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^{1}H MAS NMR AND IR STUDIES OF THE ACIDIC PROPERTIES OF REALUMINATED ZEOLITE Y

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IR and ^{1}H MAS NMR confirm that extra-framework aluminium present in dealuminated (ultrastable) zeolite Y is reintroduced into the framework by treatment with strongly basic solutions at elevated temperatures. The realuminated sample contains twice as many Brønsted acid sites than the ultrastable precursor and, with an accuracy of 20%, the same number of acid sites as the parent as-prepared zeolite. However, not as many hydroxyl groups associated with framework Al in the product are acccesible to pyridine as in the parent sample.

1. Introduction

We have recently shown [1–8] that the process of stabilization of zeolite Y, 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 at elevated temperatures. Extensive work using X-ray and neutron diffraction, ^{29}Si and ^{27}Al magic-angle-spinning (MAS) NMR, infrared and ^{27}Al quadrupole nutation NMR has thrown much light on the mechanism of the dealumination/realumination sequence, and the optimum conditions of the reaction have been established [2–4]. 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; (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; (iv) aluminium substitution takes place in ZSM-5/silicalite [8]; (v) other elements, notably gallium and boron can be similarly introduced into zeolitic frameworks.

Preliminary studies show that the catalytic performance towards the cracking of n-hexane of the "second generation" zeolite Y is very different from that of the first-generation material. Further generation materials can also be prepared, with

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still different Si, Al distributions and presumably catalytic performance. It is therefore of interest to examine directly the acidity of the new catalysts using ^{1}H MAS NMR and infrared spectroscopies.

Brønsted acidity of zeolites arises from the presence of accessible hydroxyl groups associated with framework aluminium (the so-called "bridging hydroxyl groups"). ^{1}H MAS NMR has been used [9–12] to obtain important information on the chemistry of zeolite Y. It was shown that the spectra of zeolites can be treated as distribution functions of acidity. Experiments involving different materials and loading samples with bases, such as ammonia and pyridine, which react with acid sites, have led to the assignment of the various proton resonances. Five proton resonances in zeolite Y have been assigned [11]:

Signal a at 1.3–2.3 ppm from tetramethylsilane (TMS), due to non-acidic (silanol) hydroxyls on the surface of zeolite crystallites and crystals defects sites.

Signal b at 3.8–4.4 ppm from bridging OH groups involving O_1 oxygen atoms and pointing towards the zeolitic supercages.

Signal c at ca. 5 ppm from protons on O_3 atoms and pointing towards the other oxygens in the sodalite cages.

Signal d at 6.5–7.0 ppm, due to residual NH_4^+ cations.

Signal e at 2.6–3.6 ppm, due to Al-OH groups attached to non-framework Al.

The concentration of the various types of protons in zeolites can be determined by comparing the intensities of lines with those in a standard sample with an accuracy of $\pm 10\%$. Two different types of bridging hydroxyl groups in H-Y zeolites have been assigned [11] on the basis of location of the hydroxyls groups in the framework. Thus signal *b* was found to correspond to the HF infrared band at 3650 cm^{-1} for OH groups involving O_1 oxygen atoms and signal *c* to the LF band at 3540 cm^{-1} which has been attributed to OH groups involving O_3 oxygen atoms.

The hydroxyl stretching region (3500–3800 cm^{-1}) in infrared spectroscopy also gives valuable information about the origin and nature of different types of OH groups [13–19]. Important factors governing the acidity including the number of proton-donor (Brønsted) and electron-acceptor (Lewis) sites and the respective acid strengths can be identified using the method of adsorption and thermal desorption of pyridine [20]. The various types of acidic and non-acidic hydroxyl groups have been assigned to specific vibrations in the IR spectrum as follows [15–17]:

