



Catalytic pyrolysis of cellulose using MCM-41 type catalysts



Andrés I. Casoni^a, María L. Nievas^b, Elizabeth L. Moyano^b, Mariana Álvarez^c,
Alejandra Diez^c, Mariana Dennehy^c, María A. Volpe^{a,*}

^a Planta Piloto de Ingeniería Química (PLAPIQUI), Camino Carrindanga Km 7, CP 8000 Bahía Blanca, Argentina

^b Instituto de Investigaciones Físico-Químicas de Córdoba (INFIQC), Universidad Nacional de Córdoba, Facultad de Ciencias Químicas, Ciudad Universitaria, CP5000 Córdoba, Argentina

^c Instituto de Química del Sur (INQUISUR), Dpto. de Química, Universidad Nacional del Sur, Alem 1253, CP 8000 Bahía Blanca, Argentina

ARTICLE INFO

Article history:

Received 16 September 2015

Received in revised form 4 January 2016

Accepted 14 January 2016

Available online 18 January 2016

Keywords:

Catalytic pyrolysis

Cellulose

MCM-41

Bio-oil

Levoglucosenone

ABSTRACT

The pyrolysis of microcrystalline cellulose in contact with MCM-41 and Fe⁻, Al⁻ and Cu⁻ substituted samples was carried out at 400 °C in a fixed-bed glass reactor in order to obtain high bio-oils yields. The acid properties of the catalysts were determined by potentiometric titration with *n*-butylamine, while the redox properties were studied by TPR. BET surface area, pore volume and pore size were measured by means of N₂ sorptometry. The effect of the different catalysts on the composition of the bio-oils was analyzed in the light of the characterization results. Mainly the concentration of levoglucosan (LG), levoglucosenone (LGO), 1,4:3,6-dianhydro-β-D-glucopyranose (DGP) and (1S,5R)-5-hydroxy-3,7-dioxabicyclo[3.2.1]octan-4-one (LAC) were measured. The presence of the solid catalysts increased the liquid formation and strongly modified the chemical composition of the bio-oils compared to the non-catalytic pyrolysis. All the catalysts decreased the production of LG and increased that of LGO, LAC and DPG. The mild acidity of the catalysts promoted dehydration reactions, while redox properties led to a higher production of isomerization products. A much higher LGO yield was obtained over Al-MCM-41 (53 wt% of cellulose is converted to LGO over this catalyst) than by non-catalytic pyrolysis of cellulose previously washed with phosphoric acid (7 wt% of washed cellulose is converted to LGO). In order to evaluate the reuse of the catalyst, the spent sample was submitted to calcination at 400 °C. The physico-chemical properties were not modified after the calcination treatment and the pyrolysis employing the spent sample led to a similar bio-oil composition (though with a smaller yield) as in the case of the fresh catalyst. A second regeneration of the catalyst diminished the specific surface area and the surface acidity. Concomitantly a notable decrease of the yield of LGO was observed.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Pyrolysis of lignocellulosic biomass for bio-oil production could be considered a renewable option to produce fuels and chemicals [1]. However the technologies for economic valorization of biomass from pyrolysis are under development and they cannot compete yet with traditional processes. The main reason is that bio-oils present many disadvantages: the liquids are corrosive and highly oxygenated, which preclude their use as fuels [2]. In addition, although many valuable chemicals are present in pyrolytic oils, the separation and purification processes are too complicated and expensive due to the complex nature and instability of bio-oils [2].

Catalytic pyrolysis has been followed for obtaining upgraded bio-oils and it has been concluded that the acidity of the catalysts plays a crucial role in the transformation of the molecules coming from the primary decomposition [3–9]. The use of HZSM-5 catalysts in the pyrolysis of poplar wood yielded a liquid with a high concentration of phenolic compounds [10]. Although this is a relatively simple liquid (that could be envisaged as a fuel), the yields were poor and the catalysts strongly deactivated. These disadvantages were attributed to the high acidity and to the microporosity of the catalysts. On the other hand, catalytic pyrolysis using mesoporous catalysts, with relatively large pores and mild acidity, led to higher liquid yields [6,8].

Cellulose is the main component of lignocellulosic biomass and the pyrolysis of cellulose gives relatively simple bio-oils, containing mainly furans, monosaccharides and pyran derivatives. Levoglucosan (LG) and levoglucosenone (LGO) are both high-value sugars present in the bio-oils obtained from cellulose. However, the

* Corresponding author.

E-mail address: mvolpe@plapiqui.edu.ar (M.A. Volpe).

Table 1
Properties of the samples employed for carrying out the catalytic pyrolysis.

