Hierarchic zeolites: Zeolite ZSM-5 desilicated with NaOH and NaOH/tetrabutylamine hydroxide

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ABSTRACT

The desilication of zeolite ZSM-5 (Si/Al = 31.6) was performed by the treatment with NaOH of various concentrations (0.1, 0.2, 0.5 and 1 M) and with NaOH/TBAOH mixtures of various concentrations and ratios between both bases. The information on the composition of both bulk and surface was obtained by ICP-OES and XPS, respectively. It has been found that diluted NaOH solutions extracted Si equally from the surface and bulk of ZSM-5. In more concentrated NaOH the desilication from the bulk was more effective than from the surface. The MAS NMR studies showed that Si(4Si,0Al) was less stable and was removed from the zeolite structure before Si(3Si,1Al). Higher stability of Si(3Si,1Al) was explained by the repulsion of AlO_4^- and OH^-. According to the IR results the desilication, leading to mesopore formation, increased distinctly the amount of Si–OH on mesopore walls and also the contribution of acidic Si–OH–Al. Calcination of desilicated zeolite at air atmosphere resulted in a significant loss of tetrahedral Al due to the "steaming" of zeolite with water physisorbed in mesopores facilitated by lower stability of framework injured by desilication. Both NMR and IR studies suggested that the stability of Si atoms in the zeolite framework increased in the following order: $(SiO)_3Si–OH < (SiO)_3Si–OSi < (SiO)_3Si–OAl$. Porosimetric experiments evidenced that the NaOH treatment produced mesopores with very broad pore size distribution (a majority of pore diameters was close to 20 nm). The desilication with the NaOH/TBAOH mixtures produced mesopores of higher surface area and pore volume but of smaller diameter than with NaOH alone. We suppose that in the presence of TBAOH a larger number of narrower pores is formed, or narrow pores penetrate zeolite crystal more deeply.

1. Introduction

Zeolites are crystalline aluminosilicates with integral system of well defined micropores. The micropores of diameter in the range of 0.25–1 nm create system of channels and cavities which are determined by the crystal structure, and are different for each type of framework. Due to these unique properties which are responsible for shape selectivity, high acidity, thermal stability and uniform porosity, zeolites are used in many important catalytic processes, such as cracking, isomerization, alkylation, esterification (for review see Ref. [1]), as well as in many reactions resulting in the production of fine chemicals [2]. Recently, zeolites have started to play an important role as potential catalysts in processes that are essential for environment protection [3].

For catalytic applicability of zeolites, diffusion limitations are main drawbacks. Molecular dimensions of micropores constrain the transport of reagents to and from active sites. Improved activity, selectivity and stability in a wide range of reactions have been achieved by producing hierarchical zeolites with secondary system of mesopores generated by pre- or post-synthesis treatment [4]. Mesoporous zeolites combine high acidity and thermal stability, similarly to traditional zeolites, with supreme mass transport properties, which are characteristic for other mesoporous materials. Templating, dealumination and desilication are well known strategies for the formation of additional mesopores. Carbon nanoparticles and mesoscale cationic polymers are also used during templating methods [5–7]. Dealumination and desilication are based on preferential aluminum or silicon extraction from zeolite framework, by acid or base treatment after zeolite synthesis. Depending on concentration of base or acid, duration and temperature of treatment, additional agents as well as type of zeolites, different extent of mesoporosity can be achieved. Currently, several other methods have been applied to produce hierarchical zeolites, such as zeolitization of mesoporous materials, assembly of zeolite nanocrystals and recrystallization [8].

The removal of Si from zeolite framework in an alkaline medium (e.g. NaOH, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, Na_2CO_3), has proven to be the simplest and the most economical way of effective introducing the mesoporosity in

different types of zeolites [9]. Recently, the desilication of high silica ZSM-5 zeolite with sodium hydroxide has attracted much attention. The controlled formation of extra mesoporosity produced mesopores in the range between 10 and 30 nm for zeolites with the bulk Si/Al ratio of 25–50 [10]. The effect of process temperature was investigated [11]. Additionally, Perez-Ramirez et al. [12] found that the presence of extraagents, like tetrapropylammonium hydroxide and tetrabutylammonium hydroxide, improved transport properties and catalytic performance (as shown for the benzene alkylation). Interesting data on the mechanism of zeolite desilication were described by Verboekend et al. [13] and by Groen et al. [14] and especially on the role of pore-directing agents (PDA) on mesopores formation. Not only tetra-alkil ammonium hydroxides but also Al was found to be PDA. Al which was removed from the zeolite framework during the desilication was subsequently reinserted into the tetrahedral positions of mesopore walls forming acidic hydroxyls. Verboekend et al. [13] proposed also a model of desilication relating the affinity of zeolite surface to PDA and their efficiency in mesopores formation.

In the present study zeolite ZSM-5, with initial Si/Al = 31.6, was desilicated with NaOH solution and mixtures of NaOH and tetrabutylammonium hydroxide (TBAOH), of different concentrations and ratios. Chemical analysis and XPS measurements were performed to follow the impact of desilication conditions on the composition of the whole zeolite crystal and of the surface zone, respectively. MAS NMR spectroscopy showed the effect of desilication on the arrangement of Si and Al atoms. The data concerning the pore system were obtained in porosimetric experiments. FTIR studies led to preliminary analysis of acid properties of modified zeolites on the basis of OH group spectra, and provided information on the Si–OH groups on mesopore walls, in defects and "hydroxyl nests".

