J|A|C|S
ARTICLES

Chemistry of the Silica Surface: Liquid−Solid Reactions of Silica Gel with Trimethylaluminum

Jianhua Li, Joseph A. DiVerdi, and Gary E. Maciel*

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Received July 30, 2006; E-mail: gary.maciel@colostate.edu

Abstract: The reaction of trimethylaluminum and dry, high-surface-area (500 m^2/g) silica gel in a mixed slurry was studied using multinuclear, solid−state NMR spectroscopy. The products of the initial reaction were characterized, and their progress through subsequent washing with diethyl ether and reactions with measured amounts of water was followed. The quantitative distribution of different chemical forms of carbon deposited on the silica surface by the initial reaction was measured. The products of the initial reaction are dominated by methyl species of the types $Al(CH_3)_n$ (with Si−O−Al linkages), $Si{-}O{-}CH_3$, and $(Si{-}O)_{4-n}$-$Si(CH_3)_n$; aluminum is seen to exist predominantly as a five-coordinate species. Subsequent treatment with diethyl ether fails to remove any surface species, but instead the ether becomes strongly associated with the surface and highly resistant to removal. Stepwise additions of water hydrolyze the $Al{-}CH_3$ and $Si{-}O{-}CH_3$ moieties, leading to conversion of five-coordinate aluminum to four- and six-coordinate aluminum, and affect the partial release of the surface-associated diethyl ether; $Si{-}CH_3$ moieties remain. The effect of aromatic and saturated solvents on the initial reaction was examined and found to cause a small but significant change in the distribution of products. Structures of aluminum-centered species on the silica surface consistent with the spectroscopic data are proposed.

Introduction

Derivatization and modification of the silica surface are enormously important in both pure and applied chemistry.[1−4] In addition to the popular silylation reactions that facilitate the formation of useful composites[5] and generate a variety of useful "phases" for chromatography,[1−4,6−8] silica-surface modification is extremely useful for "immobilizing" moieties with catalytic activity.[9,10]

Trimethylaluminum, $Al(CH_3)_3$, is useful for generating aluminum-based layers that subsequently can be converted to aluminum oxide[11] or aluminum nitride[12] layers. Trimethylaluminum also serves as a prototype or precursor to important cocatalysts in olefin polymerization.[13−25]

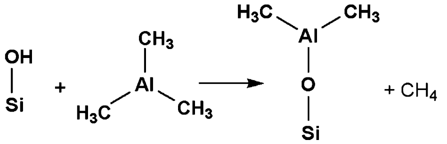
Previous work on the reaction between trimethylaluminum and dry silica gel has focused mainly on reactions occurring using gas-phase reagents (i.e., at a gas/solid interface),[26−43] with

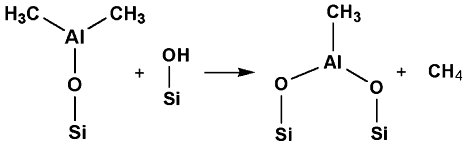
---

(1) Leyden, D. E. In *Silanes, Surfaces and Interfaces*, Silanes, Surfaces, and Interfaces Symposium, Snowmass, Colorado, 1985; Leyden, D. E., Ed.; Gordon and Breach: New York, 1986; p 599.
(2) Leyden, D. E.; Collins, W. T. In *Chemically Modified Surfaces in Science and Industry*, Chemically Modified Surfaces Symposium, Fort Collins, Colorado, 1987; Leyden, D. E.; Collins, W. T., Eds.; Gordon and Breach: New York, 1988; p 686.
(3) Scott, R. P. W. *Silica Gel and Bonded Phases: Their Production, Properties, and Use in LC*; Wiley: New York, 1993; Vol. viii, p 1.
(4) Scott, R. P. W. *Silica Gel and Bonded Phases: Their Production, Properties, and Use in LC*; Wiley: New York, 1993; Vol. viii, p 23.
(5) Hoh, K. P.; Ishida, H.; Koenig, J. L. *Polym. Compos.* **1990**, *11*, 121.
(6) Miller, M. L.; Linton, R. W.; Maciel, G. E.; Hawkins, B. L. *J. Chromatogr.* **1985**, *319*, 9.
(7) Rudzinski, W. E.; Montgomery, T. L.; Frye, J. S.; Hawkins, B. L.; Maciel, G. E. *J. Catal.* **1986**, *98*, 444.
(8) Rudzinski, W. E.; Montgomery, T. L.; Frye, J. S.; Hawkins, B. L.; Maciel, G. E. *J. Chromatogr.* **1985**, *323*, 281.
(9) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.
(10) Fink, G.; Steinmetz, B.; Zechlin, J.; Przybyla, C.; Tesche, B. *Chem. Rev.* **2000**, *100*, 1377.
(11) Higashi, G. S.; Fleming, C. G. *Appl. Phys. Lett.* **1989**, *55*, 1963.
(12) Bartram, M. E.; Michalske, T. A.; Rogers, J. W., Jr.; Mayer, T. M. *Chem. Mater.* **1991**, *3*, 953.
(13) Boleslawski, M.; Serwatowski, J. *J. Organomet. Chem.* **1983**, *255*, 269.
(14) Pasynkiewicz, S. *Polyhedron* **1990**, *9*, 429.
(15) Siedle, A. R.; Newmark, R. A.; Lamanna, W. M.; Schroepfer, J. N. *Polyhedron* **1990**, *9*, 301.
(16) Chien, J. C. W.; He, D. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1603.
(17) Korneev, N. N.; Khrapova, I. M.; Polonskii, A. V.; Ivanova, N. I.; Kisin, A. V.; Kolesov, V. S. *Russ. Chem. Bull.* **1993**, 1453.
(18) Barron, A. R. *Macromol. Symp.* **1995**, *97*, 15.
(19) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 6465.
(20) Katayama, H.; Shiraishi, H.; Hino, T.; Ogane, T.; Imai, A. *Macromol. Symp.* **1995**, *97*, 109.
(21) Lee, D.-h.; Shin, S.-y.; Lee, D.-h. *Macromol. Symp.* **1995**, *97*, 195.
(22) Sinn, H. J. *Macromol. Symp.* **1995**, *97*, 27.
(23) Winter, H.; Schnuchel, W.; Sinn, H. *Macromol. Symp.* **1995**, *97*, 119.
(24) Reddy, S. S.; Radhakrishnan, K.; Sivaram, S. *Polym. Bull. (Berlin)* **1996**, *36*, 165.
(25) Fusco, R.; Longo, L.; Masi, F.; Garbassi, F. *Macromol.* **1997**, *30*, 7673.
(26) Low, M. J. D.; Severdia, A. G.; Chan, J. *J. Catal.* **1981**, *69*, 384.
(27) Murray, J.; Sharp, M. J.; Hockey, J. A. *J. Catal.* **1970**, *18*, 52.
(28) Peglar, R. J.; Murray, J.; Hambleton, F. H.; Sharp, M. J.; Parker, A. J.; Hockey, J. A. *J. Chem. Soc. A* **1970**, 2170.
(29) Murray, J.; Jones, P.; Hockey, J. A. *Trans. Faraday Soc.* **1971**, *67*, 848.
(30) Peglar, R. J.; Hambleton, F. H.; Hockey, J. A. *J. Catal.* **1971**, *20*, 309.
(31) Yates, D. J. C.; Dembinski, G. W.; Kroll, W. R.; Elliott, J. J. *J. Phys. Chem.* **1969**, *73*, 911.
(32) Kinney, J. B.; Staley, R. H. *J. Phys. Chem.* **1983**, *87*, 3735.
(33) Bartram, M. E.; Michalske, T. A.; Rogers, J. W., Jr. *J. Phys. Chem.* **1991**, *95*, 4453.
(34) Jun, S.; Ryoo, R. *J. Catal.* **2000**, *195*, 237.
(35) Anwander, R.; Palm, C.; Groeger, O.; Engelhardt, G. *Organometallics* **1998**, *17*, 2027.
(36) Uusitalo, A. M.; Pakkanen, T. T.; Kroger-Laukkanen, M.; Niinisto, L.; Hakala, K.; Paavola, S.; Lofgren, B. *J. Mol. Catal. A* **2000**, *160*, 343.
(37) Puurunen, R. L.; Root, A.; Sarv, P.; Haukka, S.; Iiskola, E. I.; Lindblad, M.; Krause, A. O. I. *Appl. Surf. Sci.* **2000**, *165*, 193.
(38) Puurunen, R. L.; Root, A.; Haukka, S.; Iiskola, E. I.; Lindblad, M.; Krause, A. O. I. *J. Phys. Chem. B* **2000**, *104*, 6599.
(39) Lakomaa, E. L.; Root, A.; Suntola, T. *Appl. Surf. Sci.* **1996**, *107*, 107.

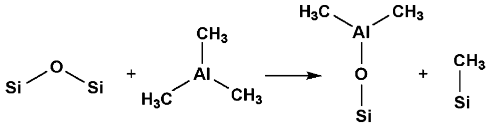
10.1021/ja065497c CCC: $33.50 © 2006 American Chemical Society

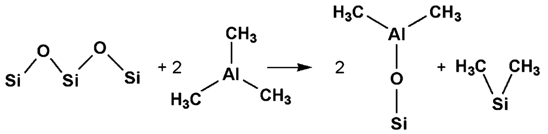
infrared spectroscopy being the most common spectroscopic method used. This previous research includes some solid-state NMR work in one study from this laboratory.[43] On the basis of the prior research, a number of reactions have been proposed to account for the various products. Equations 1 through 6 represent a consensus of chemical understanding *embodied in the prior work*. Surface silanols (SiOH) react with trimethylaluminum to produce Si−O−Al with attached $Al(CH_3)_n$ surface linkages and to generate methane (eqs 1 and 2).