Catalyst	Me wt%	S_{BET} (m ² /g)	Pore diam (nm)	Pore volumen (cm ³ /g)	H ₂ /Me ^a	E_0 (mV)	Total strength
MCM-41	–	1145	4.2	0.98	0	38	w
Al-MCM-41	3.4	848	3.8	0.93	0	98	s
Fe-MCM-41	4.3	1009	4.1	0.90	0.57	76	w
Cu1-MCM-41	1.6	876	4.3	0.89	0.60	43	w
Cu3-MCM-41	3.0	807	4.6	0.85	0.98	24	w
Cu12-MCM-41	12.2	810	4.8	0.86	0.97	17	W
Al-Fe-MCM-41	2.3–1.6	893	4.2	0.83	0.43	96	w
Nb ₂ O ₅	–	140	<2	0.58	0	138	vs
MCM-49	–	499	6.3	0.46	0	198	vs
Cu/SiO ₂	8.1	210	1.5	0.55	1.08	–11	vw

^a Moles of H₂ uptaken per mole of Fe, Cu or Al as measured by TPR.

separation of LG from the bio-oils is fairly complex, whereas in the case of LGO the separation is quite simple, and for this reason it is desirable to obtain bio-oils rich in LGO rather than in LG [11]. Phosphoric acid and ionic liquids have been used as catalysts to increase the LGO yield [12,13]. Some studies have reported on the use of heterogeneous catalysts in contact with cellulose during pyrolysis to improve LGO production, but yields were very low [14–17].

In the present work, the catalytic pyrolysis of cellulose was carried out using a series of metal-substituted MCM-41 type catalysts in order to obtain bio-oils, which can be a source of valuable products. Substitution of MCM-41 with Fe, Al or Cu increased the acidity of the pure siliceous material and in some cases redox sites were also created. It was expected that the primary molecules from cellulose pyrolysis would react over the MCM-41 surface, giving different products.

The objective of this study was twofold: to find a solid catalyst to improve LGO yield during the catalytic pyrolysis of cellulose, and try to establish a relationship between the properties of the catalyst and the yield of different compounds in the pyrolytic liquid.

The pyrolysis of microcrystalline cellulose in contact with Al-MCM-41, Fe-MCM-41, Al-Fe-MCM-41 and Cu-MCM-41 was carried out in a glass reactor at 400 °C and at low contact times. The catalysts were characterized by N₂ sorptometry, temperature-programmed reduction, transmission electron microscopy, titration with *n*-butylamine and UV–vis spectroscopy.

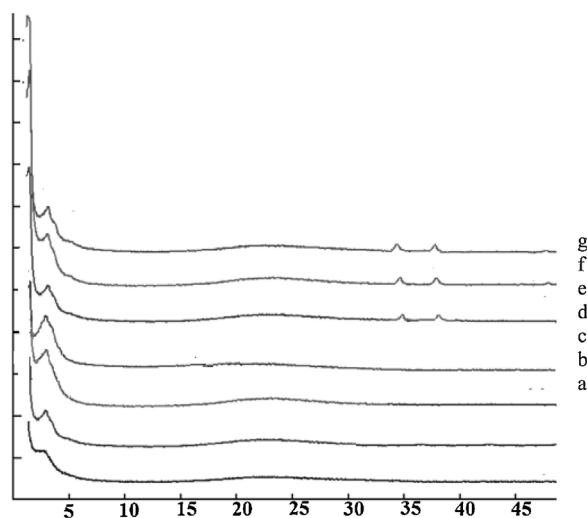


Fig. 1. XRD patterns of (a) MCM-41; (b) Al-MCM-41; (c) Fe-MCM-41; (d) Al-Fe-MCM-41; (e) Cu1-MCM-41; (f) Cu3-MCM-41 and; (g) Cu12-MCM-41.

2. Experimental

2.1. Materials

Microcrystalline cellulose from Biopack was used in the pyrolysis experiments. For some experiments cellulose was washed with solution of phosphoric acid (1.00 g of cellulose and 5 mL of phosphoric acid solution 85% w/w). Elemental analysis of both samples of cellulose were carried out in a EXCETER CE 440 equipment.

2.2. Catalysts preparation

The series of MCM-41 samples were prepared by hydrothermal synthesis [18,19]. For the pure siliceous form, MCM-41, cetyltrimethyl ammonium bromide (CTAB) was mixed with sodium silicate, with a molar ratio of 3.4SiO₂:1CTAB:286H₂O. The gel was treated under static hydrothermal conditions at 373 K for 72 h in a steel/Teflon autoclave. Finally the precursor of MCM-41 was washed with water of mili-Q quality, and dried at room temperature. CTAB was removed by heating the solid at 0.5 K/min under an inert gas flow from room temperature to 673 K. Then the solid was treated at 673 K under air for 6 h.

The substituted MCM-41 samples were prepared by adding Al, Cu or Fe nitrate (99% Merck) to the mixture of the surfactant and the silica source. The pH was kept at 10 by adding a 1 M nitric acid solution at 353 K in a Teflon reactor. After 8 h the solid was filtered and washed with water, and finally calcined at 773 K for 12 h. The Si/Me (Me = Fe, Al, Cu) molar ratio was 30. These samples are named as, Fe-MCM-41, Al-MCM-41 and Cu1-MCM-41. A bi-substituted aluminum/iron catalyst was prepared in a similar manner, with a Si/(Al + Fe) molar ratio of 30.

