



Structural study on the Al distribution in zeolites Nu-6(1) and Nu-6(2)

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ABSTRACT

This work describes the preparation of zeolites Nu-6(1) and Nu-6(2) with different Si/Al atomic ratios (24, 45, 90 and ∞) followed by the study of the Al distribution in the different available Si or Al (T atom in the zeolite) positions. Nu-6(1) is a layered zeolite that can be converted by topotactic condensation (achieved by calcination) into the framework zeolite Nu-6(2). Several Si/Al ratio samples were submitted to synchrotron radiation and to subsequent structural refinement. The results suggest that two of six possible T positions are preferred for Al from the point of view of simulated formation energy. These two positions are in terminal situation in the gallery space of the layered zeolite, i.e., near the positively charged amine template molecules. The results were corroborated by ^{29}Si and ^{27}Al solid-state NMR observations.

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1. Introduction

Several framework zeolites are obtained from layered zeolites through a mechanism of topotactic condensation. This transition usually occurs upon calcination, although it has also been observed that certain zeolites tend to crystallize by condensation of silicate sheets [1]. In a topotactic transformation the crystal lattice of the product phase shows one or more crystallographical equivalences to the generating phase [2]. In fact, during calcination, the condensation of the hydroxyl groups of the sheets helps to form the framework zeolite. Layered MCM-22 [1], PREFER [3], Nu-6(1) [4], and EU-19 [5] are examples of layered zeolites transformed into the framework zeolites MCM-22, ferrierite, Nu-6(2), and EU-20 and EU-20b, respectively.

Layered zeolites are versatile porous materials that can be modified by pillaring [1] or exfoliation [6] to increase accessibility, as many times observed by textural analysis, while preserving their thermal stability, homogeneous distribution of pores and acidic character.

The synthesis of zeolites Nu-6(1) and Nu-6(2) was first achieved by using 4,4'-bipyridine as structure-directing agent [7]. Lamellar zeolite Nu-6(1) can be described by a model in which layers are formed by $[\text{SiO}_4]$ and $[\text{SiO}_3\text{OH}]$ tetrahedra and where two crystallographically independent 4,4'-bipyridine molecules are localized in the interlayer or gallery space [4], contrarily to the layered zeolite MCM-22, where the hexamethylenimine molecule used for its

crystallization is found both in the layers and in the galleries [8]. By removal of the 4,4'-bipyridine template, Nu-6(1) is converted through the aforementioned topotactic transformation into Nu-6(2), a zeolite with the NSI-type structure. Zeolite Nu-6(2) has been used as catalytic material for dewaxing, disproportionation and isomerization [4], and due to its small pore size (eight-membered rings of 3.2×4.3 and 2.4×4.8 Å) and plate-like growth habit has been applied in the preparation of polymer-zeolite mixed matrix membranes for selective H_2 permeation [9]. On the other hand, delaminated Nu-6(1) [10,11] has BET specific surface areas in the 500–600 m^2/g range, while that of the framework zeolite Nu-6(2) is about 80 m^2/g . In addition, low BET specific surface area (151 m^2/g) delaminated Nu-6(1) has been applied to the dehydration of D-xylose into furfural [12]. Nu-6(1) has directly, i.e., without the expected swelling, been exfoliated to Nu-6(2) by treatment with CTA^+ and subsequent calcination; this material, preserving the typical XRD pattern of the NSI-type structure, has a specific surface area of ca. 300 m^2/g [13].

The Al content in the framework relates not only to the hydrophilicity and the adsorption properties but also to the number of acid sites and hence to the corresponding catalytic activity. It has recently been reported that it is possible to increase the acid site density in ferrierite by synthesizing the zeolite with two simultaneous templates which in turn allows the modification of the Al distribution in the different possible positions [14,15].

In this study we have investigated the Al distribution in Nu-6(1) and Nu-6(2) zeolites synthesized with different Si/Al atomic ratios (24, 45, 90 and ∞). To this end, the different structures of zeolites Nu-6(1) and Nu-6(2) were determined from their X-ray diffraction

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(synchrotron) patterns using commercial software. Moreover, ^{29}Si and ^{27}Al solid-state NMR data were collected for the key samples, contributing to the discussion relating to the Al distribution.

2. Experimental

2.1. Synthesis of Nu-6(1)

The lamellar precursor Nu-6(1) was synthesized as described in the literature [10,13]. The first step was the preparation of zeolite precursor dispersions with Si/Al nominal ratios of infinite, 90, 45, and 24 which were reacted in a rotating Teflon-lined stainless steel autoclave for 4 days at 120 °C. The dispersions were obtained by mixing solutions A, B, and C. Solution A was prepared by adding 4,4'-bipyridine (Fluka, purum, $\geq 99.0\%$) (0.91 g) to ethanol (Scharlab) (5.04 g). Solution B was obtained by diluting sodium silicate solution (Sigma-Aldrich, purum, $\geq 10\%$ as NaOH, $\geq 27\%$ as SiO_2) (10.03 g) with deionized water (5.96 g). Aluminum sulfate hydrate (Sigma-Aldrich, 98%) (0, 0.31, 0.62, and 1.24 g for Si/Al ratios of infinite, 90, 45, and 24, respectively) and sulfuric acid (Scharlab, 98%) (0.76 g) were dissolved in deionized water (12.11 g) to obtain solution C. Under stirring conditions, solution B was added to solution A, and solution C to the mixture of A and B. The final product, after the treatment in the autoclave, was filtered off and washed until it reached a pH of about 9. To obtain Nu-6(2), Nu-6(1) powder was calcined at 580 °C with a heating rate of 1 °C/min and maintained at 580 °C for 2 h.