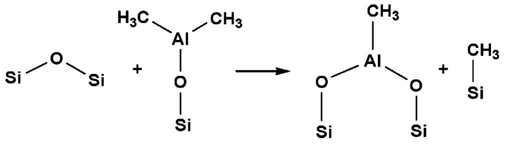

(1)


(2)

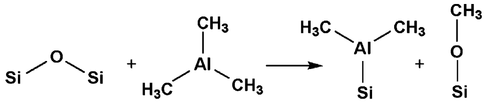
Correspondingly, surface siloxanes moieties (Si−O−Si) react to produce Si−O−Al and $Si(CH_3)_n$ surface structures without the generation of methane (eqs 3 through 5).

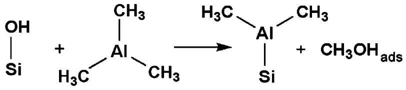

(3)

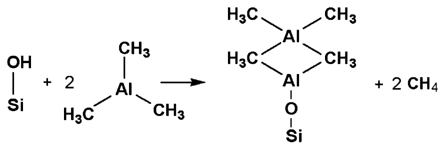

(4)

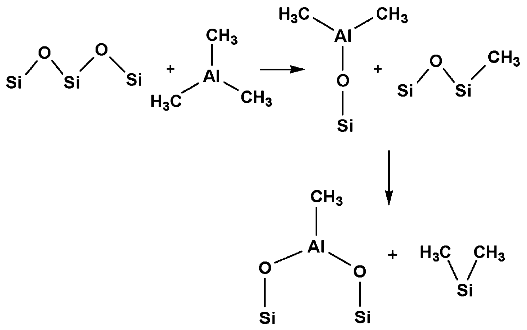

(5)

The formation of $SiOCH_3$ moieties has also been suggested (eqs 6 and 7) as well as other kinds of transformations (eqs 8 and 9).


(6)


(7)


(8)


(9)

In all but one of the above chemical equations from the literature, the surface-attached aluminum is nominally shown as three-coordinate. However, the ^{27}Al NMR results given below show the predominance of four-, five-, and six-coordinate aluminum in the products of the reaction between trimethylaluminum and silica.

Just as there has been a wide range of experimental conditions employed in the trimethylaluminum/silica reactions studied (methods of silica preparation and pretreatment, trimethylaluminum/silica reaction temperature and period, the absence or presence and identity of a liquid medium), a variety of often conflicting results have been obtained. Different conclusions have been reached regarding the occurrence or absence of Si−O−CH_3 and Si−O−$Al(CH_3)_n$ groups in the product, on the relative reactivity orders of hydrogen-bonded SiOH groups ($SiOH_h$), non-hydrogen-bonded SiOH groups ($SiOH_i$, for isolated), and siloxane moieties (Si−O−Si) at the silica surface and on the relative populations of Al−CH_3 and Si−CH_3 moieties formed at the surface.

The present work re-examines and extends the prior results in the following important ways: (1) the products of the initial reaction between trimethylaluminum and silica gel are tentatively identified (structures proposed) and their distribution is determined *quantitatively* by NMR; (2) the important reaction steps intermediate between the initial reaction and final hydrolysis are examined in detail; and (3) the chemical structures of the carbon, silicon, and aluminum centers are directly observed at each reaction step, and their transformations are followed.

Experimental Section

Materials. Silica gel (S679, Fisher Scientific, Lot 000232), with a particle diameter range of 100−200 mesh was dried by evacuation at 5×10^{-3} Torr and 150 °C for 24 h.[44] Trimethylaluminum (97%, Aldrich) was used as received. (**CAUTION**: trimethylaluminum is a pyrophoric and moisture-sensitive material.)[45] Toluene and cyclohexane (Fisher Scientific) were refluxed over sodium metal for 12 h. Diethyl ether (anhydrous, Fisher Scientific) was stored over 4A molecular sieves. Hexamethylbenzene (HMB, Aldrich), tetrakis(trimethylsilyl)silane (TTMSS, Fluka), aluminum potassium sulfate (alum, J.T. Baker), and polydimethylsiloxane (PDMS, 2.5 MDa MW, Petrarch Systems) were used as received.

---

(40) Kleisner, R. J.; Koeck, B. H.; Phillips, M. R.; Wieland, J. A.; Gutow, J. H.; Boiadjiev, V.; Tysoe, W. T. *Thin Solid Films* **2001**, *381*, 10.

(41) Boiadjiev, V.; Blumenfeld, A.; Gutow, J.; Tysoe, W. T. *Chem. Mater.* **2000**, *12*, 2604.

(42) Yamamoto, K.; Tatsumi, T. *Chem. Lett.* **2000**, 624.

(43) Tao, T.; Maciel, G. E. *J. Am. Chem. Soc.* **2000**, *122*, 3118.

(44) Chuang, I. S.; Maciel, G. E. *J. Phys. Chem. B* **1997**, *101*, 3052.

(45) The spontaneous flammability of trimethylaluminum in air demands special precautions. All transfers, storage, and reactions must be performed under an anhydrous atmosphere of pure nitrogen or argon. See the detailed discussion in Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds. *Comprehensive Organometallic Chemistry: The Synthesis, Reactions and Structures of Organometallic Compounds*; Pergamon Press: New York, 1982; Vol. 1, p 579.

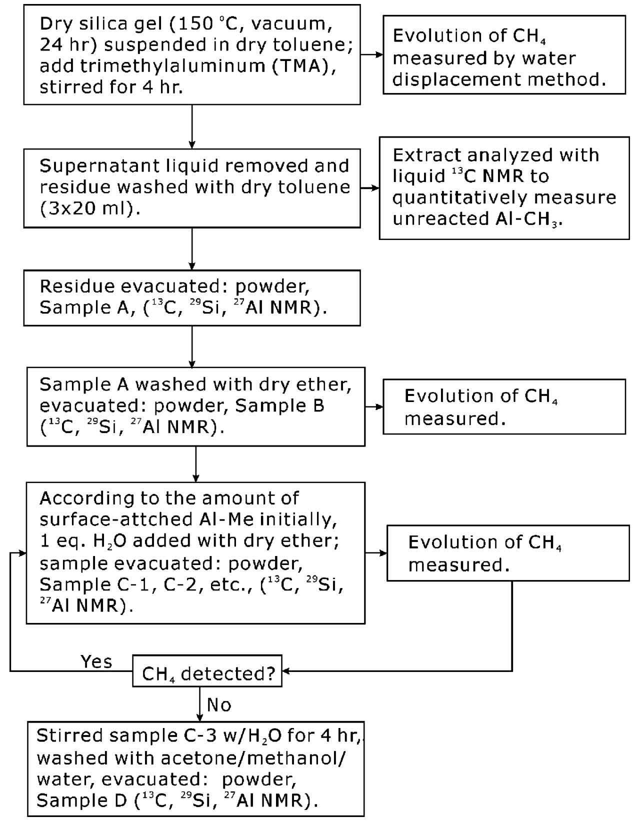


Figure 1. Scheme for the reaction between trimethylaluminum and dry silica.

Surface Properties. Values of the BET surface area, pore volume, and pore size (width) were determined by Micrometrics Analytical Services (Norcross, GA).

Sample Preparation. Trimethylaluminum (∼1.1-fold molar ratio of trimethylaluminum relative to total silica surface silanols) was added slowly to a suspension of dry silica gel in either dry toluene or cyclohexane, in a flask cooled by an ice-water bath, with the evolution of heat and gas. Gaseous helium was used to protect the reaction from oxygen and moisture in the air. The mixture was stirred over the ice-water bath for 4 h. After removal of the solution layer by a syringe, the solid was washed three times with the same solvent, and the washings were pooled for liquid-state ^{13}C NMR analysis. The solid was dried by evacuation at 5×10^{-3} Torr and 20 °C for 4 h, and a portion was removed for solid-state NMR analysis (representing the initial reaction product (sample A)).

Subsequent Reaction Steps (see Figure 1). The initial reaction product was treated in turn as follows: washed with diethyl ether and dried by evacuation at 5×10^{-3} Torr and 20 °C for at least 12 h (sample B); treated three times each with one molar equivalent of water in diethyl ether (samples C-1, C-2, C-3) and dried by evacuation at 5×10^{-3} Torr and 20 °C for at least 12 h (with no further methane evolution in the C-3 step); treated with excess water and dried by evacuation at 5×10^{-3} Torr and 20 °C for at least 12 h (sample D). The evolution of gaseous methane was monitored at each step by the use of a cryogenic trap and subsequent return to room temperature with measurement of volumetric displacement of water, and portions of the dried solids were reserved for solid-state NMR analysis. (Additional experimental details are provided in the Supporting Information.)

NMR Spectroscopy. Solid-state ^{13}C, ^{29}Si, and ^{1}H NMR spectra were obtained with magic-angle spinning (MAS), using a CMX-II type spectrometer (Otsuka Electronics, Fort Collins, CO) operating at 8.46 and 4.7 T for ^{13}C and ^{29}Si, respectively. Samples for ^{13}C and ^{29}Si spectroscopy were contained in modified 9.5 mm diameter PENCIL-II, zirconia MAS rotors equipped with six rubber O-rings, three on each end, to minimize exposure to air. Samples for ^{1}H spectroscopy were contained in 4.0 mm diameter PENCIL-II, zirconia MAS rotors with standard plastic-to-ceramic closures. Solid-state ^{27}Al NMR spectra were obtained using a CMX-Infinity type spectrometer operating at 14.1 T (600.1 MHz for ^{1}H, 156.4 MHz for ^{27}Al); samples were contained in 4.0 mm diameter PENCIL-II, zirconia MAS rotors with standard plastic-to-ceramic closures. ^{13}C and ^{29}Si NMR spectra were obtained using cross polarization[46] (CP) to develop the initial magnetization, while ^{1}H and ^{27}Al NMR spectra were obtained using direct polarization (DP). (Additional experimental details are provided in the Supporting Information.)

