Catalytic conversion of biomass pyrolysis products by mesoporous materials: Effect of steam stability and acidity of Al-MCM-41 catalysts

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Abstract

In the present study, two mesoporous aluminosilicate Al-MCM-41 materials (Si/Al = 30 or 50) were tested as catalysts for the *in situ* upgrading of biomass pyrolysis vapours in comparison to a siliceous MCM-41 sample and to non-catalytic biomass pyrolysis. The product yields and the quality of the produced bio-oil were significantly affected by the use of all MCM-41 catalytic materials. This behavior was mainly attributed to the combination of the large surface area and tubular mesopores (pore diameter ∼2–3 nm) of MCM-41 materials, with their mild acidity that leads to the desired environment for controlled conversion of the high molecular weight lignocellulosic molecules. The major improvement in the quality of bio-oil with the use of Al-MCM-41 catalytic materials was the increase of phenols concentration (useful chemicals) and the reduction of corrosive acids (undesirable in fuel bio-oils). Higher Si/Al ratios (i.e. lower Al content and lower number of acid sites) of the Al-MCM-41 samples enhanced the production of the organic phase of the bio-oil, while lower Si/Al ratios favoured the conversion of the hydrocarbons of the organic phase towards gases and coke. Moderate steaming of the Al-MCM-41 samples (at 550 and 750 °C, 20% steam partial pressure) decreased their surface area and number of acid sites by 40–60% depending on the Si/Al ratio of the samples and the steaming temperature. However, the steamed samples were still active in the *in situ* upgrading of biomass pyrolysis vapours, resulting in different product yields and bio-oil composition compared to the parent calcined samples, mainly after higher-temperature steaming.
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1. Introduction

Biomass as a term is used to describe any organic matter (excluding fossil fuels), in which the energy of sunlight is stored in chemical bonds. Breaking these bonds by digestion, combustion or decomposition releases the stored chemical energy. Biomass has always been a major source of energy for mankind and is expected to play a more substantial role in the future global energy balance. Even today it contributes to about 12% of the world's energy supply, while in many developing countries its contribution ranges from 40 to 50%. Its main advantage compared to other renewable sources (e.g. wind, solar) is that it can be converted to liquid, solid and gaseous fuels [1–5]. Apart

from the economical impact related to enhanced independency on fossil fuels for energy production, utilization of biomass will also lead to a cleaner and safer environment via reduction of greenhouse gases (CO_2, N_2O) and other toxic gases (NOx, SO_2) which are produced by the use of fossil fuels [1,2,5]. These environmental benefits are related with several biomass properties, e.g. the negligible sulfur content of biomass fuels or the fact that if grown and utilized in sustainable basis, biomass is carbon dioxide neutral, as CO_2 released during biomass conversion has been previously adsorbed from atmosphere on plants during photosynthesis [6].

Wood-based biomass consists mainly of hemicellulose, cellulose and lignin, each one of them pyrolyzing or degrading at different rates and by different mechanisms [4,7]. Generally, biomass conversion processes can be divided in two broad categories: biological (fermentation and anaerobic digestion) and thermochemical (combustion, gasification and pyrolysis)

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[6]. Among the various thermochemical conversion processes, pyrolysis is considered to be an emerging technology for the production of liquid oil, usually referred to as bio-oil (up to 75 wt.% on biomass) [2,7,8]. Pyrolysis of biomass is carried out in various types of reactors using an inert solid as heat carrier for the fast heating of biomass particles [7,8].

In the pyrolysis process, biomass is heated in the absence of oxygen, or is partially combusted in a limited oxygen supply, to produce a gas mixture (containing mainly carbon oxides, some methane and higher gaseous hydrocarbons in minor quantities), a carbon rich solid residue (char and coke) and liquid oil (bio-oil) [6]. The solid char can be used to make activated carbon, while the gas can be potentially used as a fuel gas [8]. The as-produced bio-oil can be utilized as a source of high value chemicals in the field of food aromas, adhesives, fuel enhancers, specialty chemicals, fertilizers, etc. [7]. It is also considered as a promising biofuel since it can be easily transported, be burned directly in thermal power stations, diesel engines, or gas turbines, be utilized as a feedstock in a conventional petroleum refinery and be upgraded to obtain more valuable light hydrocarbon fuels (reforming) [6,8,9].

