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Biofuels and Biomass

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Deactivation of a CoMo catalyst during catalytic hydropyrolysis of biomass. Part II: Characterization of the spent catalysts and char

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Abstract

In this work sulfided CoMo/MgAl₂O₄ catalysts used in fluid bed catalytic hydropyrolysis for the conversion of beech wood and wheat straw to liquid fuels were thoroughly characterized by Raman spectroscopy and scanning (transmission) electron microscopy together with energy dispersive X-ray spectroscopy. Potassium and calcium were transferred from the beech wood to the catalyst and the accumulated amounts increased proportionally with the time on stream (TOS) and reached 0.67 and 0.28 wt.% after 16.2 h, respectively, when beech wood was used as biomass feedstock with a feeding rate of approximately 270 g/h (4.4 kg in total) beech wood to 50 g of catalyst. The concentration of coke on the spent catalyst also increased with TOS and was 3.7 wt.% (carbon) after 3.5 h and 7.2 wt.% after 16.2 h, indicating that the coking rate decreased with time on stream. However, SEM-EDS indicated that the carbon concentration increased more on the surface than in the bulk, thereby increasing the risk of pore blocking. In addition, Raman spectroscopy showed that the initially formed coke was mostly graphitic, but the coke became less ordered as successive layers grew on top.

Doping the catalyst with K_2CO_3 , corresponding to a potassium loading of 1.9 wt.%, prior to the sulfidation, led to a higher degree of stacking and increased the slab length of the MoS_2 particles. Furthermore, SEM images of the spent catalyst indicated that the catalyst particles were encapsulated by a layer of coke during pyrolysis, but this layer was continuously removed by knock-off. This indicates that potassium acts as a catalyst for polymerization of tar and coking reactions on the catalyst.

The effect of using wheat straw, which contains 10 times more potassium than beech wood, as feedstock was also investigated. This led to defluidization due to agglomeration within the first 0.3 h on stream. SEM images showed that agglomerates of char and catalyst particles, with a diameter up to 5 mm, were formed due to polymerization of the metaplast and tar. Additionally, SEM-EDS images showed that potassium was well-distributed in the agglomerates, indicating that potassium catalyzed the formation of these agglomerates.

Abbreviations

BSE	Backscattered electron
daf	Dry, ash free basis
db	Dry basis
EDS	Energy dispersive X-ray spectroscopy
FB	Fluid bed
HAADF	High-angle annular dark-field
HDO	Hydrodeoxygenation
ICP-OES	Inductive coupled plasma optical emission spectroscopy
ND	Not determined
SEI	Secondary electron image
SEM	Scanning electron microscopy

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4	STEM	Scanning transmission electron microscopy
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6	Temp.	Temperature
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8	TOS	Time on stream
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14 36 **1 Introduction**

17 37 Several studies have shown that catalytic hydropyrolysis of biomass is a highly efficient process for the
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19 38 production of carbon based fuels^{1,2}. In catalytic hydropyrolysis, the biomass is rapidly heated in a hydrogen
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21 39 atmosphere and in the presence of a hydrotreating catalyst, which enables the conversion of the reactive
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23 40 oxygenates before they polymerize. GTI has developed a process called IH²® where a fixed bed
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25 41 hydrodeoxygenation (HDO) reactor is placed after the catalytic hydropyrolysis reactor, further reducing the
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27 42 oxygen content of the liquid fuel^{1,2}. With this process they are able to obtain a condensable organic (C₄₊)
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29 43 yield between 26 and 28 wt.% dry ash free (daf) with an oxygen content below 2.2 wt.% when using woody
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31 44 biomass. Lemna, microalgae, bagasse, macroalgae, and corn stover have also been tested in the IH²®
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33 45 process¹. Using different algae generally gave a high condensable organic yield (up to 46 wt.% daf), while
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35 46 using corn stover, a biomass with a high ash content of typically 4 to 10 wt.%³, gave a lower yield of 21
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37 47 wt.% daf¹. A 750 h pilot plant experiment with a biomass (wood) feeding rate of 50 kg per day obtained a
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39 48 condensable organic yield of 26 wt.% daf with no signs of catalyst deactivation. However, fresh catalyst was
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41 49 continuously added to the setup due to catalyst entrainment, which would (partially) mask if deactivation
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43 50 had taken place². The fresh and spent catalysts were not characterized to shed light on this. Other research
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45 51 groups have also tested a system with two reactors, where hydropyrolysis (non-catalytic) takes place in a
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47 52 fluid bed or a cyclone reactor followed by a fixed bed HDO reactor⁴⁻⁶.

53 53 Dayton et al.⁷⁻⁹ tested several different reduced catalysts in a fluid bed catalytic hydropyrolysis setup at
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55 54 temperatures between 375 and 500 °C, pressures in the range between 1 and 21 bar, and obtained a
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57 55 carbon recovery in the condensable organics between 25 and 43 %. They also conducted a 10 days
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experiment where 1 kg of biomass was fed each day and the catalyst in the fluid bed was oxidized and reduced between each day in order to remove carbon⁸. The condensable organics yield varied between 25 and 30 wt.% daf, and the oxygen content was between 2 and 5 wt.% dry basis (db). Due to catalyst loss, fresh catalyst was added to the fluid bed during the experiment⁸. Meesuk et al.^{10–12} studied catalytic hydropyrolysis of rice husk using a fluid bed reactor with a single shot biomass feeding system, and obtained bio-oil yields between 20 and 50 wt.%, but the oxygen content in the organic phase was generally above 20 wt.% and the spent catalysts were also not characterized. Chandler and Resende tested the difference between catalytic pyrolysis and catalytic hydropyrolysis in a fluid bed reactor using H-ZSM-5 as catalyst and *Arundo Donax* as biomass¹³. They observed a higher loss of catalyst surface area in catalytic pyrolysis compared to catalytic hydropyrolysis, which indicates that the hydrogen reduces the degree of pore blockage. Other groups have studied catalytic hydropyrolysis using pyroprobes or similar micro-scale equipment^{14–20}, however none of the spent catalysts were analyzed. This clearly shows that there is a lack of knowledge on how the catalysts are affected by the type of biomass, time on stream, and process conditions.