Results

Surface Properties. Values obtained for the (BET) surface area, pore volume, and average pore size of the dry silica gel were 500 m^2/g, 0.40 cm^3/g, and 3.19 nm, respectively. Corresponding values for the initial reaction product were 211 m^2/g, 0.19 cm^3/g, and 3.38 nm, respectively.

The ^{1}H MAS NMR spectrum of the dry silica gel (see Supporting Information) and the BET surface area yield an assay of 5.3 mmol OH/g. This corresponds to 6.2 OH/nm^2 or 3.2×10^{21} OH/g. ^{29}Si NMR measurements yield a silanol concentration of 5.2 mmol OH/g (vide infra).

NMR Spectroscopy. Multinuclear solid-state NMR, using ^{27}Al, ^{29}Si and ^{13}C, was applied to provide structural information on the species present on the silica gel surface after it was modified by trimethylaluminum from a toluene or cyclohexane medium. All NMR data presented in this work utilized MAS to obtain isotropic chemical shift spectra. In the case of ^{13}C and ^{29}Si, cross-polarization from protons (^{1}H → ^{13}C or ^{1}H → ^{29}Si) was used to develop observable magnetization, which favors nuclei closer to protons in the sample, although there is some experimental control over the selectivity. In the case of ^{1}H and ^{27}Al, direct-polarization (using a single $\pi/2$ or $\pi/12$ excitation pulse, respectively) was used to develop observable magnetization and excite all corresponding nuclei present in the sample regardless of their location (e.g., surface or buried). Figure 2 shows the ^{27}Al, ^{29}Si, and ^{13}C MAS spectra of the products of the initial reaction and subsequent reaction steps for the toluene medium. Corresponding results for the cyclohexane case can be found in the Supporting Information.

Products of the Initial Reaction. The bottom right-hand panel of Figure 2 shows the ^{13}C CP/MAS spectrum of the initial reaction product. Two sets of signals are observed in this spectrum: a group of methoxy carbon resonances from 57 to 47 ppm and a second group corresponding to various methyl carbons from 1 to −13 ppm. These groups of resonances are heavily overlapped, and the individual signals were isolated by manually guided spectral simulation. Two methoxy peaks were isolated at 49 and 54 ppm and assigned to $Si{-}O{-}CH_3$ and $Si(OCH_3)_2$, respectively.[33,35−39,42] Four methyl peaks were isolated at 0, −3, −7, and −12 ppm and assigned to $Si(CH_3)_3$, $Si(CH_3)_2$, $SiCH_3$, and $Al(CH_3)_n$, respectively.[33,35−39,42]

Two spinning sidebands, at 27 and −49 ppm, arise from the peak at −12 ppm and a single sideband at 84 ppm arises from the peak at 49 ppm. The intensities of the sidebands relative to that of the corresponding central peak are related to the effective chemical shift anisotropy (CSA) of the relevant nucleus.[47] In

---

(46) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.
(47) Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021.

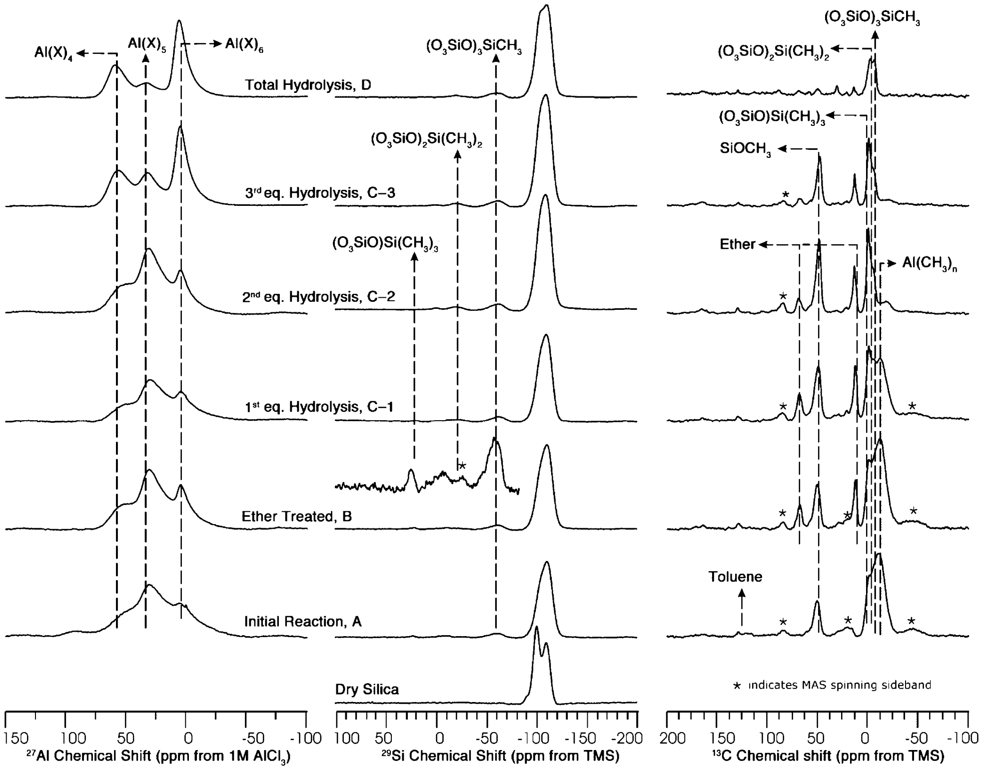


Figure 2. Composite of ^{27}Al, ^{29}Si, and ^{13}C NMR MAS spectra of samples from the trimethylaluminum/silica reaction in toluene.

this case, where the number of sidebands is few and their individual intensities are weak, it is possible to place only very broad constraints on an estimated anisotropy. The sideband intensities observed at this resolution are consistent with an axially symmetric anisotropy of roughly 50 ppm. Weak signals are also present in this spectrum at 21 and 130 ppm, which are due to the methyl group and aromatic carbons of residual toluene, the reaction solvent.

The ^{29}Si CP/MAS spectra of untreated silica gel and the initial reaction product are shown in the bottom center panel of Figure 2. The unreacted silica gel spectrum contains three partially resolved signals at −89, −100, and −109 ppm, which are assigned to surface moieties of the types $(HO)_2\mathbf{Si}(SiO)_2$ (Q_2), $HO\mathbf{Si}(SiO)_3$ (Q_3), and $\mathbf{Si}O_4$ (Q_4), respectively (where the bold symbol refers to the surface silicon on which the chemical shift is in focus).[48] The spectrum of the initial reaction product displays a complex, broad signal in the same region. Deconvolution of this complex signal is consistent with Q_4 at −109 ppm together with a small signal at −104 ppm of no more than 5% of the total ^{29}Si intensity and assigned to $(SiO)_3\mathbf{Si}{-}O{-}Al$. The Q_2 and Q_3 contributions to this region are negligible.

The change in chemical shift experienced by a ^{29}Si atom upon conversion of a single hydroxyl group to an oxo-aluminum linkage is not well defined in the current literature but can be estimated to be −104 ppm from additivity relationships based on available information (see Supporting Information). The extent to which this substitution has occurred can be quantified by deconvolution of the ^{29}Si spectrum into its component parts; such deconvolution indicates that a maximum of 5% of the total ^{29}Si intensity is due to residual Q_3 silanols (see Supporting Information).

Additional, weaker signals are present at roughly −60, −8, and 25 ppm, which are assigned to $({-}O_3SiO)_3\mathbf{Si}CH_3$, $({-}O_3SiO)_2\mathbf{Si}(CH_3)_2$, and, tentatively, $({-}O_3SiO)\mathbf{Si}(CH_3)_3$, respectively.[35−39] The single silicon species with only one methyl group attached is the most intense of this set, indicating its predominant production in the initial reaction. The weak intensities of these peaks in the ^{13}C spectrum and their overlap with the more abundant $Al(CH_3)_n$ signal limit their utility in chemical interpretations.

The ^{27}Al MAS NMR spectrum of the initial reaction product is displayed in the lower left-hand panel of Figure 2. Three incompletely resolved signals are present at 54, 32, and 6 ppm, which are assigned to four-, five-, and six-coordinate aluminum species, respectively.[35,37,49−51] On the basis of the relative intensities of the signals, the major aluminum structure on the surface is five-coordinate, with the four- and six-coordinate aluminum species being present in smaller amounts. Additional ^{27}Al NMR measurements indicate that 2.0 mmol total aluminum atoms/g silica are attached on the surface in the initial reaction product (see Supporting Information).

Quantitation of Initial Reaction Products and Effect of Reaction Solvent. Several repetitions of the initial reaction were performed, with either toluene or cyclohexane as a reaction solvent, to determine the extent of reaction and to prepare for analysis of the subsequent reaction steps. Table 1 shows the results of these measurements. Trimethylaluminum was added in excess on a molar basis relative to the total surface silanols to arrange for the latter to serve as the limiting reactant so that

---

(48) Maciel, G. E.; Sindorf, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 7606.

(49) Okuno, M.; Shimada, Y.; Schmuecker, M.; Schneider, H.; Hoffbauer, W.; Jansen, M. *J. Non-Cryst. Solids* **1997**, *210*, 41.

(50) Nyfeler, D.; Armbruster, T. *Am. Mineral.* **1998**, *83*, 119.

(51) Gore, K. U.; Abraham, A.; Hegde, S. G.; Kumar, R.; Amoureux, J.-P.; Ganapathy, S. *J. Phys. Chem. B* **2002**, *106*, 6115.

