

AEI

AlPO<sub>4</sub>-18

Al(50), P(50)

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**Contributed by** Rune Wendelbo

**Verified by** S. Kaliaguine, by E. Dumitriu, and by C. Round

**Type Material:** [Al<sub>24</sub>P<sub>24</sub>O<sub>96</sub>]

**Method:** S. T. Wilson, E. M. Flanigen [1, 2]

**Batch Composition:** Al<sub>2</sub>O<sub>3</sub> : P<sub>2</sub>O<sub>5</sub> : (TEA)<sub>2</sub>O : 60 H<sub>2</sub>O : 6 i-C<sub>3</sub>H<sub>7</sub>OH (TEA = tetraethylammonium)

**Source Materials**

distilled water

phosphoric acid (85%)

aluminum isopropoxide (Jansen, 98+ %)

tetraethylammonium hydroxide (Aldrich, 40% (TEA)OH)<sup>a</sup>

**Batch Preparation** (for 15.8 g dry product)

- (1) [36.3 g water + 15.0 g phosphoric acid + 27.2 g aluminum isopropoxide], add diluted phosphoric acid to the aluminum isopropoxide in a 250 mL polypropylene bottle and shake vigorously for one minute
- (2) [(1) + 49 g (TEA)OH solution], shake to produce a uniform gel. Transfer to the autoclave

**Crystallization**

Vessel: 200 mL Teflon-lined stainless steel autoclave (Berghof)

Incubation: 6 hours at room temperature

Time: 69 hours<sup>b</sup>

Temperature: 215°C<sup>b</sup>

Agitation: gentle<sup>c</sup>

**Product Recovery**

- (1) Recover solid product by centrifugation<sup>d</sup>
- (2) Wash once with distilled water; recover product by centrifugation<sup>d</sup>
- (3) Dry overnight at 100°C
- (4) Calcine for 4 h at 550°C in flowing dry air
- (5) Store under nitrogen. Yield near 100%

**Product Characterization**

XRD: fully crystalline AEI; competing phase: AFI<sup>e</sup>

Elemental Analysis: 24.26% Al, 20.59% P, 0.20% Si<sup>f</sup>

Crystal size and habit: square platelets 0.2-8 μm x 0.1 μm thick<sup>g</sup>

**References**

- [1] S. T. Wilson, E. M. Flanigen, US Patent 4 310 440 (1982)
- [2] R. Wendelbo, D. Akporiaye, A. Andersen, I. M. Dahl, H. B. Mostad, Appl. Catal. A: General 142 (1996) L197

## Notes

- a. This product is now traded as 35% (TEA)OH solution. I would use the same volume of the 35% solution, since the synthesis is not sensitive to a variation of the template concentration of this order. It is important that the (TEA)OH source have minimum  $K^+$  and  $Na^+$  concentrations.
- b. The synthesis temperature can probably be reduced to 200°C and the time reduced substantially, but this has not been tested.
- c. Standing autoclaves in a heated block on a "shaking table" rotated at about 60 rpm.
- d. Filtration leads to loss of fine material or goes very slowly depending on the filter.
- e. AFI appears as a contaminant.
- f. A Cameca microprobe was used averaging 5 points each 50 x 50  $\mu m$ . The analysis was done on "as synthesized material."
- g. Micropore volume 0.28 mL/g (by  $N_2$  adsorption).

AEI

SAPO-18<sup>a</sup>

Al(49), P(42), Si(9)

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**Contributed by** Jiesheng Chen and John M. Thomas

**Verified by** S. Schunk, by J. López Nieto, and by D. Akolekar

**Type Material:**  $[\text{Al}_{24}\text{P}_{20}\text{Si}_4\text{O}_{96}] : \text{mR} : \text{nH}_2\text{O}$  (R = N,N-diisopropylethylamine)<sup>b</sup>

**Method:** J. Chen, P. A. Wright, J. M. Thomas, S. Natarajan, L. Marchese, S. M. Bradley, G. Sankar, C. R. A. Catlow [1]

**Batch Composition:** 0.40 SiO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub> : 0.90 P<sub>2</sub>O<sub>5</sub> : 50 H<sub>2</sub>O : 1.60 R

**Source Materials**

distilled water

phosphoric acid (Aldrich, 85% H<sub>3</sub>PO<sub>4</sub>)

aluminum hydroxide hydrate (Aldrich, ca. 55% Al<sub>2</sub>O<sub>3</sub>)

Aerosil (Degussa, 99% SiO<sub>2</sub>)

N,N-diisopropylethylamine (Aldrich, 99% C<sub>8</sub>H<sub>19</sub>N)

**Batch Preparation (for ~2 g product)**

- (1) [19.4 g water + 3.48 g phosphoric acid + 4.64 g aluminum hydroxide hydrate], stir until homogeneous
- (2) [(1) + 0.60 g Aerosil], stir until homogeneous
- (3) [(2) + 5.10 g N,N-diisopropylethylamine], stir until homogeneous

**Crystallization**

Vessel: PTFE-lined stainless steel autoclave

Temperature: 160°C

Time: 8 days

Agitation: none

**Product Recovery**

- (1) Filter; wash with distilled water
- (2) Dry at 50°C in air
- (3) Yield: 60% based on Al<sub>2</sub>O<sub>3</sub>

**Product Characterization**

XRD: c Characteristic strong reflections at  $d = 9.1$  and  $5.1 \text{ \AA}$  for as-synthesized materials; competing phase is AFI when  $\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3 > 1.2$  or  $\text{R}/\text{P}_2\text{O}_5 < 1.2$

Elemental Analysis (exclusive of R and H<sub>2</sub>O): 0.35 SiO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub> : 0.87 P<sub>2</sub>O<sub>5</sub>

Crystal Size and Habit: small cubes less than  $2 \mu\text{m}$  in diameter <sup>d</sup>

**References**

- [1] J. Chen, P. A. Wright, J. M. Thomas, S. Natarajan, L. Marchese, S. M. Bradley, G. Sankar, C. R. A. Catlow, *J. Phys. Chem.* 98 (1994) 10216
- [2] A. Simmen, L. B. McCusker, Ch. Baerlocher, W. M. Meier, *Zeolites* 11 (1991) 654

- [3] S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan, E. M. Flanigen, J. Am. Chem. Soc. 104 (1982) 1146
- [4] H. He, J. Klinowski, J. Phys. Chem. 97 (1993) 10385

### Notes

- a. Preparation for SAPO-18 only is given. For AlPO<sub>4</sub>-18 [2], no Aerosil is added, and the amounts of reactants should be changed to give gel composition Al<sub>2</sub>O<sub>3</sub> : P<sub>2</sub>O<sub>5</sub> : 50 H<sub>2</sub>O : 1.80 R
- b. AlPO<sub>4</sub>-18 was originally prepared by using tetraethylammonium hydroxide (TEA-OH) as the template in the presence of HCl. It is not possible to prepare SAPO-18 using (TEA)-OH. [3, 4]
- c. The XRD patterns of the AEI materials are very sensitive to water molecules present in the channels of the structure.
- d. Crystals are typically cubic; crystal size increases to a certain degree as the amount of silica in the reaction mixture increases.

AEI

SAPO-18<sup>a</sup>

P(50), Al(48), Si(02)

Contributed by Rune Wendelbo

Verified by E. Dumitriu and by C. Round

Type Material:  $[\text{Al}_{23.2}\text{Si}_{0.8}\text{P}_{24}\text{O}_{96}]^{\text{b}}$ 

Method: R. Wendelbo, D. Akporiaye, A. Andersen, I. M. Dahl, H. B. Mostad [1]

Batch Composition:  $\text{Al}_2\text{O}_3 : 0.98 \text{ P}_2\text{O}_5 : 0.015 \text{ HCl} : 0.075 \text{ SiO}_2 : (\text{TEA})_2\text{O} : 70 \text{ H}_2\text{O} : 2.8 \text{ i-C}_3\text{H}_7\text{OH}^{\text{c}}$   
(TEA = tetraethylammonium)**Source Materials**

distilled water  
 aluminum isopropoxide (Jansen, 98+%)  
 phosphoric acid (85%)  
 hydrochloric acid (37%)  
 silica sol (DuPont Ludox LS-30, 30%  $\text{SiO}_2$ )  
 tetraethylammonium hydroxide (Aldrich, 40 % (TEA)OH)<sup>d</sup>

**Batch Preparation:** (for 13.8 g dry product)

- (1) [108 g water + 81.6 g aluminum isopropoxide], mix in a one liter poly-propylene bottle and shake for 1 minute
- (2) [1) + 45 g phosphoric acid], shake for 1 minute then cool under running tap water
- (3) [(2) + 0.6 g hydrochloric acid], shake bottle<sup>e</sup>
- (4) [(3) + 3.0 g silica sol], shake bottle. filter gel for 10 minutes (water suction).  
About 100 g filtrate is removed and discarded. Transfer one-third of filter cake gel to a 250 mL plastic bottle
- (5) [One-third (4) + 49 g tetraethylammonium hydroxide solution], shake

**Crystallization**

Vessel: 200 mL stainless steel, Teflon-lined autoclave (Berghof)  
 Incubation: 12 hours at room temperature  
 Time: 120 hours  
 Temp: 215°C  
 Agitation: gentle<sup>f</sup>

**Product Recovery**

- (1) Recover solid product by centrifugation.<sup>g</sup>
- (2) Wash once with distilled water; recover product by centrifugation<sup>g</sup>
- (3) Dry overnight at 100°C
- (4) Calcine for 4 hours at 550°C in flowing, dry air
- (5) Store under nitrogen. Yield near 100%

**Product Characterization**

XRD: fully crystalline AEI; competing phase AFI and CHA<sup>h</sup>  
 Elemental Analyses: 0.84% Si, 19.9% Al, 26.6% P<sup>i</sup>  
 Crystal size and habit: square platelets, 0.1-2.0  $\mu\text{m}$  x 0.1  $\mu\text{m}$  thick<sup>j</sup>

## Reference

- [1] R. Wendelbo, D. Akporiaye, A. Andersen, I. M Dahl, H. B. Mostad, Appl. Catal. A: General 142 (1996) L197

## Notes

- a. Mg APO-18 and Zn APO-18 were synthesized like SAPO-18 by using Mg and Zn nitrates in place of colloidal silica in equivalent amounts on a molar basis. The Mg and Zn nitrates were dissolved in the phosphoric acid 20 m prior to mixing with the other reagents. Products showed 0.14 Mg and 0.10 Zn (mmol/g).
- b. Based on Si content; excess P is unexplained.
- c. It is assumed that water, HCl and isopropanol are lost in equal proportions and no other components are lost in gel filtration.
- d. This product is now traded as 35% (TEA)OH solution. I would use the same volume of the 35% solution, since the synthesis is not sensitive to a variation of the template concentration of this order. It is important that the (TEA)OH source have minimum  $K^+$  and  $Na^+$  concentrations.
- e. Addition of HCl has previously been found to allow better control of Si substitution in SAPO-34 and has been used in this case for the same purpose.
- f. Standing autoclaves in a heated block on a "shaking table" rotated at about 60 rpm.
- g. Filtration leads to loss of fine material or goes very slowly depending on the filter.
- h. At lower water content, AFI appears as a contaminant; at higher water content, CHA appears.
- i. Analysis by XRF.
- j. Micropore volume 0.25 mL/g (by  $N_2$  sorption)

AEL

AlPO<sub>4</sub>-11

Al(50), P(50)

Contributed by Kristin Vinje

Verified by J. Campelo and by J. Kornatowski

Type Material: [Al<sub>20</sub>P<sub>20</sub>O<sub>80</sub>] : wH<sub>2</sub>O

Method: R. Szostak, B. Duncan, R. Aiello, A. Nastro, K. Vinje, K. P. Lillerud [1]

Batch Composition: 1.0 Al<sub>2</sub>O<sub>3</sub> : 1.25 P<sub>2</sub>O<sub>5</sub> : 2.37 DPA : 1.80 HF : 156 H<sub>2</sub>O (DPA = di-n-propylamine)

#### Source Materials

deionized water

aluminum hydroxide (Aldrich 23918-6, 50-57.5% Al<sub>2</sub>O<sub>3</sub>)<sup>a</sup>

phosphoric acid (Fisher, 85% H<sub>3</sub>PO<sub>4</sub>)

di-n-propylamine (DPA)(Kodak, ~ 100%)

hydrofluoric acid (Fisher, 48% HF)

#### Batch Preparation (for 4 g dry product)

- (1) [20.0 g water + 7.8 g aluminum hydroxide] stir well
- (2) [(1) + 14.4 g phosphoric acid]; add acid dropwise and stir until effervescence is completed
- (3) [(2) + 100 g water]; dilute and stir
- (4) [(3) + 12.0 g DPA]; add amine dropwise and stir
- (5) [(4) + 10.0 g water 3.75 g hydrofluoric acid]; stir for two hours <sup>b</sup>

#### Crystallization

Vessel: Teflon-lined steel autoclave

Temperature: 145°C

Time: 18 hours

Agitation: none

#### Product Recovery

- (1) Cool autoclave rapidly.
- (2) Filter immediately to recover solids and wash.
- (3) Dry overnight at room temperature.
- (4) Yield: ~ 70% <sup>c</sup>

#### Product Characterization

XRD: AEL only crystalline phase: no other crystalline phases or amorphous material detected

Elemental Analysis: (atomic %): 15.5 Al, 13.9 P, Al/P = 1.1<sup>d</sup>

Crystal Habit: Bow-tie crystals constructed of long needles) or needles  
~1 mm long)<sup>c</sup>

#### Reference

- [1] R. Szostak, B. Duncan, R. Aiello, A. Nastro, K. Vinje, K. P. Lillerud, in Synthesis of Microporous Materials, M. Occelli, H. Robson, (eds.), Van Nostrand Reinhold, New York (1992), pp 240-7

## Notes

- a. Consistently good results have been obtained using the Aldrich Al-source, but difficulties were encountered using other aluminum sources.
- b. Should produce a clear solution; initial pH = 5.5, final pH = 6.0
- c. After 18 hours the yield increases to 50-75% at the expense of the crystal size with smaller 5 to 10  $\mu\text{m}$  crystals resulting.
- d. Determined on a CAMECA SX 100 Microbeam



AFI

 $\text{AlPO}_4\text{-5}$  $\text{Al(50), P(50)}$ 

Contributed by Juergen Caro and Irina Girus

Verified by S. Cresswell, by B. Weckhuysen, and by G. Schulz-Ekloff

Type Material:  $\text{Al}_{12}\text{P}_{12}\text{O}_{48}$

Method: I. Girus, K. Jancke, R. Vetter, J. Richter-Mendau, J. Caro [1]<sup>a</sup>

Batch Composition:  $\text{Al}_2\text{O}_3$  : 1.3  $\text{P}_2\text{O}_5$  : 1.6 TEA : 1.3 HF : 425  $\text{H}_2\text{O}$  : 6  $\text{C}_3\text{H}_7\text{OH}$  <sup>b</sup>

