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Aluminum Insertion into High Silica Zeolite Frameworks. 1. Reaction with Aluminum Halides

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Abstract: Dealumination of zeolite frameworks is a well-known reaction. The reverse reaction of "alumination" is little known. The direct insertion of aluminum into high silica zeolite frameworks is described. This has been achieved by reaction with volatile aluminum halides and aqueous solutions of complex aluminates. Incorporation of aluminum into the framework as tetracoordinate species was confirmed by ^{27}Al MAS NMR, supported by NH_3 TPD, FTIR, and catalytic studies.

It is well-known that aluminum can be removed from zeolite frameworks without structural collapse.[1-4,21,24] The reverse process of aluminum insertion, on the other hand, has received little attention to date. We report the direct insertion of aluminum into high silica porous tectosilicate[5] frameworks. Aluminum insertion or "alumination" is effected by a high-temperature gas–solid reaction with aluminum halide vapor or with solutions of complex aluminates. Experiments with high silica ZSM-5[6,7] zeolite are described in this paper.

Experimental Methods

Materials. The zeolite was a high silica ZSM-5 (SiO_2/Al_2O_3 = 26 000) synthesized according to the method of Argauer and Landolt.[6] Anhydrous $AlCl_3$ and $AlBr_3$ were reagent grade. $(NH_4)_3AlF_6$ was obtained from ICN/K&K Life Sciences Group, Plainview, NY, and used without further purification.

Experimental Apparatus and Procedure

The apparatus used for activation with volatile halide is represented in Figure 1. The reaction vessel was a Vycor tube (18 mm i.d. × 25 cm length) with ball joints at each end. A four-way stopcock permitted carrier gas flow in either direction through the tube and out the vent. A tube furnace (electrical resistance, 650 W) heated $^2/_3$ of the length of the reaction vessel and could be moved to either end of the vessel. The unheated section constituted an air condenser, which served to collect unreacted Al halide.

In a typical experiment, a 5.5-g sample of the zeolite was loaded into the center of the Vycor tube. Anhydrous Al halide (~3.5 g) was heated to 375 °C with helium flowing (~50 mL/min) through the halide end of the tube. Unreacted Al halide condensed at the unheated end. The flow was reversed after 1 h; simultaneously, the furnace was moved over the condensed Al halide and the new downstream end chilled by a stream of cold air. The system was subjected to 12 hourly flow direction changes or cycles. At the end of every third cycle, the system was heated to 550 °C for 30 min. The product was calcined overnight at 538 °C and exchanged twice with 1 N NH_4NO_3.

No special equipment was used for aqueous solution reactions.

Analytical Methods. Infrared spectra were obtained by using a Nicolet 7199 interferometer. The sample cell was similar to that described by Moon et al.[8]

^{27}Al MAS NMR spectra were obtained on an instrument at the University of Illinois (Urbana, IL), courtesy of Professor Eric Oldfield. These spectra were measured at 360-MHz and 2.7-kHz spinning rate.

Solution ^{27}Al NMR spectra were measured at 15.54 MHz with a JEOL FX-600 spectrometer.

Temperature-programmed NH_3 desorption was carried out by using a Du Pont 951 Thermogravimetric Analyzer (TGA) equipped with an automatic titrimeter assembly.[22] *n*-Hexane sorptions were carried out with the same TGA.

Catalytic Testing. *n*-Hexane cracking activity was determined by using the method of Weisz and Miale.[9,10]

Activity for methanol conversion to hydrocarbons was determined by following the procedure of Chang and Silvestri.[11]

Experimental Results

Reaction with Volatile Halides. Anhydrous high silica ZSM-5 (SiO_2/Al_2O_3 = 26 000) was contacted with $AlCl_3$ vapor at 375 °C. An exothermic reaction ensued with evolution of HCl, giving an immediate indication that chemical reaction with silanol groups, and not ordinary physisorption, had taken place. An analogous reaction occurred when $AlBr_3$ was used. Following exposure to the aluminum halide, the zeolite samples were heated to 550 °C in the presence of flowing He to remove the bulk of unreacted halide. All samples were then thoroughly NH_4^+ exchanged to remove cationic Al and to decompose any residual aluminum halide.

