

TUN

TNU-9

Si(95), Al(5)

Contributed by Suk Bong Hong

Verified by J. Rimer, M. Hartmann, T. Okubo, W. Chaikittisilp

Type Material: $\text{Na}_{1.5}(\text{SDA})_{7.1}[\text{Al}_{9.3}\text{Si}_{182.7}\text{O}_{384}] \cdot w \text{H}_2\text{O}^a$ ($w \sim 28$)

(SDA = 1,4-bis[*N*-methylpyrrolidinium]butane (1,4-MPB))

Method: S. B. Hong, H. -K. Min, C. -H. Shin, P. A. Cox, S. J. Warrender, P. A. Wright [1]

Batch Composition: 4.5 (1,4-MPB) : 11.0 Na_2O : 1.0 Al_2O_3 : 30 SiO_2 : 1200 H_2O

Source Materials

deionized water

1,4-MPB dibromide^b

sodium hydroxide (Aldrich, 50% NaOH solution)

aluminum nitrate nonahydrate (Junsei, 98%, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)

silicon dioxide (Degussa Aerosil 200 or Cabot Cab-O-Sil M5)

Batch Preparation (for 3 g dry product)

(1) [62.62 g water + 1.18 g aluminum nitrate nonahydrate + 5.42 g sodium hydroxide (50% solution)], stir until dissolved

(2) [(1) + 5.54 g silica], mix thoroughly and stir for 30 minutes

(3) [(2) + 5.46 g 1,4-MPB dibromide], stir for 24 hours^c

Crystallization

Vessel: Teflon-lined stainless steel autoclave

Temperature: 160 °C

Time: 14 days^d

Agitation: 100 rpm

Product Recovery

(1) Dilute reaction mixture with water

(2) Filter and wash with water

(3) Dry at ambient temperature or at 90 °C

(4) Yield: 3.2 g

Product Characterization

XRD: TUN; competing phase: MOR (when $\text{SiO}_2/\text{Al}_2\text{O}_3 < 30$)

Elemental analysis: 1,4-MPB is approximately 12 wt.% and $\text{SiO}_2/\text{Al}_2\text{O}_3 = 39$ [1]

Crystal size and habit: rod-like crystals with ca. 1.0 μm in length and 0.3 μm in diameter

Reference

[1] S. B. Hong, H. -K. Min, C. -H. Shin, P. A. Cox, S. J. Warrender, P. A. Wright, J. Am. Chem. Soc. 129 (2007) 10870

- [2] S. B. Hong, E. G. Lear, P. A. Wright, W. Zhou, P. A. Cox, C. -H. Shin, J. -H. Park, I. -S. Nam, *J. Am. Chem. Soc.* 126 (2004) 5817

Notes

- a. The imbalance between the amount of Al and the sum of organic and alkali cations indicates that a fraction of the *N*-methylpyrrolidinium ions occluded within TNU-9 serves as spacefilling species rather than as charge-compensating cations.
- b. The description of template preparation is given in [2].
- c. pH of the final gel is 11.5.
- d. After about 7 days of heating, MCM- 22(P) is first crystallized. Continuing the crystallization for more than 14 days produces fully crystalline TUN.