

KFI

ZK-5

Si(77), Al(23)

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Contributed by J. P. Verduijn

Verified by J. Patarin, by J. Kornatowski, and by S. Ahmed

Type Material:  $K_{22}[Al_{22}Si_{74}O_{192}] : w H_2O$

Method: J. P. Verduijn [1]

Batch Composition:  $2.30 K_2O : 0.1 Sr(NO_3)_2 : Al_2O_3 : 10 SiO_2 : 160 H_2O$

#### Source Materials

deionized water

potassium hydroxide (Baker 0222, pellets, 86.8% KOH)

alumina (Baker 0005, 98.6%  $Al(OH)_3$ )

silicic acid (AKZO SM 604, 90%  $SiO_2$ )<sup>a</sup>

strontium nitrate (Fluka 85900)<sup>b</sup>

#### Batch Preparation (for 57 g product)

- (1) [50.00 g water + 29.76 g potassium hydroxide + 15.80 g alumina], heat to boiling until clear; cool to room temperature and correct weight loss due to boiling
- (2) [96.97 g water + 66.77 g silicic acid], mix until smooth (approximately 6 minutes)
- (3) [75.08 g water + 2.124 g strontium nitrate], mix until dissolved
- (4) [(2) + (3) + 25.12 g water (rinse)], mix for 6 minutes
- (5) [(4) + (1) + 25.08 g water (rinse)], mix for 6 minutes<sup>c</sup>

#### Crystallization

Vessel: 300 mL stainless steel autoclaved

Time: 115 hours

Temperature: 150°C<sup>f</sup>

Agitation: none

#### Product Recovery

- (1) Cool to room temperature<sup>g</sup>
- (2) Filter and wash (5 times) with 650 mL water; the pH of the last wash water = 10.5
- (3) Dry in a 150°C oven for 16 hours
- (4) Yield: 57.2 g (97% on  $Al_2O_3$ )

#### Product Characterization

XRD: KFI (only crystalline product)

Elemental Analysis:  $SiO_2/Al_2O_3 = 6.6$

Crystal Size and Habit:  $\sim 0.5 \mu m$

## Reference

- [1] J. P. Verduijn, US Patent 4 944 249 (19 February 1991)

## Notes

- a. Colloidal silicas such as Ludox HS-40 are also suitable silica sources.
- b. The  $\text{Sr}^{2+}$  sources used were  $\text{Sr}(\text{OH})_2$  and  $\text{Sr}(\text{NO}_3)_2$ ; there is no preference.
- c. The final gel is (visually) very homogeneous and pourable.
- d. No Teflon liner was used.
- e. Crystallization times (at  $150^\circ\text{C}$ ) are not critical (90-140 hours).
- f. The autoclave was placed in a room temperature oven. The oven was heated within 2 hours to  $150^\circ\text{C}$  and kept at this temperature for 115 hours.
- g. The synthesis magma (after treatment has an amorphous appearance; no free mother liquor can be seen. This is typical for this type of synthesis.

**KFI****High-silica KFI****Si(79), Al(21)**

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**Contributed by** Alain Matijasic and Joël Patarin

**Verified by** S. Schwarz, by K. Strohmaier, and by S. Miller

**Type Material:**  $K_{18}Sr[Al_{20}Si_{76}O_{192}] \cdot 72 H_2O \cdot (18-C-6)$  (18-C-6 = Cycl.  $(C_2H_4O)_6$ )

**Method:** T. Chatelain, J. Patarin, R. Farré, O. Pétigny, P. Schulz [1]

**Batch Composition:** 2.3  $K_2O$  : 0.1  $SrO$  :  $Al_2O_3$  : 10  $SiO_2$  : 220  $H_2O$  : 1.0(18-C-6)

**Source Materials**

distilled water  
potassium hydroxide (Prolabo, 86% KOH)  
aluminum hydroxide (Fluka, 99+%  $Al(OH)_3$ )  
strontium nitrate (Prolabo >97%  $Sr(NO_3)_2$ )  
silica sol (Dupont Ludox AS-40, 40%  $SiO_2$ )  
18-C-6 (Lancaster, > 98% cycl.  $(C_2H_4O)_6$ )

**Batch Preparation** (for 7 g of as-synthesized product)

- (1) [11.00 g water + 3.00 g potassium hydroxide + 1.57 g aluminum hydroxide], heat to boiling until clear, cool to room temperature and correct weight loss due to boiling <sup>a</sup>
- (2) [18.63 g water + 0.22 g strontium nitrate + 2.70 g 18-C-6 + 15.00 g silica sol], stir until homogenized
- (3) [(1) + (2)], mix for 30 min. (forms a thick gel). Transfer to a 120 mL PTFE-lined stainless steel autoclave. Final pH: 14

**Crystallization**

Vessel: PTFE-lined stainless steel autoclave  
Time: 120 hours  
Temperature: 150°C in a preheated oven  
Agitation: none; final pH: approximately 13

**Product Recovery**

- (1) Dilute the reaction mixture with distilled water
- (2) Filter and wash until pH  $\approx$  10
- (3) Dry at 60°C overnight
- (4) Yield: Total  $\approx$  7 g of as-synthesized KFI-type sample (product contains 18-C-6 as organic template,  $\sim$  one molecule per unit cell <sup>b</sup>)

**Product Characterization**

XRD: Highly crystalline KFI; can be indexed with cubic symmetry,  $a_0=18.671(1)\text{\AA}$ <sup>b</sup>

Elemental Analyses: Si/Al = 3.7<sup>b</sup>

Crystal Size and Habit: by SEM, the crystals display a cubic morphology; most of them are aggregated and their sizes range from 2 to 4  $\mu\text{m}$

## Reference

- [1] T. Chatelain, J. Patarin, R. Farré, O. Pétigny, P. Schulz, *Zeolites* 17 (1996) 328

## Notes

- a. The starting mixture is prepared in a polyethylene vessel.
- b. According to ref. [1].

## LEV

## [B]-Levyne

Si(89), B(11)

Contributed by Giuseppe Bellussi and Angela Carati

Verified by Li Shi and by S. B. Hong

Type Material:  $(\text{Na,H})_5[\text{B}_5\text{Si}_{49}\text{O}_{108}] : 8 \text{ Q} : 5 \text{ H}_2\text{O}^a$  (Q = quinuclidine)

Method: R. Millini, A. Carati, G. Bellussi [1]

Batch Composition:  $3.0 \text{ Q} : \text{B}_2\text{O}_3 : 3.0 \text{ SiO}_2 : 60 \text{ H}_2\text{O}$

### Source Materials

distilled water

quinuclidine (1-azabicyclo[2.2.2]octane) (Aldrich, 97%)

boric acid ( $\text{H}_3\text{BO}_3$ ) (Carlo Erba RPE-ACS)

silica sol (Dupont HS-40, 40%  $\text{SiO}_2$ , 0.3%  $\text{Na}_2\text{O}$ )

### Batch Preparation (for 19 g dry product)

- (1) [10 g water + 14.7 g quinuclidine], mix until dissolved
- (2) [61 g water + 10.8 g boric acid + 14.7 g quinuclidine], mix until dissolved
- (3) [39.5 g silica sol + (1)], mix until a uniform gel is obtained
- (4) [(3) + (2)], add solution (2) to gel slowly with vigorous mixing. Final slurry pH ~ 11

### Crystallization

Vessel: stainless-steel autoclave

Time: 5 days

Temperature: 170°C

Agitation: autoclave is rotated 20 rpm

### Product Recovery

- (1) Filter to recover solids
- (2) Wash with distilled water
- (3) Dry at 120°C
- (4) Yield: 90% on  $\text{SiO}_2$

### Product Characterization

XRD: LEV (only crystalline phase),  $a = 12.944 \text{ \AA}$ ,  $c = 21.914 \text{ \AA}$

Elemental Analysis:  $17 \text{ SiO}_2 : \text{B}_2\text{O}_3 : 2.7 \text{ Q}$  (dry basis)<sup>b</sup>

Crystal Size and Habit: Compact spherical aggregates (4 to 8  $\mu\text{m}$ ) of small crystals

### Reference

- [1] R. Millini, A. Carati, G. Bellussi, Zeolites 12 (1992) 265

### Notes

- a. Protonated quinuclidine ( $\text{HQ}^+$ ) or  $\text{Na}^+$  (from silica sol) act as counterions for structural boron.
- b. By thermal analysis, organic material adsorbed in extra framework pores is eliminated at 268°C. After treatment at 550°C for a few hours, a limited structure collapse is observed with formation of amorphous material and trigonal  $\text{BO}_3$  units. [1]

## LTA

## Linde Type A

## Si(50), Al(50)

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**Contributed by** R. W. Thompson and K. C. Franklin

**Verified by** B. Subotic and A. Cizmek, and by K. Hashimoto

**Type Material:**  $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] : 27 \text{ H}_2\text{O}$

**Method:** R. W. Thompson, M. J. Huber [1]

**Batch Composition:**  $3.165 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 1.926 \text{ SiO}_2 : 128 \text{ H}_2\text{O}^{\text{a}}$

### Source Materials

deionized water

sodium hydroxide (Fisher Scientific, 99+% NaOH)

sodium aluminate (Fisher Scientific,  $\text{NaO}_2 : \text{Al}_2\text{O}_3 : 3 \text{ H}_2\text{O}$ )<sup>b</sup>

sodium metasilicate (Fisher Scientific,  $\text{Na}_2\text{SiO}_3 : 5 \text{ H}_2\text{O}$ )

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

- (1) [80 mL water + 0.723 g sodium hydroxide], mix gently until NaOH is completely dissolved. Divide into two equal volumes in polypropylene bottles
- (2) [One-half of (1) + 8.258 g sodium aluminate], mix gently in capped bottle until clear <sup>c</sup>
- (3) [Second half of (1) + 15.48 g sodium metasilicate], mix gently in capped bottle until clear <sup>c</sup>
- (4) [(2) + (3)], pour silicate solution into aluminate solution quickly; a thick gel should form. Cap tightly and mix until homogenized <sup>d</sup>

### Crystallization

Vessel: 100-150 mL polypropylene bottle (sealed)

Incubation: none required

Temperature:  $99 \pm 1^\circ\text{C}$

Time: 3-4 hours<sup>e</sup>

Agitation: stirred or unstirred

### Product Recovery

- (1) Remove from heat source and cool to below  $30^\circ\text{C}$
- (2) Filter to recover solids and wash with deionized water until filtrate pH is below 9 <sup>f</sup>
- (3) Dry product on filter paper and watch glass at  $80\text{--}110^\circ\text{C}$  overnight
- (4) Yield: 28.1 g (hydrated) or 10.4 g (dry)

### Product Characterization

XRD: LTA; characteristic strong reflections at  $d = 4.107, 3.714, 3.293$  and  $2.987 \text{ \AA}$  Competing phases (if present): SOD (HS), GIS (Pc)

Elemental Analysis:  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2 \text{ SiO}_2$

Crystal Size and Habit: cubic crystals,  $2\text{--}3 \mu\text{m}$ <sup>g</sup>

## References

- [1] R. W. Thompson, M. J. Huber, *J. Cryst. Gr.* 56 (1982) 711
- [2] D. W. Breck, *Zeolite Molecular Sieves*, John Wiley, New York, 1974, p 270
- [3] J. F. Charnell, *J. Cryst. Gr.* 3 (1971) 291
- [4] H. Neels, W. Schmitz, E.-M. Berger, D. Lutz, *Krist. Tech.* 13 (1978) 1345
- [5] G. Scott, A. G. Dixon, A. Sacco, Jr., R. W. Thompson, in *Stud. Surf. Sci. Catal.* 49, P. A. Jacobs, R. A. Van Santen (eds.), Elsevier, Amsterdam, 1989, p 363

## Notes

- a. Zeolite NaA can be synthesized from a wide range of batch compositions as noted in Breck [2] and temperatures other than used in this example, e.g., 60-110°C. Also, it can be made from a variety of alumina and silica source materials other than those used in this example, e.g., pure aluminum powder<sup>h</sup> or aluminum wire, fumed silica, sodium disilicate, Ludox, silica gels, etc. The actual weights of these other sources used must be compensated for the presence of water of hydration, Na<sup>+</sup> ions, etc.
- b. Assumed 100%.
- c. Could take 10-20 minutes.
- d. May be done with laboratory mixer or vigorously by hand for 5-10 minutes.
- e. The turbid gel phase will be observed to diminish in height as the reaction proceeds, accelerating rapidly in the final stages of the crystallization, leaving a clear supernatant above the precipitated crystalline phase.
- f. One-half liter should be sufficient for this preparation.
- g. Zeolite NaA crystals are typically cubic. Dodecahedral crystals have been observed frequently, but there is little fundamental understanding of why this habit forms. Additions of triethanolamine are known to result in larger crystals, but the particle size distribution becomes broader, synthesis times are extended, and the impurity zeolite phases appear with increased abundance. [3-5]
- h. Special care must be taken if powdered aluminum is dissolved in a caustic solution to make the aluminate solution. Since its dissolution is exothermic, the solution can become quite warm and hydrogen evolves.

LTA

ZK-4

Si(59), Al(41)

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Contributed by Don Hopkins

Verified by V. Valtchev, by M. Castagnola, and by G. Kühn

Type Material:  $\text{Na}_{9.2}(\text{TMA})_{0.8}[\text{Al}_{10}\text{Si}_{14}\text{O}_{48}]$  (TMA = tetramethylammonium)

Method: G. T. Kerr [1]

Batch Composition:  $1.55 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 3.91 \text{ SiO}_2 : 4.13(\text{TMA})_2\text{O} : 320 \text{ H}_2\text{O}$

#### Source Materials

distilled water

sodium hydroxide (50% solution)

sodium aluminate (~46%  $\text{Al}_2\text{O}_3$ , 31%  $\text{Na}_2\text{O}$ ; Fisher, MC&B, Nalco)

tetramethylammonium hydroxide (TMA-OH, Southwestern Analytical Chemical, 25% aqueous solution)

silica sol (Dupont HS-40 or AS-40, 40%  $\text{SiO}_2$ )

#### Batch Preparation (for 34 g product)

- (1) [290 g water + 6.0 g sodium hydroxide solution + 21.5 g sodium aluminate], stir until dissolved
- (2) [292 g TMA-OH (25% solution) + 57.0 g silica sol], stir for approximately 30 minutes
- (3) [(1) + (2)], stir vigorously; gel pH = 14.0 to 14.5

#### Crystallization

Vessel: Teflon bottle, 1000 mL

Incubation: 24 hours at 25°C (optional)

Temperature: 100°C (oven with efficient air circulation)

Time: 16-48 hours

Agitation: none

#### Product Recovery <sup>a</sup>

- (1) Filter and wash with 0.5 to 1 L water
- (2) Dry at 100°C
- (3) Yield: approximately 34 g (100% on  $\text{Al}_2\text{O}_3$ )

#### Product Characterization

XRD: LTA,  $a_0 = 24.38 \text{ Å}$ ; competing phases: GIS (long reaction time) and EAB <sup>b</sup>

Elemental Analysis (dried at 100°C): 15.7% Al (29.7%  $\text{Al}_2\text{O}_3$ ), 23.1% Si (49.4%  $\text{SiO}_2$ ), 12.4% Na (16.7%  $\text{Na}_2\text{O}$ ), 2.24% C (3.83%  $(\text{TMA})_2\text{O}$ ) <sup>c</sup>

Crystal Size and Habit: cubes (some with penetration twinning) approximately 1.0-1.5  $\mu\text{m}$  on an edge



## References

- [1] G. T. Kerr, *Inorg. Chem.* 5 (1966) 1537
- [2] R. H. Jarman, M. T. Melchior, D. E. W. Vaughan, ACS Symposium Series 218, American Chemical Soc., Washington, D. C., 1983, p 267