Table I. Alumination of High Silica ZSM-5 (SiO_2/Al_2O_3 = 26 000)

alumination agent	NH_4^+ exchange capacity, mequiv/g	*n*-hexane sorption capacity, wt %	α
none	0.0013	10.43	0.02
$AlCl_3$ (g)	0.022	10.93	81
$AlBr_3$ (g)	0.027	10.97	106
$(NH_4)_3AlF_6$ (aqueous, pH 5.9)	0.014	9.50	2
$(NH_4)_3AlF_6$ (aqueous, pH 10.5)	0.12	9.68	49

The nature of the aluminum sites remaining in the zeolite was elucidated by various physicochemical techniques, complemented by catalytic testing.

Ion exchange and *n*-hexane sorption capacities of the zeolites

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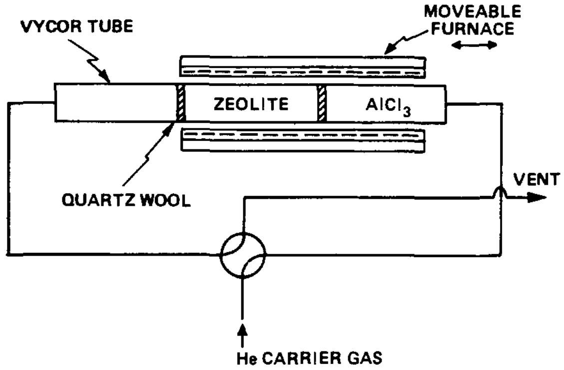


Figure 1. Apparatus for zeolite activation.

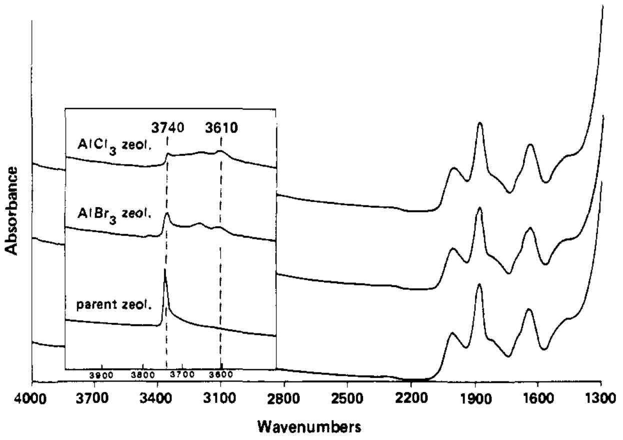


Figure 2. Fourier transform infrared spectra of ZSM-5 reacted with aluminum halides.

before and after reaction are compared in Table I. These measurements were both made by using the thermogravimetric analyzer. Ion exchange capacity was determined by temperature-programmed desorption of NH_3 followed by titrimetry.

The parent high silica ZSM-5 had a total NH_4^+ exchange capacity of 0.0013 mequiv/g and a *n*-hexane sorption capacity of 10.43% (90 °C). Upon alumination, the NH_4^+ exchange capcity of the $AlCl_3$-treated sample increased to 0.022 mequiv/g and that of the $AlBr_3$ sample to 0.027 meguiv/g, demonstrating the creation of Brønsted acid sites. *n*-Hexane sorption capacities were 10.93% and 10.97%, respectively, not significantly different from the parent, indicating that zeolite channels were largely free of occluded material.

Fourier transform IR analysis produced the absorption spectra shown in Figure 2. These spectra are normalized on the areas of the 1870- and 1980-cm^{-1} bands of the parent. The hydroxyl stretching region is enlarged in the inset. The parent zeolite shows a single band at 3740 cm^{-1} due to nonacidic silanol groups. Upon treatment with $AlCl_3$ or $AlBr_3$ followed by NH_4^+ exchange and calcination, a small but distinct band at 3610 cm^{-1} appears. This band is associated with zeolite framework Al(OH)Si groups responsible for Brønsted acidity.[12] Concomitant with the appearance of the 3610-cm^{-1} band is a sharp decrease in the 3740-cm^{-1} band, consistent with reaction of surface hydroxyl group with the aluminum halide. A band between the 3740- and 3610-cm^{-1} band also appears and is attributed to amorphous alumina or silica–alumina, which have been found to exhibit broad bands in this region.[13] Amorphous alumina would be formed through hydrolysis of residual aluminum halide during aqueous exchange.

