CATALYTIC DEOXYGENATION OF CELLULOSE PYROLYSIS VAPOURS OVER MESOPOROUS MATERIALS

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In this paper, catalytic deoxygenation of cellulose pyrolysis vapours over mesoporous materials is investigated. Three different MCM-41 mesoporous materials were employed as catalysts, namely, acidic H-MCM-41-15, H-MCM-41-20 and aluminium-free silica Na-Si-MCM-41, with cellulose beads used as a raw material. Pyrolysis/deoxygenation experiments were carried out in a dual-fluidized bed reactor. Thermal pyrolysis occurred over quartz sand and the vapours formed were upgraded in a consecutive fluidized bed, in which the mesoporours materials acted as catalysts. Both the yield and chemical composition of the pyrolysis products were affected by the catalysts. More water and CO were formed as a result of catalytic deoxygenation, compared to the non-catalytic experiment. Some of the organic compounds in the catalytic bio-oil had a lower oxygen content than the predominant levoglucosan in the non-catalytic bio-oil.

Keywords: catalytic pyrolysis, cellulose beads, mesoporous materials, MCM-41, dual-fluidized bed reactor, bio-oil

INTRODUCTION

Biomass can be transformed into liquid, solid and gaseous fuels or fuel precursors through pyrolysis, that is, thermal degradation of an organic material in the absence of oxygen.[1] Cellulose is the most abundant polymer in the world.[2] Pyrolysis of cellulose has been thoroughly investigated by several authors and close to 500 articles can be found with SciFinder.

The Broido-Shafizadeh mechanism is the most common procedure applied for the pyrolysis of cellulose, where cellulose is assumed to follow a dehydrated "active cellulose" path, to be subsequently degraded by two competing pathways to gases and char, and volatile fragments forming the bio-oil.[3] The dominant compound in the cellulose pyrolysis oil is levoglucosan - concentrations as high as 66 wt% of levoglucosan have been found in the bio-oil.[4] A low amount of alkali salts in the raw material changes the thermal degradation route of cellulose. Essig and co-workers[4] found out that low amounts of sodium chloride present in cellulose changed the yield and chemical composition of the bio-oil. A NaCl concentration of 0.01 wt% decreased the bio-oil yield from 84 to 66 wt% while, simultaneously, levoglucosan concentration decreased and the formation of glycolaldehyde and hydroxyacetone increased.[4] Recently, Wang *et al.*[5] reported similar results. At higher NaCl concentrations, the effect was more noticeable. Temperature also affects the yield and chemical composition of the bio-oil. Luo and co-workes[6] reported that the bio-oil yield attains a maximum at 600-610 °C. The yield of levoglucosan reached its maximum over the same temperature range, while the yields of glycolaldehyde and hydroxyacetone increased with temperature.

Pyrolysis of cellulose over different crystalline aluminosilicates, *i.e.* zeolites and mesoporous materials, as well as with different nanopowder metal oxides, has been studied by Fabbri *et al.*[7-9] These authors pyrolysed cellulose over several different zeolites, *i.e.* NH_4-Y, NH_4-ZSM-5 and H-Y, nanopowder metal oxides such as SiO_2, Al_2O_3, MgO and mixed oxides, $TiO_2{\cdot}SiO_2$ and $Al_2O_3{\cdot}TiO_2$, and investigated the influence of these catalysts on the distribution of chiral anhydrosugars. They reported that zeolites H-Y and NH_4-ZSM-5 favoured the formation of levoglucosenone, while the NH_4-Y did not modify the chemical composition of the bio-oil, compared to non-catalytic pyrolysis. Formation of levoglucosenone and hydroxylactone was increased[7,8] over $Al_2O_3{\cdot}TiO_2$.

Torri *et al.*[9] studied cellulose pyrolysis over different mesoporous materials of the MCM-41 type. Siliceous MCM-41 and metal-containing (Al, Mg, Ti, Sn and Zr) Me-MCM-41 were tested in batch-mode pyrolysis, under a continuous stream of nitrogen. They reported that the metal-containing mesoporous materials were more active in forming levoglucosenone and hydroxylactone than siliceous MCM-41.

