zhang, P.;
 Yang, G.; Tsubaki, N. One-Pot Hydrothermal Synthesis of Multifunctional ZnZrTUD1 Catalysts for Highly Efficient Direct Synthesis of Butadiene from Ethanol. ACS Sustain. Chem. Eng. 2021, 9 (31), 10569–10578.
- (25) Baylon, R. A. L.; Sun, J.; Wang, Y. Conversion of Ethanol to 1,3-Butadiene over Na Doped ZnxZryOz Mixed Metal Oxides. *Catal. Today* 2016, 259, 446–452.
- (26) Pomalaza, G.; Simon, P.; Addad, A.; Capron, M.; Dumeignil, F. Properties and Activity of Zn-Ta-TUD-1 in the Lebedev Process. *Green Chem.* **2020**, *22* (8), 2558–2574.
- (27) Angelici, C.; Meirer, F.; Van Der Eerden, A. M. J.; Schaink, H. L.; Goryachev, A.; Hofmann, J. P.; Hensen, E. J. M.; Weckhuysen, B. M.; Bruijnincx, P. C. A. Ex Situ and Operando Studies on the Role of Copper in Cu-Promoted SiO2-MgO Catalysts for the Lebedev Ethanol-to-Butadiene Process. *ACS Catal.* **2015**, *5* (10), 6005–6015.
- (28) Ochoa, J. V.; Bandinelli, C.; Vozniuk, O.; Chieregato, A.; Malmusi, A.; Recchi, C.; Cavani, F. An Analysis of the Chemical, Physical and Reactivity Features of MgO-SiO2 Catalysts for Butadiene Synthesis with the Lebedev Process. *Green Chem.* 2016, *18* (6), 1653–1663.
- (29) Zhu, Q.; Wang, B.; Tan, T. Conversion of Ethanol and Acetaldehyde to Butadiene over MgO-SiO2 Catalysts: Effect of Reaction Parameters and Interaction between MgO and

SiO2 on Catalytic Performance. ACS Sustain. Chem. Eng. 2017, 5 (1), 722–733.

- (30) Taifan, W. E.; Li, Y.; Baltrus, J. P.; Zhang, L.; Frenkel, A. I.; Baltrusaitis, J. Operando Structure Determination of Cu and Zn on Supported MgO / SiO2 Catalysts during Ethanol Conversion to 1, 3-Butadiene. ACS Catal. 2019, 9, 269–285.
- (31) Jiang, H.; Jiang, A.; Gao, Q.; Yang, G.; Wang, L. Understanding Ta as an Efficient Promoter of MgO–SiO2 Catalyst for Conversion of the Ethanol–Acetaldehyde Mixture into 1,3-Butadiene. *Catal. Lett.* **2021**, 1–9.
- (32) Angelici, C.; Velthoen, M. E. Z.; Weckhuysen, B. M.; Bruijnincx, P. C. A. Effect of Preparation Method and CuO Promotion in the Conversion of Ethanol into 1,3-Butadiene over SiO2–MgO Catalysts. *ChemSusChem* 2014, 7 (9), 2505–2515.
- (33) Sekiguchi, Y.; Akiyama, S.; Urakawa, W.; Koyama, T. R.; Miyaji, A.; Motokura, K.; Baba, T. One-Step Catalytic Conversion of Ethanol into 1,3-Butadiene Using Zinc-Containing Talc. *Catal. Commun.* **2015**, *68*, 20–24.
- (34) Niu, X.; Gao, J.; Miao, Q.; Dong, M.; Wang, G.; Fan, W.; Qin, Z.; Wang, J. Influence of Preparation Method on the Performance of Zn-Containing HZSM-5 Catalysts in Methanol-to-Aromatics. *Microporous Mesoporous Mater.* 2014, 197, 252–261.
- Wei, Q.; Zhang, P.; Liu, X.; Huang, W.; Fan, X.; Yan, Y.; Zhang, R.; Wang, L.; Zhou,
 Y. Synthesis of Ni-Modified ZSM-5 Zeolites and Their Catalytic Performance in n-Octane Hydroconversion. *Front. Chem.* 2020, *8*, 1–8.
- (36) Veses, A.; Puértolas, B.; Callén, M. S.; García, T. Catalytic Upgrading of Biomass Derived Pyrolysis Vapors over Metal-Loaded ZSM-5 Zeolites: Effect of Different Metal Cations on the Bio-Oil Final Properties. *Microporous Mesoporous Mater.* 2015, 209, 189–196.
- (37) Yan, T.; Yang, L.; Dai, W.; Wu, G.; Guan, N.; Hunger, M.; Li, L. Cascade Conversion of Acetic Acid to Isobutene over Yttrium-Modified Siliceous Beta Zeolites. *ACS Catal.* 2019, *9* (11), 9726–9738.
- (38) Sushkevich, V. L.; Ivanova, I. I. Ag-Promoted ZrBEA Zeolites Obtained by Post-Synthetic Modification for Conversion of Ethanol to Butadiene. *ChemSusChem* 2016, 9 (16), 2216–2225.
- (39) Qi, L.; Zhang, Y.; Conrad, M. A.; Russell, C. K.; Miller, J.; Bell, A. T. Ethanol

Conversion to Butadiene over Isolated Zinc and Yttrium Sites Grafted onto Dealuminated Beta Zeolite. *J. Am. Chem. Soc.* **2020**, *142* (34), 14674–14687.

- (40) Wang, K.; Gao, W.; Chen, F.; Liu, G.; Wu, J.; Liu, N.; Kawabata, Y.; Guo, X.; He, Y.; Zhang, P.; Yang, G.; Tsubaki, N. Hierarchical Nano-Sized ZnZr-Silicalite-1 Multifunctional Catalyst for Selective Conversion of Ethanol to Butadiene. *Appl. Catal. B Environ.* 2022, *301*, 120822–120833.
- (41) Wang, C.; Zheng, M. Catalytic Conversion of Ethanol into Butadiene over High Performance LiZnHf-MFI Zeolite. *Green Chem.* **2019**, *21* (December 2018), 1006–1010.
- (42) Rahm, M.; Zeng, T.; Hoffmann, R. Electronegativity Seen as the Ground-State Average Valence Electron Binding Energy. J. Am. Chem. Soc. 2019, 141 (1), 342–351.
- (43) Rahman, M. M.; Davidson, S. D.; Sun, J.; Wang, Y. Effect of Water on Ethanol Conversion over ZnO. *Top. Catal.* 2016, 59 (1), 37–45.
- (44) Sushkevich, V. L.; Ivanova, I. I. Mechanistic Study of Ethanol Conversion into Butadiene over Silver Promoted Zirconia Catalysts. *Appl. Catal. B Environ.* 2017, 215, 36–49.
- (45) Yan, T.; Dai, W.; Wu, G.; Lang, S.; Hunger, M.; Guan, N.; Li, L. Mechanistic Insights into One-Step Catalytic Conversion of Ethanol to Butadiene over Bifunctional Zn-Y/Beta Zeolite. ACS Catal. 2018, 8 (4), 2760–2773.
- (46) Orazov, M.; Davis, M. E. Catalysis by Framework Zinc in Silica-Based Molecular Sieves. *Chem. Sci.* 2016, 7 (3), 2264–2274.
- (47) Takewaki, T.; Beck, L. W.; Davis, M. E. Synthesis of CIT-6, a Zincosilicate with the *BEA Topology. *Top. Catal.* 1999, 9 (1–2), 35–42.
- (48) Kumar, N.; Konova, P. M.; Naydenov, A.; Heikilla, T.; Salmi, T. Synthesis of Novel Ag Modified MCM-41 Mesoporous Molecular Sieve and Beta Zeolite Catalysts for Ozone Decomposition at Ambient Temperature. *Catal. Lett.* **2004**, *98*, 1–3.
- (49) Zaykovskaya, A. O.; Kumar, N.; Kholkina, E. A.; Li-Zhulanov, N. S.; Mäki-Arvela, P.; Aho, A.; Peltonen, J.; Peurla, M.; Heinmaa, I.; Kusema, B. T.; Streiff, S.; Murzin, D. Y. Synthesis and Physico-Chemical Characterization of Beta Zeolite Catalysts: Evaluation of Catalytic Properties in Prins Cyclization of (–)-Isopulegol. *Microporous Mesoporous Mater.* 2020, *302*, 110236–110249.