In addition two other copper samples were prepared. One of them was prepared in a similar manner as Cu1-MCM-41, but with a Si/Cu ratio of 15 (Cu3-MCM-41). The other copper sample (Cu12-MCM-41) was prepared by impregnation of the support MCM-41 before removing the organic surfactant with a toluene solution of Cu(AcAc)₂ (Aldrich, 99.9%). Two additional catalysts were used in the present study: MCM-49 and Cu/SiO₂. The zeolitic catalyst (MCM-49) had a Si/Al ratio of 16.7. The supported copper catalyst (Cu/SiO₂) was prepared following the wet impregnation method from Cu(AcAc)₂ (Aldrich, 99.9%). The support used was silica supplied by Rhône Poulenc (99.7%, Na: 0.1%, SO₄²⁻: 0.1%, others: 0.1%, with a BET surface area of 210 m²/g).

2.3. Catalysts characterization

The Al, Fe and Cu loadings were determined by absorption atomic spectroscopy (AAS). The BET surface area of the samples was obtained from N₂ isotherms at 77 K, measured in a Nova 1200e Quantachrome equipment. Pore sizes were determined by the BJH method. Measurements were performed after evacuation

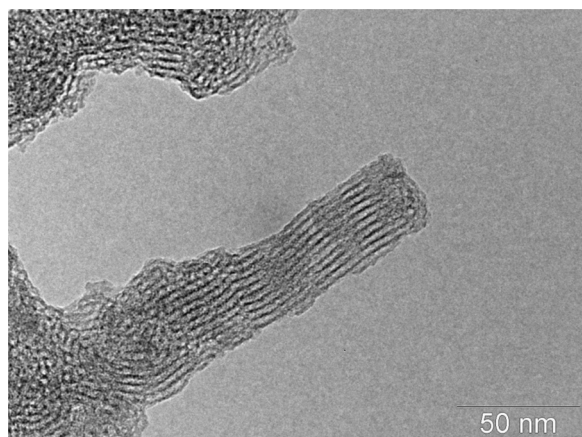


Fig. 2. Micrograph of Al-MCM-41.

at 393 K for 20 h. An X-ray diffraction (XRD) study was carried out using a Philips PW1710 BASED apparatus equipped with a graphite monochromator, operating at 45 kV and 30 mA, and with Cu K α 1 radiation (15.406 nm). The angle step was 0.035 (2θ) and the counting time was 1 s. A high-resolution transmission electron microscopy (HRTEM) study of the samples was carried out in a Philips CM200 UT microscope operating at 200 kV at room temperature.

The catalysts were also characterized by temperature-programmed reduction (TPR). The samples were calcined at 773 K in chromatographic air for 30 min, and then a N₂ purging was carried out at the same temperature. Afterwards, the samples were cooled down to 353 K, and the gas was switched to an H₂ (10%)/Ar mixture flowing at 20 cm³/min. The hydrogen concentration was measured with a TCD detector, and the sample was linearly heated at 10°/min.

Potentiometric titrations were carried out to measure the acidity of the catalysts in an AT500N Automatic Potentiometric titrator (Kyoto instrument) equipped with an M-272 Platinum electrode (Kyoto Electronics, KEM). A 0.1 M solution of *n*-butylamine in acetonitrile was used in the titration of the suspension of 0.10 g of catalyst in 90 mL of acetonitrile. The electrode potential measured 3 h after adding 0.05 mL of the titration solution (E_0) was taken as a measurement of the strength of the acid sites, while the number of such sites was calculated from the equivalents of *n*-butylamine added till a constant potential was achieved [20].

2.4. Catalytic test

The pyrolysis of cellulose was carried out in a lab-scale vertical fixed-bed glass reactor (5 mL), put inside an oven. The reactor was provided with a porous glass disk for supporting the sample, with N₂ flowing (100 mL/min) from the top. Cellulose was mixed with the catalyst, and then the solid mixture was put in a porous basket and dropped into the reactor from the top, once the temperature reached 400 °C. A thermocouple was placed 1 cm above the porous disk. The pyrolytic vapors were collected in a liquid air trap at the bottom of the reactor. After 20 min of pyrolysis, the reactor was cooled down and the charcoal-like solid was withdrawn. The reactor, the liquid collector and the sample basket were weighed before and after pyrolysis process for calculating the mass of the charcoal like product and of the liquid. The mass of gas was calculated from the corresponding mass balance. The experiments were carried out with cellulose masses in the 0.2–1.2 g range, employing cellulose/catalyst weight ratio of 10. The experiments were repeated in triplicate to check reproducibility.