#### Source Materials

- deionized water
- orthophosphoric acid (Merck, 85 wt%  $\text{H}_3\text{PO}_4$ )
- triethylamine (TriEA), (Riedel de Häen,  $(\text{C}_2\text{H}_5)_3\text{N}$ )<sup>c</sup>
- aluminum triisopropylate (Merck,  $\text{Al}(\text{C}_3\text{H}_7\text{O})_3$ )<sup>d</sup>
- hydrofluoric acid (Merck, 40 wt% HF in water)

#### Batch Preparation (for ~ 3 g product)

- (1) [7 g water + 3.84 g of phosphoric acid], mix
- (2) [(1) + 2.07 g TriEA], add TriEA dropwise and mix
- (3) [(2) + 5.23 g aluminum isopropylate], add in small amounts at 0°C with intense stirring then stir the mixture at room temperature for 2 hours
- (4) [(0.83 g hydrofluoric acid + 89.2 g water], mix
- (5) [(3) + (4)], stir for 2 hours

#### Crystallization

- Vessel: 150 mL Teflon-lined steel autoclaves<sup>e</sup>
- Temperature: 180°C (preheated oven)
- Time: 6 hours <sup>f</sup>
- Agitation: none

#### Product Recovery

- (1) Decant the supernatant liquid and discard
- (2) Wash the precipitate four times with 100 mL deionized water
- (3) Calcine in air at 600°C until product is colorless (white)<sup>g</sup>
- (4) Yield: near 100% on  $\text{Al}_2\text{O}_3$

#### Product Characterization

- XRD: Characteristic strong reflections at  $d = 11.90, 5.93, 4.48, 4.24, 3.96$ , and  $3.42\text{\AA}$ ; competing phases (if present): tridymite
- Elemental Analysis: 42.9 wt%  $\text{P}_2\text{O}_5$ , 30.5 wt%  $\text{Al}_2\text{O}_3$  ( $\text{P}/\text{Al} = 1.00$ )
- Crystal size and Habit: Hexagonal columns up to  $50\text{ }\mu\text{m}$  <sup>h</sup>

## References

- [1] I. Girnus, K. Jancke, R. Vetter, J. Richter-Mendau, J. Caro, *Zeolites* 15 (1995) 33
- [2] S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan, E. M. Flanigen, *J. Am. Chem. Soc.* 104 (1982) 1146
- [3] J. M. Bennett, J. P. Cohen, E. M. Flanigen, J. J. Pluth, J. V. Smith, *ACS Symp. Series* 218, Am. Chem. Soc., Washington, D. C., 1983, p. 109
- [4] S. Qiu, W. Pang, H. Kessler, J.-L. Guth, *Zeolites* 9 (1989) 440
- [5] A. S. T. Chiang, C.-K. Lee, Z. H. Chang, *Zeolites* 11 (1991) 380
- [6] G. Finger, J. Richter-Mendau, M. Bülow, J. Kornatowski, *Zeolites* 11 (1991) 443
- [7] D. Demuth, G. D. Stucky, K. K. Unger, F. Schüth, *Micropor. Mater.* 3 (1994) 473
- [8] I. Girnus, K. Hoffmann, F. Marlow, G. Döring, J. Caro, *Micropor. Mater.* 2 (1994) 537

## Notes

- a. The decisive difference of this synthesis from that of Wilson and Flanigen [2,3] is the use of HF as proposed by Kessler and Guth [4]. However, crystallization proceeds also in the absence of HF, but less favorably.
- b. Because Al triisopropylate is used as Al source, a fixed amount of 3 isopropyl alcohol molecules per Al is always present in the gel.
- c. The  $\text{AlPO}_4\text{-5}$  phase can be prepared with numerous templates. Good results are also reported using tripropylamine [3-5].
- d. Other Al sources as pseudoboehmite [2, 3] and Al hydroxide [6] also give good and large crystals.
- e. For microwave heating, full Teflon autoclaves.
- f. For microwave oven (heating rate 4 grd/sec), 15 minutes at 180°C. If the product remains brown or gray after 4 hours at 600°C, this can be taken as a hint that free diffusion in the one-dimensional pores is blocked (by stacking faults or by non-framework material) thus preventing oxygen from entering and oxidation products from leaving the pores. By going to 900°C, the material can be made "white," but the uptake capacity remains low.
- h. Crystals up to 50  $\mu\text{m}$  in length in the direction of the hexagonal columns are easily obtained; in optimized synthesis, Crystals up to 500  $\mu\text{m}$  are observed. Incorporation of Si [7] or Co [8] gives larger and better crystals. Numerous compositional variants are known.

AFI

SAPO-5

Al(49), P(35), Si(16)

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Contributed by David Young

Verified by R. Borade and by S. Schunk

Type Material:  $[Al_{11.8}P_{9.4}Si_{3.8}O_{48}] : rR : wH_2O$

Method: D. Young, M. E. Davis [1]<sup>a</sup>

Batch Composition: 0.15 cHA : 0.25  $[(CH_3)_2CHO]_3Al$  : 0.25  $H_3PO_4$  : 13  $H_2O$  : 0.5  $SiO_2$

#### Source Materials

deionized water  
aluminum isopropoxide (Aldrich, 98+%)  
phosphoric acid (Aldrich A.C.S. grade, 85%  $H_3PO_4$ )  
cyclohexylamine (cHA)(Aldrich, 99+%)  
silica sol (Dupont Ludox AS-40, 40%  $SiO_2$ )

#### Batch Preparation (for 1 g product)<sup>b</sup>

- (1) [4 g water + 1.44 g aluminum isopropoxide]; make slurry
- (2) [1.2 g water + 0.81 g phosphoric acid]; mix
- (3) [(1) + (2)]; add diluted phosphoric acid dropwise to the aluminum isopropoxide slurry. Stir and age the gel for one hour to ensure homogeneity
- (4) [(3) + 0.42 g cHA]; add cHA dropwise. A viscous gel results. Stir and age for 90 minutes
- (5) [(4) + 2.13 g silica sol]; check to see that gel (4) is homogeneous, then add silica sol and stir for 10 minutes<sup>c</sup>

#### Crystallization

Vessel: 15 mL Teflon-lined autoclave<sup>d</sup>  
Temperature: 200°C<sup>e</sup>  
Time: 3 hours<sup>f</sup>  
Agitation: none

#### Product Recovery

- (1) Remove reactor from the oven and quench cool
- (2) Transfer product from the liner to a beaker with a wash bottle<sup>g</sup>
- (3) Slurry with 50 mL deionized water. Allow the SAPO-5 crystallites to settle and decant off the suspended impurities. Repeat twice
- (4) Filter off product on a Buechner funnel. Wash copiously with water. Air dry
- (5) Yield: 1 g (Approximately 85% with respect to phosphoric acid)

#### Product Characterization

XRD: high purity SAPO-5 free from amorphous or crystalline impurities (SAPO-44)<sup>d</sup>  
Elemental Analysis:  $Al_{0.49}P_{0.35}Si_{0.16}O_2$ <sup>h</sup>  
Crystal size and habit: spherical or hexagonal aggregates, average size of 20  $\mu m$

## References

- [1] D. Young, M. E. Davis, *Zeolites* 11 (1991) 277
- [2] S. T. Wilson, B. M. Lok, E. M. Flanigen, US Patent 4 310 440 (1982)
- [3] J. A. Martens, C. Janssens, P. J. Grobet, H. K. Beyer, P. A. Jacobs, *Stud. Surf. Sci. Catal.* 49A (1989) 215

## Notes

- a. Developed from S. T. Wilson, et al., [2] and from J. A. Martens, et al., [3]
- b. When handling small quantities of polar liquids, the use of glassware which has been pretreated with dichlorodimethylsilane is recommended. This ensures a clean transfer of reagents.
- c. Failure to mix the reagents in this order will result in different products, i.e., the silicoaluminophosphate analogue of quartz/berlinite.
- d. Due to the rapid crystallization of the SAPO-5 product and its propensity to transform to SAPO-44 upon synthesis over-run, small reactors with a narrow aspect ratio are recommended. This synthesis is recommended for a 15 mL capacity reactor. It can be scaled up, but the gel should be split between small reactors. Even with 45 mL reactors, impure product will result.
- e. Place autoclave on a rack in a forced convection oven at 200°C.
- f. A four hour synthesis time results in SAPO-44 impurities: a two hour reaction yields an amorphous gel. Deliberate over-run of one week will yield an excellent SAPO-44.
- g. The pH of the synthesis mother liquor will peak at close to 10, which coincides with the crystallization of the SAPO-5.
- h. This indicates that the main mode of T-atom substitution is silicon for phosphorous. However, surface analysis reveals significant silicon enrichment with strong evidence for silica islanding by Si-O-Si substitution for Al-O-P. <sup>29</sup>Si NMR: P-substitution peak at -90 ppm and Si-O-Si peak at -110 ppm.

AFI

CoAPO-5

P(51), Al(45), Co(4)

**Contributed by** Myriam Uyterhoeven and An Verberckmoes**Verified by** S. Ashtekar, by P. Norby, by J. Jänchen, and by H. van Breukelen**Type Material:**  $[\text{CoAl}_{11}\text{P}_{12}\text{O}_{48}] \cdot w\text{H}_2\text{O}$  ( $w = 0.1$  to  $0.2$ )**Method:** M. G. Uyterhoeven, R. A. Schoonheydt [1, 2]**Batch Composition:**  $0.7 \text{ TriEA} : (\text{Co}_{0.08}\text{Al}_{0.92}\text{P})\text{O}_4 : 20 \text{ H}_2\text{O}$ **Source Materials**

- water (doubly distilled)
- phosphoric acid (Janssen Chimica, 85%  $\text{H}_3\text{PO}_2$ )
- cobalt nitrate,  $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$  (Janssen Chimica)
- pseudoboehmite (Catapal, Vista, 70%  $\text{Al}_2\text{O}_3$ )
- triethylamine (TriEA) (Janssen Chimica 99%)

**Batch Preparation** (for 27 g product)

- (1) [62.6 g water + 23.06 g phosphoric acid], mix; chill to  $0^\circ\text{C}$
  - (2) [(1) + 4.66 g cobalt nitrate], stir until dissolved
  - (3) [(2) + 13.4 g pseudoboehmite], add alumina under continuous stirring
  - (4) [(3) + 14.3 g TriEA], add amine under continuous stirring;<sup>a</sup> stir for one additional hour.
- Initial pH  $\approx 3$

**Crystallization**

- Vessel: stirred, Teflon-lined autoclave
- Temperature:  $200^\circ\text{C}$
- Time: 24 hours
- Agitation: Stirring is essential.<sup>b</sup> Autoclaves were “tumbled” (end-over-end) in the oven

**Product Recovery**

- (1) Filter and wash with distilled water; dry at room temperature
- (2) Yield: near 100% on T-atom basis

**Product Characterization**

- XRD: pure AFI, CHA impurity when present is evidenced by a line at  $9.5^\circ(2\theta)^c$
- Elemental Analysis:  $0.10 \text{ TriEA} \cdot (\text{Co}_{0.086}\text{Al}_{0.892}\text{P}_{1.000}\text{O}_4) \cdot 0.13 \text{ H}_2\text{O}^d$
- Crystal Size and Habit: agglomerates formed by hexagonal platelets, regularly shaped (spherical or diabolo-shaped) with dia. =  $55\mu\text{m}^{e,f}$

**References**

- [1] M. G. Uyterhoeven, R. A. Schoonheydt, *Micropor. Mater.* 3 (1994) 265
- [2] M. G. Uyterhoeven, R. A. Schoonheydt, *Proc. Ninth Int. Zeo. Conf.*, R. von Ballmoos, J. B. Higgins, M. M. J. Treacy (eds.), Butterworth-Heinemann, Boston, 1993, p. 329

## Notes

- a. TriEA addition causes an exothermic reaction; the preparation should be performed at 0°C and TriEA added drop by drop under careful temperature control.
- b. Under static conditions, co-crystallization of CHA is more probable.
- c. The co-crystallization of CHA can be suppressed by reducing the amine content and/or decreasing the cobalt content. The latter requires an increase of the Al content so that  $[Al + Co = P]$ .
- d. On T-atom basis, the product composition is almost equal to the gel composition.  $Al + Co = P$  should be approximately achieved.
- e. SEM is suited to distinguish between AFI and much smaller CHA crystals.
- f. At low cobalt content (e.g.,  $Co_{0.02}Al_{0.98}P_{1.00}$ ), single crystals are formed, shaped as hexagonal bars. Twinning can occur. Increasing cobalt content causes agglomeration giving larger, regular agglomerates. At high cobalt content (for example,  $Co_{0.08}Al_{0.92}P_{1.00}$ ) single crystal formation can be achieved by increasing dilution and increasing template content, although the latter favors the co-crystallization of CHA.

AFI

SSZ-24

Si(100)

Contributed by S. I. Zones and L. T. Yuen

Verified by A. Bell and C. Gittleman, by A. Cheetham, and by R. Lobo and D. Shantz

Type Material:  $(\text{SiO}_2)_{24} \cdot a\text{RN}^+$   $a = 0.96 \pm 0.24$  ( $\text{RN}^+ = \text{trimethyl-1-adamantammonium}$ )

Method: R. A. Van Nordstrand, D. S. Santilli, S. I. Zones [1]

Batch Composition: 5  $\text{K}_2\text{O}$  : 15  $\text{RN}^+$  : 100  $\text{SiO}_2$  : 4400  $\text{H}_2\text{O}$

#### Source Materials

deionized water

$\text{RN}^+$  (see above) 0.72 Molar [2]

potassium hydroxide (Baker reagent, 87.8% KOH)

fumed silica (Cab-O-Sil M5, 97%  $\text{SiO}_2$ , 3%  $\text{H}_2\text{O}$ )

#### Batch Preparation (for 3.5 g product)

- (1) [38.32 g water + 13.90 g (0.72M  $\text{RN}^+$ ) + 0.44 g potassium hydroxide], mix until dissolved
- (2) [(1) + 4.00 g fumed silica], mix in the Teflon liner of a 125 mL Parr stainless steel reactor <sup>a</sup>

#### Crystallization

Vessel: Parr 125 mL reactor (Teflon-lined) heated in a Blue M oven

Temperature: 150°C

Time: 7 days <sup>b,c</sup>

Agitation: none

#### Product Recovery

- (1) Upon cooling to room temperature, the product should be settled to the bottom of the reactor liner; pH with a calibrated probe should be 11.50-11.70
- (2) Filter to recover solids (medium grade glass-frit funnel)
- (3) Wash product with approximately 100 mL 0.01N KOH solution <sup>d</sup>
- (4) Wash with approximately 1 liter water
- (5) Air dry overnight while pulling a vacuum through the frit
- (6) Yield: 3.52 g; 79% yield based on  $\text{SiO}_2$

#### Product Characterization

XRD: AFI only crystalline phase

Elemental Analysis:  $\text{RN}^+$  is approximately 10 wt% and alkali cation is usually less than 0.5 wt%. The remaining material is  $\text{SiO}_2$  [3]

Crystal Size and Habit: Typically hexagonal rods composed of identical hexagonal plates on top of each other. The rods are usually about 10  $\mu\text{m}$  long

## References

- [1] R. A. Van Nordstrand, D. S. Santilli, S. I. Zones in *Molecular Sieve Science*, ACS Symp. Ser. 368, W. H. Flank, T. E. Whyte, (eds.), Am. Chem. Soc., Washington, D. C., 1988, pp. 236-245
- [2] S. I. Zones, US Patent 4 665 110 (1987)
- [3] I. Petrovic, A. Navrotsky, M. E. Davis, S. I. Zones, *Chem. Mater.* 5 (1993) 1805
- [4] R. A. Van Nordstrand, D. S. Santilli, S. I. Zones, in *Synthesis of Microporous Materials*, Vol. 1, M. L. Occelli, H. E. Robson (eds.), Van Nostrand Reinhold, New York, 1992. pp. 373-383

## Notes

- a. High speed stirring of this preparation leads to SSZ-23 formation [1].
- b. The reaction can be accelerated by seeding after some initial material has been made.
- c. The synthesis of the borosilicate [4] requires only one day; the crystals are smaller.
- d. The alkaline wash helps to prevent unreacted silica from coming out of solution during washing and causing pore-plugging.



