SOLID-STATE NMR STUDIES OF FRAMEWORK DEFECTS
IN THERMALLY TREATED ZEOLITE Ca-A

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$^{29}$Si, $^{27}$Al and $^1$H magic-angle-spinning NMR and relaxation measurements on thermally treated zeolite Na$_{1.3}$Ca$_{4.4}$-A have been carried out in order to study framework defects responsible for, and surface barriers to, molecular diffusion. Various possible mechanisms for the formation of such defects are considered in detail. We conclude that no framework dealumination takes place and no acidic hydroxyl groups are present in the zeolite. Excess aluminium occluded in the as-prepared zeolite A is responsible for the production of aluminium hydroxide during hydrothermal treatment.

1. Introduction

Sorption and desorption of paraffins on zeolite Ca-A is significantly modified by the presence of surface barriers, i.e. areas of high diffusional resistance resulting from damage to the zeolitic pore structure, on the surface of crystallites. This has been shown by NMR of thermally treated samples [1,2]. A correlation between the creation of surface barriers and the increased concentration of hydroxyl groups and extra-framework species has also been demonstrated [2]. It is therefore likely that the formation of surface barriers is controlled by a bulk reaction. The presence of aluminium species on extra-framework positions has been detected by X-ray diffraction [3] and $^{27}$Al magic-angle-spinning (MAS) NMR [4,5], while $^1$H NMR has demonstrated a relationship between the hydroxyl content on the one hand and the type of thermal treatment and the degree of calcium exchange on the other [6].

A combination of $^{29}$Si, $^{27}$Al and $^1$H MAS NMR enables detailed insights to be gained into the structure of and the defects in the zeolitic framework [7]. The aim of this work is to elucidate the mechanism of defect formation in zeolite Ca-A in the course of thermal treatment.

2. Experimental

Our starting material was zeolite Na$_{1.3}$Ca$_{4.4}$-A (Zeosorb 5AZ with mean crystallite size of $\approx 4 \mu m$ from VEB Chemiekombinat Bitterfeld, GDR). Sample preparation followed either the “deep bed” (DB) or “shallow bed” (SB) procedure. Under DB conditions the powder is heated in an open glass tube $\approx 30 \text{ mm long at atmospheric pressure. The temperature is raised at a rate of 100 K h}^{-1}$ until the chosen activation temperature is reached. After being kept at this temperature for 2h, the sample is evacuated for 20 h. Under SB conditions the thickness of the zeolite layer is less than 3 mm and the sample is heated in vacuo at a rate of $10 \text{ K h}^{-1}$ until the activation temperature is reached.

$^1$H MAS NMR measurements were carried out in Leipzig with a home-made pulse spectrometer HFS-270. Samples were placed in glass tubes sealed off under vacuum. $^{29}$Si and $^{27}$Al MAS NMR spectra were
measured in Cambridge using a Bruker MSL-400 multinuclear spectrometer. The magic-angle spinning rate for $^1$H and $^{27}$Al were 3 and 7 kHz respectively.

3. Results

Fig. 1 shows the $^{27}$Al MAS NMR spectrum of the rehydrated sample 200 DB (the number refers to the activation temperature in °C). The signal from the framework aluminium atoms is at $\approx 50$ ppm from $\text{Al(H}_2\text{O)}^+_6$, in good agreement with previous work [7]. No signal at 0 ppm, which would correspond to extra-framework hexaaquoaluminium complexes, could be found. However, an additional signal with 78.5 ppm resonance shift and 3 ppm fwhm (full width at half maximum) is present. Applying the quadrupole correction [8] of $\Delta \nu = 2.5$ ppm gives a corrected shift value of 81 ppm. The signal is attributable to $\text{Al(OH)}_4^-$ or other tetrahedrally coordinated aluminium species, e.g. $\text{Al(OH)}_3$ sorbed on a framework oxygen atom. This signal is observed only in rehydrated DB samples, and is absent in dehydrated DB and in SB samples. Extra-framework aluminium forms aluminium hydroxide and $\text{Al(H}_2\text{O)}^+_6$ species when in basic (such as zeolite Ca-A) and acidic (zeolite H-Y) intracrystalline environments, respectively. In low pH environments aluminium exists as $\text{Al(H}_2\text{O)}^+_4$. As the pH increases, this species becomes deprotonated; at high pH Al is present as tetrahedral $\text{Al(OH)}_4^-$ irrespective of concentration [4,9–11].