## Notes

- a. Although no decomposition of TMA-OH is expected, it is advisable to carry out the crystallization and product work-up in a fume hood. Temperature excursions can produce noxious and toxic by-products, *e.g.*, trimethylamine and methanol.
- b. EAB can co-precipitate with ZK-4 if the TMA-OH is added to solution (1) before the silica sol.
- c. The Si/Al of products by this recipe ranged from 1.39 to 1.43 (average 1.41). Higher and lower Si/Al products have been made using other recipes. [2]

## LTA

## Zeolite Alpha

Si(75), Al(25)

**Contributed by** Günter Kühl

**Verified by** S. Mintova and by Zhaolan

**Type Material:**  $\text{Na}_4(\text{TMA})_2[\text{Al}_6\text{Si}_{18}\text{O}_{48}]$  (TMA = tetramethylammonium)

**Method:** G. H. Kühl [1]

**Batch Composition:** 1.07  $\text{Na}_2\text{O}$  : 2.37  $(\text{TMA})_2\text{O}$  :  $\text{Al}_2\text{O}_3$  : 10  $\text{SiO}_2$  : 120  $\text{H}_2\text{O}$

### Source Materials

distilled water

sodium aluminate (MCB, 28.5%  $\text{Na}_2\text{O}$ , 42.75%  $\text{Al}_2\text{O}_3$ )

tetramethylammonium hydroxide solution (25% TMAOH)<sup>a</sup>

precipitated silica (PPG Corp. Hi-Sil 233, 88%  $\text{SiO}_2$ )<sup>b</sup>

### Batch Preparation (for 36 g product)

- (1) [46.4 g water + 15.6 g sodium aluminate], stir at room temperature until dissolved<sup>c</sup>
- (2) [(1) + 111.7 g tetramethylammonium hydroxide solution], mix
- (3) [(2) + 44.5 g precipitated silica], add silica to the aluminate solution gradually with stirring<sup>d</sup>
- (4) Stir or blend for 30 minutes<sup>d</sup>

### Crystallization

Vessel: polypropylene bottle

Incubation: 48 h at room temperature

Time: 24 - 30 hours<sup>e</sup>

Temperature: 90°C

Agitation: none

### Product Recovery

- (1) Dilute reaction mixture with water
- (2) Filter on a dense filter, such as Whatman #5, or separate by decantation, then reslurry sediment, flocculate,<sup>f</sup> and wash with water<sup>g</sup>
- (3) Dry at room temperature or at 110°C
- (4) Yield: 36 g (near 100% on  $\text{Al}_2\text{O}_3$ )

### Product Characterization

XRD: LTA (contracted unit cell); competing phase: high-silica sodalite

Elemental Analyses: 0.6  $\text{Na}_2\text{O}$  : 0.4  $(\text{TMA})_2\text{O}$  :  $\text{Al}_2\text{O}_3$  : 6  $\text{SiO}_2$

Crystal size and habit: cubes, < 1  $\mu\text{m}$  on edge

### Reference

- [1] G. H. Kühl, US Patent 4 191 663

## Notes

- a. TMA salts cannot be used because the anions tend to cause nucleation of high-silica sodalite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 10$ ).
- b. Hi-Sil 233 has a median particle size of 18-19  $\mu\text{m}$ ; precipitated silica of larger particle size tends to be insufficiently reactive. Ultrasil 320 is an acceptable substitute. If less reactive silica is to be used in this preparation, 10% of the silica should be slurried in the (TMA)OH solution prior to combining the (TMA)OH with the  $\text{NaAlO}_2$  solution.
- c. Small amounts of iron may be removed by filtration although this iron does not affect the crystallization. If the sodium aluminate does not dissolve completely, it probably contains  $\text{Al}(\text{OH})_3$  and cannot be used.
- d. Slow addition of Hi-Sil is recommended for proper dispersion. Silica-rich gel particles tend to cause nucleation of high-silica sodalite.
- e. The longer crystallization time improves the crystallinity, unless sodalite nuclei are present.
- f. Avoid flocculating in the presence of mother liquor because colloidal silica will coagulate.
- g. Alternatively, use repeated decantation and reslurrying sequences (settling may be accelerated by centrifuging), and optionally, flocculation<sup>h</sup> after having removed the bulk of the alkalinity.
- h. See Introductory Article on "Product Recovery."

LTA

GaPO<sub>4</sub>

P(50), Ga(50)

**Contributed by** Henri Kessler and Abdallah Merrouche**Verified by** P. Behrens, by P. Feng, by J. Chen, by R. Fricke, and by G. Férey**Type Material:** [Ga<sub>12</sub>P<sub>12</sub>O<sub>48</sub>][(n-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>NH<sub>2</sub>F]<sub>3</sub> : (H<sub>2</sub>O)<sub>w</sub> (w ~ 6 [1])**Method:** A. Merrouche, J. Patarin, M. Soulaire, H. Kessler, P. Anglerot [2]**Batch Composition:** 1 Ga<sub>2</sub>O<sub>3</sub> : 1 P<sub>2</sub>O<sub>5</sub> : 1 HF : 70 H<sub>2</sub>O : 6.5 DPA (DPA = di-n-propylamine)**Source Materials**phosphoric acid (Fluka, 85% H<sub>3</sub>PO<sub>4</sub>)

distilled water

gallium sulfate hydrate (Strem Chemicals, Ga<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · xH<sub>2</sub>O (wt% Ga ~ 18))

hydrofluoric acid (Fluka, 40% HF)

di-n-propylamine (Fluka, 95%)

**Batch Preparation** (for 1 g dry product)

- (1) [1.16 g phosphoric acid + 2.2 g water + 3.8 g gallium sulfate hydrate + 2.5 g water], stir until dissolved
- (2) [(1) + 0.25 g hydrofluoric acid], mix thoroughly
- (3) [(2) + 3.25 g di-n-propylamine], mix thoroughly. Initial pH = 4 to 4.5

**Crystallization**

Vessel: PTFE-lined autoclave

Temperature: 140°C

Time: 24 hours

Agitation: none

**Product Recovery**

- (1) Filter; wash with distilled water
- (2) Dry at 60°C
- (3) Yield: approximately 60% with respect to starting oxides

**Product Characterization**

XRD: characteristic strong reflections at d = 12.02, 8.50, 6.94, 6.01 Å

Elemental Analysis (anhydrous form): Ga<sub>0.49</sub>P<sub>0.51</sub>O<sub>2</sub>(DPA)<sub>0.13</sub>F<sub>0.12</sub>

Crystal Size and Habit: cubes (5 - 40 μm)

**References**

- [1] A. Simmen, J. Patarin, C. Baerlocher, in Proceedings of the 9th International Zeolite Conference, Vol. I, R. Von Ballmoos, J. B. Higgins, M. M. J. Treacy (eds.), Montreal, 1992, Butterworth-Heinemann, Stoneham, 1993, p. 433
- [2] A. Merrouche, J. Patarin, M. Soulaire, H. Kessler, D. Anglerot, in Molecular Sieves, Vol. 1, Synthesis of Microporous Materials, M. L. Occelli, H. E. Robson (eds.), Van Nostrand Reinhold, New York, 1992, p. 384

# LTL Linde Type L Si(76), Al(24)

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**Contributed by** J. P. Verduijn

**Verified by** C. Williams, by M. Uguina, and by J. Warzywoda

**Type Material:**  $K_9[Al_9Si_{27}O_{72}] : wH_2O$  ( $w = 0$  to 36)

**Method;** J. P. Verduijn [1]

**Batch Composition:**  $2.35 K_2O : Al_2O_3 : 10 SiO_2 : 160 H_2O : \text{trace } MgO$  <sup>a</sup>

## Source Materials

deionized water  
potassium hydroxide (Baker 0222 pellets, 86.8% KOH)  
alumina (Baker 0005, 92.6%  $Al(OH)_3$ )  
silica sol (Dupont Ludox HS-40, 40%  $SiO_2$ )  
magnesium nitrate (Baker,  $Mg(NO_3)_2 \cdot 6 H_2O$ )

## Batch Preparation (for ~ 59 g product)

- (1) [50.00 g water + 30.39 g potassium hydroxide + 15.82 g alumina], heat to boiling until clear. Cool to room temperature and correct water loss due to boiling
- (2) [150.24 g silica sol + 99.0 g water + 14.5 g  $Mg(NO_3)_2$  solution],<sup>b</sup> mix until homogeneous (~ 3 minutes)
- (3) [(1) + (2) + 25.00 g water (rinse)],<sup>c</sup> mix until thickening starts (~ 3 minutes) <sup>d</sup>

## Crystallization

Vessel: 300 mL stainless steel autoclave  
Temperature: 175°C  
Time: 48 hours<sup>f</sup>  
Agitation: none

## Product Recovery

- (1) Cool to room temperature
- (2) Filter and wash (5 times) with 650 mL water. The pH of the last wash water should be ~ 10
- (3) Dry at 150°C for 16 hours
- (4) Yield: After drying at 150°C, ~ 15.3 wt% based on the weight of synthesis gel in the autoclave (nearly 100% on  $Al_2O_3$ )

## Product Characterization

XRD: LTL (only crystalline product). Competing phases: MER (without  $MgO$ )  
Elemental Analysis: 6.2  $SiO_2/Al_2O_3$ , 1.0  $K_2O/Al_2O_3$   
Crystal Size and Habit: cylindrical, 0.2 to 0.4  $\mu m$  diameter, 0.4 to 0.7  $\mu m$  long ( $L/D \sim 2$ )

## Reference

- [1] J. P. Verduijn, US Patent 5 242 675 (1993)

## Notes

- a. The synthesis mixture contains 9 wt ppm of added  $\text{Mg}^{2+}$  species (based on the weight of the synthesis mixture).
- b.  $\text{Mg}(\text{NO}_3)_2$  solution: dissolve 2.5645 g magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ ) in 997.4 g water.  
This solution contains 0.24 mg  $\text{Mg}^{2+}$ /g solution. The function of the  $\text{Mg}^{2+}$  species is to avoid the formation of byproducts such as MER, and to control the particle size of the LTL product.
- c. This water is used to quantitatively transfer the aluminate solution.
- d. After 3 minutes mixing, the gel is still pourable. Longer mixing is permitted, but the gel then tends to stiffen and is difficult to transfer to the autoclave.
- e. No Teflon liner was used.
- f. Crystallization time is not critical (24 to 72 hours).

## MAZ

## Mazzite

## Si(78), Al(22)

Contributed by David Vaughan and Karl Strohmaier

Verified by S. Yang and A. Navrotsky, by C. Williams and C. Round, by Hyun-ku Rhee, and by J. Kornatowski

Type Material:  $\text{Na}_{7.3}(\text{TMA}^+)_{0.7}\text{Al}_8\text{Si}_{28}\text{O}_{72} : w\text{H}_2\text{O}$  (TMA = tetramethylammonium)

Method: D. E. W. Vaughan [1]

Batch Composition:  $3.35 \text{ Na}_2\text{O} : 1.24 (\text{TMA})\text{Br} : \text{Al}_2\text{O}_3 : 9.17 \text{ SiO}_2 : 125 \text{ H}_2\text{O} : 0.66 \text{ Na}_2\text{SO}_4$

### Source Materials

deionized water  
sodium hydroxide (J. T. Baker, ~ 99% NaOH)  
alumina (Alcoa C-31, assumed 100%  $\text{Al}_2\text{O}_3 \cdot 3 \text{ H}_2\text{O}$ )  
sodium silicate (PQ Corp. N brand, 8.9%  $\text{Na}_2\text{O}$ , 28.7%  $\text{SiO}_2$ )  
tetramethylammonium bromide (RSA)  
aluminum sulfate (J. T. Baker,  $\text{Al}_2(\text{SO}_4)_3 : 17 \text{ H}_2\text{O}$ )

### Batch Preparation (for 112 g dry product)

#### Preparation of Seed Solution [2]

- (1) [30 g water + 16 g NaOH + 3.25 g alumina] reflux until a clear solution forms, then cool to room temperature and add water back to the original weight if necessary
- (2) [54.4 g sodium silicate + 31.3 g water + (1)], add sodium aluminate solution slowly with mixing in a 200 mL Waring blender
- (3) Age for 24 hours at room temperature<sup>a</sup>

#### Preparation of Crystallization Batch

- (4) [50 g water + 19.6 g NaOH + 25.1 g alumina], reflux until clear. Cool to room temperature and add water to attain the original weight
- (5) [50 g water + 40 g tetramethylammonium bromide], mix until dissolved.
- (6) [396.4 g sodium silicate + 35 g water + 13.9 g (3) + (5)]. Add components sequentially with mixing in a Pyrex one-L reaction kettle with mixing. Heat mixture to 80°C
- (7) [50 g water + 30 g aluminum sulfate], mix until dissolved
- (8) [(6) + (4) + (7)], add sodium alumina to solution followed by alum solution with stirring at 80°C<sup>b</sup>
- (9) Increase temperature to 100°C and stir until homogeneous

### Crystallization

Vessel: one-L Pyrex reaction kettle with reflux condenser and stirrer<sup>c</sup>

Time: 40+ hours<sup>d</sup>

Temperature: 100°C

Agitation: None, except just prior to sampling

### Product Recovery

- (1) Vacuum filter on a Buchner funnel
- (2) Wash to pH < 10
- (3) Dry at 110°C
- (4) Yield near quantitative on  $\text{Al}_2\text{O}_3$

### Characterization

XRD: excellent MAZ

Elemental Analyses:  $0.92 \text{ Na}_2\text{O} : 0.1 (\text{TMA})_2\text{O} : \text{Al}_2\text{O}_3 : 7.14 \text{ SiO}_2$

Crystal size and Habit: barrel-shaped aggregates of needle-like crystals (2 to 3  $\mu$  long and 0.1  $\mu$  dia.)<sup>e</sup>

### References

- [1] D. E. W. Vaughan, Mater. Res. Soc. Symp. Proc. 111 (1988) 89
- [2] D. E. W. Vaughan, US Patent 4 178 352 (1979)

### Notes

- a. Stored at room temperature, this seed solution will be stable and usable for several months.
- b. This formulation produces a hard gel when the alum is added making it difficult to fully homogenize. A Hobart or Kitchenaid mixer is better than a blender if available. The gel breaks up at about 80°C.
- c. Alternatively, a one-L Teflon jar (Nalgene) or subdividing the gel between smaller vessels is appropriate.
- d. After about 18 hours, faujasite is fully crystallized ( $\text{Si} / \text{Al} = 2.4$ ). Continuing the crystallization for more than 40 hours produces fully-crystalline MAZ. It was still pure MAZ after 7 days.
- e.  $^{13}\text{C}$  NMR shows one site in the GME cage.



**MER**

Linde W

Si(65), Al(35)

**Contributed by** Karl Strohmaier**Verified by** P. Piccione and by Huann-Jih Lo**Type Material:**  $K_{11}Al_{11}Si_{21}O_{64} \cdot 20H_2O$ **Method:** R. M. Milton [1]**Batch Composition:** 3  $K_2O$  : 0.05  $Na_2O$  :  $Al_2O_3$  : 5  $SiO_2$  : 100  $H_2O$ **Source Materials**

deionized water

potassium hydroxide (J. T. Baker, 87.6% KOH)

alumina (Alcoa C-31, 65%  $Al_2O_3$ )colloidal silica (duPont Ludox HS-40, 40%  $SiO_2$ )<sup>a</sup>**Batch Preparation** (for 15 g dry product)

- (1) [20 g water + 12.4 g potassium hydroxide + 5.0 g alumina], heat to a gentle boil with stirring until clear. Cool to room temperature and add water to attain the original weight
- (2) [24.2 g colloidal silica + 18.5 g water + (1)]. Add components sequentially with mixing in a beaker<sup>b</sup>

**Crystallization**

Vessel: 125 Teflon-lined autoclave (Parr #4748 acid digestion bomb)

Time: 48 hours

Temperature: 150°C<sup>c</sup>

Agitation: None

**Product Recovery**

- (1) Vacuum filter on a Buechner funnel
- (2) Wash to pH < 10
- (3) Dry at 110°C
- (4) Yield 15 g, near quantitative on  $Al_2O_3$

**Characterization**XRD: excellent MER, unit cell dimensions (space group  $I4/mmm$  - No. 139)  $a = 14.15\text{\AA}$ ,  
 $c = 10.03\text{\AA}$ Elemental Analyses:  $K_2O$  :  $Al_2O_3$  : 3.66  $SiO_2$ Crystal size and Habit: barbell-shaped aggregates (40-50  $\mu\text{m}$  long and 20-30  $\mu\text{m}$  dia.) of needle-like crystals.**Reference**

- [1] R. M. Milton, US Patent 3 012 853 (1961)

**Notes**

- a. Available from Aldrich or Alpha.
- b. Solution gels in about 5 minutes.
- c. If mixture is crystallized at 100°C, a mixture of chabazite and Linde W is made.