## AFO

## SAPO-41

## Al(51),P(46).Si(3)

Contributed by A. M. Prakash and D. K. Chakrabarty

Verified by P. Mériaudeau and by J. Pérez-Pariente and J. Rodríguez

Type material:  $[(\text{Al}_{20.4}\text{P}_{18.4}\text{Si}_{1.2})\text{O}_{80}] \cdot m\text{R} \cdot n\text{H}_2\text{O}$  (R = Di-n-propylamine)

Method: A. M. Prakash, S. V. V. Chilukuri, R. P. Bagwe, S. Ashtekar, D. K. Chakrabarty [1]

Batch Composition: 1.0  $\text{Al}_2\text{O}_3$  : 1.3  $\text{P}_2\text{O}_5$  : 0.1  $\text{SiO}_2^a$  : 4.0  $\text{R}^b$  : 58.2  $\text{H}_2\text{O}^c$

#### Source Materials

deionized water

orthophosphoric acid (Merck, 85%)

pseudoboehmite (Vista; Catapal-B, assumed 70 wt%  $\text{Al}_2\text{O}_3$ )

fumed silica (Degussa, Aerosil-200)

di-n-propylamine (Merck, 99%)

#### Batch Preparation (for ~ 16 g product)

- (1) [23.06 g phosphoric acid + 25 g water], mix together
- (2) [(1) + 14.57 g pseudoboehmite], add slowly over a period of 3.5 hours and continue stirring for 1.5 hours
- (3) [0.60 g silica + 25 g water], mix together to form a slurry
- (4) [(2) + (3)], add silica slurry over a period of 30 minutes and continue stirring for 1 hour
- (5) [(4) + 40 g water], mix together
- (6) [(5) + 40.88 g di-n-propylamine], add dropwise to gel and continue stirring for 30 minutes
- (7) Adjust pH of the gel to 7.7 by slowly adding 4 mL of phosphoric acid diluted in 6 g water and stir the final gel for 30 minutes to ensure homogeneity

#### Crystallization

Vessel: 500 mL stainless steel autoclave

Temperature: 180°C

Time: 11 days

#### Product Recovery

- (1) Decant the mother liquor
- (2) Slurry with deionized water. Allow the crystallites to settle and decant the water
- (3) Repeat step (2) three times
- (4) Filter off product and wash again with water
- (5) Dry at 100°C overnight
- (6) Yield: ~ 65% based on alumina

#### Product characterization

XRD: SAPO-41 [1]<sup>d</sup> Orthorhombic;  $a = 9.7 \text{ \AA}$ ,  $b = 25.5 \text{ \AA}$ ,  $c = 8.4 \text{ \AA}$ ; competing phases: SAPO-11 and SAPO-31 at low template concentration and SAPO-46 at high silica concentration [1, 2]

Elemental Analysis (exclusive of R and  $\text{H}_2\text{O}$ ): 1.00  $\text{Al}_2\text{O}_3$  : 0.90  $\text{P}_2\text{O}_5$  : 0.11  $\text{SiO}_2$

Crystal size and habit: 5-10  $\mu\text{m}$  crystals of rectangular morphology

## References

- [1] A. M. Prakash, S. V. V. Chilukuri, R. B. Bagwe, S. Ashtekar, D. K. Chakrabarty, *Micropor. Mater.* 6 (1996), 89
- [2] P. Mériaudeau, V. A. Tuan, V. T. Nghiem, S. Y. Lai, L. Hung, C. Naccache, *J. Catal.* 169 (1997) 55

## Notes

- a. In this synthesis pure phase SAPO-41 crystallizes only at low SiO<sub>2</sub> concentration in the gel. High concentration of silica generally leads to phases such as SAPO-11, SAPO-31, SAPO-46 depending on template concentration, temperature and period of crystallization.
- b. Template concentration should be high (3 mol < R < 4 mol) for obtaining pure SAPO-41. Lower template concentration leads to SAPO-11 and SAPO-31 depending on silica concentration.
- c. H<sub>2</sub>O included water from pseudoboehmite, phosphoric acid and added water.
- d. Extra low-intensity lines between 9-18 degrees (2 $\theta$ ) have not been identified. They may indicate a lower symmetry due to retained template. However a competing phase cannot be ruled out.

AFS

MAPO-46

P(50), Al(40), Mg(10)

Contributed by Deepak B. Akolekar

Verified by H. Tian and by A. Prakash

Type Material:  $\text{Mg}_{5.54}\text{Al}_{22.4}\text{P}_{28.06}\text{O}_{112} \cdot 8.1 \text{ R} \cdot 11.0 \text{ H}_2\text{O}$  (R = di-n-propylamine)

Method: D. B. Akolekar, S. Kaliaguine [1]

Batch Composition: 2 R : 0.30 MgO : 0.85  $\text{Al}_2\text{O}_3$  : 1.0  $\text{P}_2\text{O}_5$  : 50  $\text{H}_2\text{O}$

#### Source Materials

deionized water  
orthophosphoric acid (85%, Aldrich)  
pseudoboehmite (Vista Chemical Co., 71.8%  $\text{Al}_2\text{O}_3$ )  
magnesium oxide (99.9%, Aldrich)  
n-dipropylamine (99%, Aldrich, 0.738 g/mL)

Batch Preparation (for 20 g dry, template-free product)

- (1) [65.0 g water + 25.16 g o-phosphoric acid + 13.18 g pseudo-boehmite], stir until homogeneous
- (2) [(1) + 1.32 g magnesium oxide + 32.0 g water], stir until homogeneous
- (3) [(2) + 29.9 mL n-dipropylamine], stir until homogeneous (about 35 minutes) <sup>a</sup>

#### Crystallization

Vessel: PTFE-lined stainless steel autoclave (200 mL)  
Temperature: 162°C  
Time: 240 hours  
Agitation: none

#### Product Recovery

- (1) Stir the total crystallization batch into 1.5 L deionized water. Allow to stand for a few minutes, then decant the top organic layer
- (2) Filter; wash with deionized water
- (3) Dry at 75°C
- (4) Yield: > 60% based on  $\text{Al}_2\text{O}_3$

#### Product Characterization

XRD: AFS, only crystalline product [2-4]; characteristic strong reflections at  $d = 11.43$  and  $4.12 \text{ \AA}$   
Elemental Analysis ( $\text{H}_2\text{O}$  and template-free):  $0.396 \text{ MgO} \cdot 0.80 \text{ Al}_2\text{O}_3 \cdot 1.00 \text{ P}_2\text{O}_5$   
Crystal Size and Habit: hexagonal rod-like,  $0.8 \times 8 \text{ }\mu\text{m}$

#### References

- [1] D. B. Akolekar, S. K. Kaliaguine, J. Chem. Soc., Faraday Trans. 89 (1998) 4141
- [2] S. T. Wilson, E. M. Flanigen in ACS Symp. Ser. 398, M. L. Occelli, H. E. Robson (eds.), Am. Chem. Soc., Washington, D.C., 1989, p. 329
- [3] E. M. Flanigen, R. L. Patton, S. T. Wilson, Stud. Surf. Sci. Catal. 37 (1988) 13
- [4] J. M. Bennett, B. K. Marcus, Stud. Surf. Sci. Catal. 37 (1988) 269

#### Note

- a. Uniform homogeneous gel formation is the important step for obtaining pure phase material.

ANA

Analcime

Si(68), Al(32)

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**Contributed by** B. W. Garney

**Verified by** N. Evmiridis and by F. Farzaneh

**Type Material:**  $\text{Na}_x[\text{Al}_x\text{Si}_{48-x}\text{O}_{96}] : 16 \text{ H}_2\text{O}$  ( $x = 15$  to  $17$ )

**Method:** Developed from J. F. Charnell [1], and A. Dyer, A. M. Yusof [2]

**Batch Composition:**  $4.5 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 4.5 \text{ SiO}_2 : 3.0 \text{ H}_2\text{SO}_4 : 380 \text{ H}_2\text{O} : 6.1 \text{ triethanolamine}$  <sup>a</sup>

**Source Materials**

demineralized water

aluminum sulfate [General Purpose Reagent,  $\text{Al}_2(\text{SO}_4)_3 \cdot 16 \text{ H}_2\text{O}$ ]

sodium metaasilicate (Technical Grade,  $\text{Na}_2\text{SiO}_3 \cdot 5 \text{ H}_2\text{O}$ )

triethanolamine [General Purpose Reagent,  $\text{N}(\text{C}_2\text{H}_4\text{OH})_3$ ]

**Batch Preparation** (for approximately 7 g product) [3,4]

- (1) [55 g water + 9.8 g aluminum sulfate], stir until dissolved; filter through 0.7 micron glass microfibre filter
- (2) [36.5 g water + 14.9 g sodium metasilicate + 12.2 g triethanolamine], stir until dissolved; filter through 0.7 micron glass microfibre filter
- (3) [(1) + (2)], stir gently until gel thickens (do not over-stir)

**Crystallization**

Vessel: 150 mL Teflon-lined autoclave <sup>b</sup>

Time: 24 hours

Temperature: 200°C (autoclave heated in the oven)

Agitation: none

**Product Recovery**

- (1) Cool to room temperature and filter to recover solids
- (2) Wash with distilled water until pH of filtrate < 10
- (3) De-agglomerate by adding 10 mL of 10% ethanol in water and immerse in a 150 watt ultrasonic bath for approximately 1 hour
- (4) Dry at 100°C
- (5) Yield: approximately 90%

**Product Characterization**

XRD: ANA (only crystalline phase)

Elemental Analysis:  $1.06 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 4.3 \text{ SiO}_2 : 2 \text{ H}_2\text{O}$

$\text{H}_2\text{O}$  (Wt. loss at 500°C): 8.29% ( $\pm 0.20$ )

$\text{Na}_2\text{O}$ : 14.6% ( $\pm 1.5$ )

$\text{Al}_2\text{O}_3$ : 22.7% ( $\pm 1.5$ )

$\text{SiO}_2$ : 57.3% ( $\pm 0.5$ )

Crystal Size and Habit: polycrystalline non-porous spherulites  $\leq 180 \mu\text{m}$  dia. [2]

## References

- [1] J. F. Charnell, J. Cryst. Growth 8 (1971) 291
- [2] A. Dyer, A. M. Yusof, Zeolites 7 (1987) 191
- [3] B. W. Garney, Fusion Technology 21 (1992) 604
- [4] B. W. Garney, UK Patent Application 9011151.9

## Notes

- a. This preparation gives the non-porous form of analcime. Replacing aluminum sulfate with an equivalent weight of sodium aluminate gives the porous form of analcime. Gel composition: 6.5 Na<sub>2</sub>O : Al<sub>2</sub>O<sub>3</sub> : 4.5 SiO<sub>2</sub> : 380 H<sub>2</sub>O : 6.1 triethanolamine.
- b. The method of heating the gel is very important if large crystals are required. The largest crystals were obtained when the autoclave was placed in a laboratory oven where the heat flow was uniform all around the pot. Experiments using autoclaves which were heated by electrical jackets around the sides were not so successful.

## AST

AlPO<sub>4</sub>-16

## Al(50), P(50)

Contributed by Joël Patarin

Verified by J. Shi and K. Balkus, by D. Akporiaye, and by T. Blasco

Type Material: (Al<sub>10</sub>P<sub>10</sub>O<sub>40</sub>)Q<sub>2.0</sub>F<sub>1.6</sub> : 3.0 H<sub>2</sub>O<sup>a</sup> (Q = quinuclidine)

Method: C. Schott-Darje, J. Patarin, P. Y. Le Goff, H. Kessler and E. Benazzi [1]

Batch Composition: 1 P<sub>2</sub>O<sub>5</sub> : 1 Al<sub>2</sub>O<sub>3</sub> : 1 Q : 1 HF : 60 H<sub>2</sub>O

Source Materials

distilled water  
phosphoric acid (Fluka, 85% H<sub>3</sub>PO<sub>4</sub>)  
aluminum isopropoxide (Aldrich, 98%)  
quinuclidine C<sub>7</sub>H<sub>13</sub>N (Fluka, 97%)  
hydrofluoric acid (Prolabo, 40%)

Batch Preparation<sup>b</sup> (for 1.5 g of as-synthesized product)

- (1) [4.00 g water + 2.31 g phosphoric acid + 4.17 g aluminum isopropoxide], stir until homogenized <sup>c</sup>
- (2) [6.15 g water + 1.14 g quinuclidine], stir until dissolved
- (3) [(1) + (2) + 0.50 g hydrofluoric acid], stir for 2 minutes. Gel pH = 7 to 7.5

Crystallization

Vessel: Teflon-lined stainless steel autoclave (50 cm<sup>3</sup>)  
Temperature: 150°C  
Time: 24 hours  
Agitation: none  
Final pH: approximately 8

Product Recovery

- (1) Dilute the reaction mixture with distilled water
- (2) Filter or centrifuge
- (3) Wash until the pH of the filtrate is 5.5 to 6
- (4) Dry at 60-70°C overnight
- (5) Yield: 50% based on aluminum (as-synthesized product containing quinuclidine and some water) <sup>d</sup>

Product Characterization

XRD: AST (only crystalline phase), Space group I4, a<sub>0</sub> = 9.3423(1) Å c<sub>0</sub> = 13.4760(2) Å  
Elemental Analysis (wt%): Al<sub>2</sub>O<sub>3</sub> = 32.8, P<sub>2</sub>O<sub>5</sub> = 44.8, F = 1.9, (C<sub>7</sub>H<sub>13</sub>)N = 15.4, H<sub>2</sub>O = 3.4  
Crystal Size and Habit: tetrahedra, 0.5 to 3 μm

## References

- [1] C. Schott-Daric, J. Patarin, P. Y. Le Goff, H. Kessler, E. Benazzi, *Micropor. Mater.* 3 (1994) 123
- [2] J. M. Bennett, R. M. Kirchner, *Zeolites* 11 (1991) 502

## Notes

- a. The Q/F molar ratio is lower than 1. Part of the quinuclidine is either not protonated or OH<sup>-</sup> groups are present in order to get a neutral material.
- b. The starting mixture is prepared in a polyethylene vessel.
- c. The reaction is exothermic.
- d. After calcination (removal of the organic and fluoride species) the cubic form [2] of AlPO<sub>4</sub>-16 is obtained.
- e. According to reference [1].