- (50) Larina, O. V.; Kyriienko, P. I.; Balakin, D. Y.; Vorokhta, M.; Khalakhan, I.; Nychiporuk, Y. M.; Matolín, V.; Soloviev, S. O.; Orlyk, S. M. Effect of ZnO on Acid-Base Properties and Catalytic Performances of ZnO/ZrO2-SiO2 Catalysts in 1,3-Butadiene Production from Ethanol-Water Mixture. *Catal. Sci. Technol.* **2019**, *9* (15), 3964–3978.
- (51) Zhu, Q.; Yin, L.; Ji, K.; Li, C.; Wang, B.; Tan, T. Effect of Catalyst Structure and Acid
 Base Property on the Multiproduct Upgrade of Ethanol and Acetaldehyde to C4
 (Butadiene and Butanol) over the Y–SiO2 Catalysts. ACS Sustain. Chem. Eng. 2020, 8, 1555–1565.
- (52) Su, X.; Zan, W.; Bai, X.; Wang, G.; Wu, W. Synthesis of Microscale and Nanoscale ZSM-5 Zeolites: Effect of Particle Size and Acidity of Zn Modified ZSM-5 Zeolites on Aromatization Performance. *Catal. Sci. Technol.* **2017**, 7 (9), 1943–1952.
- (53) Miyake, N.; Brezicki, G.; Davis, R. J. Cascade Reaction of Ethanol to Butadiene over Multifunctional Silica-Supported Ag and ZrO2Catalysts. ACS Sustain. Chem. Eng. 2022, 10 (2), 1020–1035.
Chapter 5 Ethanol/acetaldehyde conversion into 1,3butadiene

This chapter investigates the production of 1,3-butadiene using an ethanol/acetaldehyde mixture as the substrate over Y/ZSM-5 zeolite catalysts bearing different counter ions. A series of different counter ions in ZSM-5 zeolites with Y impregnated catalysts was used in an ethanol/acetaldehyde mixture used in the 1,3-butadiene preparation process. The influence of the counter ions in the Y/ZSM-5 zeolite catalysts on the catalytic performance was studied in detail.

This project was conducted by Kai Gao (Ph.D. student), supervisor Søren Kegnæs (Professor), and supervisor Dr. Jerrik Mielby (Senior researcher). The manuscript was finished and ready to be submitted to a peer-reviewed journal.



Graphical abstract

Mesoporous K-ZSM-5 zeolite

Figure 5-1. The production of 1,3-butadiene from ethanol/acetaldehyde mixtures over Y/K-ZSM-5 zeolites. This is a graphical abstract from the manuscript.

5.1 Introduction

Ethanol can be converted to 1,3-butadiene in the fixed-bed reactor within the catalyst through the Lebedev process as shown in Scheme 5-1. The catalytic activities of Zn- and/or Ycontaining zeolites have been extensively investigated in Chapter 3. However, the monometallic Zn-containing and Y-containing zeolite catalysts were not effective enough to produce 1,3-butadiene with high selectivity. These experimental results were not competitive to the previously published ZnO/MgO–SiO₂ catalyst with the optimum selectivity of 63.3%.¹ The synergistic effect between Zn and Y active sites in the bimetallic ZnY/NaZSM-5 zeolite catalyst improved the production of 1,3-butadiene with the selectivity of 12.4%. The layer by layer structure of catalysts arrangement of Zn/NaZSM-5 and Y/NaZSM-5 facilitated the production of 1,3-butadiene with the optimum selectivity of 39.2%. Therefore, the focus of innovation can be switched from the active site of catalysts to process innovation. Inspired by the ethanol participation in the MPV reaction, it is important to confirm that the ethanol can not be converted to acetaldehyde in the initial step of dehydrogenation. The regeneration of acetaldehyde in the MPV reaction also indicates the concentration of acetaldehyde should be limited in the initial step of ethanol dehydrogenation for the sake of promoting the MPV reaction.



Scheme 5-1. The Lebedev process of 1,3-butadiene production from ethanol.

In addition to this one-step process, another 1,3-butadiene generation method was invented by Ostromislensky, which is also known as the two-step method as shown in Scheme 5-2.² A mixture of ethanol and acetaldehyde was utilized as the substrate, which was different from the Lebedev process that used pure ethanol. In general, the two-step method consists of the initial ethanol dehydrogenation reaction to form acetaldehyde, and the acetaldehyde produced is mixed with additional ethanol to form a new mixed substrate for 1,3-butadiene production in the second step. The difference between the one- and two-step methods is the utilization of a second fixed-bed reactor and the carbon chain expansion process. In the one-step method, the carbon chain extension occurs between two acetaldehyde molecules. However, it is still not clear about the mechanism of the carbon-carbon coupling process in the two-step process between the ethanol and acetaldehyde molecules. Some researchers have suggested that ethanol was only effective in MPV reaction and carbon chain expansion only occurs between two acetaldehyde molecules via an aldol condensation reaction (which is the same as the one-step method).^{3–5} However, other scientists have mentioned that the carbon-carbon coupling process takes place between the ethanol and acetaldehyde molecules rather than two acetaldehyde molecules.⁶



Scheme 5-2. Production of 1,3-butadiene from a ethanol/acetaldehyde mixture using the twostep method.

Inspired by the substrate composition from the second step in the Ostromislensky process, it is reasonable to discard the first step of ethanol dehydrogenation to acetaldehyde since the production of acetaldehyde from ethanol is quite easy. In the second step, the focus should be on the carbon coupling reaction utilizing an ethanol/acetaldehyde mixture as the substrate to produce 1,3-butadiene. Zhang *et al.* proposed that the aldol condensation reaction proceeds via nucleophilic attack of the reactive enolate ($CH_2^{\delta-}-CH=O$) on acetaldehyde with Lewis acid sites.⁷ Many MO_x–SiO₂ (M=metal) materials have been studied in the two-step method, including Ta₂O₅–SiO₂,^{8,9} ZrO₂–SiO₂,^{10,11} and MgO–SiO₂.^{1,12–15} The researchers have paid attention to yttrium (Y) for the carbon coupling process because the Y³⁺ Lewis acid sites facilitate the carbon coupling process.^{6,16,17} Zhu *et al.* investigated the application of Y-SiO₂ catalyst in the conversion of ethanol/acetaldehyde mixture and found that the low Y loading facilitated the production 1,3-butadiene with the highest selectivity of 81.2%, while high Y loading improve the production of 1-butanol. The main reason should be ascribed to the different strengths of acid and base sites in the catalysts with various Y loadings.¹⁷

Carbon deposition is a major challenge that should be overcome in the production of 1,3butadiene because it dramatically deactivates the catalyst. Mesoporous zeolites play a crucial role as support to increase the coke tolerance due to their large pore size.^{8,18} Zhang *et al.* investigated the deactivation of MgO-SiO₂ catalyst resulting from carbon deposition found that coke formation on the acid-basic sites was the reason for catalyst deactivation. Moreover, the acid sites were occupied in the initial stage of the reaction and the basic sites were covered in the terminal step of the reaction.¹⁵ The deactivation positions indicated the different steps of the tandem reaction that occurred in respective active sites. Herein, this chapter focuses on the production of 1,3-butadiene using ethanol/acetaldehyde as the substrate over Y/ZSM-5 mesoporous zeolite catalysts bearing different counter ions. Furthermore, the effect of ethanol concentrations in the mixtures on the selectivity of 1,3-butadiene was investigated as well. The result shows that Y/K-ZSM-5 zeolite catalyst exhibits the optimum activity due to the smallest acidity, and the ethanol concentration plays an important role in the production of 1,3-butadiene.

5.2 Materials and methods

5.2.1 Materials

Ammonium nitrate (NH₄NO₃, \geq 99.0%), lithium nitrate (LiNO₃, \geq 99.0%), potassium nitrate (KNO₃, ACS Reagent, \geq 99.0%), and 1,3-butadiene (16 wt.% in hexane) were obtained from Sigma-Aldrich.

