



Short communication

Deoxygenation of *m*-toluic acid over hierarchical x zeolite

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ARTICLE INFO

Article history:

Received 15 December 2015

Received in revised form 5 February 2016

Accepted 7 February 2016

Available online 9 February 2016

Keywords:

Deoxygenation
m-Toluic acid
Mesoporosity
FAU zeolite
Toluene

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.

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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 CO₂ (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, $\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$). 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: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.2$, $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{SiO}_2 = 3.25$, $\text{H}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O}) = 17$ and $\text{Na}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O}) = 0.77$. 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 $\text{Na}_{64}\text{K}_{28}(\text{SiO}_2)_{100}(\text{AlO}_2)_{92}$ [13].

Synthesis of NaX zeolite was carried out employing a gel with molar ratios: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.44$, $\text{Na}_2\text{O}/\text{SiO}_2 = 1.32$, $\text{H}_2\text{O}/\text{Na}_2\text{O} = 39.8$. 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 $\text{Na}_{77}(\text{SiO}_2)_{115}(\text{AlO}_2)_{77}$ [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 $\text{SDBS}/\text{SiO}_2 = 0.005$ [15]. This zeolite has a silicon/aluminum molar ratio of 1.5 and an anhydrous unit cell formula of $\text{Na}_{77}(\text{SiO}_2)_{115}(\text{AlO}_2)_{77}$.

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 $\text{CuK}\alpha 1$ 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 *Axi*os instrument.

2.3. Catalytic activity

Deoxygenation reaction of *m*-toluic acid ($\text{CH}_3\text{C}_6\text{H}_4\text{COOH}$), 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

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}^d (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.

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

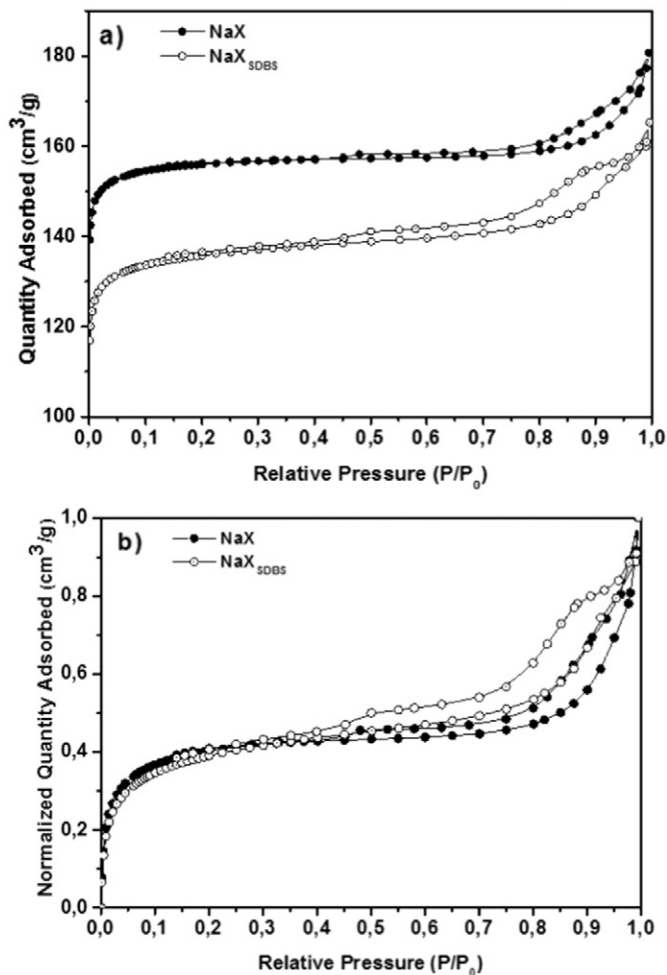


Fig. 1. a) Nitrogen adsorption/desorption isotherms at 77 K in NaX and NaX_{SDBS} as-synthesized zeolites. b) Normalized nitrogen adsorption/desorption isotherms at 77 K in NaX and NaX_{SDBS} as-synthesized zeolites.

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