In our previous research we have conducted catalytic hydropyrolysis of biomass (beech wood) in a fluid bed loaded with a sulfided Co promoted Mo catalyst followed by a fixed bed hydrotreating reactor loaded with a sulfided Ni promoted Mo catalyst and investigated the effect of varying the temperature and pressure^{21,22}. The difference between using a sulfided Co and Ni promoted Mo, and unpromoted Mo catalyst in the fluid bed reactor has also been investigated, which showed that the Co promoted Mo catalyst had the highest HDO activity at similar metal loadings at the applied temperature around 450 °C²³. Analysis of the spent catalysts showed that it contained both potassium and calcium, which most likely were transferred from the beech wood to the catalysts during the experiments²⁴, which over time may lead to catalyst deactivation²⁵. In this study the effects of time on stream, doping the fresh catalyst with potassium, and using wheat straw, with approximately 10 times higher potassium content than beech wood, were studied. In part I²⁶, the product distribution and composition were thoroughly described, while

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4 81 in this work we focus on studying the spent catalysts and char from the fluid bed catalytic hydropyrolysis
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6 82 reactor.
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11 83 **2 Material and methods**
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14 84 **2.1 Biomass feedstock**
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17 85 Beech wood (bark free) and wheat straw were used as biomass feedstocks. The beech wood has previously
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19 86 been used in catalytic hydropyrolysis experiments^{21,23,27}. The moisture and ash contents in the beech wood
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21 87 were 6.72 wt.% and 0.59 wt.% db, respectively, and the particle size was between 200-700 μm²¹. The
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23 88 moisture content in the straw was 7.4 wt.% and the ash content was 4.2 wt.% db, the particle size was
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25 89 below 710 μm and 80 % of the particles were smaller than 315 μm. The compositions of the beech wood
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28 90 and the wheat straw are shown in Table 1.
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31 91 **Table 1. Composition of bark free beech wood and wheat straw. ND means not detected/determined.**
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	Beech	Straw	
C	49.9	46.9	wt.% dry
H	6.0	6.0	wt.% dry
N	0.13	0.56	wt.% dry
O*	43.0	41.6	wt.% dry
K	0.12	1.4	wt.% dry
Ca	0.13	0.23	wt.% dry
S	48	1200	wt-ppm dry
Na	9.9	230	wt-ppm dry
Mg	350	960	wt-ppm dry
Si	140	3900	wt-ppm dry
P	75	910	wt-ppm dry
Cl	2.0	6500	wt-ppm dry
Mn	170	ND	wt-ppm dry
Fe	24	41	wt-ppm dry
Cu	2.1	ND	wt-ppm dry
Zn	4.9	ND	wt-ppm dry
Sr	4.6	ND	wt-ppm dry
Al	ND	44	wt-ppm dry
Ti	ND	540	wt-ppm dry
HHV	19.7**	18.9	MJ/kg

57 92 **Calculated by difference.*
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93 ***Calculated from Milne formula: $0.341 \times C + 1.322 \times H - 0.12 \times O - 0.12 \times N + 0.0686 \times S - 0.0153 \times ash$* ²⁸

94 **2.2 Catalysts**

95 Three Co promoted Mo catalysts (denoted: CoMo#1, CoMo#2, and CoMoK#1) were tested in the fluid bed
96 reactor. The catalysts were prepared by sequential incipient wetness impregnation of $MgAl_2O_4$ with a
97 surface area of 54-58 m²/g and a detailed description of the preparation and characterization of the oxide
98 catalyst precursors can be found elsewhere²⁶. CoMo#1 contained 3.41 wt.% Mo and 0.637 wt.% Co,
99 CoMo#2 contained 3.29 wt.% Mo and 0.615 wt.% Co, and CoMoK#1 contained 3.43 wt.% Mo and 0.603
100 wt.% Co. CoMoK#1 was after the impregnation with Mo and Co also impregnated with K_2CO_3 and the K
101 content was 1.94 wt.%. During the 5 day experiment the hydrotreating reactor was loaded with a NiMo
102 catalyst supported on an alumina carrier (denoted: NiMo/ Al_2O_3) supplied by Haldor Topsoe.

103 The catalysts were sulfided prior to the experiment and H_2S was fed during the experiment in order to
104 maintain them in their active sulfide phase. A detailed description of the sulfidation method can be found
105 in our previous work²⁶.

106 **2.3 Catalyst and char characterization**

107 The scanning electron microscopy (SEM) was performed on a FEI QUANTA600 scanning electron
108 microscope equipped with both a backscattered electron (BSE) and secondary electron detector making it
109 possible to take both BSE and secondary electron images (SEI). EDS element maps and quantifications were
110 acquired on 0.11 mm x 0.11 mm areas at 3 kV, 5 kV, 10 kV and 15 kV to probe different interaction volumes
111 between the incident electron beam and the sample. The maximum penetration depth of the incident
112 electron beam was estimated to be 0.170 μm at 3 kV and 1.60 μm at 15 kV in $MgAl_2O_4$. A more detailed
113 description of the analysis method can be found elsewhere^{23,27}.

114 Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to measure the bulk
115 concentration of alkali metals (K and Ca) on the spent catalysts. The carbon content on the spent catalysts

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were measured with a LECO CS-200, in which the sample was combusted in pure oxygen and the carbon content was calculated on the basis of the formed CO₂, which was measured with IR absorption.

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 and a detailed description of the method can be found elsewhere²³.

Raman spectra were acquired with a Horiba Jobin Yvon LabRAM HR800 Raman microscope, using a solid state laser at 488 nm as excitation source. The samples (20 mg) were pressed and crushed to 150 to 300 μm particle size and placed in a Linkam CCR1000 cell. Raman spectra were measured in a fluidized bed mode in an inert atmosphere (helium) in order to avoid sample damage by laser heating and to obtain the average carbon structures in the samples²⁹. The beam was focused on the sample with a 10× objective and the laser power was adjusted to 50 mW. First order carbon Raman spectra were obtained in the 1000–1950 cm⁻¹ range with 30 s exposure and as the average of three acquisitions. While all samples have been measured with 488 nm excitation, the spent CoMo#2 sample from experiment 1 was also measured with two additional excitation wavelengths at 532 and 633 nm, in order to check for dispersion of the main carbon bands and thereby obtain further information on the nature of the carbon.

The curve fitting of the Raman spectra was performed with the Origin 9.0 software. Many different curve fitting procedures were tested, but the best results were obtained using a model composed of seven Lorentzian bands. All fitting parameters were set free and in all cases the fits converged. The extracted parameters, i.e. band positions and full-width-at-half-maximum FWHM are in good agreement with literature data.

2.4 Experimental setup and procedure

2.4.1 Hydropyrolysis setup

An in-house designed and constructed pilot plant was used for the catalytic hydropyrolysis experiments and it is described in detail elsewhere^{21,23,27}. The setup consisted of a pressurized biomass feeding system, a fluid bed reactor and a fixed bed hydrotreating reactor, a condensation system and gas analysis by gas chromatography. The catalyst and the remaining char were removed from the fluid bed reactor after each experiment and replaced with the fresh catalyst for the next experiment. During the 5 days experiment, however, the same catalyst was used without exchanging it or adding new catalysts. A detailed description of the experimental procedure can be found elsewhere²⁶.

2.4.2 KCl transfer setup

Transfer of KCl to the catalyst was investigated by mixing KCl and CoMo#1 in a 10:1 ratio (w/w) in a crucible, placing it in a tube furnace (diameter: 6 cm), and heating it to 450 °C and varying the holding time, see Table 2. The KCl particles were larger than 355 µm and the CoMo#1 particles were smaller than 355 µm. After the experiment was finished the mixture was sieved whereby the KCl and CoMo#1 were separated and the K and Cl concentration on the spent CoMo#1 particles was investigated by SEM-EDS.