5.2.2 Catalyst synthesis

In this work, ZSM-5 zeolite (SiO₂/Al₂O₃ = 200) was prepared with a mesoporous structure using a carbon template (Carbon Black Perals, BP 2000), which was first published by Haldor Topsøe at 2000.¹⁹ The ratio of Si to Al in the ZSM-5 zeolite was different from Chapter 4 because the mesoporous structure zeolite was used in Chapter 5. Different counter ions of ZSM-5 zeolites were synthesized through the ion-exchange method.

Mesoporous Na-ZSM-5 zeolite was synthesized using a steam assistance method previously described by our group.²⁰ In brief, NaAlO₂ (0.0175 g) was dissolved in TPAOH (7.26 ml) under stirring. The resulting solution was introduced to carbon black (2 g, BP 2000) with vigorous stirring and then left in a fume hood overnight. Thereafter, TEOS (4.47 mL) was introduced dropwise to the carbon-containing solid in a small Teflon beaker. The following procedures were the same as described in Chapter 3.

The as-synthesized Na-ZSM-5 zeolite was used as the parent zeolite for the synthesis of ZSM-5 zeolite bearing different counter ions such as H⁺, Li⁺, and K⁺. via an ionic exchange method according to a literature method^{21,22} with the exception for the substitution of the chloride salt precursors into their corresponding nitrate salt precursors.²³ In general, 1 g of Na-ZSM-5 zeolite was suspended in 80 ml of NH₄NO₃, LiNO₃, and KNO₃ aqueous solutions, separately. All of the ion-exchanged ZSM-5 solutions were washed via centrifugation to remove excess nitrate salt precursor with five cycles. The oblique solid residue in the centrifuge tube was scattered with additional water via drastic vibration using an eccentric device prior to

every centrifugation step. The solid residue after centrifugation was dried at 80 °C prior to calcination at 550 °C for 4 h to obtain the desired Metal(H)-ZSM-5 zeolites.

The Y/Metal(H)-ZSM-5 was obtained by incipient wetness method with the previously prepared Metal(H)-ZSM-5 zeolite as the support. The Metal(H)-ZSM-5 (1.0 g) was dried in the vacuuming oven overnight to get rid of the remaining moisture before impregnation. The $Y(NO_3)_3 \cdot 6H_2O$ (0.0881g) was dissolved into a specific volume of water (based on zeolite pore volume from physisorption measurement) to form a colorless transparent Y precursor solution. Subsequently, the $Y(NO_3)_3 \cdot 6H_2O$ solution was added to the zeolite dropwise with fierce stirring and dried in an 80 °C oven, and then experienced calcination at 550 °C for 4 h to decompose the $Y(NO_3)_3$, and the product Y/Metal(H)-ZSM-5 zeolite catalysts were achieved after calcination.

Y/Metal(H)-ZSM-5 was obtained via an incipient wetness method using the previously prepared Metal(H)-ZSM-5 zeolite as the support. The Metal-ZSM-5 (1.0 g) was dried in a vacuum oven overnight to remove the remaining moisture prior to impregnation. The 0.0881 g of $Y(NO_3)_3 \cdot 6H_2O$ was dissolved in a specific volume of water (based on the zeolite pore volume from physisorption measurement) to form a colourless Y precursor solution. Subsequently, the $Y(NO_3)_3 \cdot 6H_2O$ solution was added dropwise to the zeolite with vigorous stirring and dried in an oven heated at 80 °C overnight and then calcined at 550 °C for 4 h with temperature ramping of 4 h to decompose the $Y(NO_3)_3$, and the Y/Metal(H)-ZSM-5 zeolite catalysts were achieved after the calcination step.

5.2.3 Catalysts characterization

The characterizations of XRD, N₂ physisorption, XPS, and SEM were the same as described in Chapter 3.

TGA was conducted on a Mettler Toledo instrument. The heating ramping for the spent sample was 5 °C/min under the air atmosphere to 800 °C.

NH₃-TPD chemisorption was performed on the AutoChem II 2920 equipped with a TCD detector. In a typical measurement, ~100 mg of the dried sample was saturated with NH₃ (Air Liquide, 5% NH₃ in He) and then heated from 100 to 500 °C resulting in the desorption of NH₃. Meanwhile, the amount of NH₃ was recorded in real-time along with time.

5.2.4 Catalytic activity measurements

The details of catalyst evaluation were described in Chapter 3 through the fixed-bed reactor. The ethanol and acetaldehyde conversions and product selectivity were calculated based on carbon balances derived from the GC peak area. In the literature, the concept of 'total conversion' has been applied, which means the ethanol/acetaldehyde mixture is regarded as a single substrate and counted together.^{5,8,9,11,15,17,24,25} The reason is speculated that the peak area of acetaldehyde increased after reaction and it was impossible to calculate the conversion of acetaldehyde. However, in our research, we found the peak area of acetaldehyde decreased after the reaction when compared to the original peak area of substrate acetaldehyde. The original peak areas were recorded using a bypass route without contact with the catalyst. Therefore, the conversions of ethanol and acetaldehyde were calculated based on their peak areas difference before and after the reaction. The selectivities of the different products were determined using the carbon balance method described in the literature.^{8,11,17,24,25}

5.3 Results and discussion

5.3.1 Characterisation results





Figure 5-2. XRD patterns obtained for the as-synthesized zeolite catalysts bearing different counter ions.

The phase crystallinity of the samples was determined using the XRD technique, as shown in Figure 5-2, and all zeolites demonstrate the typical MFI topology with major characteristic peaks observed at $2\theta = 7.9$, 8.8, 23, and 24° . This indicates both the ion-exchange and Y-

impregnation steps of the parent Na-ZSM-5 catalyst did not change the crystal zeolite structure. Y_2O_3 species are recognized to facilitate the carbon-carbon coupling or -aldol condensation reaction that occurs during the production of 1,3-butadiene from ethanol/acetaldehyde.⁶ However, they also promote the ethanol dehydrogenation reaction to form ethylene, which decreases the selectivity toward 1,3-butadiene (Chapter 4). Furthermore, the Y_2O_3 powder diffraction pattern exhibits peaks at 20.50° (211), 29.14° (222), 33.78° (400), 48.52° (440), and 57.60° (622) according to ICSD_CollCode66730. There are not very distinct peaks in the corresponding positions that indicate the Y_2O_3 has good particle distribution on the zeolite surface and inner cavity instead of being agglomerated into large clusters.

Table 5-1. Textural properties and acidities of the as-synthesized zeolite catalysts bearing different counter ions.

	Surface	Pore	Microporous pore	Pore size	Acidity b	ру
Zeolite	area	volume	volume (cm ³ /g)	(nm)	strength	$(\text{mmol/g})^{[1]}$
	(m ² /g)	(cm ³ /g)			Weak ^[2]	Strong ^[2]
H-ZSM-5	414.2	0.4617	0.04672	12.523	0.0501	0.1319
Li-ZSM-5	361.9	0.5061	0.06094	5.671	0.1451	0.0060
Na-ZSM-5	349.7	0.5202	0.05102	5.715	0.1323	0.0052
K-ZSM-5	371.4	0.4854	0.05695	5.456	0.1095	0.0006

[1] NH₃-TPD. [2] The weak and strong acidic densities of acid sites were determined using NH₃-TPD for NH₃ desorption at 100–260 and 260–500 °C, respectively.

The surface areas of the ion-exchange zeolite catalysts have significant differences among the different counter ions studied. The H-ZSM-5 zeolite has the largest surface area and the other zeolites have slightly different surface areas from the Na-ZSM-5. This means the ion exchange of alkali-metal Li and K did not have a remarkable impact on their MFI topology. The pore volume of H-ZSM-5 was slightly lower than the other three zeolites, but the pore size was remarkably increased when compared to the others. This may be attributed to the treatment of Na-ZSM-5 with NH₃·H₂O to obtain H-ZSM-5 zeolite, and the OH⁻ ions in the NH₃·H₂O solution lead to the desilication of the parent zeolite framework. However, the structural classification of H-ZSM-5 was still mesoporous when considering the isotherms obtained for the H-ZSM-5 zeolite shown in Figure 5-3 even after the weak desilication process. The pore volumes of the different zeolites only slightly fluctuate, which was also evidence of their stable structure after the ion-exchange step despite the desilication process that occurred during the formation of H-ZSM-5. The total acidity of ZSM-5 zeolites with four different counter ions increases in the sequence of K-ZSM-5 < Na-ZSM-5 < Li-ZSM-5 < H-ZSM-5. In addition, the H-ZSM-5 zeolite has the highest acidity in the strong acidic densities, which was attributed to the protons contributed from the Brønsted acid sites. Meanwhile, the lower weak acidic densities of K-ZSM-5 zeolite compared to Na-ZSM-5 zeolite implies the less likely dehydration process will occur in the production of 1,3-butadiene.