Bio-oil is composed of a very complex mixture of oxygenated organic compounds and its elemental composition approximates that of the feedstock-biomass [10]. It consists of two phases: an aqueous phase containing a wide variety of oxygenated organic compounds of low molecular weight (such as acetic acid, methanol, acetone) and a non-aqueous phase containing oxygenated compounds (such as aliphatic alcohols, carbonyls, acids, phenols, cresols, benzenedioles, guaiacol and their alkylated derivatives) and aromatic hydrocarbons which are single ring aromatic compounds (such as benzene, toluene, indene and alkylated derivatives) and polycyclic aromatic hydrocarbons (PAHs) (such as naphthalene, fluorene and phenanthrene and alkylated derivatives) [7,10,11].

The major drawbacks of the bio-oil is that it is highly oxygenated, viscous, corrosive and relative unstable [11], while its high concentration of water and oxygenated compounds reduces its calorific value and change significantly the combustion characteristics. Finally the presence of certain undesirable oxygenated compounds (organic acids and carbonyls) and of polycyclic aromatic hydrocarbons, limits its potential for direct use in engines or turbines [8,11].

In an attempt to enhance bio-oil utilization, recent research activity has focused on the optimization of biomass conversion processes towards fuels and chemicals, by applying various catalytic systems, mainly through two routes. One is the upgrading of the biomass pyrolysis bio-oil by using mainly metallic or bifunctional (hydrogenating and acidic) catalysts in hydrotreating processes, resulting in naphtha-like products as potential high-quality fuels additives [10,12–14]. The other route is the *in situ* upgrading of the biomass pyrolysis vapours in specially designed fluidized or fixed-bed or combined reactor systems, in which the vapours react directly with an acidic catalyst towards the formation of bio-oil, gases and solid residues (char and coke) [11,15–19]. In addition, *in-bed* mixing of the solid biomass with the catalyst in the pyrolysis reactor has also been tested [20]. The *in situ* catalytic upgrading of the biomass pyrolysis

vapours, which is also the subject of the present work, usually results to additional water formation and coke-solid residue (consisting mainly of formed charcoal and coke), as well as to a decrease in the yield of organic phase of the bio-oil. However, a positive effect on the quality of the organic phase was noticed and research has been directed towards the design of selective catalysts for either increasing the production of specific compounds (e.g. phenols) or minimizing the formation of undesirable compounds (e.g. acids, carbonyls).

Many catalytic applications in biomass conversion and upgrading processes involve zeolitic catalysts, such as zeolites Y and ZSM-5 [11,14,16,17]. They are both very acidic, the latter being also very shape-selective due to its two-dimensional channel-like pore system with pore diameter of ~0.55 nm. The mesoporous aluminosilicates Al-MCM-41 can be considered as promising catalysts for biomass pyrolysis due to their specific porosity and acidic properties (large surface area, relatively large pores of ca. 3 nm pore diameter, and mild-to-moderate acidity). Previous studies [21,22] have shown that Al-MCM-41 or composite catalysts which comprised Al-MCM-41 with ZSM-5 are very active in the catalytic cracking of palm oil towards the production of gasoline. In more recent studies of our group [15,18,19], various Al-MCM-41 samples were tested as catalysts in the biomass fast catalytic pyrolysis process, resulting in significant changes in the quality of bio-oil. The acid sites present in an Al-MCM-41 catalytic material can be of both Brönsted and Lewis type, each of them participating in the biomass pyrolysis via different mechanisms. However, Al-MCM-41 materials exhibit relatively low hydrothermal stability compared to zeolites [23], thus inhibiting their use in high-temperature processes in the presence of steam. Catalytic pyrolysis of biomass at 500–650 °C which produces water-vapour or the intermediate regeneration of coked catalysts at 650–750 °C in a continuous operation mode, can be considered as such processes. In the present paper, the siliceous MCM-41 and two aluminosilicate MCM-41 mesoporous materials with different Si/Al ratios were evaluated as catalysts for the *in situ* upgrading of biomass pyrolysis vapours. Furthermore, the effect of steaming of Al-MCM-41 on their porous and acidic characteristics as well as on catalytic performance in biomass pyrolysis was also investigated.