Table 2 Test conditions for KCl transfer experiments. (Temperature: 450 °C, N₂ flow: 1.0 NL/min)

Hold time (h)	48	96	375
CoMo#1 (g)	1.49	1.48	1.47
KCl (g)	14.95	14.86	14.73

3 Results and Discussion

In order to evaluate the process stability a 5 days experiment was conducted with CoMo#2 in the hydropyrolysis reactor and a commercial NiMo/Al₂O₃ catalyst in the fixed bed reactor. The total time on stream (TOS) was 16.2 hours and 4.4 kg of beech wood was processed. The temperature in the fluid bed reactor was between 452 and 455 °C, the temperature in the HDO reactor was between 366 and 373 °C and

the beech wood feeding rate was between 240 and 276 g/h. The experimental time was 3.5 hours per day, except on day 3, where the experiment was stopped after 2.2 hours due to problems with the biomass feeding system. An overview of the test conditions and mass balances is shown in Table 3. The catalyst carryover from the fluid bed to the filter was estimated to between 1 and 9 g per day and the total amount of catalyst carryover was estimated to 20 g, corresponding to 41 wt.% of the total amount of catalyst loaded. The condensable organics yield varied between 22.2±1 wt.% daf, which was within the experimental uncertainty²⁶. The effect of doping the fresh catalyst with 1.9 wt.% potassium was also investigated in experiment 2 and 3. This increased the concentration of oxygen in the condensed organics from 9.0 to 13.8 wt.% db, indicating that potassium has a large impact on the catalyst activity. The solid yield also increased from 13.3 to 14.6 wt.% daf, which was due to a lower degree of stabilization of reactive oxygenates²⁶. A detailed discussion of the product distribution and composition can be found elsewhere²⁶.

Table 3 Test conditions and yields for stability test and reference experiment. (Catalyst in HDO reactor: 173 g NiMo/Al₂O₃ supplied by Haldor Topsøe A/S)

Test	1 (day 1)	1 (day 2)	1 (day 3)	1 (day 4)	1 (day 5)	1 (average)	2	3	4	5
Test conditions										
FB Temp. (°C)	453	452	454	455	453	453	451	454	453	453
FB catalyst	CoMo#2	CoMo#2	CoMo#2	CoMo#2	CoMo#2	CoMo#2	CoMo#1	CoMoK#1	CoMo#2	CoMo#2
FB catalyst amount (g)	49.99	-	-	-	-	49.99	50.03	49.98	50.01	49.96
FB catalyst lost (g)	5	9	3	2	1	4	ND	ND	ND	ND
HDO Temp. (°C)	370	370	366	372	373	370	-	-	-	-
Biomass	beech	beech	beech	beech	beech	beech	beech	beech	straw	straw
Pressure (bar)	26	26	26	26	26	26	26	26	26	26
Feed time (h)	3.5	3.5	2.2	3.5	3.5	3.2	3.5	3.5	0.26	0.29
Feeding rate (g/h)	274	276	240	274	273	267	275	268	400	~310
H ₂ S conc.(ppm)	460	460	460	460	460	460	460	460	460	447
H ₂ flow (NL/min)	82	82	82	82	82	82	82	82	82	102
N ₂ flow (NL/min)	5	5	5	5	5	5	5	5	5	5
Yields (wt. daf %)										
Gas	29.4	30.0	29.6	30.7	31.2	30.2	26.1	24.9	ND	ND
Solid	10.9	13.8	14.6	13.2	13.6*	13.2	13.3*	14.6*	ND	ND
Aqueous phase	38.0	37.1	36.4	34.5	35.115	36.2	33.3	28.9	ND	ND
Organic phase	12.2	13.7	12.5	14.6	14.1	13.4	17.7	19.9	ND	ND
C ₄₊ in the gas	9.9	9.2	8.7	8.3	9.1	9.0	7.5	4.1	ND	ND
Organics + C ₄₊	22.1	22.9	21.2	22.9	23.2	22.5	25.2	24.1	ND	ND
Mass balance	100.3	103.7	101.8	101.2	103.1	102.0	97.8	92.5	ND	ND

* Solid = Solid in filter + solid in fluid bed – catalyst loaded

The beech wood only contained 0.12 wt.% db potassium. Therefore, the effect of using wheat straw was investigated with the test conditions shown in Table 3, experiments 4 and 5. The straw contained 1.4 wt.% potassium, thus it was assumed that deactivation by potassium would be more pronounced with straw. In the first experiment with straw, the reactor defluidized after 0.26 h, which was observed as large

temperature fluctuations of up to 130 °C (see supplementary information Figure S.1), and lead to plugging of the biomass feeding tube. The straw was tested in a second experiment with an increased gas flow rate and decreased biomass feeding rate (see Table 3) and each time a temperature fluctuation occurred the biomass feeding was paused and restarted when the temperature had stabilized, in an attempt to minimize the risk of plugging of the biomass feeding tube. The first larger temperature fluctuation was observed after 0.21 h, and five larger temperature fluctuations was observed before the biomass feeding tube plugged after 0.29 h (see supplementary information Figure S.1(C)). Due to the short operational time, not enough liquid was condensed to conduct any analysis and it was not possible to make a mass balance for the experiments with straw. However, the spent catalyst from the fluid bed was recovered, which showed that agglomeration had occurred in both experiments with straw and agglomerates with a diameter up to 5 mm was observed, as discussed in detail in section 3.1.2.

3.1 Characterization of spent catalysts and char

3.1.1 SEM-EDS

3.1.1.1 *Effect of time on stream*

The degree of coking on the spent catalysts from experiment 1 and 2 was investigated by SEM-EDS by measuring the carbon content at different acceleration voltages as shown in Figure 1(A). At low acceleration voltage (3 kV) the electron beam only penetrates about 0.17 μm into the surface of the catalyst, and thus the carbon content corresponds to the surface concentration²⁷. As the acceleration voltage increases, the beam reaches deeper into the catalyst, integrating the signals from the surface to the maximum penetration depth, which at 15 kV is 1.6 μm . The background carbon signal from the carbon tape was accounted for by subtracting the measured concentration of carbon on the fresh from the used Co promoted Mo catalyst (see supporting information Table S.1). The concentration of carbon on the CoMo#1 catalyst, with 3.5 h on stream and only 0.96 kg biomass processed, was between 1.5 (measured at 15 eV) and 3.3 wt.% (measured at 3 eV). However, the catalyst (CoMo#2) with 16.2 h on stream using 4.36 kg

