



Desilication of *BEA zeolites using different alkaline media: Impact on catalytic cracking of *n*-hexane



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ABSTRACT

The desilication of two commercial nano- and one synthesized microcrystal *BEA zeolites via different alkaline solutions have led to several observations. In the nanocrystal *BEA zeolites, the use of NaOH alone reduced the crystallinity and microporosity, which was recovered after the use of pore directing agents as tetrapropylammonium bromide (TPABr). The use of tetrabutylammonium hydroxide (TBAOH) was not as much effective with NaOH as TPABr in terms of crystallinity and microporosity recovery, as it wasn't also as much effective as was NaOH alone in introducing intracrystalline mesopores to these nanocrystals. In the microcrystal series, the use of NaOH with TBAOH was seen to be more effective than NaOH alone or NaOH with TPABr. The increase of relative Brønsted acidity was observed at lower alkaline concentrations with a pronounced decrease at higher alkaline media. The company of the pore directing agents was seen to provoke the formation of new Lewis acid sites. In the cracking of *n*-hexane, the desilication treatments were not seen to improve the catalytic performance of the requested catalysts, as the slight deactivation of the catalysts was at the basis of coke formation. The activity was seen to drop due to even the diffusional limitations occurring or due to loss of acidity after desilication. More olefin and isomers products were produced despite of coke formed which was considered non-toxic being located inside the mesopores.

1. Introduction

Being rich with unusual features, zeolites are used in wide range of applications especially in oil refining and petrochemical industries [1,2]. The success of these zeolites in the industrial catalytic reactions is surely due to their micropores in which most of the catalytic sites are located and where the reactions take place. Notwithstanding the positive effect induced by these micropores with respect to shape selectivity [3], they may still provoke negative impacts by lowering the rate of access of molecules into the crystals of the zeolites [4], and favor unwanted adsorption effects of the reactants or the products as they undergo the catalytic action [5]. Hence, it was of much importance to seek after materials that withstand the bulky molecules without distorting the main objective.

Bulky molecules that cannot diffuse properly into the zeolite micropores might induce negative impact on the efficiency and activity in the media containing such substrates. These limitations have stimulated the researchers to follow up after new zeolitic structures [6]. Various methodologies to minimize diffusion limitations and enhance catalyst effectiveness were followed. Synthesizing zeolites with larger

micropores [7–9], and decreasing the zeolite crystal size to reduce the intracrystalline diffusion path length [10–13], were two of the strategies used to overcome diffusional limitations. However, a more generally applied strategy to obtain materials with sufficient molecular transport properties is to synthesize hierarchical zeolites that combine the primary micropore system and a secondary one that consists of mesopores (2–50 nm) inside the microporous zeolite crystals [14–18]. These improved structures enhance diffusion of bulky reactants and products molecules into and out of the pores respectively which in turn facilitates the adsorptive and catalytic reactions.

The synthesis of these zeolites can be achieved by destructive methods (top-down approaches) [19,20]. It is known as post-synthetic procedures that account to subject an already synthesized zeolite to treatments that target their pore structure thereby introducing mesoporosity. Due to its simplicity and efficiency, desilication by alkaline treatments, which is a controlled way to extract silicon species from the zeolite framework [21], is one of the most widely applied methods recently to induce mesoporosity [22–25]. Nonetheless, such post-synthetic procedure may affect not only the pore system of the zeolite, but also the structural, compositional, acidic and as well the final catalytic

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performance of the catalyst. For that, it is of much importance to be aware not to induce severe changes in the intrinsic properties of the zeolites. This can be achieved by the introduction some organic molecules that afford some protection to the zeolites crystals during their dissolution in the treatment solutions [24,26,27].

The objective in this work is to study the impact of desilication of already hierarchical nanocrystal *BEA zeolites and a synthesized microcrystal *BEA zeolite (purely microporous), on the structural, elemental, textural and acidic properties of these zeolites. It is also meant to study if the increased mesoporous content (in the hierarchical series) or the introduced mesopores (in the microcrystal series) would account to any improve in the catalytic activity and selectivity of the catalysts in the catalytic cracking of *n*-hexane.

2. Experimental part

2.1. Catalysts preparation

Two commercial *BEA zeolites, CP811 of Si/Al = 12, purchased from PQ corporation, and CP814E of the same Si/Al ratio produced by Zeolyst Company, were desilicated in presence of NaOH and different pore directing agents. Series 1 zeolites was the parent CP811 zeolite (P1) and its desilicated samples in NaOH solution (NaOH: Sigma Aldrich; > 98% purity), and NaOH mixed with tetrapropylammonium bromide solution (TPABr: Sigma Aldrich; > 98% purity). 5 g of P1 was always used as a starting desilicating material. Series 2 zeolites was the parent CP814E zeolite (P2) (with 5 g as starting material) and all its desilicated samples in different concentrations of NaOH solution, and solutions of NaOH mixed with tetrabutylammonium hydroxide (TBAOH: Sigma Aldrich; 40% in H₂O), with varying the mixture's concentration and molar ratio of TBAOH. Desilication treatments were carried at 65 °C for 30 min. After each desilication, the suspension was cooled down in an ice-bath, filtered and washed with distilled water to reach neutral pH. A threefold successive Na⁺/NH₄⁺ ion exchange was done after with 0.5M NH₄NO₃ solution at 80 °C for 1 h. The final materials were calcined at 550 °C for 6 h. The conditions of desilications are reported in Table 1. P1 and P2 desilicated samples will be denoted P1-Dx and P2-Dx respectively, where x stands for the number of desilicated sample as reported in Table 1.