The number of aluminium hydroxide molecules per zeolitic supercage is determined by comparing the NMR signal with that of a reference sample. This gives $0.49 \pm 0.05$, $0.31 \pm 0.03$ and $0.14 \pm 0.02$ molecules per cavity for the fully hydrated 200 DB, 400 DB and 600 DB samples, respectively. The value for the partially hydrated (five water molecules per supercage) sample 200 DB is $0.44 \pm 0.05$. These values are significantly lower than those reported previously [5], when it was found that partially rehydrated samples contained 1.7 molecules of aluminium hydroxide per supercage. It is now clear that these earlier results were incorrect. The reason why we are now able to determine the amount of aluminium very accurately is twofold. First, we have worked at a higher magnetic field (9.4 T compared with 6.3 T in ref. [5]). Second, we have used a higher spinning rate 7 kHz compared with 3 kHz).

$^{29}$Si MAS NMR spectra of all the samples consist of just one signal at -90.5 ppm from tetramethylsilane (TMS). This is attributable to Si(4Al) structural units, i.e. to silicon atoms linked tetrahedrally, via oxygens, to four aluminium atoms. Si($n$Al) signals with $n \neq 4$ are not observed even at low intensity (see fig. 2). However, spectral linewidths increase with the severity of the thermal treatment. The fwhm increases from 1.38 ppm in the as-synthesised sample to 2.18 ppm in the 600 DB sample; it is even greater (2.57 ppm) in the 300 SB sample. This is in agreement with a previous report [5] that the $^{27}$Al quadrupole frequency increases with activation temperature. There may be two reasons for this. Firstly, the environment of the T atoms becomes less symmetric as the activation temperature increases. Secondly, the second-order quadrupole interaction of non-resonant aluminium may influence line narrowing by MAS [14]. X-ray powder diffraction measurements reveal that the cubic unit cell parameter is unchanged at $12.31 \pm 0.01$ Å. There is, however, evidence that the "amorphous" background increases with the severity of treatment. This is likely to be
related to the increasing number of framework vacancies, and therefore decreasing long-range order, rather than an appearance of a separate amorphous phase.

The concentration of hydroxyl groups per supercage in samples 200 DB, 400 DB, 200 SB and 400 SB has been found to be about 4, 3, 2 and 1, respectively. These values were measured by $^1$H NMR at liquid-nitrogen temperature for both dehydrated and rehydrated samples [2].

Fig. 3 shows $^1$H MAS NMR spectra of samples 400 DB and 400 SB. The resolution is poor, which may be caused by the heteronuclear dipole–dipole interaction between protons and $^{27}$Al nuclei, which interact strongly with the electric field gradient [14]. According to earlier work [15–17] the signal at 1.8 ppm is due to non-acidic SiOH hydroxyls similar to those at the surface of silica gel. No signal at 3.8–4.4 ppm, which would correspond to unperturbed bridging (i.e. acidic) hydroxyl groups, is found. Zeolite Na-A 20% ammonium exchanged and then converted into the hydrogen form by 400 SB activation does show the acidic signal at 4.05 ppm [17]. There is, however, a signal at 3.6 ppm. $^1$H signals at 2.6–3.6 ppm are known to be due to hydroxyl groups connected to non-framework aluminium atoms [17]. As this line is quite broad and not far from the usual position of acidic hydroxyls, a further test of acidity was applied. Treatment of the samples with two molecules of ammonia per supercage did not produce a signal at 7 ppm which is characteristic of NH$_4^+$ cations [17]. No acidic hydroxyls are therefore present. The hydroxyls are associated with non-framework aluminium and framework defects.