Other research teams[10-12] have also studied catalytic upgrading of pyrolysis vapours over modified MCM-41 type materials, although using lignocellulosic biomass as a raw material for pyrolysis. Adam *et al.*[10,11] studied pyrolysis of spruce wood in the presence of Al-MCM-41 type catalysts and reported that the yield of the undesired carbonyls and heavy products decreased over the catalysts, while the yield of the desirable hydrocarbons and phenolic products remained the same or increased. Antonakou *et al.*,[12] who studied various metal-modified Al-MCM-41 materials in the pyrolysis of beech and miscanthus for bio-fuels and chemicals, concluded that the organic fraction decreased and the water yield increased over the MCM-41 catalysts. Not only the hydrocarbons and phenolics, but also the formation of polyaromatic hydrocarbons (PAHs) increased in the presence of catalysts. Metal modification of the catalysts produced an organic fraction with high levels of phenolics and low levels of PAHs and hydrocarbons. Iron- and copper-modified MCM-41 were the optimal catalysts for producing phenols.

This paper reports the pyrolysis of cellulose beads followed by catalytic gas phase deoxygenation of the cellulose pyrolysis vapours over acidic H-MCM-41-15, H-MCM-41-20 and silica Na-Si-MCM-41 mesoporous materials, in a dual-fluidized bed reactor. The experimental procedure here applied differs from the one used by Torri *et al.*[9] in that cellulose is first pyrolysed and then the vapours are deoxygenated over the mesoporous materials. In this way, more pyrolysis vapours come into contact with the catalysts than in a static mixture.

EXPERIMENTAL

Equipment

A dual-fluidized bed reactor was used for investigating the catalytic deoxygenation of cellulose pyrolysis vapours. The set-up consisted of a cellulose feeder, a dual-fluidized bed reactor, a furnace for heating the reactors, a vapour condensing section and a gas analyser for CO and CO_2. The set-up is illustrated in Figure 1. Pyrolysis of the cellulose beads was conducted in (1) and catalytic upgrading of the pyrolysis vapours – in (2). A detailed description of the set-up can be found elsewhere.[13] The temperature of the pyrolysis reactor and of the catalysis reactor was continuously monitored.

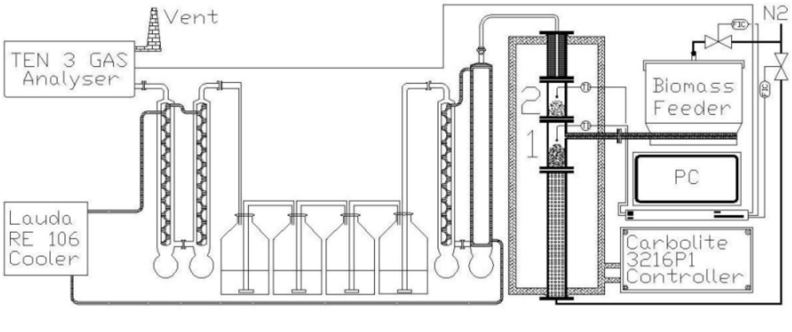

Figure 1: Pyrolysis reactor scheme

Materials

Cellulose beads produced at the Laboratory of Fibre and Cellulose Technology, at Åbo Akademi University, were used as a raw material. The raw material for the production of cellulose beads was viscose. Droplets of viscose were precipitated in sulphuric acid and cellulose beads were formed. Rosenberg[14] has described the production of cellulose beads in detail.

Acidic H-MCM-41-15, H-MCM-41-20 and

silica Na-Si-MCM-41 mesoporous materials were synthesised as described by Beck *et al.*[15] and Bernas *et al.*,[16] with some modifications. The number appearing after the name corresponds to the SiO_2-Al_2O_3 ratio. The materials were synthesised by preparing three different solutions. The first solution (1) was prepared by mixing fumed silica with distilled water, the second solution (2) – by mixing tetramethylammonium silicate with sodium silicate and then stirring for 15 min, while the third solution (3) was prepared by dissolving tetradecyl trimethyl ammonium bromide in distilled water. Solution (2) was slowly added to solution (1) and stirred for 20 min, after which solution (3) was added and stirred vigorously. Aluminium isopropoxide was then mixed with the gel and stirred for 30 min. Crystallisation of the mesoporous material was performed at 100 °C in a Teflon cup inserted in an autoclave. After crystallisation, the material was washed, dried and calcinated at 550 °C. H-MCM-41-15 and H-MCM-41-20 were obtained through the ion-exchange of the produced mesoporous material and a water solution of ammonium chloride subsequently calcinated at 500 °C. Na-Si-MCM-41 was prepared in a similar way, yet without addition of aluminium isopropoxide.

