

Isomorphous Substitution of Be²⁺ into ZSM-5 Zeolite with Ammonium Tetrafluoroberyllate

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Be²⁺ has been inserted into the framework of ZSM-5 zeolite by treatment with aqueous ammonium tetrafluoroberyllate and characterized by ⁹Be MAS NMR spectroscopy.

We report here the isomorphous substitution of Be²⁺ into the framework of ZSM-5 zeolite. Treatment of ZSM-5 with an aqueous solution of ammonium tetrafluoroberyllate resulted in lattice substitution of Al³⁺ or Si⁴⁺ with small amounts of beryllium. This is believed to be the first reported instance of tetrahedral Be²⁺ inserted into a zeolite by post-synthesis modification.

Beryllium-containing silicates and aluminosilicates, although rare, are known to exist. Known examples of beryllium silicates include beryl, Be₃Al₂Si₆O₁₈,¹ chiavennite, CaMn(BeOH)₂Si₅O₁₃·2H₂O,² lovdarite, K₄Na₁₂(Be₈-Si₂₈O₇₂)·18H₂O,³ hsianghualite,⁴ euclase⁵ and phenacite.⁵ The synthesis of zeolites ZSM-5^{6,7} and lovdarite⁸ have also been reported wherein beryllium was incorporated into the zeolite framework under hydrothermal synthesis conditions.

Our attempts to modify existing zeolite structures by post-synthesis methods have succeeded in inserting small amounts of Be²⁺ into ZSM-5 using aqueous ammonium tetrafluoroberyllate. In a typical preparation, treatment of 1 part of (NH₄)ZSM-5 (SiO₂/Al₂O₃ = 68) with 50 parts of 0.2 mol l⁻¹ aqueous (NH₄)₂BeF₄ (CAUTION: TOXIC) at 85 °C for 18 h followed by filtering and copious washing with water yielded [Be]ZSM-5 (Anal: 130 ppm Be, Si/Be = 2280).

The ⁹Be MAS NMR spectrum is given in Fig. 1. The shift of Be in ZSM-5 has been reported^{6,9} to be -5.8 ppm relative to

0.05 mol l⁻¹ BeSO₄ set to -1.73 ppm. Using -1.73 ppm for our 0.061 mol l⁻¹ BeSO₄ reference solution, the chemical shift for the Be in our sample was found to be at -5.0 ppm. The difference in shift is likely due to the difference in concentration between the two aqueous reference solutions. T₁ values were obtained for the solution (2.7 s) and [Be]ZSM-5 (90 ms) using the saturation comb technique.¹⁰ The calculated Be concentration was 0.025 ± 0.01 mequiv. per g (225 ± 90 ppm) assuming non-zero quadrupole coupling. Owing to the small amounts of beryllium inserted, NH₄⁺ exchange capacity using thermogravimetric analysis and temperature programmed desorption showed no difference between parent and product zeolites.

The chemistry of Be²⁺ insertion into ZSM-5 parallels that reported previously by Chang *et al.* for Al insertion¹¹ and Skeels *et al.* for insertion of Si,¹² Fe and Ti¹³ into zeolite frameworks using the respective aqueous metal fluoride salts. This reaction has been postulated to involve substituting existing framework metal ions with the desired metal ions resulting in the formation of various metal fluoride species. In our case, Be is substituting for either Al³⁺ or Si⁴⁺ in ZSM-5 by a similar metathesis pathway in solution. No attempts were made to characterize which metal ion the Be²⁺ substituted for by analysing the residual solution owing to the small level of insertion observed and the toxicity of the solution. Similar

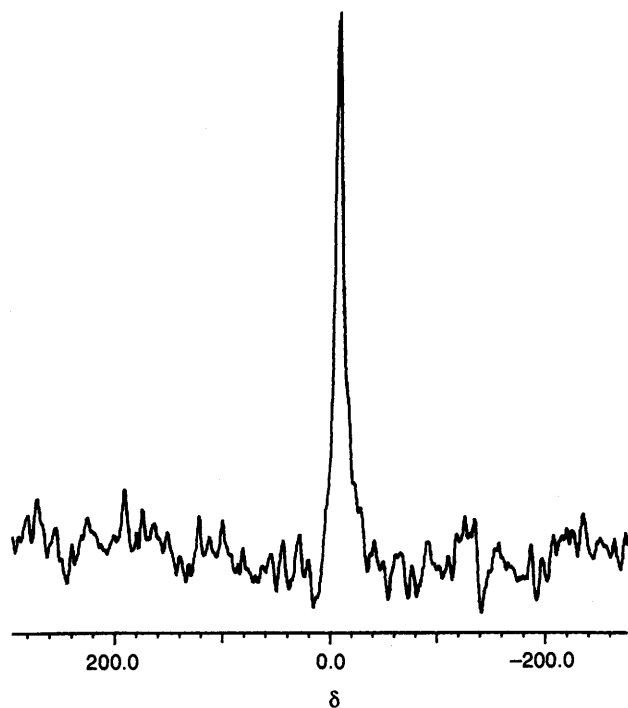


Fig. 1 28.04 MHz ^9Be MAS NMR spectrum of [Be]ZSM-5 obtained using 36 000 $6.0 \mu\text{s}$ pulses (solution $90^\circ = 7.2 \mu\text{s}$) with 55 Hz exponential line broadening applied before Fourier transform, with 0.061 mol l^{-1} aqueous BeSO_4 as reference

isomorphous substitution chemistry of zeolites in the vapour phase has been reported with Si^{14} and $\text{Al}^{11,15}$ chloride or bromide treatment.

Be^{2+} was considered to be an ideal candidate for this insertion reaction since its radius ratio [$r(\text{Be}^{2+})/r(\text{O}^{2-}) = 0.25$] favoured tetrahedral coordination.¹⁶ Although the preparation has not been completely optimized, we believe

the amount of Be inserted may be limited by difficulties in accommodating the smaller Be^{2+} ion (relative to Si^{4+} and Al^{3+}) in the ZSM-5 structure. Limited B^{3+} insertion [$r(\text{B}^{3+})/r(\text{O}^{2-}) = 0.20$] in ZSM-5 relative to less porous silicate systems has been reported.⁷

The present results along, with those published previously,¹¹⁻¹³ suggest a versatile method for preparing isomorphously substituted zeolite frameworks with various metal ion combinations.

Received, 27th April 1993; Com. 3/02418K

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