Figure 5-3. Nitrogen physisorption isotherms of the as-synthesized mesoporous zeolite catalysts.

The N₂ physisorption isotherms obtained for the as-prepared zeolite catalysts are shown in Figure 5-3. A large hysteresis loop in the relative pressure range of 0.85–0.99 and a small hysteresis loop in the range of 0.1–0.2 can be observed. All the zeolite catalysts have mesoporous structures due to the typical Type-IV isotherms and large hysteresis loop according to IUPAC classification. Furthermore, the large hysteresis loop is classified as an H1 loop with narrow and vertical characteristics, where multilayer adsorption and capillary condensation filling in the pores occurs within the p/p^{0} range of 0.85–0.99. The H1 type hysteresis loop also

confirms uniform cylindrical pores or ordered three-dimensional pore network in these ordered mesoporous materials.²⁶ The small hysteresis loop is well known to appear in microporous MFI zeolites rather than evidence of the mesoporous structure and can be attributed to the N₂ phase transformation from disordered to ordered.²⁷ The isomers at the relatively low pressure $(p/p^{\circ} < 0.015)$ have an obvious sharp knee that indicates the existence of the microporous structure. Therefore, the co-existence of mesoporous and microporous structures occurs in the zeolites and dominated by mesopores. The isotherm observed for Li-ZSM-5 is slightly different from the other three isotherms in the low relative pressure range of 0.01–0.1, which can be ascribed to the slight destruction of the microporous structure and the nitrogen molecules filling a small number of micropores quickly. However, the ion exchange step to give the Li-ZSM5 zeolite does not affect the dominant mesoporous structure. This was consistent with the smallest surface area of Li-ZSM-5 zeolite among the four different counter ions studied, as shown in Table 5-1.

SEM



Figure 5-4. SEM images of the ZSM-5 zeolites bearing different counter ions.

The uniform particle size distribution of Na-ZSM-5 gives a mean length of 2–3 μ m, and a crystalline phase with obvious protrusions on the rough surface was observed, as shown in Figure 5-4. The fissure of the fluffy particle surface is a typical mesoporous structured zeolite material, which was in good agreement with the literature.²⁰ Nevertheless, the ion exchange of LiNO₃ and KNO₃ solutions alters the surface of Na-ZSM-5 zeolite into the rough surface. Small agglomerated substances are attached to the surface and it may be ascribed to excess K₂O and Li₂O particle deposition after calcination despite the five washing steps using deionized water. However, the main morphology of the zeolite particles does not change remarkably, which means the ion-exchange step has little effect on the crystal size and structure. When compared to Li-ZSM-5 and K-ZSM-5, the H-ZSM-5 zeolite exhibits a clean and tidy surface morphology

that resembles the Na-ZSM-5. The clean and neat surface appearance of the Na/H-ZSM-5 zeolites results from different reasons. The precise controllable amount of NaAlO₂ used before the crystallization process of the parent Na-ZSM-5 zeolite means no excess Na₂O species are generated to further agglomeration to form large clusters. However, the clean and tidy appearance of H-ZSM-5 was attributed to the volatility of NH₃·H₂O during the calcination process after ion exchange of Na-ZSM-5 zeolite.





Figure 5-5. XPS signals observed for the Y/K-ZSM-5 zeolite catalysts at the Y3d level.

Two peaks at binding energies of 160.5 and 158.4 eV correspond to Y $3d_{3/2}$ and Y $3d_{5/2}$ as shown in Figure 5-5, respectively.²⁸ However, the binding energies of Y $3d_{3/2}$ and Y $3d_{5/2}$ in bulk Y₂O₃ are 158.6 and 156.7 eV, respectively. The reason for the distinctly higher binding energies observed in the Y/K-ZSM-5 zeolite is ascribed to the formation of Si-O-Y bonds.²⁹ The electron transfer from the Y to O atoms and then delivered to the Si atoms¹⁷ result in the low electron density of the Y species exhibiting Lewis acidity. Therefore, the O atom can easily interact with the electron-deficient Y atom because of the higher electron density of O when compared to the C atom in the aldehyde group because of its stronger electronegativity (the electronegativities of O and C are 3.44 and 2.55, respectively).¹⁶ The Lewis acidity of the Y species in the Si-O-Y bonds facilitate the aldol condensation step in the cascade reaction, consequently improving the selectivity toward 1,3-butadiene.¹⁷

5.3.2 Catalyst evaluation

1,3-Butadiene is produced from a mixture of ethanol and acetaldehyde, and the stoichiometric number ratio was 1:1 based on molar counting. Furthermore, the molar ratio of the mixture can be converted into a volume ratio using a calibration factor of 0.96, which is very close to 1, because they have subequal density and molar mass. Therefore, the volume ratio of ethanol and acetaldehyde was applied in this work rather than the molar ratio. The ethanol to acetaldehyde volume ratio was selected to be 1:1 to match the theoretical stoichiometric number ratio for the evaluation of zeolite catalysts bearing different counter ions.





Figure 5-6. Catalytic performance over Y/ZSM-5 zeolites bearing different counter ions.

The catalytic performance during 1.3-butadiene production from ethanol/acetaldehyde (v/v= 1:1) over Y/ZSM-5 zeolite catalysts bearing different counter ions is shown in Figure 5-6. It can be easily observed that ethylene is the main product with a selectivity of ~90% obtained using Y/H-ZSM-5 zeolite. This implies ethanol dehydrogenation was the dominant process rather than the acetaldehyde aldol condensation reaction used to increase the carbon chain. This catalytic result was in good agreement with the NH₃-TPD result showing the highest acidity of H-ZSM-5 zeolite, which exhibits strong Brønsted acidity, and also indicates the strong competitive priority for ethanol dehydrogenation by the proton even in the presence of Y species. It can also be confirmed that an ethanol conversion of 90% and acetaldehyde conversion of 30% can be achieved at the reaction temperature of 500 °C. Most of the ethanol was converted into ethylene and a small amount of ethanol undergoes intermolecular dehydration to form diethyl ether, especially in the low reaction temperature range of 300-350 °C. However, the situation exhibits a significant change after switching the counter ions to Li⁺, Na⁺, and K⁺. 1,3-Butadiene was one of the dominant products formed in the reaction temperature range of 400–500 °C, which indicates the aldol condensation and MPV reactions took place successfully with the interaction of Y species. The results indicate the introduction of alkaline-metal cations in ZSM-5 zeolite effectively suppresses the majority of the dehydration process. Nevertheless, the conversion of ethanol in the presence of the three alkaline-metal ions significantly decreases when compared to the Y/H-ZSM-5 catalyst, as shown in Figure 5-7, and thus led to the low selectivity toward the ethylene by-product. This can be attributed to the aldol condensation and MPV reactions over the Y species starting to play a dominant role to produce 1,3-butadiene rather than the dehydration of ethanol. The selectivity toward 1,3-butadiene at a reaction temperature of 450 °C over the Y/ZSM-5 zeolite catalysts bearing different counter ions decreases in the sequence of K > Na \approx Li \gg H. This was attributed to the particle size difference among the alkaline-metal ions. The larger particle size of the K cation leads to its weaker Lewis acidity when compared to the Na and Li cations. Thus, a higher electron density at the O atom was formed when compared to the Na and Li counter ions.



Figure 5-7. The summary of key indicators of the Y/ZSM-5 zeolite catalysts at an ethanol/acetaldehyde volume ratio of 1:1 at 450 °C.