ATN

MAPO-39

P(50), Al(40), Mg(9)

Contributed by Deepak Akolekar

Verified by P. Norby and by S. Sivasanker

Type Material:  $H_{1.6}[Mg_{1.6}Al_{6.4}P_8O_{32}]$

Method: D. B. Akolekar, S. K. Kaliaguine [1]

Batch Composition: 1.1 R : 0.40 MgO : 0.80  $Al_2O_3$  : 1.00  $P_2O_5$  : 41  $H_2O$  (R = di-n-propylamine)

#### Source Materials

deionized water  
orthophosphoric acid (85%, Aldrich)  
pseudoboehmite (Vista Chemical Co., 71.8%  $Al_2O_3$ )  
magnesium oxide (99.9%, Aldrich)  
n-dipropylamine (99%, Aldrich, 0.738 g/mL)

Batch Preparation (for 12 g dry, template-free product)

- (1) [70.0 g water + 32.3 g o-phosphoric acid + 15.91 g pseudoboehmite], stir until homogeneous
- (2) [(1) + 2.26 g magnesium oxide + 26 g water], stir until homogeneous
- (3) [(2) + 19.2 mL n-dipropylamine], stir until homogeneous (about 30 minutes) a

#### Crystallization

Vessel: PTFE-lined stainless steel autoclave (150 mL)  
Temperature: 150°C  
Time: 114 hours  
Agitation: none

#### Product Recovery

- (1) Stir the total crystallization batch into 1.5 L deionized water
- (2) Filter; wash with deionized water
- (3) Dry at 75°C
- (4) Yield: > 70% based on  $Al_2O_3$

#### Product Characterization

XRD: ATN [2,3], characteristic strong reflections at  $d = 4.19$  and  $3.95\text{\AA}$  for as-synthesized material  
Elemental Analysis: (exclusive of R and  $H_2O$ ) (wt%): 6.31 MgO, 34.32  $Al_2O_3$ , 59.37%  $P_2O_5$

Crystal Size and Habit: small irregular platelike particles,  $2.5 \times 3.3 \mu\text{m}$

#### References

- [1] D. B. Akolekar, S. K. Kaliaguine, *Zeolites* 14 (1994), 620
- [2] S. T. Wilson, E. M. Flanigen, in *ACS Symp. Ser. 398*, M. L. Occelli, H. E. Robson (eds.) Am. Chem. Soc., Washington, D.C., 1989, p. 329
- [3] L. B. McCusker, G. O. Brunner, A. F. Ojo, *Acta Crystallogr. A* 46 (1990), C 59

#### Note

- a. Uniform homogeneous gel formation is the important step for obtaining pure phase material.



## BEA

## Zeolite Beta

Si(93), Al(7)

Contributed by Joaquin Pérez-Pariente and Miguel Cambor

Verified by Shu-Hua Chien and Xianping Meng, and by D. Cardoso and S. Jahn

Type Material:  $\text{Na}_{0.92}\text{K}_{0.62}(\text{TEA})_{7.6}[\text{Al}_{4.53}\text{Si}_{59.47}\text{O}_{128}]^{\text{a}}$

Method: M. A. Cambor, J. Pérez-Pariente [1]

Batch Composition: 1.97  $\text{Na}_2\text{O}$  : 1.00  $\text{K}_2\text{O}$  : 12.5  $(\text{TEA})_2\text{O}$  :  $\text{Al}_2\text{O}_3$  : 50  $\text{SiO}_2$  : 750  $\text{H}_2\text{O}$  : 2.9  $\text{HCl}^{\text{b}}$

### Source Materials

deionized water

tetraethylammonium hydroxide (Alfa 40 wt% TEAOH, K < 1 ppm, Na < 3 ppm)

sodium chloride (reagent grade)

potassium chloride (reagent grade)

silica (Degussa Aerosil 200, 99+%  $\text{SiO}_2$ )

sodium hydroxide (Prolabo reagent grade, 98%)

sodium aluminate (Carlo Erba, 56 wt%  $\text{Al}_2\text{O}_3$ , 37 wt%  $\text{Na}_2\text{O}$ )

### Batch Preparation (for 20 g product)

- (1) [59.4 g water + 89.6 g TEAOH (40%) + 0.53 g sodium chloride + 1.44 g potassium chloride], stir until dissolved
- (2) [(1) + 29.54 g silica], stir until homogenized (10 minutes minimum)
- (3) [20.0 g water + 0.33 g sodium hydroxide + 1.79 g sodium aluminate], stir until dissolved
- (4) [(2) + (3)], stir for 10 minutes, (gives a thick gel)

### Crystallization

Vessel: 60 mL stainless steel autoclaves with Teflon liners

Temperature:  $135 \pm 1^\circ\text{C}$

Time: 15 to 20 hours

Agitation: autoclaves are rotated (60 rpm)<sup>c</sup>

### Product Recovery

- (1) Quench autoclaves in cold water, product pH =  $12.8 \pm 0.1$
- (2) Centrifuge (10,000 rpm), wash until pH ~ 9 and dry overnight ( $77^\circ\text{C}$ )
- (3) Yield:  $9.9 \pm 0.2$  g of solid / 100 g gel (~ 90% on Al)

### Product Characterization

XRD: zeolite beta (no other phases)

Elemental Analysis (content per unit cell):  $\text{Na}_{0.90}\text{K}_{0.62}(\text{TEA})_{7.6}[\text{Al}_{4.53}\text{Si}_{59.47}\text{O}_{128}]^{\text{d}}$

(Si/Al =  $13.1 \pm 0.1$ )

Crystal Size and Habit: The crystals are round-shaped. They do not show any particular crystal habit. Average crystal size is  $0.20 \mu\text{m}$ , and the crystal size distribution is very narrow. (The size of ~90% of crystals is between  $0.10$ - $0.30 \mu\text{m}$ )

## References

- [1] M. A. Cambor, J. Pérez-Pariente, Zeolites 11 (1991) 202
- [2] M. A. Cambor, A. Mifsud, J. Pérez-Pariente, Zeolites 11 (1991) 792

## Notes

- a. Highly siliceous beta (Si/Al~ 100 can be obtained by using tetraethyl-orthosilicate as silica source [2].
- b.  $\text{OH}/\text{SiO}_2 = 0.56$
- c. In the specific synthesis conditions given in the recipe, the agitation has practically no influence on the properties of the product. However, by using different synthesis conditions, large differences in total crystallization time, average crystal size and crystal size distribution can be found between static and agitated synthesis.
- d. Excess cations assumed to be occluded TEOH or TEA<sup>+</sup> compensating SiO-structure defects.

## BEA

## [Ti,Al] Beta

## Si(95), Ti(3), Al(2)

Contributed by Dilson Cardoso

Verified by M. Camblor and by W. S. Ahn

Type Material:  $(\text{TEA})_{1.5}[\text{Ti}_{2.0}\text{Al}_{1.5}\text{Si}_{60.5}\text{O}_{128}]$  (TEA = tetraethylammonium)

Method; S. Jahn, D. Cardoso [1,3], M. A. Camblor, A. Corma, J. Pérez-Pariente [2]

Batch Composition:  $0.033 \text{ TiO}_2 : \text{SiO}_2 : 0.0026 \text{ Al}_2\text{O}_3 : 0.269 (\text{TEA})_2\text{O} : 15.5 \text{ H}_2\text{O}$

#### Source Materials

tetraethylammonium hydroxide (Aldrich, 35% TEA-OH aqueous solution)  
tetraethylorthotitanate (Aldrich, 99%)  
silica (Degussa Aerosil 380, 99+%)  
aluminum nitrate  $(\text{Al}(\text{NO}_3)_3 \cdot 9 \text{ H}_2\text{O})$   
deionized water

#### Batch Preparation (for ~1 g product)

- (1) [13.24 g tetraethylammonium hydroxide solution + 0.44 g tetraethylortho-titanate], mix in a glove box; stir for 10 minutes<sup>a</sup>
- (2) [(1) + 3.52 g silica], stir for 15 minutes
- (3) [0.11 g aluminum nitrate + 7.69 g water], stir until dissolved
- (4) [(3) + (2)], stir until homogenized (10 minutes minimum)<sup>b</sup>

#### Crystallization

Vessel: 50 mL stainless steel autoclave with Teflon liner  
Time: 60-96 hours  
Temperature: 140°C  
Agitation: optional  
Final pH: ~12.5

#### Product Recovery

- (1) Quench autoclave in cold water
- (2) Centrifuge (7000 rpm) and wash until pH is about 9 c
- (3) Dry overnight at 80°C
- (4) Yield: 3-4 g/100 g batch (about 90% based on Al, 40% on Ti and 25% on Si)

#### Product Characterization

XRD: zeolite beta (no other phases)  
Elemental analyses:  $\text{Ti}_{2.0}\text{Al}_{1.5}\text{Si}_{60.5}\text{O}_{128}$  (for material with 96 hours crystallization. As synthesized material contains TEA<sup>+</sup> cations)  
Crystal size and habit: round-shaped particles with average size 0.28  $\mu\text{m}$  (for 96 hours crystallization) and a narrow size distribution

## References

- [1] S. L. Jahn, P. A. P. Nascente, D. Cardoso, *Zeolites* 19 (1997) 416
- [2] M. A. Camblor, A. Corma, J. Pérez-Pariente, *Zeolites* 13 (1993) 82
- [3] S. L. Jahn, D. Cardoso, in *Proceedings of 12th International Zeolite Conference*, Vol. III, M. M. J. Treacy, B. K. Marcus, M. E. Bisher, J. B. Higgins (eds.), Materials Research Soc., Warrendale, PA, USA (1998), pp 1885-1892,

## Notes

- a. Tetraethylorthotitanate hydrolyses very rapidly under normal atmospheric conditions forming extra framework  $\text{TiO}_2$ . Using this Ti-source, the gel must be prepared in a glove box. If this equipment is not available, the gel can be prepared under normal atmosphere using a solution of tetraethylortho-titanate in isopropyl alcohol (TEOTi/iPrOH molar ratio of 1/10). This results in a small loss in solid yield.
- b. It is difficult to synthesize the beta structure in total absence of aluminum. This recipe employs the minimum content of this element (Si/Al ~400).
- c. The solid particles formed during synthesis are very small, and it is very difficult to filter them. Unfortunately the appropriate method for purification is by centrifugation.

## CAN

## Cancrinite

Si(50), Al(50)

Contributed by J.-Ch. Buhl

Verified by C. Williams and by M. Bottale

Type Material:  $\text{Na}_8[\text{AlSiO}_4]_6\text{CO}_3 \cdot 4\text{H}_2\text{O}$

Method: J.-Ch. Buhl [1]

Batch Composition: 93  $\text{Na}_2\text{O}$  :  $\text{Al}_2\text{O}_3$  : 2  $\text{SiO}_2$  : 10  $\text{NaHCO}_3$  : 1386  $\text{H}_2\text{O}$ <sup>a</sup>

### Source Materials

distilled water  
sodium hydroxide (Merck pellets, analytical grade)  
kaolin (Fluka)  
sodium bicarbonate (Merck, analytical grade,  $\text{NaHCO}_3$ )

### Batch Preparation (for 0.6 g product)

- (1) [45 mL water + 14.4 g sodium hydroxide], stir until dissolved
- (2) [(1) + 0.5 g kaolin + 1.7 g sodium bicarbonate], mix until uniform slurry

### Crystallization

Vessel: Teflon-lined steel autoclave  
Temperature: 200°C  
Time: 48 hours  
Agitation: none

### Product Recovery

- (1) Cool to ambient temperature. Filter
- (2) Wash free of NaOH residuals (approximately 150 mL water)
- (3) Dry at 80°C
- (4) Yield: close to 100%

### Product Characterization

XRD: CAN; small amounts of a disordered phase between CAN and SOD and amorphous material could be detected in the polycrystalline sample [1,2]  
Elemental Analysis:  $\text{Na}_8[\text{AlSiO}_4]_6\text{CO}_3 \cdot 4\text{H}_2\text{O}$ <sup>b</sup>  
Crystal Size and Habit: small elongated needles<sup>c</sup>

### References

- [1] J.-Ch. Buhl, *Thermochimica Acta* 178 (1991) 19
- [2] G. Hermeler, J.-Ch. Buhl, W. Hoffmann, *Catalysis Today* 8 (1991) 415
- [3] C. Liu, S. Li, K. Tu, R. Xu, *J. Chem. Soc., Chem. Commun.* (1993) 1645

### Notes

- a. CAN-formation in the water-free system is reported using butane-1,3-diol. [3]
- b. Analysis of the guest anions according to the combination of simultaneous thermal analysis (TG, DTG, DTA), IR-spectroscopy and MAS NMR ( $^{13}\text{C}$ ).
- c. Single crystals can be prepared from a gel consisting of [50 mg kaolin (heated at 1400°C for two hours) + 168 mg  $\text{NaHCO}_3$  + 320 mg NaOH + 1 mL distilled water] treated at 500°C for 48 hours in a silver-lined steel autoclave.

