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. Str-
obl, G.J. Kennedy, G.C. Gobbi, C.T. Pasztor,
G.E. Barlow and S. Bradley, University of Guel-
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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 def-
ects, distribution and mobility of absorbed
organic species and temperature.

The framework structures are perturbed by sorb-
ents and temperature. Solid state MAS NMR is
more sensitive in detecting changes in the loc-
al environment of the T-atoms. Thus, the comb-
ined use of x-ray diffraction and MAS NMR pro-
vides a more complete description of the frame-
work structures of these materials.

The effect of temperature and organic molecule
adsorption on the structure of several zeol-
ites; 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,
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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-
,$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}].260H_2O$, 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 compres-
sion is concentrated within a small region of the
structure into which H_2O 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 H_2O will compress larger, and per-
haps 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, $Na_{12}Si_{12}Al_{12}O_{48}$, 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 $(Cs_4)^{3+}$.
These clusters are stable up to 850 °C but they can be
decomposed at 1000 °C to give clear colorless $CsAlSiO_2$
($Cs_{12}Si_{12}Al_{12}O_{48}$ 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 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 $Pm3m$ and
$Fm3c$. R values of the order of 0.05 have been
achieved. The cesium ions in $Cs_{12}Si_{12}Al_{12}O_{48}$ 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 $Ba_2RE_4[Ba_x+RE_{2/3-2/3x}]Ti_9O_{27}(RE=Nd,Sm)$.
By R.S. Roth, F. Beach, A. Santoro and K. Davis,
National Bureau of Standards, Gaithersburg, MD. USA,
J.L. Soubeyroux, ILL, Grenoble, France and M. Zucchi,
Univ. of Milan, Italy.

Compositions near $BaO:Sm_2O_3:5TiO_2$ 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 Nd_2O_3 analogs are more lossy. The crystal
structure of the phase previously thought to be
"$Ba_2Nd_4Ti_{10}O_{28}$" 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
$10BaO:15.5Nd_2O_3:74.5TiO_2$ and the structure analyses
revealed the formula $Ba_2Nd_4[Ba_x+Nd_{2/3-2/3x}]Ti_9O_{27}$ with
$x\approx zero$. 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 TiO_2 contains x
slightly greater than 0.25. This composition with a
small amount of rutile and $Nd_4Ti_9O_{24}$ will always be
present in a solid state preparation of the ideal
composition $BaO:Nd_2O_3:5TiO_2$.

The structure of both end members of the $[Ba,Nd]^{+2}$
solid solution were refined from neutron powder data and
the structure of the $[Sm_{2/3}]$ end member was refined from
synchrotron X-ray powder data. One half the unit cell
of this phase ($a\approx 22.3, b\approx 12.2, c\approx 3.84 x 2Å$ S.G=Pbam)
consists of $4Ba^{+2}$ in 10-fold coordination, eight Nd^{+3}
in 8-fold coordination and $2[Ba_x+(Nd,Sm)_{2/3-2/3x}]^{+2}$
also in 8-fold coordination with 18 octahedrally