The Y/K-ZSM-5 zeolite catalyst exhibits superior catalytic performance regarding the 1,3butadiene selectivity among the other zeolite catalysts bearing different counter ions. Therefore, it is necessary to screen the ethanol to acetaldehyde volume ratio to optimize the substrate composition to improve the selectivity toward 1,3-butadiene.



Figure 5-8. Catalytic performance over Y/K-ZSM-5 zeolites in the presence of different volume ratios of ethanol/acetaldehyde from 4:1 (upper left), 2:1 (upper right), 1.5:1 (bottom left) to 0.5:1 (bottom right).

The ethanol/acetaldehyde volume ratio has a significant effect on the 1,3-butadiene selectivity, as shown in Figure 5-8. . The highest 1,3-butadiene selectivity was 65%, which was obtained using ethanol to acetaldehyde volume ratio of 1.5:1, as shown in Figure 5-9. Raising volume ratio of acetaldehyde can accelerate the production of 1,3-butadiene with an ethanol/acetaldehyde volume ratios from 4:1 to 1.5:1. This can be attributed to the ratedetermination step being aldol condensation reaction at low acetaldehyde concentration because the selectivity of crotonaldehyde was lower than the other substrate ratios in the lowtemperature range (<350 °C). The low crotonaldehyde selectivity indicates that a small amount of acetaldol was produced because the acetaldol dehydration reaction to form crotonaldehyde is easy to achieve in the existence of acid sites or upon heating (Scheme 5-1). The fast dehydration process of acetaldol to α,β -unsaturated crotonaldehyde was due to the much higher inherent stability of crotonaldehyde with the formation of two double bonds when compared to acetaldol. Acetaldol was produced from the aldol condensation reaction of acetaldehyde. Therefore, the low concentration of acetaldehyde was the main reason limiting the aldol condensation process. Nevertheless, the situation was reversed upon increasing the acetaldehyde concentration. The selectivities of crotonaldehyde and 1,3-butadiene have complementary trends in the temperature range of 300-380 °C among the volume ratios of ethanol/acetaldehyde from 2:1 to 0.5:1. This means the aldol condensation was not an obstacle at high acetaldehyde concentrations. The MPV reaction becomes the rate-limiting step because ethanol participates in the MPV reaction to produce acetaldehyde. This results in an even higher acetaldehyde concentration and even lower ethanol concentration. Therefore, the MPV reaction is the rate-limiting step at a high acetaldehyde concentration in the low-temperature range of 300-380 °C. However, ethanol dehydration is the dominant process to produce ethylene at all acetaldehyde concentrations studied in the high-temperature range of 450–500 °C.



Figure 5-9. Summary of the key indicators of the Y/K-ZSM-5 zeolite catalysts among different ethanol/Acetaldehyde volume ratios at 450 °C.

5.3.3 TGA of coke deposition on the spent Y/K-ZSM-5 zeolite catalyst



Figure 5-10. TGA curve obtained for the used Y/K-ZSM-5 zeolite catalyst after the conversion of ethanol/acetaldehyde (v/v = 1.5:1).

Carbon deposits in the Y/K-ZSM-5 zeolite catalyst formed during the conversion of ethanol/acetaldehyde into 1,3-butadiene were analyzed using TGA in the temperature range of 25–800 °C. Figure 5-10 shows there are two obvious weight losses in the whole TGA analysis: A low-temperature weight loss in the range of 25–150 °C and a high-temperature weight loss in the range of 477–670 °C with quantified weight loss percentages of 0.6 and 7.2%, respectively. The low-temperature range weight loss was attributed to the evaporation of volatile compounds, such as water, absorbed products, and unreacted reactants. The high-temperature range weight loss was ascribed to the decomposition of coke compounds. The coke compounds were composed of unsaturated aldehydes and ketones dominated by 2,4-dimethyl

benzaldehyde, which was formed during the aldol condensation and cyclization reactions.²⁸ There is a different increasing tendency observed in the weight loss curve upon increasing the temperature in the range of 200–477 °C, which is unnormal in typical TGA measurements. This can be assigned to the yttrium particles being oxidized to Y_2O_3 during the TGA measurements due to the presence of air. The Y/K-ZSM-5 zeolite catalyst was obtained via calcination after the incipient wetness impregnation of the Y(NO₃)₃·6H₂O solution. Therefore, Y_2O_3 was formed in the zeolite catalyst and participates in the conversion of substrate mixture. However, ethylene was formed in the reduction of Y_2O_3 to Y. The Y particles were re-oxidized to Y_2O_3 and thus lead to an increase in the sample weight. The theoretical mass of Y_2O_3 was calculated to be 0.571 mg using the fresh Y/K-ZSM-5 zeolite catalyst and the real mass of Y_2O_3 in the zeolite catalyst was determined to be 0.445 mg upon the deduction of the zeolite support mass during the TGA measurement. The difference was acceptable when compared to the sample weight of 35.04 mg.

5.3.4 Stability and regeneration test



Figure 5-11. Stability and regeneration test using 2%Y/K-ZSM-5 in the presence of an ethanol/acetaldehyde volume ratio of 1.5:1 at 450 °C.

The catalytic stability and regeneration test using the Y/K-ZSM-5 zeolite with time on stream (TOS) was carried out at 450 °C, as shown in Figure 5-11. The maximum 1,3-butadiene selectivity was 67% during the catalyst stability test, which was slightly higher than the identical reaction conditions shown in Figure 5-8 (65%). The difference was acceptable due to the slight disturbance of the N₂ carrier gas. The Y/K-ZSM-5 zeolite catalyst maintains a stable selectivity of around 65% up to 22 h during the production of 1,3-butadiene and then slightly decreases to 57% over 3 h, whereas the conversions of ethanol and acetaldehyde exhibit a slow downward trend during the whole test period. The decreasing conversion of the substrate can

be attributed to coke formation (Figure 5-10) that hinders the effective interaction of Y sites with the substrate mixture.

5.4 Conclusions

The present work demonstrates the influence of counter ions in Y/ZSM-5 zeolite catalysts on the catalytic performance during the conversion of ethanol/acetaldehyde mixture to 1,3butadiene using a two-step method. K-ZSM-5 was identified as the most effective zeolite support used to improve the 1,3-butadiene selectivity due to the suitable acidity, which inhibits the ethanol dehydration, and the maximum 1,3-butadiene selectivity reached 65%. The activity of synthesized zeolites decreases in the order of Y/K-ZSM-5 > Y/Na-ZSM-5 \approx Y/Li-ZSM-5 \gg Y/H-ZSM-5 based on 1,3-butadiene selectivity. Furthermore, the volume fraction of acetaldehyde in the mixed substrate also played a critical role to yield 1,3-butadiene, and the optimum volume ratio of ethanol to acetaldehyde was selected to be 1.5:1 among the different tests.

