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-
ph, 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 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,
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-
,$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}].260H_2O$, 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 ($a \approx 22.3, b \approx 12.2, c \approx 3.84 \times 2$Å 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

coordinated Ti^{+4} ions. The structure can be described as being made up of chains of Ti^{+4} octahedra surrounding Ba^{+2} filled pentagonal tunnels, $[Ba_2Ti_8O_{20}]^{-4}$ alternating with chains of $[Nd_4TiO_7]^{+2}$ held together by the $[Ba_x(Nd,Sm)_{2/3-2/3x}]^{+2}$ ions. Alternately, it can be described as corner shared groups of perovskite-like molecules of $[Nd_4Ti_9O_{27}]^{-6}$ containing three kinds of tunnels, pentagonal Ba^{+2}, diamond shaped $[Ba_x(Nd,Sm)_{2/3-2/3x}]^{+2}$, and vacant triangular sites.

High resolution electron microscope lattice images taken down the c-axis show a "herring-bone weave" pattern, with angles near 60°. All postulated structures based on the 1:1:5 composition shown calculated lattice images with 90° angles. However, calculated images based on the present structure agree with the observed.

group I4). Barium atoms are surrounded by nine oxygen atoms achieving a very distorted polyhedron. The acetate ligands are involved in two kinds of coordination scheme as shown on the figure :
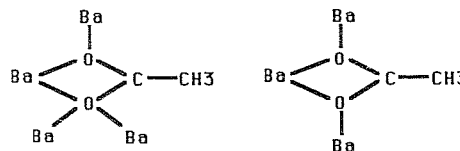
07.9-10 STRUCTURAL PRECURSORS IN THE SOL-GEL PROCESSING OF BaTiO₃.

I. Gautier-Luneau, A. Mosset and J. Galy, Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 TOULOUSE Cédex, France.

Sol-gel processed $BaTiO_3$ is prepared from barium acetate and tetraethoxy titanium(IV) in glacial acetic acid and ethanol. The so-obtained gel is dried and heat-treated until $BaTiO_3$ recrystallises at 650°C.

Three domains of temperature can be considered on the basis of a LAXS study of the amorphous solid (LAXS: Large Angle X-ray Scattering):

1) Below 250°C, there is no important change in the local order. This domain corresponds to a loss of solvents.

2) Between 250°C and 400°C, there is still a loss of solvents and the organic ligands begin to decompose.

3) Between 400°C and 600°C, the transformation of the amorphous solid is very fast, corresponding to the formation of new products. The modelling of the high temperature (600°C) solid shows that $BaTiO_3$ crystallises from a mixture of "native" barium carbonate and titanium dioxide.

The aim of the present study is to define the structural precursors in the room-temperature gel. Titanium might be present as an hexanuclear species $Ti_6 (\mu_3-O)_2 (\mu_2-O)_2 (\mu_2-OC_2H_5)_2 (\mu-CH_3COO)_8 (OC_2H_5)_6$, built up of two trinuclear oxo-centered units. This complex crystallises in the triclinic system (space group P1). The metal-oxygen-metal bridging scheme is highly asymmetrical. This asymmetry results in a great dispersion in the Ti-Ti distances and in the Ti-(μ_3-O) bonding(I. Gautier-Luneau et al., Z. Krist., in print).

Barium might be present as the $Ba(CH_3COO)_2$ acetate or a solvate like $Ba(CH_3COO)_2$. x CH_3COOH. y H_2O . The crystal structure of the first compound has been determined. It crystallises in the tetragonal system (space

07.9-11 $U_{14}Au_{51}$, A NEW PHASE IN THE SYSTEM U — Au.

F. Hulliger and A. Dommann, Laboratorium für Festkörperphysik, ETH-Hönggerberg, CH-8093 Zürich, Switzerland.

The published phase diagram of the system U-Au only shows two intermetallic compounds: U_2Au_3 and UAu_3. We synthesized the new phase $U_{14}Au_{51}$ and found its structure to be of the $GdAg_{3.6}$ type. Some speculations about this structure type will be offered.