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Evidence of zeolite-solution equilibrium for isomorphous substitution using aqueous metal fluoride complexes ☆

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Abstract

The reversibility of isomorphous substitution of tetrahedral framework metal ions using aqueous AlF_3 and $(NH_4)_2SiF_6$ treatments on zeolite ZSM-5 is reported. ^{19}F NMR studies of AlF_3 and SiF_6^{2-} D_2O solutions after reaction at 85 °C with NH_4ZSM-5 showed formation of corresponding Si and Al fluoride species. Fluorine material balances were reasonable within experimental error. These experiments qualitatively suggest an equilibrium condition exists between Al^{3+} and Si^{4+} using mild aqueous metal fluoride treatment and imply a general synthetic pathway to isomorphously substituted zeolites. As a further example, [Ga]ZSM-5 containing framework Ga^{3+} was prepared by substitution of framework Al^{3+} using aqueous GaF_3 treatment. The framework Ga^{3+} was characterized by solid-state static and magic-angle spinning (MAS) NMR and the observed Ga chemical shift (155 ± 5 ppm) was consistent with tetrahedral framework Ga^{3+} reported previously. Quantitation by Ga and Si NMR and temperature-programmed NH_3 desorption (TPAD) showed excellent agreement.

Keywords: Isomorphous substitution; Zeolite complexes; Metal complexes; Fluoride complexes

1. Introduction

Isomorphous substitution of zeolites, i.e. replacement of existing T-atom sites with various metal ions, has been of significant interest [1] since new materials with potentially interesting catalytic properties are prepared. Two synthetic pathways have been reported to isomorphously substitute tetrahedral metal ions into zeolites: (i) incorporation of the desired metal ion through crystallization under hydrothermal conditions or (ii) modification of an existing framework through various post-synthesis treatments (secondary synthesis).

There has been copious research activity in isomorphous substitution of zeolites via method (ii) above using aqueous metal fluoride complexes. Skeels and Breck reported [2] in 1983 that replacement of framework Al^{3+} with Si^{4+} was possible using aqueous $(NH_4)_2SiF_6$ solution, producing highly stable, silicon-enriched Y zeolite. Chang et al. subsequently reported [3] the reverse reaction, i.e. substitution of Al^{3+} into highly siliceous, medium-pore ZSM-5 zeolite frameworks by replacement of Si^{4+} using aqueous aluminum fluoride solutions. This treatment has been extended to incorporate Fe^{3+}, Ti^{4+}, Sn^{2+} and Cr^{3+} into various zeolite frameworks using the respective aqueous metal fluoride salts [4,5]. Later, Ga^{3+} insertion into large-pore zeolites using this method was reported [6,7]. More recently, this preparative method was extended to incorporate smaller metal ions, e.g. Be^{2+} [8] and B^{3+} [9], into ZSM-5 and Y zeolite frameworks.

The versatility of using aqueous metal fluoride compounds for T-atom replacement suggests a general synthetic pathway for isomorphous substitution. This reaction is apparently proceeding via a metathesis pathway wherein the desired metal ion inserts into a T-atom vacancy created by the formation of soluble aluminum [2] or silicon [3] fluorides. If the reaction proceeds in this manner as described in the literature, then it strongly suggests an equilibrium condition exists between the metal fluoride species in solution and the metal T-atoms of the zeolite. Certain substitutions may be preferred due to strong heats of formation, e.g. AlF_3: $\Delta G_f^\circ = -336$ kcal mol^{-1}, but all substitution

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☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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reactions should occur to some extent and equilibrium shifts would be dependent on the reactant concentrations used.

We report here studies on observing this equilibrium by ^{19}F NMR of aluminum and silicon fluoride solutions used to treat ZSM-5 zeolite with varying Si/Al ratios. Qualitative indications of equilibrium for the aluminum/silicon fluoride treatment of ZSM-5 would suggest this condition may be applicable for all zeolite metal exchange reactions using aqueous fluoride solutions. As a further example, we report the insertion of Ga^{3+} into ZSM-5 using GaF_3 and characterization of framework Ga^{3+} by solid-state NMR and temperature-programmed NH_3 desorption (TPAD).