5.5 References

- Larina, O. V.; Kyriienko, P. I.; Soloviev, S. O. Ethanol Conversion to 1,3-Butadiene on ZnO/MgO-SiO2 Catalysts: Effect of ZnO Content and MgO:SiO2 Ratio. *Catal. Lett.* 2015, 145 (5), 1162–1168.
- (2) Dussol, D.; Cadran, N.; Laloue, N.; Renaudot, L.; Schweitzer, J. M. New Insights of Butadiene Production from Ethanol: Elucidation of Concurrent Reaction Pathways and Kinetic Study. *Chem. Eng. J.* **2020**, *391*, 123586.
- (3) Ahn, C.; Kim, C.; Wook, J.; Jeon, J.; Seung, H.; Kim, Y.; Lee, S.; Lee, J.; Ha, K. Ethanol Conversion into 1, 3-Butadiene over Zn-Zr Mixed Oxide Catalysts Supported on Ordered Mesoporous Materials. *Fuel Process. Technol.* **2020**, 200, 106317.
- Klein, A.; Palkovits, R. Influence of Structural Parameters on the Conversion of Ethanol into 1, 3-Butadiene Using Mesoporous Zeolites. *Catal. Commun.* 2017, *91*, 72–75.
- (5) Kyriienko, P. I.; Larina, O. V.; Soloviev, S. O.; Orlyk, S. M.; Calers, C.; Dzwigaj, S. Ethanol Conversion into 1,3-Butadiene by the Lebedev Method over MTaSiBEA Zeolites (M = Ag, Cu, Zn). ACS Sustain. Chem. Eng. 2017, 5 (3), 2075–2083.
- (6) Qi, L.; Zhang, Y.; Conrad, M. A.; Russell, C. K.; Miller, J.; Bell, A. T. Ethanol Conversion to Butadiene over Isolated Zinc and Yttrium Sites Grafted onto Dealuminated Beta Zeolite. J. Am. Chem. Soc. 2020, 142 (34), 14674–14687.
- (7) Zhang, H.; Ibrahim, M. Y. S.; Flaherty, D. W. Aldol Condensation among Acetaldehyde and Ethanol Reactants on TiO2: Experimental Evidence for the Kinetically Relevant Nucleophilic Attack of Enolates. J. Catal. 2018, 361, 290–302.
- (8) Chae, H. J.; Kim, T. W.; Moon, Y. K.; Kim, H. K.; Jeong, K. E.; Kim, C. U.; Jeong, S. Y. Butadiene Production from Bioethanol and Acetaldehyde over Tantalum Oxide-Supported Ordered Mesoporous Silica Catalysts. *Appl. Catal. B Environ.* 2014, *150–151*, 596–604.
- (9) Kim, T.; Kim, J.; Kim, S.; Chae, H.; Kim, J.; Jeong, S.; Kim, C. Butadiene Production from Bioethanol and Acetaldehyde over Tantalum Oxide-Supported Spherical Silica Catalysts for Circulating Fluidized Bed. *Chem. Eng. J.* 2015, 278, 217–223.
- (10) Larina, O. V.; Kyriienko, P. I.; Balakin, D. Y.; Vorokhta, M.; Khalakhan, I.; Nychiporuk,Y. M.; Matolín, V.; Soloviev, S. O.; Orlyk, S. M. Effect of ZnO on Acid-Base Properties

and Catalytic Performances of ZnO/ZrO2-SiO2 Catalysts in 1,3-Butadiene Production from Ethanol-Water Mixture. *Catal. Sci. Technol.* **2019**, *9* (15), 3964–3978.

- (11) Xu, Y.; Liu, Z.; Han, Z.; Zhang, M. Ethanol/Acetaldehyde Conversion into Butadiene over Sol–Gel ZrO2–SiO2 Catalysts Doped with ZnO. *RSC Adv.* 2017, *7*, 7140–7149.
- Huang, X.; Men, Y.; Wang, J.; An, W.; Wang, Y. Highly Active and Selective Binary MgO–SiO 2 Catalysts for the Production of 1, 3-Butadiene from Ethanol. *Catal. Sci. Technol.* 2017, 7 (1), 168–180.
- (13) Taifan, W. E.; Baltrusaitis, J. In Situ Spectroscopic Insights on the Molecular Structure of the MgO/SiO2 Catalytic Active Sites during Ethanol Conversion to 1,3-Butadiene. *J. Phys. Chem. C* 2018, *122* (36), 20894–20906.
- (14) Taifan, W. E.; Li, Y.; Baltrus, J. P.; Zhang, L.; Frenkel, A. I.; Baltrusaitis, J. Operando Structure Determination of Cu and Zn on Supported MgO / SiO2 Catalysts during Ethanol Conversion to 1, 3-Butadiene. ACS Catal. 2019, 9, 269–285.
- (15) Zhang, M.; Qin, Y.; Tan, X.; Wang, L.; Yu, Y.; Jiang, H. Study of Ethanol/Acetaldehyde to 1,3-Butadiene Over MgO–SiO2 Catalyst: Comparative Investigation of Deactivation Behaviour Due to Carbon Deposition. *Catal. Lett.* **2020**, *150* (5), 1462–1470.
- (16) Yan, T.; Dai, W.; Wu, G.; Lang, S.; Hunger, M.; Guan, N.; Li, L. Mechanistic Insights into One-Step Catalytic Conversion of Ethanol to Butadiene over Bifunctional Zn-Y/Beta Zeolite. ACS Catal. 2018, 8 (4), 2760–2773.
- (17) Zhu, Q.; Yin, L.; Ji, K.; Li, C.; Wang, B.; Tan, T. Effect of Catalyst Structure and Acid
 Base Property on the Multiproduct Upgrade of Ethanol and Acetaldehyde to C4
 (Butadiene and Butanol) over the Y–SiO2 Catalysts. ACS Sustain. Chem. Eng. 2020, 8, 1555–1565.
- (18) Díaz, M.; Epelde, E.; Valecillos, J.; Izaddoust, S.; Aguayo, A. T.; Bilbao, J. Coke Deactivation and Regeneration of HZSM-5 Zeolite Catalysts in the Oligomerization of 1-Butene. *Appl. Catal. B Environ.* **2021**, *291*, 120076-120085.
- Jacobsen, C. J. H.; Madsen, C.; Houzvicka, J.; Schmidt, I.; Carlsson, A. Mesoporous Zeolite Single Crystals. J. Am. Chem. Soc. 2000, 122 (29), 7116–7117.
- (20) Rasmussen, K. H.; Goodarzi, F.; Christensen, D. B.; Mielby, J.; Kegnæs, S. Stabilization of Metal Nanoparticle Catalysts via Encapsulation in Mesoporous Zeolites by Steam-

Assisted Recrystallization. ACS Appl. Nano Mater. 2019, 2 (12), 8083–8091.

- (21) Jaumain, D.; Su, B. L. Direct Catalytic Conversion of Chloromethane to Higher Hydrocarbons over a Series of ZSM-5 Zeolites Exchanged with Alkali Cations. J. Mol. Catal. A Chem. 2003, 197 (1–2), 263–273.
- (22) Yamazaki, T.; Watanuki, I.; Ozawa, S.; Ogino, Y. Infrared Spectra of Methane Adsorbed by Ion-Exchanged Zsm-5 Zeolites. *Langmuir* **1988**, *4* (2), 433–438.
- Yuan, C.; Liu, H.; Zhang, Z.; Lu, H.; Zhu, Q.; Chen, Y. Alkali-Metal-Modified ZSM-5 Zeolites for Improvement of Catalytic Dehydration of Lactic Acid to Acrylic Acid. *Chin. J. Catal.* 2015, *36* (11), 1861–1866.
- (24) Zhu, Q.; Wang, B.; Tan, T. Conversion of Ethanol and Acetaldehyde to Butadiene over MgO-SiO2 Catalysts: Effect of Reaction Parameters and Interaction between MgO and SiO2 on Catalytic Performance. ACS Sustain. Chem. Eng. 2017, 5 (1), 722–733.
- (25) Kyriienko, P. I.; Larina, O. V; Soloviev, S. O.; Orlyk, S. M.; Dzwigaj, S. High Selectivity of TaSiBEA Zeolite Catalysts in 1, 3-Butadiene Production from Ethanol and Acetaldehyde Mixture. *Catal. Commun.* **2016**, 77, 123–126.
- (26) Giraldo, L.; Camargo, G.; Tirano, J.; Moreno-Piraján, J. C. Synthesis of Fatty Alcohols from Oil Palm Using a Catalyst of Ni-Cu Supported onto Zeolite. *E-Journal Chem.* 2010, 7 (4), 1138–1147.
- (27) Goodarzi, F.; Thumbayil, R. P.; Enemark-Rasmussen, K.; Mielby, J.; Nguyen, T. T. M.; Beato, P.; Joensen, F.; Kegnæs, S. Enhanced Catalytic Performance of Zn-Containing HZSM-5 upon Selective Desilication in Ethane Dehydroaromatization Process. *ChemCatChem* 2020, *12* (5), 1519–1526.
- (28) Yan, T.; Yang, L.; Dai, W.; Wang, C.; Wu, G.; Guan, N.; Hunger, M.; Li, L. On the Deactivation Mechanism of Zeolite Catalyst in Ethanol to Butadiene Conversion. J. *Catal.* 2018, 367, 7–15.
- (29) Dai, W.; Zhang, S.; Yu, Z.; Yan, T.; Wu, G.; Guan, N.; Li, L. Zeolite Structural Confinement Effects Enhance One-Pot Catalytic Conversion of Ethanol to Butadiene. *ACS Catal.* 2017, 7 (5), 3703–3706.