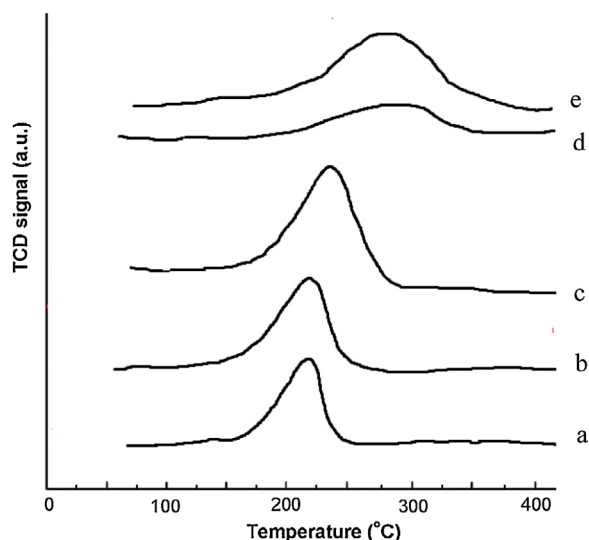


Fig. 3. TPR profile of: (a) Cu1-MCM-41; (b) Cu3-MCM-41; (c) Cu12-MCM-41; (d) Fe-MCM-41 and; (e) Al-Fe-MCM-41.

The liquid collector was washed with acetone (HPLC quality). A rotary evaporator was used to remove the solvent from the sample. Elemental analysis was carried out for some selected liquids in the same equipment employing for characterizing cellulose samples. Chemical composition of bio-oils was determined by gas chromatography in a PerkinElmer CLAIRUS 500 equipment coupled with a mass spectrometer detector. The quantification of the compounds was carried out considering that the peak area was directly proportional to the molar concentration of each compound. The weight percent of the detected product was calculated from the molar composition of the liquids. Nuclear magnetic resonance (NMR), recorded on a Bruker ARX-300 spectrophotometer, was applied for levoglucosenone identification, using a chloroform/ethyl acetate solution (80:20) for elution.

3. Results and discussion

3.1. Catalyst characterization

The list of the catalysts studied and the concentration of Al, Fe and Cu is reported in Table 1.

The small-angle XRD patterns of the catalysts (Fig. 1) exhibited a diffraction peak at $2\theta = 2.1^\circ$ (1 0 0 plane) and two other minor peaks due to (1 1 0) and (2 1 0) planes, all of them corresponding to the 2D hexagonal mesostructure with space group $p6mm$ [21]. Since all the substituted samples exhibited similar patterns as the parent MCM-41, it is concluded that all these catalysts retained the mesoporous structure upon incorporation of Al, Fe or Cu to MCM-41.

The adsorption–desorption N₂ isotherms of the catalysts corresponded to type IV (mesoporous character). BET surface areas, pore volumes and pore diameters are presented in Table 1. It clearly shows that the surface area slightly decreased upon substitution. Pore size was in the mesoporous range for all the MCM-41 samples.

A HRTEM photograph of the Al-MCM-41 catalyst is shown in Fig. 2, in which the mesoporous channels of the sample can be clearly observed.

In order to study the redox properties of the catalysts, the samples were analyzed by TPR. The profiles corresponding to the iron- and copper-containing catalysts (Cu-MCM-41, Fe-MCM-41 and Al-Fe-MCM-41) are shown in Fig. 3. No H₂ consumption was detected for MCM-41 and Al-MCM-41 (results not shown in Fig. 2). The reduction of copper species in the Cu1, Cu3 and Cu12-MCM-41 samples originated peaks with maxima at 220–230 °C. In the case

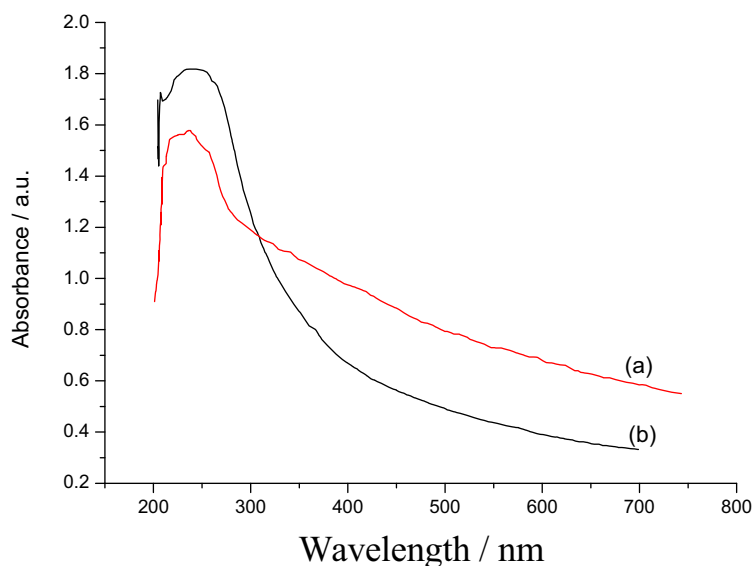


Fig. 4. UV-vis spectra of: (a) Al-Fe-MCM-41; and (b) Fe-MCM-41.

of Fe-MCM-41 and Al-Fe-MCM-41, the reduction of iron oxide took place at a higher temperature (approximately 230 °C). It is interesting to note that the TPR profile of iron-containing catalysts was not similar to those obtained for bulky iron supported on different oxides, which generally shows two peaks with maxima at temperatures higher than 400–500 °C [22,23]. The peculiar TPR profile of Fe-MCM-41 and Al-Fe-MCM-41 would be due to the high dispersion of iron species in the MCM-41 wall and to the absence of bulky iron oxide crystals.

