ChemComm

Detection of the 'invisible aluminium' and characterisation of the multiple aluminium environments in zeolite USY by high-field solid-state NMR

Colin A. Fyfe,*[a] J. L. Bretherton[a] and L. Y. Lam[b]

[a] *Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, V6T 1Z1, Canada. E-mail: fyfe@chem.ubc.ca, jerry@chem.ubc.ca*
[b] *Petrobras/Cenpes, Rio de Janeiro, Brazil.*

Received (in Irvine, CA, USA) 14th April 2000, Accepted 9th June 2000

The detection of all of the aluminium present in steamed zeolite H-Y catalysts by ^{27}Al MAS NMR at high field (18.8 T, 800 MHz for ^{1}H) is reported; further, it is shown that it is possible by ^{27}Al MAS and MQMAS measurements to clearly identify four separate aluminium environments characteristic of these materials and to unambiguously assign their coordinations.

The acid form of faujasite (zeolite H-Y) is converted to a very stable material by steam treatment at elevated temperatures, producing the universally used cracking catalyst 'ultrastable-Y' (USY). Early ^{29}Si MAS NMR studies documented the increase in the framework Si/Al ratio brought about by steaming.[1–4] ^{27}Al MAS NMR indicated that six-coordinate aluminium (Al$^{\mathrm{OCT}}$) is produced even during mild calcination and that substantial amounts of amorphous material can be generated by steaming,[1–8] characterised by a broad ^{27}Al resonance between those of the four-coordinate aluminium (Al$^{\mathrm{TET}}$, at ≈ 60 ppm) and Al$^{\mathrm{OCT}}$ (at ≈ 0 ppm). The nature of the species responsible for this signal intensity has been a matter of dispute for almost twenty years. Some workers have assigned the broad signal to a second, distorted tetrahedral species.[4,5a,8,9] More recently, various authors have shown that the chemical shift of the intensity maximum of the broad resonance corresponded to five-coordinate aluminium (Al$^{\mathrm{PENT}}$) and the broad resonance was attributed to this species.[5b,6,10,11] Despite considerable ongoing effort, there remains little overall agreement in the interpretation of ^{27}Al NMR data. Early studies also suffered from the problem of quantification of the ^{27}Al spectra:[3,4,7,9] Even using small pulse angles, some 30% of the aluminium known to be present could not be observed (the so-called 'invisible aluminium'). Therefore the nature of the aluminium and the related catalytic sites in USY are still poorly understood at the present time.

In the present work, we present preliminary results of an ultra-high field ^{27}Al MAS and MQMAS NMR investigation of a USY sample prepared from Na-Y by the conventional method of ammonium exchange followed by steam treatment at 600 °C, repeated twice. ^{27}Al NMR spectra were obtained at 208.43 MHz (18.8 T, 800 MHz ^{1}H) using a Varian INOVA Spectrometer. In this work we have been able to quantitatively observe all of the aluminium present and to identify four well defined aluminium environments.

The integrated intensities of the ^{27}Al single pulse MAS [Fig. 1(a) and (d)] and 90–180° spin–echo MAS NMR spectra of weighed samples were calibrated at both 104.26 MHz (9.4 T, 400 MHz for ^{1}H) and 208.43 MHz against spectra of weighed Na-Y and Na-A samples acquired under identical conditions. In line with previous work,[3,4,7,9] the data at 104.26 MHz not only fail to account for all of the aluminium present, but show considerable differences in intensity distributions between single pulse and echo experiments; the echo experiments detecting larger contributions from the broader resonances. However, there are no significant differences between the single pulse [Fig. 1(a)] and echo spectra at 18.8 T, where the integrated intensities of both spectra indicate that signal is observed from 100% of the aluminium present.

