



Solid-state dealumination of zeolite Y: Structural characterization and acidity analysis by calorimetric measurements



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ABSTRACT

Zeolite Y was dealuminated in the solid-state at several degrees (5, 10, 15 and 20%) using $(\text{NH}_4)_2\text{SiF}_6$ as dealumination agent. The materials were heated to 80, 100, 120, 140, 160, 180 and 200 °C to investigate the best temperature at which the samples retain their crystallinity and acidity. The solids obtained were characterized by XRD, FTIR, TG/DTG, XRF, ^{27}Al and ^{29}Si MAS NMR and N_2 physisorption. They were also subjected to pyridine adsorption and calorimetric experiments. Structural and textural results showed that lower temperatures (80 and 100 °C) and smaller degrees of dealumination (5 and 10%) maintained the zeolite crystallinity and increased its specific surface area, microporosity and mesoporosity. The study of the materials acidity indicated the presence of Brønsted acid sites with different strength, hydrogen bonding sites and Lewis sites originated from acid leaching. The calorimetric measurements showed higher enthalpy values for some of the dealuminated materials than for the parent zeolite. It also evidenced an increase for the number of acid sites between -160 and -140 kJ mol^{-1} and a reduction for the other sites, between -140 and -80 kJ mol^{-1} .

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1. Introduction

Since 1962, Y zeolites have been widely used as industrial catalysts for several commercial processes, such as, long-chain hydrocarbon cracking [1] and hydroprocessing technology [2,3]. The crystalline structure of zeolite Y is well known and shows a tridimensional channel system that can be accessed through 12-member ring pores (7.4×7.4 Å, [111] direction) formed by the union of α supercavities [4,5]. Due to its high aluminium content, Y zeolites present low thermal stability and the dealumination process is a very important method to modify and to adjust their properties [6]. The variation of the Si/Al ratio in the zeolitic framework leads to significant changes in acidity, stability and hydrophilic/hydrophobic features, which will consequently determine their catalytic and adsorption capacities [6].

The dealumination methods reported in literature are mainly related to the isomorphous substitution of framework aluminium by silicon [4] using an external agent or to the extraction of framework aluminium by steam, acids or ligands [7]. The dealumination agents used in the isomorphous process are gaseous SiCl_4 or solid $(\text{NH}_4)_2\text{SiF}_6$

(ammonium hexafluorosilicate or AHFS). The later was initially used only as aqueous solutions under controlled conditions [8]. Because of some difficulties found in aqueous phase dealumination with AHFS (e.g., reaction control, non-substitutive dealumination, etc. [9]), an alternative post-synthetic route was developed, where the isomorphous substitution of framework Al(III) by Si(IV) was conducted in the solid state by heating mixtures of zeolite samples and AHFS [9–11]. The advantage of this method is that the dealumination occurs efficiently without sophisticated experimental techniques and the products formed are soluble in water (e.g., NH_4HF_2 and NH_4AlF_4), which allows their extraction by washing at the end of the reaction [9–11]. In fact, to increase the control over the material properties (e.g., structural and acidity parameters) obtained by solid state dealumination and avoid the formation of different byproducts, the washing procedure can be conducted under controlled pH and temperature [12,13].

Different methodologies for the solid state dealumination of zeolites with AHFS have been reported using several dealumination degrees and temperatures [9,11,14,15]. However, the effects of these parameters on zeolite Y morphology and structure were limited to reaction temperatures above 120 °C [9,11,14,16]. In addition, to understand the effects of dealumination on the catalytic activity of zeolites, the investigation of their acidic properties becomes essential. In order to determine the nature, number, strength and

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distribution of acid sites in zeolitic materials, different techniques may be employed, such as FTIR, NMR, TG, TPD and calorimetry [17,18]. This later allows the direct measurement of the heat evolved from the interaction between solid acids and several basic molecules (e.g., C_5H_5N , NH_3 , CH_3CN , etc.) [18–20]. Among them, pyridine and alkyl pyridines can be used to probe the accessibility of hydroxyl Si–O(H)–Al bridges on the surface of zeolites due to their different steric hindrances [18–22].

This article studies the solid-state dealumination of zeolite Y by ammonium hexafluorosilicate at several activation temperatures (80, 100, 120, 140, 160, 180 and 200 °C) and four dealumination degrees (5, 10, 15 and 20%). The adsorption of pyridine (Py) on the materials obtained was evaluated by calorimetric experiments to assess the surface acidity modifications induced by the dealumination process. In addition, structural and textural changes were characterized by XRD, XRF, FTIR, TG/DTG, N_2 physisorption (surface area and porosity measurements) and solid state NMR.

2. Experimental

2.1. Materials

Zeolite Y in the ammonium form (NH_4Y) was obtained from Zeolyst International (CBV 300). Ammonium hexafluorosilicate (Aldrich, 98%) was used as supplied. Pyridine (Vetec, 99.5%) was distilled over CaH_2 (Merck, 98%). Cyclohexane (Vetec, 99%) was distilled over P_2O_5 (Merck, 98%) and stored over 3A molecular sieves (Aldrich).