2.2. Characterization

The zeolite was characterized by X-ray diffraction in the Grenoble Synchrotron, line BM25A with synchrotron radiation, wavelength $\lambda = 0.82637 \text{ \AA}$ with aperture $0.9 \times 0.9 \text{ mm}$ in 16 bunch mode. Data were measured from 2° to 30° in steps of 0.02° and $t = 1 \text{ s/step}$.

Scanning electron microscopy (SEM, JEOL 6400) images were obtained on Au-coated specimens operating at 20 kV. Also, transmission electron microscopy (TEM, JEOL-2000 FXII) was used at 200 kV. TEM samples were prepared by repeated dispersion in deionized water before pouring onto the carbon grid. ^{29}Si and ^{27}Al solid-state MAS NMR spectra were recorded using a Bruker AV400 WB spectrometer operating at a resonance frequency of 79.49 MHz and with a 4 mm probe. The measurements were carried out with a contact time of 3.5 ms, a pulse width of 4 μs , a recycle delay of 5 s and a spinning rate of 10 kHz. Chemical shifts were referred to 3-(trimethylsilyl)-1-propanesulfonic acid and to aqueous $\text{Al}(\text{H}_2\text{O})_6^{3+}$.

Elemental analysis was performed to determine the Si/Al ratio in Nu-6(1) and Nu-6(2) samples with a Thermo Scientific ARL ADVANT'XP X-ray fluorescence (XRF) sequential spectrometer equipped with an X-ray tube with Be window and an Rh anode. The samples were measured in a He atmosphere.

2.3. Structure refinement

The structure of zeolites Nu-6(1) and Nu-6(2) with different Al content was determined from their X-ray diffraction patterns using as basic computational platform the software Accelrys Materials Studio 4.3 supplied by Accelrys®. A combination of Rietveld [16] and Pawley [17] refinement methods was used for the optimum determination of the structures. Initially, Pawley refinement was performed until no improvement for R_{wp} was observed. The order for parameter refinement was the following: first, base line; second, parameters related to peak shape with the Pseudo-Voigt for peak profile and Berar-Baldinozzi for asymmetry models. Then

Table 1

Si/Al molar ratios for the different Nu-6(1) samples studied. Nominal Si/Al corresponds to that in the synthesis precursor gel, while XRF Si/Al was determined by X-ray fluorescence.

Sample	Nominal Si/Al	XRF Si/Al
Nu-6(1)-24	24	24
Nu-6(1)-45	45	45
Nu-6(1)-90	90	74 (± 1)
Nu-6(1)- ∞	∞	354 (± 1)

the lattice parameters were refined and finally all the parameters were refined together. The parameters related to line shift were not refined.

For Rietveld refinement, all the occupancies were first refined, followed by peak shape parameters and lattice parameters. Finally, all the parameters were refined at the same time. The initial estimation of the Nu-6(1) and Nu-6(2) structures was taken from data reported previously by Zanardi et al. [4]. The optimum structure was selected based on the achieved minimum weighted profile factor (R_{wp}) and minimum energy of the system. In some cases, the energy of the new structures was initially minimized using the Compass method approach [18].

3. Results and discussion

The Si/Al ratio obtained by XRF (Table 1) is quite close to that expected from the synthesis precursor dispersion (nominal ratio). Several samples and XRF analyses were repeated giving rise to the errors depicted in the table. The Si/Al ratio of 354 for the infinite Si/Al nominal ratio could be due to some Al contamination coming either from the reactives or from the autoclaves, since the same Teflon-lined autoclaves (after rigorous cleaning) were often used for the preparation of the zeolite with different Si/Al content.

3.1. SEM and TEM characterization

Samples of Nu-6(1) and Nu-6(2) were observed by SEM and TEM, while electron diffraction was performed on some selected samples. No significant morphological or size differences were observed as a function of Al content. As an example, Fig. 1a shows the typical plate-like shape of aggregated crystals having a laminar growth habit. The diffraction patterns (inset of Fig. 1b for Nu-6(1)) were indexed and the lattice parameters calculated. The indexation, compiled from several TEM images not shown here, was in agreement with spatial group $P2_1/a$ for both zeolites. For Nu-6(1) a , b , c , and β were 27.1, 5.0, 13.6 Å, and 103.5°, respectively, while for Nu-6(2) a , b , c , and β were 16.8, 5.0, 13.9 Å, and 107.2°, respectively. These values corroborate those reported by Zanardi et al. [4] and those obtained here from the corresponding refinements (see below).

3.2. Refinement of samples with different Si/Al ratio

From the crystallographic model proposed by Zanardi et al. [4], six different silicon positions can be identified in the structure of zeolite Nu-6(1) (labeled in Fig. 2a from Si1 to Si6). Si1, Si3, Si4 and Si6 correspond to $(-\text{SiO})_4\text{Si}$, whereas Si2 and Si5 correspond to $(-\text{SiO})_3\text{SiOH}$ sites. Upon calcination, $(-\text{SiO})_3\text{SiOH}$ are converted into $(-\text{SiO})_4\text{Si}$ sites, and the structure becomes more homogeneous in terms of Si bonding environment, as will be illustrated later when analyzing the NMR results. In principle, Al atoms can isomorphically substitute Si atoms in any of the six mentioned positions.

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