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Biofuels and Biomass

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Catalytic Hydropyrolysis of Biomass using Molybdenum Sulfide Based Catalyst. Effect of Promoters

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Abstract

Catalytic hydropyrolysis of beech wood was conducted in a fluid bed reactor at 450°C and a total pressure of 26 bar. The differences in hydrodeoxygenation activity, selectivity and the resulting product composition between sulfided Mo/MgAl₂O₄, CoMo/MgAl₂O₄ or NiMo/MgAl₂O₄ catalysts have been investigated. The acidity and molybdate species in the oxide catalyst precursors were characterized with ammonia temperature programmed desorption (NH₃-TPD) and Raman spectroscopy. The spent sulfided catalysts were also extensively characterized by scanning electron microscopy (SEM) and by scanning transmission electron microscopy (STEM) coupled with energy dispersive X-ray spectroscopy (EDS). The catalytic hydropyrolysis of beech wood produced four kinds of products: Liquid organic and aqueous phases, solid char and gases. The solid char and aqueous phase yields were not affected by the type of catalyst. The sum of condensed organics and C₄₊ gas yield varied between 24.3 and 26.4 wt.% on dry, ash free basis (daf) and was highest for the Mo catalyst and lowest for the NiMo catalyst. The NiMo catalyst had the highest hydrogenation, cracking, and de-carbonylation activity. The oxygen content in the condensed organic phase was between 9.0 and 12 wt.% on dry basis (db) and was lowest for the CoMo catalyst and highest for the

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4 24 Mo catalyst. The carbon recovery in the condensable organics was 39 % for both the CoMo and the Mo,
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6 25 and 37 % for the NiMo catalyst. These results indicate that the CoMo, due to its high deoxygenation activity
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8 26 and high carbon recovery, is the most suitable catalyst for catalytic hydrolysis. The carbon content on
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10 27 the spent CoMo was between 1.5 and 3.3 wt.% and between 0.9 and 3.1 on the spent NiMo catalyst, but
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12 28 between 5.0 and 5.5 wt.% on the spent Mo catalyst. The higher carbon content on the spent Mo catalyst
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14 29 was probably due to its lower deoxygenation and hydrogenation activity. Calcium particles and small
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16 30 amounts of potassium (≤ 1.5 wt.%) were detected on all spent catalysts using STEM-EDS, showing that alkali
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18 31 metals are transferred from the biomass to the catalyst, which potentially could lead to catalyst
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20 32 deactivation.
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Abbreviations

AED	Atomic emission detector
BET	Brunauer–Emmett–Teller
conc	Concentration
CUS	Coordinatively unsaturated sites
daf	Dry, ash free basis
db	Dry basis
DDO	direct deoxygenation
diAro	Diaromatics
DMDS	Dimethyl disulfide
EDS	Energy dispersive X-ray spectroscopy
FB	Fluid bed
FCC	Fluid catalytic cracking
FID	Flame ionization detector
GC	Gas chromatograph
HAADF	High-angle annular dark-field
HDO	Hydrodeoxygenation
HYD	Hydrogenation
ICP-OES	Inductive coupled plasma optical emission spectroscopy
mAro	Monoaromatics
MS	Mass spectrometry
Naph	Naphthenes
O-Ali	Oxygenated aliphatics
O-Aro	Larger oxygenated aromatics

Par	Paraffins
PhOH	Phenolics
Ph(OH) ₂	Dihydroxybenzene
SSA	Specific surface area
SEM	Scanning electron microscopy
STEM	Scanning transmission electron microscopy
Temp.	Temperature
TPD	Temperature programmed desorption
tetAro+	Tetra- and higher aromatics
triAro	Triaromatics

1 Introduction

Catalytic hydropyrolysis, the concerted combination of fast pyrolysis and catalytic hydrodeoxygenation (HDO), has been shown to be an efficient method for production of renewable diesel and gasoline range hydrocarbons from biomass^{1,2}. In this process the reactive oxygenates formed during pyrolysis, which otherwise may undergo polymerization reactions³, are immediately hydrogenated producing a stable product with a significantly lower oxygen content than conventional fast pyrolysis oil. Marker et al.^{1,2} were able to produce an oxygen free oil with a condensed organic and C₄₊ gas yield of 21 to 46 wt.% dry ash free (daf) basis by conducting catalytic hydropyrolysis of different types of biomass (the high yield of 46 wt.% daf was obtained with microalgae) in a fluid bed reactor followed by deep HDO in a fixed bed reactor, in a process called IH²®. Furthermore, life cycle assessments of the IH²® process have shown that its fuel products have 30-96 % lower greenhouse gas emissions compared to fossil fuels, mainly depending on the biomass feedstock where bagasse shows the highest reduction^{4,5}.

Using a fluid bed reactor, Dayton et al.⁶⁻⁸ have tested several pre-reduced catalysts, including a commercial NiMo hydrotreating catalyst and a Mo based catalyst, for catalytic hydropyrolysis of woody biomass at temperatures between 375 and 500 °C and pressures of hydrogen between 1 and 31 bar. They were able to obtain a condensed organic and C₄₊ carbon yield of 43 %, with an oxygen content in the condensed liquid of 6.2 wt.%⁸. However, the composition of the catalysts was not reported and the spent catalysts were not characterized. Gamliel et al.⁹⁻¹¹ also studied the effect of reduced metal catalysts in catalytic hydropyrolysis using a Pyroprobe analyzer focusing mainly on Ni metal on a zeolite (ZSM-5) support. The fresh catalysts were characterized, but the spent catalysts were not studied. Therefore, despite that catalytic hydropyrolysis is a promising technology, there is very little information available about the composition of catalysts and to what degree the catalysts may be deactivated e.g. by carbon deposition or transfer of alkali metals, inherently present in biomass.

Sulfided CoMo, NiMo, and Mo, which are widely used as hydrotreating catalysts in oil refineries, are also known to be active and stable in hydrodeoxygenation reactions of bio-oil and model components^{12–20}. Since most biomass sources contain sulfur²¹, a major advantage of the sulfided catalysts is that they are sulfur tolerant, as opposed to many reduced metal catalysts. It is well-known that the addition of a promoter (Co or Ni) to MoS₂ increases the formation of the coordinated unsaturated sites (CUS)^{22–24}, thus enhancing the catalytic activity^{17,25}. One of the differences between Co and Ni as promoter is that Co promotes the direct deoxygenation (DDO) pathway, while Ni promotes the hydrogenation (HYD) pathway, where aromatic rings are saturated prior to deoxygenation^{18,25–28}.