# CHA

# Chabazite

# Si(68), Al(32)

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**Contributed by** Thomas R. Gaffney

**Verified by** J. Warzywoda, by J. Cejka, and by Liu Xinjin

**Type Material:**  $K_{11}[Al_{11}Si_{25}O_{72}]:40 H_2O$

**Method:** M. Bourgogne, J.-L. Guth, R. Wey [1]

**Batch Composition:**  $0.17 Na_2O : 2.0 K_2O : Al_2O_3 : 5.18 SiO_2 : 224 H_2O$

## Source Materials

demineralized water

potassium hydroxide (J. T. Baker reagent grade, 45% KOH solution)

(Na,H) Zeolite Y (UOP LZY-64)<sup>a</sup>

## Batch Preparation (for 25 g dry product)

- (1) [198.2 mL water + 26.8 mL KOH (45% solution), mix
- (2) [(1) + 25.0 g Zeolite Y], seal in a polypropylene bottle and shake for 30 s

## Crystallization

Vessel: polypropylene bottle with a screw-top lid

Temperature: 95°C (steam chamber)

Time: 96 hours

Agitation: none

## Product Recovery

- (1) Remove bottle from the steam chamber and filter to recover solids while still hot <sup>b</sup>
- (2) Wash two times with 500 mL water per wash
- (3) Dry at ambient temperature <sup>c</sup>
- (4) Yield: 99% based on alumina, 83% based on silica

## Product Characterization

XRD: CHA with no reflections from FAU. Competing phases; FAU when insufficient crystallization times are used <sup>d</sup>

Elemental Analysis:  $0.02 Na_2O : 0.98 K_2O : Al_2O_3 : 4.32 SiO_2$  (dry basis)<sup>e,f</sup>

Crystal Size and Habit: Sub-micron crystallites, 0.1  $\mu m$  on average, multifaceted (some can be seen to be hexagonal platelets)

## Reference

- [1] M. Bourgogne, J.-L. Guth, R. Wey, US Patent 4 503 024 (1985)

## Notes

- a. The Na/Al ratio of the NaHY starting materials should be less than 0.17. LZY-64 was prepared by heating  $\text{NH}_4^+$  exchanged type Y to  $550^\circ\text{C}$  (at  $2^\circ\text{C}/\text{minute}$ ) and calcining at  $550^\circ\text{C}$  for 2 hours. Caution: ammonia is liberated during the calcination. Use adequate ventilation and safety precautions.
- b.  $\text{pH} = 13.5$  after crystallization treatment.
- c. The product is stable to drying in an oven at  $110^\circ\text{C}$ .
- d. Converting samples of Zeolite Y which contain large crystals or are formed (pelleted, beaded) to chabazite requires longer reaction times.
- e. The framework  $\text{SiO}_2/\text{Al}_2\text{O}_3$  is 4.32 by  $^{29}\text{Si}$  NMR.
- f. For preparing more siliceous product, Nalco 2326 silica (14.5%  $\text{SiO}_2$ ) was used as the silica source. Synthetic chabazite with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.3$  forms from a reaction mixture of composition:  $0.17 \text{ Na}_2\text{O} : 4.31 \text{ K}_2\text{O} : \text{Al}_2\text{O}_3 : 8 \text{ SiO}_2 : 500 \text{ H}_2\text{O}$ . Addition of more silica to the reaction mixture (batch  $\text{SiO}_2 : \text{Al}_2\text{O}_3 > 8$ ) leads to incomplete conversion of Zeolite Y, and the product is a mixture of CHA and FAU.

## CHA

## SSZ-13

## Si(93), Al(7)

Contributed by L. T. Yuen and S. I. Zones

Verified by R. Lobo and by L. Schreyeck

Type Material: (aRN, bNa)  $[\text{Al}_{2.4}\text{Si}_{33.6}\text{O}_{72}] : w\text{H}_2\text{O}^a$  ( $w = 1$  to 7)  
(RN = N,N,N, trimethyl-1-adamantammonium)

Method: S. I. Zones, R. A. Van Nordstrand [1]

Batch Composition: 10 Na<sub>2</sub>O : 2.5 Al<sub>2</sub>O<sub>3</sub> : 100 SiO<sub>2</sub> : 4400 H<sub>2</sub>O : 20 RN-OH

#### Source Materials

sodium hydroxide (1N), (Baker, reagent grade)  
N,N,N, trimethyl-1-adamantammonium hydroxide (RN-OH)(0.72M)<sup>b</sup>  
deionized water  
aluminum hydroxide (Reheis F-2000 dried gel, 50% Al<sub>2</sub>O<sub>3</sub>)  
fumed silica (Cab-O-Sil, M5 grade, 97% SiO<sub>2</sub>)

#### Batch Preparation (for 0.6 g product)

- (1) [2.00 g 1N NaOH + 2.78 g 0.72 M RN·OH + 3.22 water], add sequentially to the Teflon cup of a Parr 23 mL autoclave <sup>c</sup>
- (2) [(1) + 0.05 g aluminum hydroxide], mix until solution clears
- (3) [(2) + 0.60 g fumed silica], mix until uniform

#### Crystallization

Vessel: Teflon-lined 23 mL autoclave (Parr model 4745)  
Temperature: 160°C <sup>d</sup>  
Time: 4 days  
Agitation: none

#### Product Recovery

- (1) Cool to room temperature <sup>e</sup>
- (2) Filter in a medium frit glass funnel
- (3) Wash with about one liter of water
- (4) Air dry at room temperature with vacuum pulling through frit
- (5) Yield: 0.57 g, 74% based on TO<sub>2</sub>

#### Product Characterization

XRD: CHA (only crystalline phase); competing phases when observed: analcime or quartz; impurities can occur at this temperature or higher.  
Elemental Analyses: RN is approximately 15 wt% and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 28 by ICP  
Crystal Size and Habit: cubes of 2-5 μm with some occasional intergrowth



## References

- [1] S. I. Zones, R. A. Van Nordstrand, Zeolites 8 (1988) 166
- [2] S. I. Zones, US Patent 4 544 538 (1985)
- [3] S. I. Zones, Trans. Faraday Soc. 87 (1991) 3709

## Notes

- a. Typical values:  $a = 1.4$  to  $2.9$ ,  $b = 0.7$  to  $4.3$
- b. The description of template preparation is given in [2]. The fastest synthesis of this product is from FAU sources [3].
- c. The Teflon cup is washed between runs with HF (48%), water, KOH solution, and water again.
- d. The reactor is placed into a Blue M convection-heating oven preset at  $160^{\circ}\text{C}$ .
- e. pH of the treated batch should measure in the range of 12.20 to 12.64 using a calibrated probe

CHA

SAPO-34

Al(47), P(32), Si(21)

Contributed by A. M. Prakash

Verified by J. López Nieto and by N. Tusar

Type Material:  $mR[Al_{17}P_{12}Si_7O_{72}]$  (R = morpholine)

Method: A. M. Prakash, S. Unnikrishnan [1]

Batch Composition:  $Al_2O_3 : 1.06 P_2O_5 : 1.08 SiO_2 : 2.09 R : 66 H_2O_{a,b}$

#### Source Materials

distilled water  
phosphoric acid (Merck, 85%)  
pseudoboehmite (Vista Catapal-B, 70%  $Al_2O_3$ )  
fumed silica (Degussa Aerosil-200 99+%  $SiO_2$ )  
morpholine (Aldrich, 99%  $C_4H_9O$ )

#### Batch Preparation(for 20 g product)<sup>c</sup>

- (1) [18.0 g water + 15.37 g phosphoric acid], mix
- (2) [(1) + 9.20 g pseudoboehmite], add slowly (2 hours) with stirring
- (3) [(2) + 10 g water], stir thoroughly for 7 hours
- (4) [4.09 g fumed silica + 11.62 g morpholine + 15 g water], mix thoroughly
- (5) [(3) + (4)], add (4) dropwise to (3) while stirring
- (6) [(5) + 24 g water], stir thoroughly for 7 hours; pH of gel = 6.4 to 7.5

#### Crystallization

Vessel: 150 mL Teflon-lined autoclave  
Incubation: 24 hours at 38°C without agitation<sup>d</sup>  
Temperature: 200°C  
Time: 24 hours  
Agitation: none

#### Product Recovery

- (1) Decant the mother liquor
- (2) Dilute with distilled water and filter
- (3) Wash 3 to 4 times with distilled water
- (4) Dry at 100°C for 6 hours
- (6) Yield: 98% based on alumina

#### Product Characterization

XRD: SAPO-34 (CHA) [1],  $a_o = 13.78 \text{ \AA}$ ,  $c_o = 14.85 \text{ \AA}$ ; competing phase:  $AlPO_4$  (cristobalite)  
when silica and/or template concentration is low  
Elemental Analysis:  $1.0 Al_2O_3 : 0.68 P_2O_5 : 0.87 SiO_2 : 0.59 R : 1.07H_2O$   
Crystal size and habit: 5 to 20  $\mu m$  crystals with cubic-like rhombohedral morphology [1]

## Reference

- [1] A. M. Prakash, S. Unnikrishnan, J. Chem. Soc. Faraday Trans. 90 (1994) 2291

## Notes

- a. H<sub>2</sub>O includes water from phosphoric acid, pseudoboehmite and added water.
- b. Concentration of SiO<sub>2</sub> and organic template can vary over a range without affecting the phase purity. At low concentration of silica (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ≤ 0.3) or template (R/Al<sub>2</sub>O<sub>3</sub> ≤ 1.5), however, dense phase AlPO<sub>4</sub>-crystobalite co-crystallizes with SAPO-34.
- c. Use Teflon or stainless steel equipment throughout.
- d. Although SAPO-34 crystallizes without aging, the crystallinity of the resulting product can be improved by aging.

## CHA

## SAPO-44

## Al(48), P(34), Si(18)

Contributed by S. Ashtekar, S. V.V. Chilukuri and D. K.Chakrabarty

Verified by A. Prakash and by He Chang-Qing

Type Material: 5.0 (C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub>)[Si<sub>6.5</sub>Al<sub>17.3</sub>P<sub>12.2</sub>O<sub>72</sub>] · wH<sub>2</sub>O<sup>a</sup>

Method: S. Ashtekar, S. V.V. Chilukuri, D. K. Chakrabarty [1]

Batch Composition: Al<sub>2</sub>O<sub>3</sub> : 1.0 P<sub>2</sub>O<sub>5</sub> : 1.0 SiO<sub>2</sub> : 1.9 R : 63 H<sub>2</sub>O<sup>b</sup> (R = cyclohexylamine)

Source Materials

distilled water

orthophosphoric acid (85% H<sub>3</sub>PO<sub>4</sub>)

pseudoboehmite (Catapal-B, Vista, 70% Al<sub>2</sub>O<sub>3</sub>)

cyclohexylamine (99+%)

fumed silica (99+% SiO<sub>2</sub>)

Batch Preparation (for ~ 16 g product)

- (1) [90 g water + 34.59 g orthophosphoric acid + 21.86 g pseudoboehmite], mix thoroughly
- (2) [60 g water + 28.27 g cyclohexylamine + 9 g fumed silica], mix thoroughly
- (3) [(1) + (2)], mix thoroughly with vigorous agitation

Crystallization

Vessel: stainless steel autoclave

Temperature: 190°C

Time: 48 hours

Agitation: none

Product Recovery

- (1) Filter and wash with distilled water
- (2) Dry at 110°C
- (3) Yield near 100% on Al<sub>2</sub>O<sub>3</sub>

Product Characterization

XRD: CHA; competing phase: SAPO-5 (when gel C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio < 1.9)

Elemental Analysis: (Si<sub>0.18</sub>Al<sub>0.48</sub>P<sub>0.34</sub>)O<sub>2</sub><sup>a</sup>

Crystal Size and Habit: cubical morphology with 10-50 μm diameter [1]

Reference

- [1] S. Ashtekar, S. V. V. Chilukuri, D. K. Chakrabarty, J. Phys. Chem. 98 (1994) 4878

Notes

- a. Cations assumed to be protonated amine or surface hydroxyl.
- b. H<sub>2</sub>O includes water from pseudoboehmite and orthophosphoric acid.

**-CLO****Cloverite (GaPO<sub>4</sub>)****P(50), Ga(50)****Contributed by Céline Schott-Darie****Verified by S. Bradley, by W. Schmidt, and by R. Fricke****Type Materials:** 8{[Ga<sub>9</sub>P<sub>9</sub>O<sub>37</sub>(OH)<sub>24</sub>](QF)<sub>24</sub>(H<sub>2</sub>O)<sub>n</sub>} (Q = quinuclidine [1])**Method:** A. Merrouche, J. Patarin, H. Kessler, M. Soulard, L. Delmotte, J.-L. Guth, J. F. Joly [2]**Batch Composition:** Ga<sub>2</sub>O<sub>3</sub> : P<sub>2</sub>O<sub>5</sub> : HF : 80 H<sub>2</sub>O : 6 Q<sup>a</sup>**Source Materials**phosphoric acid (Fluka, 85% H<sub>3</sub>PO<sub>4</sub>)

distilled water

gallium sulfate [Ga<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · xH<sub>2</sub>O] (Strem Chemicals, wt.% Ga ~ 18)<sup>b</sup>

hydrofluoric acid (Fluka, 40% HF)

quinuclidine (Fluka, 97% C<sub>7</sub>H<sub>13</sub>N)**Batch Preparation (for 1 g product)**

- (1) [0.95 g phosphoric acid + 2.2 g H<sub>2</sub>O + 3.14 g gallium sulfate hydrate + 2.2 g H<sub>2</sub>O] stir until dissolved
- (2) [(1) + 0.2 g HF + 2.7 g quinuclidine], mix until uniform. Initial pH = 4 to 4.5

**Crystallization**

Vessel: PTFE-lined autoclave

Temperature: 150°C

Time: 24 hours

Agitation: none

**Product Recovery**

- (1) Filter, wash with distilled water, dry at 60°C
- (2) Yield: approximately 60% on Ga<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub>

**Product Characterization**XRD: Characteristic strong reflections at d = 25.4, 9.1 and 8.5 Å; competing phases are GaPO<sub>4</sub>-a and GaPO<sub>4</sub>-b [2] when the starting molar ratio F/Ga<sub>2</sub>O<sub>3</sub> < 0.5 [3]Elemental Analysis (anhydrous form): Q<sub>0.14</sub>Ga<sub>0.48</sub>P<sub>0.52</sub>O<sub>2</sub>F<sub>0.13</sub>Crystal Size and Habit: small cubes, less than 1 μm<sup>c</sup>

## References

- [1] M. Estermann, L. B. McCusker, C. Baerlocher, A. Merrouche, H. Kessler, *Nature* 352 (1991) 320
- [2] A. Merrouche, J. Patarin, H. Kessler, M. Soulard, L. Delmotte, J.-L. Guth, J. F. Joly, *Zeolites* 12 (1992) 226
- [3] J. Patarin, C. Schott-Darie, A. Merrouche, H. Kessler, M. Soulard, L. Delmotte, J.-L. Guth and J. F. Joly in *Proceedings from the 9th International Zeolite Conference*, R. von Ballmoos, J. B. Higgins and M. J. Treacy (eds), Butterworth-Heinemann, Stoneham, 1992, p. 263

## Notes

- a. The acceptable range for  $\text{HF}/\text{Ga}_2\text{O}_3$  is 0.75 to 2.
- b. Aldrich  $\text{Ga}_2(\text{SO}_4)_3$  acceptable substitute.
- c. Crystals are typically cubes with apparent truncatures when large (20  $\mu\text{m}$  or more). Increase in crystal size has been achieved by decreasing the amount of fluoride in the starting mixture to  $\text{F}/\text{Ga}_2\text{O}_3 < 0.5$  [3].

