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Chapter Six

MISCELLANEOUS SOLID-STATE COMPOUNDS

43. ZEOLITE MOLECULAR SIEVES

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Zeolites are three-dimensional, crystalline networks of AlO_4 and SiO_4 tetrahedra; a unit negative charge is associated with each AlO_4 tetrahedron in the framework. Their crystallization is often a nucleation-controlled process occurring from molecularly inhomogeneous, aqueous gels, and the particular framework structure that crystallizes can be strongly dependent on the cations present in these gels.[1]

Synthesis methods are described below for four very different but important zeolite structures, A,[2] Y,[3] tetramethylammonium (TMA) offretite,[4] and tetrapropylammonium (TPA) ZSM-5.[5,6] These four were selected because they span the composition range from 1:1 Si:Al to a potentially aluminum-free zeolite structure (A to ZSM-5). In addition, these syntheses provide examples of fundamental concepts in crystallization such as templating (TMA offretite and ZSM-5), low-temperature nucleation (Y), and variable reactant (silica) sources.

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The chemical description of a zeolite synthesis mixture requires special comment. It is conventional to present reaction mixtures as mole ratios of added ingredients:

$$\frac{SiO_2}{Al_2O_3}, \quad \frac{H_2O}{SiO_2}, \quad \frac{OH^-}{SiO_2}, \quad \frac{Na^+}{SiO_2}, \quad \frac{R}{SiO_2}$$

wherein R (if present) may be a component such as a quaternary ammonium cation or a potassium ion. By convention, moles of hydroxide are calculated by assuming, for example, that sodium silicate is a mixture of silica, sodium hydroxide, and water; that sodium aluminate is an analogous mixture but with alumina in place of silica; and that aluminum sulfate is a mixture of alumina, water, and sulfuric acid. In the descriptions given below, it is also recognized that alumina consumes 2 mol of hydroxide (i.e., acts as 2 mol of acid) on its incorporation into a zeolite framework as aluminate ion. Hydroxide:silica ratios are then calculated by subtracting moles of acid added from moles of hydroxide and then dividing by moles of silica present. Organics such as amines are never included in calculating $OH:SiO_2$ ratios.

Determination of purity in zeolites is a second area of concern. Elemental analysis is generally not a satisfactory criterion since almost all zeolite structures can exist in a range of compositions (i.e., of $SiO_2:Al_2O_3$ ratio). For example, the A structure has been crystallized with a $SiO_2:Al_2O_3$ ratio from 2 to 6;[7] at the other extreme, ZSM-5 has even been synthesized with essentially no aluminum.[6].

X-ray powder diffraction patterns are the most common measure of purity in zeolite samples. If the diffraction pattern shows no evidence for crystalline (or amorphous) contaminants, purity is then estimated by comparing intensities of reflections (at *d* spacings smaller than about 6 Å) with those of an authentic sample of the same composition and crystal size. Except for such large-scale commercial products as NaA and NaY, "authentic" samples are normally obtained by repeated and varied crystallization experiments.

A. ZEOLITE A[2]

$$2NaAlO_2 + 2(Na_2SiO_3 \cdot 9H_2O) \rightarrow Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.5H_2O + 4NaOH + 11.5H_2O$$

Procedure

Sodium aluminate (13.5 g, approximately 0.05 mol alumina and 0.07 mol Na_2O; commercial sodium aluminate contains about 40% Al_2O_3, 33% Na_2O and 27% H_2O) and sodium hydroxide (25 g, 0.62 mol) are dissolved in

300 mL of water in a magnetically stirred 600-mL beaker and brought to a boil. The aluminate solution is added, with vigorous stirring, to a hot solution of sodium metasilicate, $Na_2SiO_3 \cdot 9H_2O$ (14.2 g, 0.05 mol), in 200 mL water in a 1-L beaker, also equipped with a Teflon-coated magnetic stirrer. The entire mixture is heated with stirring at about 90° until the suspension will settle quickly when stirring is stopped (2–5 h). The suspension is then filtered hot and the solid washed repeatedly with water (four 100-mL portions) and dried in an oven at 110° to give about 7–8 g (80–90% yield based on SiO_2) of $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.1H_2O$.

Anal. Calcd.: Na_2O, 17.3; Al_2O_3, 28.5; SiO_2, 33.5. Found: Na_2O, 16.1; Al_2O_3, 28.8; SiO_2, 34.2. The purity of the sample is determined by inspection of its X-ray diffraction pattern.