In our previous work we conducted catalytic hydropyrolysis of beech wood in a fluid bed reactor with a commercial, sulfided CoMo/MgAl₂O₄ catalyst (supplied by Haldor Topsøe A/S), followed by a fixed bed reactor with a commercial, sulfided NiMo/Al₂O₃ hydrotreating catalyst²⁹. The effect of temperature and pressure in the fluid bed hydropyrolysis reactor was evaluated. An essentially oxygen free organic phase (oxygen < 0.01 wt.%) was obtained with a yield between 17 and 22 wt.% daf, corresponding to an energy recovery between 40 and 53 %²⁹. The concentration of aromatics could be controlled between 42 and 75 % by varying the operating conditions²⁹. Furthermore we previously studied the differences between sulfided Mo, CoMo, and NiMo, catalysts supported on MgAl₂O₄ in the hydrodeoxygenation of ethylene glycol in a fixed bed reactor¹⁷, and found that the Mo catalyst had the lowest conversion and the lowest stability, but the highest selectivity to C₂ and C₃ hydrocarbons and C-C coupling products, rather than C₁ cracking products. This indicates that it could be an advantage to use a catalyst with a moderate activity in catalytic hydropyrolysis.

In this work the differences between using a sulfided Mo, CoMo, and NiMo supported on MgAl₂O₄ in catalytic hydropyrolysis of beech wood in a fluid bed reactor was studied. Thereby the influence of the promoter type when using sulfided molybdenum catalysts for catalytic hydropyrolysis of biomass could be investigated. The oxide catalyst precursors were characterized by Raman spectroscopy and NH₃-TPD to

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4 84 obtain specific information about the surface molybdate species and acid properties. The spent catalysts
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6 85 were investigated with electron microscopy (SEM and STEM) coupled with energy dispersive X-ray
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8 86 spectroscopy (EDS) to reveal composition and elemental distribution of the catalysts as well as the
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11 87 structure and particle sizes of the catalytically active molybdenum sulfide. Furthermore, the organic phase
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13 88 products were characterized in depth with sulfur specific gas chromatography (GC) using an atomic
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15 89 emission detector (AED) and GC×GC-mass spectrometry (MS)/flame ionization detector (FID). To our
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18 90 knowledge this is the first study published in the open literature where the composition of the catalyst used
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20 91 in a continuous, bench scale catalytic hydropyrolysis setup is reported, where the catalysts are
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22 92 characterized in depth and where the influence of the catalyst type on the product properties is provided.
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26 93 **2 Experimental**

27 94 **2.1 Biomass feedstock**

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31 95 Bark free beech wood was used as biomass feedstock and was supplied by Dansk Træmel (Product number:
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33 96 10000251250390). The moisture and ash contents were 6.72 wt.% and 0.59 wt.% on dry basis (db),
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35 97 respectively²⁹. The particle sizes were between 200-700 μm. The beech wood was analyzed by Celignis
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38 98 Analytical (analysis P10) and consisted of 24 wt.% db lignin, 40 wt.% db cellulose, 18 wt.% db hemicellulose,
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40 99 3 wt.% db other polysaccharides, 3 wt.% db extractives and 12 wt.% db unknown. The potassium was 0.12
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42 100 wt.% db and calcium content was 0.13 wt.% db. A detailed elemental composition of the biomass, including
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45 101 the ash composition, can be found elsewhere²⁹.
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48 102 **2.2 Catalyst preparation**

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50 103 The CoMo, NiMo, and Mo catalysts were prepared by sequential incipient wetness impregnation of the
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52 104 MgAl₂O₄ spinel support, which was supplied by Haldor Topsøe A/S. The support was crushed to a particle
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55 105 size of 180-355 μm, to ensure a good fluidization of the fluid bed. Prior to impregnation, the support was
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4 106 calcined at 995°C for 10 hours. The calcined support had a pore volume of 0.58-0.62 g_{water}/g and 110 % of
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6 107 this volume was used for the impregnation. The specific surface area (SSA) was between 54-58 m²/g.
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10 108 The support was impregnated with an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O (Fluka≥99.0%), then aged
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12 109 with stirring for approximately 3 hours and dried over night at approximately 110°C in air. For the
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14 110 promoted catalysts, a second impregnation with Co(NO₃)₂·6H₂O (Fluka ≥ 98%) or Ni(NO₃)₂·6H₂O (Sigma-
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16 111 Aldrich ≥97%) was conducted with ageing for approximately 3 hours followed by drying over night at
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18 112 approximately 110°C in air. The calcination was conducted under a flow of technical air by heating to 500°C
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21 113 with a ramp of 5°C/min and holding for 3 hours. After calcination the catalyst was sieved to 180-355 μm
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23 114 again in order to remove any dust or agglomerates formed during the preparation. The composition of the
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25 115 catalysts is shown in Table 1. A Mo loading between 3.5 and 3.7 atoms/nm² was obtained. Mo loadings
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27 116 lower than 4 atoms/nm² should give a sub monolayer of MoO_x on MgAl₂O₄, assumed similar to γ-Al₂O₃³⁰,
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30 117 which should lead to a high dispersion of small MoS₂ particles (when sulfided) with a moderate activity,
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32 118 hence minimizing the formation of the very active type II sites³¹. The (Co/Ni) to Mo atomic ratio was aimed
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34 119 at 0.3, because this should ensure that the less active Co₉S₈ phase is not formed³². The acidity of the as
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36 120 calcined catalysts in the oxide form was measured using NH₃ adsorption and subsequent TPD. No significant
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39 121 difference in the acidity of the three catalysts was observed (see supporting information Figure S.1 and
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41 122 Table S.1), indicating that the main difference between these catalysts are the promoter.
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44 123 The catalysts were sulfided in-situ in the catalytic hydropyrolysis setup at 26 bar, 350°C with 1.8 mol % H₂S,
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46 124 11 mol % N₂ in 87 mol % H₂ by feeding 2% H₂S in H₂ (flow: 4 NL/min) and N₂ (flow: 0.5 NL/min). The
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49 125 temperature ramp was 10 °C/min and the holding time was 2 hours. After the sulfidation, the test
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51 126 conditions shown in Table 2 were established.
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Table 1 Composition of the fresh catalysts

Catalyst	Mo [wt.%]	Ni [wt.%]	Co [wt.%]	(Co/Ni)/Mo [molar]	Mo load Atoms/nm ²	BET SSA m ² /g
CoMo	3.41	-	0.637	0.30	3.6	60
NiMo	3.27	0.585	-	0.29	3.5	58
Mo	3.50	-	-	-	3.7	60

