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Creation of mesopores and structural re-organization in Beta zeolite during alkaline treatment

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ABSTRACT

Beta zeolite has a large number of applications and increasing the mesoporosity to enhance accessibility of active sites will further improve their performance. In this work we evaluated the effects of conditions of alkaline treatment (temperature and reaction time) on formation of mesoporous in Beta zeolite, starting from a Beta zeolite with SiO_2/Al_2O_3 mole ratio (SAR) of 40 and 73. The zeolite with SAR 73 suffered drastic loss in microporosity in agreement with previous literature reports. Yet, the zeolite Beta with a lower SAR (40) showed gradual variations in properties that were followed in further details. The temperature and reaction time of the treatment that offered the best compromise between meso-area, micropore volume (MiPV) and crystallinity was found. From the characterization of the samples a model of re-crystallization and re-organization of the pore structure during mesopore formation in Beta zeolite was proposed.

1. Introduction

One of the greatest problems of using zeolites in catalytic process is the diffusion limitations of bulky molecules. The formation of mesoporosity in zeolites may attenuate this limitation. The post synthesis treatment with alkaline solution has been showed to be an effective method to create mesopores in zeolites [1,2]. One of the first work reported in the literature was the method described by Ogura et al. [3]. In this study ZSM-5 zeolite was treated with a NaOH solution which resulted in an increase in external area as well as mesopore volume. Later, this method was extend for other zeolites like BEA, MOR, FER and USY [4,5].

The creation of mesopores in Beta zeolite is an interesting route to be studied since Beta can be an alternative zeolite to be used in catalytic cracking of gasoil, instead of Y zeolite or can be used in mixtures with Y. Beta zeolite has important characteristics: large pores, high silica-to-alumina synthesis ratio and a three dimensional pore network [6]. The structural characteristics mentioned above led to the common consequences observed in catalytic cracking. Compared with Y zeolites, typical Beta zeolites showed a lower capacity to promote reactions involving hydrogen transfer and coke production. They were also less selective to gasoline and produced more light products [7,8]. So it is expected that Beta with mesopores can improve the activity in FCC through the enhancement in accessibility of bulky molecules. The gain in accessibility can also improve the diffusion of the initial cracked products avoiding the overcracking of gasoline and LCO, enhancing the selectivity for these products.

In recent years, there were several publications focused on the mesopore creation on ZSM-5 [9–12].

From the extensive work done by Groen [10] on ZSM-5 zeolites it was shown that there is an optimal range of SiO_2/Al_2O_3 (SAR) to form mesopores. The experimental condition of the alkaline treatment was 3.3% of solid content, 0.2 M NaOH, reaction time of 30 min and reaction temperatures of 338 K and 358 K. The range of 50–100 of SAR showed the highest meso-area formation (of more than 250 m^2/g), with a micropore volume (MiPV) reduction of only 25%. The average size of the mesopore was about 10 nm. For ZSM-5 with SAR more than 400, an excessive silicon removal occurred and the presence of larger mesopores and macropores was shown to contribute less to mesopore surface area increase. In contrast, for SAR below 50, there was hardly any mesopore formation. It was concluded that the model of silicon dissolution was the main

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mechanism behind mesopore formation in ZSM-5. It was also highlighted that both the framework and extra framework (EFAL) aluminum were capable of inhibiting the silicon dissolution.

The creation of mesopores in Beta zeolite has been less studied in the literature than ZSM-5. Groen et al. [13] evaluated in detail the formation of mesopores in Beta zeolite by alkaline post-treatment starting from a Beta zeolite with SAR of 72. The effects of temperature (298–338 K) and reaction time (10–60 min) were evaluated. For the optimal condition reported for ZSM-5 (3.3% of solid content, 0.2 M NaOH, at 338 K for 30 min), Beta zeolite achieved external area of 370 m^2/g (much higher than 250 m^2/g, obtained for ZSM-5) but only 45% of MiPV was preserved, compared to 75% for ZSM-5. Hence, this condition was considered to be too severe to be used for Beta zeolite. On the other hand, at 318 K, mesopore area obtained was 250 m^2/g, and MiPV retention was 68%. Although the absolute values of the changes in the Beta and ZSM-5 meso-area and MiPV values were different, they showed similar responses: temperature and reaction time both caused an increase in meso-area and in silicon concentration in the filtrate accompanied by a decrease in MiPV. The conclusion was that the same mesopore formation model would apply to the two zeolites. However, the facility of mesopore creation is quite different for ZSM-5 and Beta. The latter is much more susceptible to mesoporosity formation but also more susceptible to microporosity destruction, resulting in the loss of acidic properties.

The activities of ZSM-5 and Beta were evaluated by the alkylation reaction of benzene and ethylene. The increase in meso-area in ZSM-5 increases its activity but for Beta the opposite was observed [13].

