



Catalytic cracking of bio-oils improved by the formation of mesopores by means of Y zeolite desilication



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ARTICLE INFO

Article history:

Received 24 July 2014

Received in revised form 29 October 2014

Accepted 1 November 2014

Available online 13 November 2014

Keywords:

Bio-oils

Fuels

Desilication

Y zeolite

Mesopores

ABSTRACT

Y zeolite was desilicated by means of alkaline treatments (NaOH 0.05, 0.10 and 0.20 M) during 15 min to produce varying mesoporosity over it. Catalysts were made with a SiO₂ matrix and a binder. Pine sawdust bio-oil was produced by pyrolysis and immediately upgraded, without intermediate condensation, on a downstream bed of the compound catalysts. The experiments were produced in a fixed bed reactor at 550 °C using different catalyst to reactants relationships. The desilicated zeolites were more effective than the parent zeolite to deoxygenate bio-oil and produce more hydrocarbons, with higher selectivity to olefins (more than 35 wt.%) and lower selectivity to aromatics (less than 60 wt.%) in gasoline. The selectivity to C₄⁻ and gasoline olefins increased if the mesoporosity was higher, and the coke formed was less condensed. These observations were the result of improvements in the diffusion of bulky molecules in bio-oils, such as phenolic ethers, increasing their conversion to hydrocarbons.

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1. Introduction

Residual lignocellulosic biomass is a renewable, low price resource, which could be used for the production of energy, transportation fuels and chemicals [1,2]. The pyrolysis of this biomass allows obtaining up to 70 wt.% of a liquid product named bio-oil, which is a very complex mixture of oxygenated compounds (oxygen, more than 40 wt.%) and water (more than 15 wt.%). Bio-oils cannot be used directly as transportation fuels and are unstable during storage due to the occurrence of carboxylic acids and phenolic compounds, which tend to polymerize [3].

The main problem in upgrading bio-oils into fuels is how to remove the oxygen efficiently. Some options are hydrotreating over conventional catalysts [4] and cracking over acidic solids such as zeolites and mesoporous materials [5–8]. Even though high levels of deoxygenation in bio-oils can be achieved by means of hydrotreating (up to 90%) [4], the large amount of water hinders their processing with typical catalysts. Moreover, the high hydrogen consumption in the process makes their transformation into useful transportation fuels very expensive [6]. In contrast, while zeolites are very important in oil processing, the peculiar characteristics of bio-oils, which strongly differ from fossil hydrocarbons, impose that new approaches are necessary to process biomass

derived feedstocks with them, the overall efficiency depending on both process conditions and catalyst formulation [9].

The use of zeolite catalysts with different crystalline structure, then, could induce changes of varying degree in the product distributions of the conversion of bio-oils. It can be mentioned that various zeolites, such as ZSM-5, Y, beta, mordenite and silicalite, have been studied in cracking bio-oils, but only a few showed to be efficient enough. For example, Yu et al. [10] showed that the zeolite structure impacts on the conversion of oxygenated compounds in bio-oil according to their molecular dimensions; thus, phenolic ethers, such as guaiacol, syringol and their derivatives were not converted on ZSM-5 and mordenite zeolites due to steric hindrance. On the contrary, Y and beta zeolites were the most effective in deoxygenating this type of compounds due to their larger micropore sizes. Previous studies by Adjaye and Bakhshi [11] about the conversion of maple sawdust bio-oil reported that ZSM-5 and mordenite zeolites produced more aromatic hydrocarbons (toluene, xylenes and trimethylbenzenes) and less coke than Y zeolite and silicalite, which produced more C₆–C₉ aliphatic hydrocarbons (mainly alkylated cyclopentenes, cyclopentane, pentane and hexene). Williams and Horne [12] and Vitolo et al. [13] obtained similar results concerning coke yields with Y and ZSM-5 zeolites in the conversion of bio-oils from various sawdusts, and suggested that this is due to the singular crystalline structure of ZSM-5 zeolite impeding the formation of coke precursors.

These facts confirm that Y zeolite is effective in deoxygenating bio-oils, and particularly phenolic ether components, and producing less aromatic hydrocarbons than other zeolite; moreover, the

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distribution of hydrocarbon products is different, as mentioned above. Thus, they are attractive as a catalyst for bio-oil upgrading.

Many molecules which occur in bio-oils are not subjected to strong diffusion resistances in the structure of various zeolites, but others are. In effect, some studies reveal that many bulky molecules in bio-oils, such as some phenolic ethers (vanillin or eugenol, among others), react only on the external surfaces of the crystals of different zeolites such as ZSM-5, Y, beta and silicalite, also blocking pores and contributing significantly to catalyst deactivation [11,14].

The mass transfer of reactants and products in a zeolite pore system could be improved if mesopores can be induced over the crystals [15]. It is possible to remove part of the Si atoms in the crystalline framework of a zeolite by means of leaching in an alkaline medium, inducing a partial collapse of the network and thus producing the occurrence of mesopores in the crystals [16]. Different reports, based on TEM evidences, showed that the mesopores produced by the desilication methods, which consist in a network of interconnected cavities and cylindrical channels, are located not only in the outer portions of the zeolite crystals, but also in the inner fractions (see, e.g., [17–21]). Gueudré et al. [22] used a gravimetric technique to study the diffusion of 2,2-dimethylbutane in ZSM-5 zeolite and found that the mesopores induced by alkaline leaching enhanced diffusion by a factor of five in comparison with the purely microporous parent material; the authors claim that the reason for the improvement was the interconnected network of micro and mesopores within the zeolite crystals.