EAB

TMA-E

Si(74), Al(26)

---

Contributed by Rosario Aiello and Flaviano Testa

Verified by B. Schoeman and by B. Subotic'

Type Material:  $[\text{Na}_{6.84}(\text{TMA})_{3.05}] [(\text{AlO}_2)_{9.25}(\text{SiO}_2)_{26.75}] \cdot 17.12 \text{ H}_2\text{O}^a$  (TMA = tetramethylammonium)

Method: R. Aiello, R. M. Barrer [1]

Batch Composition:  $5 (\text{TMA})_2\text{O} : 3 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 15 \text{ SiO}_2 : 500 \text{ H}_2\text{O}$

#### Source Materials

distilled water

tetramethylammonium hydroxide (Fluka, purum, 25% aqueous solution)

sodium hydroxide (Carlo Erba, pellets, reagent grade, 30% aqueous solution)

alumina (Pfaltz and Bauer,  $\text{Al}(\text{OH})_3$ , 65%  $\text{Al}_2\text{O}_3$ )

silica (Sigma, fumed, 99+%  $\text{SiO}_2$ )

#### Batch Preparation (for 1.4 g dry product)

- (1) [13.78 g water + 9.10 g tetramethylammonium hydroxide solution + 2.00 g sodium hydroxide solution], mix until dissolved
- (2) [(1) + 0.39 g alumina], mix until homogeneous
- (3) [(2) + 2.25 g silica], mix thoroughly

#### Crystallization

Vessel: Teflon container

Time: 14 days

Temperature:  $80 \pm 2^\circ\text{C}$

Agitation: container is rotated

#### Product Recovery

- (1) Filter and wash thoroughly
- (2) Dry at ambient temperature
- (3) Yield: near 100% on  $\text{Al}_2\text{O}_3$

#### Product Characterization

XRD: EAB (only phase observed); competing phase: FAU (trace sometimes present)<sup>b</sup>

Elemental Analyses:  $(\text{Na}_2\text{O})_{0.74} : ((\text{TMA})_2\text{O})_{0.33}\text{Al}_2\text{O}_3 \cdot 5.74 \text{ SiO}_2$  <sup>c</sup>

Crystal Size and habit: 1-2  $\mu\text{m}$  faceted spherulites <sup>d,e</sup>

#### Reference

- [1] R. Aiello, R. M. Barrer, J. Chem. Soc. A (1970) 1470

## Notes

- a. Excess cations attributed to  $\text{SiO}^-$  fragments in the framework.
- b. FAU traces were observed from systems with lower TMA/Na ratio and with lower  $\text{H}_2\text{O}$  content.
- c. As reported in Ref. [1] for samples obtained both from batches with  $\text{Na}^+ / (\text{TMA})^+ = 0.5/0.5$  and  $0.2/0.8$ .
- d.  $\text{TMA}^+$  could not be removed by  $\text{NaNO}_3$  exchange.
- e. By thermal analysis, water is first lost endothermally, followed by exothermal oxidative decomposition of  $\text{TMA}^+$ .



EDI

Barrer K-F

Si(50), Al(50)

---

Contributed by Juliusz Warzywoda

Verified by T. Gier and by M. Sato

Type Material:  $K_{10}(Al_{10}Si_{10}O_{40}) \cdot wH_2O$  ( $w \sim 8$ )

Method: R. M. Barrer, B. M. Munday [1]

Batch composition:  $19.9 K_2O : Al_2O_3 : 2 SiO_2 : 378 H_2O$

#### Source Materials

deionized water

potassium hydroxide (pellets, 85% KOH min.)

kaolin ( $\sim Al_2Si_2O_5(OH)_4$ )

#### Batch Preparation (for 0.8 g product)

(1) [18.2 g water + 7.95 g potassium hydroxide]; dissolve KOH pellets in HDPE <sup>a</sup> bottle

(2) [(1) + 0.78 g kaolin]; seal the bottle and shake for 15 seconds <sup>b</sup>

#### Crystallization

Vessel: HDPE bottle

Temperature: 80°C

Time: 12 days

Agitation: occasional shaking

#### Product Recovery

(1) Filter to recover solids

(2) Wash with deionized water until pH of wash water is neutral

(3) Dry at 80°C

(4) Yield: 0.83-0.86 g (dry) (90% on Al or Si)

#### Product Characterization

XRD: Barrer K-F (no competing phases) [2]

Elemental Analyses:  $K_2O \cdot Al_2O_3 \cdot 2 SiO_2 \cdot 3 H_2O$  [3]

Crystal Size and Habit: inter-penetrating prismatic crystals, 2  $\mu m$  or less

#### References

[1] R. M. Barrer, B. M. Munday, J. Chem. Soc. (A) (1971) 2914

[2] J. D. Sherman in ACS Symp. Series 40, J. R. Katzer (ed.), Am. Chem. Soc., Washington, D. C., 1977, p. 30

[3] R. M. Barrer, J. W. Baynham. J. Chem. Soc. (1956) 2882

#### Notes

a. High density polyethylene

b. Upon addition of kaolin to the KOH solution, a slowly settling suspension of solids, rather than a homogeneous gel, is formed.

EDI

Linde Type F

Si(50), Al(50)

---

Contributed by Juliusz Warzywoda

Verified by T. Gier and by M. Sato

Type Material:  $K_{10}(Al_{10}Si_{10}O_{40}) \cdot wH_2O$  ( $w \sim 8$ )

Method: J. Warzywoda, R. W. Thompson [1]

Batch Composition: 5.26  $K_2O$  :  $Al_2O_3$  : 3  $SiO_2$  : 94.5  $H_2O$

#### Source Materials

deionized water  
potassium hydroxide (pellets, 85% KOH min.)  
aluminum (wire, 99.999% Al)  
silica (Cab-O-Sil M5, amorphous fumed  $SiO_2$ )

#### Batch Preparation (for 4 g product)

- (1) [20.0 g water + 9.26 g potassium hydroxide]; dissolve KOH pellets in HDPE a bottle. Divide into two equal portions
- (2) [First half (1) + 0.719 g aluminum];<sup>b</sup> dissolve the Al wire in half of the KOH solution by heating under reflux in a Teflon flask. Cool, filter and store in a HDPE bottle
- (3) [Second half (1) + 2.42 g silica]; dissolve the silica in the remaining KOH solution and heat at 80-95°C in a HDPE bottle. Cool, filter and store in a HDPE bottle<sup>c</sup>
- (4) [(2) + (3)]; heat (2) and (3) in HDPE bottles to 80-95°C and mix together.<sup>d</sup> Mix the resulting gel for 1-2 minutes at 1000 rpm with a mechanical stirrer to homogenize it<sup>e</sup>

#### Crystallization

Vessel: HDPE bottle  
Temperature: 95°C  
Time: 96 hours  
Agitation: static conditions with occasional mixing

#### Product Recovery

- (1) Filter to recover solids
- (2) Wash with deionized water until the pH of wash water is neutral
- (3) Dry at 80°C
- (4) Yield: 4.4 to 4.7 g (near 100% based on  $Al_2O_3$ )

#### Product Characterization

XRD: Linde Type F (ref. [2], Table III, page 35)  
Elemental Analyses:  $K_2O$  :  $Al_2O_3$  :  $2SiO_2$  :  $3H_2O$  [3]  
Crystal size and habit: small submicron prismatic crystals forming 0.5 to 3  $\mu m$  aggregates

## References

- [1] J. Warzywoda, R. W. Thompson, *Zeolites* 11 (1991) 577
- [2] J. D. Sherman, in *ACS Symp. Series 40*, J. R. Katzer (ed.), Am. Chem. Soc., Washington, D.C., 1977, p 30
- [3] R. M. Barer, J. W. Baynham, *J. Chem. Soc.* (1956) 2882

## Notes

- a. High density polyethylene.
- b. The dissolution of aluminum powder in these caustic solutions generates heat and hydrogen and can be somewhat violent.
- c. To avoid precipitation of solids from solutions (2) and (3), carry out crystallization immediately after solution preparations is complete.
- d. A viscous aluminosilicate gel is formed instantaneously.
- e. If no mechanical stirring is used, the gel appears to be very viscous with no visible fluid phase, and homogenization may be difficult. Brief heating of the gel at 95°C will give a fluid phase and hand shaking can be used to homogenize it.

## EMT

## EMC-2

## Si(79), Al(21)

Contributed by Jens Weitkamp

Verified by Kuei-jung Chao and by T. Chatelain

Type Material:  $\text{Na}_{20}[\text{Al}_{20}\text{Si}_{76}\text{O}_{192}] \cdot (18\text{-crown-6})_4$  [1]

Method: J. Weitkamp, R. Schumacher [1-3]

Batch Composition: 2.2  $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$  : 10  $\text{SiO}_2$  : 140  $\text{H}_2\text{O}$  : 0.87 (18-crown-6)

### Source Materials

demineralized water  
sodium hydroxide (Fluka reagent grade)  
sodium aluminate (Riedel-de Haën; 54%  $\text{Al}_2\text{O}_3$ , 41%  $\text{Na}_2\text{O}$ )  
crown ether (Fluka 18-crown-6)  
silica sol (Bayer AG, VP 4039, 30%  $\text{SiO}_2$ )

### Batch Preparation (for 19 g product)<sup>a</sup>

- (1) [39 g water + 6.05 g NaOH solution (50%) + 7.26 g sodium aluminate + 8.81 g (18-crown-6)], dissolve under continuous stirring
- (2) [(1) + 77 g silica sol], stir vigorously

### Crystallization

Vessel: stainless steel autoclave (150 mL)  
Incubation: one day at room temperature  
Temperature: 110°C  
Time: 12 days  
Agitation: none

### Product Recovery

- (1) Filter and wash extensively with demineralized water
- (2) Dry at 120°C for 16 hours
- (3) Yield: approximately 19 g (still containing the template and some adsorbed water), 56% based on Alb

### Product Characterization

XRD: EMT; competing phases: GIS and FAU  
Elemental Analyses:  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 7.6$  (by AES/ICP and  $^{29}\text{MAS}$  NMR) [2]  
Crystal Size and Habit: hexagonal, 4-5  $\mu\text{m}$  mean diameter, 0.5 to 1.0  $\mu\text{m}$  thick

### References

- [1] F. Delprato, L. Delmotte, J.-L. Guth, L. Huve, Zeolites 10 (1990) 546
- [2] J. Weitkamp, R. Schumacher, in Proceed. Ninth Int. Zeo. Conf., R. von Ballmoos, J. B. Higgins, M. M. J. Treacy, (eds.), Butterworth-Heinemann, Boston, 1993, p. 353
- [3] J. Weitkamp, R. Schumacher, U. Weiß, Chem.-Ing. Tech. 64 (1993) 1109

### Notes

- a. This synthesis has been successfully scaled-up by a factor of four (yield 69 g).
- b. Calcination at 540°C in air for 16 hours removes template.

EUO

[Ga] EU-1

Si(96.5), Ga(3.5)

Contributed by A. N. Kotasthane

Verified by S. Lambert, by H. Kessler, and by T. Loiseau

Type Material:  $\text{Na}_5[\text{Ga}_4\text{Si}_{108}\text{O}_{224}] : w\text{H}_2\text{O}$  ( $w \sim 26$ )

Method: G. N. Rao, V. P. Shiralkar, A. N. Kotasthane, P. Ratnasamy [1]

Batch Composition:  $7.0 \text{ Na}_2\text{O} : \text{Ga}_2\text{O}_3 : 36.6 \text{ SiO}_2 : 4.0 \text{ R} : 5.55 \text{ H}_2\text{SO}_4 : 926 \text{ H}_2\text{O}^a$   
(R = hexamethonium dibromide ( $\text{C}_{12}\text{H}_{30}\text{N}_2\text{Br}_2$ ))

#### Source Materials

demineralized water  
sodium hydroxide, reagent grade (97%)  
silica sol (27.4%  $\text{SiO}_2$ , 0.5%  $\text{Na}_2\text{O}$ )  
sulfuric acid (AR BDH, 98%)  
gallium(III)sulfate (Aldrich 99.99%)  
hexamethonium bromide monohydrate (HM-Br<sub>2</sub>, Aldrich)

#### Batch Preparation (for 24 g product)

- (1) [30.0 g water + 5.41 g sodium hydroxide], mix until dissolved,  $\text{pH} = 13.8 \pm 0.2$
- (2) [81.0 g silica sol + 20 g water], mix until uniform,  $\text{pH} = 9.8 \pm 0.2$
- (3) [(1) + (2)], mix until uniform,  $\text{pH} = 13.6 \pm 0.2$
- (4) [30 g water + 2.6 g sulfuric acid + 4.3 g gallium sulfate], mix until dissolved; heating on hot plate for 15 minutes essential,  $\text{pH} = 0.08 \pm 0.02$
- (5) [(3) + (4)], add (4) drop-wise to (3) with good mixing
- (6) [30 g water + 15.2 g HM-Br<sub>2</sub>], mix until dissolved.  $\text{pH} = 7.2 \pm 0.2$
- (7) [(5) + (6)], add (6) to (5) with good mixing. Adjust final batch to  $\text{pH} = 12.6$  with 1 M NaOH <sup>b</sup>

#### Crystallization

Vessel: stainless-steel autoclave (Parr, 300 mL capacity)  
Temperature: 170°C  
Time: 6 days  
Agitation: propeller mixer (250 RPM)

#### Product Recovery

- (1) Cool and filter to recover solids. Slurry  $\text{pH}$  after crystallization =  $10.5 \pm 0.2$
- (2) Wash extensively with demineralized water until filtrate  $\text{pH} < 9$
- (3) Dry at 110°C for 12 to 15 hours
- (4) Yield: approximately 24 g (56% on  $\text{Ga}_2\text{O}_3$ , 79% on  $\text{SiO}_2$ )

#### Product Characterization

XRD: Pure EU-1 phase (EUO framework topology) having characteristic strong reflections at  $d = 4.30, 3.99$  and  $3.28\text{\AA}$  without any impurity phases. On longer crystallization (above 6 days), alpha quartz appears

Elemental Analysis: 92.4%  $\text{SiO}_2$ , 5.24%  $\text{Ga}_2\text{O}_3$ , 2.36%  $\text{Na}_2\text{O}$  ( $\text{SiO}_2/\text{Ga}_2\text{O}_3 = 55.0$ ,  $\text{Na}_2\text{O}/\text{Ga}_2\text{O}_3 = 1.36$ )<sup>c,d</sup>

Crystal Size and Habit: Homogeneously distributed small spheres (2-3  $\mu\text{m}$ )

## Reference

- [1] G. N. Rao, V. P. Shiralkar, A. N. Kotasthane, P. Ratnasamy, in *Synthesis of Microporous Materials*, Vol. I, M. L. Occelli, H. E. Robson (eds.), Van Nostrand Reinhold, New York (1992) p 153

## Notes

- a. Increasing  $\text{SiO}_2/\text{Ga}_2\text{O}_3$  in gel from 35 to 70 and to 110 gives  $\text{SiO}_2/\text{Ga}_2\text{O}_3$  in product of 79 and 100 respectively. For products with  $\text{SiO}_2/\text{Ga}_2\text{O}_3$  greater than 100, the preferred template is equimolar benzyldimethylamine + benzyl chloride. [1]
- b. The  $\text{Na}_2\text{O}$  content of the silica source is significant. If gel pH is less than 12.0, it should be adjusted with NaOH solution.
- c. By thermal analysis: template burnout 300-700°C (approximately 10% weight loss).
- d. By  $^{71}\text{Ga}$  MAS NMR: chemical shift  $\delta = 170$  ppm ( $\text{Ga}_{3+}$  in tetrahedral environment).