2.3 Experimental setup

The catalytic hydropyrolysis experiments were conducted in a bench scale setup shown schematically in Figure 1 and described in detail elsewhere²⁹. In brief, the setup consisted of a feeding system, which included a gas mixing system and a screw feeder for biomass feeding, a fluid bed hydropyrolysis reactor, a filter for char removal and a three stage condensation system (20°C, 2°C, and -40°C). The uncondensed gases were sent to a flare. A small fraction of the gas was set to an online gas GC, which measured the gas composition (H₂, N₂, H₂S, CO, CO₂, C₁ to C₅ and C₆₊ hydrocarbons) every 10 min. The piping between the fluid bed, filter and condensation section was heated to 350°C in order to avoid condensation. During the experiments 52 NL/min hydrogen passed through a sinter plate in the bottom of the fluid bed reactor and 30 NL/min hydrogen and 5 NL/min nitrogen passed through the biomass feeding tube, thus ensuring a rapid transfer of the biomass from the screw feeder to fluid bed reactor. The fluid bed temperature was approximately 450°C, the biomass feeding rate was between 271 and 275 g/h, the total pressure was 26 bar, and the experimental time was 3.5 h. The condensed liquid was collected after the experiment had ended.

The total mass of the condensed liquid was determined by weighing and the organic phase and the aqueous phase were separated with a separation funnel. The mass of the aqueous phase was measured and the mass of the organic phase was determined by subtracting the mass of the aqueous phase from the total mass of condensed liquid. The H₂S dissolved in the liquid phases was for safety reasons removed by bubbling with N₂ until hydrogen sulfide test strips (Sigma Aldrich) showed no sign of H₂S. This lead to a mass loss between 0 and 4.8 wt.% for the organic phase and between 1.0 and 1.5 wt.% of the aqueous

phase. The mass loss in the organic phase was mainly due to vaporization of light hydrocarbons while the mass loss in the aqueous phase was mainly due to vaporization of water.

After each experiment the catalyst and the remaining char was removed from the fluid bed, and replaced with the fresh catalyst for the subsequent experiment. The sum of char (un-vaporized biomass residue) and coke (carbon on the catalysts) yield was calculated by subtracting the mass of loaded catalyst from the total mass of solids collected from the filter and fluid bed.

Regarding the experimental uncertainty, a previously reported repeated experiment³³ has shown that the largest uncertainty is the aqueous phase yield, where the difference between two experiments was 1.2 wt.% daf. The difference in the C₁-C₃ yield was <0.1 wt.% daf, CO and CO₂ yield was 0.4 wt.% daf, char and coke yield was 0.1 wt.% daf, and condensed organics and C₄₊ in the gas yield was 0.1 wt.% daf. It is therefore assumed that the experimental error is less than 0.5 wt.% daf for the char and coke yield, 0.2 wt.% daf for the C₁-C₃ yield, 0.5 wt.% daf for the total CO and CO₂ yield, 1.5 wt.% for the aqueous phase yield, and less than 0.5 wt.% daf for the condensed organics and C₄₊ in the gas yield.

Figure 1. Simplified piping and instrumentation diagram of the catalytic hydropyrolysis setup

2.4 Analysis methods

2.4.1 Organic phase

Several methods were used to analyze the condensed organic phase and a more detailed description can be found elsewhere²⁹. The hydrogen content was measured with the ASTM method D7171. The sulfur content was measured according to ASTM D4294. The density at 40 °C was measured with ASTM method D 4052 and the water content was measured with Karl Fisher titration.

The oxygen content in the condensed organic phase was analyzed at DB Lab A/S using a Flash 2000 elemental analyzer (Thermo Scientific). The uncertainty of this measurement was 3.0 %, defined as two standard deviations for the measurement uncertainty, corresponding to a confidence interval of 95 %.

The condensed organic liquid samples were characterized by GC×GC-ToF/MS or –FID and a detailed description can be found elsewhere²⁹. Based on the GC×GC-ToF/MS analysis the compounds were classified

into seven groups: paraffins, naphthenes, mono-, di- and tri- and higher aromatics, oxygenated aliphatics, phenolics, dihydroxybenzenes, larger oxygenated aromatics, and sterols. The relative uncertainty for this analysis is estimated to be below 5 %.

Selective analysis of sulfur containing compounds was conducted using a GC with an atomic emission detector (AED)²⁹.

2.4.2 Aqueous phase

The carbon content in the aqueous phase samples was determined with GC-AED using an Agilent 7890A GC coupled to a JAS 2370 AED in carbon selective mode. The carbon emission line at 193 nm was used in combination with a helium makeup gas flow of 80 ml/min. The cavity temperature was 320°C and the transfer line temperature was 380°C. The GC column was a Phenomenex ZB-5 Inferno (30m X 0.25mm X 0.25µm) in connection with a JAS PTV inlet in split mode (1:100) held at 325°C and 0.5 µl injection. The oven was held at 40°C for 1 min and then ramped to 380°C @ 10°C/min. The quantification was done by external standards using benzyl alcohol dissolved in water. Calibration concentrations ranged from 10 ppm to 1100 ppm carbon. No identification of individual compounds was done and the total detected carbon was taken as a figure of the total carbon content in the aqueous sample. No sample pretreatment was done prior to analysis.

The aqueous phase was also analyzed on a Shimadzu GC-MS/FID as previously described²⁹. Based on the GC-FID/MS analysis the components were classified into 8 groups: unidentified, ethers, ketones, alcohols, sugars, phenols, acids and furans. The relative amount (FID area-%) of each component class was estimated as the sum of all the detected peaks in that class divided by the total peak area.

2.4.3 Catalyst characterization

The composition (Co, Ni, Mo) of the fresh catalysts was determined with inductive coupled plasma optical emission spectroscopy (ICP-OES) and the surface area was measured with N₂-physisorption (BET). Temperature programmed ammonia desorption (NH₃-TPD) of the fresh catalysts were conducted on a

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Mettler Toledo TGA/DSC 1. A complete blank measurement was first conducted with an empty crucible. The sample was subjected to the same procedure, which was heating at 20°C/min to 500 °C, where the sample was held for 60 min in 75 ml/min 31 % He and 69 % Ar. Thereafter the sample was cooled to 150°C (-20°C/min), and left to settle at 150°C for 20 minutes. The gas was then changed to 75 ml/min 2 % NH₃ in 29% He and 69% Ar for 30 min and the sample was flushed in the Ar/He mixture for 233 min. Afterwards the sample was cooled to 140°C and the NH₃ desorption ramp (10 C°/min) up to 600°C was initiated. To assess the desorbed NH₃ the weight loss in the temperature interval 150-500°C was used.