2. Experimental

2.1. Synthesis-preparation of MCM-41 mesoporous materials

All MCM-41 mesoporous materials were synthesized in the laboratory based on a modified procedure of the method that has been initially presented by Beck et al. [24]. In a typical synthesis of an aluminosilicate MCM-41 material (Al-MCM-41), a mixture of tetraethylorthosilicate (TEOS) and aluminum isopropoxide (AIP) was slowly added under stirring at room temperature to an aqueous solution of cetyltrimethylammonium bromide (CTAB) which has been previously become alkaline (pH 10–11) by the addition of ammonia solution. The formed gel was further stirred for 1 h and was then transferred to a

polypropylene bottle and was hydrothermally aged at 100 °C for 5 days. The white product was filtered, washed with double distilled water and dried at room temperature. The Si/Al mole ratio in the synthesis gel was modified in order to prepare two Al-MCM-41 samples, with Si/Al ratio of 30 and 50 (labelled Al-MCM-41(30) and Al-MCM-41(50), respectively). A silicate MCM-41 sample (labelled MCM-41) was synthesized following the above procedure with the absence of the Al source. All dried samples were further calcined at 540 °C for 7 h in air in order to combust the organic template (CTAB) and produce the H^+-form of the samples. The Al-MCM-41 calcined samples were further steamed at 550 and 750 °C for 3 h at 20% steam partial pressure, in order to test the gradual effect of steaming on their acidic, porous and catalytic properties.

2.2. Characterization of catalytic mesoporous materials

The catalytic materials tested in this work were characterized by: (a) ICP-AES for the determination of the chemical composition (wt.% of Al and Na), using a Plasma 400 (Perkin Elmer) spectrometer, equipped with Cetac6000AT+ ultrasonic nebulizer, (b) powder X-ray diffraction (XRD) for the determination of the mesophases of MCM-41 materials, using a Siemens D-500 X-ray diffractometer with Cu Kα radiation, in the range of 2–10° 2θ at a scan rate of 1° min^{-1}, (c) N_2 adsorption-desorption experiments at −196 °C for the determination of surface area (BET method), pore volume and pore size distribution (BJH method) of the samples that were previously outgassed at 150 °C for 16 h under 1×10^{-3} Torr vacuum, using an Automatic Volumetric Sorption Analyzer (Autosorb-1, Quantachrome), (d) temperature programmed desorption (TPD) of ammonia for the determination of the number of acid sites, using a commercial TPD apparatus (Altamira AMI-1) and an on-line mass spectrometer (Baltzers, Omnistar) for the detailed analysis of all the desorbed gases.

2.3. Biomass pyrolysis tests and feedstock properties

A commercial wood biomass feed (Lignocel HBS 150-500) originating from beech wood was used in all experiments of the current study. The properties of the feed biomass are shown in Table 1. The pyrolysis of biomass with the mesoporous catalytic materials was performed at 500 °C, using a bench-scale fixed bed reactor (i.d. 1.25 cm), made of stainless steel 316 and heated by a 3-zone furnace. A specially designed piston system was used to introduce the biomass feedstock into the reactor. The reactor was filled with 0.7 g catalyst and the piston with 1.5 g biomass. A constant stream of N_2 was fed from the top of the reactor during the pyrolysis experiments for the continuous withdrawal of the products and the maintenance of the inert atmosphere during pyrolysis. As soon as the reactor reached the desired reaction temperature (500 °C) the solid biomass feedstock entered the reactor with the aid of the piston and was initially pyrolyzed on a hot glass-wool layer placed on the top of the catalyst bed. With the aid of flowing N_2 (100 cm^3/min for 15 min) the produced biomass pyrolysis vapours were fed to the catalyst, while additional purging with N_2 (30 cm^3/min) was performed for another 30 min. A typical residence time of the vapour phase was ∼4.5 s. A more detailed description and a schematic diagram of the unit are given elsewhere [15,19]. For comparison, tests with a non-catalytic solid (glass beads) instead of the mesoporous catalytic materials were also performed.