## MFI

## High-Alumina ZSM-5

## Si(93), Al(7)

Contributed by Hans Lechert and Ralph Kleinwort

Verified by A. Palmqvist and by J. Brendle and H. Kessler

Type Material:  $\text{Na}_7[\text{Al}_7\text{Si}_{89}\text{O}_{192}] : w\text{H}_2\text{O}$

Method: H. Lechert, R. Kleinwort<sup>a</sup>

Batch Composition:  $3.25 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 30 \text{ SiO}_2 : 958 \text{ H}_2\text{O}$  (exclusive of seeding gel)

**Source Materials**

distilled water  
sodium hydroxide (Merck, pure)  
tetrapropylammonium hydroxide (Fluka, 20% solution)  
silicic acid (Merck, technical grade,  $\text{SiO}_2 : 0.5 \text{ H}_2\text{O}$ )  
sodium aluminate (Roth,  $\text{Al}_2\text{O}_3 : 1.24 \text{ Na}_2\text{O} : 0.57 \text{ H}_2\text{O}$ )

**Seeding Gel Preparation<sup>b</sup>**

- (1) [710.3 g water + 13.8 g sodium hydroxide + 117.0 g TPA-OH solution], dissolve and mix thoroughly
- (2) [(1) + 158.9 g silicic acid], add silica in portions under stirring. Shake the resulting mixture for one hour at ambient temperature. Age at  $100^\circ\text{C}$  for 16 hours

**Synthesis Gel Preparation (for ~87 g product)**

- (1) [867.8 g water + 8.8 g sodium hydroxide + 10.3 g sodium aluminate], dissolve and mix thoroughly
- (2) [(1) + 113.1 g silicic acid], add silica in portions under stirring. Shake vigorously for one hour at ambient temperature
- (3) [(2) + 50 g seeding gel],<sup>c</sup> shake for one hour

**Crystallization**

Vessel: 50 mL PTFE-lined stainless steel autoclaves  
Temperature:  $180^\circ\text{C}$  <sup>d</sup>  
Time: 40 hours <sup>e</sup>  
Agitation: none

**Product Recovery**

- (1) Recover product by filtration
- (2) Wash thoroughly with distilled water
- (3) Dry at  $105^\circ\text{C}$  for 24 hours
- (4) Pulverize dried product in an agate mortar <sup>f</sup>

**Product Characterization**

XRD: fully crystalline MFI; <sup>g,h</sup> competing phase: mordenite (at lower Si/Al ratios in the gel)  
Elemental Analysis:  $\text{Si}/\text{Al} = 12$  to  $13.5$  <sup>i</sup>  
Crystal Size and Habit:  $6 \mu\text{m}$  crystals

## References

- [1] G. Bellussi, G. Perego, A. Carati, U. Cornaro, V. Fattore, in *Innovation in Material Science*, P. J. Grobet, W. J. Mortier (eds.), Elsevier, Amsterdam, 1988
- [2] H. Kacirek, A. Meyer, German Patent 3 402 842 A1
- [3] R. Kleinwort, PhD Thesis, University of Hamburg (1995)
- [4] A. Nastro, C. Collella, R. Aiello, in *Stud. Surf. Sci. Catal. Vol. 24*, B. Drzaj, S. Hocevar, S. Pejovnik (eds.), Elsevier, Amsterdam, 1985, p 19
- [5] J. M. Berak, R. Mostowicz, in *Stud. Surf. Sci. Catal., Vol. 24*, B. Drzaj, S. Hocevar, S. Pejovnik (eds.), Elsevier, Amsterdam, 1985
- [6] W. Schwieger, K. H. Bergk, U. Haedcke, German Patent 2 83 1 26 (1990)
- [7] H. P. Rieck, German Patent OS 3 242 352 (1984)
- [8] P. Chu, E. J. Rosinski, European Patent Appl. 110650 (1983)

## Notes

- a. According to Bellussi, [1] the ZSM-5 structure crystallizes in batches of the composition:  $\text{NaAlO}_2 \cdot n[\text{Na}_m\text{H}_{4-m}\text{SiO}_4] \cdot p\text{H}_2\text{O}$  in the ranges  $n = 20$  to  $50$ ,  $m = 0.1$  to  $0.2$  and  $p = 400$  to  $500$ . For  $m < 0.1$ , generally amorphous products were observed. Above  $m = 0.2$ , mordenite crystallizes. For  $n < 20$ , ferrierite was found and above  $n = 50$ , zeolite Q. The Si/Al ratio in the product was nearly equal to the Si/Al in the batch. Compared to batches with template, those without template usually show a distinctly enhanced crystallization time. The enhancement is especially due to an increased induction period, leading to the conclusion that the crystallization should be carried out with the use of seeds. Another hope of the application of seeds is that the area of the formation of ZSM-5 in the crystallization field can be extended to higher  $m$  and lower  $n$  by suppressing the formation of mordenite which crystallizes preferably in that region.
- b. A quite active seeding agent is obtained by carefully aging a gel giving silicalite. [2] For this gel, only a small amount of TPA-OH is necessary which does not influence the Si/Al ratio of the final product.
- c. Good results have been obtained using 1-10 wt% seeding gel in the mixture.
- d. Good results have been obtained at temperatures from  $145^\circ$  to  $190^\circ\text{C}$ . At  $190^\circ\text{C}$ , the crystallization is finished at about 10 hours.
- e. The crystallization kinetics have been checked by comparison of the crystallinity with an industrial sample by X-ray. [3]
- f. The final products were kept in a desiccator over saturated  $\text{CaCl}_2$ - solution for 24 hours before further characterization.
- g. The kinetic experiments showed that the described seeding gel led to a drastically reduced induction period of crystallization and to a considerable increase in the crystallinity of MFI. This shows that the area of MFI crystallization can be extended into the range where mordenite or ferrierite has been found.
- h. Crystallinity of the products was determined by comparing the sum of the peak areas between  $2\theta = 23.2^\circ$  and  $24.5^\circ$  with that of a well-crystallized industrial sample which was used as a standard throughout the experiments.
- i. For lower Si/Al ratios in the batch, mordenite could not be avoided. For higher Si/Al ratios in the batch, Si/Al of the products increased but remained slightly below Si/Al of the batch. Further information about the crystallization of MFI in template-free systems can be found in references [4-8].

MFI

Silicalite-1

Si(100)

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Contributed by A. C. Faust and C. Schott-Daric

Verified by J. Cejka and by B. Schoeman

Type Material:  $\text{Si}_{96}\text{O}_{192}\text{F}_4(\text{TPA})_4$  (TPA = tetra-n-propylammonium)

Method: J.-L. Guth, H. Kessler, R. Wey [1]

Batch Composition: 1  $\text{SiO}_2$  : 0.08 (TPA)Br : 0.04  $\text{NH}_4\text{F}$  : 20  $\text{H}_2\text{O}$

#### Source Materials

distilled water  
tetrapropylammonium bromide (Fluka, 98%)  
ammonium fluoride (Fluka, 98%)  
silica (Degussa Aerosil 130, 99+%)

#### Batch Preparation (for 12 g product)

- (1) [72 g water + 4.26 g tetrapropylammonium bromide + 0.296 g ammonium fluoride], stir until dissolved
- (2) [(1) + 12 g silica], mix with a spatula, and then stir until homogenized. Initial pH = 6

#### Crystallization

Vessel: PTFE-lined autoclave  
Time: 15 days<sup>a</sup>  
Temperature: 200°C  
Agitation: none

#### Product Recovery

- (1) Filter, wash with distilled water
- (2) Dry at 80°C
- (3) Yield: 12.7 g; near 100% based on silica

#### Product Characterization

XRD: characteristic strong reflections at  $d = 11.01, 3.829, 3.806$  and  $3.698 \text{ \AA}$   
Elemental Analyses:  $\text{Si}_{96}\text{O}_{192}\text{F}_4(\text{TPA})_4$   
Crystal Size and Habit: prisms  $95 \times 80 \mu\text{m}$

#### Reference

- [1] J.-L. Guth, H. Kessler, R. Wey, in *Stud. Surf. Sci. Catal.*, Vol. 28, Y. Murakami, A. Iijima, J. W. Ward (eds.), Kodansha-Elsevier, Tokyo, 1986, p. 121

#### Note

- a. Increasing  $\text{NH}_4\text{F}$  leads to a decrease in crystallization time (2 days for  $\text{NH}_4\text{F}/\text{SiO}_2 = 1$ ).

**MFI**

**[B] ZSM-5**

**Si(98), B(2)**

**Contributed by** Rob de Ruiter

**Verified by** Z. Gabelica, by U. Deforth, and by A. Cichocki

**Type Material:**  $\text{Na}_{0.4}(\text{TPA})_{0.4}[\text{B}_2\text{Si}_{94}\text{O}_{192}] : w\text{H}_2\text{O}$  (TPA = tetra-n-propylammonium)

**Method:** R. de Ruiter, J. C. Jansen, H. van Bekkam [1]

**Batch Composition:** 2.1  $\text{Na}_2\text{O}$  :  $\text{B}_2\text{O}_3$  : 2.4  $\text{SiO}_2$  : 4 TPABr : 1050  $\text{H}_2\text{O}$

**Source Materials**

distilled water  
silica (Aerosil 200-Degussa)  
sodium hydroxide (J. T. Baker, reagent grade)  
tetrapropylammonium bromide (TPABr)(CFZ Zaltbommel)  
boric acid (Merck p.a.)

**Batch Preparation** (0.12 to 0.14 g product/35 mL autoclave)

- (1) [280 g water + 2.66 g silica + 3.1 g sodium hydroxide], shake overnight at room temperature
- (2) [(1) + 19.7 g tetrapropylammonium bromide], stir until dissolved
- (3) [90 g water + 2.92 g boric acid], stir until dissolved
- (4) [20 mL of (2) + 5 mL of (3)], mix thoroughly; initial pH ~11

**Crystallization**

Vessel: Teflon-lined stainless steel autoclave, 35 mL  
Time: 5 days  
Temperature: 180°C  
Agitation: none

**Product Recovery**

- (1) Filter and wash
- (2) Yield: 60-70% on  $\text{SiO}_2$

**Product Characterization**

XRD: Pure MFI, no extraneous phases  
Elemental Analysis: 93.5%  $\text{SiO}_2$ , 1.25%  $\text{B}_2\text{O}_3$ , 2% TPABr, 0.25%  $\text{Na}_2\text{O}$   
Crystal Size and Habit: prismatic to lath morphology depending on boron content, the crystal thickness (in b-direction) decreases with boron content of framework

**Reference**

- [1] R. de Ruiter, J. C. Jansen, H. van Bekkam, in *Synthesis of Microporous Materials*, Vol. I, M. L. Occelli, H. E. Robson (eds.), Van Nostrand Reinhold, New York, 1992, p 167

MFI

[Fe] ZSM-5

Si(96), Fe(4)

Contributed by Angelika Brückner

Verified by Y. Kiyozumi and by P. Fejes

Type Material:  $\text{Na}_{0.3}(\text{TPA})_{3.7}[\text{Fe}_4\text{Si}_{92}\text{O}_{192}] : w\text{H}_2\text{O}$  (TPA = tetra-n-propylammonium)

Method: A. Brückner, R. Lück, W. Wieker, B. Fahlke [1]

Batch Composition:  $30 \text{ Na}_2\text{O} : \text{Fe}_2\text{O}_3 : 30 \text{ SiO}_3 : 1040 \text{ H}_2\text{O} : 5 (\text{TPA})\text{Br} : 25 \text{ H}_2\text{SO}_4$

#### Source Materials

distilled water

sulfuric acid (reagent grade, 98%  $\text{H}_2\text{SO}_4$ )

iron(III) sulfate (reagent grade,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9 \text{ H}_2\text{O}$ )

sodium metasilicate (reagent grade,  $\text{Na}_2\text{SiO}_3 \cdot 9 \text{ H}_2\text{O}$ )<sup>a</sup>

tetrapropylammonium bromide (TPABr) (Fluka, CH-9470 Buchs)

#### Batch Preparation (for ~20 g volatile-free product)

- (1) [100 g water + 22 g sulfuric acid + 5.62 g iron(III) sulfate], stir until dissolved
- (2) [163.4 g water + 85.26 g sodium metasilicate], stir until dissolved
- (3) [(1) + (2)], add silicate slowly to iron(III) sulfate solution with good mixing
- (4) [(3) + 13.31 g TPABr], mix vigorously until uniform (~ 400 rpm)

#### Crystallization

Vessel: stainless steel autoclaves

Temperature: 170°C

Time: 72 hours

Agitation: autoclaves are rotated axially

#### Product Recovery

- (1) After cooling, filter and wash with water several times
- (2) Dry over  $\text{P}_4\text{O}_{10}$
- (3) Calcine at 550°C for 4 hours to remove template

#### Product Characterization

XRD: ZSM-5 (only phase)

Elemental Analysis:  $0.07 \text{ Na}_2\text{O} : \text{Fe}_2\text{O}_3 : 48 \text{ SiO}_2 : w\text{H}_2\text{O}$

Crystal Size and Habit: 1-6  $\mu\text{m}$ , snowball-like

#### Reference

- [1] A. Brückner, R. Lück, W. Wieker, B. Fahlke, Zeolites 12 (1992) 380

#### Note

- a. Al(III), a common impurity in silica sources, displaces Fe(III) from T-atom positions in MFI. [1]

**MFI**

**[Ti] ZSM-5**

**Si(98.6), Ti(1.4)**

**Contributed by** Jan H. C. van Hooff and Arjan van der Pol

**Verified by** D. Serrano and by Z. Gabelica

**Type Material:**  $[\text{Ti}_{1.3}\text{Si}_{94.7}\text{O}_{192}] : w\text{H}_2\text{O}$

**Method:** M. Taramasso, G. Perego and B. Notari [1-3]

**Batch Composition:**  $\text{TiO}_2 : 70 \text{ SiO}_2 : 1980 \text{ H}_2\text{O} : 30 \text{ TPA-OH}$  (TPA = tetra-n-propylammonium)

**Source Materials**

distilled water

tetraethylorthosilicate  $[\text{Si}(\text{OC}_2\text{H}_5)_4]$  (Merck 800658)

tetraethylorthotitanate  $[\text{Ti}(\text{OC}_2\text{H}_5)_4]$  (Merck 821083)

tetrapropylammonium hydroxide (Alfa 17456, 40% solution in water)

**Batch Preparation (for 43 g product)**

- (1) [163.3 g tetraethylorthosilicate + 2.56 g tetraethylorthotitanate], mix at 35°C
- (2) [(1) + 170 g tetrapropylammonium hydroxide (40% solution)], add slowly at 0°C to prevent hydrolysis
- (3) Heat at 80°C to evaporate ethanol
- (4) Add water to restore initial volume; final pH 12.2

**Crystallization**

Vessel: 500 mL stirred autoclave

Temperature: 175°C

Time: 2 days

Agitation: 120 rpm

**Product Recovery**

- (1) Centrifuge to recover solids and wash with water (three times)
- (2) Dry at 120°C
- (3) Heat in air to 550°C (heating rate 5°C/min.) and hold at 550° for 3 hours
- (4) Yield: ~ 90% on  $\text{SiO}_2$

**Product Characterization**

XRD: orthorhombic MFI (only crystalline phase)

Elemental Analysis: 1.37 mol% Ti (72  $\text{SiO}_2/\text{TiO}_2$  by AAS)<sup>a</sup>

Crystal Size and Habit: 0.3  $\mu\text{m}$  cubes (SEM)

**References**

- [1] M. Taramasso, G. Perego, B. Notari, US Patent 4 410 501 (1983)
- [2] A. J. H. P. van der Pol, J. H. C. van Hooff, Appl. Catal. 92 (1992) 93
- [3] J. A. Martens, P. Buskens, P. A. Jacobs, A. van der Pol, J. van Hooff, P. J. Kooyman, H. van Bekkum, Appl. Catal. 99 (1993) 71
- [4] A. Tuel, Y. Ben Taarit, Zeolites 14 (1994) 272

**Note**

- a. No extra-framework  $\text{TiO}_2$  can be observed by IR or UV-VIS. No IR bands around 700  $\text{cm}^{-1}$  and no UV-VIS bands above 250 nm were observed [4].

