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Dealumination of zeolite Y by H_4EDTA

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Solid-state NMR shows that the treatment of zeolite Y by H_4EDTA dealuminates the zeolite framework. Since no extra-framework aluminium is found, all the Al removed from the framework is subsequently washed out of the crystallites in the form of an H_4EDTA complex. Unlike with hydrothermal dealumination or treatment with $SiCl_4$, H_4EDTA gives defective crystals in which framework vacancies created by the expulsion of aluminium are not healed by silicon from other parts of the framework. The likely reason for this is the slow intracrystalline diffusion of $Si(OH)_4$ at low temperatures. ^{29}Si CP/MAS NMR and infrared spectra confirm the creation of hydroxyl nests in the zeolitic framework. A small amount of disordered siliceous phase responsible for a low intensity ^{29}Si MAS NMR shoulder at -110 ppm is produced in the process.

Keywords: Highly siliceous zeolites; $SiCl_4$; CP MAS NMR; hydroxyl nests

1. Introduction

Hydrothermal synthesis yields zeolites X and Y with $Si/Al = 1.0–3.4$, and more highly siliceous materials cannot be directly prepared by conventional methods [1]. However, the use of crown-ether-based supramolecules as templates allows zeolite Y with a higher Si/Al ratio to be synthesised [2]. Since the acidity and the catalytic properties of zeolites are largely governed by their aluminium content [3], it is important to be able to control this parameter. This can be done in both directions, starting from either the siliceous or the aluminous members of the substitutional series [4–8].

Several dealumination processes have been described. One example is the "ultrastabilization" of zeolite Y, a process which is used commercially [5,6]. In this process the ammonium ion-exchanged form is heated to 400–550°C in the presence of water vapour. Aluminium is expelled from the framework, and the vacancies

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are subsequently re-occupied by silicon from other parts of the crystal. The precise mechanism of this process is unknown, but presumably involves intracrystalline diffusion of $Si(OH)_4$ at high temperatures. As a result, a siliceous, more thermally stable ("ultrastable") material is prepared. Ultrastabilization is often combined with acid leaching to enable a nearly complete extraction of aluminium from the framework [8].

Dealumination with silicon-containing species such as $SiCl_4$ (in the gas phase) and $(NH_4)_2SiF_6$ (in solution) is well documented [7,9,10]. Aluminium can also be extracted from zeolites by CCl_4, $COCl_2$, SO_2Cl_2 and other volatile non-siliceous compounds, and by chelating agents such as H_4EDTA, tartaric acid, diethylenotriaminopentaacetic and diaminocyclohexano-N,N,N′,N′-tetraacetic acids at moderate temperatures [11,12]. It is thought that all these methods lead to imperfect zeolitic frameworks, the generation of "hydroxyl nests" and secondary mesopore systems [13,14]. We have examined samples of zeolite Y dealuminated with H_4EDTA.

2. Experimental

Parent zeolite Y with $(Si/Al)_{bulk} = 2.67$ (sample 1) was dealuminated with H_4EDTA to give sample 2 with $(Si/Al)_{bulk} = 3.35$ and sample 3 with $(Si/Al)_{bulk} = 4.23$ (by chemical analysis). Dealumination was carried out by 1 h treatment of a zeolite suspension (water : zeolite = 15 : 1) using a 0.4% solution of H_4EDTA at 100°C. Dealuminated samples were washed with hot water and dried at 160°C. The amount of H_4EDTA used was adjusted according to the desired level of dealumination. XRD diffraction patterns do not show any distinct loss of crystallinity of the samples. However, it has been shown that when dealumination is taken further, a loss of crystallinity is observed [11].

Solid-state magic-angle-spinning (MAS) NMR spectra were recorded at 104.22 and 79.5 MHz for ^{27}Al and ^{29}Si, respectively. ^{1}H–^{29}Si cross-polarization (CP/MAS) experiments were carried out to investigate the status of hydrogen in the samples. Zirconia rotors were spun in air at 5 kHz for ^{29}Si MAS and CP/MAS and at 15 kHz for ^{27}Al MAS experiments. The magic angle was set precisely by observing the ^{79}Br resonance of KBr. ^{29}Si MAS spectra were acquired with $\pi/4$ pulses. The ^{29}Si CP/MAS experiments were carried out with single contacts and contact times of 5 ms. The Hartmann–Hahn condition was set using a sample of kaolinite [14]. ^{27}Al NMR Bloch decays were recorded at 104.26 MHz with very short, 0.7 μs (less than 10°), radiofrequency pulses and 0.5 s recycle delays. XRD patterns were collected on a Philips automatic diffractometer fitted with a vertical goniometer using Cu Kα radiation.

For IR studies zeolites were pressed into self-supporting wafers (5 mg/cm^2) and activated in situ in an IR cell at 723 K for 1 h. The IR spectra were recorded by and UR-10 spectrometer (Carl Zeiss, Jena).