The liquid products (bio-oil) were collected in a liquid bath (−17 °C) and quantitatively measured in a pre-weighted glass receiver. The two phases usually present in bio-oil (organic and aqueous) were separated using an organic solvent (dichloromethane). The gaseous products were collected and measured by the water displacement method. The amount of the solid residue (named as coke) left in the reactor or deposited on the catalyst surface, consisted mainly of unconverted biomass, charcoal and coke-on-catalyst (formed by thermal and catalytic cracking) and was measured by direct weighting. Gaseous products were analyzed in a HP 6890 GC, equipped with four columns (Precolumn:OV-101; Columns: Porapak N, Molecular Sieve 5A and Rt-Qplot (30 m × 0.53 mm i.d.)) and two detectors (TCD and FID). Liquid products were analyzed by GC-MS analysis in a HP 5989 MS ENGINE (electron energy 70 eV; emission 300 V; helium flow rate: 0.7 cm^3/min; column: HP-5MS (30 m × 0.25 mm i.d. × 0.25 μm)). Internal libraries were used for the identification of the compounds found in the bio-oil and their categorization into main functional groups.

3. Results and discussion

3.1. Characterization of MCM-41 mesoporous catalytic materials

The XRD patterns of the calcined and steamed MCM-41 mesoporous (alumino)silicate samples are shown in Fig. 1. The siliceous MCM-41 presents a pattern that corresponds to highly ordered hexagonal arrangement of the mesopores. Insertion of Al in the samples results in a partial destruction of the hexagonal ordering, as can be seen from the broadening of the (1 0 0) diffraction peak and the significant decrease of the intensity of the (1 1 0) and (2 0 0) reflections. As the Al content increases, from sample Al-MCM-41(50) to sample Al-MCM-41(30), this effect becomes more intense. Upon steaming at relatively moderate conditions (750 °C, 20% steam, 3 h) the siliceous sample retains its integrity to a high extent while the two aluminosilicate MCM-41 samples suffer a more pronounced damage of

Table 1
Properties of biomass feedstock (Lignocel HBS 150-500)

Ash/solid residue (wt.%)	0.53
C (wt.%)	49.41
H (wt.%)	6.73
N (wt.%)	0.16
O (determined by difference)	42.96
GHV (MJ/kg)[a]	18.22
Na (mg/kg)	43.8
K (mg/kg)	326
Moisture (wt.%)	8.25

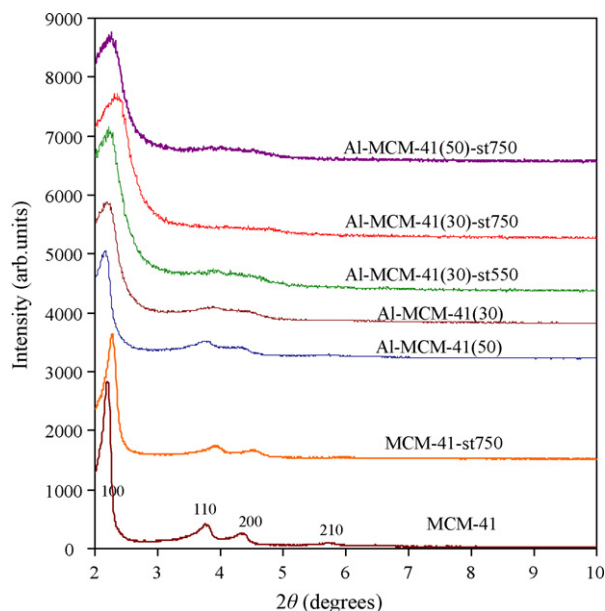[a] GHV: Gross Heating Value (or higher heating value, HHV) determined by ASTM-D4809.

Fig. 1. XRD patterns of calcined silicate and aluminosilicate MCM-41 samples and of the respective samples after steaming at 550 °C or 750 °C at 20% steam for 3 h.

their hexagonal structure, as can be seen from the respective XRD patterns.