**MFI**

[Ti, Al] ZSM-5

Si(97.5), Ti(1.3), Al(1.2)

**Contributed by** D. P. Serrano, G. Ovejero, R. Van Grieken and J. A. Melero

**Verified by** M. Anderson and by J. Rocha and A. Ferreira

**Type Material:**  $H_{1.2}[Al_{1.17}Ti_{1.23}Si_{93.6}O_{192}] : wH_2O$

**Method:** G. Ovejero, R. Van Grieken, M. A. Uguina, D. P. Serrano, J. A. Melero [1]

**Batch Composition:** 1  $TiO_2$  : 0.25  $Al_2O_3$  : 40  $SiO_2$  : 216  $H_2O$  : 7.44 (TPA)OH  
(TPA = tetra-n-propylammonium)<sup>a</sup>

#### Source Materials

tetraethylorthosilicate [Alfa,  $Si(OC_2H_5)_4$ ]  
hydrochloric acid (0.2 N) (reagent grade)  
isopropyl alcohol for analysis (Panreac)  
aluminum isopropoxide, [Aldrich,  $Al(OC_3H_7)_3$ ]  
tetrapropylammonium hydroxide (TPAOH)  
[Alfa, 40 wt%  $(C_3H_7)_4NOH$  in water]  
titanium tetrabutoxide [Alfa,  $Ti(OC_4H_9)_4$ ]

#### Batch preparation (for ~ 2.9 g dried cogel)

##### A. Acid hydrolysis-condensation

- (1) [8 g tetraethylorthosilicate + 5 g hydrochloric acid (0.2 N)], mix at room temperature for 45 minutes
- (2) [2.5 g isopropyl alcohol + 0.098 g aluminum isopropoxide], mix until dissolved
- (3) [(1) + (2)], add (2) to (1) dropwise. Mix at room temperature for 45 minutes.
- (4) [4 g TPAOH (40 wt%) + 4 g  $H_2O$ ], mix
- (5) [(3) + 0.75 g (4)], add 20 wt% TPAOH slowly at room temperature. Stir at 0°C for 15 minutes
- (6) [0.327 g titanium tetrabutoxide + 2 g isopropyl alcohol], mix until homogeneous
- (7) [(5) + (6)], add (6) to (5) slowly at 0°C. Stir at 0°C for an additional 20 minutes

##### B. Basic Gelation:

- (8) [(7) + approximately 1.9 g (4)], add 20 wt% TPAOH slowly at room temperature; mix until gelation
- (9) Dry overnight at 110°C to remove alcohol and water. Grind to give a powdered material
- (10) [(9) + approximately 4.6 g (4)], impregnate the dried and powdered cogel to incipient wetness with 20 wt% TPAOH. Charge to autoclaves

#### Crystallization

Vessel: Teflon-lined autoclaves (50 mL)  
Time; 24 hours  
Temperature: 170°C  
Agitation: none



### Product Recovery

- (1) Centrifuge to recover crystalline product; wash with double-distilled water (three times)
- (2) Dry overnight at 110°C
- (3) Calcine in air at 550°C (heating rate 5°C/minutes and hold at 550°C for 5 hours)
- (4) Yield; ~ 95% on SiO<sub>2</sub>

### Product Characterization

XRD: MFI structure, orthorhombic

Elemental Analysis: SiO<sub>2</sub>/TiO<sub>2</sub> = 76, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 160 (by XRF)<sup>b,c</sup>

Crystal Size and Habit: 0.4-0.5 μm, cuboid shape

### References

- [1] G. Ovejero, R. Van Grieken, M. A. Uguina, D. P. Serrano, J. A. Melero, *Catal. Lett.* 41 (1996) 69
- [2] G. Bellussi, A. Carati, M. G. Clerici, A. Esposito, *Stud. Surf. Sci. Catal.* 63 (1991) 421
- [3] L. Forni, M. Pellozi, A. Giusti, G. Fornasari, R. Millini, *J. Catal.* 122 (1990) 44
- [4] A. Thangaraj, R. Kumar, S. Sivasanker, *Zeolites* 12 (1992) 135
- [5] D. Trong On, S. Kaliaguine, L. Bonnevot, *J. Catal.* 157 (1995) 235
- [6] F. Geobaldo, S. Bordiga, A. Zecchina, E. Gianello, G. Leofanti, G. Petrini, *Catal. Lett.* 16 (1992) 109

### Notes

- a. Ti and trivalent metal ions, Al<sup>3+</sup>, Ga<sup>3+</sup>, Fe<sup>3+</sup> and B<sup>3+</sup>, can be co-incorporated into ZSM-5 by conventional methods based on hydrothermal crystallization of a liquid gel obtained from respective alkoxides hydrolyzed in basic medium. [2-5]
- b. By DR UV-VIS, adsorption around 330 nm is not detected either in the sample or in the cogel, showing the absence of bulk TiO<sub>2</sub> phases. [6]
- c. By <sup>29</sup>Si and <sup>27</sup>Al MAS-NMR, atoms are located in tetrahedral environments in the starting cogel and in the synthesized sample.

## MOR

## Mordenite

## Si(90), Al(10)

Contributed by Wha Seung Ahn

Verified by G. Price, by K. Satya Narayana Reddy, and by Yan Sun

Type Material:  $\text{Na}_5[\text{Al}_5\text{Si}_{43}\text{O}_{96}] : w \text{ H}_2\text{O}$

Method: G. J. Kim, W. S. Ahn [1]

Batch Composition:  $6 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 30 \text{ SiO}_2 : 780 \text{ H}_2\text{O}$

#### Source Materials

distilled water

sodium hydroxide (Junsei Co., 95% NaOH)

sodium aluminate (Junsei Co., 32.6%  $\text{Na}_2\text{O}$ , 35.7%  $\text{Al}_2\text{O}_3$ )

silica powder (Zeosil from Kofran Co., 91.8%  $\text{SiO}_2$ , 8.2%  $\text{H}_2\text{O}$ )<sup>a</sup>

#### Batch Preparation (for 56 g dry product)

- (1) [40 g water + 19 g sodium hydroxide], stir until dissolved
- (2) [(1) + 14.3 g sodium aluminate], stir until dissolved
- (3) [(2) + 645 g water], mix
- (4) [(3) + 98.2 g silica], stir for 30 minutes

#### Crystallization

Vessel: Teflon-lined stainless steel autoclave

Incubation: none<sup>b</sup>

Temperature: 170°C

Time: 24 hours<sup>c</sup>

#### Product Recovery

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

#### Product Characterization:

XRD: 100% mordenite, characteristic peaks at  $d = 3.45, 3.97, 9.02, 3.27$  and  $3.21 \text{ \AA}$ ; competing phases: quartz, analcime, gismondine

Elemental Analysis:  $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 17.2 \text{ SiO}_2$

Crystal Size and Habit: irregular spherical to prismatic,  $\sim 5 \mu\text{m}$ <sup>d</sup>

#### Reference

- [1] G. J. Kim, W. S. Ahn, *Zeolites* 11 (1991) 745

#### Notes

- a. Sodium silicate can also be used as a silica source, but crystallization rates are lower.
- b. Incubation is not required when using silica powder as  $\text{SiO}_2$  source; aging at room temperature resulted in larger crystals but lower crystallization rates.
- c. Seeding with 5 wt% mordenite in the reaction batch substantially improved the crystallization rate.
- d. Typically needle-shaped crystals, but siliceous crystals can be plate or flat prismatic shape.

MTN

ZSM-39

Si(100)

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Contributed by Valentin Valtchev

Verified by S. Ernst and by A. Iwasaki

Type Material:  $(\text{SiO}_2)_{136} : q \text{ R}; q \approx 10, (\text{R} = \text{TMA}^+ \text{ and } \text{TrMA})^a$

Method: I. Vergilov, V. Valtchev [1]

Batch Composition:  $15 \text{ Na}_2\text{O} : 16 \text{ TrMA} : 16 (\text{TMA})\text{Cl} : 55 \text{ SiO}_2 : 3387 \text{ H}_2\text{O} : 10 \text{ H}_2\text{SO}_4^{b,c}$

#### Source Materials

bidistilled water

sodium silicate (Riedel de Haen, 63%  $\text{SiO}_2$ , 18%  $\text{Na}_2\text{O}$ , 18%  $\text{H}_2\text{O}$ )

sulfuric acid (98%  $\text{H}_2\text{SO}_4$ )

trimethylammonium (TrMA) chloride (Merck, 98%  $\text{TrMA} \cdot \text{HCl}$ )

tetramethylammonium (TMA) chloride (Merck, > 98%  $(\text{TMA})\text{Cl}$ )

#### Batch Preparation (for 30 g dry product)

- (1) [300 g water + 52.5 g sodium silicate], heat and stir until dissolved <sup>d</sup>
- (2) [150 g water + 10.7 g sulfuric acid]
- (3) [(1) + (2)], mix thoroughly
- (4) [15.29 g trimethylammonium chloride + 17.54 g tetramethylammonium chloride + 150 g water], mix thoroughly
- (5) [(3) + (4)], mix thoroughly; pH 9.2 to 9.5

#### Crystallization

Vessel: stainless steel or Teflon jar

Time: 12 to 14 days

Temperature: 200°C

Agitation: none

#### Product Recovery

- (1) After crystallization, pH 10.5
- (2) Filter to recover solids, and wash with hot water
- (3) Dry at ambient temperature (drying at 90–110°C acceptable)
- (4) Yield: 88% based on silica

#### Characterization

XRD: MTN only crystalline phase,<sup>e</sup>  $a_0 = 19.39 \text{ \AA}$ , single crystal structure refinement [2];

competing phases: NU-1 (when gel contains aluminum), quartz (when pH of starting gel > 11.5)

Elemental Analysis:  $0.0018 \text{ Na}_2\text{O} \cdot \text{SiO}_2^f$

Crystal Size and Habit: octahedral morphology, 100 to 200 nm dia. [1]

## References

- [1] I. Vergilov, V. Valtchev, *Zeolites* 11 (1991) 387
- [2] J. Macicek, V. Valtchev, G. Kirov, in *Collected Abstracts, 14th Congress and General Assembly Int. Union of Crystallography*, H. C. Freeman (ed.), Lamb Printers, Perth, Australia, 1987, C-134

## Notes

- a. Crystalline product is 7.4 wt% TMA<sup>+</sup> and TrMA by thermal analysis.
- b. With TMA<sup>+</sup> only, complex crystal twins are formed.
- c. H<sub>2</sub>O includes water from sodium silicate, sulfuric acid and added water.
- d. Sodium silicate solution must be heated and stirred until converted to a clear solution.
- e. XRD patterns of as-synthesized product and product after 600°C calcination do not differ significantly.
- f. Analysis of ZSM-39 calcined for 1 hour at 950°C in air gave 94.7% SiO<sub>2</sub>, 0.17% Na<sub>2</sub>O, and a remainder, probably consisting of carbonaceous material and water.

MTT

ZSM-23

Si(97), Al(3)

Contributed by Stefan Ernst

Verified by R. Ravishankar and by Wha-Seung Ahn

Type Material:  $\text{Na}[\text{AlSi}_{23}\text{O}_{48}] \cdot w\text{H}_2\text{O}$  ( $w \approx 4$ )

Method: S. Ernst, R. Kumar, J. Weitkamp [1]

Batch Composition:  $20.6\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 100\text{SiO}_2 : 4610\text{H}_2\text{O} : 46.2\text{Pyrr} : 18.8 \text{H}_2\text{SO}_4$

#### Source Materials

demineralized water  
sodium hydroxide, reagent grade (Riedel-de Haën)  
pyrogenic silica (Cab-o-Sil M5)<sup>a</sup>  
pyrrolidine (Pyrr), (Fluka)  
aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , Fluka)  
sulfuric acid (96 wt%  $\text{H}_2\text{SO}_4$ , Fluka)

#### Batch Preparation (for 14 g product)<sup>b</sup>

- (1) [195.8 g water + 4.40 g sodium hydroxide], mix until dissolved
- (2) [(1) + 16.5 g silica], add silica to solution (1) over the course of ~5 minutes under continuous stirring
- (3) [24.4 g water + 8.81 g pyrrolidine + 1.79 g aluminum sulfate], mix until dissolved
- (4) [(2) + (3)], add solution (3) to solution (2) with good mixing
- (5) [(4) + 4.33 g sulfuric acid], add acid dropwise with stirring; final gel pH = 12.6

#### Crystallization

Vessel: stainless steel autoclave (300 mL)<sup>c</sup>  
Temperature: 180°C  
Time: 50 hours  
Agitation: autoclaves are rotated ~ 30/minutes

#### Product Recovery

- (1) Cool and filter
- (2) Wash extensively with demineralized water
- (3) Dry at 100°C for 16 hours
- (4) Yield: approx. 14 g

#### Product Characterization

XRD: MTT (only crystalline phase), competing phases: MFI (contaminated autoclave)  
cristobalite (occasional overheating, or pH too high)  
Elemental Analysis:  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 78$  (AES/ICP)<sup>d</sup>  
Crystal Size and Habit: bundles of needles<sup>e</sup>

## Reference

- [1] S. Ernst, R. Kumar, J. Weitkamp, in *Zeolite Synthesis*, Am. Chem. Soc. Symposium Series 398, M. Occelli, H. Robson (eds.), 1989, pp 560-573

## Notes

- a. Cab-O-Sil M5 must be used; other silica sources, such as silica sol or sodium silicate, lead to different products.
- b. The synthesis has been successfully scaled up to a 5 liter autoclave (stirring rate: 120/minutes, yield: 250 g).
- c. The crystallization vessels have to be cleaned very thoroughly in order to avoid seeding effects from residual crystallites of ZSM-5, for example.
- d. With pyrrolidine as template, the molar ratio can be varied between 70 and 150.
- e. Platelet-like  $\sim 1 \mu\text{m}$  can be synthesized using C<sub>7</sub>-diquat  $[(\text{CH}_3)_3\text{N}-(\text{CH}_2)_7-\text{N}(\text{CH}_3)_3]\text{Br}_2$  as template. [1]

## MTW

## ZSM-12

## Si(97), Al(3)

Contributed by Girolamo Giordano

Verified by Nguyen Huu Phu, by A. Souza de Araujo, and by G. Kühl

Type Material:  $\text{Na}_{0.5}(\text{MTEA})_{1.3}[\text{Al}_{0.8}\text{Si}_{27.2}\text{O}_{56}] : 0.6 \text{ H}_2\text{O}$  (MTEA = methyltriethylammonium)