If the selective removal of Si atoms in the zeolite crystals is achieved, provided that activity is maintained in the desired levels, then, it would be possible to improve the yield of the hydrocarbons which are formed in the conversion of the bio-oils, as the result of the reaction of heavier molecular weight compounds. It should be noted that it is possible to exert some degree of control on the resulting physical properties of the zeolite, provided some experimental conditions such as the concentration of the alkaline agent and the contact time are controlled, impacting on the method's severity [23]. This approach has not been used extensively on Y zeolite [20,24,25].

In view of the possible use of lignocellulosic biomass through the upgrading of bio-oils into transportation fuels and chemical raw materials, it is the objective of this work to evaluate the effect of the occurrence of mesoporosity in Y zeolite on the upgrading of pine sawdust bio-oil, emphasis being given to the quality of the product hydrocarbons which are of interest in the production of fuels and chemicals (light olefins and hydrocarbons in the range of gasoline) and to coke yield.

2. Experimental

2.1. Materials

The catalysts were prepared by adding Y zeolite, which was previously subjected to desilication with varying severities, to an essentially inactive matrix (mesoporous silica, chromatographic grade, Merck) and a colloidal silica binder (Ludox AS-40, Aldrich). The parent zeolite was a commercial ultrastable Y zeolite (H-USY, Zeolyst CBV 760). In the desilication method [20] 0.05, 0.10 and 0.20 M NaOH solutions were contacted with the zeolite during 15 min; after that, the suspensions were neutralized with a 1.0 M HCl solution. These zeolites were exchanged with 0.50 M NH_4Cl (Carlo Erba, 99.5%) solutions, at 1 g zeolite/5 mL solution, and then thoroughly washed with deionized water, dried at 110 °C during 16 h and finally calcined at 550 °C during 4 h to have the zeolites in their protonic form. The zeolites were named Z-00 (no treatment), Z-05, Z-10 and Z-20, in consistency with the NaOH concentration

in the treating solutions. Then, the zeolite samples were steamed (100% steam) at 788 °C during 5 h in order to stabilize them. The zeolite, the matrix and the binder were mixed to form the catalysts at 30, 50 and 20 wt.%, respectively, reproducing typical formulations of the catalysts used in the process of catalytic cracking of hydrocarbons (FCC). Finally, the catalysts were dried at 110 °C during 16 h and calcined in an oven at 550 °C during 4 h in air. The solids were grounded and sieved to the 75–125 μm range. The catalysts were named Cat-00, Cat-05, Cat-10 and Cat-20, in consistency with the corresponding zeolites.

Pine sawdust was dried at 100 °C during 18 h, the contents of its main components being cellulose 35 wt.%, hemicellulose 29 wt.%, lignin 28 wt.%, ash 0.3 wt.% and water 10.2 wt.%, and its elemental composition C (51.6 wt.%), H (5.2 wt.%) and O (43.2 wt.%).

2.2. Catalyst characterization

The X-ray diffraction patterns of the various zeolite samples were collected in a Shimadzu XD-D1 diffractometer in the $5^\circ < 2\theta < 40^\circ$ range. Unit cell sizes (UCS) were calculated according to the ASTM D 3942 method and the crystallinity according to the ASTM D 3906 method. The zeolite Si/Al relationships in the various samples were calculated from UCS data following the Breck–Flanigen correlation [26].

The textural properties of the catalysts were determined by means of the adsorption of nitrogen at -196°C in a Quantachrome Autosorb-1 sorptometer. The specific surface area (S_{BET}) was assessed following the BET method in the $0.15 < P/P_0 < 0.30$ range, the total pore volume (V_{TOT}) was estimated at $P/P_0 \sim 0.98$ and the micropore volume (V_{MICRO}) and the specific surface area of the mesopores (S_{MESO}) were estimated with the t -plot method in the $3.5 \text{ \AA} < t < 5.0 \text{ \AA}$ range. The average mesopore size was assessed with the Barrett–Joyner–Halenda (BJH) model.

The nature, amount and strength of acidic sites in the different zeolites were determined by means of the FTIR analysis of adsorbed pyridine (Merck, 99.5%) as a probe molecule in a Shimadzu FTIR Prestige-21 equipment. Approximately 100 mg of the zeolite were pressed at 1 ton/ cm^2 in order to produce self supporting wafers with density 440 g/ m^2 , which were then placed into a cell with CaF_2 windows. Samples were initially degassed at 450 °C during 2 h and a background spectrum was collected at room temperature. Pyridine adsorption was performed at room temperature and after successive desorptions at 150, 300 and 400 °C, spectra were recorded at room temperature with a resolution of 4 cm^{-1} at pressure of 10^{-4} Torr. The amounts of Brönsted and Lewis acid sites were calculated from the integrated absorbance of the bands at 1545 and $1450\text{--}1460 \text{ cm}^{-1}$, respectively, by means of the integrated molar extinction coefficients, which are considered independent from the catalyst and site strength [27,28].

2.3. Catalytic upgrading of bio-oil

The experiments of conversion of bio-oil over the catalysts prepared from the Y zeolites were performed in an integrated pyrolysis – catalytic upgrading fixed bed reactor. The reactor (see Fig. 1) has two zones which are heated electrically; the first one where the purely thermal pyrolysis occurs and the second one where the pyrolysis vapors (bio-oil) are contacted with a catalytic bed. The experiments were carried out at 550 °C during 7 min, under a 30 ml/min flow of nitrogen. The biomass was located in a stainless steel basket which was introduced instantly in the pyrolysis zone when it reached the target reaction temperature; in this way, secondary polymerization and condensation reactions of the pyrolysis products, which decrease the yield of bio-oil, are minimized. Pyrolysis vapors were then immediately converted, without

