

MFI

[Ti,Al] ZSM-5

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

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Type Material $H_{1.2}[Al_{1.17}Ti_{1.23}Si_{93.6}O_{192}] : w H_2O$

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

Batch Composition 1 TiO₂ : 0.25 Al₂O₃ : 40 SiO₂ : 216 H₂O : 7.44 (TPA)OH (TPA tetra-n-propylammonium) ^a

Source Materials

tetraethylorthosilicate [Alfa, Si(OC₂H₅)₄]

hydrochloric acid (0.2 N) (reagent grade)

isopropyl alcohol for analysis (Panreac)

aluminum isopropoxide, [Aldrich, Al(OC₃H₇)₃]

tetrapropylammonium hydroxide (TPAOH) [Alfa, 40 wt% (C₃H₇)₄NOH in water]

titanium tetrabutoxide [Alfa, Ti(OC₄H₉)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 H₂O], 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) Calcme in air at 550°C (heating rate 5°C/minutes and hold at 550°C for 5 hours)
- (4) Yield; 95% on SiO₂

Product Characterization

XRD: MFI structure, orthorhombic

Elemental Analysis: SiO₂/TiO₂ = 76, SiO₂/Al₂O₃ = 160 (by XRF) ^{b,c}

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. 56. Catal.* 63 (1991) 421
- [3] L Forni, M. Pellozi, A. Giusti, G. Fornasari, R Milhini, *J. Catal.* 122 (1990) 44
- [4] A. Thangaraj, R. Kumar, S. Sivasanker, *Zeolites* 12 (1992) 135
- [5] D. Trong On, S. Kaliaguine, L Bonneviot, *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⁺³, Ga⁺³, Fe⁺³ and B⁺³, 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 TiO₂ phases. [6]
- c. By ²⁹Si and ²⁷Al MAS-NMR, atoms are located in tetrahedral environments in the starting cogel and in the synthesized sample.