Magic-Angle-Spinning Nuclear Magnetic Resonance and Adsorption Studies of Dealumination and Realumination of Zeolite ZSM-5

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ABSTRACT

Adsorption of nitrogen, 27Al and 1H magic angle spinning nuclear magnetic resonance show that non-framework aluminium species created by deep dealumination of zeolite H-ZSM-5 can be partially reintroduced into the framework upon treatment (2 h, 350 K) with 0.1 M aqueous solution of NaOH. However, the treatment also causes a loss of micropore volume and creates a secondary pore system. No realumination or loss of porosity are observed after dealumination performed under mild hydrothermal conditions, i.e. when the Si/Al ratio of the dealuminated material is less than ca. 25.

INTRODUCTION

It has recently been shown [1–4] that the process of zeolite stabilization, during which Al is removed from the framework and deposited in the zeolitic channels and cavities, can be reversed using a simple hydrothermal method consisting of treating the sample with a concentrated solution of a strong base. Extensive work using X-ray and neutron diffraction, 29Si, 27Al and 1H magic-angle-spinning nuclear magnetic resonance (MAS NMR) and infrared spectroscopy has thrown much light on the mechanism of the dealumination/realumination sequence. It was found that: (i) the extent and efficiency of the reaction depend on the temperature, duration of treatment and especially on
the kind and concentration of the basic solution; (ii) the degree of crystallinity and the thermal stability of the products are primarily controlled by the composition of the parent material; and (iii) the distribution of Si and Al in the aluminated product is strikingly different from that in the as-prepared sample of the same composition.

Preliminary studies show that the catalytic performance towards the cracking of n-hexane of the mildly dealuminated zeolites H-ZSM-5 is enhanced in comparison with the parent material [5,6]. On the other hand, dealumination is used to increase the Si/Al ratio of the zeolitic framework, which increases its thermal stability but also decreases the amount of acidity. Despite information provided by MAS NMR [7], the precise nature of the aluminium species created during a hydrothermal treatment of zeolites is not clear. We show, using adsorption of nitrogen and $^{27}$Al and $^1$H MAS NMR, that the ease with which the ZSM-5 framework can be realuminated depends on the degree of dealumination.

**EXPERIMENTAL**

Parent zeolite ZSM-5 (Si/Al=15), synthesized without organic template [6] was provided by Dr. Schwieger. Hydrogen ion exchange was carried out at room temperature using a 0.5 M aqueous solution of HCl. Hydrothermal treatment of 2-g samples was performed in a horizontal tubular quartz furnace of 50 mm inner diameter with a maximum bed-depth of 8 mm. Temperature was increased at a rate of 10 K/min in a dry nitrogen stream at a flow-rate of 1 1/min. Steaming was carried out at 810 K for 150 min under pressure which was varied by controlling the temperature of the nitrogen gas.

Hydrothermally dealuminated samples were dried and partially with a 0.1 M aqueous solution of NaCl or NaOH during 2 h at 350 K and then washed. X-Ray diffraction pattern shows that, except for one sample, no significant loss of crystallinity occurred during this procedure. Nitrogen isotherms were measured at 77 K using a Sartorius balance.

$^{27}$Al MAS NMR measurements were carried out at 104.26 MHz using powerful 0.6 µs radiofrequency pulses with a 0.2-s recycle delay on samples equilibrated in a desiccator for 48 h over aqueous NH$_4$Cl. Samples were spun at 3.4 kHz in an aluminium-free probehead and Vespel rotors. Chemical shifts are quoted in ppm from external Al(H$_2$O)$_6^{3+}$. 10000 transients were acquired for each spectrum.

For the $^1$H MAS NMR measurements the samples were pretreated in a glass tube of 5.5 mm inner diameter and with 10 mm bed-depth of zeolite under conditions similar to those used for shallow-bed activation. The temperature was increased at a rate of 10 K/h. The samples were kept at the final activation temperature of 670 K under a pressure below 10$^{-2}$ Pa for 24 h and then cooled and sealed. The home-made MAS equipment for the rotation of the fused-glass
ampoules was carefully cleaned to avoid spurious proton signals. Since identical quantities of each sample were taken for all experiments, spectral intensities are directly comparable. $^1$H MAS-NMR spectra were measured at 400.13 MHz with a Bruker MSL 400 spectrometer and a home-made probehead. Phase cycling with 6.0 $\mu$s $\pi$ per 2 pulses and recycle delay of 4 s was used. 400 transients were recorded for each spectrum. Identical quantities of each sample were taken for the experiments, which means that spectral intensities are directly comparable. The samples were spun in air at 2.5 kHz.