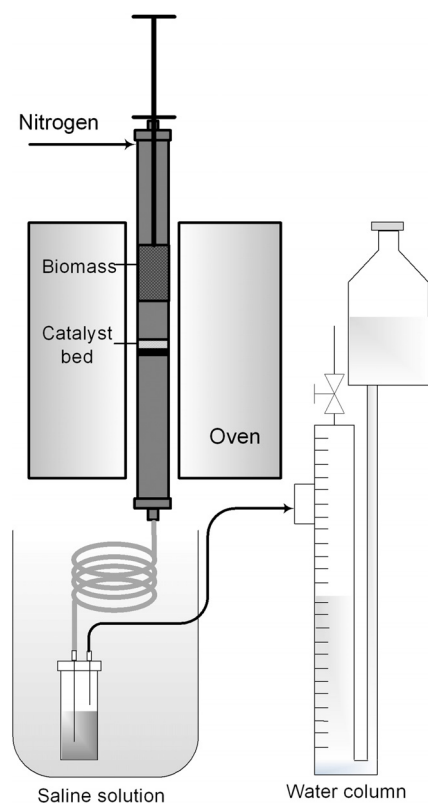


Fig. 1. Experimental setup for integrated pyrolysis – catalytic upgrading experiments.

intermediate condensation, on the catalytic bed which is supported on a porous metal plate.

The experiments were carried out with the catalysts formulated with the parent and the modified zeolites; moreover, an experiment with the mesoporous silica (the matrix supporting the zeolites) was performed at Cat/Oil 3.5. The cumulative Cat/Oil relationship was calculated based on the organic compounds present in the bio-oil, which represented about 30 wt.% of the dry biomass. Besides these experiments, a test without catalyst (purely thermal pyrolysis) was performed to produce background information. The reactor effluents passed through a condenser immersed in a saline solution at -5°C , where liquids were retained, and the gases were collected in a water column and quantified by water displacement. After the reaction time elapsed, the reactor was swept with flowing nitrogen during 7 min. Mass balances (recoveries) were higher than 90% in all the cases.

2.4. Product characterization

Both the liquid and gas products were analyzed by means of conventional capillary gas chromatography. The liquids were analyzed in a Varian GC 450 equipment, using a 30 m long, 250 μm diameter and 0.25 μm film thickness, non-polar, dimethylpolysiloxane HP-1 column and flame ionization detection. The gases were analyzed in an Agilent 6890N equipment, with a 30 m long, 530 μm diameter and 3.0 μm film thickness, bonded monolithic carbon-layer GS-CARBONPLOT column, with TCD detection. The identification of products was performed with the help of standards and GC/MS technique. The calibration of the peak areas was done using response factors specific for each of the chemical groups, which in turn were determined with mixtures of standards and a reference compound (tetralin for liquids and methane for gases). Unidentified peaks, which in all the cases represented less than 0.5% of the

total chromatographic area, were assigned a response factor which was the average value of the factors for the other groups.

The content of water in the liquid product was determined by means of Karl-Fischer titration (IRAM 21320). The amount of coke on the catalyst was assessed with a combined method of thermal programmed oxidation (TPO; initial temperature, 250°C during 15 min; heating ramp, $16^{\circ}\text{C}/\text{min}$; final temperature, 700°C , during 16 min) and further conversion of the carbon oxides formed to methane on a Ni catalyst, which was quantified with a FID detector.

The yield of the various products was calculated as the relationship between the mass of the given product and the mass of dried biomass used.

3. Results and discussion

3.1. Catalyst properties

Table 1 shows the textural and crystalline properties of the zeolite samples used to prepare the catalysts. It can be seen that as the concentration of the NaOH solution in the alkaline leaching increases, the zeolite UCS increases slightly, thus showing a reduction in the zeolite Si/Al relationship. Moreover, the UCS were low in all the cases, indicating that a low number of Al atoms per unit cell existed and, consequently, a high proportion of isolated acidic sites is to be expected [29].

Concerning the textural properties, it can be seen that mesoporosity (mesopore volume and mesopore surface area) clearly increases when the desilication severity increases, reflecting on the increase in the average mesopore size (see Table 1). This change comes from a loss of crystallinity due to the removal of Si atoms from the zeolite network and consequent partial collapse of the crystals [20,30].

The characterization of the zeolite acidic properties was based on the FTIR analysis of adsorbed pyridine. Results in Table 2 show the amount of Brönsted and Lewis acid sites after desorption at 150, 300 and 400°C . It can be seen in all the cases that the amount of acidic sites (mass basis) increased after the treatment of the zeolites. This effect can be noticed both in total acidity (as expressed by the lowest desorption temperature 150°C) and in the other ranges of acid strengths. It must be noted that the lixiviation process is highly selective to leaching out silica-rich domains [16]; thus, aluminium-rich domains and, consequently, tetrahedral Al atoms would remain relatively unchanged, thereby increasing acidity on a mass basis. This behavior was especially observed in zeolites Z-05 and Z-10, which did not lose crystallinity severely, as opposed to zeolite Z-20, which showed a smaller increase.

The strongest acid sites (evidenced by pyridine desorption at 400°C) also increased in the desilication procedure. Different results were reported by Gayubo et al. [19] who, in desilicating ZSM-5 zeolite (Si/Al = 15) with NaOH solutions observed that total acidity decreased and that acid strength was lower. This should not be considered inconsistent, since it has been shown that process parameters (such as alkali, concentration, organic templating agents, contact time, temperature, etc.) and zeolite topology and composition strongly impact on the results of desilication procedures [23,24].

