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Short communication

Deoxygenation of m-toluic acid over hierarchical x zeolite

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ABSTRACT

Catalytic activity of FAU zeolites was tested on the deoxygenation of *m*-toluic acid at atmospheric pressure and without feeding hydrogen. Sodium dodecylbenzenesulfonate was used as template to obtain a certain mesoporosity in the NaX zeolite. The mesoporosity improved the catalytic activity. This zeolite showed a good activity catalytic increasing the toluene yield to 40%, reducing the oxygen content in the reaction products, and decreasing the esterification reaction. The catalytic activity was kept without deactivation of the catalyst.

1. Introduction

The production of biofuels from wood, vegetable oils and animal fats has been considered a good alternative to supply large quantities of fuels. However, it requires significant changes to become an acceptable transportation fuel [1–3]. These biofuels contain a complex mixture of acids, alcohols, aldehydes, esters, ketones, phenols, carbohydrates, furans, alkenes, aromatics and nitrogen compounds. In these mixtures, a high content of oxygenated groups involves high viscosity, poor thermal stability, low calorific value and high corrosivity, which limits their applicability. Therefore, the presence of oxygenated compounds decreases the quality of biofuels and the deoxygenation, the removal of oxygen atoms present in the molecules, is needed to enhance fuel enthalpies, decrease its viscosity and corrosivity and stabilize the biofuels increasing their chemical and thermal stability. Biofuels obtained after deoxygenation will be acceptable and economically attractive. Deoxygenation of biofuels has been mainly studied over acid catalysts, silica-alumina or zeolites, with consumption of hydrogen at high pressure and with formation of coke and tar as well as of by-product undesirables [4,5]. Deoxygenation of biofuels can also be carried out by direct elimination of the carboxylic groups releasing CO_2 (decarboxylation) and/or CO (decarbonylation) over supported metal catalyst such as Pd/C [6,7]. An alternative to these catalysts are the basic solid catalysts, which can produce decarbonylation and decarboxylation reactions with lower hydrogen consumption, lower temperature and less coke formation. Among the possible basic solid catalysts for use in these reactions are the basic zeolites. Resasco et al. have published studies about the use of CsNaX zeolite as catalyst in the decarbonylation and decarboxylation of methyl octanoate and benzaldehyde. The highly polar environment of the micropores of the zeolite seems to play an essential role in the adsorption and decomposition of adsorbed molecules without hydrogen consumption [8,9]. However, some of the compounds obtained in biofuels, which could be deoxygenated, are too bulky to diffuse through the zeolite pores. In this sense, the use of zeolites with hierarchical porosity would be very interesting. Hierarchical zeolites have emerged as an important class of materials, since the presence of porosity on different scales lead to improved catalytic performance compared to their microporous parents. Successful methods for the direct preparation of mesoporous zeolites with high silicon/aluminum molar ratio and MFI and Beta frameworks have been developed. In these syntheses ordered mesoporous carbons or carbon nanotubes, functionalized polymers, hybrid organic–inorganic surfactants, cationic polymers, etc. were employed as templates [10]. However, there are few studies about synthesis of zeolites with FAU framework and low silicon/aluminum molar ratio. Xiao et al. reported on the synthesis of mesoporous NaX zeolite with silicon/aluminum molar ratio of 1.3 using organic templates of cationic polymer (polydiallyldimethylammonium chloride) and spirulina [11]. Mesoporous in the range of 4–5 nm were obtained and the calcium ion-exchange rate was higher than that of conventional NaX zeolite. Inayata et al. synthesized X zeolite with a low Si/Al ratio of 1.0–1.5 using **3-**(trimethoxysilyl)propyl hexadecyl dimethyl ammonium chloride as amphiphilic organosilane achieved mesopores with a mean size of 7 nm but with intracrystalline mesopores [12]. Undoubtedly, the development and use of hierarchical zeolites with low silicon/aluminum molar ratio will increase in coming years and it would be interesting to study the potential templates and their basic catalytic properties.

In this study the synthesis of NaX zeolite with mesoporosity was carried out using as template an anionic surfactant, sodium

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dodecylbenzenesulfonate (SDBS, $CH_3(CH_2)_{11}C_6H_4SO_3Na$). This zeolite was employed as catalyst on the *m*-toluic acid deoxygenation reaction.