Chapter 6 Conclusions and future work

The objective of this dissertation aimed to investigate the applications of metal-supported zeolite catalysts in the process of 1,3-butadiene production from ethanol or ethanol-acetaldehyde mixtures. The ethanol conversion to 1,3-butadiene is a complex tandem reaction with four consecutive steps: (1) ethanol dehydrogenation to acetaldehyde; (2) aldol condensation to acetaldol and further dehydration to crotonaldehyde; (3) crotyl alcohol formation from crotonaldehyde through MPV reaction; (4) crotyl alcohol dehydration to 1,3-butadiene. The critical point for the production of 1,3-butadiene is an exploration of active sites for all steps and then obtaining the synergistic effect among these active sites. Therefore, this thesis investigated the pivotal parameters in the process of 1,3-butadiene production from the local to the overall with the progressive improvement.

Chapter 3 focuses on the process of ethanol dehydrogenation to acetaldehyde over Zncontaining zeolites with MFI topology. The Zn/Silicalite-1 (5 wt%) zeolite exhibited the optimum activity towards the production of acetaldehyde through ethanol dehydrogenation with the conversion and the selectivity of 65% and 95%, respectively. The Zn/NaZSM-5 (5 wt%) zeolite was also effective in the formation of acetaldehyde from ethanol with the conversion and the selectivity of 55% and 92%, separately. The high activities of Zn/Silicalite-1 and Zn/NaZSM-5 should be ascribed to the ZnO species that acted as the dehydrogenation sites compared to their naked zeolites. The ethanol dehydration to ethylene was the main reaction over Zn/HZSM-5 and Zn/DeAlZeolite due to the strong Brønsted acid sites which resulted from the sufficient silanol groups in the zeolite framework.

Chapter 4 describes the direct conversion of ethanol to 1,3-butadiene over Zn and/or Y containing zeolites with MFI and BEA topologies. The monometallic Zn/Zeolite or Y/Zeolite catalysts were inactive to produce 1,3-butadiene with high selectivity due to the absence of Lewis acid sites and dehydrogenation sites, respectively. The synergistic effect of Zn and Y species in the bimetallic ZnY/NaZSM-5 played a prominent part in the process of 1,3-butadiene production from ethanol conversion with the highest selectivity of 12.4%. However, the arrangements of Zn/NaZSM-5 and Y/NaZSM-5 zeolites demonstrated an obvious improvement of the 1,3-butadiene production. The zeolite arrangement structures of physical mixture and layer by layer have the optimum 1,3-butadiene selectivities of 37% and 39%,

separately. The significant improvement of 1,3-butadiene selectivity indicated that the distance of Zn and Y active sites was a critical factor for the direct conversion of ethanol to 1,3-butadiene.

Chapter 5 investigates the conversion of ethanol/acetaldehyde mixtures to 1,3-butadiene over Y/NaZSM-5 zeolites with different counter ions. The activity of synthesized zeolite catalysts decreased in the order of Y/K-ZSM-5 > Y/Na-ZSM-5 \approx Y/Li-ZSM-5 \gg Y/H-ZSM-5 according to the selectivity of 1,3-butadiene. The Y/KZSM-5 zeolite catalyst exhibited the optimum activity for the 1,3-butadiene production with the maximum selectivity of 65%. The high selectivity should be attributed to the suitable acidity and the molar ratio of the substrate composition. Nevertheless, the proton-form ZSM-5 zeolite was inactive for the production of 1,3-butadiene, and the selectivity of ethylene reached 90% that was assigned to the strong Brønsted acidity of the zeolite.

The highest selectivity of 1,3-butadiene in this dissertation is still lower than the state-ofthe-art literature either in the direct conversion of ethanol or the conversion of ethanol/acetaldehyde mixture. The complex tandem reaction makes it a great challenge to invent a novel catalyst with multifunctional active sites and moderate acidity for the effective production of 1,3-butadiene. Therefore, future research about the ethanol conversion to 1,3butadiene should focus on the three aspects:

(1) the application of monometallic zeolite catalyst in the direct conversion of ethanol to 1,3butadiene through other metals with sufficient dehydrogenation sites, Lewis acid sites, and Brønsted acid sites;

(2) the quantitative relationship of distance between Zn active sites and Y active sites may be an interesting project because it involves the adsorption and desorption of ethanol and acetaldehyde molecules;

(3) the production of 1,3-butadiene from ethanol/acetaldehyde mixture is relatively easier than the direct conversion of ethanol. However, the mechanism of the carbon-carbon bond coupling is remained to be investigated through advanced techniques such as in-site IR, and DFT calculation.

Appendix A Supporting information of Chapter 5

TEM



Figure A-1. TEM images of ZSM-5 zeolites bearing different counter ions.

Appendix B Phenol hydrogenation to cyclohexanol

This project is not included in the thesis.



Figure B-1 Different reaction barriers in the process of phenol hydrogenation. Adapted with permission from literature.¹



Scheme B-1. Reaction pathway of phenol hydrogenation to cyclohexanol.

Experimental section

Phenol (0.1 g) and nonane (0.1 mL, internal standard) were mixed in a Teflon inlet of the high-pressure autoclave. The as-prepared catalyst and $ZnCl_2$ were added into the Teflon inlet followed by 5 ml CH₂Cl₂ as solvent. The hydrogen (10 bar) was purged into the autoclave for the reaction at the reaction temperature (100 °C) and time (16 h). After the reaction time was reached, the autoclave was quenched down to room temperature quickly in an ice bath.

Results



Figure B-2. Phenol conversion over different catalysts. AC: activated carbon.

References

(1) Chen, H.; He, Y.; Pfefferle, L. D.; Pu, W.; Wu, Y.; Qi, S. Phenol Catalytic Hydrogenation over Palladium Nanoparticles Supported on Metal-Organic Frameworks in the Aqueous Phase. *ChemCatChem* **2018**, *10* (12), 2558–2570.

Appendix C Disseminations

Publication list

- (1) Kai Gao, Jerrik Mielby, Søren Kegnæs. Catalytic dehydrogenation of ethanol over zinccontaining zeolites, *Catalysis Today*, 2022, Under review.
- (2) Kai Gao, Jerrik Mielby, Søren Kegnæs. 1,3-Butadiene production from ethanol and acetaldehyde mixtures over Y/ZSM-5 zeolites with different counter ions, 2022, Manuscript finished.

Oral presentations

- (1) Mechanistic study of the conversion of ethanol to 1,3-butadiene by DRIFT analysis, DTU Chemistry Ph.D. symposium, 28 January 2021, Lyngby, Denmark.
- (2) Ethanol conversion to 1,3-butadiene over Zn zeolite catalysts, *Centre for Catalysis and Sustainable Chemistry, DTU Chemistry, 13 October 2020, Lyngby, Denmark.*
- (3) Phenol hydrogenation to cyclohexanol using metal-encapsulated zeolite catalysts, Centre for Catalysis and Sustainable Chemistry, DTU Chemistry, 08 January 2019, Lyngby, Denmark.

Poster presentations

- (1) Phenol hydrogenation to cyclohexanol using noble metal incorporated in hierarchical zeolites, *Europacat XIV*, *August 18-23, 2019, Aachen, Germany*.
- (2) Hydrogenation of phenol using Pd incorporated in hierarchical zeolites, *DTU Chemistry Ph.D. symposium, November 8-9, 2019, Helsingør, Denmark*

Appendix D Co-author statement

PhD Administration & Development



Declaration of co-authorship at DTU

If a PhD thesis contains articles (i.e. published journal and conference articles, unpublished manuscripts, chapters, etc.) written in collaboration with other researchers, a co-author statement verifying the PhD student's contribution to each article should be made.

If an article is written in collaboration with three or less researchers (including the PhD student), all researchers must sign the statement. However, if an article has more than three authors the statement may be signed by a representative sample, cf. article 12, section 4 and 5 of the Ministerial Order No. 1039, 27 August 2013. A representative sample consists of minimum three authors, which is comprised of the first author, the corresponding author, the senior author, and 1-2 authors (preferably international/non-supervisor authors).