The hydrothermal stability of the modified zeolites was evaluated by means of a steaming process, their consequences on crystal and textural properties being shown in Table 1. As it is well known, steaming produced the loss of crystallinity and specific surface area (both BET and mesopore), which was more intense on the more severely desilicated samples. Similar results were observed by Martínez et al. [21] after steaming over Y zeolite treated with NaOH and EDTA. Steaming also increased the average mesopore size in the desilicated zeolites, probably due to coalescence of the mesopores

Table 1
Properties of the parent zeolite and desilicated samples.

Sample	Cryst. (%)	UCS (Å)	Si/Al Breck-Flanigen	S_{BET} (m ² /g)	S_{MESO} (m ² /g)	V_{MICRO} (cm ³ /g)	V_{MESO} (cm ³ /g)	Average mesopore size (Å)
SiO ₂	Amorphous	–	–	438	438	0.000	0.751	87.9
Z-00	100 ^a	24.23	86.7	838	226	0.350	0.282	19.0
Z-05	75	24.24	33.0	835	358	0.272	0.387	21.3
Z-10	66	24.25	27.3	828	366	0.266	0.420	25.4
Z-20	54	24.26	23.2	724	454	0.158	0.652	38.5
Z-00-S	95	24.24	33.0	681	111	0.241	0.274	30.3
Z-05-S	52	24.22	56.5	624	140	0.203	0.339	34.8
Z-10-S	29	24.21	86.7	639	172	0.198	0.387	36.6
Z-20-S	18	24.20	184.0	352	170	0.076	0.754	94.4

$$V_{\text{MESO}} = V_{\text{TOT}} - V_{\text{MICRO}}$$

^a Reference sample.

Table 2
Distributions of acid sites (pyridine FTIR; $\mu\text{mol/g}$; B: Brönsted and L: Lewis sites) in the parent zeolite and desilicated samples, both fresh and steamed.

Sample	Temperature (°C)					
	150 °C		300 °C		400 °C	
	B	L	B	L	B	L
Z-00	60	23	53	15	21	16
Z-05	69	34	50	15	30	14
Z-10	126	49	83	40	30	27
Z-20	73	41	52	23	23	21
Z-00-S	2	29	1	17	1	14
Z-05-S	10	25	8	14	2	7
Z-10-S	9	31	2	32	2	8
Z-20-S	6	30	5	13	1	8

[17,31], although the ranking of pore sizes for the various zeolites was maintained unaltered.

In relation to the physical properties of the compound catalysts (zeolite plus matrix plus binder), it is expected that mesoporosity be the result of the contribution from the desilicated zeolite, the matrix and the binder. Similar results were determined for all the catalysts, average values being S_{BET} about 350 m²/g, V_{MESO} about 0.55 cm³/g and mesopore size about 70 Å.

Table 2 also includes the acidity of the catalysts after steaming. A strong decrease in both total and strong Brönsted and Lewis acidity can be observed, which affected Brönsted acidity particularly. Particular attention will be given to Brönsted acidity in view of its mechanistic importance, since it has been stated that cracking and deoxygenation reactions proceed on those sites [10,32].

3.2. Product distributions in the conversion of bio-oils

The design and operation of the experimental setup permit the immediate contact and conversion of the bio-oil vapors over the catalyst bed without previous condensation, thus saving energy resources and avoiding collection problems. It is possible in this way to analyze the effect of the addition of a catalyst to the pyrolysis system, comparing results against those of the purely thermal pyrolysis. The pyrolysis of pine sawdust produced 61.4 wt.% bio-oil, 17.2 wt.% gases, which were mainly composed by carbon dioxide and methane, and 21.4 wt.% char (solid carbonaceous deposits).

In the experiment of pyrolysis and immediate contact of the bio-oil vapors with a bed of silica only, at Cat/Oil 3.5, yields of 57.8 wt.% of liquid products and 17.0 wt.% of gas products were observed, that is, very similar to those in the pyrolysis experiment. The experiments where a catalytic bed was included produced less liquid products, ranging from 49.2 to 56.7 wt.%, and more gases, ranging from 18.8 to 22.7 wt.%. This effect was more significant when the

Table 3
Distribution of products in the pyrolysis and the catalytic experiments at Cat/Oil 8.5 (wt.%, dry basis).

	Pyrolysis	Cat-00	Cat-05	Cat-10	Cat-20
Hydrocarbons	1.5	3.1	3.9	4.3	4.0
Oxygenated compounds	28.3	16.5	17.4	15.5	17.5
Water	24.9	29.5	29.9	30.1	30.4
CO ₂	14.3	19.2	17.5	16.5	16.7
Hydrogen	1.6	1.9	1.4	1.6	1.0
Char	21.4	22.6	23.0	24.2	23.5
Coke	–	5.5	5.7	6.6	6.8
Unidentified	7.9	1.6	1.0	1.0	0.0

catalyst load increased, due to the larger number of catalytic sites available for adsorption and reaction.

Table 3 shows the distribution of products in the pyrolysis and the catalytic experiments at the highest Cat/Oil relationship. It can be observed that the catalysts increased up to three times the yield of hydrocarbons in comparison to the pyrolysis and reduced the yield of oxygenated compounds about 40%. Moreover, when mesopores existed in the catalysts, the yield of hydrocarbons increased up to 40%.

The yield of CO₂ in the combined process of pyrolysis plus catalytic conversion was between 14.9 and 19.2 wt.% and, for the case of water, between 29.5 and 30.4 wt.% considering all the experiments. These results do not diverge significantly from previous reports where wood sawdusts were pyrolyzed into bio-oils which were later converted over zeolites [1,33,34].

