Neutron Diffraction Studies of Realuminated Zeolite Y

Patrick J. Barrie,[a] Lynn F. Gladden[b] and Jacek Klinowski[a]

[a] Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK
[b] Department of Chemical Engineering, University of Cambridge, Pembroke Street, Cambridge CB2 3RA, UK

Neutron diffraction measurements together with solid-state NMR results support the claim that aluminium is reinserted into the framework of steamed samples of zeolite Y upon treatment with highly alkaline solutions.

A number of ways of increasing the framework aluminium content of zeolites have been devised.[1-4] The most recent involves enriching the framework of the commercially important zeolite Y in aluminium by treating the steamed (ultrastable) form with highly alkaline solutions at ca. 80 °C.[3,5,6] The method leads to novel zeolites, which have the same structure and similar Si : Al ratios as the parent material, but very different distributions of aluminium and silicon within the framework, and thus modified thermal stability and catalytic activity. We present here, for the first time, powder neutron diffraction results on base-treated zeolite Y as further proof that realumination does occur.

Dealuminated zeolite Y (sample USY) was prepared by steaming a 78% NH_4-exchanged zeolite Y (Si : Al = 2.65) at 500 °C for 12 h. Two realuminated samples (ReAl-1 and ReAl-2) were prepared by treating the steamed sample with 0.5 and 1 mol dm^{-3} KOH respectively at 80 °C for 24 h. All samples were then ion exchanged to the potassium form so that comparisons between samples could be made without complications from varying cations. ^{29}Si magic-angle-spinning (MAS) NMR spectra were recorded on a Bruker MSL-400 spectrometer using 45° radiofrequency pulses with 20 s recycle time. MAS rotors were spun in air at 2.5 kHz. Neutron diffraction patterns on dehydrated samples of K-Y, K-USY, ReAl-1 and ReAl-2 were obtained at 5 K on the D1A diffractometer at the Institut Laue-Langevin, Grenoble, with neutrons of 1.909 Å wavelength. The patterns were analysed using the GSAS Rietveld refinement package developed at Los Alamos Laboratories. The space group $Fd3m$ was used in all refinements, and the highly asymmetric (111) peak was excluded.

^{29}Si MAS NMR spectra shown in Fig. 1 consist of up to five signals corresponding to different Si(nAl) environments, where n denotes the number of aluminium atoms linked, via a bridging oxygen, to a given silicon. Deconvolution of the peak areas enables the framework Si : Al ratios to be calculated.[7] These are shown in Table 1 which indicates that substantial framework realumination has taken place.

Rietveld analysis of the neutron diffraction patterns gave R_{wp} values in the range 6.0–7.9% after refining instrumental, framework and cation parameters. The calculated diffraction profile for the sample ReAl-1 is shown in Fig. 2. This also gives the difference plot, which indicates that the main source of error remaining is in the modelling of the peak shapes at low 2θ angles. The structural parameters obtained from the refinement of ReAl-1 are given in Table 2. The refined lattice parameters shown in Table 1 correlate well with the changes in Si : Al ratio calculated from the NMR spectra. Since all our samples are in the potassium form, the argument[8] that the variations in lattice parameter on treating zeolite Y with strong bases may be due to changed cationic species cannot be correct.

The occupancy of the tetrahedral sites was refined while constraining the Si : Al ratio to be that determined from the ^{29}Si MAS NMR spectra. Both realuminated samples had refined occupancies greater than 95% (Table 1), indicating that substantial dissolution of the sample did not occur during the treatment. This is in marked contrast to the results of Aouali et al.[9] who used X-ray diffraction to obtain a value of only 73% for the tetrahedral occupancy in a sample which had been treated with a base after dealumination. They suggested that the basic treatment removed silicon from the sample
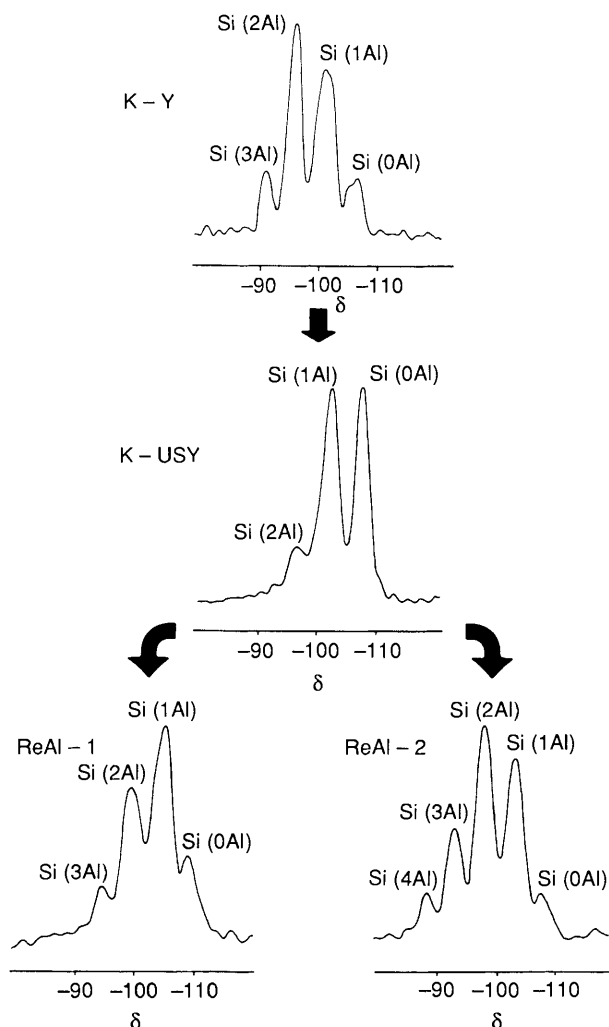
Fig. 1 ^{29}Si MAS NMR spectra of samples K-Y, K-USY, ReAl-1 and ReAl-2