The amount of hydrogen consumed, expressed as mole of gas per mole of the corresponding metal (iron or copper), is reported in Table 1. Cu1/MCM-41, Fe-MCM-41 and Al-Fe-MCM-41 showed relatively low hydrogen consumption. This result indicates that certain amounts of iron or copper species were not engaged in the redox process, probably due to the fact that such species were incorporated inside the MCM-41 structure [24]. On the other hand, Cu3 and Cu12-MCM-41 showed relatively high hydrogen consumptions, which correspond to the total reduction of CuO to Cu°.

The UV-vis spectra of the Al-Fe-MCM-41 and the Fe-MCM-41 catalysts are shown in Fig. 4. Both samples showed an absorption band in the 200–350 nm range with a maximum at approximately 240 nm. This band is assigned to isolated iron(III) ions due to charge-transfer transition from the oxygen ligand associated with species in tetrahedral coordination sites [25].

The acid properties of the catalysts were analyzed by potentiometric titration with *n*-butylamine. Total acidity was calculated through the potentiometric titration curves (see Fig. 5), and the strength of the sites was estimated from the corresponding E_0 value. The total amount of acid sites per g of catalyst, the strength of the sites and the E_0 values are reported in Table 1. It can be observed that all the samples exhibited an acid character; however, the acidity was mild for the bare MCM-41 and both copper-substituted samples. On the other hand, Fe-MCM-41, Fe-Al-MCM-41 and Al-MCM-41 showed a higher acidity than the parent MCM-41 sample. The following order of increasing acidity can be established: MCM-41 \cong Cu-MCM-41 < Al-Fe-MCM-41 < Fe-MCM-41 < Al-MCM-41.

For the sake of comparison, two other samples were also characterized by titration with *n*-butylamine: MCM-49 and Cu/SiO₂, which showed a high and very low acid character, respectively.

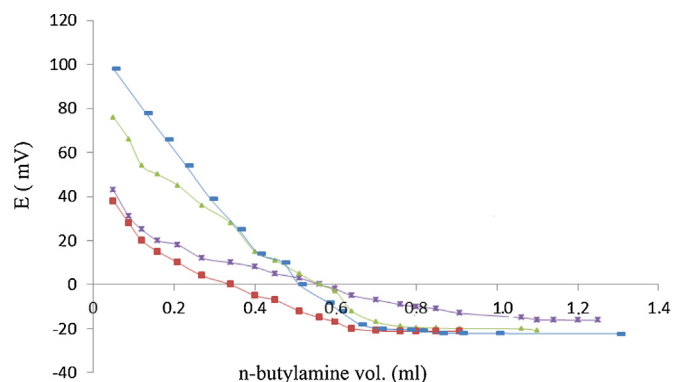


Fig. 5. Potentiometric titration employing *n*-butylamine for: (○) Al-MCM-41; (■) MCM-41; (*) Cu1-MCM-41; and (▲) Fe-MCM-41.

3.2. Catalytic pyrolysis of cellulose

The weight percent of bio-oils obtained during the non-catalytic pyrolysis and the catalytic pyrolysis of 1.0 g of cellulose are reported in Table 2. These percentages were practically constant for pyrolysis carried out using cellulose masses in the 0.2–1.2 g range.

The percentage of bio-oil was relatively high when mesoporous catalysts were used. On the other hand, the pyrolysis carried out using Nb₂O₅, Cu/SiO₂ and MCM-49 led to a low amount of liquids. The relatively large pore volume and pore size of the mesoporous catalysts allow for the free diffusion of the molecules of the primary thermal decomposition of cellulose, which are converted to liquid products. In addition, Cu/SiO₂ and Nb₂O₅ give rise to diffusional barriers due to the microporosity of these solids. Thus, a lower thermal attack of the biomass and consequently a lower production of liquids occur. For Cu/SiO₂ and Nb₂O₅, the fraction of residual solid was high, giving 22 wt%. Both catalysts with relatively small pores unfavorably decelerated the diffusion of the generated anhydrosugars into the gas phase, leading to a repolymerization and concomitantly to a higher formation of char. The catalytic pyrolysis over MCM-49 produced a low amount of liquid due to the formation of a high amount of permanent gases. The gas phase was collected in a Tedlar bag, and it was determined (by means of GC analysis) that the composition of the gas phase upon pyrolysis over MCM-49 was CO₂, CO, CH₄, H₂, and small amounts of other gases.

Table 2
Weight percents of bio-oil and of products obtained in the pyrolysis of cellulose.