Table 1. Summary of Initial Reaction Stoichiometry for Both Solvents[a]

	toluene solvent	cyclohexane solvent
surface silanols in silica reactant (as Si−OH)[b]	63.3 ± 4.1 mmol	64.2 ± 3.1 mmol
trimethylaluminum reactant (as CH_3)	223 ± 16 mmol	222 ± 16 mmol
methane product (as CH_4)	36.4 ± 2.7 mmol	37.5 ± 3.0 mmol
unreacted Al−CH_3[c]	176 ± 23 mmol	102 ± 22 mmol
silica surface methyl product[d]	38.0 ± 4.1 mmol	55.8 ± 2.4 mmol
total methyl and methane recovered	248 ± 19 mmol	196 ± 24 mmol
total	108 ± 4%	88 ± 5%

[a] Results of six replicate reactions for each solvent. Uncertainties are estimated standard deviations. [b] The sample sizes of each reaction run were slightly different, which is why the average number of surface silanols in the silica reactant differ for the two solvents. [c] Measured in the supernatant liquid, including the initial solvent wash. [d] All methyl groups attached, in any way, to the surface in the initial reaction products.

bridging of surface silanols by a single trimethylaluminum would not limit the reaction.

From the quantitative ^{13}C CP/MAS spin counting results (see Supporting Information) it is seen that, at the surface, the ratio of the number of methyl groups bound directly to aluminum to the number of methyl groups bound directly to silicon is about 4.5. This is a considerably larger number than previously reported for the trimethylaluminum/silica reaction.[26,27,33,35] The atomic C/Al ratio (about 1.6) is closer to values previously reported.[26,29,33,35] The methyl groups are well accounted for with toluene as a solvent. On the basis of the methane evolution, approximately 60% of the surface silanols have reacted to generate CH_4. In cyclohexane, roughly 88% of the surface silanols have reacted, but roughly 12% of the methyl groups are incompletely unaccounted for. On the basis of the integrated ^{13}C NMR intensities of the regions shown in Figure 2, roughly 60% of the surface-attached methyl groups detected are Al$(CH_3)_n$ and about 12% belong to the Si−O−CH_3 moiety.

Effects of Diethyl Ether on Initial Reaction Products. For the purposes of examining the effect of a solvent more polar than toluene on the initial reaction product, for example, to at least partially dissolve a weakly physisorbed surface complex, the initial $Al(CH_3)_3$/silica product was washed with diethyl ether. The ^{13}C CP/MAS NMR spectrum of the anhydrous diethyl ether-washed and dried initial reaction products is shown in the lower right panel of Figure 2. Some redistribution of the intensity of the various signals is observed, for example, for the Si−O−CH_3 peak, which increases, and for the intensity of the $Al(CH_3)_n$ region, which decreases, although this trend is not readily apparent in the particular pair of spectra displayed in this figure (more apparent in some of the other replicate experiments and in the spin-counting data). This small apparent change suggests that, during the diethyl ether treatment, surface $Al(CH_3)_n$ is partially converted to Si−O−CH_3, because there is no methyl reagent added to the system; the only source is methyl groups already present on the surface from the initial reaction. Additionally, the two signals from diethyl ether (methylene and methyl at 69 and 14 ppm, respectively) appear in the spectrum. It is notable that the structural units of diethyl ether remain on the surface even after exposing the sample to high vacuum at room temperature, a treatment that is highly effective in removing diethyl ether from the unmodified silica gel surface.

No significant changes in the ^{27}Al and ^{29}Si NMR spectra nor CH_4 evolution were observed in this ether treatment step (see Supporting Information).

Limited Hydrolysis. In our earlier study of reactions between silica gel and methyl−metal compounds, including $Al(CH_3)_3$,[43] the initial reaction products were treated with excess H_2O prior to spectroscopic observation. For the purpose of examining the effect of water on Al−CH_3 in greater detail, treatment with H_2O was studied in stepwise treatments (1 equiv of H_2O at a time). The center right panels of Figure 2 show the ^{13}C CP/MAS NMR spectra at each stage of limited hydrolysis. As hydrolysis proceeds, the $Al(CH_3)_n$ signal is significantly reduced in intensity at each step. During the limited hydrolysis, the other signals, corresponding to Si−O−CH_3, $Si(CH_3)_3$, $Si(CH_3)_2$, and $SiCH_3$, at 49, 0, −3, and −7 ppm, respectively, are essentially unaffected, indicating that the limited water added to the surface has targeted only the $Al(CH_3)_n$ species. The signals corresponding to diethyl ether units have also decreased over these stages. The ^{29}Si CP/MAS spectra corresponding to each of these steps, shown in the central panels of Figure 2, are essentially unchanged, indicating that none of the silicon species are affected. The center left panels of Figure 2 show the ^{27}Al MAS spectra at the corresponding stages of limited hydrolysis. With stepwise addition of water, which reacts with the $Al(CH_3)_n$ moieties, the intensity of the five-coordinate aluminum species at 32 ppm decreases, while intensity associated with four- and six-coordinate species, at 54 and 6 ppm, respectively, increases. In sum, the ^{13}C signals due to $Al(CH_3)_n$ and $(CH_3CH_2)_2O$ and the ^{27}Al intensity of five-coordinate aluminum all decrease with increasing hydrolysis, suggesting an association between these types of species.

No significant changes in the ^{29}Si NMR spectrum were observed at this step (see the central panels of Figure 2).

Exhaustive Hydrolysis. The top panels of Figure 2 show the ^{13}C CP/MAS, ^{29}Si CP/MAS and ^{27}Al MAS NMR spectra of exhaustively hydrolyzed reaction product. At this stage the Si−O−CH_3 and $Si(CH_3)_3$ signals have completely disappeared and the only carbon species left on the surface are $Si(CH_3)_2$ and $SiCH_3$. This configuration corresponds approximately to that observed previously.[43] The diethyl ether peaks have also disappeared at this stage. The $Si(CH_3)_n$ signals remain essentially unchanged during exhaustive hydrolysis, for $n = 1, 2$. The five-coordinate aluminum signal has decreased to a minimum, while the four- and six-coordinate species signals have increased to their maxima.

Dynamics of Methyl Groups on the Silica Surface. Knowledge of relaxation times, T_1^{H}, T_{CH}, and $T_{1\rho}^{\mathrm{H}}$, is necessary for carrying out quantitative analysis in the ^{13}C CP/MAS spin counting of surface methyl moieties. These parameters can also reveal useful information about molecular-level motion. A detailed examination of the relevant relaxation times, T_1^{H}, T_1^{C}, T_{CH}, and $T_{1\rho}^{\mathrm{H}}$, that were measured on some of the samples represented in this work are described in detail elsewhere.[52] Relaxation times from that examination are consistent with a view that (1) on the surface, initially formed Al−CH_3 methyl groups are more rigid than Si−O−CH_3 methyl groups and (2) diethyl ether molecules, introduced during the diethyl ether treatment, interact with surface-attached $Al(CH_3)_n$ species

---

(52) Li, J. M. S. Thesis, Colorado State University, Fort Collins, Colorado, 2006.

and such interactions can be perturbed by toluene in some respects.

The ^{13}C signals of Al(CH$_3$)$_n$ species have a large width (∼12 ppm), compared to the line widths for other species (no greater than ∼4 ppm) shown in the spectra. At a MAS speed of 3.6 kHz, which was used in obtaining the ^{13}C spectra, the Al(CH$_3$)$_n$ signal shows significant spinning sidebands, which indicates that the effective CSA of the Al(CH$_3$)$_n$ resonance is substantial. This spinning sideband behavior indicates that the Al(CH$_3$)$_n$ species are in a motionally restrained environment (otherwise, much of the CSA effect responsible for the spinning sidebands would be motionally averaged); this can be rationalized in terms of a view in which at least some portion of the Al−CH$_3$ moieties interact with (e.g., are bonded to) the surface by more than one linkage. The large CSA behavior, which gives rise to large spinning sidebands, was also observed for the ^{13}C peak at around 49 ppm (see Figure 2), which has the second largest intensity among signals of surface methyl groups.

Discussion

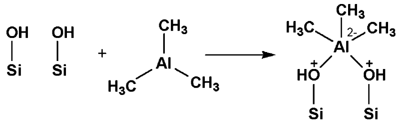
Initial Reaction Products. The experimental results shown above from the present work on the reaction of trimethylaluminum and silica gel in the presence of a solvent (i.e., at a liquid/solid interface) are generally consistent with the picture embodied in eqs 1 through 9. All the ^{13}C and ^{29}Si species expected for the gas/solid reaction (Si−O−Al, Al(CH$_3$)$_n$, Si(CH$_3$)$_n$, Si−O−CH$_3$) are observed in the corresponding NMR spectra of the initial reaction product and are consistent with the concomitant elimination of the surface Si−OH species as they are consumed. The replacement of Si−OH with Si−O−Al linkages is almost but not quite complete, occurring at the 95% level.

Among the methyl moieties formed initially on the silica surface in the trimethylaluminum/silica reaction, Si−O−CH$_3$, Si(CH$_3$)$_n$, and Al(CH$_3$)$_n$, the ^{13}C spin-counting results show that Al(CH$_3$)$_n$ are the most abundant moieties formed. The Al(CH$_3$)$_n$ moieties constitute about 70% of the total amount of surface-attached methyl groups detected by ^{13}C NMR. The amounts of Si−O−CH$_3$, Si(CH$_3$)$_3$, and Si(CH$_3$)$_2$ moieties are approximately equal to each other and together amount to about 30% of the total amount of methyl groups detected on the surface.