without any reinsertion of aluminium, but were unable to explain how this could lead to an increase in lattice parameter, or the changes in IR and ^{29}Si MAS NMR spectra. The high occupancy of the tetrahedral sites in our samples is also in agreement with the fact that their crystallinity relative to the dealuminated sample is improved upon basic treatment. This has also been observed by Bezman.[5] It has also been seen that the crystal morphology of zeolite Y remains largely unchanged on treatment with high alkaline solutions.[8] These observations support the proposed realumination mechanism that extra-framework aluminium dissolves in concentrated base to form tetrahedral aluminate ions which can then enter the framework at sites vacated by silicon atoms.

It is usually assumed that all the T sites in the faujasite structure are equivalent (as in the space group $Fd3m$). However, the distribution of Si and Al over these sites is not completely random, being constrained by the Loewenstein rule[10] (which states that Al–O–Al linkages are avoided) and by other longer-range ordering effects. The distribution of Al in the realuminated samples is strikingly different from that in the parent zeolite, as can be seen from the variations in the Si(nAl) peak intensities between samples of similar Si : Al ratio.[6] It may be possible to distinguish more than one tetrahedral site, arising from the local ordering of the T atoms. ^{29}Si MAS NMR provides one method by which Si and Al ordering within faujasite may be probed,[11] and neutron diffraction may provide another as there is a significant difference between Si and Al scattering lengths. There is,

Table 1 Summary of neutron diffraction refinement results; values in parenthesis give the estimated standard deviations in the last figure

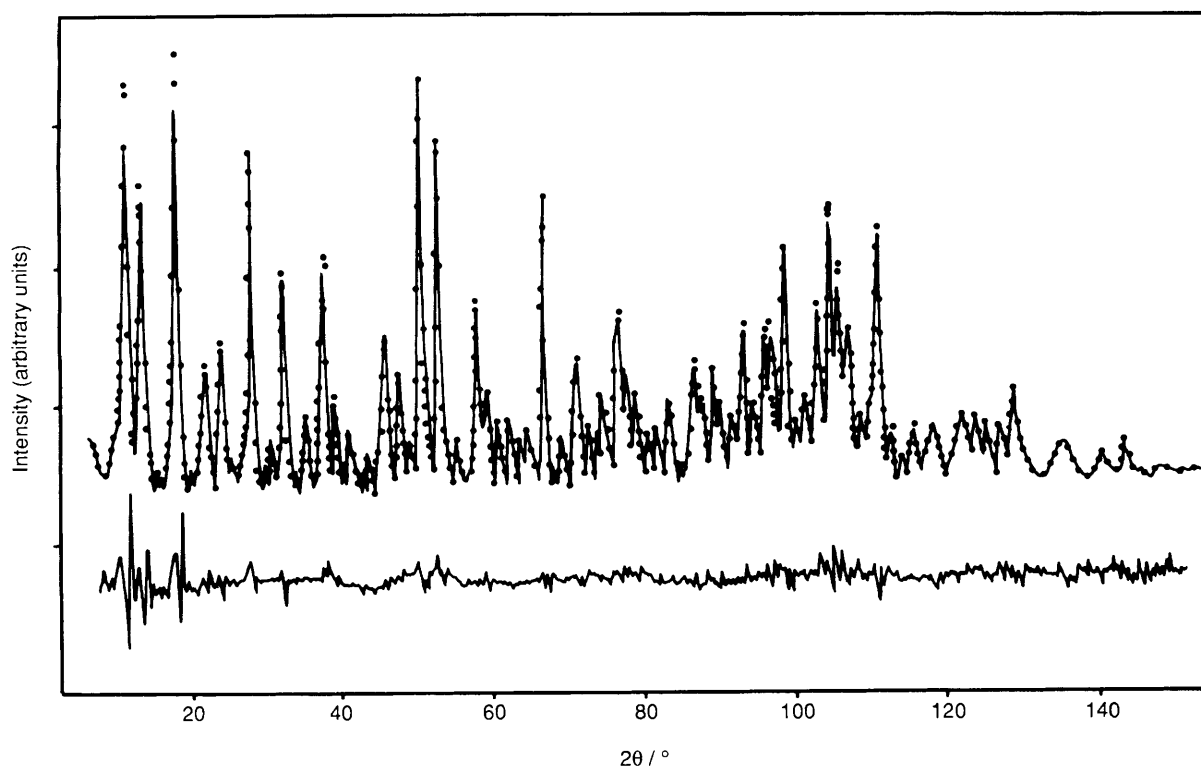| Sample	Si : Al	R_{wp} (%)	a_0/Å	T_{occ} (%)
K-Y	2.65	7.3	24.9041(4)	99.6(9)
K-USY	5.5	6.0	24.6218(7)	98.5(10)
ReAl-1	2.90	7.0	24.8606(9)	95.1(10)
ReAl-2	2.15	7.9	24.9641(5)	95.3(9)