	Liq	LG	LGO	DGP	LAC	X ^a	Yield _{LGO} ^b
–	52	85.2	0.80	0	0	14.0	4
MCM-41	55	21.1	29.2	40.3	0	10	16
Al-MCM-41	60	2.5	88.9	6.8	0	1.8	53
RAI-MCM-41 ^c	51	4.2	88.0	3.5	1	3.3	41
RRAl-MCM-41 ^c	47	25.2	27.8	35.6	0	11.7	13
Fe-MCM-41	57	7.5	77.9	1.1	10.0	3.5	44
Cu1-MCM-41	52	17.6	31.9	44.8	0	5.7	17
Cu3-MCM-41	51	14.1	26.5	12.5	39.6	9	14
Cu12-MCM-41	49	14.4	25.6	9.1	43.8	7.1	13
Al-Fe-MCM-41	55	5.1	84.5	7.8	2.2	0.4	47
Nb ₂ O ₅	40	35.4	23.9	1.1	–	39.6 ^d	10
MCM-49	38	0	0	0	–	100 ^d	0
Cu/SiO ₂	39	81.0	2.5	0	–	16.5	10
Acid pretreat ^e	9	6.2	81.2	5.6	4.4	1.7	7

Reaction conditions: 1 g of cellulose, 100 mg of catalyst, 400 °C, 100 mL/min N₂ flow.

^a Mainly furans.

^b Yield to LGO, expressed as wt% of LGO per g of starting cellulose.

^c RAI-MCM-41 (once regenerated), RR-Al-MCM-41 (twice regenerated).

^d Only hydroxyacetone.

^e Pyrolysis carried out over cellulose previously washed with a phosphoric acid solution.

Table 3
Elemental analysis of microcrystalline cellulose, pre-treated cellulose and of selected bio-oils.

Sample	%C	%H	%O
Cellulose	44.21	6.26	49.53
T-cellulose ^a	45.80	6.19	48.01
Bio-oil ^c	47.37	6.01	46.62
Bio-oil (Al-MCM41) ^d	56.33	4.73	38.94
Bio-oil (MCM-41) ^b	52.32	5.23	42.45

^a Microcrystalline cellulose previously washed with phosphoric acid.

^b Liquid from the catalysis free pyrolysis.

^c Liquid from the pyrolysis using 100 mg of Al-MCM-41, 400 °C, 1 g of cellulose, 100 mL/min N₂.

^d Liquid from the pyrolysis using 100 mg of MCM-41, 400 °C, 1 g of cellulose, 100 mL/min N₂.

The chemical composition of the bio-oil is shown in Table 2, as weight percent of the different components in the liquid. The bio-oil obtained by non-catalytic pyrolysis presented a relatively high concentration of LG, whereas furans (mainly 5-methylfuran-2-one, 5-methyl-2-furancarboxaldehyde, and 4-hydroxy-5,6-dihydropyran-2-one) were observed in minor concentrations. Oligomers of cellulose with lower degree of polymerization were not observed in the liquid. At the relative high pyrolysis temperature (400 °C) the complete depolymerization of cellulose took place. The results of the Elemental Analysis characterization of this liquid are reported in Table 3. If only LG would be present in the liquid a similar concentration of C, O and H should be expected. The presence of furans in the liquids led to a lower concentration of H and O than in the starting cellulose.

A notable effect of the different catalysts on the chemical composition of the bio-oils was observed (see Table 2). The mesoporous series led to a lower concentration of LG, while it increased that of other sugars, LGO (levoglucosenone), DGP (1,4:3,6-dianhydro-β-D-glucopyranose) and LAC ((1S,5R)-5-hydroxy-3,7-dioxabicyclo[3.2.1]octan-4-one), which are formed from the dehydration of LG. The mild acidity of the mesoporous samples would account for the dehydration of LG and the higher production of other anhydrosugars such as LGO, DGP and LAC. The bio-oil produced during the pyrolysis using Al-MCM-41 presented the highest concentration of LGO, indicating that LG losses two water molecules over the catalytic surface of this sample. The elemental analysis of the liquid obtained from the pyrolysis using Al-MCM-41 present a concentration of C, H and O which is in line its high concentration of LGO (see Table 3). Since the weight percent

to the liquid obtained from the pyrolysis employing Al-MCM-41 is high, the weight yield of LGO is also the highest for this catalyst (see last column of Table 2).

Approximately the same trends as in the case of Al-MCM-41 were observed for Al-Fe-MCM-41 and Fe-MCM-41. On the other hand, MCM-41 and Cu-MCM-41 catalyzed the loss of only one water molecule, increasing the concentration of DGP and LAC in the corresponding bio-oils.

Regarding the effect of the redox sites of the different catalysts on the composition of bio-oils, it is interesting to compare Cu1-MCM-41, Cu3-MCM-41 and Cu12-MCM-41 with the parent MCM-41 sample, since the copper-containing samples presented almost the same acidic properties as the pure siliceous catalyst, and at the same time the Cu-MCM-41 catalysts presented redox sites associated with copper species. Almost the same composition was found for the bio-oils coming from MCM-41 and Cu1-MCM-41 (Table 2). Probably the copper loading in Cu1-MCM-41 was not high enough to introduce appreciable differences between this catalyst and the parent MCM-41. It is important to point out that the amount of H₂ consumed, as measured by TPR, for Cu1-MCM-41 was much lower than that corresponding to Cu3 and Cu12-MCM-41. On the other hand, the liquids corresponding to both high loaded Cu3 and Cu12-MCM-41 showed a higher concentration of LAC than the one coming from the pyrolysis using MCM-41. It is possible that copper redox sites promote the isomerization of DGP to LAC.