3745 cm^{-1}	terminal Si-OH
3700–3600 cm^{-1}	Si-OH groups at defect sites and/or OH groups associated with extra-framework Al (EFAL) species
3610 cm^{-1}	extra-framework hydroxyls
3670–3600 cm^{-1}	hydroxyls involving O_1 oxygen atoms (HF band)
3580–3545 cm^{-1}	hydroxyls involving O_3 oxygen atoms (LF band)

When pyridine (Py) is adsorbed at room temperature and degassed at 250 °C, only the low-acidity (non-framework) hydroxyls or those which are not accessible to pyridine remain in the hydroxyl region of the IR spectrum. Adsorption of pyridine on the acidic hydroxyls forms pyridinium ions (PyH^+) and on non-framework Al species Py-Al complexes. The type, strength and number of a particular acidic site formed by the adsorption and desorption of pyridine can be characterized from the IR spectrum in the wavenumber region of pyridine ring vibrations (1350–1700 cm^{-1}) assigned as follows:

1545 cm^{-1} (B) PyH^+ ions (Brønsted acidity)
1454 cm^{-1} (L) Py-Al complexes (Lewis acidity).

2. Experimental

SAMPLE PREPARATION

The parent sample 1 was 62% ammonium-exchanged zeolite Na,NH_4-Y with Si/Al = 2.56. It was hydrothermally treated at 525 °C for 18 hours in a horizontal tubular quartz furnace under deep-bed conditions while water was slowly injected into the tube by a peristaltic pump, keeping the partial pressure of H_2O above the zeolite bed at 1 atm, to give the dealuminated sample 2. The realuminated sample 3 was prepared by treatment of 0.5 g of sample 2 in 50 ml 0.25 M KOH at 80 °C for 24 hours. Sample 3 was ammonium exchanged in 2 M NH_4NO_3 at 80 °C and calcined overnight at 400 °C in an air oven to give sample 4. Samples were evacuated at 300 °C for 2 hours before being sealed in a glass ampoule which could be spun inside a MAS rotor.

X-RAY DIFFRACTION

Powder X-ray diffraction (XRD) patterns were acquired on a Philips PW1710 vertical goniometer using Cu Kα radiation selected by a graphite monochromator in the diffracted beam. Unit cell parameters were calculated using silicon powder as an internal standard. Si/Al ratios of the samples were calculated from unit cell parameters using a well-established relationship [21].

INFRARED MEASUREMENTS

IR spectra were measured at room temperature using the KBr wafer technique. For the IR of the hydroxyl region, the samples were calcined at 550 °C and dehydrated under vacuum (10^{-4} Torr) at 400 °C for 16 hours prior to measurements. 10–50 mg of pyridine was used for the sorption/desorption experiments. Adsorption was performed at room temperature and desorption at 250, 350 and 400 °C at 10^{-4} Torr pressure. The aluminium content of the samples has been calculated from the IR results using the correlation [22] between the fraction of

aluminium in the framework and the frequency of the main asymmetric band, ν_{as}, based on regression analysis of 37 points taken from the literature:

$$\frac{\text{Al}}{\text{Al} + \text{Si}} = 4.454 - 4.099 \cdot 10^{-3} \nu_{as}$$

MAGIC-ANGLE-SPINNING NMR (MAS NMR)

^{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 μs $\pi/2$ 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 sample was spun at 2.5 kHz.

^{29}Si MAS NMR spectra were measured at 79.5 MHz. Samples were spun in Andrew-Beams rotors at 2.6 kHz using air as the spinning gas. Radiofrequency pulses of 4 μs duration were applied with 20 s recycle delay. 1000 transients were acquired for each spectrum. ^{29}Si chemical shifts are quoted in ppm from external tetramethylsilane (TMS).