Experimental

Pyrolysis was carried out in a fluidized bed reactor. Approximately 40 g of quartz sand, with a particle size distribution of 100-150 μm, was used as a bed material in the pyrolysis fluidized bed. The mesoporous material powders were pressed, crushed and sieved to 250-355 μm. For catalytic deoxygenation experiments, the upper fluidized bed reactor was loaded with 3 g of mesoporous material. Approximately 15 g of the cellulose beads were used as a raw material in each experiment. The catalyst-to-biomass ratio was close to 0.2. All materials were dried at 100 °C overnight, prior to the experiments.

Fluidization was obtained by feeding 1.3 L/min of nitrogen through the bottom of the reactor; to assure an easier feeding of the biomass, an additional flow of 2 L/min was introduced through the feeder.

The initial temperatures of the pyrolysis and catalysis reactors, of 450 and 485 °C, respectively, were obtained by heating the furnace to 520 °C. The temperature of the glycol used as coolant in the coolers was of -20 °C. When the desired temperatures of the reactors and coolers were reached, feeding of the cellulose beads started. Once the whole material was introduced into the reactor and the concentrations of CO and CO_2 diminished to zero, feeding and heating were discontinued.

Most of the char remained in the lower fluidized bed and was determined gravimetrically. The amount of collectable bio-oil was determined by weighing both the coolers and the collectors. The quantity of bio-oil condensed in the gas quenchers was evaluated by total organic carbon analysis (TOC) and solid phase micro extraction (SPME) on the water in the gas quenchers, followed by gas chromatography mass spectra (GC-MS). The amount of organics in the quench water was determined by dividing the amount of carbon (TOC) by relative carbon concentration (SPME). The water content in the collected bio-oil was determined by Karl Fischer titration. The gas phase was continuously analysed for CO and CO_2. The amount of coke was investigated by thermogravimetric analysis (TGA), in a synthetic air flow of 100 mL/min. The heating rate in the TGA was 10 °C/min, ranging from room temperature to 800 °C, with an isothermal drying period of 15 min at 100 °C.

The spent catalysts were regenerated by burning away the formed coke, at 450 °C, for 2 h. A stepwise temperature programme was applied for regeneration. First, the temperature of the oven was raised to 250 °C, at a heating rate of 4.5 °C/min, then kept at 250 °C for 40 min and thereafter raised to 450 °C, at a heating rate of 5.0 °C/min. The regeneration temperature of 450 °C was maintained for 2 h, followed by slow cooling down to room temperature.

Product analysis

The chemical nature of the bio-oil was analysed by different chromatographic techniques. Approximately 0.2 g of the bio-oil was diluted in 4 mL of distilled water and analysed by high performance liquid chromatography (HPLC). The water soluble fraction of the mixture was filtered prior to the analysis. The column used in the HPLC was an Animex HPX-87C connected to a refractive index (RI) detector. The response factors for several known components had been previously determined. Furthermore, 0.1 g of the organic phase was extracted by MTBE and analysed by GC-MS.

As already mentioned, the coke formed on the mesoporous materials was quantified by TGA. The qualitative nature of the coke was investigated by two different methods. The first was performed by extracting the coke of 0.2 g of the spent material with 4 mL of dichloromethane and further analysed by GC-MS. The second method consisted in first destroying the structure of the mesoporous material (0.15 g) with hydrofluoric acid (2.5 mL) and then extracting the coke again by dichloromethane (10 mL). Principially, by performing the two different procedures of extraction, information on the external and internal coke could be gained.

Characterization of mesoporous materials

The surface area of the mesoporous materials was measured by nitrogen adsorption (Sorptometer 1900, Carlo Erba) and calculated with the B.E.T. equation. The fresh and regenerated samples were evacuated at 150 °C and the spent sample at 100 °C, for 3 h, prior to the measurements.

The strength of the Brønsted and Lewis acid sites of the fresh and regenerated mesoporous materials was measured by infrared spectroscopy (ATI Mattson FTIR), using pyridine as a probe molecule. No acidity determinations were made for the spent samples. A thin self-supported wafer of mesoporous material was pressed and then placed into the FTIR-cell. The cell was evacuated and the temperature was raised to 450 °C and kept for 1 h, after which it was decreased to 100 °C, and the background spectra of the sample were recorded. Pyridine was adsorbed on the sample for 30 min at 100 °C, followed by desorption at 250, 350 and 450 °C for 1 h, the spectra of the sample being recorded in-between every temperature ramp. Scanning was performed under vacuum at 100 °C. The spectral bands at 1545 cm^{-1} and 1450 cm^{-1} were used to identify the Brønsted (BAS) and Lewis (LAS) acid sites, respectively. The BAS and LAS amounts were calculated with the constants of Emeis.[17]

The structure and phase purity of the synthesised mesoporous materials were determined by X-ray powder diffraction (XRD) using a Philips PW1820 diffractometer.