Further characterization was made by using solid-state high-resolution NMR. The ^{27}Al MAS NMR of ZSM-5 consists of a single, sharp resonance,[14] whose chemical shift varies slightly with field, from δ 53 ± 1 at 360 MHz to δ 55 ± 1 at 500 MHz (relative to $Al(H_2O)_6^{3+}$). This peak position is within the range generally assigned to tetrahedral Al bound to Si atoms through oxygen.[15]

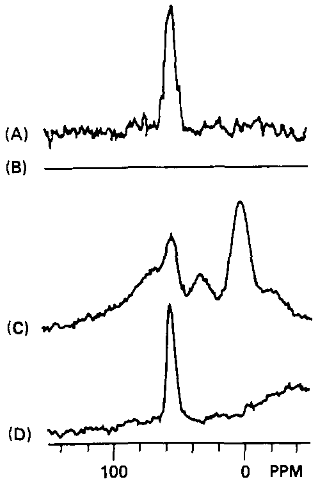


Figure 3. ^{27}Al MAS NMR spectra of ZSM-5 reacted with various aluminum compounds. (A) and (B) = parent; (C) = treated with $AlCl_3$; (D) treated with aqueous AlF_4^-.

Table II. Methanol Conversion to Hydrocarbons over $AlCl_3$-Activated High Silica ZSM-5 (370 °C, 1 LHSV, 1 atm)

	parent high silica HZSM-5 (SiO_2/Al_2O_3 = 26 000)	activated high silica ZSM-5	HZSM-5 (SiO_2/Al_2O_3 = 1000)
$\sum NH_4^+$ exchange capacity, mequiv/g	0.0013	0.022	0.033
conversion, %	<2	99+	99+
hydrocarbon distribution, wt %			
methane + ethane	16.9	2.3	0.6
ethene	1.3	7.9	8.2
propane	6.1	5.2	2.2
propene	11.9	7.1	9.8
C_4	28.1	17.7	15.6
C_5^+ aliphatic	35.7	25.0	38.1
aromatics		34.8	25.5

^{27}Al MAS NMR spectra are shown in Figure 3. These spectra were plotted on a fixed peak-height basis and therefore are not intended for quantitative comparison. Spectrum A is that of the parent material showing a single resonance at δ 56. Because of its extremely low Al content (50 ppm framework Al_2O_3) a large number of scans (89 800 FID) was required to achieve acceptable signal-to-noise ratios. Spectrum B is the result of decreasing the number of scans on the parent material to 3592 FID's. Other spectra on Figure 3 were obtained at this lower number of scans.

Spectrum C is that of the $AlCl_3$-treated zeolite. The spectrum consists of a 56 ppm peak, assigned to zeolitic framework Al, and peaks at 5 (T_d) and 70 (O_h) ppm showing the presence of a γ-Al_2O_3 type component. This indicates incomplete removal of nonframework Al during workup. These NMR data are consistent with IR results and confirm that Al is inserted into the zeolite framework by reaction with volatile aluminum halides. Spectrum D in Figure 3 is discussed presently.

The catalytic activity of the aluminated zeolites was determined for two reactions: paraffin cracking and methanol conversion to hydrocarbons. Paraffin cracking activity was evaluated by means of the "α-test".[9,10] This measures the rate of *n*-hexane cracking over the test sample relative to an amorphous SiO_2/Al_2O_3 standard. The α values obtained are listed in Table I. It is seen that whereas the parent zeolite had an α = 0.02, the aluminated zeolites showed high cracking activity with α = 81 for the $AlCl_3$-treated sample, and α = 106 for $AlBr_3$, all zeolites tested in their H-form.