3. Results and discussion

^{29}Si MAS NMR spectra of faujasitic zeolites consist [23] of up to five signals corresponding to Si(nAl) building blocks where n, which can be 0, 1, 2, 3 and 4, is the number of framework Al atoms linked, via bridging oxygens, to a given Si. The *framework* Si/Al ratios can be calculated from the relative intensities, I_n, of the individual Si(nAl) signals [23–25]:

$$\left(\frac{\text{Si}}{\text{Al}}\right)_{\text{NMR}} = \frac{I_4 + I_3 + I_2 + I_1 + I_0}{I_4 + \frac{3}{4}I_3 + \frac{1}{2}I_2 + \frac{1}{4}I_1}.$$

^{29}Si spectra of realuminated samples are very different from those of the starting dealuminated materials [1,3,4]. The intensities of the Si(0Al) signals are greatly reduced, and the intensities of the Si(1Al), Si(2Al), Si(3Al) and Si(4Al) signals correspondingly increased, signifying that a considerable amount of aluminium has entered the zeolitic framework. Further, the spectra of re-aluminated samples are very different from that of the parent sample despite the fact that the composition of all four samples is similar, showing that the distribution of Si and Al among the tetrahedral sites is different in each case.

The unit cell parameters and Si/Al ratios calculated from IR, XRD and ^{29}Si NMR are listed in table 1. The Si/Al ratios from NMR and IR are in particularly good agreement. The IR spectra of samples 2 and 4 at room temperature show typical absorptions with frequencies listed in table 2.

The ^{1}H MAS NMR spectra of our samples, given in fig. 1, are relatively poorly resolved because of the strong proton-proton dipolar interaction [12]. Spectral

Table 1
Unit cell parameters and the composition of samples

Sample	a_0 (Å)	Framework Si/Al ratio		
		XRD	NMR	IR
1	24.69	2.34	2.56	2.8
2	24.51	4.22	5.08	5.2
4	24.69	2.34	2.88	2.7

deconvolution into Gaussian components was used to obtain relative intensities of the various signals, and fig. 2 shows such deconvolution of the central (as opposed to the sidebands) signal of the spectrum of the realuminated sample 4. All five types of hydroxyls described above are clearly in evidence. The spectrum of the parent zeolite H-Y (fig. 1) consists of three signals corresponding to different kinds of protons: signal *b* at 4.0 ppm due to bridging OH groups involving O_1 atoms and pointing towards the zeolitic supercages, signal *c* at ca. 4.9 ppm to protons on O_3 atoms pointing towards the other oxygens in the sodalite cages; signal *a*, corresponding to Si-OH groups, is weak, which indicates that the sample contains only few defects. Dealumination 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. In the spectrum of realuminated material, besides the shoulder attributable to line *a* and the signal *e*, there are signals in the chemical shift region corresponding to lines *b* and *c*. Their intensity is increased in comparison with the spectrum of dealuminated material (sample 2). There is also a weak signal due to the residual ammonium cations (line *d*). Measurement of the intensity of NMR signals indicates that there are 4.2 ± 0.4 bridging OH groups per supercage in sample 1, 2.1 ± 0.3 OH groups in sample 2 and 4.4 ± 0.4 OH groups in the realuminated sample 4. The total number of bridging hydroxyl groups in the realuminated sample is therefore approximately the same as in the parent sample 1. On the other hand, the intensity of signal *c* is significantly higher in sample 4 than in sample 1, indicating that in the latter sample aluminium is preferentially substituted into sites associated with OH groups involving O_3 oxygen atoms.

The IR spectrum of sample 2 (table 2) contains symmetric and assymmetric stretches typical of partially dealuminated zeolite Y. The realuminated sample 4

Table 2
Infrared vibrational frequencies (cm^{-1})

Sample	Asymmetric stretch			Symmetric stretch		Double ring		T-O bend	Pore
2	1403	1164	1047	808	748	584	510	453	394
4	1401	1146	1021	786	730	573	502	452	390