RESULTS

Pyrolysis

The initial temperatures of the pyrolysis and catalysis reactors were 450 and 487 °C, respectively. The cellulose beads were rapidly introduced into the pyrolysis reactor and, consequently, a sharp decrease in the temperature of the pyrolysis reactor could be noticed. When monitoring the temperature of the catalysis reactor, a sharp increase in temperature could be noticed at the beginning of the experiment, probably due to the adsorption heat of the organic pyrolysis vapours on the fresh catalyst. After an initial increase, the temperature of the catalysis reactor decreased to some extent and then returned close to the initial value. The temperature profile of the experiment with H-MCM-41-15 is illustrated in Figure 2. In all cases, the temperature of the pyrolysis reactor decreased to approximately 390 °C. The initial temperature increase in the catalytic reactor for H-MCM-41-15, H-MCM-41-20 and Na-Si-MCM-41 was approximately 20 °C, 25 °C and 3 °C, respectively.

The yield of the pyrolysis products is given in Table 1. More than 85 wt% of the raw material could be observed as the total amount of different pyrolysis products. A mass balance closure of 85 wt% can be considered acceptable, if taking into account the small amount of raw material used in the experiments. The distribution of product phases is affected by the mesoporous materials applied as catalysts in deoxygenation of the pyrolysis vapours. More water and CO are produced as a result of deoxygenation reactions. Na-Si-MCM-41 silica mesoporous material afforded more CO and less water, compared to acidic H-MCM-41-15. H-MCM-41-20 showed the highest water and CO yields. Similar observations have been reported by Lee *et al.*,[18] although dealing with a different feedstock.

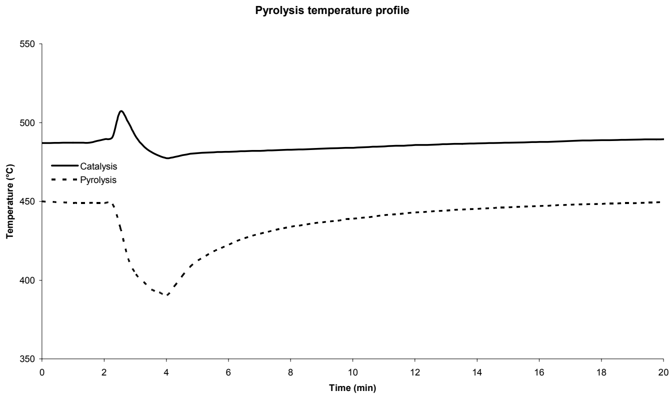

Figure 2: Reactor temperature profiles for H-MCM-41-15 pyrolysis experiments

It was reported that the water and gas yields increased over different mesoporous materials, compared to non-catalytic pyrolysis, as the yield of the organic phase decreased. Coke is also formed on the mesoporous materials during the experiments. Interestingly, char yield is lower in the catalytic experiments than in the non-catalytic ones. In theory, char yield should not be affected by the catalysts, since these two solid materials are never in close contact. The most probable explanation for the lower char yields is that some of the produced char exits the reactor with the fluidization gas.

Characterization of mesoporous materials

Specific surface area, strength and distribution of the acid sites were determined for the fresh, spent and regenerated mesoporous materials, the results being given in Table 2.

The surface area of the spent materials is much lower than that of the fresh ones. The relative decrease in the surface area is higher for the acidic H-MCM-41-15 and H-MCM-41-20 than for Na-Si-MCM-41. Only 13.1% of the initial surface area of the H-MCM-41-20 and 14.5% of the H-MCM-41-15 was retained after the experiment, while the relative surface area of Na-Si-MCM-41 was 66.9% of the initial one. Most of the surface area can be regained through regeneration of the spent sample. The relative values of the regenerated samples surface areas are 84.3%, 81.6% and 94.4% for H-MCM-41-15, H-MCM-41-20 and Na-Si-MCM-41, respectively. To regain more of the surface area, regeneration should be conducted either at higher temperature or for a longer time.