The relaxation results indicate that Al(CH$_3$)$_n$ and Si−O−CH$_3$ groups are relatively immobile on the silica surface. More concretely, they lack large amplitude motions on the 10^3 Hz (or faster) time scale. This motional restriction is also signaled by the presence of spinning sidebands of corresponding ^{13}C signals. Any molecular motions faster than the magnitude of the CSA will average the CSA effect toward zero and cause the amplitudes of the sidebands to be attenuated. Conversely, the Si(CH$_3$)$_n$ groups are mobile on this same time scale, as evidenced by the absence of sidebands from their signals. The data presented here are too limited to support a detailed description of the motions at present.

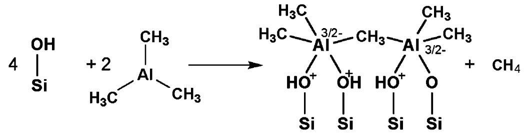
To the extent that chemical reactions of types represented by eqs 6 and 7 occur in the trimethylaluminum/silica system studied here, surface species involving Si−Al bonds would be formed. Although there are no ^{29}Si NMR data available in the literature on structures closely related to the Si−Al species represented in eqs 6 and 7, one can make a tentative estimate of roughly 70−100 ppm for the ^{29}Si chemical shift of such species (see Supporting Information). This is in the range of ^{29}Si chemical shifts of Q$_2$ and Q$_3$ silicons. While there is no evidence of such a peak (or shoulder) in the ^{29}Si NMR spectra of the initial trimethylaluminum/silica reaction products of this study, the potential for serious peak overlap and the difficulty of making a reliable chemical shift prediction preclude a definitive statement on the presence or absence of Si−Al structures at this time.

In eqs 1 through 7, and in most of the relevant literature, all surface-attached Al(CH$_3$)$_n$ moieties are represented with an implied aluminum coordination number of three. However, there is no evidence of three-coordinate aluminum in any of the ^{27}Al NMR spectra of Figure 2. The ^{27}Al NMR spectrum of the initial reaction product indicates that the predominant form of aluminum present on the surface is five-coordinate with a smaller concentration of four- and six-coordinate aluminum species. This suggests the following hypothetical and speculative kinds of surface-attached species and their net generating reactions (where Si−OH represents a surface silanol, which might, in principle, be a single-silanol or geminal-silanol site and, in



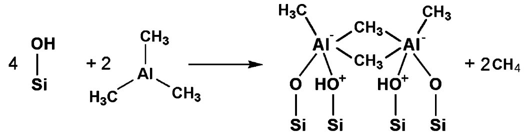
I

(10)



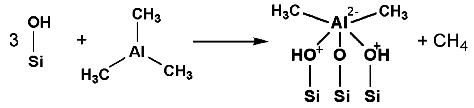
II

(11)



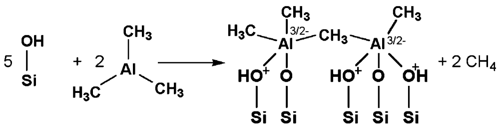
III

(12)



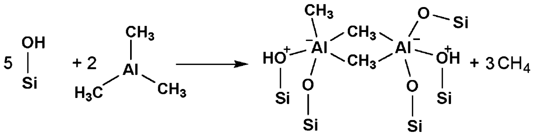
IV

(13)



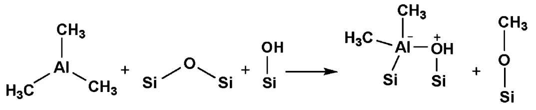
V

(14)



VI

(15)



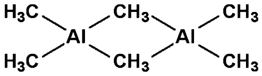
VII

(16)

principle, may or may not be hydrogen-bonded). Analogous hypothetical reactions for the formation of species with four-coordinate and six-coordinate aluminum are given in the Supporting Information.

In some of the hypothetical reactions represented in chemical eqs 11−16, and in others presented in the Supporting Information, the postulated structures in which two or three aluminum atoms are involved in “bridging” between precursor-silanol sites require a substantial concentration of silanols on the unreacted silica surface. The measured value of about 6.2 OH/nm^2 is consistent with a working model of the silica surface in terms of intersecting segments of ⟨100⟩−like and ⟨111⟩−like faces of β-cristobolite (corresponding to geminal- and single-silanol silica sites, respectively). This model is consistent with the total *number* of Si−O−Al linkages, and structurally is readily compatible with *two* such linkages to a *specific* aluminum atom; however, this model must be strained dramatically to accommodate *three* Si−O−Al linkages to a *specific* aluminum atom and would require a model with a substantial degree of patchy clustering of silanols more closely packed in clusters.

In all the above chemical equations (eqs 11 through 16), trimethylaluminum is nominally represented in its monomeric form, recognizing that in fact this substance may exist and function in its dimeric form or some more complex oligimeric form.



Effects of Diethyl Ether on Initial Reaction Products. Surface species of types I through VI would be expected to be substantially reactive toward exposure to potential electron donors, for example, when the surface is treated with diethyl ether. The oxygen atom of diethyl ether is electron rich and would be capable of coordinating with the aluminum atom, even replacing the interaction between the aluminum atom and methyl in a Al−CH$_3$−Al bridge. Hence, a variety of transformations, some of them depicted in the Supporting Information, might be expected to lead to the incorporation of diethyl ether into the surface-attached aluminum species.

$$\mathrm{AlX}_n + (\mathrm{CH_3CH_2})_2\mathrm{O} \rightarrow (\mathrm{CH_3CH_2})_2\mathrm{O{-}AlX}_n \qquad (17)$$

$$\mathrm{X}_n\mathrm{Al{-}CH_3{-}AlX}_m + (\mathrm{CH_3CH_2})_2\mathrm{O} \rightarrow \mathrm{X}_n\mathrm{Al{-}CH_3} + (\mathrm{CH_3CH_2})_2\mathrm{O{-}AlX}_m \qquad (18)$$

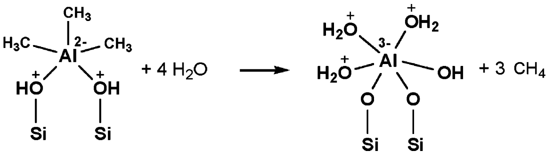
Here no formal charges are shown and X stands for any ligand (e.g., CH$_3$, OH, OH$_2$, not necessarily the same). These kinds of transformations would also explain why a significant amount of diethyl ether is retained after it has been evacuated at 10^{-3} Torr. This observation reinforces the argument that there is a strong interaction between ether molecules and the surface species in the initial reaction product.

Limited Hydrolysis. The amount of surface-associated diethyl ether decreases with the limited sequential hydrolysis treatment but is not completely eliminated, indicating that it interacts strongly with the treated surface. The association or interaction sites are most likely the aluminum of the various Al(CH$_3$)$_n$ species (i.e., an electron-deficient center), a view supported by the coincident decrease in the populations of both diethyl ether and the Al(CH$_3$)$_n$ species with increasing hydrolysis. The Si(CH$_3$)$_n$ and Si−O−CH$_3$ species are unaffected by limited hydrolysis, indicating their (relative) stability to this treatment.

As limited hydrolysis proceeds, the five-coordinate aluminum species begins to disappear from the surface, while four- and six-coordinate aluminum species simultaneously appear. The most likely target of the added water is the highly reactive Al−CH$_3$ moieties. These changes can be understood in terms of reactions in which Al−CH$_3$ moieties are replaced by Al−OH and/or Al−OH$_2$, with the simultaneous generation of CH$_4$.

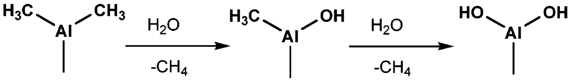
$$\mathrm{Al{-}CH_3} + \mathrm{H_2O} \rightarrow \mathrm{Al{-}OH}\ (\text{or } \mathrm{Al{-}OH_2}) + \mathrm{CH_4} \qquad (19)$$

There are a variety of hypothetical processes and structures that represent transformations where five-coordinate structures of Al(CH$_3$)$_n$ species (I, II, and III) are converted by water to four-coordinate and six-coordinate structures. A representative example is shown in eq 20. Some other possible hydrolysis processes are given in the Supporting Information.

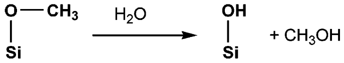


(20)

Exhaustive Hydrolysis. Only in the final hydrolysis step, in which a large excess of water is used, does Si−O−CH$_3$ disappear from the surface, implying that excess water reacts with Si−O−CH$_3$ linkages. The following two reactions are hypothetical summaries that describe chemical changes that could occur with the addition of water (again, with no implied knowledge of the aluminum coordination number, which is indicated here as three only for simplicity):



(21)



(22)

After the final hydrolysis, when peaks at 49 and 0 ppm have disappeared, peaks at −2 and −7 ppm are the only signals left in the ^{13}C NMR spectra, showing that Si−CH$_3$ and Si(CH$_3$)$_2$ species are inert to water, as expected, and are the only methyl groups that still remain from the initial reaction.

Comparing the ^{13}C NMR spectra of sample C-2 (second equiv water treatment) and C-3 (third equiv water treatment) in Figure 2, one sees that the signal intensities due to Si−O−CH$_3$ (49 ppm) and Al(CH$_3$)$_n$ (0 ppm) both dropped as a result of the treatment with a third equiv of water; this implies that, after most of the Al(CH$_3$)$_n$ moieties have reacted with water, the reactivities of Si−O−CH$_3$ and residual AlCH$_3$ toward water may be roughly similar.