Raman spectroscopy on the calcined oxide catalyst precursors was performed at ambient conditions with a Labram 800 HR from Jobin Yvon using a Koheras solid state 488 nm laser.

The scanning electron microscopy (SEM) was performed on a FEI QUANTA600 scanning electron microscope with tungsten filament and equipped with a liquid nitrogen cooled EDAX ultra-thin window (UTW) EDS detector. All samples were sprinkled on carbon tabs on Al-stubs and conducted without any coating to prevent charging in the sample chamber.

EDS element quantifications were acquired on 0.11 mm x 0.11 mm areas on the surface of the catalyst grains at acceleration voltages of 3 kV, 5 kV, 10 kV and 15 kV to probe different interaction volumes between the incident electron beam and the sample. The composition of the sample was determined in EDAX software (version 5.2.42) using a normalized, standardless, ZAF-corrected and SEC-factor corrected quantification of the acquired EDS-spectra. The maximum penetration depth of the incident electron beam in MgAl₂O₄ was estimated with the CASINO Monte Carlo Software v.3.3.04 (see Table S.2, Figures S.2 and Figure S.3) to be approximately 0.170 µm for 3 kV and 1.60 µm for 15 kV, and serves as a rough indication of the maximum depth from where the detected X-rays may have been generated. The standard deviation for the carbon measurement was 1.5 wt.% at 3 kV, 0.8 wt.% at 5 kV, 1.0 wt.% at 10 kV and 1.5 wt.% at 15 kV, and the standard deviation for the potassium measurements was 0.6 wt.% at 5 kV, 0.3 wt.% at 10 kV, and 0.2 wt.% at 15 kV.

The transmission electron microscopy was performed on a FEI Talos™ F200X transmission electron microscope equipped with high-brightness field emission gun (X-FEG) and Super-X G2 EDS detector. The catalyst powders were crushed in a mortar and dispersed dry on a Cu TEM grid covered by a continuous carbon film (SPI Supplies). Images and elemental EDS maps were acquired in scanning transmission mode (STEM) with a camera length of 125 cm. Elemental EDS maps of 512 pixels x 512 pixels (2.1 μm x 2.1 μm) were acquired for 22 min in Brüker software (Esprit 1.9) using a probe current of 0.7 nA. It is noted that the EDS sulfur K-line (S-K_α 2.309 keV) may overlap with the molybdenum L-line (Mo-L_α 2.292keV) as the separation in energy is less than the EDS resolution of about 0.13 keV (full-width-half-maximum of Mn-K_α peak). Therefore, the elemental maps were processed in Esprit by a Bremsstrahlung background subtraction and series deconvolution of the EDS pixel spectra (using a 4x-binning) to display the net counts of Mo-K_α (17.480 keV), S-K_α (2.309 keV), Co-K_α (6.931 keV), Ni-K_α (7.480 keV), K-K_α (3.314 keV), and Ca-K_α (3.692 keV) respectively. The EDS analyses were complimented by high-resolution STEM imaging (probe size about 0.16nm) using the high-angle annular dark field detector (HAADF). For particle size measurements, HAADF-STEM images of 1024 pixels x 1024 pixels were recorded with a pixel size of 0.061 nm thus enabling the lattice spacing of 2H-MoS₂ (001) of 0.615 nm to be resolved. The sizes of the identified particles were measured manually from the images using ImageJ software.

3 Results and Discussion

The reaction conditions, mass balance and properties of the condensed liquid phases are shown in Table 2. The mass balance for the experiments closed between 96.7 and 99.1 wt.% daf. A more detailed gas composition is shown in supporting information Table S.3.

Table 2 Summary of reaction conditions and mass balance for catalytic hydropyrolysis of beech wood in fluid bed reactor with sulfided CoMo, NiMo and Mo as catalysts. (Catalyst used: 50.0 g catalyst, feed time: 3.5 hours, Pressure 26 bar, H₂ flow: 82 NL/min, N₂ flow: 5 NL/min, and H₂S conc: 460 ppm)

Test:	CoMo	NiMo	Mo
Test conditions			
Hydropyrolysis Temp. (°C)	451	451	452
Feeding rate (g/h)	275	271	275

Yields (wt. daf %)			
Gas	26.1	28.2	23.3
Char and coke	13.3	13.2	13.5
Aqueous phase	33.3	33.4	33.6
Organic phase	17.7	16.5	20.0
C ₄₊ in the gas	7.5	7.8	6.4
Organics + C ₄₊	25.2	24.3	26.4
Mass balance	97.8	99.1	96.7
Carbon recovery (%)			
C ₁ -C ₃	19	20	17
C ₄₊	13	13	11
CO+CO ₂	11	12	9.3
Char	Na	Na	Na
Organic phase	26	24	28
Aqueous phase	3.2	2.8	4.2
C ₄₊ + organic phase	39	37	39
Organic phase composition			
Water (wt.%)	3.3	2.6	4.1
C (wt.% db) ^a	81	80	79
H (wt.% db)	9.39	9.44	9.26
O (wt.% db)	9.0	10.2	11.7
S (wt.% db)	0.22	0.26	0.38
Organic phase density			
Density at 40°C (g/ml)	0.9428	0.9396	0.9560
Aqueous phase carbon content			
C (wt.%)	4.3	3.7	5.6
Gas composition (wt.% daf)			
CO	3.5	7.6	4.8
CO ₂	9.2	9.4	9.5
C ₁ -C ₃	10.3	11.2	8.9
C ₄₊	7.5	7.8	6.4

^aCalculated by difference

3.1 Product distribution

The product distribution for three experiments using the CoMo, NiMo and Mo as catalysts at similar reaction conditions is shown in Figure 2. The combined char and coke yield varied between 13.2 and 13.5 wt.% daf, which indicates that it is not influenced by the promoter. However, a significant difference in the total gas yield (between 23.3 and 28.2 wt.% daf) was observed. The C₁-C₃ yield varied between 8.9 and 11.2 wt.% daf and was highest for the NiMo catalyst and lowest for the Mo catalyst. A similar trend was observed for the total CO and CO₂ yield, which was 17.0 wt.% daf for the NiMo, 15.8 wt.% for the CoMo, and 14.4 wt.% daf for the Mo. Interestingly, the CO₂ yield was almost the same for all catalysts (9.2-9.5 wt.% daf), thus the differences was due to changes in the CO yield (4.8-7.6 wt.% daf), indicating differences in the catalyst’s decarbonylation activity. However, the CO could also be formed through decarboxylation