## FAU

## Linde Type X

## Si(55), Al(45)

Contributed by Hans Lechert and Philip Staelin

Verified by D. Ginter, by E. Basaldella, and by E. Fallabella Sousa-Aguiar

Type Material:  $\text{Na}_{86}\text{Al}_{86}\text{Si}_{106}\text{O}_{384} : w\text{H}_2\text{O}$  (w ~ 260)

Method: H. Lechert, H. Kacirek [1, 2]

Batch Composition:  $\text{NaAlO}_2 : 4 \text{SiO}_2 : 16 \text{NaOH} : 325 \text{H}_2\text{O}^{\text{a,b}}$

#### Source Materials

distilled water

sodium hydroxide (99+% NaOH)

alumina trihydrate (Merck, 65%  $\text{Al}_2\text{O}_3$ )<sup>c</sup>

sodium silicate solution (27.35%  $\text{SiO}_2$ , 8.30%  $\text{Na}_2\text{O}$ , 1.37 g/mL)

#### Batch Preparation (for 42 g product)

- (1) [100 g water + 100 g sodium hydroxide], stir until dissolved
- (2) [(1) + 97.5 g alumina trihydrate], stir at 100°C until dissolved, cool to 25°C
- (3) [(2) + 202.5 g water], mix
- (4) [100 g of solution (3) + 612 g water + 59.12 g sodium hydroxide], mix until dissolved
- (5) [219.7 g sodium silicate solution + 612 g water + 59.12 g sodium hydroxide], mix until dissolved
- (7) [(4) + (5)], combine quickly and stir for 30 minutes<sup>d</sup>

#### Crystallization

Vessel: polyethylene bottles

Temperature: 90°C<sup>e</sup>

Time: 8 hours

Agitation: none

#### Product Recovery

- (1) Filter and wash to pH < 10
- (2) Dry at 100°C, equilibrate over saturated aqueous NaCl
- (3) Yield: near 100% on  $\text{Al}_2\text{O}_3$

#### Product Characterization

XRD: 100% FAU,  $a_0 = 24.92 \text{ \AA}$ , competing phases: LTA, GIS, ANA, SOD

Elemental Analysis:  $\text{NaAlO}_2 \cdot 1.24 \text{SiO}_2^{\text{f}}$

Crystal Size and Habit: spherical aggregates, 0.8  $\mu\text{m}$  dia.

#### References

- [1] H. Lechert, H. Kacirek, Zeolites 11 (1991) 720
- [2] H. Lechert, H. Kacirek, Zeolites 13 (1992) 192
- [3] G. H. K hl, Zeolites 7 (1987) 451

## Notes

- a. NaX zeolites are easily obtained with gel  $\text{SiO}_2/\text{NaAlO}_2 = 1.4\text{--}5.0$ ,  $\text{NaOH}/\text{NaAlO}_2 = 3.8\text{--}20$  and  $\text{H}_2\text{O}/\text{NaAlO}_2 = 150\text{--}400$ .
- b. Crystallization at lower water contents suffers from the high initial viscosities of the batches, thus preventing sufficient homogenization. NaX can be obtained without precautions down to  $\text{H}_2\text{O}/\text{NaAlO}_2 = 80$ . The crystallizing zeolite and its composition depend strongly on the alkalinity being held in the solution phase during the nucleation and growth of the zeolite. For a given batch composition, if the water content is decreased appreciably, the alkalinity will increase. If there are reasons to decrease the water content, the NaOH content should be decreased. Good results were obtained by reducing the alkali content proportional to the water content.
- c. For the batch preparation, the authors would always prefer sodium aluminate instead of alumina trihydrate. Problems often occurred with the solubility of the  $\text{Al}(\text{OH})_3$  at the given NaOH concentration, depending on the alumina source. Sodium aluminate is usually available only in technical-grade quality. If only small quantities of NaX or pure substances are desired, it was preferable to use  $\text{AlCl}_3$  as the alumina source and to increase the NaOH content of the batch by 3 NaOH on the given batch composition to:  $\text{AlCl}_3 : 4 \text{SiO}_2 : 20 \text{NaOH} : 325 \text{H}_2\text{O}$ . The resulting NaCl does not disturb the crystallization.
- d. Longer times of homogenization give narrower particle size distributions.
- e. Preferable crystallization temperatures:  $67^\circ$  to  $97^\circ\text{C}$ . For safety the crystallization time should be increased to 12 to 14 hours. Experiments have shown that in the given batches up to 30 hours at  $90^\circ\text{C}$  no other zeolite impurities were observed.
- f. The Si/Al ratio of the product depends strictly on the NaOH concentration in the batch. Below 2.0 NaOH/liter, the nucleation rate of NaX goes almost to zero and nucleation of GIS occurs, which grows faster than NaX. Pure FAU with  $\text{Si}/\text{Al} > 1.5$  in the product cannot be obtained without seeding. Above about 3.0 NaOH/liter, analcime or sodalite is obtained. Below  $\text{Si}/\text{Al} = 12.4$ , NaA appears. [3]



## FAU

## Low-silica Type X (LSX)

Si(50.5), Al(49.5)

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Contributed by Günter Kühl

Verified by M. Ludvig and by D. Millar

Type Material:  $\text{Na}_{73}\text{K}_{22}\text{Al}_{95}\text{Si}_{97}\text{O}_{384} : w\text{H}_2\text{O}$

Method: G. H. Kühl [1]

Batch Composition: 5.5  $\text{Na}_2\text{O}$  : 1.65  $\text{K}_2\text{O}$  :  $\text{Al}_2\text{O}_3$  : 2.2  $\text{SiO}_2$  : 122  $\text{H}_2\text{O}$ <sup>a-c</sup>

### Source Materials

distilled water

sodium aluminate (Nalco 680, 45.6%  $\text{Al}_2\text{O}_3$ , 29.65%  $\text{Na}_2\text{O}$ )

potassium hydroxide, reagent grade (usually ~86% KOH)

sodium hydroxide, reagent grade (usually ~97% NaOH)

sodium silicate solution (PQ Corp. N-brand clarified, 28.7%  $\text{SiO}_2$ , 8.9%  $\text{Na}_2\text{O}$ )

### Batch Preparation ( for 29 g dry product)<sup>d</sup>

- (1) [30 g water + 22.37 g sodium aluminate], stir until dissolved
- (2) [70 g water + 21.53 g potassium hydroxide + 31.09 g sodium hydroxide], stir until dissolved
- (3) [(1) + (2)], mix thoroughly<sup>e</sup>
- (4) [(3) + 71.8 g water + 46.0 g sodium silicate solution], mix thoroughly<sup>f</sup>

### Crystallization

Vessel: sealed polypropylene or Teflon jar

Incubation: 3 hours at 70°C without stirring

Temperature: 93-100°C

Time: 2 hours

Agitation: either with or without stirring

### Product Recovery

- (1) Dilute the reaction mixture with distilled water
- (2) Filter and wash with 0.01 N NaOH<sup>g</sup>
- (3) Dry at ambient temperature (drying at 110-125°C acceptable)
- (4) Yield: 99+% based on alumina

### Product Characterization

XRD: FAU ( $a_0 = 25.03 \text{ \AA}$ );<sup>h</sup> competing phases: LTA (when gel  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.0$ ), SOD (concentration is too high), P (extended aging or crystallization times)

Elemental Analysis: 0.77  $\text{Na}_2\text{O}$  · 0.23  $\text{K}_2\text{O}$  ·  $\text{Al}_2\text{O}_3$  · 2.04  $\text{SiO}_2$

Crystal Size and Habit: multi-faceted spherulites of 2-6  $\mu\text{m}$  dia. with 111 faces exposed [1]

### Reference

- [1] G. H. Kühl, Zeolites 7 (1987) 451

## Notes

- a.  $\text{H}_2\text{O}$  includes water from sodium aluminate, waterglass, free and bound water in  $\text{NaOH} + \text{KOH}$ , and added water.
- b.  $(\text{K}_2\text{O} + \text{Na}_2\text{O})/\text{SiO}_2$  can be reduced to 2.25 without loss of product quality. However, at least for the initial crystallizations, a value of 3.25 is recommended.
- c. The ratio:  $\text{Na}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O})$  is critical; it should be in the range 0.77 to 0.78.
- d. Use plastic or stainless steel equipment throughout.
- e. Solution (1) should be perfectly clear, but it is probably acceptable if a clear solution (3) is obtained after adding  $\text{NaOH}$  and  $\text{KOH}$ .
- f. The mixture must not gel before it is well mixed. It usually takes several minutes before a gel is formed.
- g. Wash or exchange in 0.01 N  $\text{NaOH}$  to prevent hydrolysis; low-silica X hydrolyzes as easily as NaA.
- h. The lower  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio enhances the line intensities, the presence of  $\text{K}^+$  attenuates them.

## FAU

## Linde Type Y

## Si(71), Al(29)

Contributed by David Ginter

Verified by G. Price and by C. Kuntz

Type Material:  $\text{Na}_{56}[\text{Al}_{56}\text{Si}_{136}\text{O}_{384}] : 250 \text{ H}_2\text{O}$

Method; D. M. Ginter, A. T. Bell and C. J. Radke [1]

**Batch composition<sup>a</sup>**

Seed Gel (5% of Al):  $10.67 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 10 \text{ SiO}_2 : 180 \text{ H}_2\text{O}$

Feed Stock Gel (95% of Al):  $4.30 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 10 \text{ SiO}_2 : 180 \text{ H}_2\text{O}$

Overall Gel:  $4.62 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 10 \text{ SiO}_2 : 180 \text{ H}_2\text{O}$

**Source Materials**

deionized water

sodium aluminate solid (Strem Chemical,<sup>b</sup> 1.27 Na/Al, 6.1%  $\text{H}_2\text{O}$ )

sodium hydroxide pellets (J. T. Baker, 99% NaOH)

sodium silicate solution (PQ Corp, N Brand, 28.7 wt%  $\text{SiO}_2$ , 8.9 wt%  $\text{Na}_2\text{O}$ )<sup>c</sup>

**Batch Preparation (for 32 g anhydrous product)**

**Seed Gel:**

- (1) [19.95 g water + 4.07 g sodium hydroxide + 2.09 g sodium aluminate], stir in 50 mL plastic bottle until dissolved
- (2) [(1) + 22.72 g sodium silicate solution], stir moderately for at least 10 minutes; after stirring, cap the bottle and let the solution age at room temperature for 1 day<sup>d</sup>

**Feedstock Gel:<sup>e</sup>**

- (3) [130.97 g water + 0.14 g sodium hydroxide + 13.09 g sodium aluminate], stir in a 500 mL plastic beaker until dissolved
- (4) [(3) 142.43 g sodium silicate solution], stir vigorously with a high-shear turbine mixer<sup>f</sup> until the gel appears somewhat smooth; cover the beaker until the addition of the seed gel

**Overall Gel:**

- (5) [(4) + 16.50 g of (2)], slowly add seed gel (2) to feedstock gel (4) under high shear;<sup>f</sup> move the beaker during mixing to ensure the entire gel volume encounters the high shear from the turbine (up to 20 minutes)<sup>g</sup>

**Crystallization**

Vessel: 300 mL polypropylene bottle (sealed)

Incubation: One day at room temperature <sup>g</sup>

Temperature: 100°C <sup>g</sup>

Time: After about 5 h, the gel will separate into a solid (containing the NaY Zeolite) that will settle to the bottom, and a hazy supernatant liquid. Continue heating until the supernatant is clear indicating complete crystallization (no more than 2 additional hours)<sup>g</sup>

### Product Recovery

- (1) Centrifuge; decant supernatant
- (2) Filter the wet solid product; wash with distilled water until pH of filtrate is below 9
- (3) Dry at 110°C
- (4) Yield: approximately 32 g of anhydrous NaY (about 98% on  $\text{Al}_2\text{O}_3$ )

### Product Characterization

XRD: FAU; characteristic strong reflections at  $d = 14.28, 8.75$  and  $7.46 \text{ \AA}$ ,  $a_0 = 24.72 \text{ \AA}$ .

Competing phases (if present): GIS, GME, CHA

Elemental Analysis;  $\text{NaAlO}_2 \cdot 2.43 \text{ SiO}_2$

Crystal Size and Habit: octahedral crystals,  $< 1 \text{ }\mu\text{m}$

### References

- [1] D. M. Ginter, A. T. Bell, C. J. Radke, in *Synthesis of Microporous Materials*, Vol. I, Molecular Sieves, M. L. Occelli, H. E. Robson (eds.), Van Nostrand Reinhold, New York, 1992, p 6
- [2] T. Linder, C. Kurtz, personal communications

### Notes

- a. This procedure is reliable only for the production of submicron NaY crystals and is limited in the range of sizes and compositions that can be produced using slight procedural modifications.
- b. Also available as solutions with this Na/Al ratio from Alcoa and U. S. Aluminate.
- c. It should be clear of precipitated material.
- d. Solution is clear when prepared; during aging, a loose gel forms which contains the NaY seeds.
- e. May be prepared concurrently with the seed gel or just prior to mixing the overall gel.
- f. 1600 rpm with 2.5 inch diameter, 4 paddle radial mixer (minimum) recommended.
- g. If a GIS (NaP) impurity is produced, it can be eliminated by reducing the Na aluminate in (1) to 1.40 g and aging the seed gel for 1 to 5 days prior to blending it into the feedstock. Further aging of the composite is optional with this seed, and pure product has been obtained after crystallization at 90°C for 22 hours [2]

## FAU

## High-silica Faujasite EMC-1<sup>a</sup>

Si(79), Al(21)

Contributed by Joël Patarin

Verified by C.-n. Wu, by J. Dwyer, and by J. Zhao

Type Material:  $\text{Na}_{40}[\text{Al}_{40}\text{Si}_{152}\text{O}_{384}] \cdot (15\text{-Crown-5})_8 : (\text{H}_2\text{O})_{60}$

Method: T. Chatelain, J. Patarin, M. Soulard, J.-L. Guth, P. Schulz [1]

Batch Composition: 2.1  $\text{Na}_2\text{O}$  : 10  $\text{SiO}_2$  :  $\text{Al}_2\text{O}_3$  : 0.5(15-crown-5) : 100  $\text{H}_2\text{O}$

### Source Materials

distilled water  
crown ether (Aldrich 15-crown-5, 98%)  
sodium hydroxide (Fluka, 98%)  
sodium aluminate (Carlo Erba, 56%  $\text{Al}_2\text{O}_3$ , 37%  $\text{Na}_2\text{O}$ )  
silica sol (Ceca, 40%  $\text{SiO}_2$ )

### Batch Preparation<sup>b</sup> (for 15 g product)<sup>c</sup>

- (1) [17.75 g water + 2.25 g crown ether], dissolve under continuous stirring
- (2) [(1 + 1.65 g sodium hydroxide), dissolve under continuous stirring
- (3) [(2) + 3.64 g sodium aluminate], dissolve under continuous stirring
- (4) [(3) 30.00 g silica sol] stir with a magnetic bar at approximately 200 rpm Continue stirring for 24 hours at room temperature.<sup>d</sup> Gel pH = 13.5-14

### Crystallization

Vessel: Teflon-lined stainless steel autoclave (150 mL)  
Temperature: 110°C  
Time: 8 days  
Agitation: none  
Final pH = approximately 12.5

### Product Recovery

- (1) Filter and wash with distilled water until pH of the filtrate is close to 6
- (2) Dry at 60-70°C overnight
- (3) Yield: 99% based on alumina (as-synthesized product containing the organic template and some water)<sup>e</sup>

### Product Characterization

XRD: FAU,  $a_0 = 24.57 \text{ \AA}$   
Elemental Analysis:  $\text{SiO}_2/\text{Al}_2\text{O}_3$  7.6 (by atomic absorption spectroscopy and  $^{29}\text{Si}$  MAS NMR)  
Crystal Size and Habit: truncated octahedra, 1  $\mu\text{m}$  dia.