Fig. 2 The observed (dots) and simulated (solid line) neutron diffraction profiles of sample ReAl-1. The difference plot between experimental and calculated data points is given below.

Table 2 Structural parameters obtained from the refinement of sample ReAl-1; values in parentheses give the estimated error in the last figure[a]

Atom	x/a	y/b	z/c	Occ.	$N_{unit\ cell}$
T(1)	0.12523(17)	0.94523(18)	0.03559(15)	0.951(10)[b]	183(1)
O(1)	0.10746(14)	0.89254(14)	0		
O(2)	0.25322(13)	0.25322(13)	0.13991(21)		
O(3)	0.17388(13)	0.17388(13)	0.96363(21)		
O(4)	0.18133(15)	0.18133(15)	0.31878(20)		
K(I)	0	0	0	0.368(30)	5.9(5)
K(I')	0.0707(8)	0.0707(8)	0.0707(8)	0.402(21)	12.9(7)
K(II)	0.2495(3)	0.2495(3)	0.2495(3)	0.938(30)	30.0(10)

Bond length/Å		Bond angles/°			
T(1)–O(1)	1.641(5)	O(1)–T(1)–O(2)	111.4(4)	T(1)–O(1)–T(1)	136.1(5)
T(1)–O(2)	1.645(5)	O(1)–T(1)–O(3)	110.6(4)	T(1)–O(2)–T(1)	149.8(5)
T(1)–O(3)	1.648(5)	O(1)–T(1)–O(4)	109.1(4)	T(1)–O(3)–T(1)	146.0(5)
T(1)–O(4)	1.656(5)	O(2)–T(1)–O(3)	107.9(4)	T(1)–O(4)–T(1)	142.4(5)
		O(2)–T(1)–O(4)	105.6(4)		
		O(3)–T(1)–O(4)	112.2(4)		

[a] R_{wp} = 6.98%, R_p = 5.13%, R_{exp} = 7.75%; a_0 = 24.8606(9) Å; U = 559.6; V = −360.1, W = 624.5, asym = 28.95. [b] Assuming an Si : Al ratio of 2.9 as determined by MAS NMR on T1 sites.

however, no evidence from the diffraction patterns for a lowering of symmetry from the space group used.

The distribution of aluminium within the framework will also affect the occupancies of the cation sites. However, it is difficult to quantify these changes as cation positions are very sensitive to the Si : Al ratio and to the residual water content. Our refinements give occupancies of sites I, I' and II which differ from published work on dehydrated potassium-exchanged zeolite Y.[12] For example, the number of potassium atoms per unit cell for zeolite K-Y is K(I) 8.1; K(I') 12.0; K(II) 32.0, and for sample ReAl-1 K(I) 5.9; K(I') 12.9; K(II) 30.0. These refined occupancies agree well with the known cation content from the Si : Al ratio. It is interesting to note that the preference for the K(I') site over the K(I) site is larger in the realuminated zeolite, and this may be reflecting the difference in the ordering of the Al in the hexagonal prisms between the starting and realuminated zeolite. However, the difference in the cation occupancies between the two materials might also arise from the small variation in Si : Al ratio and would be affected by any residual water content.

Powder neutron diffraction patterns of samples of realuminated zeolite Y are therefore consistent with the reinsertion of Al into the framework. Further work on the details of the realuminated materials on the basis of neutron and NMR results is in progress.

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