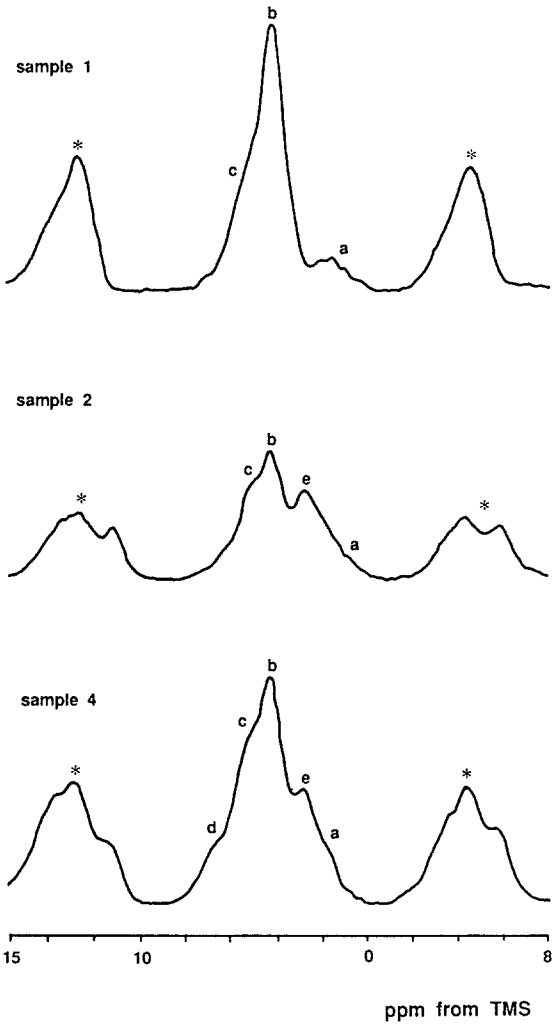

Fig. 1. ^{1}H MAS NMR spectra in the absolute intensity mode. Parent zeolite NH_4-Y (sample 1) after activation; ammonium-exchanged hydrothermally dealuminated material (sample 2), and ammonium-exchanged realuminated material (sample 4). For the assignment of the various signals see text; asterisks denote spinning sidebands.

shows the general shift of the composition-sensitive bands to lower frequencies indicating an increase in the framework aluminium content [1–4]. The parameters of the spectra in the hydroxyl region are shown in table 3, while fig. 3 shows the IR spectra of dealuminated zeolite Y (sample 2) before and after adsorption of pyridine and degassing at 400 °C. The spectrum taken before adsorption indicates a large amount of silanols at defect sites (3696 cm^{-1}) and a small amount of terminal hydroxyl groups (3742 cm^{-1}). In addition, there is a substantial amount of acidic hydroxyls corresponding to the tetrahedral framework aluminium (LF, HF) and a fair amount of hydroxylated extra-framework aluminium at

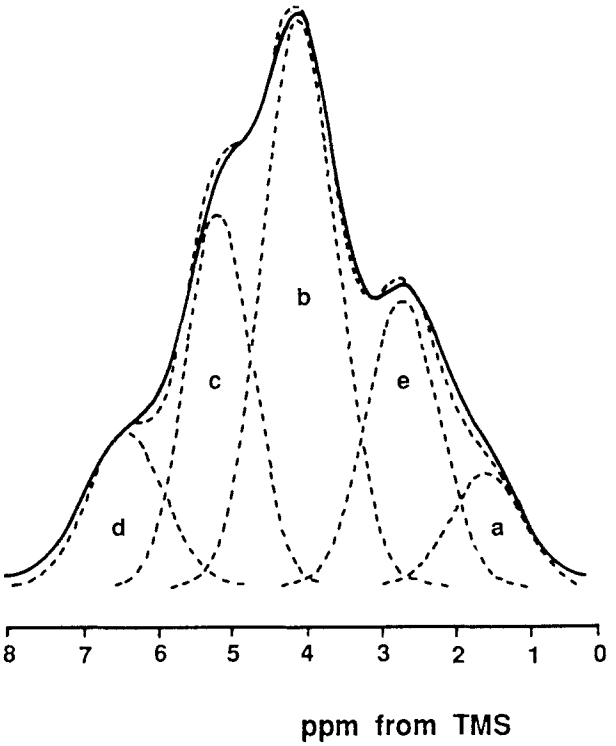

Fig. 2. Spectral deconvolution (dotted lines) into Gaussian components of the ^1H MAS NMR spectrum of the realuminated sample 4 (solid line, see fig. 1). The labelling of the various signals is as described in the text.