In the immediate processing of bio-oils over a silica bed the yield of oxygenated compounds was 24.5 wt.%, which is very similar to the values in the purely thermal pyrolysis (see Table 3). Polyaromatic hydrocarbons with more than 14 carbon atoms per molecule were observed plus a low yield of coke. These high molecular weight compounds are derived from the thermal conversion of oxygenated compounds in bio-oils, which is favored by the high specific surface area from the silica bed. It is well known that the oxygenated compounds in the bio-oils, mainly phenolic ethers, furans and some ketones, react thermally following condensation–polymerization mechanisms to yield heavier compounds which form an alquitranous fraction adhering to reactor walls and transfer lines [13,14,35].

According to the reaction scheme by Huber and Corma [36], the conversion of the oxygenated compounds in the bio-oils over acidic zeolites follows two pathways: one of them involves decarbonylation and reforming reactions to produce hydrogen and CO₂, and the other one includes hydrogenation, hydrogen transfer, dehydration and condensation, among others, which consume hydrogen and produce water, hydrocarbons and coke. When the mesoporosity in the zeolite component increased, water, hydrocarbons and coke yields increased slightly, and CO₂ and hydrogen yields decreased

Table 4
Distribution of hydrocarbons (wt.%) in the pyrolysis of pine sawdust and the catalytic experiments at Cat/Oil 8.5.

	Pyrolysis	Cat-00	Cat-05	Cat-10	Cat-20
C1–C2 hydrocarbons	54.7	23.7	29.9	34.2	30.7
Methane	34.4	7.5	9.0	8.6	6.6
Ethane + ethylene	20.3	16.2	20.9	25.6	24.1
C3–C4 hydrocarbons	20.3	17.6	21.7	21.7	21.2
Propane + propylene	11.6	8.9	12.4	13.0	14.8
Propadiene	1.0	0.4	0.3	0.3	0.3
Isobutane	2.9	1.9	1.7	1.3	0.9
Butenes	4.8	6.4	7.3	7.0	5.2
C5–C9 aliphatic hydrocarbons	11.3	9.0	9.1	9.4	10.7
<i>n</i> -Pentane	0.0	0.2	0.3	0.3	0.2
Isopentane	0.0	0.2	0.2	0.2	0.4
C5 Olefins	0.0	4.7	4.7	6.0	6.4
C6 Olefins	8.9	3.6	3.5	2.5	2.9
C6* Aliphatic	2.4	0.3	0.4	0.4	0.8
Aromatics	13.7	49.4	39.2	34.8	37.3
Benzene	1.3	3.9	0.6	0.3	2.7
Toluene	0.3	4.1	1.1	1.5	2.1
C11+ aromatics	12.1	41.4	37.5	33.0	32.5

(see Table 3), thus suggesting the desilication favors the second bio-oil reaction pathway.

Dehydration of oxygenated compounds is carried out on acidic active sites. When mesoporosity increases, the accessibility to acidic sites in the inner surfaces of the zeolites, which are hardly accessible to many of the compounds in the bio-oils, improves. According to a reported mechanism, partially dehydrated molecules can oligomerize to produce more water and slightly condensed coke [36]. This coke can act as a hydrogen donor in hydrogenation and hydrogen transfer reactions [37], considering the low yields of molecular hydrogen (see Table 3) and naphthenics (another possible hydrogen donors, see Table 4) observed in the catalytic conversion of bio-oil. Similar observations were reported by Corma et al. [38] in the conversion of glycerol over equilibrium FCC catalysts, mesoporous alumina and USY zeolite. As shown in Table 3, increases in catalyst mesoporosity imply higher coke yields and, as it will be shown later (Fig. 3), this coke is less condensed. This fact could justify the higher offer of hydrogen for hydrogen transfer reactions, which support the second branch of the conversion of bio-oil over acidic zeolites.

In the combined process of pyrolysis plus immediate catalytic conversion the reduction in the yield of oxygenated compounds translates into higher yields of hydrocarbons and coke, as well as of deoxygenation products (CO₂ and water). Fig. 2 shows the yields of hydrocarbons and oxygenated compounds as a function of the Cat/Oil relationship for all the catalysts. A higher deoxygenation was observed at higher Cat/Oil relationships in all the cases, as shown by the decrease in the yield of oxygenated compounds, the lowest reduction being observed in catalyst Cat-00. This catalyst also showed a reduction in the yield of hydrocarbons as a function of Cat/Oil, but the yield of coke increased, thus leading to an overall positive delta. The higher deoxygenation in the catalysts whose zeolite component had been subjected to desilication and consequently exhibited higher mesoporosity, can be assigned to the improved accessibility.

Acidity could have an impact on the deoxygenation activity of the catalysts. This can be especially compared in the cases of catalysts Cat-10 and Cat-20; in effect, hydrocarbon yield is higher in Cat-10 (the most acidic), which, however, has lower mesoporosity than Cat-20. This maximum in deoxygenation activity can be based on the fact that the loss of crystalline material overwhelms the benefits from higher accessibility in more mesoporous catalysts. A similar observation was reported by Li et al. [39] in the

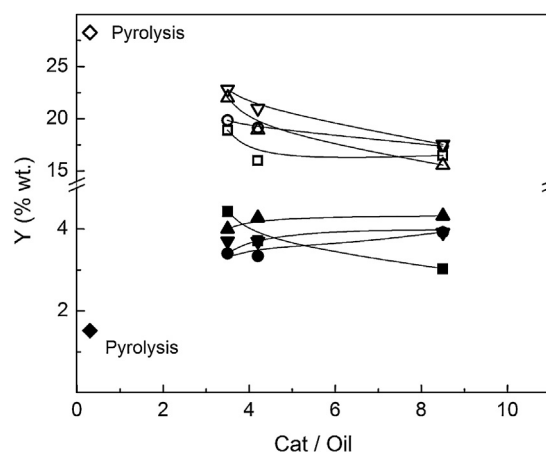


Fig. 2. Yields in the pyrolysis and the pyrolysis plus immediate catalytic conversion of pine sawdust bio-oil processes. Symbols: closed, hydrocarbons; open, oxygenated compounds. ♦, pyrolysis; ■, Cat-00; ●, Cat-05; ▲, Cat-10; ▼, Cat-20.