The MQMAS experiment introduced by Frydman and Harwood[12] (Fig. 2) correlates peaks in the MAS dimension (F2) to signals in the isotropic dimension (F1), with shifts in this dimension being a linear combination of isotropic chemical and

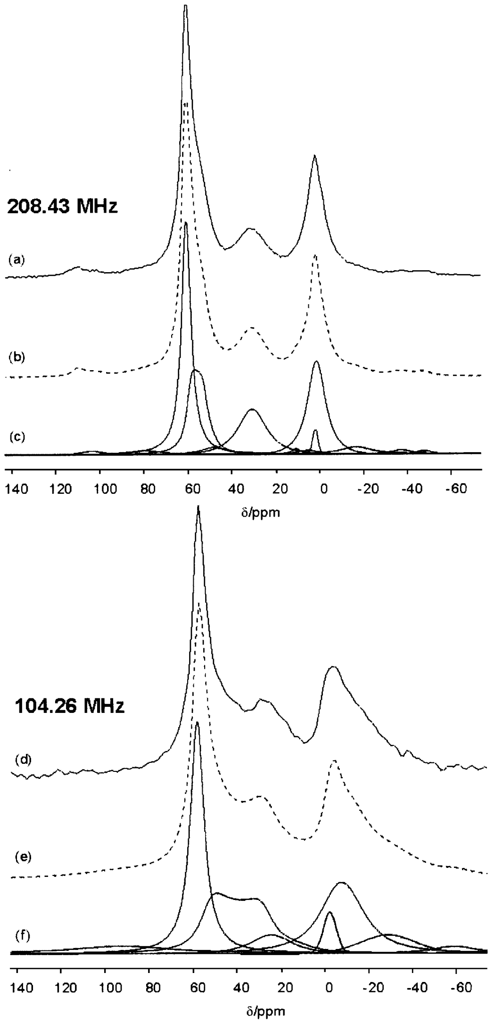

Fig. 1 (a) ^{27}Al single pulse MAS spectrum of USY at 208.43 MHz, recorded at a spinning speed of 10.2 kHz. (b) Simulation of (a). (c) Deconvolution of (b). (d) ^{27}Al single pulse MAS spectrum of USY at 104.26 MHz, recorded at a spinning speed of 9.8 kHz. (e) Simulation of (d). (f) Deconvolution of (e). Chemical shift is referenced to 1 M Al(NO$_3$)$_3$ aqueous solution. Spectral simulations and deconvolutions were made using 'Dmfit 98'.[15] Isotropic peaks are simulated by half-integer spin quadrupolar lineshapes (parameters given in Table 1) with superimposed exponential broadenings. Spinning sideband intensity is approximated by peaks with mixed Lorentzian and Gaussian character.

DOI: 10.1039/b003081n

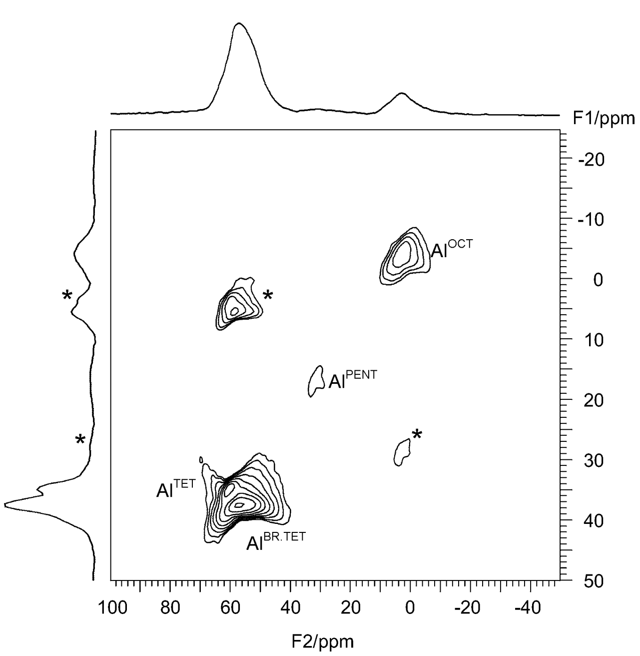

Fig. 2 ^{27}Al MQMAS spectrum of USY at 208.43 MHz, recorded at a spinning speed of 10.2 kHz. Chemical shift is referenced to 1 M $Al(NO_3)_3$ aqueous solution. Coherences were generated using a three-pulse, Rotationally Induced Adiabatic Transfer pulse sequence and selected with a 24-step phase cycle. A shearing transformation was performed after the first Fourier transform. Skyline projections along both axes are shown. * indicates spinning sidebands.

second order quadrupolar shifts. Using this technique, many of the problems caused by peak overlap in the MAS experiment are alleviated, allowing the coordinations to be clearly established.

