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Hydroxyl groups of the non-framework aluminium species in dealuminated Y zeolites

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By comparing dealuminated Y zeolites with and without non-framework aluminium species it is shown that the bands at 3693 and 3606 cm^{-1} in the i.r. spectrum and the line at 2.6 ppm in the ^1H *MAS* n.m.r. spectrum represent hydroxyl groups associated with non-framework aluminium.

Keywords: Y zeolites; dealumination; non-framework aluminium; hydroxyl groups; ^1H *MAS* n.m.r. spectroscopy; i.r. spectroscopy

INTRODUCTION

The thermochemical treatment of NH_4Y zeolites[1] causes characteristic changes within the zeolite crystals. Framework aluminium is converted into non-framework species, secondary mesopores[2] are created and it appears likely that part of the structure becomes amorphous. These structural transformations are combined with changes in the concentration of hydroxyl groups within the parent HY zeolite and with the formation of new hydroxyl groups. The number of bridging OH groups located in the neighbourhood of the framework aluminium decreases in proportion to the framework aluminium content. Silanol groups are formed on the walls of the mesopores and OH groups associated with the non-framework aluminium species or with vacancies and amorphous parts of the structure may be created.

To prove especially the presence of OH groups on the non-framework aluminium species, Y zeolites with and without non-framework aluminium have been studied both by i.r. and ^1H *MAS* n.m.r. spectroscopy.

RESULTS AND DISCUSSIONS

The samples are listed in *Table 1*. The two dealuminated samples were prepared either by deep bed treatment (sample 2) or by steaming (sample 3). From these up to ~ 80% of the non-framework aluminium species were extracted by acid leaching[3] (samples 2e, 3e' and 3e). In contrast to the deep bed treatment and steaming, the acid leaching effected no additional measureable dealumination of the framework. The dissolved amount of non-framework aluminium was determined directly by chemical analysis from the solution. The Si/Al ratio of the framework (*Table 1*) were estimated from the i.r.[4] and ^{29}Si n.m.r.[5] spectra. One further effect of the acid treatment is the exchange of the residual sodium ions against protons.

The adsorption capacity as determined from the adsorption isotherms (*Table 1*) provides a sensitive check on the crystallinity of the samples. The loss of the framework aluminium reduces the number of zeolitic structure units and consequently the cavity volume per gramme[6] (*Table 1*, compare samples 2 and 3 with sample 1). In addition, a structure breakdown of up to ~ 20% is observed after acid leaching (samples 2e and 3e) but without dealumination of the residual structure units.

Column 7 of *Table 1* contains the maximum number of bridging OH groups per 1/8 unit cell

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Table 1 Characterization of the samples

Sample number	Conditions of sample preparation	Si/Al of the framework from ^{29}Si n.m.r.	No. of non-framework Al atoms per 1/8 u.c.	Adsorption capacity n-hexane (25°C)		Number of bridging OH groups per ⅛ unit cell	
				(mmol g^{-1})	(% related to sample 1)	Estimated from sample comp.[a]	From ^{1}H n.m.r. spectra[b]
1	Deammonization of 70 NH_4Y	2.43	0[e]	2.2	100	5.0	–
2	70 HY dealuminated by deep bed treatment (770°C, 20 min)	5.0	3	1.9	86	2.0	0
2e	From sample 2 by acid leaching[c]	5.0	0.6	1.7	77	4.0	2.2
3	92 HY dealuminated by steaming (750°C, 3h)	20	5.9	1.6	73	0.6	0.7
3e	From sample 3 by acid leaching[d]	20	3.0	–	–	–	–
3e	From sample 3 by acid leaching	20	1.2	1.2	55	1.1	1.0

[a]Assuming that each framework aluminium atom which is not compensated by sodium gives rise to an OH group
[b]Corrected by the structure destruction
[c]With the stoichiometric amount of 0.1 N HCl at room temperature
[d]With the half of the stoichiometric amount of 0.1 N HCl
[e]Assumed for the parent zeolite

estimated on the supposition that those framework aluminium atoms whose charges are not compensated by sodium ions give rise to OH groups.