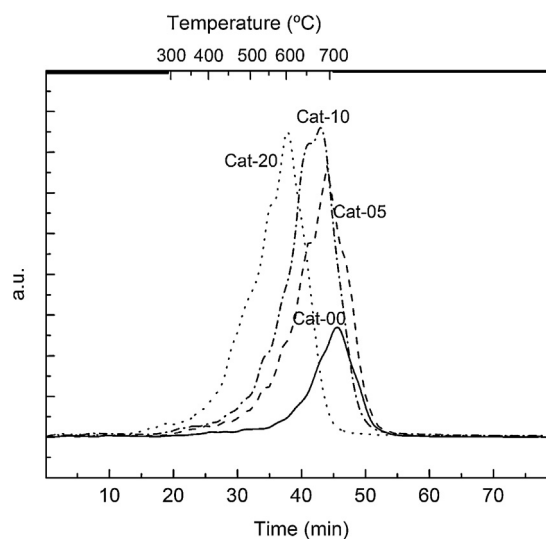


Fig. 3. Coke combustion profiles. Catalysts used in the pyrolysis plus immediate catalytic conversion of pine sawdust bio-oil process. Lines: solid, Cat-00; dash, Cat-05; dash-dot, Cat-10; dot, Cat-20. Cat/Oil 8.5.

catalytic pyrolysis of beech sawdust at 550 °C over ZSM-5 zeolite. As it will be discussed later, it was noticed that the deoxygenation was selectively different for the various oxygenated compounds.

The yield of coke was higher in the catalysts with the Y zeolite having a more extensive degree of desilication, which in all the cases increased with the Cat/Oil. Thus, coke yield in Cat-00 was between 2.8 and 5.5 wt.%, and in Cat-20 it was between 6.3 and 6.8 wt.%. Particularly in Cat-20, this high coke yield partially deactivated the deoxygenating activity of the catalyst and, consequently, could also contribute to support the fact that its hydrocarbon yield was slightly lower than that of catalyst Cat-10. Using ZSM-5 zeolite with mesoporosity increased by means of alkaline desilication, Park et al. [40] observed increases in the yield of coke in the conversion of pine sawdust bio-oil from 13.6 to 21.3 wt.%, while Foster et al. [32] reported that coke yield increased from 6.2 to 10.5 wt.% in the conversion of furan. These authors consider that the higher coke yield is the consequence of more free space in the catalyst pore system, which permits the polymerization of polyaromatic compounds leading to coke.

Coke combustion profiles are shown in Fig. 3. The profiles reflect that the higher the mesoporosity, the higher the coke yields (see Table 3). However, it is interesting to note that the maxima in the

combustion peaks shifted to lower temperatures as the severity of the desilication procedure increased; for example, it was 700 °C for Cat-00 and 603 °C for Cat-20, suggesting that the condensation degree of the coke was lower when the mesoporosity increased. It can be considered that, in FCC catalysts, coke is located mostly on the mesopores of the matrix component, arranged in polyaromatic domains which are heterogeneously distributed and which also include trapped molecules of saturated hydrocarbons [41]. An analogy could be speculated between mesopores in the matrix and these new mesopores over the zeolite, with coke agglomerates also including hydrocarbon and light oxygenated molecules which, as the desilication is more severe and the mesoporosity is higher, confer an increasingly less condensed character to the coke. Consistently, Hartmann [42] mentioned that mesopores in zeolites would ease the burning-off of coke in regeneration processes.

In the experiments with a silica bed, coke yields were lower than 1.3 wt.%, that is, much lower than in the experiments with a catalyst, their TPO peaks being located at a much lower temperature (571 °C). This coke probably derives from thermal condensation and polymerization reactions of bio-oil components, as pointed out by various authors [11,43].

3.3. Hydrocarbons

The distribution of hydrocarbon products in the pyrolysis and the experiments with a catalyst resulted very different, as shown in Table 4. Gaseous hydrocarbons predominated in the pyrolysis; for example 75 wt.% selectivity to C₄⁻ compounds and selectivity to methane four to five times larger than in the experiments with catalysts. Oppositely, the catalysts produced more liquid hydrocarbons: 44–60 wt.% selectivity to C₅⁺ compounds and selectivity to aromatics two to three times larger than in the experiments without catalysts. Particularly the selectivity to aliphatic C₅–C₉ liquid hydrocarbons was similar in both thermal and catalytic processes, but having a very different distribution: while the pyrolysis produced exclusively 2-methyl-1,4-pentadiene, 2-hexene, cyclooctane and decane, which are products typically present in wood sawdust bio-oils [44,45], when a catalyst was present C₅ and C₆ olefins predominated.

In the desilicated catalysts, light C₄⁻ olefins predominate in the group of gaseous hydrocarbons, while simultaneously the selectivity to aromatic hydrocarbons decreases. This effect seems not to be directly related to the acidic properties (Table 2) but to the increasing mesoporosity (Table 1), and reflects the fact that the products of the primary cracking and deoxygenation of the bio-oil components diffuse faster and are not strongly engaged in secondary oligomerization, cyclization and hydrogen transfer reactions [36,46]. This effect seems to prevail over the increased possibility of accommodating larger or bimolecular reaction intermediates as those, for example, needed in hydrogen transfer reactions which would increase the selectivity to aromatic hydrocarbons.