Properties[7]

The product, NaA, is a white crystalline solid with a crystal density of 1.27 g/cm^3. Its crystals are normally 1-2μm in diameter and have cubic symmetry. A typically unit cell formula is $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27H_2O$; the sodium ions are readily exchanged in aqueous solution by cations such as calcium or potassium. In the sodium form, after dehydration at 350–400° *in vacuo*, zeolite A will sorb about 0.25 g H_2O per gram of ash (at room temperature, 4 torr), but it will not sorb hexane. In the dehydrated calcium form, 0.27 g H_2O per gram (4 torr) and 0.145 g hexane (10 torr) per gram are sorbed, but benzene is not. The X-ray diffraction pattern of NaA is as follows:

hkl	*d* (Å)	*I*/*I* (0)
100	12.29	100
110	8.71	69
111	7.11	35
210	5.51	35
211	5.03	2
220	4.36	6
221, 300	4.107	36
311	3.714	53
320	3.417	16
321	3.293	47
410	2.987	55

B. ZEOLITE Y[3]

$$2NaAlO_2 + 5SiO_2 + xH_2O \rightarrow Na_2O \cdot Al_2O_3 \cdot 5SiO_2 \cdot xH_2O$$

Procedure

A solution of 13.5 g sodium aluminate (0.05 mol alumina and 0.07 mol Na_2O) and 10 g sodium hydroxide (0.25 mol) in 70 g water is prepared in a 200-mL beaker and added, with vigorous magnetic stirring, to 100 g 30% silica sol (0.5 mole SiO_2; commercial colloidal silica suspensions typically contain 30% SiO_2 together with 0.1–0.5% Na_2O, as stabilizer) in a 250-mL polypropylene bottle. The reaction mixture, which is defined by the following mole ratios of components:

$$\frac{SiO_2}{Al_2O_3} = 10 \qquad \frac{H_2O}{SiO_2} = 16 \qquad \frac{OH^-}{SiO_2} = 0.6 \qquad \frac{Na^+}{SiO_2} = 0.8$$

is then set aside to age. After 24–48 h at room temperature, the bottle is placed in a steam chest at about 95°. After 48–72 h, daily samples of the solid in the bottom of the bottle are taken, filtered, washed, dried, and analyzed by X-ray diffraction for crystallinity. Special care should be taken during sampling to avoid mixing the sample or inadvertently seeding the mixture. When the diffraction pattern reaches a limiting intensity, the hot mixture is removed from the steam chest and filtered and the solid washed with water (four times 100 mL) and dried at 100°. About 30 g of NaY (50–60% based on SiO_2) is obtained, with an approximate molar composition of $Na_2O \cdot Al_2O_3 \cdot 5.3SiO_2 \cdot 5H_2O$.

Anal. Calcd.: Na_2O, 10.5; Al_2O_3, 17.3; SiO_2, 53.9. Found: Na_2O, 10.9; Al_2O_3, 17.2; SiO_2, 53.4. A final X-ray diffraction pattern is taken for inspection and for comparison with that of an authentic sample of NaY.

Properties[7]

The NaY produced is a white crystalline solid with a crystal density of 1.27 g/cm^3. Its crystals are usually smaller than 1 µm and have cubic symmetry. A typical unit-cell formula would be $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}] \cdot 250H_2O$, about 70% of the sodium ions being readily exchanged by cations such as ammonium ion. The remainder can be exchanged with persistence. Ammonia can be removed from the resultant NH_4Y by heating to about 450°. In the sodium form, after dehydration at 350–400° *in vacuo*, zeolite Y will sorb about 25% of its weight in water (1 torr, 25°), about 19% in hexane (10 torr), and about 25% in benzene (10 torr). The X-ray diffraction pattern of NaY is as follows:

hkl	*d* (Å)	*I*/*I* (0)
111	14.29	100
220	8.75	9
311	7.46	24
331	5.68	44
333, 511	4.76	23
440	4.38	35
620	3.91	12
533	3.775	47
444	3.573	4
711, 551	3.466	9
642	3.308	37
731, 553	3.222	8
733	3.024	16

C. TMA OFFRETITE[4]

Procedure

A solution of 5.2 g sodium aluminate (0.02 mol alumina and 0.03 Na_2O), 14.6 g NaOH (0.36 mol), and 8.2 g KOH (0.15 mol) in 76 g water is prepared in a 200-mL beaker equipped with a magnetic stirrer. To this is added 11.0 g 50% tetramethylammonium chloride (0.05 mol), and the resultant solution is poured quickly into 112 g 30% silica sol (0.56 mol SiO_2) in a 250-mL polypropylene bottle. The mixture, which has the following composition

$$\frac{SiO_2}{Al_2O_3} = 27 \qquad \frac{H_2O}{SiO_2} = 16 \qquad \frac{OH^-}{SiO_2} = 1.0 \qquad \frac{Na^-}{SiO_2} = 0.75$$

$$\frac{K^+}{SiO_2} = 0.27 \qquad \frac{TMA^+}{SiO_2} = 0.09$$

is vigorously shaken and placed in a steam chest at 95° to crystallize. After 48–72 h, daily samples of the solid in the bottom of the bottle are taken, filtered out, washed, dried, and analyzed by X-ray diffraction for crystallinity. When the diffraction pattern reached a limiting intensity, the mixture is removed from the steam chest and filtered, and the solid washed with water (four times 100 mL) and dried at 100°. About 16 g of TMA offretite (25–30% based on SiO_2) is obtained, with an approximate molar composition of 0.3 $(TMA)_2O \cdot 0.5K_2O \cdot 0.4Na_2O \cdot Al_2O_2 \cdot 7.7SiO_2 \cdot 7.1H_2O$.