Method; S. Ernst, P. A. Jacobs, J. A. Martins, J. Weitkamp [1], P. Chu, G. H. Kühl [2]

Batch Composition:  $10 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 100 \text{ SiO}_2 : 2000 \text{ H}_2\text{O} : 20 \text{ MTEA Br}$

### Source Materials

distilled water  
sodium hydroxide (Carlo Erba RPE, 99+% NaOH)  
aluminum hydroxide hydrate  $[\text{Al}(\text{OH})_3]$  (Aldrich)  
methyltriethylammonium bromide [MTEA Br] (Fluka)  
precipitated silica (BDH, 99+%  $\text{SiO}_2$ )

### Batch Preparation (for ~ 2.5 g product)

- (1) [9 g distilled water + 0.4 g sodium hydroxide + 0.078 g aluminum hydroxide hydrate], stir until dissolved
- (2) [9 g distilled water + 1.96 g MTEA Br], stir until dissolved
- (3) [(1) + (2)], stir until homogenized
- (4) [(3) + 3 g precipitated silica], stir for 1 hour at room temperature and seal in the reactor

### Crystallization

Vessel: Teflon-lined autoclave, 20 mL  
Time: 6 days  
Temperature:  $140^\circ\text{C}$   
Agitation: none

### Product Recovery

- (1) Cool to room temperature and filter to recover solids
- (2) Wash with distilled water until filtrate pH = 9
- (3) Dry at  $105^\circ\text{C}$

### Product Characterization

XRD: MTW only crystalline phase; competing phases: MFI (high alumina), cristobalite (high temperature or high pH)  
Elemental Analyses:  $0.66 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 66.7 \text{ SiO}_2 : 1.5 \text{ H}_2\text{O} : 1.58 (\text{MTEA})_2\text{O}$   
Crystal Size and Habit: rice-grain shaped, length  $5 \mu\text{m}$

### References

- [1] S. Ernst, P. A. Jacobs, J. A. Martens, J. Weitkamp, Zeolites 7 (1987) 458
- [2] P. Chu, G. H. Kühl, US Patent 4 452 769 (1983)
- [3] A. Katovic, G. Giordano, Chem. Express 6 (1991) 969

### Note

- a. MTW zeolite can also be obtained when tetraethylammonium bromide (TEA Br) substitutes for MTEA Br in the hydrogel described in the Batch Composition section. In this case spheroidal crystals of about  $0.6 \mu\text{m}$  diameter are obtained. [3]

MTW

[Ga] ZSM-12

Si(93), Ga(7)

Contributed by Susan Lambert

Verified by K. Reddy and by M. Mertens

Type Material:  $\text{Na}_2[\text{Ga}_2\text{Si}_{26}\text{O}_{56}] : 4 \text{ H}_2\text{O}$ 

Method: S. L. Lambert [1]

Batch Composition:  $4.5 \text{ Na}_2\text{O} : \text{Ga}_2\text{O}_3 : 52.4 \text{ SiO}_2 : 13.7 \text{ TEMA Br} : 867 \text{ H}_2\text{O}$   
(TEMA = triethylmethyllummonium)**Source Materials**

deionized water  
 sodium hydroxide (Mallinkrodt dry pellets, > 98.5% NaOH)  
 gallium oxide (Alfa, 99.99%)  
 triethylmethyllummonium bromide (TEMA Br) (Fluka, purum)  
 silica sol (Dupont Ludox AS-40, 40%  $\text{SiO}_2$ )<sup>a</sup>

**Batch Preparation (for 13 g dry product)**

- (1) [21.72 g NaOH + 37.04 g water + 11.37 g  $\text{Ga}_2\text{O}_3$ ], heat in a closed pressure vessel (Teflon-lined Parr acid digestion bomb) at 110°C for 23 hours
- (2) [4.65 g of solution (1) + 29.22 g water + 10.78 g TEMA Br], stir until dissolved
- (3) [(2) + (31.47 g silica sol + 11.63 g  $\text{H}_2\text{O}$ )], add diluted silica sol to (2) with stirring using an eye dropper over course of 15 min. Batch pH 13-14<sup>b</sup>

**Crystallization**

Vessel: two Teflon-lined Parr acid digestion bombs (125 mL)  
 Time: 20 days<sup>c</sup>  
 Temperature: 150°C  
 Agitation: none

**Product Recovery**

- (1) Supernatant liquid pH 12.5
- (2) Filter and wash with 600 mL distilled water
- (3) Dry at 100°C
- (4) Yield: 13.64 g white solids (12.25 g volatile free), 91% recovery on  $\text{SiO}_2$  or 87% on  $\text{Ga}_2\text{O}_3$

**Product Characterization**

XRD: MTW framework by comparison to ZSM-12 crystallinity reference, best is [Al] MTW.  
 Minor impurity: cristobalite; no other phases present  
 Elemental Analyses (volatile-free): 93.4%  $\text{SiO}_2$ , 5.35%  $\text{Ga}_2\text{O}_3$ , 0.62%  $\text{Na}_2\text{O}$ , 0.14%  $\text{Al}_2\text{O}_3$ . Loss on ignition at 900°C: 10.17%<sup>d</sup>  
 Molar Composition:  $0.35 \text{ Na}_2\text{O} : 0.05 \text{ Al}_2\text{O}_3 : \text{Ga}_2\text{O}_3 : 54.4 \text{ SiO}_2 : 22 \text{ H}_2\text{O}$ <sup>e</sup>



## Reference

- [1] S. L. Lambert in Proceedings of the 9th International Zeolite Conference, R. von Ballmoos, J. B. Higgins, M. M. J. Treacy (eds.), Butterworth-Heinemann, London, 1993, p. 223

## Notes

- a. Dupont's Ludox HS-40 is an acceptable substitute.
- b. pH values were measured with ColorpHast pH indicator paper (range 5-10 or 7.5-14, from E. M. Science, Gibbstown, NJ, USA)
- c. Crystallinity vs. (Al) ZSM-12 reference: 70% after 16 days, 88% after 18 days, 90% after 20 days. The crystallization proceeds more rapidly as the amount of gallium in the synthesis batch is reduced.
- d. Template burnout occurs at 460°C in air.
- e. By  $^{29}\text{Si}$  MAS NMR,  $\text{Si}/(\text{Ga} + \text{Al}) = 14$ ; excess  $\text{SiO}_2$  by elemental analysis is attributed to amorphous silica.  $^{71}\text{Ga}$  static NMR: one symmetrical Ga line at 158.5 ppm (ref.  $\text{Ga}(\text{NO}_3)_3$ ).

MWW

MCM-22

Si(94), Al(6)

Contributed by Avelino Corma

Verified by J. Weitkamp and by N. Kumar

Type Material:  $\text{Na}_{0.08}[\text{Al}_4\text{Si}_{68}\text{O}_{144}] : (\text{C}_6\text{H}_{12}\text{NH})_{10.8}$  [1]<sup>a</sup>

Method; A. Corma, C. Corell, J. Pérez-Pariente [1]

Batch Composition: 2.7  $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 30 \text{SiO}_2 : 1347 \text{H}_2\text{O} : 15 \text{HMI}^b$  (HMI = hexamethyleneimine)

#### Source Materials

deionized water  
sodium aluminate (Carlo Erba, 56%  $\text{Al}_2\text{O}_3$ , 37%  $\text{Na}_2\text{O}$ )  
sodium hydroxide (98% NaOH)  
hexamethyleneimine  $\text{C}_6\text{H}_{12}\text{NH}$  (Aldrich, 99% HMI)  
silica (Degussa, Aerosil 200, or Cab-O-Sil M5)

#### Batch Preparation (for 12.8 g dry product)<sup>c</sup>

- (1) [124.20 g water + 0.92 g sodium aluminate + 0.60 g sodium hydroxide], stir until dissolved <sup>d</sup>
- (2) [(1) + 7.61 g hexamethyleneimine], mix thoroughly<sup>e</sup>
- (3) [(2) + 9.23 g silica], mix thoroughly<sup>f</sup>

#### Crystallization

Vessel: PTFE-lined stainless steel autoclaves  
Time: 7 days  
Temperature: 150°C  
Agitation: 60 rpm

#### Product Recovery

- (1) Dilute the reaction mixture with distilled water
- (2) Filter and wash with distilled water
- (3) Dry at 100°C overnight
- (4) Yield: 99% based on alumina

#### Product Characterization

XRD: MCM-22 [2]; competing phases: FER (when crystallized under static conditions), ZSM-5 (when gel  $\text{SiO}_2/\text{Al}_2\text{O}_3 > 100$ ), ZSM-12 (when gel  $\text{SiO}_2/\text{Al}_2\text{O}_3 > 200$ )

Elemental Analysis: 0.02  $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 34 \text{SiO}_2$

Crystal Size and Habit: small thin platelets occasionally forming spherical aggregates of 6-8  $\mu\text{m}$  <sup>g</sup>

#### References

- [1] A. Corma, C. Corell, J. Pérez-Pariente, Zeolites 15 (1995) 2
- [2] M. K. Rubin, P. Chu, US Patent 4 954 325 (1990)

## Notes

- a. Missing cations assumed to be protonated HMI.
- b. H<sub>2</sub>O includes water from sodium aluminate and added water.
- c. Use polypropylene vessel and vigorous stirring for 30 minutes.
- d. Clear solution
- e. Slightly yellow clear solution
- f. White and fluid gel
- g. Toluene sorptive capacity at 0.1 KPa, 42°C : 10.07 mmol/g. The sample was heated in oxygen flow (30 cm<sup>3</sup>/min<sup>-1</sup>) up to 500°C and outgassed overnight at 500°C in a vacuum better than 1 mPa.

# NAT [Ga] Natrolite Si(62), Ga(38)

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Contributed by Mario Occelli

Verified by J. Buhl and by R. Aiello

Type Material:  $(\text{NaK}_8\text{R}_6)[\text{Ga}_{15}\text{Si}_{25}\text{O}_{80}] \cdot w\text{H}_2\text{O}$  (R = benzyl trimethylammonium (BTMA))

Method: M. L. Occelli, E. Goldish, H. Eckert [1]

Batch Composition: 5.30 Na<sub>2</sub>O : 2.21 K<sub>2</sub>O : 2.12 R<sub>2</sub>O : Ga<sub>2</sub>O<sub>3</sub> : 12.54 SiO<sub>2</sub> : 298 H<sub>2</sub>O : 31.4 CH<sub>3</sub>OH

## Source Materials

deionized water

sodium hydroxide, reagent grade (~97% NaOH)

potassium hydroxide, reagent grade (85% KOH)

gallium oxide (99.99% Ga<sub>2</sub>O<sub>3</sub>)

sodium silicate (PQ N-brand, 29,9% SiO<sub>2</sub>, 10.0% Na<sub>2</sub>O)

benzyl trimethyl ammonium hydroxide (Excel Co., 40% in methanol)

## Batch Preparation

- (1) [50 g water + 9.92 g sodium hydroxide + 29.0 g potassium hydroxide] mix until dissolved
- (2) [(1) + 18.7 g gallium oxide], stir at the boiling point until the solution clears
- (3) [(2) + 50 g water], mix and cool to ambient temperature<sup>a</sup>
- (4) [(3) + 167.2 g BTMA·OH solution]
- (5) [251.3 g sodium silicate + 274.3 g water] mix for 4 hours
- (6) [(5) + (4)], add gallate mixture dropwise to the vigorously stirred, diluted sodium silicate; stir for 10 hours at ambient temperature

## Crystallization

Vessel: Teflon-lined, stirred autoclave

Incubation: 10 h at ambient temperature with stirring.

Temperature: 125±2°C

Time: 7 days

Agitation: 100 rpm

## Product Recovery

- (1) Filter and wash to pH < 10
- (2) Dry at 110°C
- (3) Yield: near 100% on Ga<sub>2</sub>O<sub>3</sub>

## Product Characterization

XRD: NAT; no other crystalline phases or amorphous material observed

Elemental Analyses: Ga<sub>2</sub>O<sub>3</sub>·3.28 SiO<sub>2</sub>·0.11 Na<sub>2</sub>O·0.56 K<sub>2</sub>O·0.39 (BTMA)<sub>2</sub>O

Crystal Size and Habit: Anisotropic columns 10-20 μm long with an almost square cross section often bounded at both ends by pyramids. Twinning and intergrowths are common

## Reference

- [1] M. L. Occelli, E. Goldish, H. Eckert, in *Stud. Surf. Sci. Catal.* 84, J. Weitkamp, H. G. Karge, H. Pfeifer, W. Hölderich (eds.), 1994, p. 597

## Note

- a. Diluted gallate solution must be clear.

# OFF Linde Type T Si(78), Al(22)

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Contributed by Andrzej Cichocki

Verified by S. Khvoshchev and M. Shubaeva, by J. Warzywoda, by J. Parise, M. Kleinsorge and S. Park, and by Conghua Liu

Type Material:  $\text{Na}_{2.9}\text{K}_{5.4}[\text{Al}_{8.3}\text{Si}_{27.7}\text{O}_{72}] \cdot w\text{H}_2\text{O}$  (w ~7)

Method: A. Cichocki, P. Koscielniak [1, 2]

Batch Composition: 4.18  $\text{Na}_2\text{O}$  : 1.25  $\text{K}_2\text{O}$  :  $\text{Al}_2\text{O}_3$  : 16.5  $\text{SiO}_2$  : 175  $\text{H}_2\text{O}$

## Source Materials

distilled water  
sodium hydroxide (97% NaOH)  
potassium hydroxide (86% KOH)  
silica sol (Rudniki Chemical Works, 29.5%  $\text{SiO}_2$ , 0.2%  $\text{Na}_2\text{O}$ )  
sodium aluminate solution (26.6%  $\text{Al}_2\text{O}_3$ , 19.6%  $\text{Na}_2\text{O}$ ) =  $\text{NaAlO}_2$

## Batch Preparation (for 14 g dry product)

- (1) [9.57 g water + 4.67 g sodium hydroxide + 3.24 g potassium hydroxide], dissolve and cool to room temperature
- (2) [67.0 g silica sol + (1)], mix in a porcelain mortar and stir for 2 minutes <sup>a</sup>
- (3) [(2) + 7.64 g sodium aluminate solution], add  $\text{NaAlO}_2$  drop by drop to the stirred silicate over a 10 min. interval and continue stirring for 20 minutes

## Crystallization

Vessel: stainless steel autoclave, 120  $\text{cm}^3$  capacity  
Aging: 24 h at room temperature  
Temperature: 140°C  
Time: 7 days  
Agitation: none

## Product Recovery

- (1) Cool; transfer the reaction mixture to a mortar and grind
- (2) Filter and wash in a Buechner funnel until pH of the filtrate is ~ 10
- (3) Dry at 110°C
- (4) Equilibrate in laboratory air for a few days
- (5) Yield: near 95% on  $\text{Al}_2\text{O}_3$  and 41.5% on  $\text{SiO}_2$ <sup>b</sup>

## Product Characterization

XRD: pure OFF;<sup>c</sup> competing phases: PHI, CHA, LTL<sup>d</sup>  
Elemental Analysis: 0.35  $\text{Na}_2\text{O}$  · 0.65  $\text{K}_2\text{O}$  ·  $\text{Al}_2\text{O}_3$  · 6.65  $\text{SiO}_2$   
Crystal Size and Habit: rods and "bones" type crystals ~ 9  $\mu\text{m}$  long on average (longest ~22  $\mu\text{m}$ )

## References

- [1] A. Cichocki, P. Koscielniak, M. Michalik, M. Bus, *Zeolites* 18 ( 1997) 25
- [2] A. Cichocki, P. Koscielniak, *Micropor. Mesopor. Mater.* 29 (1999) 369
- [3] A. Cichocki, *Zeolites* 11 (1991) 758
- [4] R. Aiello, R. M. Barrer, *J. Chem. Soc.* 1970 (A), 1470

## Notes

- a. The use of a porcelain mortar gives a good mix of the reagents, particularly aluminate and silica sol.
- b. 39.9% of the sum of  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  masses introduced into the reaction mixture. Synthetic erionite with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 6.55$  forms from a reaction mixture of composition 8.09  $\text{Na}_2\text{O} : 2.38 \text{ K}_2\text{O} : \text{Al}_2\text{O}_3 : 27.0 \text{ SiO}_2 : 448 \text{ H}_2\text{O}$  when crystallization is carried out in a stainless steel autoclave at the temperature 373 K and time 7 days, but the yield is reduced to 22.5%. This composition differs slightly from that given in ref. [3] where NaOH and KOH were assumed 100%.
- c. The Na/K-system synthetic product shows domains of erionite and offretite in a single crystal. The XRD pattern agrees with natural offretite (PDF), but the product shows adsorption properties of erionite. Unfaulted erionite crystallized in the Na/ $\text{Me}_4\text{N}$ -system. [4]
- d. Formation of PHI is favored by decreasing relative alkalinity ( $\text{OH}^-/\text{SiO}_2$ ). Decreasing the temperature of crystallization favors CHA. Increasing relative alkalinity leads to formation of LTL.