Fig. 2 shows the N_2 adsorption–desorption isotherms for the calcined and steamed aluminosilicate MCM-41 samples. The shape of the isotherms of the two calcined Al-MCM-41(50) and Al-MCM-41(30) samples is similar to those of highly ordered siliceous MCM-41 mesoporous materials, revealing that the porous characteristics of the aluminosilicate samples have not
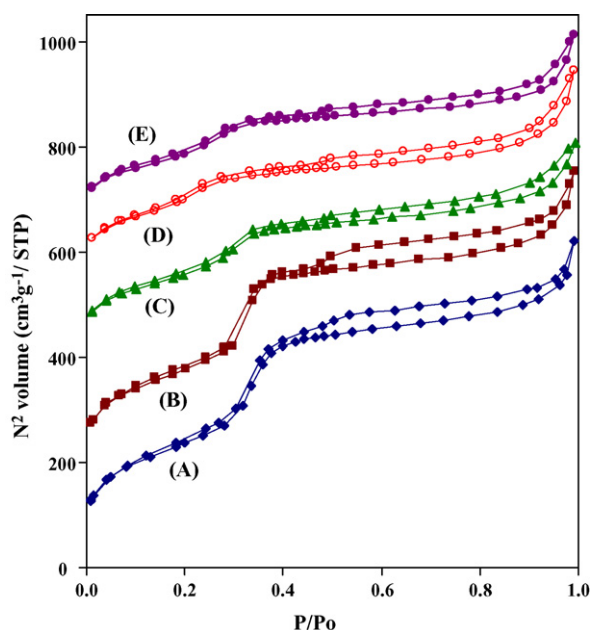

Fig. 2. N_2 adsorption–desorption isotherms for calcined samples (A) Al-MCM-41(30) and (B) Al-MCM-41(50) (offset by 150 cm³ g⁻¹), and for steamed samples (C) Al-MCM-41(30)-st550 (offset by 400 cm³ g⁻¹), (D) Al-MCM-41(30)-st750 (offset by 550 cm³ g⁻¹), and (E) Al-MCM-41(50)-st750 (offset by 650 cm³ g⁻¹).

been damaged to the extent that the XRD patterns indicated. On the other hand, steaming of the aluminosilicate samples resulted in significant changes in the shape of the isotherms, since the characteristic N_2 uptake (step) at P/P_o ∼0.3–0.4 has been significantly decreased. The surface area and the pore size/volume of the samples derived from the N_2 isotherms are given in Table 2. All calcined MCM-41 samples, both silicate and aluminosilicates, exhibit very high surface areas (∼830–950 m²/g) and mean pore diameters of ∼2.7–2.9 nm. Steaming of the samples resulted in lower surface areas and pore volumes, as well as to slightly decreased mesopores mean diameters. This effect was clearer in the aluminosilicate samples and was more intense at higher steaming temperatures. The surface area of both aluminosilicate samples was reduced by ∼40%, compared to the respective calcined samples, after steaming at 750 °C. The total pore volume (including both framework mesopores and textural meso/macropores) decreased from ∼0.95 to 0.85 cm³/g (in the calcined samples) to ∼0.70–0.55 cm³/g (in the steamed), depending on the Si/Al ratio and the severity of the steaming (Table 2).

The chemical composition (Al, Na) and the number of acid sites (measured by NH_3-TPD) of the samples are also shown in Table 2. As expected, the siliceous MCM-41 sample possesses negligible acidity. In the case of the aluminosilicate samples, the total number of acid sites increases with the Al content of the samples. As with the surface area, the number of acid sites in the steamed samples decreases, the reduction being higher at higher steaming temperature (e.g. 60% reduction of acid sites of Al-MCM-41(30) after steaming at 750 °C).

The steaming conditions applied in this work (550 °C or 750 °C, 20% steam, 3 h) can be characterized of relatively moderate severity, mainly due to the low steam partial pressure. They were selected in order to simulate the hydrothermal conditions occurring during biomass pyrolysis at temperatures of 500–650 °C, since one of the main products is water. In addition, if a continuous circulating fluidized-bed catalytic pyrolysis process is designed, the catalysts will need intermediate regeneration between reaction steps since a significant amount of coke or unconverted biomass is usually deposited on their surface. During regeneration at high temperatures, water is also produced, thus subjecting the catalysts to relatively severe hydrothermal treatment-deactivation. Both the above scenarios indicate the importance of the hydrothermal stability of the catalysts used in catalytic biomass pyrolysis. Under the moderate steaming applied in the present study, the surface area of the steamed samples was significantly reduced, but it was still higher than ca. 500 m²/g. In addition, the mesopores diameter remained always higher than ca. 2.1 nm, while the total pore volume was higher than ca.0.55 cm³/g in all steamed samples. All the above show that the steamed samples possess still the appropriate pore size/volume and surface area in order to be able to convert relatively big reactant molecules, such as those present in biomass pyrolysis vapours.