3. Results and discussion

The Si/Al ratio in the aluminosilicate framework may be calculated directly from the ^{29}Si MAS NMR spectrum using the formula [15,16]

$$(\mathrm{Si/Al})_{\mathrm{NMR}} = \frac{I_4 + I_3 + I_2 + I_1 + I_0}{I_4 + 0.75 I_3 + 0.5 I_2 + 0.25 I_1}, \qquad (1)$$

where I_n denotes the intensity (peak area) of the NMR signal corresponding to the Si(nAl) building unit. By comparing $(\mathrm{Si/Al})_{\mathrm{NMR}}$ values with the results of chemical analysis, which gives *bulk* composition, the amount of extra-framework aluminium can normally be calculated, which is important when dealing with chemically modified zeolites. Because our parent sample is already quite siliceous, the Si(4Al) signal is missing.

Formula (1) works well with as-prepared and utrastabilized zeolites X and Y. Thus the ^{29}Si MAS NMR spectrum of sample 1 (see fig. 1a) can be deconvoluted to yield relative intensities of signals corresponding to Si(3Al), Si(2Al), Si(1Al) and

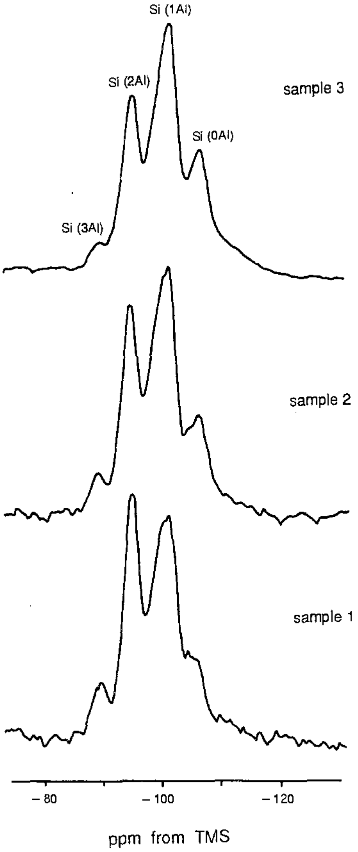

Fig. 1. ^{29}Si MAS NMR spectra of our samples.

Si(0Al) environments. Formula (1) then leads to the value of $(Si/Al)_{NMR}$ which is in good agreement with that obtained from chemical analysis (see table 1).

Problems arise as dealumination progresses *without* the resubstitution of the vacant sites created by the expulsion of framework aluminium. As aluminium is removed, the number of Si(0Al) [i.e. Si(4Si)] units is changed, and Si(3Al, 1Si) units give rise not to Si(2Al, 2Si) and Si(1Al, 3Si) units, but rather to Si(2Al, 1OH) and Si(1Al, 2OH) groupings [16]. These units are known to give rise to ^{29}Si NMR signals at −100 and −90 ppm, respectively, the intensity of which is strongly enhanced upon cross-polarization (see fig. 2). The various signals overlap with other signals in the spectrum, and their individual intensities cannot be directly determined, since cross-polarization is not a quantitatively reliable technique. This means that formula (1) is only approximately applicable to our samples 2 and 3 (see table 1). ^{27}Al MAS NMR spectra of all the samples (not shown) exhibit each only one line corresponding to aluminium atoms situated at tetrahedral framework positions. No signal from six-coordinated (extra-framework) Al is found, and XRD shows that no other crystalline or amorphous phase is present. We conclude that dealumination by H_4EDTA removes aluminium not only from the framework into interstitial positions, but also from the crystal, in contrast to numerous hydrothermal [11] or $SiCl_4$ treatments [9,17]. For hydrothermally treated zeolites the amount of such extra-framework Al can be significantly higher than in a $SiCl_4$ treated sample [17].

An additional estimation of the framework Si/Al ratio was based on its relationship with the cubic unit cell parameter established by XRD. Several such relationships have been published [18–20]. We believe that the formula

$$\left(\frac{\mathrm{Al}}{\mathrm{Si}+\mathrm{Al}}\right)_{\mathrm{framework}} = 0.591a_0 - 14.305 \tag{2}$$

given by Kubelková et al. [20] is the most reliable and also applies to samples containing a certain amount of hydroxyl nests. The results are compared with Si/Al ratios obtained from chemical analysis (table 1). We note that results obtained for the *parent* zeolite by chemical analysis, NMR and XRD are very close. For dealuminated zeolites, however, the values of $(Si/Al)_{XRD}$ and $(Si/Al)_{NMR}$ are lower than

Table 1
^{29}Si MAS NMR line intensities and silicon to aluminium molar ratios derived from chemical analysis, XRD patterns and Gaussian deconvolution of silicon spectra for parent zeolite Na–Y and the dealuminated samples

Sample	$(Si/Al)_{bulk}$	a_0	$(Si/Al)_{XRD}$	$(Si/Al)_{NMR}$	NMR line intensity (%)			
					Si(3Al)	Si(2Al)	Si(1Al)	Si(0Al)
1	2.67	24.69	2.49	2.84	8	35	47	10
2	3.35	24.65	2.80	3.10	5	30	54	11
3	4.23	24.61	3.18	3.28	3	27	59	11