2. Experimental

2.1. Starting materials

The ZSM-5 powders used in this study were prepared according to published methods [10]. ZSM-5 zeolites in NH_4^+ form were used in all the reactions and were prepared by ion-exchange with 1.0 M NH_4NO_3, washing with distilled water, and drying at 120 °C. The NH_4ZSM-5 zeolites used had the following Si/Al ratios: AlF_3 treatment, 13 000/1; $(NH_4)_2SiF_6$ treatment, 35/1; GaF_3 treatment, 15.5/1. The AlF_3 species used was the soluble hydrate, $AlF_3 \cdot nH_2O$ where $n = 3$–9, prepared according to a published procedure [11]. $(NH_4)_2SiF_6$, $GaF_3 \cdot 3H_2O$, D_2O, $Ga(NO_3)_3$ and β-Ga_2O_3 were obtained as reagents from Aldrich or Alfa.

2.2. AlF_3 treated ZSM-5

In a plastic bottle, 5.0 ml of a 0.02 M $AlF_3 \cdot nH_2O$ (assumed $n = 3$) in D_2O were reacted with 3.0 g of NH_4ZSM-5 at 85 °C for 60 h. The solution was then filtered and analyzed. The AlF_3 starting solution was also analyzed by NMR.

2.3. SiF_6^{2-} treated ZSM-5

In a plastic bottle, 5.0 ml of a 0.02 M $(NH_4)_2SiF_6$ solution in D_2O were reacted with 3.0 g of NH_4ZSM-5 at 85 °C for 60 h. The solution was then filtered and analyzed. The $(NH_4)_2SiF_6$ starting solution was also analyzed by NMR.

2.4. ^{19}F NMR experiments

^{19}F NMR spectra were taken in Kel-F 10 mm NMR tubes at 56.26 MHz resonance frequency with a 4 s recycle time. Kel-F is poly-(dichlorodifluoroethylene) so it gives a broad fluorine NMR background signal. The solutions were quantitated against a 0.9766 M $NH_4F \cdot HF$ solution.

2.5. GaF_3 treated ZSM-5

To 10.0 g of NH_4ZSM-5 were added 4.0 g of $GaF_3 \cdot 3H_2O$ in 150 ml of distilled water. The mixture was reacted overnight (18 h) in a plastic bottle at 85 °C. The product was filtered while hot and washed with 600 ml of distilled water. The solid was then stirred with 400 ml of distilled water for 48 h, filtered, and washed with 1 l of water. The product was dried at 120 °C and ion-exchanged with NH_4NO_3. *Anal.*: Si, 36.52; Al, 0.15; Ga, 10.39%.

2.6. TPAD studies

TPAD studies were performed using a DuPont 951 thermogravimetric analyzer coupled to a Metrohm automatic titrator as described elsewhere [12]. A constant heating rate of 20 °C/min was maintained during TPAD measurements.

2.7. GaF_3 ZSM-5 NMR studies

^{71}Ga spectra were obtained static at 109.82 MHz at the University of Illinois using a ringless echo pulse sequence [13] and were obtained MAS at 60.86 MHz. The Ga^{3+} spectrum was referenced to acidified 1 M aqueous $Ga(NO_3)_3$. The Si NMR spectrum was obtained MAS at 39.64 MHz using direct excitation with 60° pulses at 15 s intervals. Ninety degree solution pulse widths were 5.7 μs for Ga and Si at 4.69 T and 8.5 μs for Ga at 8.46 T.

3. Results and discussion

Previous works on Si^{4+} substitution into large pore zeolites using $(NH_4)_2SiF_6$ solution [2] and Al^{3+} substitution into ZSM-5 using $(NH_4)_3AlF_6$ [3] suggest an equilibrium condition may exist for isomorphous substitution using aqueous metal fluoride complexes. The equilibrium expression for this system could be expressed as:

$$\mathrm{Al(zeolite)} + \mathrm{SiF}_x\mathrm{(aq.)} \rightleftharpoons \mathrm{Si(zeolite)} + \mathrm{AlF}_y\mathrm{(aq.)} \qquad (1)$$

Thus, zeolites may be silicon or aluminum enriched by aqueous reaction with the appropriate metal fluoride reagent. Our attempts at demonstrating this concept on a qualitative level centered on using ^{19}F NMR for AlF_3 and SiF_6^{2-} solutions used to treat ZSM-5 zeolite.

