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Solid State NMR Studies of Alkali Metal Loaded Zeolites

The regular intracrystalline channels and cavities of a dehydrated zeolite constitute a periodic array of cation-lined nanoscale spaces in which discrete chemical species - or alternatively, tiny fragments of bulk materials - may be assembled and arranged with a well defined geometry relative to one another. One advantage often sought by following this synthetic approach is an enhancement in either the stability or the desired properties of the 'guest' component through encapsulation within the aluminosilicate framework of the host zeolite. In contrast, alkali metal loaded zeolites exhibit a qualitatively different form of host - guest interaction. This interaction is sufficiently strong to result in the spontaneous ionization of the incoming guest metal atoms to form a wide range of inclusion compounds whose properties bear little resemblance if any to those of the parent alkali metals. The phenomenon of alkali metal inclusion has been likened to the 'dissolution' of alkali metals in the solid zeolite solvent. The electrons released in this process may be trapped in a rich variety of spatially localized chemical species, ranging from paramagnetic and diamagnetic cationic clusters such as Na_4^{3+} and Cs_4^{2+} to alkalide anions such as Na^- , or may be partly or wholly delocalized within the zeolite structure. The unique ability of the zeolite to organize these into regular arrays, whose geometry is imposed by the zeolite structure, has placed alkali metal loaded zeolites at the forefront of current research into materials design.

Although a considerable amount was known about the nature of the many paramagnetic species and structures formed within alkali metal zeolites, at the outset of this research programme there was a huge gap in our knowledge with respect to the diamagnetic species which are known to account for the greater part of metal incorporated. In particular, only a handful of NMR studies had been attempted. During the course of three years we recorded NMR spectra from more than fifty different compounds. A preliminary survey of the common zeolites, X, Y and A quickly established zeolite A (LTA) as the most promising zeolite host for these measurements. Through the success of the synthetic element in our programme we have been able to complete an extensive series of experiments on alkali metal loaded zeolite A samples, including several metal-rich compounds not previously synthesized. These measurements have demonstrated the power of solid state NMR, and in particular the use of the framework nuclei ^{27}Al and ^{29}Si , as a key probe of cluster formation and distribution in zeolite frameworks. In addition, with the help of ^{23}Na NMR experiments, we have established the probable location of Na^- in the LTA structure. Experiments on a range of sodium and potassium loaded sodalites have demonstrated the importance of the careful preparation and detailed characterization, through both NMR and diffraction methods, of materials produced. We have also fulfilled our promise to investigate loading with different metals and zeolites, resulting in the preparation of Cd/Cd-A, and a promising new series of compounds based on the RHO structure. In summary, the results obtained constitute the first substantial NMR examination of this important class of compounds and lay the groundwork for future NMR studies.