In catalytic cracking and pyrolysis catalytic processes, such as the biomass pyrolysis, the acidic properties of the catalytic materials play an important role since the acid sites catalyze the cracking, isomerization, oligomerization–aromatization,

Table 2
Chemical composition, porosity and acidity characteristics of mesoporous (alumino)silicate MCM-41 materials used as catalysts for biomass pyrolysis

Sample	Chemical composition		Porosity characteristics			Total acid sites[a]
	Al (wt.%)	Na (wt.%)	Surface area[b] (m^2/g)	Pore size[c] (nm)	Pore volume[d] (cm^3/g)	(mmol NH_3/g)
MCM-41	0.02	0.08	946	2.87	0.86	~0.02
Al-MCM-41(30)[e]	1.27	0.04	869	2.75	0.96	0.28
Al-MCM-41(50)	0.74	0.03	827	2.70	0.93	0.20
MCM-41-st750	–	–	796	2.58	0.67	~ 0
Al-MCM-41(30)-st550	–	–	591	2.52	0.63	0.21
Al-MCM-41(30)-st750	–	–	537	2.14	0.61	0.11
Al-MCM-41(50)-st750	–	–	502	2.38	0.56	0.16

[a] Determined from TPD-NH_3.
[b] Multi-point BET surface area.
[c] Determined by BJH method from nitrogen adsorption data.
[d] At $P/P_o = 0.99$.
[e] Numbers in parentheses correspond to the molar Si/Al ratio of the synthesis gel.

decarboxylation and dehydration reactions that take place. Catalyst's activity and selectivity depend greatly, not only on the number of total acid sites, but also on the nature (Brönsted or Lewis) and strength of acid sites. The Al-MCM-41 materials exhibit both Lewis and Brönsted type acidity of relatively mild-moderate acid strength [23]. In the case of gas-oil cracking or conversion of large hydrocarbon molecules, their activity as catalysts is enhanced compared to strongly acidic but with small pores zeolitic catalysts, such as USY, and is significantly higher compared to classical silica-alumina catalysts [23]. However, after severe steaming treatment they become almost inactive since the mesoporous structure collapse almost completely and acidity is greatly reduced [25]. In the present work, the relatively moderate steaming severity decreased the number of acid sites of the Al-MCM-41 samples, this decrease being more intense after steaming at higher temperature (Table 2). However, all steamed samples retained half or more of the acid sites of the parent calcined samples.

3.2. Catalytic activity and product selectivity in biomass pyrolysis

The product yields (total liquids, organic phase of liquids, gases and coke) in the catalytic biomass pyrolysis tests with the inert solid (glass beads) and the MCM-41 materials are shown in Table 3. In addition, the composition of the produced pyrolysis gases is given in Table 4. It can be clearly seen that the use of the siliceous mesoporous MCM-41 catalyst induces a con-

Table 3
Product yields (wt.% on biomass) from catalytic pyrolysis of biomass with mesoporous (alumino)silicate MCM-41 materials[a]

Catalyst	Total liquid products[b]	Organics in TLP	Gases[c]	Coke[d]
Non-catalytic (glass beads)	46.20	20.97	12.29	34.86
MCM-41	55.68	19.81	9.87	32.74
Al-MCM-41(50)	48.38	22.55	7.49	37.43
Al-MCM-41(30)	38.57	9.42	14.34	38.08
Al-MCM-41(30)-st550	40.53	9.20	11.59	39.03
Al-MCM-41(50)-st750	38.75	12.92	11.19	41.10

[a] The mass balance in all pyrolysis experiments was higher than 90 wt.% based on initial biomass.
[b] Total liquid products (TLP) refers to total pyrolysis bio-oil consisting of the organic and water phase.
[c] See Table 4 for gases composition.
[d] "Coke" refers mainly to unconverted biomass and catalytically produced charcoal and coke-on-catalyst.