2. Experimental

2.1. Catalysts

X zeolite syntheses with different silicon/aluminum molar ratio were carried out via the hydrothermal method according to previous studies. All the solids obtained were washed, dried at 373 K overnight and calcined at 823 K for 3 h (heating rate 1.8 °C/min).

Synthesis of KNaX zeolite was carried out employing a gel with molar ratios: $SiO_2/Al_2O_3 = 2.2$, $(Na_2O + K_2O)/SiO_2 = 3.25$, $H_2O/(Na_2O + K_2O) = 17$ and $Na_2O/(Na_2O + K_2O) = 0.77$. Aging and crystallization were carried out at 343 K for 14 h. This zeolite has a silicon/aluminum molar ratio of 1.1 and an anhydrous unit cell formula of $Na_{64}K_{28}(SiO_2)_{100}(AlO_2)_{92}$ [13].

Synthesis of NaX zeolite was carried out employing a gel with molar ratios: $SiO_2/Al_2O_3 = 3.44$, $Na_2O/SiO = 1.32$, $H_2O/Na_2O = 39.8$. Aging and crystallization stages were carried out at 298 K for 24 h and at 373 K for 7 h, respectively. This zeolite has a silicon/aluminum molar ratio of 1.5 and an anhydrous unit cell formula of $Na_{77}(SiO_2)_{115}(AlO_2)_{77}$ [14]. Synthesis of NaX_{SDBS} was carried out in the same way, but using sodium dodecylbenzenesulfonate (SDBS) during the synthesis. The concentration of SDBS in the mixture gel was 5.2 mM (1.8 times the critical micelle concentration of the SDBS at 298 K) with a molar ratio $SDBS/SiO_2 = 0.005$ [15]. This zeolite has a silicon/aluminum molar ratio of 1.5 and an anhydrous unit cell formula of $Na_{77}(SiO_2)_{115}(AlO_2)_{77}$.

Commercial 13X (NaX) and USY zeolites were supplied by Sigma-Aldrich and Grace Davison, respectively.

2.2. Characterization

N_2 adsorption–desorption isotherms were obtained at −77 K using a MICROMERITICS ASAP 2020. Total surface area and pore volume were determined using the Brunauer–Emmett-Teller (BET) equation and the single-point method, respectively. Pore size distribution (PSD) curves were calculated by Barrett–Joyner-Halenda (BJH) method. X-ray diffraction (XRD) patterns were recorded on a SIEMENS-D501 diffractometer with CuKα1 radiation with scanning range of 2θ between 5° and 50° with a step size of 0.1°. Chemical composition was determined by means of X-ray fluorescence (XRF) in an Aχios instrument.

2.3. Catalytic activity

Deoxygenation reaction of *m*-toluic acid ($CH_3C_6H_4COOH$), as probe molecule, was carried out at 698 K in a fixed bed reactor with continuous nitrogen flow (20 mL min^{-1}) at atmospheric pressure. Previously, the zeolites were calcined at the reaction temperature, 698 K, in nitrogen stream for 1 h. Reaction conditions employed were catalyst weight/feed rate of reactants (W/F) of 13 g h mol^{-1} and 1 wt.% of *m*-toluic acid in a solvent. Samples from the reaction were analyzed by Gas Chromatography in a Varian CP-3800 equipped with a capillary column (30 m) and flame ionization detector (FID).

3. Results and discussion

3.1. Catalyst characterization

XRD profiles exhibited the characteristic peaks of the FAU framework, without amorphous halo and with high crystallinity in all zeolites.

Table 1 shows the physical characteristics of the commercial and as-synthesized zeolites.