When the severity of desilication increased, liquid C₅–C₉ aliphatic hydrocarbons, mainly C₅–C₆ olefins, were produced more selectively; on the contrary, the yield of the heaviest hydrocarbons, C₁₁⁺, decreased due to their easier access to the catalytic sites and further cracking to lighter aromatics such as benzene and toluene [47] (see Table 4).

3.4. Composition of the gasoline cut

The yield of liquid hydrocarbons in the gasoline boiling range is of particular interest in the field of the production of fuels from residual lignocellulosic biomass. The selectivity to those hydrocarbons was low in the pyrolysis (11.3 wt.%), but higher in the experiments with catalysts, (between 22.3 and 30 wt.%), especially when the catalyst Cat-00 was used. Desilicated catalysts showed

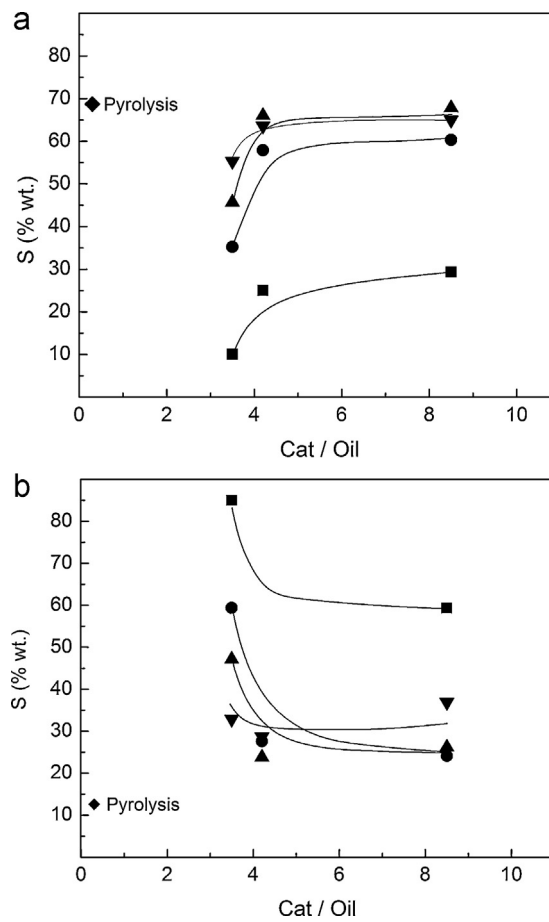


Fig. 4. Proportions of C₅–C₁₂ olefins and C₆–C₁₂ aromatic hydrocarbons in gasoline in the pyrolysis and the pyrolysis plus immediate catalytic conversion of pine sawdust bio-oil processes. (a) Olefins. (b) Aromatic hydrocarbons. Symbols: □, pyrolysis; ■, Cat-00; ●, Cat-05; ▲, Cat-10; ▼, Cat-20.

selectivities to gasoline from 12.5 to 17.0 wt.%, a consequence of the lower yield of aromatic hydrocarbons (see Table 4). The selectivity to the non-aromatic hydrocarbons in the cut was between 9.0 and 10.8 wt.% for all the catalysts, which increased slightly with mesoporosity (see Table 4).

In all the cases the gasoline cut was mostly made up by olefins and aromatic hydrocarbons, as shown in Fig. 4, with low proportions of paraffins (up to 15 wt.%) and naphthenics (up to 4 wt.%). Important differences were observed between Cat-00 and the alkaline desilicated catalysts, the first one producing selectively much more aromatics and less olefins in gasoline than the other catalysts. In all the cases aromatics decreased and olefins increased as long as the Cat/Oil relationship increased. These observations can be rationalized under the view of the discussion in the previous section.

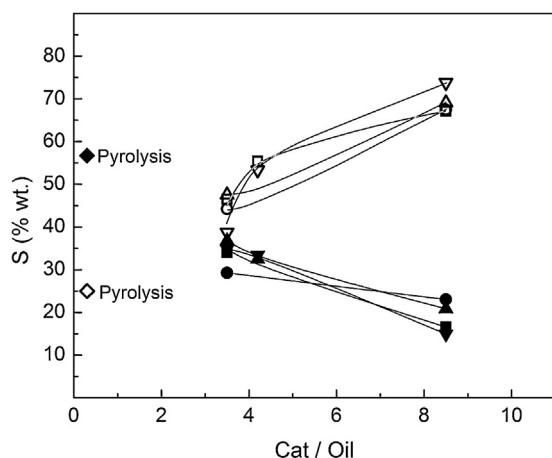
3.5. Oxygenated compounds

The effect of the modification of the textural properties of the zeolites on their deoxygenating activity can be observed in Table 5, where the distribution of oxygenated products in the catalytic tests is compared with that in the thermal pyrolysis. When the catalyst is present, the selectivity to acids, esters, aldehydes, ketones and alcohols decreased notably, while the selectivity to phenols (mainly phenol and alkylated phenols) increased. Moreover, the higher the catalyst mesoporosity, the more significant the effect. This fact could be due to the improved accessibility of the phenolic

Table 5

Distribution of oxygenated compounds (wt.%) in the pyrolysis of pine sawdust and the catalytic experiments at Cat/Oil 8.5.