3.1. ^{19}F NMR of starting solutions

The ^{19}F NMR spectra of SiF_6^{2-} and AlF_3 in D_2O are given in Fig. 1. The SiF_6^{2-} solution spectrum showed a sharp peak at −128 ppm [14]. Close examination of the spectrum showed the expected 2% splitting into a 106 Hz doublet [15]. T_1 was measured at 1.23 s. The AlF_3 solution spectrum showed two peaks in about a 7:1 ratio at −154 and −155 ppm each with T_1 of about 200 ms. The peak at −154 ppm has been assigned to the $AlF(H_2O)_5^{2+}$ species [16] and it is likely the lower field peak is due to $AlF_2(H_2O)_4^+$ [16,17]. No AlF_4^- species was observed due to the lack of NH_4F complexing agent in the solution. The SiF_6^{2-} peak is quite sharp with a linewidth in the order of 1 Hz. The AlF_3 lines are much broader, about 30–40 Hz. A mixture of the two solutions showed no change after three days at room temperature.

3.2. ^{19}F NMR of product solutions

Reaction of the zeolite with AlF_3 resulted in clean conversion of the starting two peak mixture to a single fluorine species with a sharp peak at −119 ppm. This spectrum is given in Fig. 2. Quantitation of the peaks resulted in an acceptable material balance of 108% on fluorine. The shift in the SiF_6^{2-} peak is undoubtedly due to an intermediate silicon fluoride hydrolysis species. A second reaction mixture run analogously gave the expected SiF_6^{2-} product peak at −128 ppm.

The results for SiF_6^{2-} treated ZSM-5 were not as clean. The spectrum is given in Fig. 3. In this reaction, the initial SiF_6^{2-} peak at −128 ppm became two peaks at −118 and −151 ppm. This suggests that SiF_6^{2-} reacted in solution to the hydrolyzed intermediate silicon fluoride species observed previously (−118 ppm) and reacted with the zeolite to form an aluminum fluoride product (−151 ppm). The fluorine material balance of the second reaction was 75%. This inaccuracy in the material balance is likely due to formation and deposition on the zeolite of various less-soluble aluminum fluoride compounds and complexes such as AlF_3, $(NH_4)AlF_4$, etc. On the other hand, hexafluorosilicate salts are more soluble and, when formed in the AlF_3+ZSM-5 reaction, may be totally accounted for in solution.

These ^{19}F NMR experiments qualitatively demonstrate that the Si/Al aqueous fluoride system for iso-

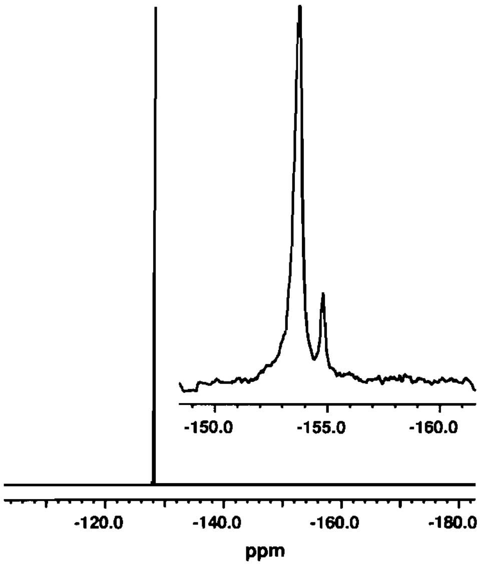

Fig. 1. ^{19}F NMR spectra of $(NH_4)_2SiF_6$ (1 Hz sharp peak at −128 ppm, bottom) and $AlF_3 \cdot nH_2O$ (30–40 Hz broad peaks at −154 and −155 ppm, inset) in D_2O solution.