Fig. 1 shows the nitrogen adsorption/desorption isotherms recorded at 77 K of the as-synthesized zeolites with and without SDBS. Zeolite NaX displays the typical shape of the microporous materials, exhibiting adsorption at low relative pressure ($p/p_0 < 0.03$). Nitrogen adsorption hardly took place between $p/p_0 = 0.1$ and 0.8, with a variation in the quantity adsorbed of 2.8%. The isotherm belongs to type I in the IUPAC classification with H4 hysteresis loop, attributed to the aggregation of particles. On the other hand, NaX_{SDBS} shows the initial high adsorption ($p/p_0 < 0.03$), in the same way that the NaX zeolite, due to the filling of micropores [16], but with higher variation (7.0%) in the quantity adsorbed in the p/p_0 range between 0.1 and 0.8. In addition, the hysteresis loop is wider, starting at p/p_0 0.4, and with more difference between desorption and adsorption branches, which indicates a broad pore size distribution. The adsorption isotherm for this zeolite NaX_{SDBS} belongs

Table 1
Physical properties of the zeolites.

	13X (NaX)	USY	KNaX	NaX	NaX_{SDBS}
Si/Al[a] (mol)	1.3	3.1	1.1	1.5	1.5
%Na[a] wt.% u.c.	26.5	6.3	18.2	23.6	24.9
%K[a] wt.% u.c.	0	0	13.5	0	0
S_{BET}[b] (m^2/g)	877	782	713	641	551
S_{micro}[c] (m^2/g)	842	722	676	613	499
S_{meso}[c] (m^2/g)	35 (4%)	60 (7.7%)	36 (5%)	28 (4.4%)	52 (9.4%)
V_{pore}[d] (cm^3/g)	0.336	0.333	0.284	0.266	0.247

wt.% u.c.: weight percentage per unit cell.

[a] Composition determined from XRF data.

[b] Specific surface calculated from N_2 adsorption data applying BET method.

[c] Micropore surface calculated from N_2 adsorption data applying t-plot method.

[d] Mesopore surface calculated from N_2 adsorption data applying t-plot method.

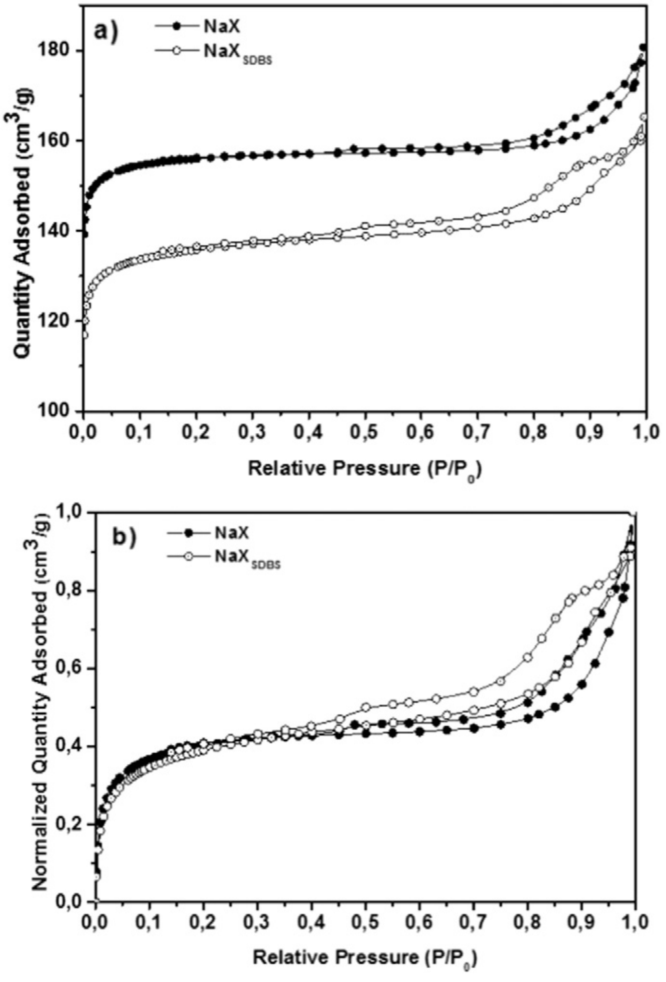

Fig. 1. a) Nitrogen adsorption/desorption isotherms at 77 K in NaX and NaX_{SDBS} as-synthesized zeolites. b) Normalized nitrogen adsorption/desorption isotherms at 77 K in NaX and Na_{XSDBS} as-synthesized zeolites.

to the type I + IV with H3 hysteresis loop. The difference between both zeolites is more clearly appreciated in Fig. 1b, where is displayed the normalized quantity adsorbed. Fig. 2 shows the pore size distribution (PSD) obtained applying the BJH model (using the KJS correction) to the desorption branch of the isotherm. NaX_{SDBS} presents a broad band with high intensity centered at ca. 11.5 nm, indicating a pore size distribution narrower than those of the NaX zeolite. Therefore, the use of SDBS during the synthesis procedure allows obtaining hierarchical porosity in the NaX zeolite.