3610 cm^{-1}. When pyridine is adsorbed at room temperature and degassed at 250 °C only the non-acidic hydroxyls (3742, 3702 and 3603 cm^{-1}) and part of the LF hydroxyl groups (3544 cm^{-1}) remain. This indicates that although the LF hydroxyl groups are strongly acidic, some of them are inaccessible to pyridine. This is further confirmed by the IR spectra [fig. 3(b)] in the pyridine ring vibration region. Adsorption and desorption of pyridine at 250, 350 and 400 °C

Table 3
IR vibrational frequencies in the hydroxyl and acidity region. (vs) very strong; (s) strong; (m) moderate; (w) weak; (vw) very weak

Sample	Hydroxyl region n (cm^{-1})					Acidity	
	Silanol terminal	Silanol defect	Bridging (HF)	Bridging (LF)	EFAL	Brønsted 1545	Lewis 1454
2	3742 (s)	3696 (m)	3675 (vs)	3544 (vs)	3610 (m)	s	vw
2 + Py	3742 (m)	3702 (s)	3603 (s)	3547 (s)		vs	w
4	3694 (s)	3640 (vs)		3543 (s)		m	s
4 + Py	3740 (m)	3696 (s)		3540 (s)		s	vs

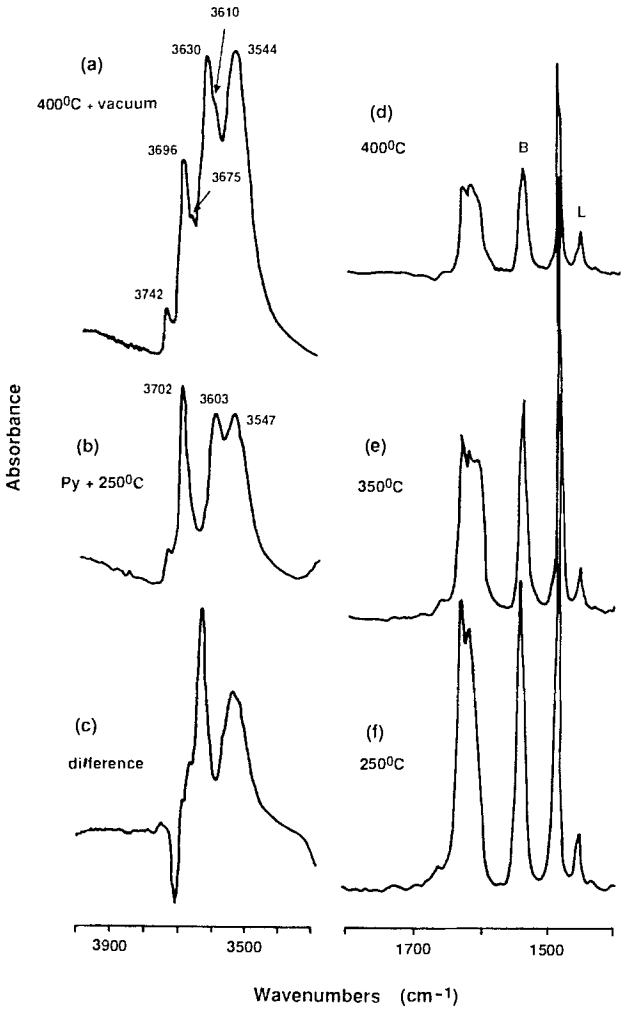

Fig. 3. Infrared spectra of (a) ultrastable zeolite Y (sample 2) calcined at 1.33×10^{-3} Pa and 400 °C overnight; (b) after sorption of pyridine at room temperature and desorption under vacuum at 250 °C for 1 hour; (c) difference spectrum; (d) after sorption of pyridine at room temperature and desorption under vacuum at 400 °C for 1 hour; (e) after sorption of pyridine and desorption at 350 °C for 1 hour; (f) after sorption of pyridine and desorption at 250 °C for 1 hour. B denotes Brønsted, L Lewis acidity.