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4 257 followed by reverse water gas shift. It can therefore be assumed that the NiMo catalyst has the highest
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6 258 decarbonylation/decarboxylation activity.
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10 259 The C₂-C₃ paraffins yield for the NiMo catalyst (4.6 wt.% daf) was significantly higher than for the CoMo (3.1
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12 260 wt.% daf), and Mo (2.8 wt.% daf), while the olefins yield was lower for the NiMo catalyst (2.6 wt.% daf)
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14 261 than for the CoMo (3.6 wt.% daf) and Mo catalyst (3.1 wt.% daf), see supporting information Figure S.4.
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16 262 Thus the paraffins to olefins ratio was 1.8 for the NiMo, but 0.90 for both the CoMo and Mo catalysts,
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18 263 showing that the NiMo catalyst had the highest hydrogenation activity, which is in agreement with
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21 264 experiments using 2-ethylphenol as a model components at significantly lower temperatures (340°C) and
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23 265 higher pressures (70 bar)²⁵.
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26 266 The aqueous phase yield varied between 33.3 and 33.6 wt.% daf, which is the same for all catalysts within
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28 267 the experimental uncertainty. The highest observed condensable organics yield was 26.4 wt.% daf for the
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30 268 Mo and the lowest was 24.3 wt.% daf for the NiMo. Thus, an inverse relationship between the gas yield and
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33 269 condensable organics yield was observed, as opposed to our previous study where the temperature in the
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35 270 fluid bed reactor was varied and an inverse relationship between the gas and char yield was observed ²⁹.
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37 271 This shows that the char yield is mainly influenced by the process conditions ²⁹ and the condensable organic
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40 272 yield is mainly influenced by the catalyst properties, while the gas yield is very dependent on both the
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Figure 2 Product distribution for catalytic hydrolysis of beech wood using sulfided CoMo, NiMo and Mo as catalyst. Conditions: Fluid bed temperature: 451-452°C, total pressure: 26 bar, biomass feeding rate: 271-275 g/h, biomass used: 946-964 g, H₂ flow: 82 NL/min, N₂ flow: 5 NL/min, and H₂S conc: 460 ppm.

The difference between sulfided CoMo, NiMo and Mo supported on MgAl₂O₄ has also been studied for HDO of ethylene glycol, a model compound for aliphatic oxygenates formed during pyrolysis of cellulose and hemicellulose, in a continuous flow setup by our group¹⁷. It was observed that Mo had the lowest cracking activity, based on the lower yields of CO, CO₂ and CH₄, but that the cracking activities of the CoMo and NiMo were similar. The difference in the relative cracking activity for the CoMo and NiMo catalysts in this study and the study on ethylene glycol as model compound for HDO¹⁷ was probably because ethylene glycol is a simple molecule, while the real biomass used here is significantly more complex. Laurent et al.³⁴ also studied the difference between sulfided CoMo and NiMo catalyst for HDO of pyrolysis oil model compounds in a batch reactor and found that the NiMo catalysts had the highest decarboxylation activity. Krause et al.¹²⁻¹⁶ studied the hydrodeoxygenation of different model compounds with sulfided CoMo and NiMo catalysts. They also found that the NiMo catalyst had the highest hydrogenation activity and carboxylation/carbonylation activity. Thus the results obtained in this study are in agreement with the HDO literature.

The CO to CO₂ molar ratio for the CoMo was 1.1, while in our previous hydropyrolysis study, where a commercial CoMo/MgAl₂O₄ was used in the fluid bed reactor, the CO to CO₂ molar ratio was 3.1²⁹. However, the commercial CoMo/MgAl₂O₄ had a higher activity, the oxygen content in the condensed

organic phase was only 1.8 wt.%, compared to 9.0 wt.% for the CoMo catalyst tested in this study. Thus, the difference in CO to CO₂ ratio is most likely because the more active commercial catalyst also catalyzed water gas shift and reforming reactions almost to equilibrium (see supporting information Figure S.5).

3.2 Chemical composition of the condensed liquids

The chemical composition of the condensed organic phases is shown in Table 2. The oxygen content in the condensed organic phase for the CoMo catalyst was 9.0 wt.% db, 10 wt.% db for the NiMo, and 12 wt.% db for the Mo catalyst, thus indicating that the deoxygenation activity of the catalysts followed the trend: CoMo>NiMo>Mo. The carbon efficiency for the C₄₊ organics is 39 % for both the CoMo and the Mo, but only 37 % for the NiMo, thus the trend for the carbon efficiency is: CoMo≈Mo>NiMo. Furthermore, since the oxygen content in the produced organics is lower for the CoMo compared to the Mo, the CoMo catalyst is considered to be favorable.

The organic phase from the experiment with the NiMo catalyst had a slightly higher hydrogen content (9.44 wt.% db), than the CoMo (9.39 wt.% db) and Mo (9.26 wt.% db), however the difference is within the experimental uncertainty. The density of the organic phase was also lower using the NiMo (0.9396 g/ml), compared to when the CoMo (0.9428 g/ml) and the Mo (0.9560 g/ml) were used. The lower density is most likely due to the observed cracking activity for the NiMo.

The sulfur content in the condensed organics, when the Mo catalyst was used, was 0.38 wt.% db, which is significantly higher than when the CoMo (0.22 wt.% db) and the NiMo (0.26 wt.% db) were used. Since the beech wood only contained 43 wt.-ppm S most of the sulfur in the organic phase must come from incorporation of S from the H₂S in the gas phase, through the activity of the sulfided catalysts. In order to obtain a better understanding of the sulfur containing species in the condensed organics, the samples were analyzed with sulfur specific GC-AED, see Figure 3 (a detailed list of the detected compounds is shown in supporting information tables S.4-S.6). This showed that there was between 382 and 572 ppm H₂S dissolved in the samples, despite the N₂ stripping procedure employed. The main sulfur containing