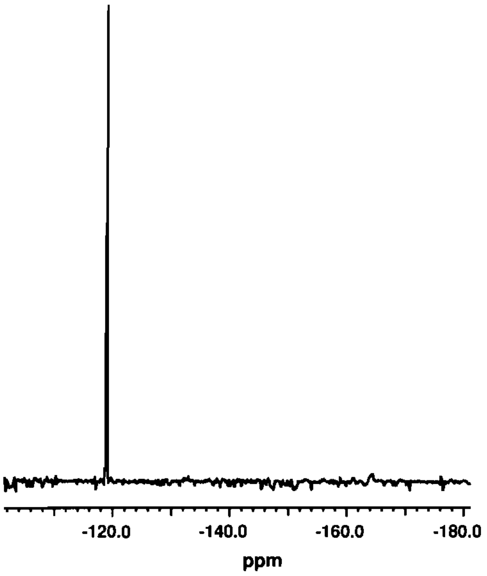

Fig. 2. ^{19}F NMR spectrum of D_2O solution obtained by treating NH_4ZSM-5 with aqueous AlF_3 at 85 °C for 60 h.

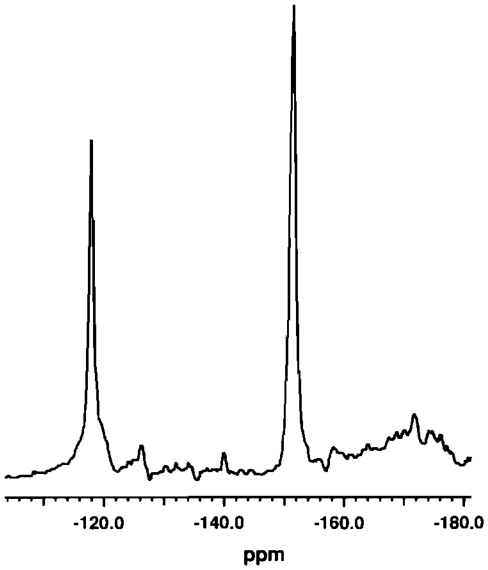

Fig. 3. ^{19}F NMR spectrum of D_2O solution obtained by treating NH_4ZSM-5 with aqueous $(NH_4)_2SiF_6$ at 85 °C for 60 h.

morphous substitution is reversible and indicative of an equilibrium condition. Material balances obtained were reasonable within experimental error, particularly for the case where aluminum fluoride compounds with low solubilities are formed from SiF_6^{2-}. It is suggested that this equilibrium condition may be applicable for all isomorphous exchange reactions using various metals in aqueous fluoride media. To further prove that this route can be a general synthetic pathway to modified zeolites, we prepared a [Ga]ZSM-5 using the above preparative method and characterized the Ga^{3+} in the product as framework Ga^{3+} consistent with prior literature reports.

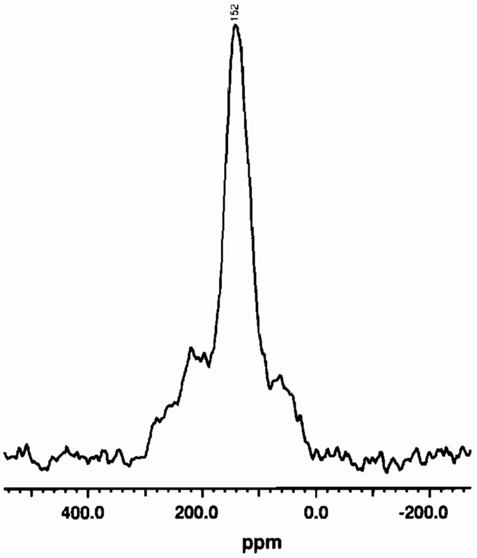

Fig. 4. 60.86 MHz Ga MAS NMR spectrum of [Ga]ZSM-5 obtained using 24 000 scans at 75 ms intervals processed with 250 Hz line broadening.

