PAU Paulingite (Seeded) Si(76), Al(24)

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Type Material $(Na_{87}K_{72}TEA_{15})[Al_{164}Si_{508}O_{1344}] : wH_2O$ (TEA = tetraethylammonium)

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

Batch Composition 0.5 K_2O : 0.7 Na_2O : 1.3 $(TEA)_2O$: Al_2O_3 : 9 SiO_2 : 0.4 Na_2SO_4 : 135 H_2O

Source Materials

deionized water
sodium hydroxide (J.T. Baker, ~99% NaOH)
alumina (Alcoa C-31, >99% $Al_2O_3 \cdot 3\ H_2O$)
sodium silicate (PQ Corp. N-brand, 8.9% Na_2O, 28.7% SiO_2)
potassium hydroxide (J. T. Baker, >99% KOH. 0.5 H_2O) silica
sol (Dupont HS-40, 40% SiO_2, 0.4% Na_2O)
tetraethylammonium hydroxide (RSA Corp., 40% $N(C_2H_5)_4OH$)
aluminum sulfate (> 99%$Al_2(SO_4)_3 \cdot 17\ H_2O$)

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[a]

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[b]

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 Al_2O_3)

Product Characterization

XRD: excellent PAU
Elemental analyses: 0.44 K_2O : 0.53 Na_2O : 0.09 $(TEA)_20$: Al_2O_3 : 6.18 SiO_2
Crystal size and habit: spherical aggregates (2 to 30 μm) of submicron crystals (0.1 to 0.3 μm)[c]

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^-/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. ^{13}C-NMR shows two sites; ^{29}Si-NMR shows three broad peaks.