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4 198 biomass had a carbon content of 27 wt.% when measured at 3 kV and 15 wt.% at 15 kV. The results indicate
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6 199 that there is a gradient of carbon in the particles, and that the carbon content increases with increasing
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9 200 amount of biomass processed. The increasing carbon content particularly at the face of the catalyst
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11 201 particles could over time lead to pore blocking.
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14 202 Potassium was detected on the spent samples as shown in Figure 1 (B). Since potassium is a heavier
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16 203 element than carbon it cannot be excited at 3 kV, hence the surface concentration was not measured. The
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18 204 potassium content on the catalyst with 3.5 h on stream (CoMo#1) was between 0.4 and 0.8 wt.% and it was
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21 205 between 1.5 and 2.4 wt.% for the catalyst with 16.2 h on stream (CoMo#2). No traces of potassium were
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23 206 detected on the fresh catalysts, indicating transfer of potassium in the beech wood to the catalyst and that
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25 207 the potassium content increases with the amount of beech wood used.
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44 208 **Figure 1 Carbon (A) and potassium (B) contents measured with SEM combined with EDS on the spent catalyst from a one-day 3.5**
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46 209 **h experiment and the five days, 16.2 h experiment. Catalytic hydropyrolysis temp.: 451-455°C, Total pressure: 26 bar, beech**
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48 210 **wood feeding rate: 240-277 g/h, hydrogen flow: 82 NL/min, nitrogen flow: 5 NL/min, and hydrogen disulfide conc.: 460 ppm.**
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50 211 A small amount of spent catalyst from the fluid bed reactor from experiment 1 and 2 were separated from
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52 212 the char particles and the bulk concentration of calcium and potassium were measured with ICP-OES and
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55 213 the bulk carbon content was measured by combustion (see Figure 2). This showed that for CoMo#1, with
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57 214 short time on stream, the carbon content measured with SEM-EDS (between 1.5 and 3.3 wt.%) is in fairly
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good agreement with the carbon content of 3.69 wt.% measured by combustion. However, for CoMo#2, with 16.2 hours on stream, the carbon content measured by EDS was between 15 and 27 wt.% but the average carbon content measured by combustion was only 7.19 wt.%. This further shows that there are strong gradients in the carbon content from the surface to the center of the particle, especially after long time on stream. The potassium content measured by ICP-OES was 0.141 wt.% for CoMo#1 and 0.666 wt.% for CoMo#2, which was lower compared to when it was measured by SEM-EDS: 0.4-0.8 wt.% for CoMo#1 and 1.5-2.4 wt.% for CoMo#2. The reason for the too high measurement with SEM-EDS is that at low potassium concentrations the EDS signal becomes too low for an accurate measurement. Calcium is also detected with ICP-OES: 0.0750 wt.% for CoMo#1 and 0.278 wt.% for CoMo#2.

Figure 2 Carbon, calcium, and potassium content on the spent catalyst in the fluid bed from experiment 1 and 2 and the NiMo/Al₂O₃ HDO reactor catalyst from experiment 1. Catalytic hydropyrolysis temp.: 451-455°C, total pressure: 26 bar, beech wood feeding rate: 240-277 g/h, hydrogen flow: 82 NL/min, nitrogen flow: 5 NL/min, and hydrogen disulfide conc.: 460 ppm. The calcium and potassium contents were measured with ICP-OES and the carbon content was measured by combustion.

Interestingly, the potassium and calcium content increases proportionally with the time on stream (see Figure 2), hence proportionally with the amount of biomass processed. Similarly, deposition of metal sulfides (mainly vanadium sulfide) on hydrotreating catalysts generally increases linearly with time on stream when hydrotreating atmospheric residue³⁰. Interestingly the amount of potassium transferred to the catalyst after 3.5 h corresponds to 28 % saturation of the acidic sites (measured on the calcined oxide

catalyst precursor²⁶), while the amount transferred after 16.2 h corresponds to 115 % saturation of acidic sites. It should be noted that the acidity of the catalyst most likely changes during the sulfidation, because the sulfided phase also possesses Brønsted acidity³¹. Olsen et al.³² studied the potassium mobility in vanadia based SCR catalysts and observed a saturation of Brønsted acidic sites, after which no more potassium diffused into the catalyst. Analysis of catalysts from longer catalytic hydropyrolysis experiments is therefore needed to investigate if the catalysts are saturated with potassium, after which potassium is expected to no longer transfer from the biomass to catalyst.

The concentration of carbon on the spent catalyst from the fluid bed indicates that the coke deposition rate decreases with TOS, which is well-known in hydrotreating of fossil oil^{30,31,33}. The reason for the decreasing coke deposition rate could be that coke builds up at the surface of the catalyst (see Figure 1) making coking inside the pores diffusion limited³⁰. Another possible explanation could be that the coke initially builds up as a monolayer on the support material^{34,35}, thus leading to a decreasing coking rate as the support becomes covered with coke. The concentration of carbon on the spent NiMo/Al₂O₃ from the downstream, fixed bed hydrotreating reactor in experiment 1 was 3.07 wt.% (see Figure 2) after 16.2 h, showing that some coking has taken place in this reactor too. However, the initial stabilization of the vapors, which occurs in the catalytic hydropyrolysis reactor, has most likely decreased the degree of coking in the HDO reactor.

3.1.1.2 Effect of doping the catalyst with potassium

The spent CoMoK#1 catalyst was studied with SEM using both a BSE and SEI detector. As shown in Figure 3(A), many of the spent catalyst particles were covered with a carbon layer (dark particles), which encapsulated the particles. An EDS measurement at spot “a” in Figure 3(D), showed that the layer consisted of 95.7 wt.% carbon (see Table 4), hence that this layer is coke. As observed by the EDS spot measurement “b” in Figure 3(D) and Table 4, the part of the spent catalyst, which was not encapsulated only gave a carbon signal of 15.9 wt.%. This number is higher than the actual carbon content since it is not corrected

for the background signal from the carbon tape. Accounting for the background signal gives a carbon content of 93.7 wt.% at spot “a” and 12.9 wt.% at spot “b”. The SEM images (Figure 3(A), (B), and (C)) indicate that the coke primarily grows from the already deposited coke on the catalyst, which can also explain the lower concentration at point “b” than “a” in Figure 3(D). Furthermore, this can also explain why some particles do not contain a coke layer. A coke flake is observed in Figure 3(C), which indicates that the coke was continuously removed during the experiment by attrition (or knock-off) in the fluid bed. This encapsulation of the catalyst particles was not observed for the CoMo#1 and CoMo#2 catalysts and has not been observed in our previous studies ^{22,23,27}, indicating that it is caused by the high concentration of potassium on the catalyst.

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Figure 3 SEM images of the spent CoMoK#1 catalyst acquired with a BSE-detector (A) and (C) and with a SEI-detector (B) and (D). Catalytic hydropyrolysis temp.: 454°C, total pressure: 26 bar, beech wood feeding rate: 268 g/h, hydrogen flow: 82 NL/min, nitrogen flow: 5 NL/min, and hydrogen disulfide conc.: 460 ppm. Inside the red circle in (C) is seen a piece of carbon which has fallen off a catalyst particle.