# OFF

# Offretite

# Si(79), Al(21)

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Contributed by Hans Lechert

Verified by M. Mertens and by R. Russu

Type Material:  $\text{Na}_{0.2}\text{K}_{0.9}[\text{Al}_4\text{Si}_{14}\text{O}_{36}] : w\text{H}_2\text{O}^a$

Method: H. Lechert, H. Weyda [1]

Batch Composition:  $3.0 \text{ Na}_2\text{O} : 1.0 \text{ K}_2\text{O} : \text{Al}_2\text{O}_3 : 20.8 \text{ SiO}_2 : 1.73 (\text{TMA})\text{Cl} : 324 \text{ H}_2\text{O}^b$   
(TMA = tetramethylammonium)

## Source Materials

distilled water

sodium hydroxide, reagent grade (99+% NaOH)

aluminum tri-isopropylate  $[\text{Al}(\text{OC}_3\text{H}_7)_3]$

potassium hydroxide, reagent grade (87% KOH)

silica (Merck, precipitated and dried, 87%  $\text{SiO}_2$ )

tetramethylammonium chloride [Merck,  $\text{N}(\text{CH}_3)_4\text{Cl}$ ]

## Batch Preparation (for 64 g dry product)

- (1) [28.1 g water + 16.8 g sodium hydroxide], mix until dissolved
- (2) [(1) + 42.5 g aluminum tri-isopropylate], stir at  $100^\circ\text{C}$  and evaporate to reduce to 42.0 g
- (3) [(2) + 58 g water], stir and cool to ambient temperature; dilute to 100 g total
- (4) [379.3 g water + 8.4 g sodium hydroxide + 13.4 g potassium hydroxide], mix until dissolved
- (5) [(4) + 149.4 g silica], mix for 30 minutes
- (6) [(5) + (3)], mix for 30 minutes
- (7) [(6) + 126.4 g water], mix for 30 minutes
- (8) [(7) + 19.7 g tetramethylammonium chloride], mix for 30 minutes

## Crystallization

Vessel: Teflon-lined autoclave

Temperature:  $160^\circ\text{C}$

Time: 20 hours

Agitation: none

## Product Recovery

- (1) Centrifuge
- (2) Wash to near neutrality
- (3) Dry at  $100^\circ\text{C}$
- (4) Yield: near 100% on  $\text{Al}_2\text{O}_3$

## Product Characterization

XRD: Strong OFF, no extraneous phases; competing phases: erionite,<sup>c</sup> Zeolite P (GIS), analcime

Elemental Analysis:  $0.10 \text{ Na}_2\text{O} : 0.46 \text{ K}_2\text{O} : \text{Al}_2\text{O}_3 : 7.72 \text{ SiO}_2^d$

Crystal Size and Habit: "rice grains," length 5-10  $\mu\text{m}^e$

## Reference

- [1] H. Lechert, H. Weyda, in *Synthesis of Microporous Materials*, Vol. I, M. L. Occelli, H. Robson (eds.), Van Nostrand Reinhold, New York, 1992, p. 77

## Notes

- a. Missing cations assumed to be  $\text{TMA}^+$  or (after calcination)  $\text{H}^+$ .
- b. OFF can be obtained without template in the temperature range 87-107°C with a gel ( $6.2 \text{ Na}_2\text{O} : 3.5 \text{ K}_2\text{O} : \text{Al}_2\text{O}_3 : 25 \text{ SiO}_2 : 390 \text{ H}_2\text{O}$ ), but slight deviations from this composition give appreciable amounts of erionite or gismondine. At higher temperatures Zeolite P (GIS) and analcime co-crystallize with offretite.
- c. ERI can be distinguished from OFF in the XRD pattern by lines at  $d = 9.13, 5.37, 4.60, 4.17, 3.28$ , and  $2.82 \text{ \AA}$ .
- d. The template content of the product is quite low (less than one  $\text{TMA}^+$  per UC).
- e. At 190°C, pure erionite can be obtained from a batch composition:  $8.0 \text{ Na}_2\text{O} : 1.7 \text{ K}_2\text{O} : \text{Al}_2\text{O}_3 : 24 \text{ SiO}_2 : 1.7 \text{ TMACl} : 410 \text{ H}_2\text{O}$ . At this temperature the offretite is needles of about  $1 \text{ }\mu\text{m}$  diameter  $\times 25 \text{ }\mu\text{m}$  long. At crystallization times longer than 4 hours at 190°C, an increasing amount of analcime is observed.



## OFF

## [Ga] Offretite

## Si (65), Ga (35)

Contributed by Mario Occelli

Verified by F. Machado and by S. Iwamoto

Type Material:  $K_{2.2}Na_{0.1}(TMA)_{4.1}Ga_{6.4}Si_{11.6}O_{36} : wH_2O$  (TMA = tetramethylammonium)

Method: M. L. Occelli [1]

Batch Composition:  $2.25 K_2O : 1.61 Na_2O : 0.5 (TMA)_2O : Ga_2O_3 : 11.7 SiO_2 : 250 H_2O : 1.0 HCl$

#### Source Materials

deionized water  
sodium hydroxide, reagent grade (~97% NaOH)  
potassium hydroxide, reagent grade (~87% KOH)  
gallium oxide (99.99%)  
silica sol (Dupont HS-40, 39%  $SiO_2$ , 0.5%  $Na_2O$ )  
tetramethylammonium chloride [99+% (TMA)Cl]

#### Batch Preparation

- (1) [50 g water + 12.0 g sodium hydroxide + 29.0 g potassium hydroxide], mix until dissolved; heat to boiling
- (2) [(1) + 18.7 g gallium oxide], stir at boiling point until a clear solution is obtained
- (3) [(2) + 30 g water], mix and cool to ambient temperature<sup>a</sup>
- (4) [20 g water + 11.0 g (TMA)Cl], mix until dissolved
- (5) [(3) + (4)], mix thoroughly
- (6) [180.3 g silica sol + 234.8 g water], mix for 4 hours
- (7) [(6) + (5)], add gallate mixture dropwise to the vigorously-stirred diluted silica sol. Continue stirring in a round-bottomed flask for 10 hours

#### Crystallization

Vessel: 1000 mL round bottomed flask with agitator and reflux condenser  
Incubation: 10 h at ambient temperature with stirring  
Temperature: 98°C<sup>b</sup>  
Time: 3 days<sup>c</sup>  
Agitation: Continue stirring until temperature reaches 98°C, then discontinue stirring for balance of crystallization period

#### Product Recovery

- (1) Filter and wash with deionized water until pH < 10
- (2) Dry at 110°C
- (3) Yield: near 100% on  $Ga_2O_3$

#### Product Characterization

XRD: OFF, no other crystalline products or amorphous material detected  
Elemental Analyses: 49.5%  $SiO_2$ , 42.2%  $Ga_2O_3$ , 7.2%  $K_2O$ , 1.1%  $Na_2O$ <sup>d</sup>

## References

- [1] M. L. Occelli, US Patent 5 133 951 (1992)
- [2] M. L. Occelli, H. Eckert, C. Hudalla, A. Auroux, P. Ritz, P. S. Iyer, *Micropor. Mater.* 10 (1997) 123-135
- [3] M. L. Occelli, H. Eckert, C. Hudalla, A. Auroux, P. Ritz, P. S. Iyer, in *Proceedings of the 11th International Zeolite Conference*, Seoul, Korea, Hakze Chon, Son-Ki Ihm (eds.), Elsevier, Amsterdam, 1997, p 1981
- [4] M. L. Occelli, H. Eckert, P. S. Iyer, P. Ritz, in *Synthesis of Porous Materials*, M. L. Occelli, H. Kessler (eds.), Marcel-Dekker (1997), p. 283

## Notes

- a. Diluted Na,K gallate solution must be clear.
- b. Stirring is continued as temperature is increased to 98°C, then discontinued for the remainder of the crystallization treatment.
- c. Methods to reduce crystallization time are given in ref. [1].
- d. After calcination in nitrogen for 2 hours at 500°C followed by calcination in air for 10 hours at 550°C; the BET surface area was 404 m<sup>2</sup>/g. Characterizations of similar gallium offretites are given in references [2-4].

PAU

ECR-18

Si(76), Al(24)

Contributed by David Vaughan

Verified by P. Piccione and by B. Subotic

Type Material:  $(\text{Na}_{82}\text{K}_{66}\text{TEA}_{16})[\text{Al}_{164}\text{Si}_{508}\text{O}_{1344}] : w\text{H}_2\text{O}$  (TEA = tetraethylammonium)

Method: D. E. W. Vaughan, K. G. Strohmaier [1,2]

Batch Composition:  $0.4 \text{ K}_2\text{O} : 0.6 \text{ Na}_2\text{O} : 1.4 (\text{TEA})_2\text{O} : \text{Al}_2\text{O}_3 : 9 \text{ SiO}_2 : 0.3 \text{ Na}_2\text{SO}_4 : 140 \text{ H}_2\text{O}$

#### Source Materials

deionized water

potassium hydroxide (J. T. Baker, >99% KOH · 0.5 H<sub>2</sub>O)

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

alumina (Alcoa C-31, >99% Al<sub>2</sub>O<sub>3</sub> · 3 H<sub>2</sub>O)

silica sol (Dupont HS-40, 40% SiO<sub>2</sub>, 0.4% Na<sub>2</sub>O)

tetraethylammonium hydroxide (SACHEM, 35% N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>OH)

aluminum sulfate (reagent grade, > 99% Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 17H<sub>2</sub>O)

#### Batch Preparation (for 20 g dry product)

- (1) [8.0 g water + 1.79 g potassium hydroxide + 2.8 g sodium hydroxide + 5.1 g alumina], reflux until a clear solution is obtained; cool to room temperature. Replace water lost by evaporation
- (2) [10 g aluminum sulfate + 10 g water], mix and warm if necessary to make a solution
- (3) [49.7 g silica sol + 43.3 g tetraethylammonium hydroxide + (1) + 5.29 g (2) + 19 g water], add sequentially with mixing in a beaker

#### Crystallization

Vessel: 125 mL Teflon jar (Nalgene)

Incubation: 3 days at room temperature

Time: 12 to 16 days<sup>a</sup>

Temperature: 100°C

Agitation: none

#### Product Characterization

XRD: excellent PAU

Elemental Analysis:  $0.4 \text{ K}_2\text{O} : 0.5 \text{ Na}_2\text{O} : 0.1 (\text{TEA})_2\text{O} : \text{Al}_2\text{O}_3 : 6.2 \text{ SiO}_2 : \text{H}_2\text{O}$

Crystal size and Habit: spherical aggregates (1 to 10 μm) of submicron crystals (< 0.1 to 0.2 μm)<sup>b</sup>

#### References

- [1] D. E. W. Vaughan, K. G. Strohmaier, U. S. Patent 5 013 536 (1991)
- [2] D. E. W. Vaughan, K. G. Strohmaier, Micropor. Mesopor. Mater. 28 (1999) 233

#### Notes

- a. Both 12 and 16 day samples were excellent PAU.
- b. <sup>13</sup>C-NMR shows two sites; <sup>29</sup>Si-NMR shows three broad peaks.

# PAU

## Paulingite (seeded)

## Si(76), Al(24)

Contributed by David Vaughan and Karl Strohmaier

Verified by P. Piccione and by B. Subotic

Type Material:  $(\text{Na}_{87}\text{K}_{72}\text{TEA}_{15})[\text{Al}_{164}\text{Si}_{508}\text{O}_{1344}] \cdot w\text{H}_2\text{O}$  (TEA = tetraethylammonium)

Method: D. E. W. Vaughan, K. G. Strohmaier [1,2]

Batch Composition:  $0.5 \text{ K}_2\text{O} : 0.7 \text{ Na}_2\text{O} : 1.3 (\text{TEA})_2\text{O} : \text{Al}_2\text{O}_3 : 9 \text{ SiO}_2 : 0.4 \text{ Na}_2\text{SO}_4 : 135 \text{ H}_2\text{O}$

### Source Materials

deionized water  
sodium hydroxide (J.T. Baker, ~99% NaOH)  
alumina (Alcoa C-31, >99%  $\text{Al}_2\text{O}_3 \cdot 3 \text{ H}_2\text{O}$ )  
sodium silicate (PQ Corp. N-brand, 8.9%  $\text{Na}_2\text{O}$ , 28.7%  $\text{SiO}_2$ )  
potassium hydroxide (J. T. Baker, >99%  $\text{KOH} \cdot 0.5 \text{ H}_2\text{O}$ )  
silica sol (Dupont HS-40, 40%  $\text{SiO}_2$ , 0.4%  $\text{Na}_2\text{O}$ )  
tetraethylammonium hydroxide (RSA Corp., 40%  $\text{N}(\text{C}_2\text{H}_5)_4\text{OH}$ )  
aluminum sulfate (> 99%  $\text{Al}_2(\text{SO}_4)_3 \cdot 17 \text{ H}_2\text{O}$ )

### Batch Preparation (for 17 g dry product)

#### Preparation of Seed Solution [3,4]

- (1) [30 g water + 16 g NaOH + 3.25 g alumina] reflux until a clear solution forms, then cool to room temperature and add water back to the original weight if necessary
- (2) [54.4 g sodium silicate + 31.3 g water + (1)], add sodium aluminate solution slowly with mixing in a 200 mL Waring blender
- (3) Age for 24 hours at room temperature<sup>a</sup>

#### Preparation of Crystallization Batch

- (4) [6 g water + 2.28 g potassium hydroxide + 2.16 g sodium hydroxide + 4.57 g alumina], stir at 100°C until clear, then cool in an ice bath to below room temperature. Adjust to original weight with water
- (5) [45.9 g silica sol + 4.53 g seed solution + 33.4 g tetraethylammonium hydroxide + (4)], add sequentially with continuous mixing
- (6) [6 g water + 3.2 g aluminum sulfate], mix until dissolved
- (7) [(5) + (6)], add alum solution slowly with continuous mixing
- (8) [(7) + 17 g water], adjust the total weight of gel to 125 g by the addition of water<sup>b</sup>

### Crystallization

vessel: 125 mL Teflon jar or bottle (Nalgene)  
time: 22 days  
temperature: 100°C  
agitation: none

### Product Recovery

- (1) Vacuum filter on a Buechner funnel
- (2) Wash to pH < 10
- (3) Dry at 110°C
- (4) Yield: 17 g (~85% on  $\text{Al}_2\text{O}_3$ )

**Product Characterization**

XRD: excellent PAU

Elemental analyses: 0.44 K<sub>2</sub>O : 0.53 Na<sub>2</sub>O : 0.09 (TEA)<sub>2</sub>O : Al<sub>2</sub>O<sub>3</sub> : 6.18 SiO<sub>2</sub>

Crystal size and habit: spherical aggregates (2 to 30 μm) of submicron crystals (0.1 to 0.3 μm)<sup>c</sup>

**References**

- [1] D. E. W. Vaughan, K. G. Strohmaier, US Patent 5 013 536 (1991)
- [2] D. E. W. Vaughan, K. G. Strohmaier, Micropor. Mesopor. Mater. 28 (1999) 233
- [3] D. E. W. Vaughan, U S Patent 4 178 352
- [4] D. E. W. Vaughan, Mater. Res. Soc. Symp. Proc. 111 (1988) 89

**Notes**

- a. Stored at room temperature, this seed solution will be stable and usable for several months.
- b. The control of OH<sup>-</sup>/Si ratios can be done either by adding part of the Al as aluminum sulfate, or by using only aluminate and balancing the alkalinity with mineral acid (such as sulfuric acid).
- c. <sup>13</sup>C-NMR shows two sites; <sup>29</sup>Si-NMR shows three broad peaks.