Table 1
Yield of pyrolysis products (wt%) based on dry raw material

	non-catalytic	H-MCM-41-15	H-MCM-41-20	Na-Si-MCM-41
Char	14.5	11.3	12.0	9.9
Organics	55.1	46.2	42.5	45.1
Water	7.0	14.0	14.5	12.5
Gases	8.6	10.8	16.7	14.0
Coke	0.0	4.5	5.0	4.2
Unidentified	14.8	13.2	9.3	14.3
CO	2.9	5.4	9.0	7.3
CO_2	5.7	5.3	7.7	6.8
CO/CO_2	0.5	1.0	1.2	1.1

Table 2
Characterization results, specific surface area, Brønsted and Lewis acid sites (μmol/g)

	H-MCM-41-15			H-MCM-41-20			Na-Si-MCM-41		
	fresh	spent	reg	fresh	spent	reg	fresh	spent	reg
Surface area (m^2/g)	594	86	501	759	100	619	1126	753	1063
Brønsted acid sites									
weak	39	N/A	36	23	N/A	17	0	N/A	0
medium	17	N/A	5	16	N/A	10	0	N/A	0
strong	10	N/A	14	5	N/A	5	0	N/A	0
Lewis acid sites									
weak	40	N/A	49	21	N/A	26	26	N/A	18
medium	20	N/A	13	11	N/A	10	7	N/A	6
strong	12	N/A	3	7	N/A	6	3	N/A	2

The strength and distribution of the acid sites were determined by FTIR, using pyridine as a probe molecule. In Table 2, the acidities are listed as weak, medium and strong acid sites. Weak and medium acid sites are defined as the amount of pyridine desorbed from the sample between 250 and 350, 350 and 450 °C, respectively. The strong acid sites are defined as the amount of pyridine still adsorbed on the sample after desorption at 450 °C. As expected, no Brønsted acidity could be detected in Na-Si-MCM-41, since this material contains no aluminium. More acid sites could be detected on H-MCM-41-15 than on H-MCM-41-20. Moreover, the catalysis-regeneration cycle changes the strength of the acid sites. Slightly more weak and strong Brønsted and weak Lewis acid sites could be detected in the regenerated H-MCM-41-15 sample, comparatively with the fresh one. Otherwise, the acidities were lower for the regenerated than for the fresh materials.

The XRD pattern of Na-Si-MCM-41 is given in Figure 3. The sample phase was indentified as a high crystalline MCM-41 type phase. No other crystalline phases were detected. The sample phases of H-MCM-41-15 and H-MCM-41-20 were of low and medium crystalline MCM-41 type phase, respectively.

Chemical composition of pyrolysis products

Bio-oil analysis

The chemical composition of the organic phase of the bio-oil was analysed by HPLC. The concentration of some pre-calibrated chemicals is given in Table 3. As seen, the chemical composition of the different bio-oils is affected by the different mesoporous materials applied as catalysts in deoxygenation experiments. The predominant chemical in the non-catalytic bio-oil is levoglucosan. In the catalytically upgraded bio-oils, levoglucosan is transformed into hydroxyacetone, glycolaldehyde, furfural, formaldehyde, glyceraldehyde and 5-methylfurfural. Since the oxygen content in hydroxyacetone, furfural and 5-methylfurfural is lower than in levoglucosan, contact of pyrolysis vapours with the catalysts resulted in successful deoxygenation of the bio-oil.

In a similar manner, Adam *et al.*[10] reported that levoglucosan was transformed into smaller molecules, such as acetic acid, furfural and furanes in the pyrolysis of biomass, in the presence of Al-MCM-41 type catalysts. A recent paper of Lin *et al.*[19] described the kinetics and mechanism of cellulose pyrolysis. A mechanism was proposed for pyrolysis, in which cellulose is first decomposed into oligosaccharides and furthermore decomposed to sugars. The major product at this stage is levoglucosan.