The compositions of the bio-oils obtained in the pyrolysis performed over Fe-MCM-41 and Al-Fe-MCM-41 were very similar to that of the bio-oil obtained using Al-MCM-41 (which did not present redox sites according to TPR characterization). The surface concentration of redox sites associated with iron species was probably too low, and they were not involved in the transformation mechanism of anhydrosugars. At this point it is important to note that the hydrogen consumption, as measured by TPR, was relatively low for Al-Fe-MCM-41 and Fe-MCM-41. Besides, it is not possible to increase iron loading in MCM-41 and the concentration of approximately 4 wt% cannot be surpassed. Thus the effect of iron concentration on the composition of the bio-oil cannot be analyzed.

The use of Cu/SiO₂ catalyst in the pyrolysis tests produced a low liquid yield, which would be associated with small pore size of this solid. The corresponding bio-oil was quite similar to that obtained by non-catalytic pyrolysis.

Nb₂O₅ and MCM-49 with strong acidic character originated a deep degradation of cellulose. The primary products of the pyrolysis of cellulose were transformed over MCM-49, which catalyzes

CC bond breaking, leading to a liquid in which only hydroxyacetone was detected. It was also observed that the amount of gases produced by the pyrolysis of cellulose over this catalyst was higher (50%) than for mesoporous catalysts (30% approximately). The same trend was observed for the Nb₂O₅ catalyst, although to a minor extent.

Based on the results discussed above, it was concluded that the heterogeneous catalysts under study notably affect the composition of the bio-oils obtained by pyrolysis of cellulose.

3.3. Reuse of the catalysts

The possibility to reuse catalysts is an aspect of paramount importance for any process, both from practical and economical point of views. The Al-MCM-41, Fe-MCM-41 and Al-FeMCM-41 catalysts were selected to study the reusability of the samples in the pyrolysis of cellulose. The charcoal left by the catalytic pyrolysis was withdrawn from the reactor and washed many times with water. Then it was submitted to calcination at 500 °C in a furnace. It was observed that for the three cases, the catalyst turned slightly darker than its original light color. It was also confirmed that the specific surface area of the treated sample was nearly the same as that of the fresh catalyst.

The pyrolysis carried out with the regenerated catalysts produced slightly lower amount of bio-oil (see Table 2). The diminution cannot be attributed to morphological changes of the recycled catalyst, since the characterization by sorptometry showed no difference between fresh and spent catalysts. On the contrary the composition of the bio-oil was different to that obtained with the fresh sample (see Table 2). For Al-MCM-41 the differences are slight, but for the other two samples, the amount of LGO produced is notably lower than in the case of the fresh samples. The concentration of iron in the used samples was lower than for the fresh ones (as measured by AAS). Thus it is concluded that Al-Fe-MCM-41 and Fe-MCM-41 cannot be reused.

Al-MCM-41 was regenerated for a second time. A slight decrease in the specific surface area was detected (from the original value of 848 m²/g to 720 m²/g). Besides, the strength of the acid sites also diminished (from the original 98 mV to 75 mV). The modification in the physicochemical properties of Al-MCM-41 within the cycles of pyrolysis could be attributed to the formation of carbonaceous products strongly adsorbed on the catalyst. These species would be produced during the regeneration treatment. The variation of the physicochemical properties of Al-MCM-41 upon the second regeneration led to a strong diminution in the concentration of LGO in the corresponding liquid. In line with this, the weight yield of LGO was also depleted.

3.4. Pyrolysis of cellulose previously washed with phosphoric acid

Previous works have reported that washing cellulose with phosphoric acid prior to pyrolysis increases the concentration of LGO in the bio-oil [12]. Based on these reports, the pyrolysis of microcrystalline cellulose washed with phosphoric acid was carried out non-catalytic conditions. The corresponding results are shown in Table 2. Firstly it was observed that the acid pre-treatment led to a much lower amount of bio-oils (9%) than in the case of untreated cellulose (45%). This may be attributed to the fact that acid dehydrates the cellulose, protecting in some way the fibers against the thermal attack during pyrolysis. This effect was previously observed [26]. It was indeed detected that the LGO concentration achieved for the acid-washed material was higher than in the case of the untreated cellulose. Nevertheless, as this increase was accompanied by a strong decrease in the amount of bio-oil produced, thus the LGO yield was too low (7 wt%).

Acid-washed cellulose was put in contact with Al-MCM-41 for carrying out pyrolysis. The catalyst had virtually no effect in this case, probably because of the protection that the treatment originates in cellulose fibers.