The above findings led us to suggest that the model to form mesopores in Beta and ZSM-5 may not be entirely the same. In this work we investigated the formation of mesopores in Beta zeolite under different conditions to have a better description of the evolution of this zeolite upon alkaline treatment. A zeolite with a lower SAR than the one used in the literature was the main sample in this study (SAR 40 instead of 70). Zeolite with higher amount of framework alumina was known to form mesopore less readily and hence may be a better precursor for following the stepwise transformation during alkaline treatment.

2. Experimental

2.1. Starting zeolites for alkaline treatment

A commercial Beta zeolite (CP814C) with nominal SAR of 40 supplied by *Zeolyst* (Beta 40) was the principal zeolite used in this work. To study the influence of SAR in Beta zeolite, a Beta zeolite with nominal SAR of 73 (Beta 73) was prepared by the treatment of Beta 40 with HCl 0.1 M. In short, 1 kg of Beta 40 was mixed with 19 L of HCl 0.1 M and heated up to 353 K. This suspension was stirred for 2 h. After this, the suspension was cooled until room temperature. Then, the solid was filtered and washed three times using 20 L of deionized water. This procedure with HCl was repeated twice to achieve the SAR of 73.

2.2. Alkaline treatment

For the first series of experiments, 20 g of Beta zeolite of each SAR was moderately stirred in 800 mL of 0.2 M NaOH solution maintained at 338 K for a period of time (10–240 min). The codes attributed to the samples in this set of experiments are the time values used in the treatment.

Then, to obtain a detail picture of the mesopore formation, Beta 40 was subjected to treatments in an extended range of temperature 303–373 K for 240 min. In this case, the codes attributed to the samples are the temperature values used in the treatment.

After the treatment, the suspension of Beta zeolite with both SAR was centrifuged. The alkaline treated samples were converted into the H-form by three consecutives steps with 0.1 M ammonium sulfate solution followed by deionized water, dried at 393 K and finally calcined in static air at 773 K for 3 h. The heating rate was 20 K/min. Before characterization, all the samples were calcined at 873 K for 1 h.

2.3. Characterization

2.3.1. N_2 adsorption

Textural properties were carried out in a TriStar 3000-Micromeritcs equipment by N_2 adsorption at 77 K. The samples were pretreated at 575 K under vacuum for 1 h. The BET method was used to determine specific area and the *t*-plot method was used to determine MiPV and external area (meso-area) in the range of 3.2–5.5 Å. The pore size distribution was calculated according to the BJH model in the range from 2 to 60 nm, as applied to the adsorption branch of the isotherm.

2.3.2. X-ray diffraction (XRD)

XRD patterns were obtained in a Rigaku X-Ray diffractometer with Bragg-Brentano geometry, using Cu Kα radiation and a diffracted beam graphite monochromator. The voltage was 40 KV and the current was 35 mA. Diffractograms were obtained between $2\theta = 7^\circ$ and 70° using a step of 0.033° and 60 s per pass. The crystallinity was accounted using the sum of peak areas between 19° and 24° and comparing with the same peaks of a commercial sample chosen as reference.

2.3.3. X-ray fluorescence (XRF)

Si and Al concentrations in the solid materials obtained upon alkaline treatment were determined by wavelength dispersive X-ray fluorescence spectrometry (WDXRF) using a Panalytical spectrometry, model: Axios Max (25 KV, 160 mA).

2.3.4. ICP-OES

Concentrations of silicon and aluminum in the mother liquor of the treated samples were determined by the Inductively Coupled Plasma-Optical Emisson Spectroscopy (ICP-OES) on a Perkin–Elmer Optima 5300.

2.3.5. NMR analysis

^{27}Al MAS and ^{29}Si MAS and CP/MAS experiments were carried out in an Agilent DD2-400 (9.4 T) NMR equipment at room temperature using 7.5 and 4.0 mm rotors (for ^{29}Si and ^{27}Al analysis, respectively).

Single pulse ^{27}Al MAS spectra were acquired using a 1.0 μs rf pulse ($\prod/20$), 50 kHz of spectral width, 16 ms of acquisition time and 0.5 s of pulse delay. 5000 transients were accumulated at 10 kHz of MAS spinning speed. $AlCl_3 \cdot 6H_2O$ (0 ppm) was used for referencing and a 50 Hz line broadening was applied for processing the spectra.

For ^{29}Si MAS spectra a pulse of 90° (3.9 μs), 50 kHz of spectral width, 20 ms of acquisition time and 20 s of pulse delay were employed. The spinning speed at MAS was 5 kHz and 500 transients were accumulated. Kaolin (−91.5 ppm) was used as a secondary reference and 50 Hz of line broadening was applied for processing the spectra. For ^{29}Si CP/MAS spectra the Hartmann–Hahn condition was adjusted and a 1 ms of contact time and 5 s pulse interval were employed.