For the rest of zeolites the shape of the nitrogen adsorption/desorption isotherm at 77 K was the typical for microporous materials, similar to that of the NaX as-synthesized zeolite.

3.2. Deoxygenation of m-toluic acid

Among the different compounds formed in the pyrolysis, bio-oils noted for their high presence the aromatic derivatives, so in this work we studied the deoxygenation of *m*-toluic acid as probe molecule.

The low concentration employed was due to two reasons. Firstly, the concentration of this kind of compounds (aromatic acids) in the bio-oils is low. The other reason was related with technical problems. Formation of crystals of *m*-toluic acid was detected at the reactor outlet, after the reaction zone. Even the pipe was blocked at high concentration of *m*-toluic acid (>5 wt.%). This problem did not allow closing mass balance due to part of feed *m*-toluic acid was accumulated in this point of the experimental installation. Anyway, as this happens after the catalyst, the reaction was carried out being expressed the results only as yields. However, that was not an impediment to check the catalytic activity of these zeolites in the deoxygenation of aromatic acids, as the *m*-toluic acid.

The expected product of the deoxygenation, using methanol as solvent, was toluene. However, since the methanol can produce hydrogen and formaldehyde over this kind of zeolite [17], hydrogenation products, as xylenes, and methylation products, as ethylbenzene, xylenes or trimethylbenzenes, could be formed. All these products would be desired products since they have lost the oxygen atoms. On the other hand, the esterification reaction to produce methyl **3-**methylbenzoate would be an undesired reaction because it did not reduce the oxygen content.

A wider product distribution was obtained in the reaction without catalyst (*blank test*) due to the thermal cracking of the *m*-toluic acid, with a low yield to deoxygenation products (≈2%). Fig. 3 displays the product distribution in the reaction with the different zeolitic catalysts using methanol and acetonitrile as solvents.

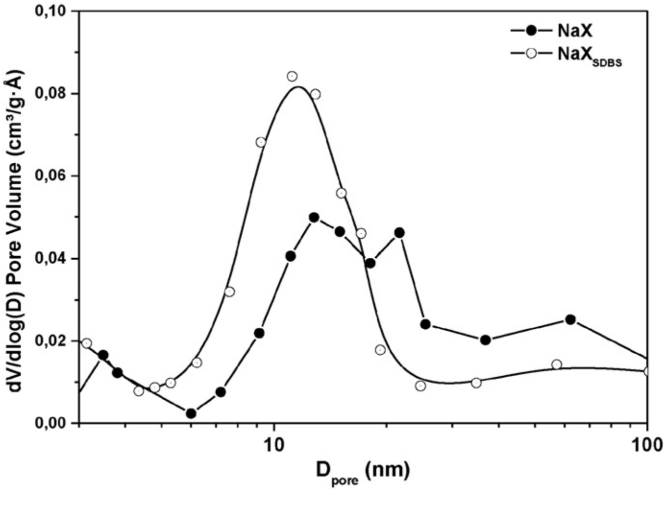

Fig. 2. Pore size distribution in NaX and NaX_{SDBS} as-synthesized zeolites, obtained from the desorption branch.