show a substantial increase in intensity of the B band corresponding to PyH^+ ions indicating the presence of strong Brønsted acidity. There is a small number of Lewis acid sites indicating that only a small amount of non-framework Al atoms in dealuminated zeolite Y exhibits electron-accepting properties.

The IR spectra of the realuminated sample 4 in fig. 4 are similar to those of dealuminated samples and consist of at least four types of OH groups. There is no EFAL signal (3610 cm^{-1}). However, there is a fair amount of terminal silanols

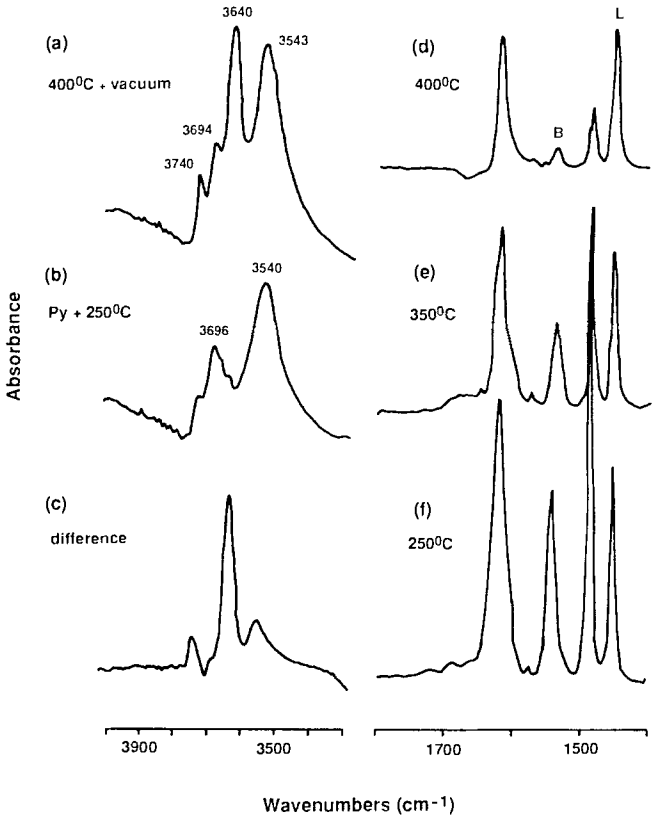

Fig. 4. Infrared spectra of (a) ammonium exchanged realuminated zeolite Y (sample 4) calcined at 1.33×10^{-3} Pa and 400 °C overnight; (b) after sorption of pyridine at room temperature and desorption under vacuum at 250 °C for 1 hour; (c) difference spectrum; (d) after sorption of pyridine at room temperature and desorption under vacuum at 400 °C for 1 hour; (e) after sorption of pyridine and desorption at 350 °C for 1 hour; (f) after sorption of pyridine and desorption at 250 °C for 1 hour.

(3694 and 3640 cm^{-1}) at the terminal and defect sites and a large amount of acidic framework hydroxyls (HF and LF). Adsorption and desorption of pyridine at 250 °C affects only the HF hydroxyls. In contrast to sample 2, most of the LF acid sites in sample 4 are inaccessible to pyridine. The IR spectra of pyridine stretching region in fig. 4 show an increase in both Brønsted and Lewis acidity upon adsorption and desorption.

IR and ^{1}H MAS NMR results are therefore in good agreement. The realuminated zeolite Y clearly contains much more framework aluminium than the dealuminated precursor. However, IR indicates that not all hydroxyls bridged to these aluminiums are accessible to pyridine.

Acknowledgements

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