Jensen et al.³⁶ investigated the effect of impregnating KCl on cellulose, hemicellulose and lignin in pyrolysis with a thermo-gravimetric analyzer using a heating rate of 10 °C/min and heating the samples up to 700 °C. They found that impregnating cellulose with KCl increased the char yield with a factor of 4, while KCl only had a minor influence on the char yield during the pyrolysis of hemicellulose and lignin. Their results indicate that potassium can act as a catalyst for char formation, which can explain the formation of coke on the surface of the CoMoK#1 catalyst, and this is probably also the reason for the higher char and coke yield for the CoMoK#1(14.6 wt.%) compared to CoMo#1 (13.3 wt.%).

Table 4 SEM-EDS measured concentrations of carbon, oxygen, sulfur, and potassium at spots a and b in Figure 3 (D). (Measured at 15 kV)

Spot	a	b
C (wt.%)	95.7	15.9
O (wt.%)	3.0	23.2
S (wt.%)	1.4	10.1
K (wt.%)	0	1.4

3.1.1.3 Effect of using straw

Investigations of the spent catalyst from the catalytic hydrolysis reactor when using wheat straw as biomass showed that agglomeration had taken place. Some of the particles retrieved from the fluid bed reactor had a diameter of approximately 5 mm, while the fresh catalyst had a diameter between 180-355 μm . The observed defluidization was therefore due to agglomeration. To obtain a deeper understanding of the agglomeration, the agglomerates were studied with SEM. As shown in Figure 4 the catalyst particles were trapped in a grid with no sign of carbon coating of the catalyst surface as observed with the CoMoK#1 catalyst in Figure 3. Instead, Figure 4 indicates that solidified tar and/or metaplast, a heavy intermediate formed during fast pyrolysis³⁷, have formed an agglomerate, which has captured several catalyst particles. Remarkably, no sign of the original cell structure of the straw is observed in this agglomerate, which indicate that the biomass has been molten, by forming a metaplast, during the pyrolysis and then solidified. This phenomenon is not observed for wood because the metaplast from wood evaporate as tar products. The organic straw agglomerates appear because the straw alkali catalyze secondary char formation from the metaplast.

Figure 4 SEM-BSE images of the formed agglomerates from experiment 4. Catalytic hydrolysis temp.: 453°C, total pressure: 26 bar, wheat straw feeding rate: 400 g/h, hydrogen flow: 82 NL/min, nitrogen flow: 5 NL/min, and hydrogen disulfide conc.: 460 ppm.

On some of the spent catalyst particles a grid was deposited on the surface, see Figure 5(A). EDS-element maps indicated that this grid mainly consisted of carbon (Figure 5(D)), and the carbon content was considerably lower on the part of the particle, which was not covered by the grid. It can therefore be assumed that this grid is not formed due to normal coke formation on the surface of the particle due to reacting vapors/gases, but must come from solidification of tar or metaplast. Furthermore potassium and chlorine were also detected in the grid, see Figure 5(B) and (C). The potassium and chlorine were observed at the same places, indicating that they are chemically bound as KCl. Both potassium and chlorine were also observed on the part of the particle, which was not covered by the carbon grid, indicating that these elements are transferred to the catalyst independently of the tar and metaplast solidification. Since both potassium and chlorine are known for their abilities to deactivate HDO catalysts^{25,38}, these results indicate that even if agglomeration is avoided, it could be difficult to use straw as feedstock without removing these species by pretreating it, e.g. by washing.

Figure 5 SEM-SEI micrograph (A) and EDS element maps of chlorine (B), potassium (C), and carbon (D) on a spent catalyst particle from experiment 4. Catalytic hydropyrolysis temp.: 453°C, total pressure: 26 bar, wheat straw feeding rate: 400 g/h, hydrogen flow: 82 NL/min, nitrogen flow: 5 NL/min, and hydrogen disulfide conc.: 460 ppm.

3.1.1.4 Char morphology and structural transformation

The char from the experiments was also studied with SEM. Figure 6(A) shows a sample taken from the fluid bed reactor from experiment 2 using beech wood. The bright particles are the spent catalyst, while the darker particles are char. Two types of char particles are observed; one is elongated and has maintained the cell structure of the beech wood, while the other is shorter and more rounded (highlighted with red color). Two of the char particles have several bright spots on the surface and EDS analysis of a similar particle indicates that these spots are calcium rich particles (see supplementary information Figure S.2 and Table S.2). Figure 6(B) and (C) show two similar char particles from experiment 2. The cell structure is almost absent for the char particle in Figure 6(B), however, only a few calcium particles are observed on this char particle, while several calcium particles are observed in the char particle shown in Figure 6(C),

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which indicates that an up-concentration of the calcium takes place. These results indicate that some of the beech wood particles partly melt during the catalytic hydropyrolysis. This has also been observed in other similar experiments conducted with the same beech wood (see supplementary information Figure S.2).

Figure 6 SEM images of solid particles from catalytic hydropyrolysis of beech wood in experiment 2 (A-C), and straw in experiment 4 (D-F) and experiment 5 (G-I). Catalytic hydropyrolysis temp.: 451-454°C, total pressure: 26 bar, biomass feeding rate: 275-400 g/h, hydrogen flow: 82-102 NL/min, nitrogen flow: 5 NL/min, and hydrogen disulfide conc.: 460 ppm. Inside the red squares in (A) is shown two char particles, which has lost some of the cell structure from beech wood. Inside the red squares in (H) is shown two primary char particles that has maintained the cell structure from straw, but is incorporated into a larger agglomerate of solidified tar or metaplast.

The melting of the biomass was more apparent when using straw compared to wood. Figure 6(D)-(F) show a large agglomerate from experiment 4, where most of the char particles (primary char) have maintained the structure from the straw, but has been stuck together by a solidified tar or metaplast (secondary char). EDS measurements showed that the agglomerate consisted of 68-71 wt.% carbon, 16-19 wt.% oxygen, 5-8 wt.% potassium, 1-3 wt.% chlorine, 1-3 wt. % silicon, 1-2 wt. % calcium and traces of magnesium, aluminum, sulfur, and phosphorus were also detected (see supplementary information Figure S.3 and Table S.3). The agglomerate from experiment 5 (Figure 6(G)-(I)) was somewhat different from the one shown in Figure 6(D)-(F) (from experiment 4), as only few fiber like particles can be identified. Figure 6(H) shows two primary char particles (marked with red color) that has maintained the structure from the straw, but has been incorporated into a larger agglomerate of solidified tar or metaplast. The agglomerate in Figure 6(G)-(I) was also studied with EDS (see supplementary information Figure S.4 and Table S.4), which showed that its composition was similar to the composition of the agglomerate in Figure 6(D)-(F), showing that the biomass had formed a melt during the pyrolysis, which solidified into the larger agglomerate mainly consisting of secondary char. This would also explain the formation of the agglomerate shown in Figure 4 and the carbon grid located on the catalyst particle in Figure 5. Furthermore, a catalyst particle with a partly melted char particle attached has been observed (see supplementary information Figure S.5). Partly hollow char particles have also been observed (see supplementary information Figure S.6), indicating that the core of the biomass particle has melted, leaving the outer original framework. These results clearly show that the biomass particles can form a melt (metaplast) at the applied conditions, which can lead to agglomeration if the melt solidifies around the primary char and catalyst particles. Furthermore, agglomerates formed here from solidification of an organic melt are different from the agglomerates formed during combustion or gasification of alkaline rich fuel, where agglomerates of inorganic, alkaline melts are formed³⁹⁻⁴².