DTU has implemented the Danish Code of Conduct for Research Integrity, which states the following regarding attribution of authorship:

"Attribution of authorship should in general be based on criteria a-d adopted from the Vancouver guidelines¹, and all individuals who meet these criteria should be recognized as authors:

- a. Substantial contributions to the conception or design of the work, or the acquisition, analysis, or interpretation of data for the work, and
- b. drafting the work or revising it critically for important intellectual content, and
- c. final approval of the version to be published, and
- d. agreement to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved."2

For more information regarding definition of co-authorship and examples of authorship conflicts, we refer to DTU Code of Conduct for Research Integrity (pp. 19-22).

By signing this declaration, co-authors permit the PhD student to reuse whole or parts of coauthored articles in their PhD thesis, under the condition that co-authors are acknowledged in connection with the reused text or figure.

It is important to note that it is the responsibility of the PhD student to obtain permission from the publisher to use the article in the PhD thesis³

This form was last updated December 2021 page 1/3

¹ International Committee of Medical Journal Editors – Recommendations for the Conduct, Reporting, Editing, and Publication of Scholarly Work in Medical Journals, updated December 2016 ² DTU Code of Conduct for Research Integrity (E-book p. 19)

³ Many journals will allow you to use only the post-print version of your article, meaning the accepted version of the article, without the publisher's final formatting. In the event that your article is submitted, but still under review, you should of course use the latest submitted version of your article in your thesis. Always remember to check your publisher's guidelines on reuse of published articles. Most journals, unless open access, have an embargo period on published articles, meaning that within this period you cannot freely use the article. Check your publisher's rules on this issue.



PhD Administration & Development

Title of article		
Catalytic dehydrogenation of eth	anol over zinc-containing zeolites	
Journal/conference	and a second	
Catalysis Today		
Author(s)		
Kai Gao, Jerrik Mielby, Søren Ke	gnæs	
Name (capital letters) and signat	ture of PhD student	
KAI GAO		
PhD student's date of birth		
1 st July, 1991		
Declaration of the PhD student's	s contribution	
For each category in the table below not fill in with names or x's)	ν, please specify the PhD student's contribu	tion to the article as appropriate (please do
Category	Minor contribution to the work (please specify the nature of the PhD student's contribution)	Substantial contribution to the work (please specify the nature of the PhD student's contribution)
Formulation of the conceptual framework and/or planning of the design of the study including scientific questions		Contributed with relevant scientific input of the whole project; discussed with co-authors for the direction of the project
Carrying out of experiments/data collection and analysis/interpretation of results		Carry out all the experimental work and data treatment; discuss the explanation of data with co-authors
Writing of the article/revising the manuscript for intellectual content		Writing the initial draft of the manuscript with all figures and explanations; discussing the improvement of the draft with co- authors
Signatures	Gras	a da Britan de Spantantes en

This form was last updated December 2021| page 2/3

PhD Administration & Development



Title of article			
Catalytic dehyd	drogenation of ethanol	over zinc-containing zeolit	es
Journal/confer	rence		
Catalysis Toda	y		
Author(s)			
Kai Gao, Jerrik	Mielby, Søren Kegnæs	5	
Name (capital	letters) and signature	of PhD student	
KAI GAO	K	AT GAD	
PhD student's	date of birth	112 01110	
1 st July, 1991	al an inneres ong		
Date	Name	Title	Signature
25 th January, 2022	Kai Gao	PhD student	bei brano
25 th January, 2022	Jerrik Mielby	Senior Researcher	Janik Milley
25 th January, 2022	Søren Kegnæs	Professor	Squen Versnos

Please note that by signing this declaration, co-authors permit the PhD student to reuse whole or parts of co-authored articles in their PhD thesis, under the condition that co-authors are acknowledged in connection with the reused text or figure.

This form was last updated December 2021| page 3/3



Declaration of co-authorship at DTU

If a PhD thesis contains articles (i.e. published journal and conference articles, unpublished manuscripts, chapters, etc.) written in collaboration with other researchers, a co-author statement verifying the PhD student's contribution to each article should be made.

If an article is written in collaboration with three or less researchers (including the PhD student), all researchers must sign the statement. However, if an article has more than three authors the statement may be signed by a representative sample, cf. article 12, section 4 and 5 of the Ministerial Order No. 1039, 27 August 2013. A representative sample consists of minimum three authors, which is comprised of the first author, the corresponding author, the senior author, and 1-2 authors (preferably international/non-supervisor authors).

DTU has implemented the Danish Code of Conduct for Research Integrity, which states the following regarding attribution of authorship:

"Attribution of authorship should in general be based on criteria a-d adopted from the Vancouver guidelines¹, and all individuals who meet these criteria should be recognized as authors:

- a. Substantial contributions to the conception or design of the work, or the acquisition, analysis, or interpretation of data for the work, and
- b. drafting the work or revising it critically for important intellectual content, and
- c. final approval of the version to be published, and
- agreement to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved."²

For more information regarding definition of co-authorship and examples of authorship conflicts, we refer to DTU Code of Conduct for Research Integrity (pp. 19-22).

By signing this declaration, co-authors permit the PhD student to reuse whole or parts of coauthored articles in their PhD thesis, under the condition that co-authors are acknowledged in connection with the reused text or figure.

It is **important** to note that it is the responsibility of the PhD student to obtain permission from the publisher to use the article in the PhD thesis³

This form was last updated December 2021 page 1/3

¹ International Committee of Medical Journal Editors – Recommendations for the Conduct, Reporting, Editing, and Publication of Scholarly Work in Medical Journals, updated December 2016

² DTU Code of Conduct for Research Integrity (E-book p. 19)

³ Many journals will allow you to use only the post-print version of your article, meaning the accepted version of the article, without the publisher's final formatting. In the event that your article is submitted, but still under review, you should of course use the latest submitted version of your article in your thesis. Always remember to check your publisher's guidelines on reuse



PhD Administration & Development

Title of article

1,3-Butadiene production from ethanol and acetaldehyde mixture over Y/ZSM-5 zeolites with different counter ions

Journal/conference

To be submitted

Author(s)

Kai Gao, Jerrik Mielby, Søren Kegnæs Name (capital letters) and signature of PhD student

KAI GAO

PhD student's date of birth

1st July, 1991

Declaration of the PhD student's contribution

For each category in the table below, please specify the PhD student's contribution to the article as appropriate (please do not fill in with names or x's)

Minor contribution to the work (please specify the nature of the PhD student's contribution)	Substantial contribution to the work (please specify the nature of the PhD student's contribution)
	Literature study of the project, Design the synthesis of Y/ZSM-5 zeolite catalysts with different counter ions, discuss the key points of reaction conditions about 1,3-butadiene production
	Carry out all synthesis of Y/ZSM-5 catalysts and characterizations except SEM and TEM, perform experiments and data treatment; discuss the explanation of results with co-authors
	Writing the initial draft of the manuscript with all result figures and explanations; discussing the improvement of the draft with supervisors
	(please specify the nature of the PhD student's contribution)

of published articles. Most journals, unless open access, have an embargo period on published articles, meaning that within this period you cannot freely use the article. Check your publisher's rules on this issue.

This form was last updated December 2021| page 2/3



PhD Administration & Development

1,3-Butadiene proc ons Iournal/conferenc Fo be submitted	duction from ethanol a e	and acetaldehyde mixtu	re over Y/ZSM-5 zeolites with different counter
ons Iournal/conferenc Fo be submitted	е		
lournal/conferenc Fo be submitted	e		
Fo be submitted			
the second se			
Author(s)			
Kai Gao, Jerrik Mie	elby, Søren Kegnæs		
Name (capital lett	ers) and signature of I	PhD student	
KAI GAO	KAL GE	10	
PhD student's date	e of birth	4-3	
1 st July, 1991			
Date N	ame	Title	Signature
23 rd January, Ka 2022	ai Gao	PhD student	kai hao
23 rd January, Je 2022	errik Mielby	Senior researcher	Jeme Mielby
23 rd January, Se 2022	øren Kegnæs	Professor	Spen Vegnes

Please note that by signing this declaration, co-authors permit the PhD student to reuse whole or parts of co-authored articles in their PhD thesis, under the condition that co-authors are acknowledged in connection with the reused text or figure.

This form was last updated December 2021 page 3/3