siderable increase of total liquid products (TLP), mainly due to higher water formation, leaving the organic phase almost unaffected. The acidic Al-MCM-41 samples showed less production of TLP compared to MCM-41. The Al-MCM-41(30) sample with the higher number of acid sites resulted in significantly lower TLP and at the same time reduced the organic phase by ~55% compared to MCM-41 and the non-catalytic experiment. The observed activity of the high-surface area siliceous MCM-41 could be attributed to enhanced thermal cracking and/or dehydration of the biomass pyrolysis products/vapours within

Table 4
Composition of pyrolysis gases (wt.% on biomass)

Catalyst	H_2	CO	CO_2	CH_4	C_2H_4	C_3H_6	C_2–C_6 alkanes
Non-catalytic (glass beads)	0.01	4.32	6.57	0.47	0.15	0.12	0.64
MCM-41	0.02	3.13	5.14	0.55	0.15	0.15	0.73
Al-MCM-41(50)	~0	3.63	2.59	0.24	0.09	0.10	0.84
Al-MCM-41(30)	0.02	5.52	6.63	0.62	0.26	0.45	0.84
Al-MCM-41(30)-st550	0.01	3.51	6.12	0.49	0.19	0.29	0.99
Al-MCM-41(50)-st750	0.02	2.44	6.69	0.53	0.17	0.21	1.12

the tubular mesopores which inhibit heat transfer phenomena in the catalyst particle and may generate "hot surfaces" leading to increased conversion rates compared to the non-porous glass beads (non-catalytic experiment). However, introduction of sufficient amounts of acid sites (as in the case of Al-MCM-41(30)) limits the above effect of increasing the liquid products, by converting a significant part of the organic phase via acid-catalyzed reactions, such as cracking and oligomerization, towards gases and coke. The suggested reaction scheme for Al-MCM-41(30) is in accordance with the observed increased yields of coke and gases (Tables 3 and 4), mainly ethylene and propylene which are considered as primary cracking products. On the other hand, the use of Al-MCM-41(50) with lower Al content and number of acid sites compared to Al-MCM-41(30), resulted in relatively high yields of liquid products, with the organic phase being even higher than that in the case of siliceous MCM-41 and the non-catalytic experiment. From the above it can be suggested that an optimum Al content and acidity of the Al-MCM-41 samples is required so as to maximize the organic phase of the bio-oil. Relatively low Si/Al ratios (i.e. high Al contents) and consequently high numbers of acid sites seem to favour conversion of the hydrocarbons of the organic phase towards gases and coke.

Moderate steaming of the Al-MCM-41 samples resulted in decreased surface area (retaining a significant part of the mesoporous structure) and lower number of acid sites, as it is discussed above. From the data in Tables 3 and 4 it can be seen that steaming of Al-MCM-41(30) at 550 °C and 20% steam resulted to minor changes in product yields compared to the parent calcined sample. The above steamed sample possesses still relatively high surface area (591 m^2/g) and considerable amount of acid sites (0.21 mmol NH$_3$/g). On the other hand, steaming of Al-MCM-41(50) at 750 °C and 20% steam, led to significant decrease of the total liquid products, and more specifically of the organic phase. Although the remarkable selectivity of the calcined Al-MCM-41(50) sample towards the organic phase has been limited, the steamed sample still retains considerable activity as the rest of the samples.

With regard to the composition of the organic liquid phase, the porosity and acidity of the MCM-41 samples played a crucial role. The yields of important compounds in the organic phase, which affect greatly the quality of the produced bio-oil, are shown in Figs. 3 and 4. All calcined and steamed Al-MCM-41 materials induced higher concentrations of phenols and carbonyls and similar concentrations of alcohols, compared to the non-catalytic experiment. On the other hand, the siliceous MCM-41 decreased all the above compounds (Fig. 3). It can thus be suggested that acidity is important in the formation of the above compounds, although a certain trend based solely on acidity cannot be deduced. This is clear in the case of the high-added-value phenols which are higher with the moderately acidic Al-MCM-41(50) sample, compared to the non-acidic MCM-41 and the most acidic Al-MCM-41(30) samples. Surface area seems also to be important and enhance the formation of phenols, as it is shown from the comparison of the calcined Al-MCM-41(50) with the steamed Al-MCM-41(30) at 550 °C, both having similar number of acid sites but the former hav-
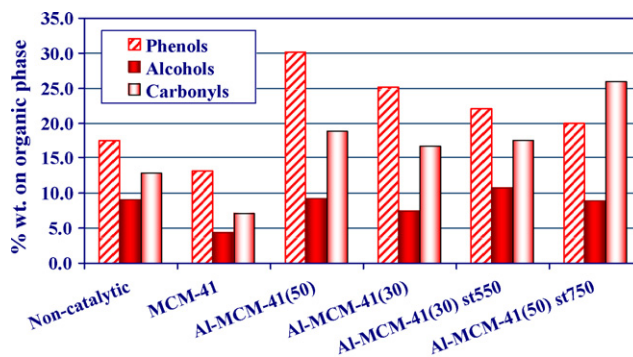