## PHI

## Phillipsite

Si(72), Al(28)

Contributed by David Hayhurst

Verified by A. Cichocki, by A. Rodriguez, by E. Falabella Sousa-Aguiar, and by R. Thompson and A. Giaya

Type Material:  $K_{3.1}Na_{0.9}[Al_4Si_{12}O_{32}] \cdot wH_2O$ 

Method: D. T. Hayhurst, L. B. Sand [1]

Batch Composition: 6.95  $Na_2O$  : 3.50  $K_2O$  :  $Al_2O_3$  : 18.5  $SiO_2$  : 325  $H_2O$ 

## Source Materials

distilled water  
potassium hydroxide (Mallinckrodt reagent grade, 87% KOH)  
sodium silicate solution (PQ Corp., N-brand, 8.9%  $Na_2O$ , 28.7%  $SiO_2$ )  
sodium aluminate (Nalco, 30.5%  $Na_2O$ , 45.6%  $Al_2O_3$ )

## Batch Preparation (for 100 g dry product)

- (1) [636 g water + 91.6 g potassium hydroxide + 826.9 g sodium silicate solution]. Dissolve in a stirred flask at 100°C under reflux
- (2) [(1) + 45.28 g sodium aluminate], continue mixing at 100°C for crystallization

## Crystallization

Vessel: 3 L, 3-neck flask under reflux  
Temperature: 100°C  
Time: 6 to 8 hours  
Agitation: mechanically stirred

## Product Recovery

- (1) Filter to recover solids
- (2) Wash to pH < 10
- (3) Dry at 120°C
- (4) Yield: 100% on  $Al_2O_3$

## Product Characterization:

XRD: PHI (only crystalline product); Competing phases; MOR,<sup>a</sup> ERI,<sup>a</sup> LTL,<sup>b</sup> GIS,<sup>b</sup> ANA<sup>c</sup>  
Elemental Analysis: 0.8  $K_2O \cdot 0.2 Na_2O \cdot Al_2O_3 \cdot 5.24 SiO_2$   
Crystal Size and Habit: multi-crystalline aggregates, ~5  $\mu m$  dia.

## Reference

- [1] D. T. Hayhurst, L. B. Sand, in ACS Symposium Series 40, J. R. Katzer (ed.), Am. Chem. Soc., Washington, D. C., 1977, p. 219

## Notes

- a. Higher silica batch composition
- b.  $K^+/(Na^+ + K^+) > 0.4$
- c.  $K^+/(Na^+ + K^+) < 0.1$

## PHI

## High-alumina Phillipsite

Si(67), Al(33)

Contributed by Andrzej Cichocki

Verified by J. Bronić and by G. Kühl

Type Material:  $\text{Na}_{6.3}\text{K}_{4.2}[\text{Al}_{10.5}\text{Si}_{21.5}\text{O}_{64}] \cdot 23 \text{H}_2\text{O}^{\text{a}}$ 

Method: A. Cichocki [1,2]

Batch Composition:  $1.53 \text{ Na}_2\text{O} : 0.44 \text{ K}_2\text{O} : \text{Al}_2\text{O}_3 : 5.0 \text{ SiO}_2 : 82.7 \text{ H}_2\text{O}$ 

## Source Materials

distilled water

sodium hydroxide (reagent grade, 97% NaOH)

potassium hydroxide (reagent grade, 86% KOH)

silica sol (Rudniki Chemical Works, 29.5%  $\text{SiO}_2$ , 0.22%  $\text{Na}_2\text{O}$ )sodium aluminate solution (26.6%  $\text{Al}_2\text{O}_3$ , 19.6%  $\text{Na}_2\text{O}$ )<sup>b</sup>

## Batch Preparation (for 26 g product)

- (1) [36.0 g water + 1.53 g sodium hydroxide + 3.78 g potassium hydroxide], dissolve and cool to room temperature
- (2) [67.0 g silica sol + (1), mix in a porcelain mortar and stir for 2 minutes
- (3) [(2) + 25.22 g sodium aluminate solution], add sodium aluminate drop by drop to the stirred silicate over a 10 minute period and continue stirring for 20 minutes

## Crystallization

Vessel: stainless steel autoclave, 120 cm<sup>3</sup> capacity

Aging: 24 hours at room temperature

Temperature: 100°C

Time: 7 days

Agitation: none

## Product Recovery

- (1) Cool to room temperature; transfer the reaction mixture to a porcelain mortar and grind
- (2) Filter and wash in a Buechner funnel until pH of the filtrate is ~10
- (3) Dry at 110°C
- (4) Equilibrate in laboratory air for a few days
- (5) Yield: 25.8 g (near 100% on  $\text{Al}_2\text{O}_3$ )<sup>c</sup>

## Product Characterization

XRD: Pure phillipsite (ZK-19 [3] in ASTM Powder Diffraction File) competing phases: ANA, CHA, ERI, LTL

Elemental Analysis:  $0.60 \text{ Na}_2\text{O} \cdot 0.41 \text{ K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4.07 \text{ SiO}_2 \cdot 4.30 \text{ H}_2\text{O}^{\text{d}}$ Crystal Size and Habit: ~0.5 to 3  $\mu\text{m}$  diameter, round twinned polycrystals

## References

- [1] A. Cichocki, Zeolites 11 (1991) 758
- [2] A. Cichocki, PL Patent 161 557 (1993)
- [3] G. H. Kuehl, Am. Mineral. 54 (1969) 1607
- [4] A. Cichocki, PL Patent 100 912 (1979)
- [5] A. Cichocki, J. Grochowski, L. Lebioda, Kristall. Technik 14 (1979) 9
- [6] A. Cichocki, PL Patent 162 653 (1993)

## Notes

- a. Al content of the unit cell varies from 9.5 to 12.8. More siliceous synthetic-type phillipsite forms when (1) higher silica batch composition is used or (2) borosilicate glass corrodes in the alkaline reaction mixture. Phillipsite with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 6.27$  crystallized in a stainless steel autoclave from a reaction mixture of composition  $7.16 \text{ Na}_2\text{O} : 2.81 \text{ K}_2\text{O} : \text{Al}_2\text{O}_3 : 26.5 \text{ SiO}_2 : 442 \text{ H}_2\text{O}$ . [4,5] Phillipsite with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.34$  forms from a reaction mixture of composition  $1.29 \text{ Na}_2\text{O} : 0.37 \text{ K}_2\text{O} : \text{Al}_2\text{O}_3 : 4.20 \text{ SiO}_2 : 69.5 \text{ H}_2\text{O}$  when crystallization is carried out in a borosilicate glass vessel. These compositions differ slightly from those given in reference [4] and [6] where NaOH and KOH were assumed 100%.
- b. Prepared by the reaction of aluminum shavings with concentrated sodium hydroxide solution (~30 wt% NaOH).
- c. Dry product contains 72.0% of the sum of  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  masses introduced into the reaction mixture.
- d. Sorptive Capacity (g/g at  $p/p_0 = 0.2$ ): 0.185 for  $\text{H}_2\text{O}$  at 298 K, 0.002 for Ar at 77 K.



## RHO

## High-silica Rho

## Si(80), Al(20)

Contributed by Alain Matijasic and Joël Patarin

Verified by S. Schwarz, by T. Cholley, and by G. Gbery and K. Balkus

Type Material:  $\text{Na}_{6.8}\text{Cs}_{3.0}[\text{Al}_{9.8}\text{Si}_{38.2}\text{O}_6] : (18\text{-C-6}) \cdot w\text{H}_2\text{O}$  ( $w \approx 29$ )

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

Batch Composition:  $1.8\text{Na}_2\text{O} : 0.3\text{Cs}_2\text{O} : \text{Al}_2\text{O}_3 : 10\text{SiO}_2 : 0.5(18\text{-C-6}) : 100\text{H}_2\text{O}$

### Source Materials

distilled water

18-C-6 (Lancaster, > 98% cycl.  $(\text{C}_2\text{H}_4\text{O})_6$ )

cesium hydroxide (Aldrich, 50% CsOH in water)

sodium hydroxide (SDS, > 98% NaOH)

sodium aluminate (Carlo Erba, 56%  $\text{Al}_2\text{O}_3$ , 37%  $\text{Na}_2\text{O}$ , 7%  $\text{H}_2\text{O}$ )

silica sol (Dupont Ludox AS-40, 40%  $\text{SiO}_2$ )

### Batch Preparation (for ~6 g product)<sup>a</sup>

- (1) [7.84 g water + 1.35 g 18-C-6 + 1.80 g cesium hydroxide solution + 0.59 g sodium hydroxide], stir until dissolved<sup>b</sup>
- (2) [(1) + 1.82 g sodium aluminate], stir until homogenized
- (3) [(2) + 15.00 g silica sol], stir until homogenized (formation of a gel) Continue stirring with magnetic stirrer for 24 h., then transfer to a PTFE-lined stainless-steel autoclave. Gel pH = 14

### Crystallization

Vessel: 120 mL PTFE-lined stainless steel autoclave

Time: 192 hours

Temperature: 110°C in a preheated oven

Agitation: none. Final pH approximately 12

### Product Recovery

- (1) Dilute the reaction mixture with distilled water
- (2) Filter and wash until pH  $\approx 10$
- (3) Dry at 60°C overnight
- (4) Yield: ~ 6 g as-synthesized RHO-type sample (product containing about one molecule 18-C-6 as organic template per unit cell)<sup>b</sup>

### Product Characterization

XRD: Strong RHO pattern showing cubic symmetry. ( $a_0=15.031(1)\text{\AA}$ );<sup>c</sup> no visible impurities

Elemental Analyses: Si/Al is close to 3.9<sup>b</sup>

Crystal size and habit: The crystals display a sphere-like shape with an average size of 1  $\mu\text{m}$

### Reference

- [1] T. Chatelain, J. Patarin, E. Fousson, M. Soulard, J. L. Guth, P. Schulz, Micropor. Mat. 4 (1995) 231

### Notes

- a. This recipe has been successfully scaled up by a factor of six.
- b. The starting mixture is prepared in a polyethylene vessel.
- c. According to Ref. [1].

## SOD

## NaBr-Sodalite

## Si(50), Al(50)

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Contributed by Andreas Stein

Verified by B. Schoeman and by S. Kowalak

Type Material:  $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24} : 2 \text{ NaBr}$  <sup>a,b</sup>

Method: A. Stein, G. Ozin, G. Stucky [1, 2]<sup>c</sup>

Batch Composition:  $\text{Al}(\text{OH})_3 : \text{SiO}_2 : 12.5 \text{ NaOH} : 7.5 \text{ NaBr} : 144 \text{ H}_2\text{O}$

### Source Materials

deionized water  
sodium hydroxide (Mallinckrodt, 98.7%)  
sodium bromide (Mallinckroft, 99.0%)  
silica sol (DuPont Ludox HS-40, 40%  $\text{SiO}_2$ )  
aluminum hydroxide (Fisher, 99.8%)

### Batch Preparation (for 34 g dry product)

- (1) [300 mL water + 60.0 g sodium hydroxide + 154.3 g sodium bromide], stir until dissolved
- (2) [(1) + 30.0 g silica sol], stir rapidly, heat to 95°C
- (3) [200 mL water + 40.0 g sodium hydroxide + 15.6 g aluminum hydroxide], stir, heat at 95°C until dissolved
- (4) [Add hot (3) with hot (2)], shake gel vigorously for 5 minutes

### Crystallization

Vessel: 1000 mL capped Teflon bottle  
Time: 24 hours  
Temperature: 95°C  
Agitation: none

### Product Recovery

- (1) Cool to ambient temperature
- (2) Filter <sup>d</sup>
- (3) Wash with deionized water until filtrate is bromide-free and  $\text{pH} \approx 7$
- (4) Dry at 110°C
- (5) Yield; close to 100% on silica and alumina

### Product Characterization

XRD: SOD, no other crystalline or amorphous material detected  
Elemental Analysis:  $\text{Na}_{7.5}\text{Br}_{1.8}(\text{AlSiO}_4)_6$  <sup>e</sup>  
Crystal Size and Habit: 50-500 nm<sup>f</sup> dodecahedra, some malformed dodecahedra and penetration twins

## References

- [1] A. Stein, G. A. Ozin, G. Stucky, *J. Am. Chem. Soc.* 114 (1992) 5171
- [2] A. Stein, G. Ozin, in *Advances in the Synthesis and Reactivity of Solids*, Vol. 2, JAI Press, Greenwich, CT, 1994, p. 93
- [3] D. J. Schipper, C. Z. van Doorn, P. T. Bolwijn, *J. Am. Ceram. Soc.* 55 (1972) 256
- [4] R. R. Neurgaonkar, F. A. Hummel, *Mater. Res. Bull.* 11 (1976) 61
- [5] I. F. Chang, *J. Electrochem. Soc.* 121 (1974) 815
- [6] S. C. Zilio, V. S. Bagnato, *J. Phys. Chem.* 88 (1984) 1373

## Notes

- a. Other anions that can be introduced by various methods include  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{BrO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{N}_3^-$ ,  $\text{B}(\text{OH})_4^-$ ,  $\text{Al}(\text{OH})_4^-$ ,  $\text{HCO}_2^-$ ,  $\text{CH}_3\text{CO}_2^-$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{MnO}_4^-$ ,  $\text{SeO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{TeO}_4^{2-}$ ,  $\text{WO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{e}^-$ .
- b. Synthesis of NaOH-SOD:  $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24} \cdot 2 \text{NaOH} \cdot 8 \text{H}_2\text{O}$ : batch  $\text{Al}(\text{OH})_3 : \text{SiO}_2 : 5 \text{NaOH} : 41 \text{H}_2\text{O}$ . [1]  
Extensive washing, especially with hot water, results in extraction of hydroxide and sodium ions.
- c. Other methods for sodalite synthesis include sintering [3, 4] and structure conversion. [5]
- d. Alternately: centrifuge for 20 minutes, decant mother liquor, add fresh water and disperse the solid phase by shaking, followed by centrifuging. Repeat six times.
- e. Low cation and anion content is due to formation of some  $\text{OH}^-$  containing cages (or anion-free cages in washing). These can be removed by heating the sodalite with NaBr. [6]
- f. The larger crystallites are obtained in more dilute solutions.