molecules identified in the organic phase were thiols, thiophenes, and benzothiophenes, including dibenzothiophenes. Methyl-ethylsulfide and dimethyl disulfide (DMDS) were also detected in the organic phase, but a large fraction of the sulfur compounds was not identified. Since the applied temperature in the fluid bed reactor is close to the temperature used in fluid catalytic cracking (FCC)^{35,36}, it is possible that the sulfur from the H₂S is incorporated into the organics by similar reactions routes as in FCC. The concentration of thiophenes was significantly higher from the experiment with the Mo catalyst, Figure 3, than from the experiments with the CoMo, and NiMo indicating that hydrodesulfurization also takes place in the fluid bed reactor. The concentration of thiols was 23 wt-ppm S when the NiMo catalyst was used and 55 and 88 wt-ppm S when the CoMo and Mo was used, respectively. This is probably because of the higher hydrogenation activity of the NiMo catalyst, which decreased the concentration of olefins, thus minimizing the incorporation of H₂S through recombination between olefins and H₂S³⁷⁻⁴⁰. Alternatively the thiols could have been formed from the alcohols through a nucleophilic substitution^{12,16}. It should be noted that in order to minimize the cracking activity, the HDO and HDS activity for these catalysts were purposely fairly low, which is part of the reason for the high sulfur content in the condensed organics. In our previous work we showed that it is possible to reduce the sulfur content in the organic phase to 0.06 wt.% by using a second HDO reactor²⁹. Since sulfur compounds are commonly encountered in petrochemical refining and removed by hydrotreating the high sulfur concentration is of minor concern.

Figure 3 Concentration of sulfur species in the condensed organic phase from experiments with the CoMo, NiMo, and Mo catalyst analyzed with S specific GC-AED. Conditions: Fluid bed temperature: 451-452°C, pressure: 26 bar, biomass feeding rate: 271-275 g/h, biomass used: 946-964 g, H₂ flow: 82 NL/min, N₂ flow: 5 NL/min, and H₂S conc: 460 ppm.

The composition of the condensed organic phases was studied with GC×GC-ToF/MS or –FID and concentrations of paraffins (Par), naphthenes (Naph), monoaromatics (mAro), diaromatics (diAro), triaromatics (triAro), and larger aromatics (tetAro+), oxygenated aliphatics (O-Ali), phenols (PhOH), dihydroxybenzenes (Ph(OH)₂) and oxygenated di- and larger aromatics (O-Aro) were measured, see Figure 4. Comparing the CoMo, Figure 4A, with the NiMo, Figure 4B, the concentration of paraffins, naphthenes, and oxygenated aliphatics are almost the same. However, the concentration of diaromatics and larger aromatics were 16 % for the CoMo and 13 % for the NiMo. This is most likely because the NiMo catalyst mainly removes oxygen (and sulfur) by first hydrogenating the aromatic ring and then removing the oxygen (HYD pathway)^{25,28}, while the CoMo catalyst removes the oxygen without first hydrogenating the ring (DDO pathway)^{18,25–27}. At the applied reaction conditions the monoaromatics-naphthenes equilibrium is shifted towards aromatics²⁹, which makes it more difficult for the NiMo catalyst to remove the oxygen resulting in a slightly higher phenols yield. Thus, the lower concentration of di- and larger aromatics and higher concentration of monoaromatics and phenols for the NiMo catalyst is probably due to its higher hydrogenation activity, since hydrogenation of di- and higher aromatics is not equilibrium limited. Furthermore, the number of carbon atoms in the molecules is lower for the NiMo than the CoMo catalyst, due to its higher cracking activity.

Figure 4 The composition of the condensed organic phases using the CoMo catalyst (A), the NiMo catalyst (B), and the Mo catalyst (C). Conditions: Fluid bed temperature: 451-452°C, pressure: 26 bar, biomass feeding rate: 271-275 g/h, biomass used: 946-964 g, H₂ flow: 82 NL/min, N₂ flow: 5 NL/min, and H₂S conc: 460 ppm.

The organic phase from the experiment with the Mo catalyst, Figure 4C, contains more oxygenated aliphatics (21 %) than for the CoMo (19 %) and NiMo (18 %) catalysts. This indicates that Mo has a lower HDO activity than the CoMo and NiMo, as expected. The concentration of phenols is lowest for the Mo, however, this could be due to a higher concentration of other oxygenated hydrocarbons, which decreases the relative FID-area for the phenols. The lower concentration of naphthenes shows that the Mo has the lowest hydrogenation activity. Traces (<0.2 % area-FID) of sterols were detected in all the condensed organic phases.

In fast pyrolysis it is generally assumed that the aromatics and phenols comes from the lignin in the biomass, while the heterocyclic compounds such as furans and sugars originates from cellulose and hemicellulose⁴¹. The high concentration of aromatics and phenols (approximately 65 %-area FID) in the condensed organic phase indicates that it mostly originates from the lignin fraction of the biomass. However, tests with pure cellulose, hemicellulose and lignin are needed to support this hypothesis.

The carbon recovery and the composition of the aqueous phases are shown in Table 2. The carbon recovery in the aqueous phase was 2.8 % for the NiMo catalyst and 3.2 % for the CoMo catalyst, which is not a significant difference. The higher carbon recovery for Mo (4.2 %) in the aqueous phase is probably due to the higher oxygen content in the organic phase which makes it more miscible with water.

Figure 5 Composition of the aqueous phase when the CoMo (A), NiMo (C), and Mo(C) catalyst was used. Conditions: Fluid bed temperature: 451-452°C, pressure: 26 bar, biomass feeding rate: 271-275 g/h, biomass used: 946-964 g, H₂ flow: 82 NL/min, N₂ flow: 5 NL/min, and H₂S conc: 460 ppm.

The composition of the aqueous phases was similar for the three catalysts, see Figure 5. It mainly consisted of alcohols (66-69 %), which was mostly methanol and ethanol (see supporting information tables S.7-S.9), and ketones (18-20 %) in the C₂-C₅ range. The amount of phenol was between 2.1 and 6.7 %, the amount of furans was 0.43 % independent of the type of catalyst, and the amount of acids was 6.9 % for the Mo, but only 3.3 and 3.8 % for the NiMo and the CoMo, respectively. Acetic acid was the only acid or ester detected in the aqueous phase in the experiment with the NiMo and CoMo, while butyl formate was also observed for the Mo. The observed acetic acid indicate, that if catalytic hydrolysis is conducted without the additional HDO reactor, the downstream equipment should be acid resistant. Dabros⁴² tested hydrodeoxygenation of acetic acid over a NiMo catalyst and observed plugging above the catalyst bed after 2 h on stream due to coke formation. Therefore, it would be desirable to remove as much of the acetic acid as possible during the initial catalytic hydrolysis step.