4. Conclusions

The catalytic pyrolysis of cellulose at 400 °C using MCM-41, Al-MCM-41, Fe-MCM-41, Al-Fe-MCM-41 or Cu-MCM-41 notably increased the production of the liquid fraction. The acidity of the catalysts promoted dehydration reactions, lowering the production of levoglucosan, while increasing that of the other anhydrosugars. For Al-MCM-41 the highest yield of levoglucosone is obtained, being this yield higher than that obtained for the non-catalytic pyrolysis of microcellulose previously washed with phosphoric acid.

Acid sites over the heterogeneous catalysts would be responsible for an enhanced dehydration of levoglucosan. Cu-MCM-41 with 3 or 12% wt of copper present active redox sites for pyrolysis, which would promote the formation of a relatively high concentration of (1S,5R)-5-hidroxi-3,7-dioxabicyclo[3.2.1]octan-4-one. The spent Al-MCM-41 catalyst can be reused following a calcination pre-treatment at high temperature, showing almost the same properties as the parent sample. However a second cycle of pyrolysis using this catalyst led to a liquid with a low concentration of LGO.

Acknowledgments

This work was generously supported by CONICET, ANPCyT and SGCyT-UNS from Argentina.

References

- [1] A. Bridgwater, Biomass pyrolysis, in: A.V. Bridgwater, H. Hofbauer, S. van Loo (Eds.), Thermal Biomass Conversion, CPL Press, 2009, 37–78, 423–429.
- [2] A. Oasmaa, S. Czernik, Energy Fuel 13 (1999) 914–921.
- [3] T. Carlson, G. Tompsett, W. Conner, G. Hub, Top. Catal. 52 (2009) 241–252.
- [4] J. Adam, M. Blazsó, E. Mészáros, M. Stöcker, M. Nilsen, A. Bouzga, J. Hustada, M. Gronli, G. Oye, Fuel 84 (2005) 1494–1502.
- [5] T. Carlson, G. Tompsett, W. Conner, G. Huber, Top. Catal. 52 (2009) 241.
- [6] T. Carlson, T. Vispute, G. Huber, ChemSusChem 1 (2008) 397–400.
- [7] L. Qiang, L. Wen-zhi, Zh. Dong, Zh Xi-Feng, J. Anal. Appl. Pyrolysis 84 (2009) 131–138.
- [8] E. Antonakou, A. Lappas, M. Nilsen, A. Bouzga, M. Stocker, Fuel 85 (2006) 2202–2212.
- [9] M. Nilsen, E. Antonakou, A. Bouzga, A. Lappas, K. Mathisen, M. Stocker, Microporous Mesoporous Mater. 105 (2007) 189–203.
- [10] E. Iliopoulou, S. Stefanidis, K. Kalogiannisa, A. Delimitia, A. Lappas, K. Triantafyllidis, Appl. Catal. B: Environ. 127 (2012) 281–290.
- [11] C. Torri, I.G. Lesci, D. Fabbri, J. Anal. Appl. Pyrolysis 85 (2009) 192–196.
- [12] G. Dobelev, G. Rossinskaja, T. Dizhbite, G. Telysheva, D. Meier, O. Faix, J. Anal. Appl. Pyrolysis 74 (2005) 401–405.
- [13] S. Kudo, Z. Zhenwei, K. Norinaga, J. Hayashi, Green Chem. 13 (2011) 3306–3311.
- [14] G. Dobelev, G. Rosinskaja, G. Telinsheva, D. Meier, O. Faix, J. Anal. Appl. Pyrolysis 49 (1999) 307–317F.
- [15] D. Fabbri, C. Torri, I. Mancini, Green Chem. 9 (2007) 1374–1379.
- [16] P. Rutkowski, J. Anal. Appl. Pyrolysis 98 (2012) 115–122.
- [17] Z. Wang, Q. Lu, X.-F. Zhu, Y. Zhang, ChemSusChem 4 (2001) 79–84.
- [18] M. McNall, R. Laurence, W. Conner, Microporous Mesoporous Mater. 44 (2001) 709–716.
- [19] V. Gutiérrez, A. Diez, M. Dennehy, M. Volpe, Microporous Mesoporous Mater. 141 (2011) 201–213.
- [20] Covarrubias, R. Quijada, R. Rojas, Microporous Mesoporous Mater. 117 (2009) 118–125.
- [21] Y. Shu, Y. Shao, X. Wei, X. Wang, Q. Sun, Q. Hng, L. Li, Microporous Mesoporous Mater. 214 (2015) 88–94.
- [22] J. Ashok, S. Kawi, Appl. Catal. A: Gen. 490 (2015) 24–35.
- [23] L. Wang, D. Li, M. Koike, S. Koso, Y. Nakagawa, Y. Xu, K. Tomishige, Appl. Catal. A: Gen. 392 (2011) 248–255.
- [24] V. Gutiérrez, M. Alvarez, M. Volpe, Appl. Catal. A: Gen. 413 (2012) 358–365.
- [25] B. Li, K. Wu, T. Yuan, C. Han, J. Xu, X. Pang, Microporous Mesoporous Mater. 151 (2012) 277–281.
- [26] M. Nieva, M. Volpe, E. Moyano, Cellulose 2 (2014) 1–20.