SEM images of additional agglomerates from experiment 4 using straw are shown in Figure 7. The structure of these agglomerates were similar to the agglomerate from experiment 5 also using straw shown in Figure

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4 361 6(I)-(G),. It is seen that agglomerates mainly consisting of secondary char were formed in both experiments
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6 362 with straw. In one of these agglomerates a primary char particle was observed (see Figure 7(B) and (C)) and
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9 363 several bright crystals were observed on the surface of the primary char particle. The composition of these
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11 364 crystals was investigated with EDS (see Figure 7(C) and detailed compositions are shown in the
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13 365 supplementary information Table S.5. The EDS data showed that these crystals are silicates since they
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15 366 consisted of oxygen and silicon with an O/Si ratio between 2.4 and 3.4. In the secondary char small bright
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18 367 spots were observed (see Figure 7(D) and (E)) and EDS measurements showed that these particles were KCl
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20 368 (detailed composition shown in supplementary information Table S.6). Additionally, an EDS element map of
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22 369 the secondary char showed that potassium was also well distributed in this phase (supplementary
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24 370 information Figure S.7). The potassium observed in the secondary char indicates that potassium acts as a
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27 371 catalyst for the formation of secondary char, which is in agreement with observations from experiment 3
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29 372 using the potassium impregnated catalyst (see section 3.1.1.2). It should be noted that the agglomeration is
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31 373 not due to melting of the biomass as such, but because potassium catalyzes polymerization of the tar
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33 374 and/or metaplast to a secondary char, thereby capturing catalyst and primary char particles in the process.

56 376 Figure 7 SEM image of a char agglomerate from experiment 4 using straw (A), SEM image of primary char found in the
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58 377 agglomerate (B,C), and SEM image of solidified metaplast (D,E). EDS measurements of the O/Si molar ratio at 6 different spots in
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(C) is highlighted with yellow and the K/Cl molar ratio at 9 different spots are highlighted with blue in figure (E). Catalytic hydropyrolysis temp.: 453°C, total pressure: 26 bar, wheat straw feeding rate: 400 g/h, hydrogen flow: 82 NL/min, nitrogen flow: 5 NL/min, and hydrogen disulfide conc.: 460 ppm.

Dall'Ora et al.⁴³ studied pyrolysis of pine and beech wood at 1000 and 1300 °C and investigated the morphology of the produced char particles. They also observed a melting behavior of the biomass: the char produced from pine was porous spherical particles, while the morphology changes were less drastic for beech wood. Likewise Cetin et al.⁴⁴ studied the char morphology from pyrolysis of pine and eucalyptus sawdust, and bagasse both at high and low heating rates and at pressures between 1 and 20 bar. They also observed that at high heating rates the char showed signs of melting and at both high heating rate and high pressure the particles fused together to form hollow particles with a smooth surface. Furthermore, they observed smaller morphology changes for bagasse than for pine and eucalyptus, however, when both high heating rate and pressure were applied, it lost some of its structural integrity⁴⁴. Trubetskaya et al.⁴⁵ also studied the morphology of char from pyrolysis of different types of biomass at temperatures between 350 and 1400 °C and heating rates between 10 and 3000 °C/s and found that the morphology changes appeared at 350 °C. Furthermore they found that at high heating rates, bridge-breaking occurred before the cross-linking started, and thus the biomass became a fluid (metaplast)⁴⁵. However, with straw the fluidity was reduced, which was ascribed to high levels of potassium and calcium, which acted as a catalyst for formation of char links⁴⁵. The reason for the more apparent solidification when using straw instead of beech wood is therefore most likely that the metaplast formed by wood evaporates while potassium catalyze solidification of the metaplast from straw.

3.1.2 HAADF-STEM

The spent catalysts from experiments 1 to 3 were also studied with high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), see Figure 8, which showed a nanometer sized slab

structure of bright contrast well distributed on the surface of the larger support particles, which have less image contrast. The CoMo#1 and CoMo#2 slabs were mainly found as single layer slabs (see Figure 8(C) & (F)), but a few slabs with 2 or more layers (up to 4) were observed. As shown in Figure 8(A), when two layer stacks were observed, the interlayer-distance between the slabs was 0.62 nm, corresponding to the (001) lattice spacing of 2H-MoS₂. On this basis, the slab structures were identified as single, double- or multilayer MoS₂ nanocrystals oriented with the (001) basal plane parallel to the electron beam, as previously reported⁴⁶. Based on 111-238 measured slabs for each sample, the MoS₂ nanocrystals in CoMo#1 and CoMo#2 consisted of >95 % single layer slabs with an average stacking of approximately 1.05. However, for the CoMoK#1 only 44% of the slabs were found as single layer structures and up to 13 layers stacked on each other was observed (see Figure 8 (I)), thus the average stacking for CoMoK#1 was 1.77. The measured slab length (Figure 8 (B) & (E)) for CoMo#1 and CoMo#2 was between 1.0 and 9.5 nm and the mean was 2.9 nm for CoMo#1 and 3.2 nm for CoMo#2. The slab size and distribution was thus comparable for CoMo#1 and CoMo#2 and it is therefore assumed that the MoS₂ edge dispersions of these samples were similar. However, the slab length for CoMoK#1 was between 1.2 and 27 nm with an average of 4.3 nm, hence significantly higher than for CoMo#1 and CoMo#2. This indicates that potassium affects the sulfidation of the CoMo catalyst and promotes the formation of multilayer slabs and increases the slab length, which was also observed by Fan et al.⁴⁷. The observed formation of multilayer slabs could be due to weaker Mo-O-Al bonds⁴⁸ and indicates that the more active type II CoMoS structure is formed instead of type I. Furthermore, stacking also decreases the number of available Brim sites, which are known for catalyzing hydrogenation reactions^{48,49}. It was observed that doping the catalyst with potassium, decreased its cracking, hydrogenation, and hydrodeoxygenation activity, leading to more decarboxylation. The concentration of oxygen in the condensed organics was 9.0 wt.% db for CoMo#1 and 13.8 wt.% db for CoMoK#1²⁶. It cannot be ruled out that the difference in the degree of stacking and slab length could be part of the reason for difference in their deoxygenation activity, however, it does not explain the observed

encapsulation of the CoMoK#1 catalyst. These results therefore indicate that potassium catalyzes the coking of the catalyst, and thus increased the catalyst deactivation rate.