2.2. Preparation of the samples

The amount of AHFS used in the solid-state dealumination experiments were based on the Al(III) content of the parent zeolite to obtain different dealumination degrees (5, 10, 15 and 20 mol%) at different temperatures. Each mixture of NH_4Y and $(NH_4)_2SiF_6$ prepared was heated in a vacuum oven for 2 h at the desire temperature (80, 100, 120, 140, 160, 180 or 200 °C) and then washed twice with hot water to remove byproducts [8]. After that, the solids were dried in an oven at 100 °C and calcined at 550 °C for 8 h in a muffle furnace. The modified materials were named by the reaction temperature and degree of dealumination, e.g., Y(80)5, zeolite Y dealuminated at 80 °C and 5 mol%.

2.3. X-ray diffraction (XRD)

XRD patterns were obtained at 1° min^{-1} on a Bruker D8 FOCUS X-ray diffractometer with $CuK\alpha$ (1.5418 Å) radiation at 40 kV and 30 mA. Silicon was mixed with the samples (15 wt%) and used as internal standard (reflection at [111]) for quantitative analysis. The method used for the determination of mean unit cell parameters (a_0) was described elsewhere [8,21–23].

2.4. Surface area and porosity measurements

N_2 physisorption measurements were performed at -196°C on a Micrometrics ASAP[®] 2020 apparatus. Before the analysis, all samples were dried at 300 °C under vacuum (10 μmHg) for 4 h. Surface area and porosity data were obtained from N_2 adsorption/desorption isotherms. Microporous surface area (S_{micro}) and micropore volume (V_{micro}) were determined from MP method [24], since the t-plot method can be unreliable in materials containing both micro- and mesopores [25]. Mesoporous surface area (S_{meso}) and mesopore volume (V_{meso}) between 1.7 and 300.0 nm were determined from BJH method. The total surface area (S_{total}) of the samples was calculated using Equation (1).

$$S_{\text{total}} = S_{\text{micro}} + S_{\text{meso}} \quad (1)$$

The crystallinity (%C) of the samples was calculated by comparing the total amount of N_2 (Q_{ads}) adsorbed in the micropores by the samples and the parent zeolite (Equation (2)) [4,26]:

$$\%C = [Q_{\text{ads sample}}/Q_{\text{ads parent}}] \times 100\% \quad (2)$$

2.5. Scanning electron microscopy (SEM)

The micrographs were obtained on a JSM-7001F scanning electron microscope (JEOL) at high vacuum. The materials were coated with gold in a Leica SCD 5500 High Vacuum Sputter Coater equipment.

2.6. Infrared spectroscopy (FTIR)

FTIR spectra were obtained on a Nicolet 6700 spectrometer (Thermo Scientific) equipped with a DTGS detector using 128 scans and 2 cm^{-1} resolution. All materials were diluted in KBr with 1 wt% of zeolite.

2.7. X-ray fluorescence spectroscopy (XRF)

The analyses were made under vacuum on a Shimadzu EDX-720 spectrophotometer equipped with a rhodium X-ray tube. The degree of dealumination of the samples was calculated using Equation (3):

$$\%dealumination = 100 - \left[\left(100 \times Al_{\text{sample}} \right) / (Al_{\text{standard}}) \right] \quad (3)$$

where Al_{sample} is the total amount of aluminium in the dealuminated sample and Al_{standard} is the total amount of aluminium in the parent zeolite.

2.8. ^{29}Si and ^{27}Al MAS NMR spectroscopy

Solid state NMR experiments were conducted at 7.05 T on a Varian Mercury Plus equipped with a 7 mm CP/MAS probe. ^{29}Si MAS spectra (59.60 MHz) were obtained at a speed of 3 KHz, pulse length of 5.5 μs ($\pi/2$), a recycle delay of 20 s and 500 scans. The spectra were referenced to Kaolin and deconvoluted with the Omnic software from Thermo Scientific. ^{27}Al MAS spectra (78.17 MHz) were obtained at a speed 6 KHz, pulse length of 1.0 μs ($\pi/2$), a recycle delay of 0.4 s and 6000 scans. The spectra were referenced to $Al(H_2O)_6^{3+}$.

2.9. Liquid phase adsorption and calorimetry experiments

Before the adsorption and calorimetry experiments, all samples were dried at 300 °C under vacuum for 4 h in a glass reactor built in our laboratory.

In a N_2 atmosphere dry box, 0.25 g of zeolite and 25 mL of cyclohexane were added to a round-bottom flask and adapted to an automatic burette (Metrohm 665 Dosimat) loaded with a solution of Py in cyclohexane (0.1 mol L^{-1}). After the equilibrium had been reached for each base addition, a 0.5 mL sample was removed from the solution. To keep a constant volume, 0.5 mL of cyclohexane was added into the system. The singular absorbance of Py (251 nm) was measured with a Beckman DU 650 UV-Vis spectrophotometer. The data collected were used to calculate the base concentration in solution at equilibrium.

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