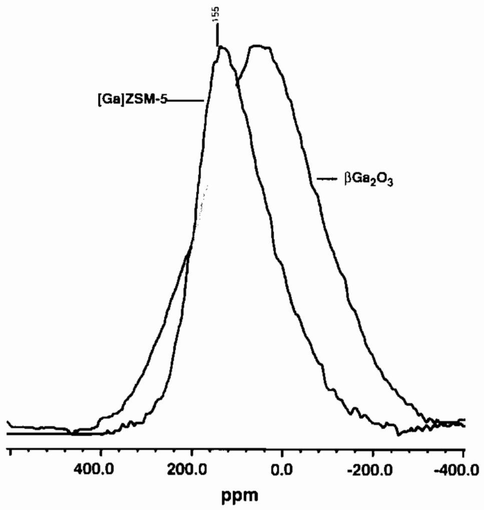

Fig. 5. Comparison of 109.82 MHz static echo spectra of β-Ga_2O_3 and [Ga]ZSM-5.

Table 1
Quantitation of [Ga]ZSM-5

Method	mequiv./g
Al, elemental	0.14
Ga, elemental	1.49
Ga, 200 MHz MAS NMR	0.65
Ga, 360 MHz static NMR	0.69
Ga, by Si MAS NMR [a]	0.69
TPAD	0.66

[a] From relative areas of $Si(O\text{-}Si)_4$ peak and −102 ppm peak.

3.3. [Ga]ZSM-5 from GaF_3 treatment

The [Ga]ZSM-5 obtained from reaction with GaF_3 was characterized using Ga and Si solid-state NMR. Fig. 4 shows the Ga MAS NMR spectrum for the product zeolite and Fig. 5 shows a comparison of the Ga static echo spectra for [Ga]ZSM-5 versus β-Ga_2O_3. Table 1 gives elemental analyses and NMR and TPAD quantitation values in mequiv./g for [Ga]ZSM-5.

The Ga NMR studies clearly show incorporation of framework Ga^{3+} into ZSM-5. From Fig. 1, an observed chemical shift of 152 ppm (155 ± 5 ppm for both 200 and 360 MHz) is indicative of tetrahedral framework Ga^{3+} and agrees well with literature values obtained for [Ga]ZSM-5 prepared hydrothermally (156 ppm) [18] and [Ga]AlY zeolites prepared from GaF_3 (151–154 ppm) [6,7]. Fig. 2 shows that the Ga^{3+} species in [Ga]ZSM-5 from GaF_3 is clearly different from the tetrahedral and octahedral Ga^{3+} present in β-Ga_2O_3. The low Al content by elemental analysis (Table 1) indicates substantial Ga^{3+} substitution for framework Al^{3+} with this treatment. By elemental analyses, the product Si/Al ratio for [Ga]ZSM-5 was 234 (15.5/1 ratio for parent) and the Si/Al+Ga ratio was 8.4/1.

The NMR and TPAD quantitations agreed well. Table 1 shows that framework Ga^{3+} quantitation by 200 MHz Ga MAS NMR (0.65 mequiv./g), 360 MHZ Ga static NMR (0.69 mequiv./g), Si MAS NMR (0.69 mequiv./g) and TPAD (0.66 mequiv./g) resulted in excellent agreement among different methods. The high Ga content by elemental analysis suggested non-framework Ga species are present, likely due to the preparation containing excess GaF_3 starting reagent.

Conclusive isomorphous substitution of Ga^{3+} in ZSM-5 by replacement of framework Al^{3+} with aqueous GaF_3, along with prior literature reports involving other metals and zeolites [2–9] implies a general equilibrium condition exists involving the aqueous metal fluoride and the zeolitic T-atoms. This has been qualitatively demonstrated for the Si^{4+}/Al^{3+} system in ZSM-5 above and there is no reason to suggest this condition does not exist for other zeolites with other appropriately-sized, tetrahedrally-coordinated metal ions. Thus, aqueous metal fluoride treatment constitutes a general synthetic pathway for isomorphous substitution in zeolites.

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