3.3 Characterization of the catalysts

3.3.1 Raman spectroscopy of the calcined oxide catalyst precursors

Raman spectroscopy was used in order to determine the phases and dispersion for the oxide precursors, see Figure 6. Three spectra were recorded for each sample at different spots. The slight variations between the spectra for the same catalyst sample indicate some degree of heterogeneity. For the CoMo catalyst the

bands for the carrier MgAl_2O_4 are observed at 760, 673 and 405 cm^{-1} . The peak observed close to 872 cm^{-1} can be assigned to hydrated CoMoO_4 and would represent a Mo-O distance of $1.75\text{ \AA}$, according to the observed relationship for Mo-O stretching frequencies and bond distances proposed by Hardcastle and Wachs⁴³. This could be a Mo-O-X (X = carrier or active metal) entity. The broad convoluted peak observed at $923\text{--}945\text{ cm}^{-1}$ in all the samples corresponds to a Mo-O distance of around $1.7\text{ \AA}$ and could come from terminal Mo=O units. The presence of crystalline MoO_3 , which exhibit a sharp Mo=O stretching mode at 992 cm^{-1} , can be ruled out and thus the peak assembly probably originated from hydrated, amorphous MoO_x phases⁴⁴. Dabros et al.¹⁷ observed peaks at 315 and 910 cm^{-1} and assigned them to tetrahedral monomolybdate, thus the observed peak at 320 and $923\text{--}945\text{ cm}^{-1}$ could be this species. The monolayer coverage of Mo on Al_2O_3 is around 4.5 Mo/nm^2 ⁴⁴, which means that these samples exhibit around 80% of a monolayer coverage. Therefore, some interaction between molybdenum oxide species would be expected and the existence of truly isolated sites is not likely. Since the MgAl_2O_4 phase is quite porous, capillary condensation of water inside the pores is likely to occur, and the observed species are probably mixtures of e.g. $\text{MoO}_4^{2-}(\text{aq})$ (isolated, tetrahedral), $\text{Mo}_7\text{O}_{24}^{6-}$ and $\text{Mo}_8\text{O}_{26}^{4-}(\text{aq})$ (the two latter both polymerized octahedral) dissolved in the ambient air exposed calcined samples. MoO_4^{2-} would contribute at 897, 837 and 317 cm^{-1} , $\text{Mo}_7\text{O}_{24}^{6-}$ at 943, 903, 570, 362 and 210 cm^{-1} , while $\text{Mo}_8\text{O}_{26}^{4-}$ at 965, 925, 590, 370 and 230 cm^{-1} ^{44,45}. Given the relatively high MoO_x surface density combined with the major contributions of the $940\text{--}960\text{ cm}^{-1}$ features it seems likely that the observed species are hydrated pre-cursors for polymeric molybdenum oxides. Co_3O_4 would have its major contribution at 692 cm^{-1} , which is not observed, which indicates that Co is mainly present as hydrated CoMoO_4 .

For the NiMo catalyst the 954 cm^{-1} band coincides with $\alpha\text{-NiMoO}_4$ and the 878 cm^{-1} band with its hydrated form. No obvious peaks of crystalline MoO_3 ($992, 820, 667\text{ cm}^{-1}$) were observed. However, it is possible that the peak at 326 and 954 cm^{-1} is due to a mixture of the previously mentioned hydrated molybdates. No pure Ni oxide phase was observed, indicating that the Ni was located as NiMoO_4 . This indicates that Ni after the sulfidation is located in the so-called NiMoS phase²⁴ and not the less active NiS_x phase¹⁷. The bands

Figure 6 Baseline corrected Raman spectra of CoMo, NiMo, and Mo in the oxide phase (calcined, not dehydrated). The Raman bands were assigned to hydrated, MoO_x (gray), hydrated CoMoO_4 (cyan), alpha NiMoO_4 (red), hydrated NiMoO_4 (green), and MgAl_2O_4 (yellow).

3.3.2 Characterization of the spent catalysts

The carbon and potassium contents on the spent and fresh catalysts were measured with SEM combined with EDS. In order to account for the carbon signal from the carbon tabs the actual carbon content on the catalysts were calculated by subtracting the measured carbon content on the fresh catalysts from the measured carbon content on the spent catalysts, and the results is shown as a function of the acceleration voltage in Figure 7. With increased acceleration voltage the electron beam penetrates slightly deeper into the sample, therefore at low acceleration voltages (3 kV) the surface concentration on the catalyst particles is measured, while at high acceleration voltages (15 kV) the concentration slightly into the particle is measured. The estimated interaction depth ranges from 170 to 1600 nm with acceleration voltage between 3 and 15 kV, respectively, see Table S.2. Due to the relatively high molar mass of potassium it is not possible to excite its core electrons at 3 kV (K- K_α line at 3.31 keV). The carbon content on the spent Mo catalyst was between 5.0 and 5.5 wt.%, while it was between 0.9 and 3.3 wt.% for the spent CoMo and NiMo catalysts (Figure 7A), showing that the lower hydrodeoxygenation activity for the Mo catalyst lead to an increased degree of coking. The carbon content on the spent NiMo and CoMo decreased with increasing accelerating

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voltage, showing that more coke was located at the surface of the catalysts. The potassium content on the spent catalysts (Figure 7B), was between 0.3 (in the bulk) and 2.4 wt.% (at the surface) and no significant difference between the catalysts was observed. Potassium was not detected on the fresh catalysts (See supporting information Table S.10), showing that the potassium has been transferred from the biomass to the surface of the catalysts. Potassium is a known poison for HDO catalysts^{40,46}, thus the transfer of potassium from the biomass to the catalyst could potentially deactivate it. This should be investigated further in the future by longer experiments and/or tests with catalysts pre-impregnated with potassium.

Figure 7 Carbon (A) and potassium (B) content on the spent measured with SEM combined with EDS. The carbon and potassium for the fresh and spent catalysts are shown in supporting information Table S.10. Conditions: Fluid bed temperature: 451-452°C, pressure: 26 bar, biomass feeding rate: 271-275 g/h, biomass used: 946-964 g, H₂ flow: 82 NL/min, N₂ flow: 5 NL/min, and H₂S conc: 460 ppm.