Fig. 2 clearly shows four aluminium environments. At 61 ppm in F2 there is a sharp Al^{TET} resonance, whose F2 shift closely matches the sharp peak from the framework aluminium in Na-Y spectra. In addition there is clearly a separate and much broader $Al^{BR.TET}$ resonance with an intensity maximum at 57 ppm in F2. Upfield of the four-coordinate resonances are similarly broad Al^{PENT} and Al^{OCT} peaks, with intensity maxima in F2 at shifts typical of five- and six-coordinate aluminium species previously reported.[6,13,14]

Fig. 1(b) and (c) shows a simulation of the single pulse MAS spectrum [Fig. 1(a)] using the program 'Dmfit 98'.[15] The complete intensity profile is based on only the intensity from four peaks (and their spinning sidebands) corresponding to the signals observed in the MQMAS spectrum (Fig. 2). A small, sharp resonance in the octahedral region due to monomeric octahedral aluminium has been observed in the ^{27}Al NMR spectra of USY samples of lower Si/Al. For completeness, a similar peak is included in the simulated spectra of the sample used in this study [Fig. 1(c)], although it has no significant influence on the proportions of the different coordinations calculated to be present (Table 1).

The same parameters (Table 1) yield simulations of similar quality for the ^{27}Al MAS spectra of the same sample taken at 104.26 MHz [Fig. 1(d), (e)] and 156.38 MHz (14.4 T, 600 MHz for ^1H). They also reproduce the observed MQMAS isotropic (F1) shifts to within ±5 ppm at both 104.26 and 208.43 MHz, with the positions of the two tetrahedral peaks being predicted to within an accuracy of ±1 ppm. From these data it is apparent that the broad peak at $\approx$ 30 ppm observed in the spectrum at 104.26 MHz [Fig. 1(d)] has contributions from both broad tetrahedral and five-coordinate aluminium. Spectra at the two higher fields show that each of these account for $\approx$ 20% of the total spectral intensity.

Framework Si/Al ratios of the Na-Y starting material (calculated from ^{29}Si MAS NMR) and of the USY sample (calculated both by ^{29}Si NMR and IR) suggest that 33% of the aluminium remains in the USY framework following steaming.

Table 1 Summary of USY single pulse ^{27}Al MAS spectral simulation parameters[a]

	$\delta_{CS}{}^{b}$/ppm	Average $C_Q{}^{c}$/kHz	η_Q	% of total intensity[d]
Al^{TET}	60.7	360	0.53	33
$Al^{BR.TET}$	60.4	940	0.1	21
Al^{PENT}	32.2	578	0.1[e]	20
Al^{OCT}	3.2	492	0.1[e]	26

[a] Chemical shift and quadrupolar coupling distributions are accounted for by an exponential broadening function with a chemical shift component proportional to the magnetic field strength and a quadrupolar coupling component inversely proportional to the magnetic field. [b] Isotropic chemical shift. [c] Calculated to ±3% for 208.43 MHz spectrum using spinning sideband intensities approximated by lineshapes with mixed Lorenzian and Gaussian character. [d] $C_Q = 3e^2qQ/2I(2I - 1)\hbar$. [e] The parameter η_Q has a minimal effect on the simulated MAS spectrum [Fig. 1(b)].

This is in good agreement with the intensity ratios of the simulated spectrum [Fig. 1(c)] in which 33% of the overall intensity is contained within the Al^{TET} peak (Table 1) suggesting that all of the aluminium contained within the fully intact framework could be represented by the Al^{TET} peak at 61 ppm.

In summary, this study shows that high magnetic field strengths solve the problem of the "invisible aluminium" associated with USY materials and that these quantitative ^{27}Al MAS spectra consist of intensity from four distinct aluminium environments. A complete account of this work and its extension to related systems is currently in preparation. We believe that this represents the most complete and self-consistent investigation of the aluminium species present in USY materials to date. Further investigations of the exact nature of the framework and non-framework aluminium species in these steamed zeolite systems is also being carried out.

This research was performed in the Environmental Molecular Sciences Laboratory (a national scientific user facility sponsored by the U.S. DoE Office of Biological and Environmental Research) located at the Pacific Northwest National Laboratory, operated by Battelle for the DoE. We thank Dr David Hoyt and the EMSL staff for their kind assistance and for access to their facility, without which this work would not have been possible. C. A. F. acknowledges the financial assistance of the NSERC of Canada in the form of operating and equipment grants.

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