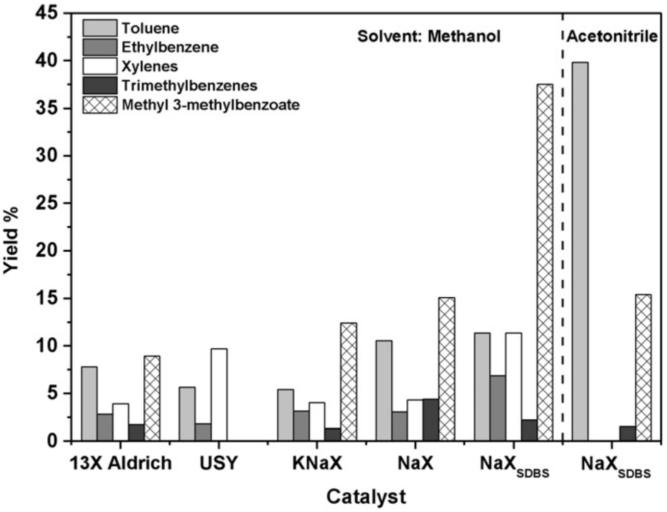

Fig. 3. Product distribution in the deoxygenation reaction of *m*-toluic acid. Reaction conditions: time: 1 h; W/F: 13 g h mol^{-1}; temperature: 698 K, *m*-toluic acid (1 wt.%) and methanol or acetonitrile (99 wt.%).

It can be observed that the reaction with USY zeolite left mainly to other products (80%) and without formation of methyl 2methylbenzoate. This was the only zeolite that did not produce the esterification reaction. Among the desired products the main product were xylenes (10%), which confirms the acid character of this zeolite since the toluene methylation over acid catalyst leads to the ring methylation [17]. This zeolite produced the catalytic cracking of the *m*-toluic acid to products with low molecular weight, which were not detected by FID detector, due to its acid character (cations/aluminum molar ratio <1). However, the yield to desired products (≈17%) was similar to these of the 13× Aldrich and KNaX zeolites, but over these zeolites, esterification product was mostly obtained, especially over the KNaX zeolite (12%). Among these three zeolites, the 13× Aldrich zeolite presented the highest desired/undesired molar ratio, around 2. Therefore, the KNaX as-synthesized zeolite, with potassium and lower silicon/aluminum molar ratio, did not improve the catalytic activity in the deoxygenation reaction of *m*-toluic acid in spite of being the most basic zeolite. There are two reactions competing with the active sites, deoxygenation and esterification, and both of them are produced over FAU zeolites.

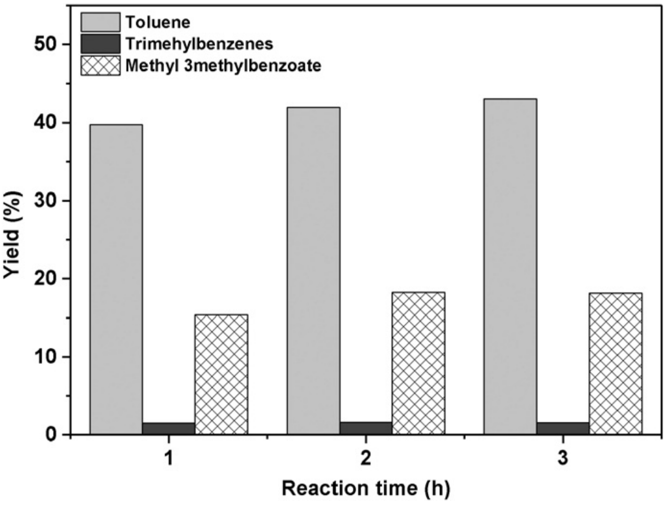

Fig. 4. Catalytic activity of the NaX_{SDBS} zeolite in the reaction with acetonitrile as solvent. W/F: 13 g h mol^{-1}; temperature: 698 K, *m*-toluic acid (1 wt.%).

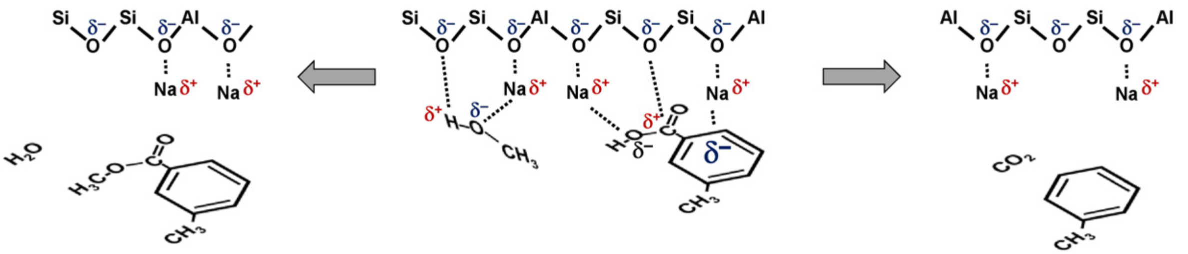

Fig. 5. Mechanism of reaction.