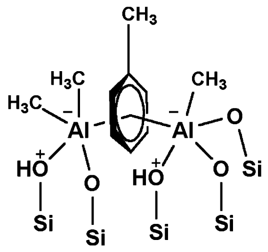
In the ^{27}Al spectrum of sample D, after the final hydrolysis step, it can be seen that four-coordinate and six-coordinate aluminum species become the major aluminum-containing structures on the surface and the five-coordinate aluminum population on the surface has almost disappeared. After final hydrolysis, almost all the Al(CH$_3$)$_n$ species turn into aluminum structures with tetrahedral and octahedral coordination.

Comparing the ^{13}C NMR results (Figure 2) from sample C-1 to those of sample C-3, it can be seen that, along with the corresponding intensity drop for $Al(CH_3)_n$ species, the signal intensity due to diethyl ether units also dropped upon treatment with water. This implies that it is unhydrolyzed $Al(CH_3)_n$ species that have a strong interaction with diethyl ether molecules and help retain them on the surface.

Comparison of Toluene and Cyclohexane Reaction Systems. Table 1 summarizes the tracking of methyl groups in repetitive experiments on the trimethylaluminum/silica reaction in toluene and cyclohexane media. The amounts of CH_4 released in both reaction systems (toluene or cyclohexane) are about the same, which implies that there is no significant difference in the manner of generating CH_4; when an $Al-CH_3$ group encounters a hydroxyl hydrogen, it releases CH_4. But, if comparison is made between the number of methyl groups observed on (somehow attached to) the surface after the initial reaction, the difference observed between solvent systems implies that there are different solvent effects in attaching and/or keeping the methyl groups on the surface.

Since the main reactions occurring on the surface are between trimethylaluminum and surface Si−OH groups, it is convenient, in examining the role of solvent, to consider the ratio of the number of methyl groups attached to the surface to the number of silanols on the unreacted surface. This CH_3(surface)/Si−OH ratio is about 0.6 for the toluene reaction (Table 1) and about 0.9 for the cyclohexane reaction. Thus, in the toluene reaction each surface Si−O group has, on average, about 0.6 CH_3 attached; about 0.9 CH_3 groups, on average, are attached to each surface Si−O group derived from Si−OH in the cyclohexane reaction (see Supporting Information). These numbers imply that, among the five-coordinate aluminum structures introduced above, the following relationships obtain: (1) Structures of types I and II are not major products in the initial reaction for either solvent system; each of these two structures has a CH_3(surface)/Si−OH ratio > 1. (2) Structures of type III and V might be major products in the cyclohexane reaction system, since type III has a CH_3(surface)/Si−OH ratio of 1 and type V has a CH_3(surface)/Si−OH ratio of 0.8. This conclusion is also consistent with relaxation results from ^{13}C NMR,[52,53] which indicate that methyl groups in surface-attached $Al(CH_3)_n$ moieties (with proton T_1 values as large as 7.2 s) are likely to exist as $Al-CH_3-Al$ linkages with adjacent aluminum atoms. (3) Structures of type IV and VI might be major products on the surface in the toluene reaction, since type IV has a CH_3(surface)/Si−OH ratio of 0.67 and type VI has a CH_3(surface)/Si−OH ratio of 0.6.

The following rationalization of these results can be given: From the methyl tracking information in Table 1 it can be seen that the $Al-CH_3$ detected by liquid-state ^{13}C NMR in the cyclohexane system is less than it is for the toluene system. In the trimethylaluminum/silica reaction reported here, trimethylaluminum was added in excess to favor reactions in which only one of the three methyl groups in $Al(CH_3)_3$ reacts with a given surface site. There remains a considerable amount of unreacted $Al-CH_3$ in the reaction solvent, and these unreacted $Al-CH_3$ species remain chemically reactive. The $Al-CH_3$ species in cyclohexane may be more chemically reactive than those in toluene, because of the putative ability of toluene to stabilize unreacted $Al-CH_3$ species through its electron-rich aromatic ring, which the paraffinic cyclohexane lacks. In the cyclohexane system, it is therefore possible that some portion of the unreacted $Al-CH_3$ species remaining in the solvent after the initial reaction might be more reactive than in the toluene case and undergo some chemical changes unrelated to the main reaction before the measurements take place. In the toluene case, in competition with $Al-CH_3-Al$ bridges, some structures of the following type might form:



V'

In addition, knowing that the interaction of toluene with silanols is stronger than that between cyclohexane and silanols,[53] one could argue that the activity of $Al-CH_3$ moieties in solution would be greater in toluene than in cyclohexane. Such differences could translate into measurably different reactivity patterns in the trimethylaluminum/silica gel system.

Summary

The main points made clear in this study are as follows: (1) Aluminum-containing structures in the initial trimethylaluminum/silica gel reaction product are dominated by five-coordinate aluminum, which is largely converted to four- and six-coordinate aluminum by treatment with water. (2) There are three main types of methyl-containing species generated by the trimethylaluminum/silica gel reaction: $Al(CH_3)_n$ (with one or more Si−O−Al linkages to the surface), $Si-OCH_3$, and $(Si-O)_{4-n}Si(CH_3)_n$; only the last of these three types (with $n = 1, 2$) is stable to harsh hydrolysis conditions. (3) The interaction of diethyl ether with the $Al(CH_3)_3$-modified silica surface is far stronger than that with untreated silica, suggesting a strong interaction with $Al(CH_3)_n$ moieties.

Taken together, the whole pattern of all our results on trimethylaluminum/silica chemistry can be interpreted mainly in terms of eqs 10 through 22 (and related material in the Supporting Information), describing the formation and subsequent transformations of a variety of aluminum-centered surface species with aluminum coordination numbers of four, five, and six. It seems likely that discrepancies between the results of the work reported here and prior literature on the trimethylaluminum/silica system, as well as inconsistencies within the prior literature, are due largely to different details of the experimental systems, for example, silica preparation/pretreatment methods and trimethylaluminum−silica reaction conditions.

Acknowledgment. The authors gratefully acknowledge support of this project from the U.S. Department of Energy, Grant DE-FG02-95ER14558.

Supporting Information Available: Additional NMR spectroscopy experimental details; ^{1}H MAS spectra of dry silica gel;

---

(53) Liu, G.; Li, Y.; Jonas, J. *J. Chem. Phys.* **1991**, *95*, 6892.

^{1}H−^{13}C and ^{1}H−^{29}Si CP/MAS spectra of initial reaction product with deconvolution into component species; ^{1}H−^{13}C and ^{1}H−^{29}Si CP/MAS spectra and ^{27}Al MAS spectra of all stages of sample preparation in both toluene and cyclohexane solvents; ^{1}H−^{13}C CP/MAS spectra and methane measurements on replicate initial reactions in both toluene and cyclohexane solvents; proposed five-coordinate aluminum structural framework; the estimation of selected ^{29}Si chemical shift values; additional hypothetical equations for the formation reactions of initial reaction products and their subsequent reactions with diethyl ether and water and additional references. This material is available free of charge via the Internet at http://pubs.acs.org.

JA065497C

SUPPORTING INFORMATION

Chemistry of the Silica Surface: Liquid–Solid Reactions of Silica Gel with Trimethylaluminum

Jianhua Li, Joseph A. DiVerdi, and Gary E. Maciel*

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

E-mail: gary.maciel@colostate.edu

NMR Spectroscopy

^{13}C MAS spectra were obtained with a rotor speed of ~3.5 kHz. Conditions for cross–polarization (CP) experiments[1] were ^{1}H RF field strength of 45.5 kHz for CP contact and decoupling, ^{13}C RF field strength adjusted for maximal signal on a reference sample of solid HMB, a contact time of 5.0 ms and a recovery time of 3.0 s. Typically, 10000 transients were accumulated. A Lorentzian line broadening of 90 Hz was applied prior to Fourier transformation. ^{13}C spectra were externally referenced to liquid tetramethylsilane (TMS, 0 ppm) based on substitution of the secondary reference solid of HMB (16.9 and 132.3 ppm).

^{29}Si NMR spectra[2-7] were obtained with a rotor speed of 3.5 kHz. Conditions for cross polarization (CP) experiments were ^{1}H RF field strength of 39.2 and 38.5 kHz for contact and decoupling, respectively, ^{29}Si RF field strength adjusted for maximal signal on a reference sample of solid untreated silica gel, a contact time of 5.0 ms and a recovery time of 2.0 s. Typically, 10000 transients were accumulated. A Lorentzian line broadening of 50 Hz was applied prior to Fourier transformation. ^{29}Si spectra were externally referenced to liquid TMS (0 ppm), based on substitution of the secondary reference solid of TTMSS (–8.1 and –134.3 ppm).

^{27}Al NMR spectra were obtained with a rotor speed of 16.5 kHz. Conditions for direct polarization (DP) experiments were ^{27}Al RF field strength of 95 kHz set using a reference sample of solid alum, and a recovery time of 0.5 s. Typically, 2000 transients were accumulated using a 15° excitation pulse length.[8, 9] A Lorentzian line broadening of 40 Hz was applied prior to Fourier transformation. ^{27}Al spectra were externally referenced to a 1 M $AlCl_3$ aqueous solution (0 ppm), based on substitution of the secondary reference of solid alum (0.2 ppm).

^1H NMR spectra were obtained with a rotor speed of 12.5 kHz. Conditions for DP experiments were ^1H RF field strength of 62.5 kHz using a reference sample of solid PDMS. Typically, 64 transients were accumulated using a 90° excitation pulse with a recovery time of 30 s.[10, 11] A Lorentzian line broadening of 20 Hz was applied prior to Fourier transformation. ^1H spectra were externally referenced to liquid TMS (0 ppm), based on substitution of the secondary reference of solid PDMS (0 ppm).