The microcrystal *BEA zeolite (MC) of Si/Al = 35 was synthesized according to a procedure followed previously [28]. The synthesis was done according to the following molar ratios: 1 mol SiO₂ (sourced by tetraethyl orthosilicate: Sigma Aldrich; > 99% purity); 0.033 mol Al (Sigma Aldrich; powder Al > 91%); 0.573 mol TBAOH (Sigma Aldrich; 35% in H₂O); 0.573 mol HF (Fischer Scientific; 47–51% HF); 7.033 mol H₂O. The synthesis was carried by adding the exact amounts

of aluminum (Al), tetraethylammonium hydroxide solution (TEAOH) and tetraethoxysilane (TEOS), to a teflon beaker. The mixture was kept under stirring for two days at room temperature. After two days the amounts of water and hydrofluoric acid (HF) were added and the mixture was well mixed, then the beaker was put in turn in an autoclave then in an oven at 170 °C for 14 days. The final suspension was also filtered, washed several times, then dried and calcined at 550 °C for 6 h. Three desilication treatments were done after (with 3 g of starting MC material for each treatment) by: a) 0.2 M NaOH solution to yield MC-D1, b) solution of 0.2M NaOH and 0.2M TPABr to yield MC-D2, and c) solution of 0.12M NaOH and 0.2M TBAOH (with a molar fraction of 0.63) to yield MC-D3. Same ion exchange and calcination procedures were also done as in series 1 & 2. Table 1 reports also the desilication conditions of this zeolites series (series 3).

2.2. Characterization methods

All the XRD patterns were obtained on a D5005 BRUKER AXS diffractometer using a CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$) as incident beam, obtained by submitting a copper anode to a tension of 40 kV and an intensity of 30 mA.

The sample compositions of silicon and aluminum, and consequently the global Si/Al ratio, were determined through Induced Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), on a Perkin Elmer Optima 2000 DV apparatus. The zeolite framework aluminum (Al_{fram}) content was determined by infrared spectroscopy measurements on a FT-IR Magna 550 Nicolet spectrometer. The position of the zeolite structure bands (450–1250 cm⁻¹) and especially that of the asymmetric stretching vibration (ν_{TOT}) at 1080–1200 cm⁻¹ allowed calculating the Al_{fram} from the correlation given in literature [29]. The TOT bands were determined using KBr wafers containing 0.5 wt% of samples.

The morphology of the samples was determined by transmission electronic microscopy (TEM) using a Philips CM 120 microscope equipped with a LaB₆ filament.

A Micromeritics 2000 ASAP was used for nitrogen sorption measurements. Around 20–30 mg of each calcined zeolite sample was out-gassed prior to each experiment, to a residual pressure of 4 mbar at 350 °C for a minimum of 4 h during the night. Nitrogen sorption measurements were performed at -196 °C. Specific surface areas were determined from the Brunauer–Emmett–Teller (BET) equation in the p/p_0 range between 0.03 and 0.16. The total pore volume was determined from the nitrogen adsorbed volume at $p/p_0 = 0.99$ and the t -plot method was used to distinguish micropore from mesopore. The pore size distribution of the zeolites were determined by BJH method.

The Brønsted [PyH⁺] and Lewis [PyL] acidities were determined by

Table 1
Conditions of desilication of series: (1–3).

Series	Sample	[NaOH] (M)	DPA	[DPA] (M)	[HO ⁻] (M)	TBAOH molar ratio
1 (Commercial) (CP811)	P1	–	–	–	–	–
	P1-D1	0.2	–	–	0.2	–
	P1-D2	0.2	TPABr	0.2	0.2	–
2 (Commercial) (CP814E)	P2	–	–	–	–	–
	P2-D1	0.1	–	–	0.1	–
	P2-D2	0.2	–	–	0.2	–
	P2-D3	0.5	–	–	0.5	–
	P2-D4	0.15	TBAOH	0.1	0.075	0.2
	P2-D5	0.225	TBAOH	0.025	0.1	0.04
	P2-D6	0.12	TBAOH	0.2	0.13	0.625
	P2-D7	0.202	TBAOH	0.134	0.13	0.385
3 (Synthesized)	MC	–	–	–	–	–
	MC-D1	0.2	–	–	0.2	–
	MC-D2	0.2	TPABr	0.2	0.2	–
	MC-D3	0.12	TBAOH	0.2	0.13	0.625

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