	Pyrolysis	Cat-00	Cat-05	Cat-10	Cat-20
Acids and esters	28.9	4.3	4.7	0.8	0.0
Ketones and aldehydes	24.3	15.3	13.3	18.5	14.9
Furans	4.2	1.3	9.7	2.6	0.0
Alcohols	12.2	10.1	3.9	6.4	3.4
Phenols	25.3	66.8	67.5	69.4	73.8
Alkylated phenols	6.7	60.4	60.5	63.6	63.3
Phenolic ethers	18.6	6.4	7.0	5.8	10.5
Other cyclic oxygenated compounds	5.0	2.1	0.9	2.1	7.9

**Fig. 5.** Proportions of oxygenated compounds in the pyrolysis and the pyrolysis plus immediate catalytic conversion of pine sawdust bio-oil processes. Symbols: closed, (aldehydes, ketones and furans; open, phenolic compounds. □, pyrolysis; ■, Cat-00; ●, Cat-05; ▲, Cat-10; ▼, Cat-20.

ethers to the acidic sites in the zeolite as the consequence of lesser diffusion restrictions given the increased mesoporosity.

The groups which showed less significant changes in selectivity, such as aldehydes and ketones, indeed exhibited variations in their distributions; for example, the proportion of high molecular weight ketones decreased and the proportion of acetone, which is a product from the catalytic conversion of other oxygenated compounds in bio-oils [48] increased as a function of increasing mesoporosity.

Fig. 5 shows the selectivities to the main groups of oxygenated compounds as a function of the Cat/Oil relationship. The proportion of phenolic compounds, which are the consequence of the conversion of the lignin in the biomass, in the experiments with catalysts was from two to four times higher than in pyrolysis, due to the fact that some of them also originate from the conversion of other compounds over the catalysts. On the contrary, those compounds which derive from cellulose and hemicellulose, such as acids, esters, aldehydes, ketones and furans, decreased their concentration in the catalytic processes, suggesting elevated conversions (refer to Fig. 5). Among phenols, phenolic ethers such as guaiacol, syringol and their derivatives, decreased notably due to their high reactivity. On the contrary, phenol and alkylated phenols such as cresol and dimethyl phenol increased their proportions; indeed these compounds can also be the products of the conversion of phenolic ethers, aromatics and alcohols [45,46], and they had been observed in the catalytic cracking of pine sawdust bio-oil over a commercial equilibrium FCC catalyst [49], and of various wood sawdusts bio-oils over Y and ZSM-5 zeolites [11,12,35].

It is to be noted that in all the catalysts the selectivity to phenolic compounds (mainly phenol and alkylated phenols) increased as a function of the Cat/Oil relationship. The change was most significant in the catalyst with the highest mesoporosity (Cat-20),

Table 6

Selectivities (wt.%) of oxygenated compounds in bio-oil as a function of catalysts properties. Case example at Cat/Oil 3.5.

	Critical diameter (Å) ^a	Cat-00	Cat-05	Cat-10	Cat-20
Catalysts properties					
Average pore size (Å) ^b		19.0	21.3	25.4	38.5
Cristallinity (%)		100	75	66	54
Oxygenated compounds					
Furfural	6.7	3.5	7.7	7.8	10.0
4-Ethyl-1,3-benzenediol	7.5	0.5	0.2	0.2	0.1
4-Vinylguaiacol	7.9	2.4	0.5	0.3	0.0
Trimethoxybenzenes	9.2	9.2	1.4	1.9	0.8

^a From Ref. [10].^b Corresponding to the zeolite component.

from 37% to 74%, thus suggesting a higher conversion of the phenolic ethers, which are their main precursors [46].

The conversion of phenolic ethers, which are the most bulky compounds in bio-oils, over zeolites is hindered by diffusion restrictions, as compared to other oxygenated compounds with smaller molecular size, such as methanol, acetone, phenol and furfural. For all the catalysts the conversion of phenolic ethers increased as a function of Cat/Oil, as evidenced by their lower concentration in the group of phenolic compounds. For example, for catalyst Cat-20, it decreased from 20.8 wt.% at Cat/Oil 3.5 to 14.2 wt.% at Cat/Oil 8.5.

The knowledge of the critical diameter of a given molecule [50] could assist this discussion; however, this property is known only for a few oxygenated molecules [10]. Table 6 shows the selectivity of some bulky phenolic and aromatic ethers for the various catalysts at Cat/Oil 3.5, at which the highest oxygenated yields were observed (see Fig. 2). It can be seen that the selectivity to these compounds decreased significantly when the catalysts' mesoporosity increased, thus suggesting higher conversions. This effect was more evident on bulkier molecules, such as trimethoxybenzenes; in particular, for the catalyst with more severe desilication on its zeolite component (Cat-20), the selectivity to these compounds was essentially nil.

On the contrary, those oxygenated compounds in bio-oils with smaller molecular size can access the sites more easily and their conversion would not be influenced by the pore size. Furfural was included in Table 6 as an example of these molecules in bio-oils, since it is not a product, such as acetone, methanol and phenol [49], from the catalytic conversion of other components. It can be seen that, contrary to the observations for bulky molecules, the selectivity to furfural increased at higher mesoporosities, indicating lower conversion, and supporting the assumption that its conversion is more dependent on zeolite crystallinity or acidic properties rather than on mesoporosity.

4. Conclusions

It is possible to control the textural properties of Y zeolite via desilication with alkaline treatments, in order to formulate compound catalysts such as those of FCC, increasing the contribution from mesopores to the catalyst's specific surface area. In this way, it is possible to use them more efficiently in the conversion of a renewable energy source.

The catalytic properties to process bio-oils are impacted positively. The increased mesoporosity in the desilicated catalysts improved the diffusion of bulky reactants such as phenolic ethers.

This approach resulted in a high degree of deoxygenation and high yield of hydrocarbons. Desilicated zeolites were also more selective to olefins and much less selective to aromatics than the parent zeolite.

Acknowledgments

This work was performed with the financial assistance of University of Litoral (Santa Fe, Argentina), Secretary of Science and Technology, Proj. CAID 2011 #501-201101-00546LI; CONICET, PIP 1257/09 and the National Agency for Scientific and Technological Promotion, PICT 2010/2123.

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