In *Figure 1* the i.r. spectra of the samples 1, 2 and 2e are represented. These were obtained from self-supporting zeolite pellets on an i.r. spectrometer Specord M–80 (VEB Carl Zeiss Jena, GDR). The spectrum of sample 1 shows the well-known high frequency (h.f.) and low frequency (l.f.) bands which are characteristic of bridging OH groups. After dealumination (sample 2) a diminished absorbancy is observed. Bands at ~ 3600 cm^{-1} and 3700 cm^{-1} have often been described in the literature for dealuminated zeolites. Concerning the origin of these bands, assignments to species within the modified zeolitic framework[7], to hydroxyaluminium ions (e.g. $Al(OH)^{2+}$ [8]) and recently to boehmite-like non-framework aluminium clusters[9,11], have all been proposed. The strong decline in the intensity of these bands after dissolution of the non-framework aluminium (sample 2e) implies that these bands are due to AlOH groups within the non-framework species.

It is interesting to note that no bridging OH groups were detected in sample 2 which is in agreement with the n.m.r. results (see below). After acid treatment the bands of the bridging OH groups appear at 3632 cm^{-1} and 3557 cm^{-1}. The h.f. band is shifted distinctly to smaller wavenumbers in comparison to sample 1, in agreement with the following dependence on the Si/Al ratio (described elsewhere[10]):

Si/Al	Frequency of h.f. band
2.4	3642 cm^{-1}
5	3632 cm^{-1}
95	3620 cm^{-1}

The terminal OH groups (silanol groups) give rise to the band at 3745 cm^{-1} which is enhanced in its intensity after dealumination and acid leaching, as expected.

After loading with ammonia it was observed that at small ammonia equilibrium pressures only the bridging OH groups interact, whereas, > 1 Pa the bands due to AlOH are reduced[12]. This confirms the known fact that the OH groups giving rise to the bands at 3600 cm^{-1} and 3700 cm^{-1} are less acidic than the bridging hydroxyl groups (i.e. the origin of the h.f. and l.f. bands).

Recently, hydroxyl groups have also been studied by proton magic angle spinning nuclear magnetic resonance (*MAS* n.m.r.) spectroscopy, and qualitative results may be derived concerning the concentration of the various species[13–15].

Figure 2 shows ^{1}H *MAS* n.m.r. spectra of the samples under study. Three lines at 1.8, 2.6 and 4.2 ppm are observed. Assuming the assignments given in Ref. 13, the signals at 1.8 ppm and 4.2 ppm are due, respectively, to terminal OH groups and bridging OH groups. After acid leaching the line at 2.6 ppm vanishes (samples 2e and 3e) or is reduced (sample 3e'), consequently, it may be assigned to