The $AlCl_3$-treated zeolites were also tested for the methanol-to-hydrocarbon reaction.[11] Typical data are listed in Table II and demonstrate the high activity for this reaction. The product distribution is similar to that obtained with a ZSM-5 having an as-synthesized NH_4^+ exchange capacity of 0.03 mequiv/g. These

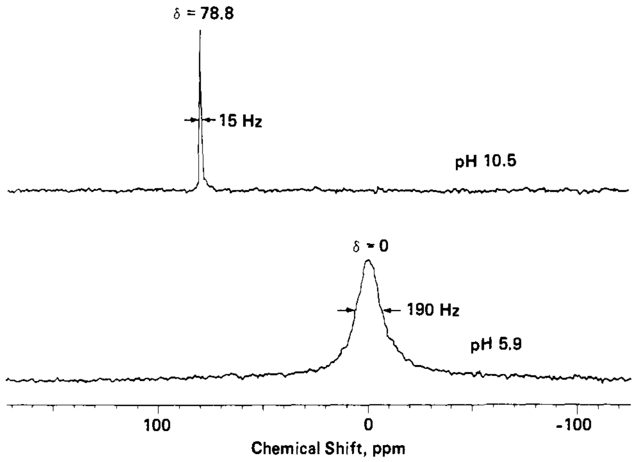


Figure 4. 15.54-MHz ^{27}Al NMR spectra of aqueous ammonium hexafluoaluminate solutions at pH 5.9 (0.02 M) and 10.5 (0.01 M).

data are also shown for comparison. By contrast, the parent zeolite has minimal activity for this reaction, as shown in Table II.

Reaction with Aqueous Fluoaluminates. Aluminum fluoride, unlike the chloride and bromide, is involatile and refractory. Nevertheless, this compound has been found active for alumination once it is placed within the zeolite pore. This is achieved by solubilization via complexation of AlF_3 with excess aqueous fluoride and contacting the zeolite with this solution. Aqueous NH_4F was found to be most effective, although the solubility of AlF_3 is generally limited in most aqueous media.

High silica ZSM-5 (SiO_2/Al_2O_3 = 26000) samples were impregnated with 0.02 M aqueous solutions of $(NH_4)_3AlF_6$. The samples, containing ~0.1% AlF_3, were heated to 130 °C and held at this temperature until dry. The samples were then exchanged with 1 N NH_4NO_3 and then calcined at 538 °C.

The pH of the fluoaluminate solutions had a strong influence on the reaction. A 0.02 M aqueous $(NH_4)_3AlF_6$ solution is slightly acidic with pH 5.9. Zeolites aluminated with this solution had a final cracking activity $\alpha = 3$ (Table I). By comparison, fluoaluminate solutions whose pH had been adjusted to 10.5 by addition of NH_4OH were more effective, increasing the zeolite cracking activity to $\alpha = 49$ (Table I). Moreover, a high α is obtained despite the fact that the solubility of the fluoaluminate is halved at the higher pH.

These fluoaluminate solutions were examined by ^{27}Al NMR. Figure 4 illustrates the effect of increasing pH on the aluminum-27 spectrum of hexafluoaluminate. Freshly dissolved $(NH_4)_3AlF_6$(0.02 M) at pH 6 is octahedral [$\delta(^{27}Al)$ 0] with a line width of 190 Hz. The large line width of the signal is presumably due to unresolved $^{27}Al-^{19}F$ couplings and/or exchange broadening. Upon basification to pH 10.5, the fluorides are displaced by hydroxyls to give a sharp ($\Delta\nu_{1/2}$ = 15 Hz), tetrahedral aluminum-27 signal at 78.8 ppm.