On the other hand, the most active catalyst was the NaX as-synthesized zeolite with and without SDBS (Fig. 3). NaX as-synthesized zeolite reached a yield to desired products around 22%, upper than the yield to methyl **3-**methylbenzoate (15%), obtaining a desired/undesired molar ratio of 1.5. Among deoxygenation products, the production of toluene was especially significant with a yield around 10%. However, the main product was methyl **3-**methylbenzoate (15%).

Noteworthy results were obtained with the NaX_{SDBS} zeolite, reaching a total yield to desired and undesired near 70%. Therefore, the presence of a certain mesoporosity in the zeolite increased the catalytic activity of the NaX zeolite since it improved the access to the active site and the formation of bulky molecules as the methyl **3-**methylbenzoate, reaching a yield of 37%. The yield to desired products also increased to 32% (10% more than with the NaX as-synthesized zeolite), achieving a desired/undesired molar ratio around 0.9. The main desired products were toluene (11%), xylenes (11%) and ethylbenzene (7%).

In spite of the better activity with the NaX_{SDBS} as-synthesized zeolite, the yield to oxygenated products was still high, upper to the yield to deoxygenated products. Acetonitrile, as solvent, was employed in order to cut down to a minimum the formation of the ester and, hence, to direct the reaction mechanism toward the toluene formation. These results are shown in Fig. 3. Meaningful decrease in the yield to methyl **3-**methylbenzoate, from 37% on methanol to 15% on acetonitrile, was observed. This was due to the lesser methylation capacity of acetonitrile compared to that of methanol. Associated to the less methylation capacity, the main product was toluene, reaching a yield of 40%, four times higher than with methanol. The desired/undesired molar ratio was increased to almost 3. Therefore, when methanol was used as solvent, the formation of ethylbenzene, xylenes or trimethylbenzenes was produced from toluene methylation.

Fig. 4 shows the variation of the catalytic activity with the reaction time in the reaction with acetonitrile as solvent. There was no detected decrease in the catalytic activity with the reaction time. The yields were steady for 3 h, with a slight increase. The same behavior was observed with the NaX and NaX_{SDBS} zeolites in the reaction with methanol as solvent. Moreover, the color of the zeolites after the reaction was beige, not black. It is well known that the solid base catalysts, unlike solid acid catalysts, tend not to form coke on the surface since basic sites lack in cracking ability [18].

The reaction scheme is shown in Fig. 5. Aromatic ring, with negative charge, is linking to the sodium cation allowing the interaction of the oxygen atoms of the zeolite with the carbon atom of the carboxyl group, producing the elimination of CO_2. The elimination of CO_2 is not a remarkable problem, since biofuels are renewable and do not affect to the carbon dioxide balance. On another hand, if methanol is used as solvent, the esterification reaction is also possible since the methyl of methanol could be linked to the oxygen of hydroxyl group of the *m*-toluic acid producing methyl **3**-methylbenzoate.

4. Conclusions

This is the first report on the use of sodium dodecylbenzenesulfonate (SDBS), as template, for the synthesis of X zeolite with a certain mesoporosity. This as-synthesized zeolite was found to be better for deoxygenation reaction of *m*-toluic acid since the mesoporosity improved the access of the reactant to the active sites. The desired/undesired molar ratio was near 3. The production of xylenes was due to the methylation of toluene, not the hydrogenation of m-toluic acid. Therefore, a solvent with low methylation capacity, as acetonitrile, is necessary to obtain toluene as main product, avoiding the methylation of toluene (ethylbenzene, xylenes, etc.). The NaX_{SDBS} zeolite could be used in the deoxygenation of biofuels at low pressure and without external consumption of hydrogen.

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