Anal. Calcd.: Na_2O, 3.1; N, 1.0; C, 3.5; K_2O, 5.8; Al_2O_3, 12.5; SiO_2, 56.9. Found: Na_2O, 2.9; N, 1.0; C, 3.6; K_2O, 5.9; Al_2O_3, 12.6; SiO_2, 56.9. A final X-ray diffraction pattern is taken for inspection and for comparison with that of an authentic sample of TMA offretite.

Properties[7]

Tetramethylammonium offretite has a crystal density of 1.55 g/cm^3. Its crystals are usually oval agglomerates, about 0.3 × 1.5 μm in size, with hexagonal symmetry. A typical unit-cell formula would be $TMA \cdot 2K \cdot Na[(AlO_2)_4(SiO_2)_{14}] \cdot 7H_2O$, the TMA (and a portion of the potassium ions) being trapped within gmelinite-and ε-cages, respectively, and therefore not readily exchanged by sodium or ammonium ions. In the as-synthesized form, after calcination to 500° in air, this zeolite will sorb about 12% of its weight in butane and 7% isobutane (100 torr). Its X-ray diffraction pattern is as follows:

hkl	*d* (Å)	*I*/*I*(0)
100	11.45	100
001	7.54	16.5
110	6.63	55.2
101	6.30	9.9
200	5.74	15.0
201	4.57	26.5
210	4.34	43.3
211, 002	3.76	89.2
102	3.59	43.0
220	3.31	18.6
202	3.15	17.4

In particular, a pure sample of TMA offretite will not show reflections at $d = 9.2$, 5.34, and 4.16 Å, which are the "odd-l" lines of erionite.

D. ZSM-5

Procedure

A solution of 0.9 g $NaAlO_2$ (0.0035 mol alumina, 0.01 mol NaOH) and 5.9 g NaOH (0.15 mol) in 50 g water is prepared in a 200-mL beaker equipped with magnetic stirrer and labeled "solution A." In a second beaker, a solution ("B") is prepared by adding 8.0 g tetrapropylammonium bromide (0.03 mol) to a stirred mixture of 6.2 g of 96% H_2SO_4 (0.12 mol) and 100 g H_2O. Solutions A and B are poured simultaneously into a solution of 60 g 30% silica sol (0.3 mol SiO_2, 0.003 mol Na_2O, and 50 g H_2O in a 250-mL polypropylene bottle). The bottle is immediately capped and vigorously shaken to form a gel with the composition

$$\frac{SiO_2}{Al_2O_3} = 85 \qquad \frac{H_2O}{SiO_2} = 45 \qquad \frac{OH^-}{SiO_2} = 0.1 \qquad \frac{Na^+}{SiO_2} = 0.5 \qquad \frac{TPA^+}{SiO_2} = 0.1$$

It is then placed in a steam chest at 95° to crystallize. After 10–14 days, periodic samples of the solid in the bottom of the bottle are taken, filtered out, washed, dried, and analyzed by X-ray diffraction for crystallinity. When the diffraction pattern reaches a limiting intensity, the mixture is removed from the steam chest and filtered, and the solid washed with water (four times 100 mL) and dried at 110°. (Crystallization times can be reduced to 1 day or less when conducted in a stirred autoclave at higher temperatures; at 140–180°, for example.) About 19 g of ZSM-5 (85% yield based on SiO_2) is obtained with a molar composition of $1.8(TPA)_2O \cdot 1.2Na_2O \cdot 1.3Al_2O_3 \cdot OSi_2 \cdot 7H_2O$.

Anal. Calcd.: Na_2O, 1.1; N, 0.7; C, 7.4; Al_2O_3, 1.9; SiO_2, 85.3. Found: Na_2O, 1.1; N, 0.7; C, 8.0; Al_2O_3, 1.9; SiO_2, 84.6 A final X-ray diffraction pattern is taken for inspection and for comparison with that of an authentic sample of ZSM-5.

Properties[5,6,8,9]

ZSM-5 has a crystal density of 1.77 g/cm^3. Its crystals have orthorhombic symmetry, as synthesized, and can vary widely in size. Compositionally ZSM-5 is unusual, in comparison with the examples given above, in that it can be prepared in the absence of aluminum. Organics can be removed from ZSM-5 samples by careful oxidative calcination at about 500°. Alkali-metal cations, if present, can be exchanged by ammonium ion, for example, to produce NH_4ZSM-5. Calcined samples of NH_4ZSM-5 will sorb about 11%hexane (25°, 20 torr). The X-ray diffraction pattern of ZSM-5 is characterized by the following significant lines:

d (Å)	Relative Intensity
11.1	S
10.0	S
7.4	W
7.1	W
6.3	W
6.04	W
5.97	
5.56	W
5.01	W
4.60	W
4.25	W
3.85	VS
3.71	S
3.04	W
2.99	W

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44. SUBSTITUTED β-ALUMINAS

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β-Alumina has the empirical formula $Na_2O \cdot 11Al_2O_3$. In reality the compound is massively defective and contains considerably more (~ 25%) Na_2O

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