

07.9-6 THE EFFECT OF TEMPERATURE AND SORBENTS ON THE STRUCTURE OF ZEOLITES ZSM-5, 11 and 39. G.T. Kokotailo, C.A. Fyfe, H. Strobl, G.J. Kennedy, G.C. Gobbi, C.T. Pasztor, G.E. Barlow and S. Bradley, University of Guelph, Guelph, Ont. N1G2W1, Canada

Zeolites are an important class of materials whose catalytic and sorption properties are dependent on their unique structural features, such as pore geometry, distribution of T-atoms in the framework, presence of strains and defects, distribution and mobility of adsorbed organic species and temperature.

The framework structures are perturbed by sorbents and temperature. Solid state MAS NMR is more sensitive in detecting changes in the local environment of the T-atoms. Thus, the combined use of x-ray diffraction and MAS NMR provides a more complete description of the framework structures of these materials.

The effect of temperature and organic molecule adsorption on the structure of several zeolites; ZSM-5, 11, and 39 will be discussed.

07.9-7 STRUCTURAL STUDIES OF SODIUM ZEOLITE X AT HIGH PRESSURES. By H.E. King, Jr. and J.M. Newsam, Exxon Research and Engineering Company, Route 22 East, Annandale, NJ 08801 U.S.A.

The technological importance of zeolites reflects to a large extent their unique crystal structures which are uniformly microporous on a molecular length scale. As a result of this microporosity, the zeolite's response to hydrostatic pressure is molecule size dependent. To be described are a series of X-ray diffraction experiments on several single crystals of sodium zeolite X,  $\text{Na}_{96}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 260\text{H}_2\text{O}$ , enclosed within diamond-anvil pressure cells. The bulk modulus for the hydrated material is about 25% larger than that for the dehydrated zeolite (using anhydrous methanol as the pressure-transmitting fluid). The results of full structure refinements for the hydrated crystals at a series of pressures up to 2.5 GPa show that the compression is concentrated within a small region of the structure into which  $\text{H}_2\text{O}$  apparently cannot penetrate. The Na-O bond lengths for site I change by ~10% in 2.5 GPa, whereas other distances in the structure vary only by ~1%. This non-uniform deformation suggests that molecules larger than  $\text{H}_2\text{O}$  will compress larger, and perhaps intuitively less rigid parts of the structure. Thus for methanol whose penetration into the sodalite cage is restricted, a smaller bulk modulus is predicted. Larger molecules should act on a still longer length scale with correspondingly smaller bulk moduli. The limit of this progression will occur when the molecular size is such as to prevent penetration into any of the micropores. The effect of pressure on the hydrated sodium zeolite X structure is seen to be similar to that of substitution of the sodium ion by a smaller and more polarizing cation. The high pressure Na-X structure is similar to that of Ni-Faujasite (Olson, *J. Phys. Chem.* 72, 4366 (1968)); although the effective "chemical pressure" generated by nickel substitution is slightly greater than that experienced by Na-X at 2.5 GPa.

07.9-8 CESIUM VAPOR REDUCES ALL OF THE SODIUM IONS IN ZEOLITE A. THE EXCESS CESIUM ATOMS SORBED CAN BE BAKED OUT AT 1000 °C. By N. H. Heo and K. Seff, Department of Chemistry, University of Hawaii, Honolulu, Hawaii, U.S.A.

Dehydrated Zeolite A,  $\text{Na}_{12}\text{Si}_{12}\text{Al}_{12}\text{O}_{48}$ , reacts with cesium vapor (about 0.1 torr) at 350 °C or above to give a black product. The crystals are black because excess cesium atoms have been accepted into the crystal structure to form the linear cationic clusters  $(\text{Cs}_4)^{3+}$ . These clusters are stable up to 850 °C but they can be decomposed at 1000 °C to give clear colorless  $\text{CsAlSiO}_2$  ( $\text{Cs}_{12}\text{Si}_{12}\text{Al}_{12}\text{O}_{48}$  per 12.3 Å cubic unit cell).

This redox method of ion-exchange, for which no conventional solvent is present, has allowed the preparation of this composition. It has been difficult to achieve because the large  $\text{Cs}^+$  ions must necessarily be unusually closely crowded together within the limited volume available in the zeolite cavities. It is to ameliorate this that excess atoms of cesium are retained by the zeolite, and that charged clusters have formed.

In this work, diffraction data sets have been relatively large (about 300 unique reflections with  $I > 3\sigma(I)$ ). Refinements have been carried out in both of the approximately appropriate space groups  $\text{Pm}\bar{3}\text{m}$  and  $\text{Fm}\bar{3}\text{c}$ . R values of the order of 0.05 have been achieved. The cesium ions in  $\text{Cs}_{12}\text{Si}_{12}\text{Al}_{12}\text{O}_{48}$  are located as follows: on threefold axes, two in the sodalite unit and seven in the large cavity; on fourfold axes, three at the centers of 8-rings. The cesium form of zeolite A has a substantially greater thermal stability than the sodium form (750 °C) or the potassium or calcium forms (830 °C).

07.9-9 STRUCTURE OF THE NONSTOICHIOMETRIC SOLID SOLUTIONS  $\text{Ba}_2\text{RE}_4[\text{Ba}_x+\text{RE}_{2/3-2/3x}]\text{Ti}_9\text{O}_{27}$  (RE=Nd, Sm).

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Compositions near  $\text{BaO}:\text{Sm}_2\text{O}_3:5\text{TiO}_2$  are useful as microwave filter devices because of high dielectric constant, very low dielectric loss, and zero temperature coefficient of the dielectric constant, although the  $\text{Nd}_2\text{O}_3$  analogs are more lossy. The crystal structure of the phase previously thought to be " $\text{Ba}_2\text{Nd}_4\text{Ti}_{10}\text{O}_{28}$ " was determined by single crystal x-ray diffraction analyses and refined by the neutron powder diffraction Rietveld technique. The crystal was obtained from a partially melted specimen of  $10\text{BaO}:15.5\text{Nd}_2\text{O}_3:74.5\text{TiO}_2$  and the structure analyses revealed the formula  $\text{Ba}_2\text{Nd}_4[\text{Ba}_x+\text{Nd}_{2/3-2/3x}]\text{Ti}_9\text{O}_{27}$  with  $x \approx 0$ . Solid state synthesis of compositions containing this formula show that a single phase solid solution exists with  $x$  varying from 1.0 to zero and the composition in equilibrium with  $\text{TiO}_2$  contains  $x$  slightly greater than 0.25. This composition with a small amount of rutile and  $\text{Nd}_4\text{Ti}_9\text{O}_{24}$  will always be present in a solid state preparation of the ideal composition  $\text{BaO}:\text{Nd}_2\text{O}_3:5\text{TiO}_2$ .

The structure of both end members of the  $[\text{Ba},\text{Nd}]^{+2}$  solid solution were refined from neutron powder data and the structure of the  $[\text{Sm}_{2/3}]$  end member was refined from synchrotron X-ray powder data. One half the unit cell of this phase ( $a \approx 2.3$ ,  $b \approx 12.2$ ,  $c \approx 3.84 \times 2 \text{Å}$ ,  $S.G. = \text{Pbam}$ ) consists of  $4\text{Ba}^{+2}$  in 10-fold coordination, eight  $\text{Nd}^{+3}$  in 8-fold coordination and  $2[\text{Ba}_x+(\text{Nd},\text{Sm})_{2/3-2/3x}]^{+2}$  also in 8-fold coordination with 18 octahedrally