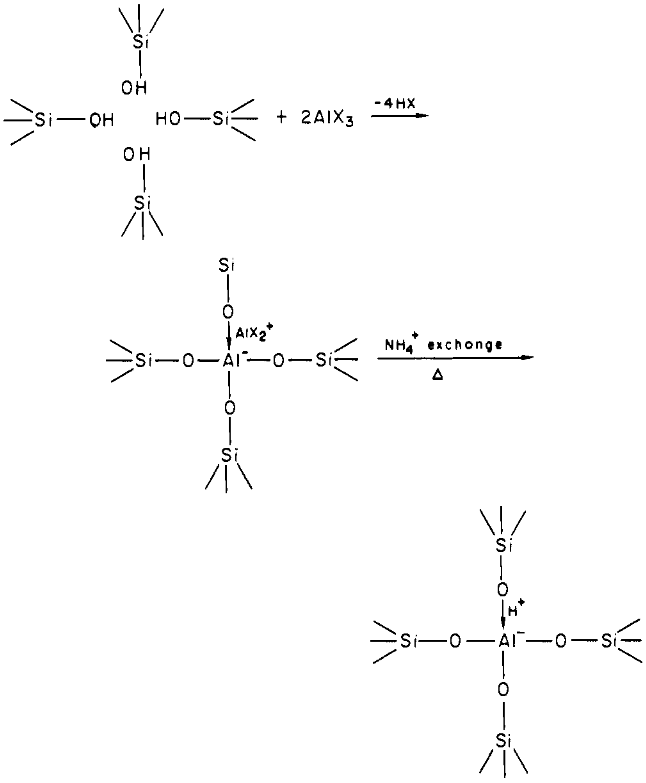
Results of sorption measurements are shown in Table I. The NH_4^+ exchange capacities appear to be disproportionately large as compared with the cracking activities. This is a consequence of the particular alumination procedure developed for the fluoride. Much of the unreacted fluoride may remain in the zeolite pore as occluded AlF_3 after calcination. This is reflected in the reduction in *n*-hexane capacity to 9.5–9.7% as seen in Table I. Occluded AlF_3 will, as a Lewis acid, sorb NH_3 and yield anomalously high NH_3 TPD results.

^{27}Al MAS NMR of the 49α sample is shown in Figure 3, curve D. A single sharp resonance at δ 56 due to tetrahedral framework Al appears.

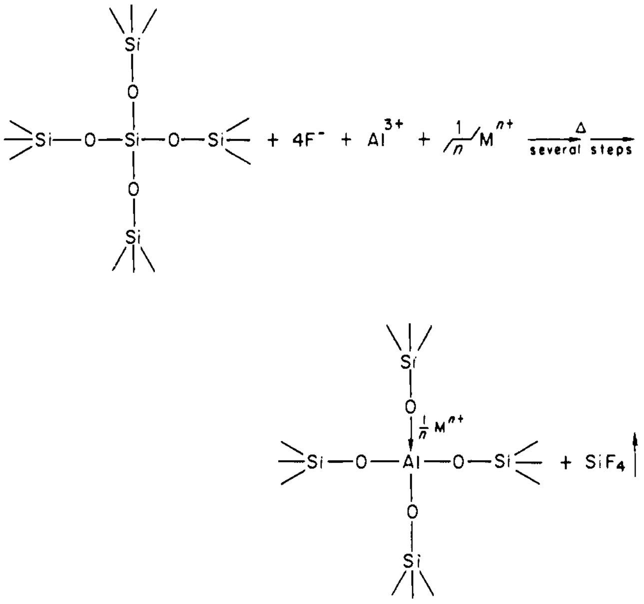
Discussion

The reaction of $AlCl_3$ with Y zeolites is disclosed in several patents.[16,17] Reaction with these low SiO_2/Al_2O_3 zeolites is basically a vapor phase exchange of the original zeolite cations with Al^{3+}. Breck and Skeels[18] have proposed that, under certain conditions, hydrolytic dealumination of NH_4Y is reversible. These workers did not investigate the effect of Al from an external (nonzeolitic) source.

Scheme I

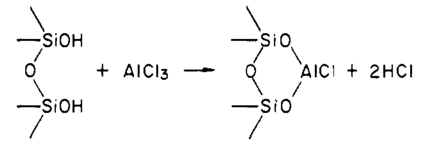


Scheme II



The present study provides direct evidence of Al insertion into zeolite frameworks in tetrahedral coordination.