## References

- [1] T. Chatelain, J. Patarin, M. Soulard, J.-L. Guth, P. Schulz, *Zeolites* 15 (1995) 90
- [2] D. Anglerot, F. Fitoussi, P. Schulz, T. Chatelain, F. Dougnier, J. Patarin, J.-L. Guth, in *Synthesis of Porous Materials, Zeolites, Clays and Nanostructures*, M. L. Occelli, H. Kessler (eds.), Marcel Dekker, New York, 1996, p. 325

## Notes

- a. EMC-1 = Elf Mulhouse Chemistry number one.
- b. The starting mixture is prepared in a polypropylene bottle.
- c. This synthesis has been successfully carried out at the kilogram scale [2].
- d. The mixture is aged in a closed polypropylene bottle.
- e. Calcination at 450°C in air removes the template.

FAU

[Ga] Type Y

Si (61), Ga (39)

Contributed by Mario Occelli

Verified by F. Machado, by S. Iwamoto, and by M. Levinbuk

Type Material:  $\text{Na}_{76}\text{Ga}_{76}\text{Si}_{116}\text{O}_{384} : w\text{H}_2\text{O}$ 

Method: M. L. Occelli [1]

Batch Composition:  $4.0 \text{ Na}_2\text{O} : \text{Ga}_2\text{O}_3 : 9.8 \text{ SiO}_2 : 150 \text{ H}_2\text{O}$ **Source Materials**

deionized water  
sodium hydroxide, reagent grade (usually ~97% NaOH)  
gallium oxide (99.99%)  
silica sol (Dupont HS-40, 39%  $\text{SiO}_2$ , 0.5%  $\text{Na}_2\text{O}$ )

**Batch Preparation**

- (1) [32.0 g water + 32.0 g sodium hydroxide + 18.7 g gallium oxide], dissolve gallium oxide in 50% NaOH at 80°C with stirring until a clear solution is obtained. Cool to ambient temperature
- (2) [(1) + 70.6 g water], mix <sup>a</sup>
- (3) [150.2 g silica sol + 70 g water], mix
- (4) [(3) + (2)], add the sodium gallate solution dropwise to the vigorously-stirred, diluted silica sol. Continue stirring for 16 hours at ambient temperature

**Crystallization**

Vessel: one-liter round-bottomed flask with reflux condenser  
Incubation: 16 h at 25°C with stirring  
Temperature: 95°C<sup>b</sup>  
Time: 90 hours<sup>c</sup>

**Product Recovery**

- (1) Filter and wash with deionized water until pH < 10
- (2) Dry at 110°C
- (3) Yield: near 100% on  $\text{Ga}_2\text{O}_3$

**Product Characterization**

XRD: FAU; no other crystalline phases or amorphous material observed  
Elemental Analyses: 38.7 wt%  $\text{Ga}_2\text{O}_3$ , 38.0 wt%  $\text{SiO}_2$ , 12.5 wt%  $\text{Na}_2\text{O}$  ( $0.98 \text{ Na}_2\text{O} \cdot \text{Ga}_2\text{O}_3 \cdot 3.06 \text{ SiO}_2$ )<sup>d</sup>

**References**

- [1] M. L. Occelli, US Patent 4 803 060 (1989)
- [2] M. L. Occelli, A. E. Schweizer, H. Eckert, A. Auroux, P. S. Iyer, Appl. Catalysis (to be submitted)

**Notes**

- a. Diluted sodium gallate solution must be clear.
- b. The temperature of the stirred, cold-aged hydrogel is raised to 95°C. When the hydrogel reaches 95°C the stirring is immediately stopped.
- c. Method to reduce crystallization time given in ref. [1, 2]
- d. After calcination at 600°C for 2 h; BET surface area 541  $\text{m}^2/\text{g}$ .

FAU

SAPO-37

Al(47), P(36) Si(17)

**Contributed by** M. J. Franco and J. Pérez-Pariente**Verified by** J. Patarin and by M. Ribeiro**Type Material:** (7TMA, 13TPA)[Al<sub>90</sub>Si<sub>33</sub>P<sub>69</sub>O<sub>384</sub>]

(TMA = tetramethyl ammonium, TPA = tetra-n-propyl ammonium)

**Method:** M. J. Franco, J. Pérez-Pariente, A. Mifsud, T. Blasco, J. Sanz [1]**Batch Composition:** 0.025(TMA)<sub>2</sub>O : 1.0(TPA)<sub>2</sub>O : 1.0Al<sub>2</sub>O<sub>3</sub> : 1.0P<sub>2</sub>O<sub>5</sub> : 1.0SiO<sub>2</sub> : 50H<sub>2</sub>O**Source Materials**

deionized water

phosphoric acid (Riedel-de Hæn, 85% H<sub>3</sub>PO<sub>4</sub>)alumina (pseudoboehmite, Vista, 70% Al<sub>2</sub>O<sub>3</sub>)<sup>a</sup>tetrapropylammonium hydroxide (TPAOH), Alfa, 40% aqueous solution)<sup>b</sup>tetramethylammonium hydroxide (TMAOH · 5H<sub>2</sub>O, Aldrich, 99%)

fumed silica (Aerosil 200, Degussa)

**Batch Preparation (for 6.2 g product)<sup>c</sup>**

- (1) [20.69 g water + 23.04 g phosphoric acid + 14.56 g alumina]. Mix water and phosphoric acid at 293K and add the alumina very slowly with vigorous stirring (1500 rpm). Continue stirring for 8 hours at 293K in a temperature-controlled bath
- (2) [101.68 g tetrapropylammonium hydroxide (40% solution) + 0.90 g tetra-methylammonium hydroxide + 6.00 g silica]. Dissolve the TMAOH in the TPAOH solution in a separate glass beaker. To this solution add the silica under vigorous stirring. Continue stirring for one hour
- (3) [(1) + (2)] Add silicate solution (2) slowly to aluminate slurry (1) under vigorous stirring. Continue stirring for 24 hours at 293K. The final gel pH should be approximately 7.5

**Crystallization**

Vessel(s): 60 mL Teflon-lined stainless steel autoclave(s)

Temperature: 200°C <sup>d</sup>

Time: 13 hours

Agitation: none

**Product Recovery**

- (1) Quench autoclave in cold water
- (2) Recover solids by centrifugation (6000 rpm)
- (2) Wash with cold distilled water
- (4) Dry at 80°C for 16 hours
- (5) Yield: 3.7 g solid/100 g of gel (19% on Al<sub>2</sub>O<sub>3</sub>)



### Product Characterization

XRD: FAU-type, pure. Competing phases: AFI and SOD when other compositions and/or crystallization treatments are used

Elemental Analysis:  $(\text{Si}_{0.17}\text{Al}_{0.47}\text{P}_{0.36})_{192}\text{O}_{384} \cdot 3.5(\text{TMA})_2\text{O} \cdot 6.5(\text{TPA})_2\text{Oe}$

Crystal Size and Habit: Crystals are quite homogeneous in size (approximately  $4.0\ \mu\text{m}$  dia.) and show interpenetrating octahedra morphology <sup>f</sup>

### Reference

- [1] M. J. Franco, J. Pérez-Pariente, A. Mifsud, T. Blasco, J. Sanz, *Zeolites* 12 (1992) 386

### Notes

- a. B.E.T. surface area  $271\ \text{m}^2/\text{g}$ ; the alumina may be critical. Aluminum isopropoxide gave negative results.
- b. Commercial 20% TPAOH can be vacuum stripped to 40%; however it is critical to make sure that there has not been decomposition of the TPAOH. For this reason, it is necessary to make a  $\text{OH}^-$  titration before and after the evaporation process to check that the total amount of  $\text{OH}^-$  has not changed.  $(\text{Na} + \text{K}) < 340\ \text{ppm}$
- c. During preparation of the gel, it is very important to use a closed vessel and a temperature controlled bath (293K) to ensure a constant water concentration in the gel. This vessel can be a polypropylene bottle with a hole in the cap to fit the rotating shaft of the stirring device. A stirring device with two movable Teflon blades is recommended.
- d. Heat-up rate:  $2.5^\circ/\text{min.}$ ; autogenous pressure.
- e. Flow thermogravimetric analysis showed three different weight losses: 373 to 473K (water desorption), 473 to 688K (decomposition of  $\text{TPA}^+$  in the alpha cages), 588 to 973K (decomposition of  $\text{TMA}^+$  in the sodalite cages).
- f. Increasing  $(\text{TPA})_2\text{O}/\text{Al}_2\text{O}_3$  in gel from 1.0 to 1.5 (keeping  $\text{TPA}^+/\text{TMA}^+ = 40$ ) decreased average crystal diameter from 4 to  $2\ \mu\text{m}$  and increased product yield by 100%. [1]

**FER**

**ZSM-35**

**Si(87), Al(13)**

**Contributed by** Jinxiang Dong

**Verified by** S. Weigel, by L. Schreyeck, and by T. Beelen

**Type Material:**  $\text{Na}_5[\text{Al}_5\text{Si}_{31}\text{O}_{72}] : w\text{H}_2\text{O}$  ( $w \sim 18$ )

**Method:** P. A. Jacobs, J. A. Martens [1]

**Batch Composition:**  $1.85 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 15.2 \text{ SiO}_2 : 592 \text{ H}_2\text{O} : 19.7 \text{ C}_2\text{DN}^a$  ( $\text{C}_2\text{DN} = \text{ethylenediamine}$ )

**Source Materials**

distilled water  
sodium hydroxide (Merck, reagent grade)  
sodium aluminate (Hopkin & Williams, technical grade)<sup>b</sup>  
silica sol (Dupont Ludox AS-30, 30%  $\text{SiO}_2$ )  
ethylenediamine (Merck, reagent grade)

**Batch Preparation (for 10 g dry product)**

- (1) [129 g water + 0.7 g sodium hydroxide + 3.3 g sodium aluminate], stir until dissolved
- (2) [46.47 g silica sol + 18.3 g  $\text{C}_2\text{DN}$ ], mix
- (3) [(1) + (2)], mix thoroughly

**Crystallization**

Vessel: stainless steel autoclaves (250 mL)  
Temperature:  $177^\circ\text{C}$   
Time: 10 days  
Agitation: 15 rpm, tumbling [2]

**Product Recovery**

- (1) Filter solid products and wash with distilled water
- (2) Dry at  $120^\circ\text{C}$
- (3) Yield: 60% on  $\text{SiO}_2$

**Product Characterization**

XRD: FER (only crystalline phase); Competing phases: quartz, MOR, MFI  
Elemental Analysis:  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 13$   
Crystal Size and Habit: irregular, approximately  $1 \mu\text{m}$  long

**References**

- [1] P. A. Jacobs, J. A. Martens, *Stud. Surf. Sci. Catal.* 33 (1987) 217
- [2] L. Schreyeck, personal communication
- [3] C. L. Kibby, A. J. Perrota, F. E. Massoth, *J. Catal.* 35 (1974) 256
- [4] W. Xu, J. Li, W. Li, H. Zhang, B. Liang, *Zeolites* 9 (1989) 468

**Notes**

- a. Hydrothermal syntheses using different organic additives are reported in the literature, particularly pyrrolidine [1] and tetramethyl-ammonium cation [3]. Nonaqueous methods based on ethylenediamine plus triethyl-amine give good crystallinity and improved yield.[4]
- b. Assumed 1.28 Na/Al, 16%  $\text{H}_2\text{O}$

## GIS

## Zeolite P

Si(54), Al(46)

Contributed by Lovat V. C. Rees

Verified by Yingcai Long, by P. Sidheswaran, and by G. Price

Type Material:  $(\text{NaAlO}_2)_7(\text{SiO}_2)_9$

Method: L. V. C. Rees and S. Chandrasekhar [1]

Batch Composition:  $\text{Al}_2\text{O}_3 : 2.2 \text{ SiO}_2 : 5.28 \text{ NaF} : 105.6 \text{ H}_2\text{O}$

### Source Materials

distilled water

sodium fluoride (BDH Analor)

kaolinite ( $\text{Al}_2\text{O}_3 : 2.2 \text{ SiO}_2 : 2 \text{ H}_2\text{O}$ )<sup>a</sup>

### Batch Preparation (for 10 g dry product)

- (1) [87.7 g water + 10.4 g sodium fluoride], stir and make a slurry
- (2) [(1) + 12.7 g kaolin], mix thoroughly

### Crystallization

Vessel: sealed polypropylene

Time: 60 days

Temperature: 85°C

Agitation: none

pH: initial 7.5, final 9-10

### Product Recovery

- (1) Filter and wash thoroughly with distilled water
- (2) Exchange twice with NaCl solution
- (3) Wash with distilled water (adjusted to pH = 10 with NaOH)
- (4) Dry at 85°C for 24 hours
- (5) Rehydrate over water vapor from saturated NaCl solution

### Product Characterization

XRD: Strong zeolite P; competing phases: CHA, no SOD

Elemental Analysis:  $\text{NaAlO}_2 \cdot 1.18 \text{ SiO}_2$  (by atomic absorption spectroscopy)<sup>b,c</sup>

Crystal Size and Habit: spherulitic particles of approximately 10  $\mu\text{m}$  dia.

### Reference

- [1] L. V. C. Rees, S. Chandrasekhar, *Zeolites* 13 (1993) 535

### Notes

- a. Kaolinite from Trivandrum, Kerela, India
- b. Dissolution of the zeolite sample for atomic adsorption: 0.1 g sample was treated with 30 mL of a mixture of HCl (37%), HF (48%) and distilled water (ratio 1:1:1); the same was kept for two to three days for complete dissolution.
- c.  $^{29}\text{Si}$  MAS NMR gave five lines with chemical shifts of -86.79, -91.55, -97.19, -102.86 and -107.10 ppm.  $^{27}\text{Al}$  MAS NMR gave two lines, intense Al (tet) at 58.58 and weak (oct) at -0.42 ppm.