Figure 8 HAADF-STEM images of CoMo#1 (A), CoMo#2 (D), and CoMoK#1 (E), slab size distribution of CoMo#1 (B), CoMo#2 (E), and CoMoK#1 (H), stacking on CoMo#1 (C), CoMo#2 (F), and CoMoK#1 (I). The images in (A), (D), and (G) were contrast adjusted to improve visibility. Catalytic hydropyrolysis temp.: 451-455°C, total pressure: 26 bar, beech wood feeding rate: 240-277 g/h, hydrogen flow: 82 NL/min, nitrogen flow: 5 NL/min, and hydrogen disulfide conc.: 460 ppm.

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Figure 9 shows the composite element map of Co, Mo, and S in the spent catalysts (individual element maps are shown in supporting information Figures S.8-S.10). For CoMo#1 and CoMo#2 Mo S were highly distributed on the support, indicating a good dispersion of the MoS₂ phase in consistency with Figure 8. For CoMoK#1, the Mo and S were also highly distributed on the support, but the MoS₂ phase were less dispersed due to the longer slabs and higher degree of stacking of the MoS₂ nanocrystals (Figure 8).The cobalt was mainly located together with the molybdenum, which indicates an incorporation of cobalt into the MoS₂ structure, the so-called CoMoS phase⁵⁰. A large CoMoS particle (~100 nm) was also observed for the CoMoK#1, which is most likely a highly stacked CoMoS particle. However, larger Co particles (20-60 nm) were observed on CoMo#2 (Figure 9(E)), indicating that not all the cobalt was incorporated into the MoS₂ structure and the Co particles are most likely the less active Co₉S₈ phase⁵⁰. A single Co particle (~50 nm), most likely Co₉S₈, was also observed on the CoMoK#1. The reason for the formation of cobalt sulfide particles is unknown, but since it is observed for both CoMo#2 and CoMoK#1 it could be related to the potassium, which was found on all the spent catalysts and was fairly homogeneously distributed on the analyzed samples. Calcium was observed on both CoMo#1 (Figure 9 (C)) and CoMo#2 (Figure 9(F)) as larger particles and was inhomogeneously distributed. The calcium particles on CoMo#1 had diameters between 20 and 60 nm, while the particle diameters were below 20 nm on CoMo#2. Calcium was not observed on CoMoK#1 in the selected image area, however, calcium may be inhomogeneously distributed as for the CoMo#1 and #2 samples, and may have been found if more areas were inspected.

Figure 9 HAADF-STEM micrographs and molybdenum, cobalt, sulfur, potassium, and calcium EDS element maps on CoMo#1 (A-C), CoMo#2 (D-F), and CoMoK#1 (G-I). Catalytic hydropyrolysis temp.: 451-455°C, total pressure: 26 bar, beech wood feeding rate: 240-277 g/h, hydrogen flow: 82 NL/min, nitrogen flow: 5 NL/min, and hydrogen disulfide conc.: 460 ppm.

3.1.3 Raman spectroscopy

Raman spectroscopy was used to study the chemical nature and bonding of the carbon deposits formed during the different experiments. While Raman spectroscopy can provide valuable information on carbon structures with sp^3 hybridized carbon atoms when visible lasers (400-700 nm) are used for excitation, the contribution of structures that contain sp^2 hybridized carbon atoms are typically dominating the spectra

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4 460 due to the two orders of magnitude higher Raman cross-section of the latter ones⁵¹. Here, the Raman
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6 461 spectra of all samples have been analyzed according to the three stage model developed by Ferrari et al.⁵¹,
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9 462 which describes the stepwise transformation of a perfect graphitic structure into amorphous carbon.
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12 463 Generally, the Raman spectra were complex and required a curve fit composed of seven components (less
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14 464 components never gave converging fitting results). As an example, in Figure 10 the experimental Raman
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16 465 spectrum of the spent CoMo#2 sample is shown together with the spectral deconvolution and the
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19 466 corresponding assignments. The extracted parameters are included in the table in the insert on Figure 10. A
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21 467 brief overview of the assignments for the different bands is given in Table 5. The carbon in the spent
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23 468 CoMo#2 sample is composed of a mixture of nano-crystalline graphitic structures (D-and G-bands) with
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25 469 different levels of defects and functional groups containing –C-O bonds (Ox-band). This indicates that some
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Figure 10 Example of Raman spectra deconvolution and assignments (Spent catalyst CoMo#2 from exp. 1 measured with 488 nm excitation).

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Table 5 Assignment of Raman bands

Band (obs. frequency range)	Band assignment	Ref.
D2 (1601 – 1607 cm ⁻¹)	The physical origin is the same as for the G-band, but related to graphitic surface layers, i.e. graphene-type layers, that are missing an adjacent top or bottom layer. Typically observed for nano-crystalline graphite with a high surface to volume ratio.	52
G (1570 – 1582 cm ⁻¹)	The G (“Graphite”) band, corresponding to an ideal graphitic lattice vibration mode with E _{2g} symmetry.	51
D3 (1525 – 1549 cm ⁻¹)	Interstitial amorphous sp ² -carbon structures, formed between graphitic particles.	53
D4’ (1430 – 1442 cm ⁻¹)	Transpolyacetylene segments at grain boundaries and surfaces, caused by sum combination of C=C chain stretching and C-H wagging modes. Linked to the D4 band, but usually obscured by intense D1 band. Excitation at 488 nm, enhances separation of the two bands.	54
D1 (1353 – 1358 cm ⁻¹)	The most prominent and typically most intense D (“Defect”) band, characteristic for disordered graphitic structures and corresponding to a graphitic lattice vibration with A _{1g} symmetry, which becomes Raman active due to in-plane defects (can also be caused by the presence of a large relative amount of graphitic layer edges).	51
Ox (1251 – 1266 cm ⁻¹)	Tentatively assigned to C-O stretching vibrations from –COOH and –C-OH functional groups attached to aromatic rings.	55,56
D4 (1147 – 1183 cm ⁻¹)	Transpolyacetylene segments at grain boundaries and surfaces, caused by difference combination of C=C chain stretching and C-H wagging modes. Linked to D4’ band.	54

The experimental Raman spectra of all spent samples are plotted together with the spectral deconvolution in supplementary information Figure S.11 and the parameters extracted from the analysis of the Raman spectra are summarized in supplementary information Table S.7. Even though the spectra are rather complex, all samples could be fitted by the same set of seven bands, which means that they are structurally related and allows to group all formed carbon structures to a transition stage between nano-crystalline graphite and amorphous carbon. This conclusion is based on the following general observations: i) absence of a second-order Raman spectrum, ii) small dispersion of the G band for different excitation wavelengths (position at ~1580 cm⁻¹ for λ = 488 nm, and $\sim\Delta$ = 10 cm⁻¹ when using λ = 633 nm, see supplementary information Figure S.12, iii) the A(D1)/A(G) integral band ratio of ~2 (indicating domain sizes between 15 to 20 Å).