4. Discussion

Hydroxyl groups are created by thermal dissociation of water in the presence of divalent cations in the intracrystalline spaces. We shall consider the following possible models for their formation: (A) hydration of aluminium oxide species randomly occluded within zeolite crystals during synthesis; (B) hydroxylation of aluminium atoms released from the framework; (C) formation of CaOH$^+$ cations and bridging hydroxyl groups.

The starting point for model (A) is the fact that the Si/Al ratio of as-synthesised zeolite Na-A (by
chemical analysis) is $0.95 \pm 0.01$ and is unaffected by cation exchange. Since there are no Al–O–Al bonds in the framework (the Loewenstein rule) the 4.7\% excess of aluminium over the minimum Si/Al= 1.00 ratio must correspond to 0.57 extra-framework Al atoms per cavity present in an oxide or hydroxide species. No aluminate ions could be found in hydrated 400 DB Na-A or SB Na,Ca-A samples. If we assume that under self-steaming conditions in the presence of Ca$^{2+}$ polymeric oxide species are transformed into the smaller, mobile hydroxide, 

$$\text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 \quad (1)$$

the products would tend to migrate to the surface of the crystallites. At higher temperatures or at lower partial pressures of water vapour hydroxide may again condense leading to the formation of surface barriers. There is evidence that aluminium-bearing species accumulate on the surface of zeolite Y in the course of thermal treatment (ultrastabilisation) [18–21]. However, X-ray photoelectron spectroscopy does not indicate increased aluminium concentration on the surface of particles of thermally treated zeolite Na, Ca-Y [27].

Model (B) involves the following reaction during which an aluminium atom is released from the framework and two framework hydroxyls are formed:

$$\text{Ca}^{2+} \quad \text{OH}^{\text{Ca(H)}_4} \quad \text{Al}^{\text{Si}_2} + 3 \text{H}_2\text{O} \rightarrow \text{Al}^{\text{OH}}_2 \quad (2)$$

In zeolite H-Y the defect site created by the release of framework aluminium is reoccupied by a silicon atom and the crystal structure is thus preserved. A similar reaction in zeolite A would inevitably lead to the formation of Si–O–Si bonds. In fact, Fyfe et al. [22] have shown that complete framework dealumination leading to a structure in which only Si–O–Si linkages are present is possible with zeolite ZK-4, which is isomorphous with zeolite A. However, $^{29}\text{Si}$ MAS NMR detects no Si–O–Si linkages in any of our samples of zeolite Ca-A. Secondly, reaction (2) requires that Si(3Al,OH) silicon sites are generated. Again, $^{29}\text{Si}$ MAS NMR does not support this, as no signal at $-100$ ppm is detected [23]. Finally, reaction (2) requires that an oxygen atom be released from the framework, which would lead to serve structural distortion.

According to Planck [24] model (C) involves the following reaction:

$$\text{Ca}^{2+} \quad \text{OH}^{\text{Ca(H)}_4} \quad \text{Al}^{\text{Si}_2} + \text{H}_2\text{O} \rightarrow \text{Al}^{\text{OH}}_2 \quad (3)$$

In zeolites Ca-X and Ca-Y this mechanism is supported by IR spectra. While two IR bands are unambiguously attributable to the bridging hydroxyls, this is not the case with CaOH$^{+}$ cations [25,26]. By contrast, $^1\text{H}$ MAS NMR of zeolite Ca-A provides no evidence for the existence of bridging hydroxyls. This result is consistent with the basic chemical character of zeolite Ca-A, which leads to the formation of aluminium hydroxide rather than acidic Al(H$_2$O)$_3^{3+}$ complexes. Model (C) cannot therefore account for the presence of hydroxyl groups on non-framework aluminium as found experimentally. Thus only model (A) remains.

We propose the following mechanism for the formation of aluminium hydroxide complexes which is in agreement with all experimental results. In SB samples aluminium non-framework complexes (about 1/2 aluminium atom per cavity) are located inside sodalite cages. In DB zeolites activated at $\geq 200^\circ\text{C}$ the excess aluminium is released from the sodalite cages. Aluminium complexes are transformed into small and mobile hydroxide species during deep bed activation.

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**References**