Figure 8 shows HAADF-STEM images of the spent CoMo, NiMo, and Mo catalysts and reveal nanometer-sized slab structures of bright contrast distributed on the surface of larger support grains (about 10-30 nm in size) of less image contrast. Occasionally, the slab structures were found with 2 or more layers (up to 4) stacked with an interlayer-distance of 0.62 nm, consistent with a MoS₂ (001) spacing (Figure 8A). The bright-contrasted slab structures are therefore attributed to single, double- or multilayer layer MoS₂ nanocrystals viewed with the (001) basal plane along the electron beam direction, and situated with the basal plane along the surfaces of the larger MgAl₂O₄ grains, as previously reported⁴⁷. Based on 10 images per catalyst, and measuring between 111 and 128 slabs per sample, the MoS₂ nanocrystals were

predominantly found as single layer structures (>98%), and the slab lengths were measured (Figure 8E-F). The slab lengths were between 1 and 5.5 nm with an average between 2.8 and 2.9 nm for all the catalysts. Thus the slab size and distribution was similar for all the spent catalysts, which indicates that the MoS₂ edge dispersions of the tested catalysts were comparable. Furthermore, the single layer structure indicates that the catalysts were in the less active type I CoMoS phase³¹, which together with their low loading is the reason for their relatively low activity.

Figure 8 HAADF-STEM images of CoMo (A), NiMo (B), and Mo (C), and single layer slab size distribution of CoMo (D), NiMo (E), and Mo (F). The images in (A)-(C) were contrast adjusted (gamma) to improve visibility. Conditions: Fluid bed temperature: 451-452°C, pressure: 26 bar, biomass feeding rate: 271-275 g/h, biomass used: 946-964 g, H₂ flow: 82 NL/min, N₂ flow: 5 NL/min, and H₂S conc: 460 ppm.

The distribution of the promoter, molybdenum and sulfur on the spent catalysts is shown on the elemental maps in Figure 9 (For single element EDS maps see supporting material Figures S.6-S.8). The molybdenum (and sulfur) is well distributed on the MgAl₂O₄ support for the three catalysts, consistent with a uniform and high degree of MoS₂ dispersion (Figure 8). Furthermore, the promoter (Co/Ni) is also highly dispersed and mainly located the same places as molybdenum, as shown in Figure 9B and Figure 9E, suggesting

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4 475 successful incorporation of promoters into the MoS₂ structures in the so-called CoMoS or NiMoS phase²⁴.
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6 476 Thereby, the similarity in MoS₂ slab sizes of the three catalysts and the highly distributed promoters
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8 represents a good data set for directly comparing the effect of the promoters. Besides the expected
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10 (promoted) MoS₂ structures, calcium particles were observed on all the spent catalysts. The calcium
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12 originates from the biomass ash. However, since calcium was only detected as larger particles (40-200nm),
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14 it has only blocked a low fraction of the catalyst surface, thus it can be assumed that the calcium only has a
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16 small influence on the catalytic activity. Potassium was likewise also observed on all the spent catalysts and
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18 was well-distributed on the particles, which might have decreased the catalyst activity ^{40,46}. Thus the results
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20 from the STEM-EDS images supports the results obtained from SEM-EDS.
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Figure 9 STEM-HAADF micrograph of molybdenum, cobalt, sulfur, potassium, and calcium EDS element distribution on CoMo (A-C), molybdenum, nickel, sulfur, potassium and calcium EDS element distribution on NiMo (D-F), and molybdenum, sulfur, potassium and calcium EDS element distribution on Mo (G-I). Conditions: Fluid bed temperature: 451-452°C, pressure: 26 bar, biomass feeding rate: 271-275 g/h, biomass used: 946-964 g, H₂ flow: 82 NL/min, N₂ flow: 5 NL/min, and H₂S conc: 460 ppm.

4 Conclusion

Catalytic hydropyrolysis of beech wood was conducted in a fluid bed reactor at 450°C and 26 bar with three different sulfided catalysts: CoMo/MgAl₂O₄, NiMo/MgAl₂O₄, and Mo/MgAl₂O₄. BET surface area, elemental analysis, Raman spectroscopy and STEM images of the spent catalysts showed that the three catalysts had similar morphology and a comparable metal content, therefore the influence of the promoters on catalytic activity and selectivity could be investigated. The char and aqueous phase yields were not affected by the applied promoter type. The NiMo/MgAl₂O₄ catalyst had the highest cracking, decarbonylation/decarboxylation, and hydrogenation activity, while the Mo/MgAl₂O₄ catalyst had the lowest. The highest condensed organics and C₄₊ yield was obtained with the Mo/MgAl₂O₄ (26.4 wt.% daf) and the lowest with the NiMo/MgAl₂O₄ (24.3 wt.% daf). However, the organic phase from the experiment with the Mo/MgAl₂O₄ had an oxygen content of 12 wt.% db, while it was 10 wt.% db and 9.0 wt.% db when the NiMo/MgAl₂O₄ and CoMo/MgAl₂O₄ were used, respectively. This difference, was ascribed to the main reaction pathway, hydrogenation for the NiMo and direct deoxygenation for the CoMo, for the deoxygenation of phenols. The carbon recovery (C₄₊ and condensed organics) was 39 % for both the CoMo/MgAl₂O₄ and Mo/MgAl₂O₄, but 37 % for the NiMo/MgAl₂O₄. Therefore, this study indicates that CoMo/MgAl₂O₄ is favorable for use in catalytic hydropyrolysis compared to NiMo/MgAl₂O₄ and Mo/MgAl₂O₄.

The carbon content on the spent Mo/MgAl₂O₄ catalyst was higher than on the CoMo/MgAl₂O₄ and NiMo/MgAl₂O₄, which was probably because of its lower activity, which increased the degree of coking. Calcium and potassium were transferred from the biomass ash to the catalysts under reaction conditions. Calcium was observed as larger (40-200 nm) single particles, which only had a minor impact on the catalytic activity. Potassium was highly dispersed on the catalyst particles, which has potentially decreased the catalytic activity. The transfer of alkali metals from the biomass to the catalyst could be a serious problem in full scale applications, and should be further investigated in order to better understand how the alkali

metals are transferred and their effect on the catalytic activity. Such investigations are on-going in our laboratories.

5 Associated content

5.1 Supporting information

NH₃-TPD of the calcined oxide catalyst precursors; estimated penetration depth for electron beam in MgAl₂O₄; detailed gas composition; equilibrium calculations; overview of sulfur containing molecules detected with sulfur specific GC-AED and hydrocarbons detected in the aqueous phase; carbon and potassium content on the calcined oxide catalyst precursors; elemental maps (STEM-EDS) of the spent catalysts

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