The Elucidation of Zeolite Structure by Solid State ^{29}Si Magic Angle Spinning NMR Spectroscopy

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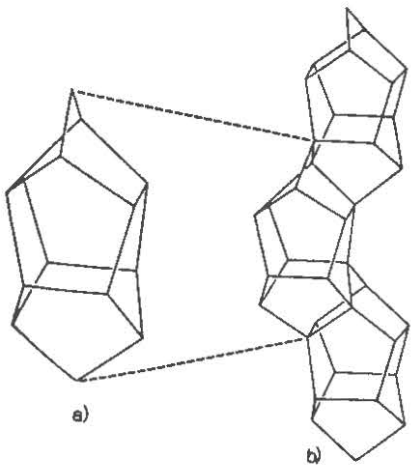
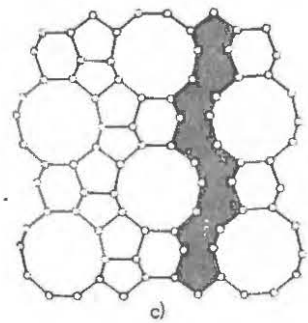
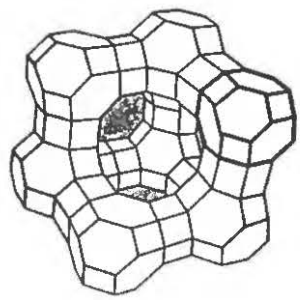
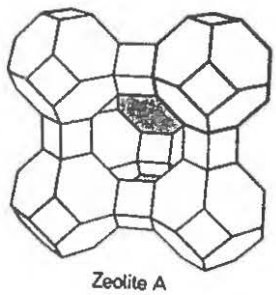
Zeolites are microporous, crystalline aluminosilicates of the general formula $M^{n+}_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot mH_2O$ which have networks of interconnected channels and cavities of molecular dimensions. Zeolites, because of their thermal stability and shape selectivity, are used extensively in industry for the cracking of petroleum and also for molecular sieving, ion exchange and highly selective catalysis. X-ray crystallography can determine the overall framework structure of many zeolites, but it cannot determine the Si,Al ordering within the tetrahedral framework because of the similar scattering powers of Si and Al, and also because of the difficulty in obtaining single crystals of adequate size and quality (this is especially true for synthetic zeolites). Structures of three representative zeolites are depicted in the figures below.







Faujasite (zeolites X and Y)



Zeolite A

a) pentasil subunit
b) pentasil subunits linked into chains
c) The ac structural projection of the ZSM-5 str.

Thus far the technique that has best elucidated the Si,Al distribution in zeolites is solid state magic angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR) [1,2]. In this technique the powder sample is spun rapidly (~3 kHz) about an axis that is oriented at an angle of 54.7° with respect to the direction of the magnetic field. At this so-called magic angle the line broadening due to dipole-dipole coupling and chemical shift anistropy is reduced to zero [3,4]. Optimization of synthetic and instrumental techniques on the highly siliceous ZSM-5 have led to resolution of a linewidth at half height of 5Hz which is the best thus far reported for a rigid crystalline solid [5].

Shortly after the first publication in 1978 of the ^{29}Si MAS-NMR of silicates, enough empirical evidence had been gathered to enable prediction of ^{29}Si chemical shifts based on $Si(OAl)_n(OSi)_{4-n}$ linkages and Si-O-T (T=Si or Al) bond angles [6,7]. Using this information combined with Loewenstein's rule which prohibits Al-O-Al linkages, the Si/Al ratio for a range of zeolites has been accurately determined [8,9]. The MAS-NMR technique also enables the facile study of the structural changes accompanying the activation of zeolites and the solid state or gas-solid reactions within these zeolites.[10] Studies of the changes in the spectra of ZSM-5 with changes in temperature and/or introduction of sorbates may lead to a detailed understanding of the structural changes which accompany these variables [11,12].

^{29}Si MAS-NMR is a valuable technique which provides an excellent complement to other techniques such as CPMAS NMR, IR, electron microscopy and Rietveld neutron diffraction profile analysis for examining the structure of zeolites. The prospect for additional work in this area is great because of the large variety of synthetic pathways, framework atoms and exchangeable cations available for preparing new zeolites.

References

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