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Powder X-ray Diffraction Studies of Yttrium-Exchanged Zeolite-A

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Introduction: In order to develop new or to improve existing zeolite and zeolite-supported catalytic materials information needs to be gathered on the interactions between absorbed species and the zeolite framework. Diffraction methods are useful in determining long range order but it is often unclear from diffraction methods alone as to where the absorbed species binds to the framework. As the majority of these interactions involve the framework oxygen atoms, ^{17}O NMR would provide valuable information about the binding of absorbed species. However, little work has been carried out on ^{17}O NMR of aluminosilicates and no correlation between charge-balancing cation, amount of absorbed water or other absorbed molecular species and the observed ^{17}O chemical shift has been established. Work by Pingel et al [1] has shown that for hydrated Na-A there is a correlation between the isotropic chemical shift and the T-O-T bond angle. However, we have shown that this simple correlation breaks down for Ca^{2+} and Sr^{2+} ion-exchanged zeolite-A [2], where the presence of the divalent cation results in unoccupied cation sites and therefore 'bare' framework oxygen atoms. These 'bare' oxygen atoms have a higher ^{17}O chemical shift than has previously been observed. To test this hypothesis further samples containing trivalent cations (Y^{3+} and Sc^{3+}) were produced. However, to date there is no structural information on Y^{3+} exchanged zeolite-A and in order to interpret our NMR spectra we needed a structural model from which we could obtain the cation positions and the T-O-T angles.

Methods and Materials: Y^{3+} exchanged zeolite-A was prepared from as-synthesized Na-A using conventional ion-exchange methods. 10g of the zeolite was stirred overnight in a 0.1M solution of yttrium nitrate at 80°C . The mixture was then filtered, washed with deionised water and repeated a further 3 times. ^{23}Na MAS NMR showed that complete ion-exchange had not taken place and the actual formula was $\text{Y}_{3.5}\text{Na}_{1.5}(\text{Al}_{12}\text{Si}_{12}\text{O}_{48})\cdot x\text{H}_2\text{O}$. A small amount of the sample was packed into a 0.5mm quartz capillary for diffraction studies. The capillary was mounted on a goniometer and a line was attached to a vacuum pump, which would allow the sample to be heated under vacuum. A wavelength of 0.91976Å was used.

Results: Least-squares refinement was carried out using the GSAS suite of programs. The starting model used was that of the zeolite framework of dehydrated Zn-A [3] in the primitive space group Pm-3m with a lattice parameter of approximately 12Å. After refinement of the background (automated linear interpolation), lattice parameter, peak profiles and framework atomic positions difference Fourier maps were used to locate the extra-framework cations. Two sites were found, one located in the six-ring displaced along the body diagonal into the sodalite cage (0.20, 0.20, 0.20) and at the center of the sodalite cage (0, 0, 0). Inclusion of these sites as yttrium improved the fit. After further refinement of the atomic positions and fractional occupancies, the atom at the center of the sodalite cage was removed as the low fractional occupancy suggested that any electron density at this site was merely an artifact. Calculation of further Fourier maps could not locate a sodium site, therefore as yttrium and sodium have similar bond distances, sodium was placed on the same site as the yttrium. After further refinement of isotropic temperature factors and peak profile parameters the refinement converged with $\chi^2=5.437$, $R_{\text{wp}}=1.88\%$ and $R_p=1.40\%$. Examination of the bond distances however, indicates that there is a considerable amount of strain in the structure as two of the Si-O bonds distances are $\sim 0.2\text{Å}$ shorter than is usually observed in zeolite-A and also the lattice parameter of 11.789Å is one of the smallest reported for zeolite-A. Further work is currently being carried out to examine the effect of hydration level on the framework distortion.

Conclusions: Least-squares refinement has shown that in Y,Na-A both the yttrium and sodium cations occupy the same site in the six-ring, in a position similar to that found in Ca-A and Sr-A [4, 5].

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References: 1) U-T. Pingel, J-P. Amoureux, T. Anupold, F. Bauer, H. Ernst, C. Fernandez, D. Freude and A. Samoson, *Chem. Phys. Letts.*, **345**, **294**, 1998 2) J. E. Readman, N. Kim, M. Ziliox and C. P. Grey, *Chem Commun.*, in press, 3) L. B. McCusker and K. Seff, *J. Phys. Chem.*, **405** **85**, 1981, 4) J. J. Pluth and J. V. Smith, *J. Am. Chem. Soc.*, **1192**, **105**, 1983 5) J. J. Pluth and J. V. Smith, *J. Am. Chem. Soc.*, **6977**, **104**, 1982