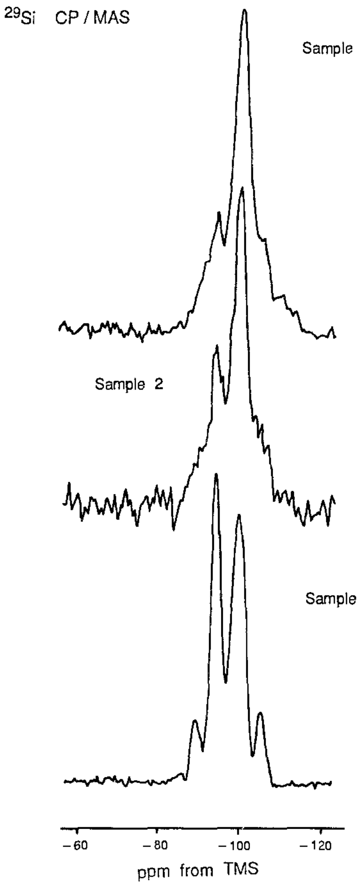

Fig. 2. ^{29}Si CP/MAS NMR spectra of our samples.

$(Si/Al)_{bulk}$, and the difference increases with the amount of extracted aluminium. This suggests that the crystals may contain a small amount of an extra-framework siliceous species which is "invisible" to NMR. This might be due to a long T_1 relaxation time, as it is well established that ^{29}Si in amorphous materials relaxes significantly slower than in crystalline aluminosilicates [21]. The ^{29}Si MAS NMR spectra of dealuminated samples (figs. 1b and 1c) do suggest the presence of a very broad signal at ca. −110 ppm which we assign to a highly siliceous amorphous aluminosilicate and/or an ill-ordered silica-type phase [14].

The compositions of zeolites dealuminated by H_4EDTA, hydrothermal and $SiCl_4$ treatment have been compared [17]. Our sample 3 (29% of Al extracted from framework by H_4EDTA) was compared with sample A1 of ref. [16] (24% of framework Al extracted hydrothermally) and with sample B1 (30% of framework Al extracted by $SiCl_4$). The most striking difference between them is the ^{29}Si NMR line corresponding to Si(0Al) (i.e. Si(4Si)) groupings. In zeolites dealuminated by hydrothermal and by $SiCl_4$ treatment [17] this signal is 4–5 times more intense than in our samples 2 and 3 where the Al vacancies remain unfilled, so that the intensity of this line remains practically constant (table 1). This is another indication that framework vacancies are not re-occupied by silicon.

Since the SiO_4 tetrahedron is smaller than the AlO_4 tetrahedron, substitution of Al by Si during dealumination should result in a contraction of the unit cell. Contraction of the framework of zeolite Y upon dealumination is well documented [9,17]. It is found in our case (see table 1), but the effect is smaller than expected, probably because of the "bulkiness" of the hydroxyl nests. For sample 3 the cubic cell parameter diminishes by 0.32% in comparison with the parent material. If all vacancies were to be filled by Si atoms and no extra-framework Si were present, the cell contraction calculated from chemical analysis should be as much as 0.93%. The difference between the observed and the expected values means that the vacancies are not re-occupied.

Final evidence for the creation of "hydroxyl nests" comes from infrared spectroscopy. The extraction of aluminium from the zeolite framework without filling tetrahedral vacancies by silicon should result in an increase in the infrared band of Si–OH silanol groups giving rise to signal at 3730 cm^{-1}. As seen in fig. 3, this is indeed the case. The 3737 cm^{-1} IR band is absent from the spectrum of the parent sample, which shows that silanol groups are absent. The signal appears in the spectrum of sample 2 and increases with the progress of dealumination.

Reoccupation of framework vacancies by silicon requires diffusion of $Si(OH)_4$

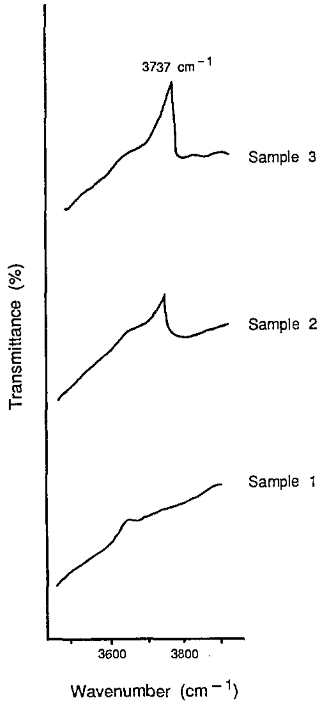

Fig. 3. IR spectra of our samples in the hydroxyl stretch region showing the 3737 cm^{-1} Si–OH band.

through the crystal. Such diffusion must be very slow, especially at relatively low temperatures used in the H_4EDTA treatment, and it is why the most vacancies formed by the extraction of aluminium from the framework remain unoccupied. By contrast, $SiCl_4$ treatment at 100°C fills all the vacancies [17] because the dealuminating agent contains the necessary silicon atoms.

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