Deconvolution of Spectra into Component Parts

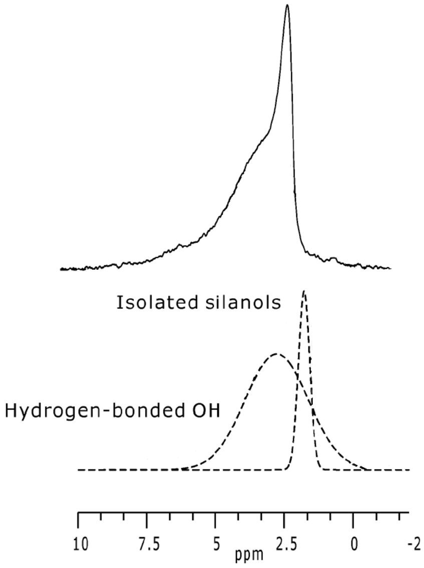


Figure SI-1. ^1H MAS spectra of silica gel dried by evacuation at $5x10^{-3}$ Torr and 150 oC for 24 h and deconvolution into component species.

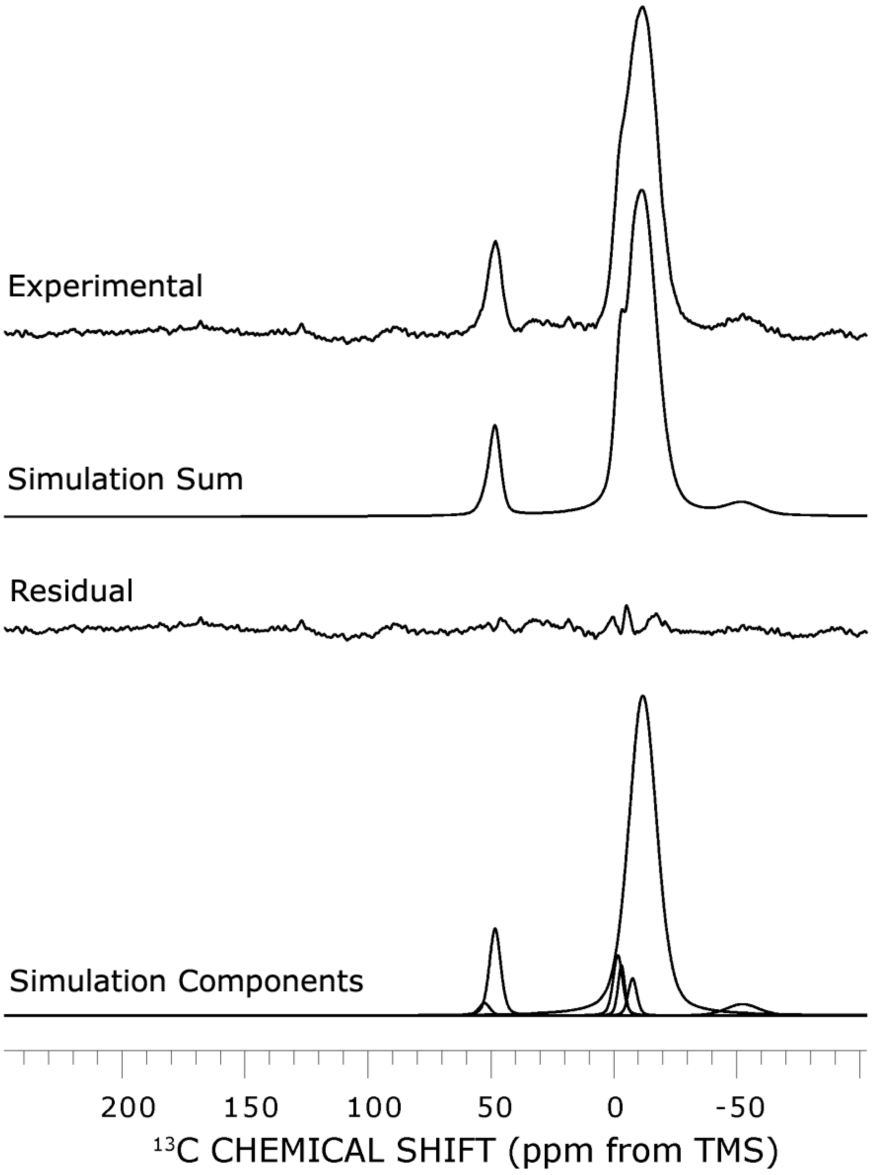


Figure SI-2. ^{3}C NMR spectra of the initial reaction product prepared in toluene: (A) raw experimental spectrum; (B) simulated individual components spectra; (C) simulated spectrum created by summing individual components; (D) Difference spectrum of raw experimental and synthetic spectra.

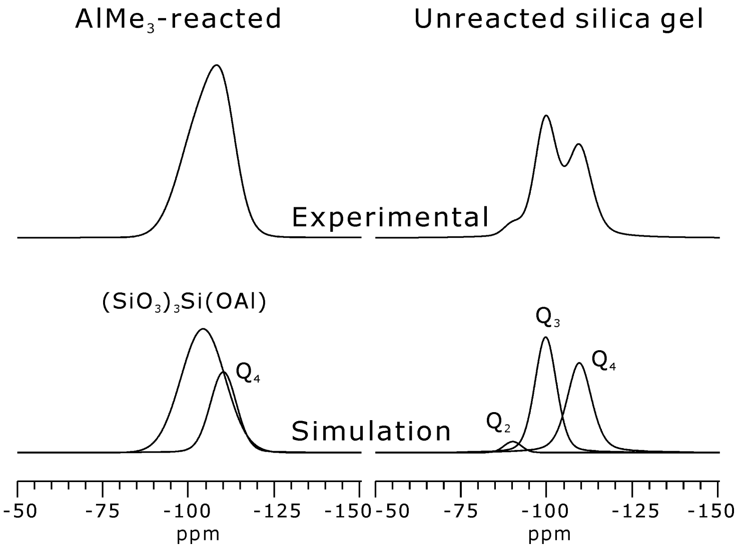


Figure SI-3. ^{29}Si CP/MAS spectra of dry silica gel and initial reaction product prepared in toluene. The raw experimental spectra and simulated individual components spectra are shown above and below, respectively.

NMR Spectroscopy of Individual Steps in the Reaction Between Trimethylaluminum and Silica in Toluene

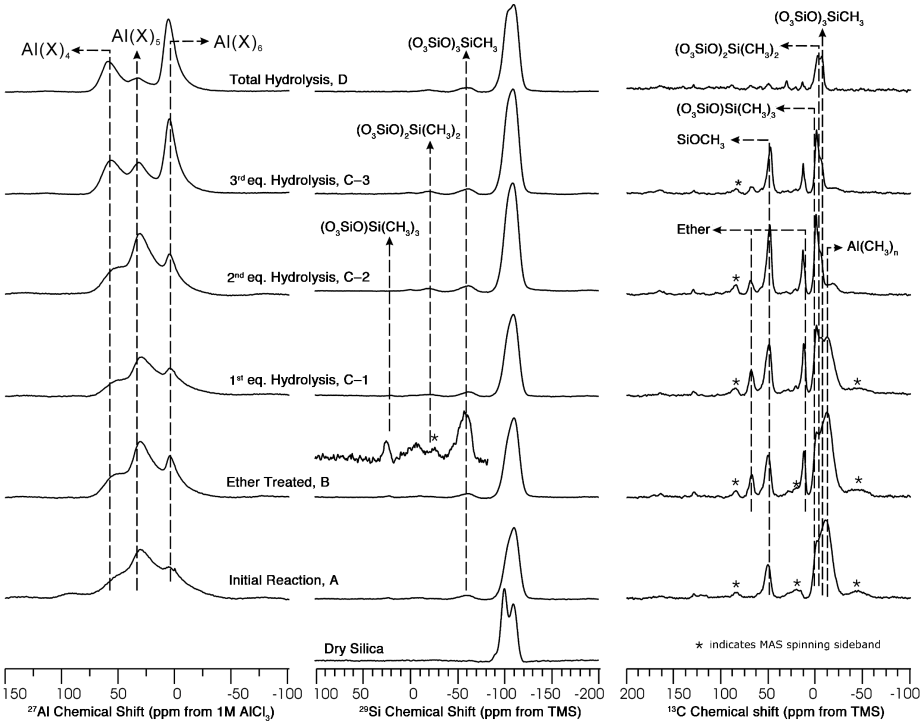


Figure SI-4. ^{27}Al, ^{29}Si, and ^{13}C MAS spectra of the reaction between trimethylaluminum and dry silica gel in toluene, subsequent treatment with ether, and partial and full hydrolysis steps.

^{13}C Spin Counting in the Individual Steps in the Reaction Between Trimethylaluminum and Silica in Toluene

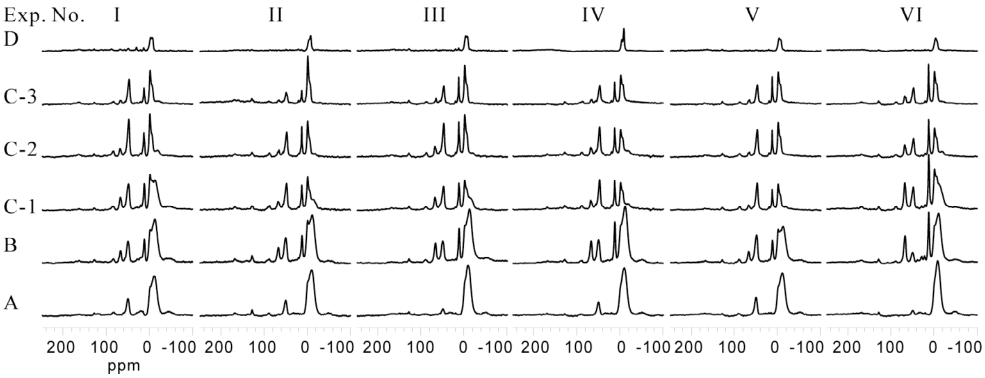


Figure SI-5. ^{13}C MAS spectra of the reaction between trimethylaluminum and dry silica gel in toluene, subsequent treatment with ether, and partial and full hydrolysis steps. The results of six separate reactions are shown.

