

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

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

Type Material [Si₆₄O₁₂₈]

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 SiO₂ : 0.51 TMAOH : 0.51 HF:10 H₂O^a
(TMAOH = 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)^b
hydrofluoric acid (Aldrich, 48% HF)

Gel Preparation (for 5 g product)

- (1) [15.60 g TEOS + 86.10 g TMAOH (aq. 0.435 mol/1000 g)], stir until ethanol evaporation is completed and until the water is reduced as required to give H₂O/SiO₂ = 10 after addition of HF^c
- (2) [(1) + 1.56 g hydrofluoric acid], stir manually^d

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 SiO₂)

Product Characterization

XRD: STT (no other crystalline phases); competing phases: CHA, SSZ-31^a
Elemental Analysis (wt%): 1.20 N, 13.50 C, 2.16 H, 1.32 F^{e,f}
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 SiO₂ are consumed during the hydrolysis of TEOS and are eliminated from the reaction mixture according to $\text{Si}(\text{OEt})_4 + 2 \text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4 \text{EtOH}$
 - (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 H₂O/SiO₂ range between 3 and 20). At the reported H₂O/SiO₂ ratio of 10, SSZ-23 is the only phase observed between 11 and 45 days of crystallization.
- b. Concentration of 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 K₂CO₃·1.5H₂O was added and the mixture was cooled in an ice bath. 13.14 g of CH₃I was then added followed the next day by a second portion of CH₃I (6.5 g). After 7 days, the mixture was filtered and the solid washed with CHCl₃. 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 ¹H NMR of the reaction mixture.
- d. A white fluid slurry is obtained after addition of HF.
- e. Corresponding to [(TMAda⁺)_{4.1}F⁻_{3.3}(OH⁻)_{0.8}(H₂O)_{1.6}][SiO]₆₄ per unit cell (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).