RESULTS AND DISCUSSION

In the low pressure region (up to 100 Pa) nitrogen adsorption isotherms of deeply dealuminated and NaOH-treated samples show a decrease of 20% in the micropore volume in comparison with the parent zeolite. Deep dealumination also causes hysteresis between adsorption and desorption isotherms in the high pressure region (40-100 kPa). This is due to the presence of a secondary pore structure, as suggested by Lohse and Mildebrath [8] for zeolite Y. However, the secondary pore volume should be equivalent to the portion of aluminium in the framework, which is much less for the zeolite ZSM-5 in comparison with zeolite Y. For deeply dealuminated zeolite ZSM-5 treatment with NaOH also results in a dissolution of a portion of the aluminosilicate framework [2,3].

The change of the framework Si/Al ratio upon dealumination and realumination and the decrease of micropore volume and the increase of the total pore volume are clear from Table 1. After mild dealumination by steaming at up to 4 kPa no realumination or significant change of pore volume by treatment with NaOH takes place. However, dealumination caused by more severe steaming conditions can be partially reversed by treatment with NaOH, which also de-

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<th>Water pressure (k Pa)</th>
<th>Dealuminated zeolites</th>
<th>Realuminated zeolites</th>
<th>Si/Al ratio</th>
<th>Decrease of micropore volume (%)</th>
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creases the micropore volume and increases the secondary pore volume. NaCl treatment does not change the Si/Al ratio of the dealuminated samples while the re-exchange of the NaOH-treated samples into the hydrogen form does not change the framework Si/Al ratio. Fig. 1 shows the $^{27}$Al MAS NMR spectra of the dealuminated and realuminated samples steamed at 13 and 80 kPa.

The $^1$H MAS NMR spectrum of the parent zeolite given in Fig. 2A consists of two lines corresponding to different kinds of protons; signal b at 4.3 ppm is due to bridging OH groups and signal a at ca. 1.7 ppm to framework defects.

Fig. 1. $^{27}$Al MAS NMR spectra in the absolute intensity mode of the dealuminated (A) and (C) and realuminated (B) and (D) samples steamed at 13 kPa (A) and (B) and 80 kPa (C) and (D).
Fig. 2. $^1$H MAS NMR spectra in the absolute intensity mode. (A) Parent zeolite H-ZSM-5 (Si/Al = 15) after activation; (B) hydrothermally dealuminated sample (Si/Al = 59); (C) realuminated sample (Si/Al = 25); (D) realuminated sample after hydrogen exchange. Framework Si/Al ratios were determined by $^{27}$Al MAS NMR. Asterisks denote spinning sidebands. For a, b and c see text.

Dealumination (Fig. 1B) results in a marked decrease of the intensity of signal b and the appearance of signal e, due to Al–OH groups attached to non-framework Al at ca. 3 ppm. The low intensity signal at ca. 6.5–7.0 ppm is due to the residual NH$_4^+$ cations. After treatment with NaOH the concentration of SiOH groups increases to 1.8 per unit cell (line a in Fig. 2 A) in comparison with 0.7 SiOH groups unit cell (line a in Fig. 2 C) in the parent sample. This is caused by the removal of framework silicon atoms during the treatment with NaOH. After converting the zeolite into the hydrogen form by treatment with 0.1 M
HCl the intensity of signal b increases in comparison with that of the dealuminated material. Measurement of the intensity of the individual NMR signals indicates that there are 4.8, 1.3, 0.9 and 2.3 bridging OH groups per unit cell in the parent sample, the sample dealuminated at 80 kPa, the NaOH-treated sample and its hydrogen form, respectively. This means that only 30% of the bridging hydroxyl groups removed during hydrothermal dealumination have been reconstituted via realumination followed by hydrogen exchange.

REFERENCES