The reaction of $AlCl_3$ with silica gel has been studied and shown to involve the surface hydroxyls according to the scheme[19]



We propose a similar mechanism for the alumination of high silica zeolite with volatile aluminum halides. We assume that the reactive hydroxyls in the zeolite comprise both external surface silanols and intracrystalline defect sites such as "hydroxyl nests".[20] High rates of ^{18}O exchange have been observed by von Ballmoos[23] for ZSM-5 zeolites, lending support for the presence of such defects. Reaction of aluminum halides with these defects followed by ion exchange would result in the creation of Brønsted sites as depicted in Scheme I.

The incorporation of Al into the zeolite framework as a tetracoordinate species generates a negative framework charge. This can be balanced either by a haloaluminum cation (as illustrated) or by a proton. Subsequent NH_4^+ exchange and calcination converts all of the sites into Brønsted acid sites.

A similar mechanism may be invoked for the reaction with fluoaluminate complexes. However, in this case, alumination could proceed even in the absence of defect sites, due to the high reactivity of inorganic fluorides toward silica. Thus the direct substitution of framework Si may occur, as shown in Scheme II.

As shown previously, the alkaline fluoaluminate solution contained 4-coordinate Al species, revealed through ^{27}Al NMR. Such 4-coordinate species may be more effective than their 6-coordinate counterpart in the Al insertion reaction because of its smaller size, hence higher intracrystalline diffusivity. Four-coordinate species may also have some steric advantage in their initial interaction with framework defect sites.

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Folded and Extended Structures of Homooligopeptides from α,α-Dialkylated Glycines. A Conformational Energy Computation and X-ray Diffraction Study

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Abstract: Conformational energy computations on a derivative and a homodipeptide of α,α-di-*n*-propylglycine were performed. In both cases the N- and C-terminal groups are blocked as acetamido and methylamido moieties, respectively. To analyze the effect of side-chain length, we carried out computations also on *N*-acetyl-α-methyl-α-ethyl-D-glycine methylamide. Literature data on *N*-acetyl-α,α-dimethylglycine methylamide were compared with our results. It was found that the minimum energy conformations for the α,α-di-*n*-propylglycine derivative and homodipeptide correspond to the fully extended conformation. A comparison with the derivatives of α-methyl-α-ethyl-D-glycine and α,α-dimethylglycine indicates that the preference from a folded to a fully extended conformation increases with increasing bulkiness of the C^{α}-substituents. The results of the theoretical analysis of the conformation of the derivative and homodipeptide of α,α-di-*n*-propylglycine are in agreement with their conformational properties in the solid state, determined by X-ray diffraction and also described in this work. In this latter study the N- and C-terminal groups are blocked as trifluoroacetamido and *N',N'*-dibenzylacylhydrazido moieties, respectively.

α,α-Dialkylated glycyl residues have been shown to represent a useful new type of conformational constraint in peptides.[2-4] Through this modification of the α-carbon, information may be obtained about the active conformation of a peptide at the receptor site and biological potency may be increased, possibly, at least in part, because of enhanced resistance to enzyme degradation. The replacement of the two α-hydrogens in glycyl derivatives by alkyl moieties has profound structural consequences. In particular, chirality may still be absent, as in α,α-dimethylglycine (also called α-aminoisobutyric acid, Aib), α,α-diethylglycine (Deg), α,α-di-*n*-propylglycine (Dpg), or may be introduced, as in α-methyl-α-ethylglycine (also called isovaline, Iva), depending on the nature of the replacements.

Among the α,α-dialkylated glycyl residues the only systematic conformational studies have been those on the Aib residue.[2-11] The inherent interest in Aib-rich peptides results not only from their restricted conformational space but also from their tendency to adopt ϕ,ψ sets of values typical of the 3_{10}- and α-helices. In addition, Aib residues characterize a family of naturally occurring membrane-active antibiotics, the peptaibol antibiotics.[4,9,10,11] Some of these antibiotics contain also a limited number of R-Iva residues (an R- or D-Iva residue is an L-alanine in which the α-hydrogen is replaced by an ethyl substituent).[12]

The structural modifications induced by substitution of protein amino acids by other α,α-dialkylated glycyl residues in bioactive

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