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4 487 Comparing the Raman spectra for the spent CoMo#1, CoMo#2, and CoMoK#1 when using beech wood
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6 488 indicates that the carbon formed on the surface of the catalyst particles is initially more graphitic (ordered)
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9 489 and becomes less ordered as successive layers of carbon grow on top, which is evidenced by the increasing
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11 490 band width for D1, as shown in Figure 11(A)⁵⁷. An increasing coke domain size with time on stream is also
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13 491 observed, which is shown by the increasing value for L_a in Figure 11(B). Comparing the Raman spectra for
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15 492 the spent CoMo#1 catalyst (using beech wood) and char particles taken from the filter shows a larger D1
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18 493 band width (see Supplementary Information Figure S.11 and Table S.7), thus less graphitic, and a larger
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20 494 coke domain size for the char. In contrast, the Raman spectra of spent CoMo#2 using straw as biomass and
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22 495 the corresponding separated agglomerate (Raman conducted on the agglomerate shown in Figure 7) are
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24 496 more similar (see Supplementary Information Figure S.11 and Table S.7). This is in agreement with the
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27 497 observations from SEM (Section 3.1.1.3) and confirms that the carbon formation in the experiments with
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29 498 straw is mainly due to solidification of tar or metaplast, rather than related to carbon growth on the
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31 499 catalyst particles.
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Figure 11 Effect of the amount of biomass used and TOS on the degree of ordering and crystal size for the coke on the spent CoMo#1, CoMo#2, and CoMoK#1 catalysts. *The amount of biomass used and TOS for CoMoK#1 has been calculated by extrapolation of the observed relationship between K and TOS in Figure 2, assuming that the potassium content on the catalyst increases proportionally with TOS.

3.2 Potassium and Chlorine transfer from KCl

Since it was observed that potassium accumulated on the catalyst when beech wood was used as biomass and would most likely also have been observed for wheat straw if the fluid bed had not defluidized because of agglomeration, the transfer of potassium was further investigated. Fresh CoMo#1 catalyst was mixed with KCl particles and heated to 450 °C for between 48 and 375 h in a nitrogen atmosphere and the potassium and chlorine contents on the catalyst were investigated with SEM-EDS and shown as a function of time in Figure 12. The content of potassium is highest at 5 kV, indicating that the potassium transfer could be limited by internal diffusion. Since the potassium uptake is known to be correlated with the

number of acidic sites³², the increase in the potassium between 96 and 375 h indicates that the acidic sites are not fully saturated at 96 h. Less chlorine compared to potassium is transferred to the catalyst, both on mass and molar basis, indicating that KCl reacts with the Brønsted acid site and produces HCl which is mainly released to the gas phase, while potassium occupies the site, through the following reaction³²:

Furthermore, the chlorine concentration does not increase after 48 h, indicating that the catalyst reaches a dynamic pseudo equilibrium between transfer and evaporation of Cl. The transfer of potassium to the catalyst could also be dependent on the type of potassium compound used, thus a different potassium concentration on the catalyst would possibly have been observed if K₂CO₃ or KOH had been used. Nevertheless, these results indicate that potassium and chlorine can move from the biomass to the catalyst by reaction followed by diffusion.

Figure 12 Potassium (A) and chlorine (B) contents on CoMo#1 after KCl transfer experiments measured with SEM-EDS. Conditions: 450 °C, 1 atm, nitrogen flow: 1 NL/min, catalyst to KCl ratio: 1:10 (g/g). The concentration at 0 hours is the concentration on the fresh catalyst before mixing with KCl.

4 Conclusions

Spent CoMoS/MgAl₂O₄ catalysts from a bench scale catalytic hydropyrolysis setup, using beech wood as feedstock, have been characterized with HAADF-STEM, SEM-EDS, and ICP-OES. The results show that both

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529 calcium and potassium are transferred from the biomass to the catalyst and that the concentration of these
530 alkali metals increases proportionally with time on stream. After 16.2 h feeding 4.4 kg beech wood to 50 g
531 of catalyst the concentration of calcium was 0.28 wt.% and the concentration of potassium was 0.67 wt.%
532 on the catalyst. Calcium was mainly found as 20 to 60 nm particles on the spent catalysts, while potassium
533 was well-distributed, which could potentially decrease the catalytic activity. Mixing KCl particles and a fresh
534 CoMo catalyst and heating it in N₂ to 450 °C for 48-375 h showed that potassium is transferred to the
535 catalyst by solid-solid contact followed by diffusion in the catalyst particle. The concentration of carbon on
536 the spent catalyst from the catalytic hydropyrolysis reactor was 3.7 wt.% after 3.5 h which increased to 7.2
537 wt.% after 16.2 h, indicating that the coking rate decreases over time.

538 In order to investigate the effect of potassium on the catalyst, a CoMo catalyst was prior to the sulfidation
539 impregnated with K₂CO₃ corresponding to 1.9 wt.% potassium and compared to a similar CoMo catalyst
540 without potassium. Interestingly, impregnation with potassium also altered the sulfidation by increasing
541 the degree of stacking of the MoS₂ slabs and increasing the slab lengths. SEM images of the spent
542 potassium impregnated catalyst showed that some of the catalyst particles were covered with coke, but
543 indicated that the coke was also removed as flakes in the fluid bed by knock-off/attrition. This was not
544 observed previously using fresh catalysts, which indicates that potassium can act as a catalyst for
545 polymerization reactions forming coke on the catalysts.

546 The effect of using straw, which has a potassium content of 1.4 wt.%, instead of beech wood, which has a
547 potassium content of 0.12 wt.%, was also studied. However, using straw led to defluidization within 0.29 h.
548 Investigations of the catalyst and char from the fluid bed showed that severe agglomeration had taken
549 place, thus the particle size in some cases had increased from 180-355 μm to approximately 5 mm. SEM
550 images showed that agglomerates were formed by solidified organic melts. The agglomerates contained
551 besides the solidified melts primary char particles with intact cell structure and catalyst particles that had
552 formed an agglomerate due to the adhesive melt that bind them together. The formation of these

agglomerates was ascribed to repolymerization of the metaplast and tar. Potassium was well distributed in the agglomerates, again indicating that potassium catalyzes polymerization reactions, thus being the reason for the organic melt solidification.

Raman spectroscopy on the spent catalysts, char, and agglomerates showed that the carbon in the agglomerates had a functionality that was similar to the carbon on the spent catalyst, while the carbon in the char particles was different from the carbon on the spent catalysts. This verifies the hypothesis that the agglomerates were formed by polymerization of the metaplast.

Overall, the results indicate that alkali metal containing feedstocks may be challenging to use in catalytic hydropyrolysis, where catalysts and feed are mixed at elevated temperature. Therefore experiments at extended run-time are needed to clarify this issue.

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Scanning electron microscopy