2. Experimental

The parent NH_4ZSM-5 zeolite (Si/Al = 31.6) was provided by Zeolyst International (NH_4-form, CBV 5524G). Desilication was carried out in the solutions of NaOH and the mixtures of NaOH and TBAOH (tetrabutylammonium hydroxide) at the temperature of 353 K for 5 h. 100 ml of solution was added to 3.0 g of zeolite. If desilication was done with NaOH only, 0.1, 0.2, 0.5 and 1 M solutions were used. The NaOH/TBAOH mixtures had concentrations 0.1, 0.2 and 0.5 M. For the 0.1 M mixture TBAOH/(NaOH + TBAOH) ratios (denoted shortly as R) were 0.1 and 0.4, for the 0.2 M solutions R ratios were 0.1, 0.4, and 0.7. For the 0.5 M mixture R ratio was 0.1. After desilication suspension was cooled down in ice-bath, filtred and washed until neutral pH. Next a fourfold ion-exchange with 0.5 M NH_4NO_3 was performed at 330 K for 1 h. Finally, the zeolites were again filtrated, washed and dried overnight at room temperature. The calcination was subsequently performed at 820 K for 5 h with 2 K/min step of heating.

Si and Al concentrations in the parent and desilicated zeolites as well as in filtrates were determined by the ICP OES method with an Optima 2100DV (PerkinElmer) spectrometer. The powder X-ray diffraction (XRD) measurements were carried out using a Bruker D2 Phaser equipped with a LYNXEYE detector in the 2θ angle range of 2–60°.

The X-ray photoelectron spectra (XPS) were measured on a Prevac photoelectron spectrometer equipped with a hemispherical VG SCIENTA R3000 analyzer. The photoelectron spectra were measured using a monochromatized aluminum AlKα source (E = 1486.6 eV) and a low energy electron flood gun (FS40A-PS) to compensate the charge on the surface of nonconductive samples. The base pressure in the analysis chamber during the measurements was 5×10^{-9} mbar. Spectra were recorded with constant pass energy of 100 eV for the survey and for high resolution spectra.

The binding energies were referenced to the Si 2p core level (103.0 eV). The composition and chemical surrounding of the sample surface were investigated on the basis of the areas and binding energies of Al 2p, Si 2p and O 1s photoelectron peaks. The fitting of high resolution spectra was provided through the CasaXPS software.

The solid state MAS NMR spectra were acquired on an APOLLO console (Tecmag) at the magnetic field of 7.05 T (Magnex). For the ^{29}Si MAS-NMR spectra a 3 μs rf pulse (π/2 flipping angle) was used, 4 kHz spinning speed, and 256 scans with the delay of 40 s were acquired. The ^{27}Al spectra were recorded using the 2 μs rf pulse (π/6 flipping angle), 8 kHz spinning speed, and 1000 scans with acquisition delay 1 s. The frequency scales in ppm were referenced to TMS and to 1 M solution of Al(NO_3)$_3$, for the ^{29}Si and ^{27}Al spectra, respectively.

For the FTIR study all samples were pressed into the form of self-supporting wafers (ca. 5 mg/cm^2) and activated in situ in an IR cell at 823 K under vacuum for 1 h. Spectra were recorded with the resolution of 2 cm^{-1} by using a Bruker Equinox 55 spectrometer equipped with a MCT detector. The spectra of OH groups were recorded at 443 K.

The N_2 adsorption and desorption processes at 77 K were studied on an ASAP 2010 Micromeritics after activation in vacuum at 623 K for 12 h. The t-plot method with the Harkins–Jura reference isotherm was used to determine the micropore volume (V_{micro}). Pore size distribution was obtained by the BJH model following the adsorption branch of the isotherm. The same model was applied for the calculation of surface area (S_{meso}) and volume (V_{meso}) of mesopores.

Transmission electron microscopy was carried out with a JEOL JSM-7500F microscope.

3. Results and discussion

3.1. Chemical analysis of bulk and surface

The Si/Al ratios in the zeolite ZSM-5 parent and treated with 0.1, 0.2, 0.5 and 1 M NaOH are presented in Table 1. The decrease in the Si/Al ratio with increasing concentration of NaOH is due to more extensive Si dissolution in concentrated NaOH. The analysis of the filtrate evidenced that not only Si, but also some amounts of Al were removed from the zeolite. For relatively diluted NaOH (0.1 and 0.2 M) the amounts of Al removed were small (about 1–2% of total Al content), but concentrated NaOH (0.5 and 1 M) extracted substantial amounts of Al (18% and 63%, respectively). The intensive Al extraction may be the result of dissolving of large fragments of zeolite grains. According to XRD data (shown in Supplementary material) desilication performed in 0.5 M NaOH led to partial destruction of zeolite framework and upon treatment with 1 M NaOH – in total collapse of the structure. On the contrary, structure destruction was not observed if desilication was done with more diluted NaOH (0.1 and 0.2 M).

The XPS analysis was done in order to answer the question if desilication was more effective from the zeolite surface or from the bulk. For this purpose, the values of the (Si/Al)$_{surf}$/(Si/Al)$_{bulk}$ factor were compared. According to the data presented in Table 1, for the parent zeolite (Si/Al)$_{surf}$/(Si/Al)$_{bulk}$ factor was 0.79 indicating a deficiency of Si and an excess of Al in the surface zone, compared to the bulk. A similar effect of the enrichment of zeolite surface in Al and an excess of Si occurred in the bulk was reported by several authors e.g. [15,16]. The treatment with diluted NaOH (0.1 and 0.2 M) did not result in any substantial change of (Si/Al)$_{surf}$/(Si/Al)$_{bulk}$ indicating that there was no preference of desilication i.e. Si was extracted uniformly from both the surface and bulk, and the deficit of Si on the surface and the excess of Si