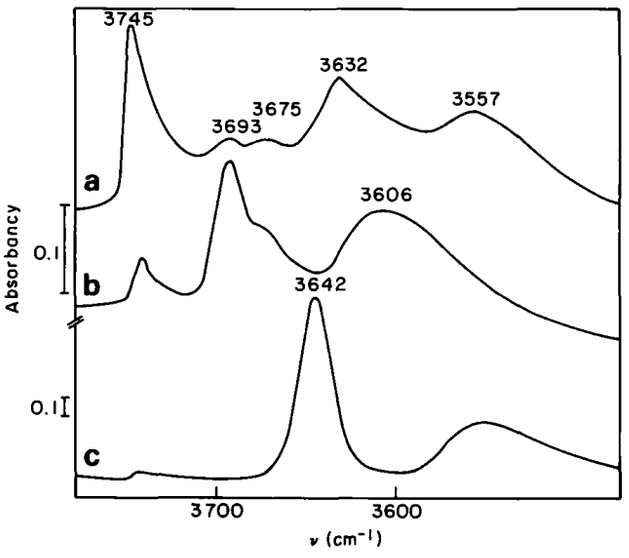

Figure 1 I.r. spectra: (a) sample 2e, (b) sample 2, (c) sample 1

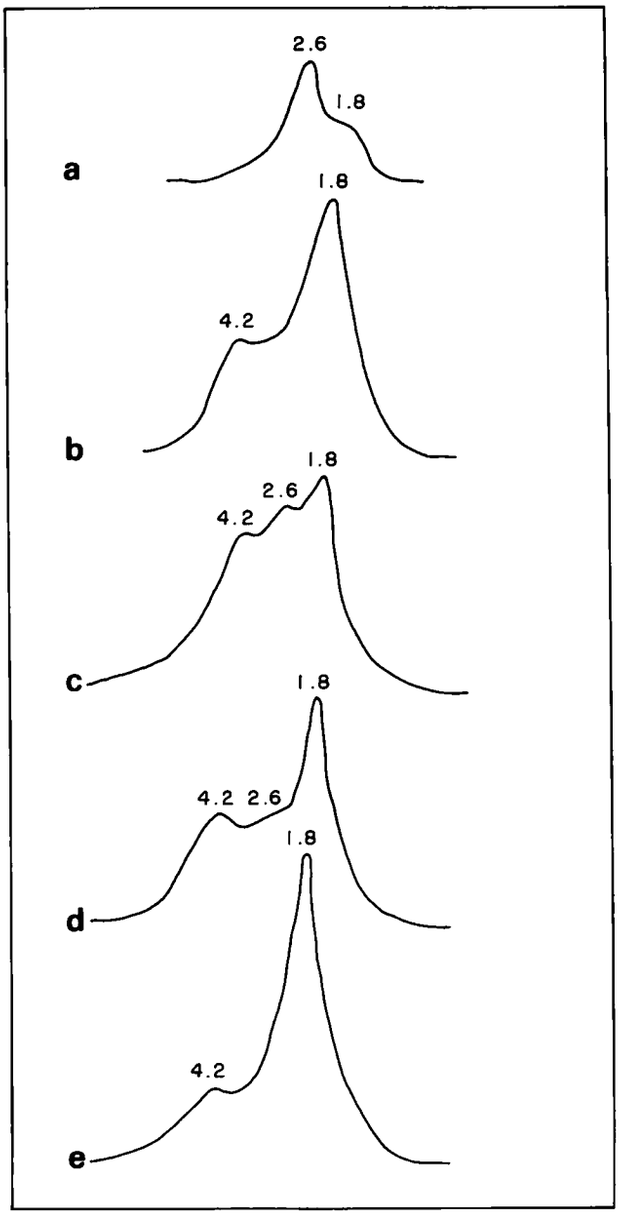

Figure 2 ^{1}H *MAS* n.m.r. spectra: (a) sample 2, (b) sample 2e, (c) sample 3, (d) sample 3e, (e) sample 3e'. The numbers give the p.m.r. shift in ppm (internal TMS)

AlOH groups on the non-framework aluminium species. In full agreement with the i.r. spectra the signal at 4.2 ppm is missing in sample 2. In addition, the enhancement in the intensity of the 1.8 ppm line for sample 2e correlates with changes in intensity of the 3745 cm^{-1} band. The number of bridging OH groups as estimated from the ^{1}H *MAS* n.m.r. spectra is listed in *Table 1*, column 8. For the highly dealuminated samples 3 and 3e the values agree with those predicted from the chemical composition of the samples.

In contrast, for samples 2 and 2e the n.m.r. values are smaller by a constant number of ~ 2 bridging OH groups per 1/8 unit cell. The increase of the concentration of bridging OH groups through acid leaching of sample 2e is caused by an extraction of two residual sodium ions per 1/8 unit cell, the differences between the values derived from the sample composition and the n.m.r. spectra, however, should be clarified by further investigations.

The ratio of the number of AlOH groups to the number of non-framework aluminium atoms is small (~ 0.1 for sample 2) and decreases further for samples steamed for a long time[16]. It seems that the process of condensation to higher molecular weight species of the monomeric $Al(OH)_3$ molecules which are formed in the first step of framework hydrolysis can be followed by studying the AlOH group concentrations in suitable samples.

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