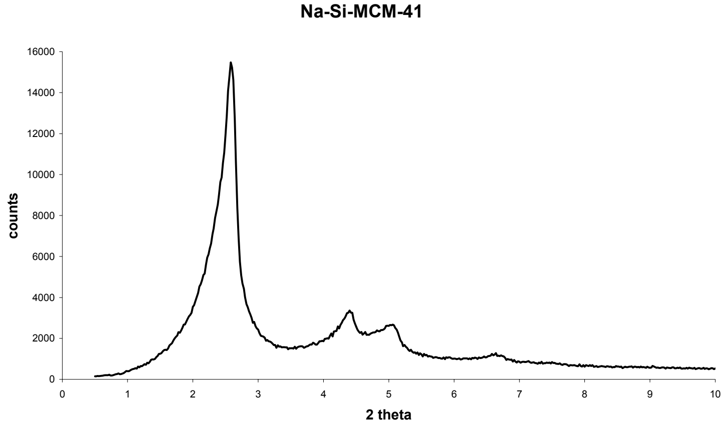

Figure 3: XRD pattern for Na-Si-MCM-41

Table 3
Chemical composition of bio-oils organic phase (wt%)

Chemical	non-catalytic	H-MCM-41-15	H-MCM-41-20	Na-Si-MCM-41
Acetic acid	8.1	8.2	8.4	9.2
Formic acid	1.5	1.9	1.3	1.6
Propionic acid	0.8	0.8	1.1	
Formaldehyde	2.4	5.1	5.7	7.0
Glycolaldehyde	4.1	6.4	8.9	10.2
Glyceraldehyde	12.4	13.3	11.8	17.3
Levoglucosan	22.8	8.7	7.0	6.8
Hydroxyacetone		8.7	6.5	7.6
Furfurylalcohol	0.9	1.2	1.6	1.2
5-hydroxymethylfurfural	3.5	2.8	3.0	3.3

Furfural	2.8	3.7	4.5	4.3
5-methylfurfural	0.4	2.5	3.2	2.3
Total	59.7	63.4	62.8	70.9
Oxygen content	49.9	48.7	48.2	49.3

Dehydration and isomerisation reactions of levoglucosan form other anhydrosugars, which can be further transformed by fragmentation/retroaldol condensation, dehydration, decarboxylation and decarbonylation to smaller molecules, such as furfural, 5-hydroxymethylfurfural, hydroxyacetone, glyceraldehyde, glycolaldehyde, CO, CO_2 and water.

The calculated oxygen content of the pre-calibrated chemicals in the bio-oils organic phase is also listed in Table 3. Calculation was performed by multiplying the oxygen content in each compound by their concentration in the organic phase and divided by the sum. A small decrease in the oxygen content can be seen for all mesoporous materials, compared to the non-catalytic bio-oil, confirming successful deoxygenation. The acidic H-MCM-41-20, followed by H-MCM-41-15, were able to remove more oxygen than in the case of silica Na-Si-MCM-41 and absence of any catalyst.

Coke analysis

An attempt to extract the external coke was performed by directly mixing the coked catalysts with dichloromethane. No peaks originating from the coke molecules could be found by GC-MS analysis.

The internal coke of the spent materials was investigated by first destroying the mesoporous structure with hydrofluoric acid, after which the internal coke was extracted with dichloromethane. The extracted coke of H-MCM-41-15 consisted mostly of linear alkanes and alkenes, ranging from C14 to C20. Similar coke has been found in the pyrolysis of pine wood over microporous zeolites.[13,20] With the applied coke analysis method, ethyl palmitate was the only oxygen-containing coke molecule found. None of the long-chain hydrocarbons were detected in the attempt of extracting the external coke, which also excludes the possibility of DCM contamination.

CONCLUSIONS

Catalytic deoxygenation of cellulose thermal pyrolysis vapours over mesoporous catalysts was performed in a dual-fluidized bed reactor. The application of catalysts changed the distribution of product phases. More water and CO were formed over the catalysts, as the organic oil yield simultaneously decreased. Deoxygenation over H-MCM-41-20 formed more water and CO compared to other mesoporous materials. H-MCM-41-15 generated more water and less CO than the siliceous Na-Si-MCM-41. The chemical composition of the bio-oils was also affected by the catalysts, leading to products containing less oxygen than levoglucosan, which was the dominant chemical in the non-catalytic bio-oil. The organic phase of the H-MCM-41-20 bio-oil had the lowest oxygen content, followed by H-MCM-41-15, Na-Si-MCM-41 and by a non-catalytic experiment. The surface area of the mesoporous materials decreased, due to coking during the experiments. Most of the surface area could be regained through regeneration of the spent catalysts. The coke formed on the catalysts consisted mostly of linear alkanes and alkenes. The coke could not be extracted only by dichloromethane washing.

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