STT

SSZ-23

Si(100)

**Contributed by** M. A. Cambor and M. J. Díaz-Cabañas

**Verified by** S. Zones, and by Y. Kubota and R. Bandyopadhyay

**Type Material:** [Si<sub>64</sub>O<sub>128</sub>]

**Method:** M. A. Cambor, M. J. Díaz-Cabañas, P. A. Cox, I. J. Shannon, P. Lightfoot, P. A. Wright, R. E. Morris [1]

**Gel Composition:** SiO<sub>2</sub> : 0.51 TMAdaOH : 0.51 HF : 10 H<sub>2</sub>O<sup>a</sup>  
(TMAdaOH = N,N,N-trimethyl-1-adamantammonium hydroxide)

**Source Materials**

tetraethylorthosilicate (TEOS), Merck, (> 98%)

N,N,N-trimethyl-1-adamantammonium hydroxide (0.435 mol/1000 g)<sup>b</sup>

hydrofluoric acid (Aldrich, 48% HF)

**Gel Preparation (for 5 g product)**

- (1) [15.60 g TEOS + 86.10 g TMAdaOH (aq. 0.435 mol/1000 g)], stir until ethanol evaporation is completed and until the water is reduced as required to give H<sub>2</sub>O/SiO<sub>2</sub> = 10 after addition of HF<sup>c</sup>
- (2) [(1) + 1.56 g hydrofluoric acid], stir manually<sup>d</sup>

**Crystallization**

Vessel: 60 mL stainless steel autoclave with Teflon liner

Time: 11 days

Temperature: 150 ± 2°C

Agitation: autoclaves rotated at 60 rpm

**Product Recovery**

- (1) Quench autoclaves in cold water; final pH ≈ 8
- (2) Filter contents; wash the solid with deionized water and dry overnight at 100°C
- (3) Yield: 20 g of solid/100 g gel (98% based on SiO<sub>2</sub>)

**Product Characterization**

XRD: STT (no other crystalline phases); competing phases: CHA, SSZ-31<sup>a</sup>

Elemental Analysis (wt%): 1.20 N, 13.50 C, 2.16H, 1.32 F<sup>e,f</sup>

Crystal size and habit: large plate-like twinned crystals; broad crystal-size distribution with crystals up to 30 x 20 x 2 μm

**References**

- [1] M. A. Cambor, M. J. Díaz-Cabañas, P. A. Cox, I. J. Shannon, P. Lightfoot, P. A. Wright, R. E. Morris, submitted to Chem. Mater.
- [2] S. I. Zones, Eur. Patent 231 018 (1987)
- [3] S. I. Zones, R. A. van Nordstrand, D. S. Santilli, D. M. Wilson, L. Yuen, L. D. Samparia, Stud. Surf. Sci. Catal. 49 (1989) 299

## Notes

- a. Final gel composition: In the calculation of the final water to silica ratio two things should be taken into account:
  - (1) Two water molecules per  $\text{SiO}_2$  are consumed during the hydrolysis of TEOS and are eliminated from the reaction mixture according to  $\text{Si}(\text{OEt})_4 + 2 \text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4 \text{EtOH}\uparrow$
  - (2) Evaporation of water must be accounted for (see gel preparation). The water to silica ratio has a large effect on the phase selectivity of the crystallization: at low ( $<6$ ) and high ratios ( $>15$ ) pure silica CHA and SSZ-31, respectively, crystallize after short heating, although SSZ-23 is the crystallization product after prolonged heating (in the  $\text{H}_2\text{O}/\text{SiO}_2$  range between 3 and 20). At the reported  $\text{H}_2\text{O}/\text{SiO}_2$  ratio of 10, SSZ-23 is the only phase observed between 11 and 45 days of crystallization.
- b. Concentration of  $\text{OH}^-$ : TMAda OH may be prepared by anion exchange of the iodide, which can be obtained by reaction of 1-adamantamine with an excess of methyl iodide at room temperature. In a typical synthesis 1-adamantamine (4.667 g) was dissolved in 50 g of chloroform. Then, 11.350 g of  $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$  was added and the mixture was cooled in an ice bath. 13.14 g of  $\text{CH}_3\text{I}$  was then added followed the next day by a second portion of  $\text{CH}_3\text{I}$  (6.5 g). After 7 days, the mixture was filtered and the solid washed with  $\text{CHCl}_3$ . The iodide was converted to the hydroxide by anion exchange with Dowex 1 resin. The yield in the anion exchange of TMAda-I to TMAdaOH is typically  $>90$ - $95\%$ .
- c. Evaporation of ethanol plus water can be monitored by the change in weight. In this example a total weight loss of 76.61 g was necessary. The time needed for this process depends on many factors (total batch weight, size of the vessel, temperature, etc.) and is typically several hours. Complete evaporation of ethanol may be checked by  $^1\text{H}$  NMR of the reaction mixture.
- d. A white fluid slurry is obtained after addition of HF.
- e. Corresponding to  $[(\text{TMAda}^+)_{4.1}\text{F}^-_{3.3}(\text{OH}^-)_{0.8}(\text{H}_2\text{O})_{1.6}][\text{SiO}_2]_{64}$  per unit cell ( $\text{OH}^-$  is included for electroneutrality and relates to a small concentration of connectivity defects in the as-made material).
- f. Al may be introduced into SSZ-23 either in hydroxide medium (as in Ref. [2] and [3]) and, apparently more favorably, in fluoride medium (unpublished results).

# TON

## ZSM-22

### Si(95), Al(05)

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Contributed by Günter Kühl

Verified by M. Derewinski and by Y. Oumi

Type Material:  $K_{0.1}Al_{0.6}Si_{23.4}O_{48}(DAO)_{0.86}^a$  (DAO = 1,8-diamino-octane)

Method: E. W. Valyocsik [1]

Batch Composition: 8.9  $K_2O$  :  $Al_2O_3$  : 90  $SiO_2$  : 3  $K_2SO_4$  : 27.3 DAO : 3588  $H_2O$

#### Source Materials

deionized water

aluminum sulfate (99+%  $Al_2(SO_4)_3 \cdot 18 H_2O$ )

potassium hydroxide (87.9% KOH)

1,8-diamino-octane (99+%)

silica sol (Dupont AS-30, ammonia stabilized, 30%  $SiO_2$ )

#### Batch Preparation (for 7.5 g dry product)

- (1) [18.2 g water + 1.76 g aluminum sulfate], stir until dissolved
- (2) [18.2 g water + 4.0 g potassium hydroxide], stir until dissolved
- (3) [72.8 g water + 10.4 g 1,8-diamino-octane], stir until dissolved
- (4) [26.95 g water + 47.65 g silica sol], mix well
- (5) [(1) + (2)], mix well
- (6) [(3) + (5)], add (3) to (5); blend
- (7) [(4) + (6)], add (4) to (6), stir for 30 minutes<sup>b</sup>

#### Crystallization

Vessel: stirred autoclave with stainless steel liner

Incubation: 24 hours at room temperature<sup>c</sup>

Temperature: 160°C

Time: 2-3 days

Agitation: vigorous stirring<sup>d</sup>

#### Product Recovery

- (1) Dilute reaction mixture with water
- (2) Filter and wash with water
- (3) Dry at ambient temperature or at 110°C
- (4) Yield: 7.5 g (near 100% on  $Al_2O_3$ )

#### Product Characterization

XRD: TON; competing phase: MEL (trace)<sup>d</sup>

Elemental Analysis: 0.2  $K_2O$  :  $Al_2O_3$  : 39  $SiO_2$  : 1.44 DAO

Crystal size and habit: needles<sup>e</sup>

#### Reference

- [1] E. W. Valyocsik, US Patent 4 902 406

## Notes

- a. Missing cations assumed to be protonated DAO.
- b. Reaction mixture becomes cloudy but does not gel.
- c. It is not certain that aging (or seeding) is beneficial.
- d. Ref. [1] recommends a stirring rate of 400 rpm; static preparations or slow stirring produce MEL or mixtures of MEL + TON.
- e. The size of the crystallites decreases with increasing stirring rate.

## VFI

## VPI-5 (DPA method)

## Al(53), P(47)

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Contributed by Heyong He and Jacek Klinowski

Verified by A. Karlsson and by W. Schmidt

Type Material:  $[\text{Al}_{19}\text{P}_{17}\text{O}_{72}] : 0.4 \text{ DPA} : 42 \text{ H}_2\text{O}$  (DPA = di-*n*-propylamine)

Method: H. He, J. Klinowski [1]

Batch Composition: 1.00  $\text{Al}_2\text{O}_3$  : 1.00  $\text{P}_2\text{O}_5$  : 40  $\text{H}_2\text{O}$  : 1.00 DPA<sup>a</sup>

### Source materials

- distilled water
- pseudoboehmite (Catapal B, 68.01 wt%  $\text{Al}_2\text{O}_3$ )
- phosphoric acid (Aldrich, 88.30 wt%  $\text{H}_3\text{PO}_4$ )
- di-*n*-propylamine (DPA) (Aldrich, > 98% pure)

### Batch Preparation (for ~18 g dry product)

- (1) [64.60 g water + 15.00 g pseudoboehmite], disperse alumina in water
- (2) [(1) + 22.20 g phosphoric acid], stir until homogeneous (for several minutes) and age for 2 hours without stirring
- (3) [(2) + 10.11 g di-*n*-propylamine], stir for 2 hours<sup>b</sup>

### Crystallization

- Vessel: Teflon-lined autoclave
- Time: 4 hours
- Temperature: 142°C
- Agitation: none

### Product Recovery

- (1) Dilute the reaction mixture with distilled water
- (2) After the crystals precipitate, decant the upper layer of liquid and discard. Repeat the operation three times
- (3) Filter and wash the crystals with distilled water
- (4) Dry in an air oven below 50°C

### Product Characterization

- XRD: VFI ( $a_0 = 18.9752 \text{ \AA}$ ,  $c_0 = 8.1044 \text{ \AA}$ , space group  $\text{P6}_3$ ); competing phase:  $\text{AlPO}_4\text{-11c}$
- Elemental Analysis: 0.04 DPA :  $\text{Al}_2\text{O}_3$  : 0.9  $\text{P}_2\text{O}_5$
- Crystal Size and Habit: Crystals are spherical and aggregated, ~ 100  $\mu\text{m}$  dia.

### Reference

- [1] H. He, J. Klinowski, J. Phys. Chem. 98 (1994) 1192

### Notes

- a. The amount of water quoted includes water in pseudoboehmite (100% - wt%  $\text{Al}_2\text{O}_3$ ), phosphoric acid (100% - wt%  $\text{P}_2\text{O}_5$ ).
- b. After adding DPA, the gel is very viscous. Homogeneous stirring is therefore essential.
- c.  $\text{AlPO}_4\text{-11}$  is found when stirring during Batch Preparation (3) is not vigorous enough.



## VFI

## VPI-5 (TBA method)

## Al(50), P(50)

Contributed by Heyong He and Jacek Klinowski

Verified by A. Karlsson and by W. Schmidt

Type Material:  $[\text{Al}_{18}\text{P}_{18}\text{O}_{72}] : 42 \text{ H}_2\text{O}$

Method: H. He, J. Klinowski [1]

Batch Composition:  $1.00 \text{ Al}_2\text{O}_3 : 1.00 \text{ P}_2\text{O}_5 : 50 \text{ H}_2\text{O} : 1.12 \text{ TBA-OH}$   
(TBA-OH = tetrabutylammonium hydroxide)

### Source materials

distilled water

pseudoboehmite (Catapal B, 68.01 wt%  $\text{Al}_2\text{O}_3$ )

phosphoric acid (Aldrich, 88.30 wt%  $\text{H}_3\text{PO}_4$ )

tetrabutylammonium hydroxide (Fluka, 58.08 wt% TBA-OH)

### Batch Preparation

- (1) [61.63 g water + 15.00 g pseudoboehmite], disperse alumina in water
- (2) [(1) + 22.20 g phosphoric acid], stir until homogeneous (for several minutes) and age for 2 hours without stirring
- (3) [(2) + 50.04 g tetrabutylammonium hydroxide], stir for 2 hours

### Crystallization

Vessel: Teflon-lined autoclave

Time: 20 hours

Temperature:  $150^\circ\text{C}$

Agitation: none

### Product Recovery

- (1) Dilute the reaction mixture with distilled water
- (2) After the crystals precipitate, decant the upper layer of liquid and discard. Repeat the operation three times
- (3) Filter and wash the crystals with distilled water
- (4) Dry in an air oven below  $50^\circ\text{C}$

### Product Characterization

XRD: VFI ( $a_0 = 18.9752 \text{ \AA}$ ,  $c_0 = 8.1044 \text{ \AA}$ , space group  $\text{P6}_3$ ); competing phases:  $\text{AlPO}_4\text{-H}_2$  and H3 [2]

Elemental Analysis:  $0.006 \text{ TBA}^+ : \text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5$

Crystal Size and Habit: needle-like and aggregated into bundles,  $\sim 10 \mu\text{m}$  dia.

### References

- [1] H. He, J. Klinowski, J. Phys. Chem. 98 (1994) 1192
- [2] F. d'Yvoire, Bull. Soc. Chim. 372 (1961) 1762

### Note

- a. The amount of water quoted includes water in pseudoboehmite (100% - wt%  $\text{Al}_2\text{O}_3$ ), phosphoric acid (100% - wt%  $\text{P}_2\text{O}_5$ ), and tetrabutylammonium hydroxide (100% - wt% TBA-OH).

## SUZ-4

Si(86), Al(14)

Contributed by Geoffrey L. Price

Verified by M. Camblor, by P. Piccione, and by E. Creighton

Type Material:  $K_x(TEA)_{5-x}[Al_5Si_{31}O_{72}] \cdot wH_2O$  (TEA = tetraethylammonium)

Method: G. L. Price

Batch Composition 7.35  $K_2O$  :  $Al_2O_3$  : 33.3  $SiO_2$  : 3.10  $(TEA)_2O$  : 681  $H_2O$

### Source Material

distilled, deionized water  
potassium hydroxide (Fisher A.C.S. pellets, 86% KOH)  
aluminum pellets (Aldrich, 99.99+% Al)  
tetraethylammonium hydroxide (Aldrich aqueous solution, 35% TEA-OH)  
silica sol (Dupont Ludox AS-40, ammonium stabilized, 40%  $SiO_2$ )

### Batch Preparation (for 13 g dry product)<sup>a</sup>

- (1) [33.98 g water + 6.709 g potassium hydroxide], stir until dissolved
- (2) [(1) + 0.3776 aluminum pellets], stir overnight or until Al pellets dissolve completely in a loosely capped plastic bottle (hydrogen gas evolved)
- (3) [18.226 g tetraethylammonium hydroxide + 35.00 g silica sol + 29.04 g water]. Stir together
- (4) [(2) + (3)], mix well

### Crystallization

Vessel: 200 mL stainless steel autoclave  
Temperature: 150°C  
Time: 4 days  
Agitation: rotated autoclave<sup>a</sup>

### Product Recovery

- (1) Cool to ambient temperature; decant and discard liquid
- (2) Wash with water to pH < 10
- (3) Dry at 100°C
- (4) Yield: near 100% on  $Al_2O_3$

### Product Characterization

XRD: strong SUZ-4 [1,2]; competing phases MOR<sup>b</sup> plus an unidentified phase<sup>c</sup>  
Elemental analysis: wt% Si 36, Al 5.5, K 1.5  
Crystal size and habit: rods, 0.1  $m\mu$  dia. x 1  $m\mu$  long

### References

- [1] S. L. Lawton, J. M. Bennett, J. L. Schlenker, M. J. Rubin, J. Chem.Soc.,Chem.Comm.(1993) 894
- [2] D. B. Lukyanov, V. L. Zholobenko, J. Dwyer, S. A. I. Barri, W. J. Smith, J. Phys. Chem B 103 (1999) 197

### Notes

- a. This preparation has been successfully scaled up to a one-liter stirred autoclave.
- b. Na<sup>+</sup> level too high.
- c. Produced by inadequate agitation during crystallization. XRD lines observed at 14.0°(2 $\theta$ ) m, 22.8° ms, 28.3 s, 29.8° ms, 30.6 m and 40.9 mw.