Fig. 3. Concentration of phenols, alcohols and carbonyls in the organic phase of the bio-oil produced from the pyrolysis of lignocellulosic biomass with MCM-41 mesoporous catalytic materials.

ing much higher surface area. The concentration of acids in the organic phase (not shown), which should be avoided due to their corrosive properties, was reduced from ~3% to ≤2% by the use of all MCM-41 catalytic materials.

The polycyclic aromatic hydrocarbons were significantly increased when the siliceous MCM-41 was used as catalyst, compared to the non-catalytic experiment, and this could be attributed to the high thermal cracking activity of this sample. With increasing number of acid sites of the calcined Al-MCM-41 samples, PAHs are reduced due to acid catalyzed cracking reactions. The concentration of hydrocarbons (aliphatic C$_5$–C$_{20}$ alkanes and alkenes, benzene and alkylated derivatives) increased with higher number of acid sites of the calcined Al-MCM-41 materials while steaming inhibited their formation as expected due to decreased acidity of the catalysts. The yields of heavier compounds were increased by the use of all the MCM-41 catalysts, except in the case of Al-MCM-41(50), compared to the non-catalytic experiments. In general, direct correlation between catalyst porous/acidic properties and products yields/selectivities in the *in situ* upgrading of biomass pyrolysis vapours is still a difficult task that requires further study of both the initial step of biomass pyrolysis towards lower molecular weight products/vapours and the consequent conversion of these products towards high quality bio-oils.
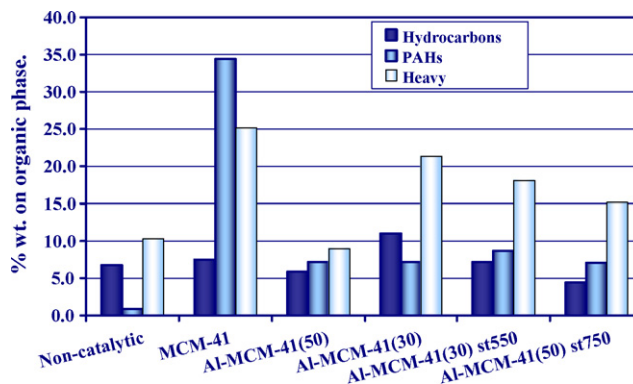

Fig. 4. Concentration of hydrocarbons, PAHs-polycyclic aromatic hydrocarbons and heavy compounds in the organic phase of the bio-oil produced from the pyrolysis of lignocellulosic biomass with MCM-41 mesoporous catalytic materials.

4. Conclusions

The use of Al-MCM-41 mesoporous aluminosilicates as catalysts in the *in situ* upgrading of biomass pyrolysis vapours appears to be promising, with respect to improving the quality of bio-oil as source of useful chemicals via increasing the concentration of phenols, compared to the non-catalytic process. The siliceous MCM-41 catalytic material was also very active in the above process, producing high amounts of total liquid products via enhanced thermal cracking and/or dehydration of the biomass pyrolysis products/vapours on the surface of the mesopores. The relatively moderate steaming pretreatment of Al-MCM-41 samples resulted in active catalytic materials, although they possessed relatively lower surface area and number of acid sites compared to the parent calcined samples. Product yields and composition of bio-oil was mainly affected by the higher temperature steaming of Al-MCM-41 samples. Fine tuning between acidity and porosity of the MCM-41 based catalytic materials seems to be necessary in order to improve product selectivity and the quality of the produced bio-oil.

Acknowledgements

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