Table SI-1. CH_4/CH_3 counting in replicate reactions in toluene (quantities in mmol).

Si-OH [a]	62	56	68	64	64	66
Al-Me added [b]	243	243	243	243	212	212
CH_4 during reaction [c]	-	31.7	37.8	36.8	38.6	37.3
Al-Me in liquid [d]	-	196.6	170.7	202.6	149.0	162.4
Surface Me [e]	34.7	32.2	38.8	37.3	41.7	43.0
Total Me[f]	-	260	247	275	229	233
%	-	107.2%	101.5%	113.2%	107.7%	109.5%

[a.] Determined by ^{1}H MAS spin counting. Estimated standard deviation, 2%.

[b.] Determined by trimethylaluminum added. Estimated standard deviation, 5.7%.

[c.] Determined by volume evolution during the reaction.

[d.] Determined by ^{1}H MAS spin counting in liquid-state NMR.

[e.] Determined by ^{13}C CP-MAS spin counting.

[f]. Estimated standard deviation, 10%

^{13}C Spin Counting in the Individual Steps in the Reaction Between Trimethylaluminum and Silica in Cyclohexane

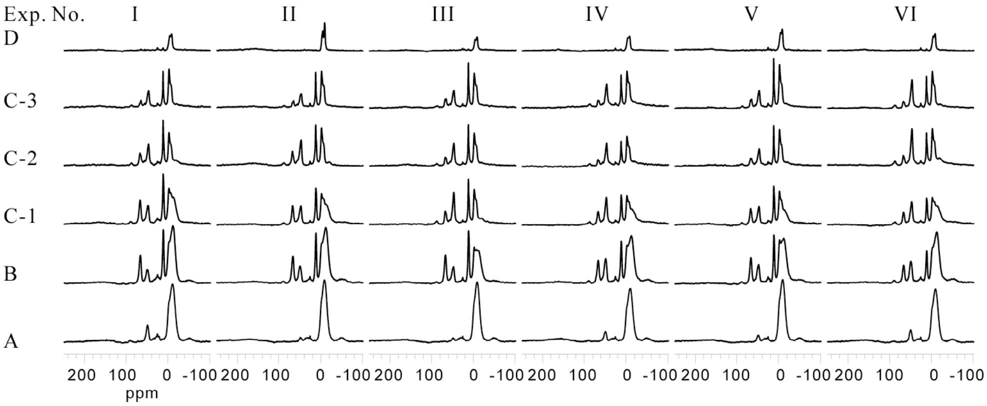


Figure SI-6. ^{13}C MAS spectra of the reaction between trimethylaluminum and dry silica gel in cyclohexane, subsequent treatment with ether, and partial and full hydrolysis steps. The results of six separate reactions are shown.

Table SI-2. CH_4/CH_3 counting in replicate reactions in cyclohexane (quantities in mmol).

Si-OH [a]	59	67	66	62	65	66
Al-Me added [b]	243	243	212	212	212	212
CH_4 during reaction [c]	34.1	38.2	42.8	36.0	38.0	36.0
Al-Me in liquid [d]	125.2	135.3	83.4	93.3	94.0	83.4
Surface –Me [e]	57.3	59.6	53.6	54.5	56.2	53.4
Total Me[f]	217	233	180	184	188	173
%	89.2%	96.0%	84.6%	86.5%	88.6%	81.3%

[a] Determined by ^{1}H MAS spin counting. Estimated standard deviation, 2%.

[b] Determined by trimethylaluminum added. Estimated standard deviation, 5.7%.

[c] Determined by volume evolution during the reaction.

[d] Determined by ^{1}H MAS spin counting in liquid-state NMR.

[e] Determined by ^{13}C CP-MAS spin counting.

[f]. Estimated standard deviation, 10%

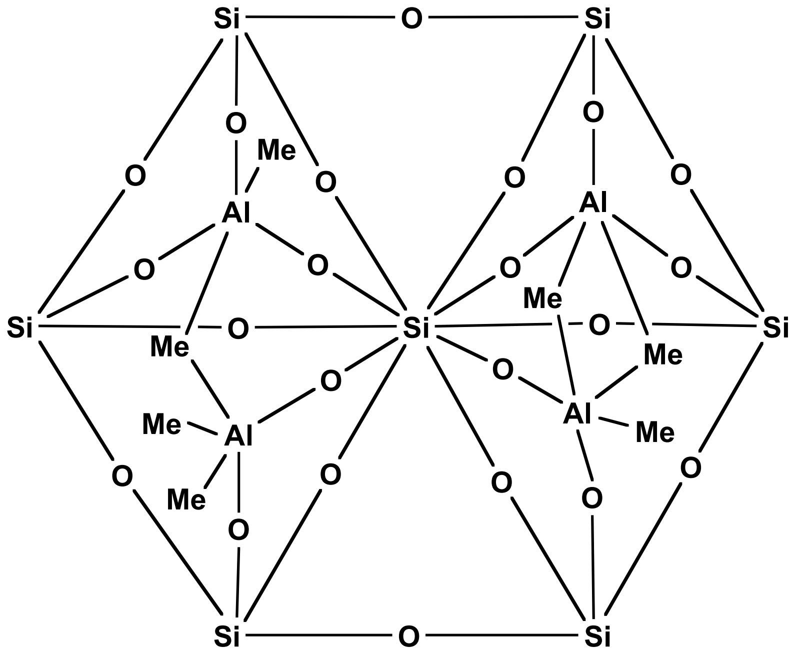
Estimation of ^{29}Si chemical shift of Si-O-Al. It is helpful to consider the **Si**-O-H → **Si**-O-Al change in terms of the following two steps: 1) **Si**-O-H → **Si**-O-**Si** and 2) **Si**-O-**Si** → **Si**-O-Al. For the first step, it is already known that replacing the $(SiO)_3$**Si**(OH) moiety by $(SiO)_3$**Si**(OSi) changes the ^{29}Si chemical shift of **Si** from –99 to –109 ppm. For the second step, the $(SiO)_4$**Si** moiety and the $(SiO)_3$**Si**(OAl) moiety are the fundamental structural units in zeolite structures and the chemical shifts of **Si** in $(SiO)_4$**Si** and $(SiO)_3$**Si**(OAl) are well studied in the same materials, as represented in Table SI-4. The zeolites from leucite to chabazite in the Table are natural zeolite minerals; and below these are synthetic zeolites. It can seen that the chemical shift change of **Si** from $(SiO)_4$**Si** to $(SiO)_3$**Si**(OAl) is fairly consistent, averaging around +5 ppm. On this basis it is reasonable to expect the **Si**-OH → **Si**-O-Al chemical shift change for the species observed in this work to be roughly: –5 ppm (–10 + 5 ppm), and the ^{29}**Si** chemical shift of the $(SiO)_3$**Si**–O–Al moiety to occur at about:–104 ppm (–99 – +5 ppm).

Table SI-4. ^{29}Si chemical shifts in zeolites.[12-14]

Type of zeolite	(SiO)$_3$**Si**(OAl) (ppm)	(SiO)$_3$**Si**(OSil) (ppm)	Chemical Shift Change (ppm)
Leucite	-97.4	-101.0	+3.6
Heulandite	-99.0	- 1080	+9.0
Clinoptilolite	-100.5	-112.8	+12.3
Stilbite	-101.5	-108.0	+6.5
Chabazite	-104.8	-110.0	+5.2
Omega	-98.8	-103.4	+4.6
NaK-L	-101.5	-107.4	+5.9
NaK-P1	-102.4	-107.0	+4.6
ZK-5	-103.5	-108.6	+5.1
NaK-chabazite	-104.4	-109.5	+5.1
Na-mordenite	-105.7	-112.1	+6.4
Ferrierite	-105.9	-110.5	+4.6
ZSM-11	-105.0	-113.0	+8.0
ZK-4	-106.1	-110.7	+4.6
ZSM-5	-106.0	-112.0	+6.0
ZSM-35	-108.0	-113.0	+50
TMA-Sodalite	-110.5	-116.2	+5.7

Estimation of the ^{29}Si chemical shift of (Si–O)$_3$Si–Al. Recognizing that replacement of –OSi by –Al in R$_3$**Si**–OSi (where R = alkyl) to yield R$_3$**Si**–Al, as reflected in the reported ^{29}Si chemical shift[15] of [(*t*-Bu)$_3$Si]$_2$Al–Al[(*t*-Bu)$_3$Si]$_2$, the 29Si chemical shift of a SiO)$_3$Si–Al moiety can be estimated as about -100 ppm (for (SiO)$_3$Si–OSi) + 20 = –80 ppm.

Five–Coordinate Aluminum Structures. Regarding structural types IV to VI, in which an aluminum atom is connected to three oxygen atoms of the silica surface, one might question the possibility of formation of this kind of structure. The following picture is a top–down representation of five–coordinate aluminum species on a β–cristobalite <111> face. This surface is commonly used as a model for single silanols on a silica surface.[16]



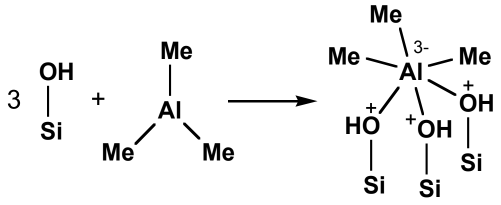
The normal interatomic distances represented in the above picture are:[17-25] Si–Si = 5.04 Å, Si–O = 1.60 Å, Al–O = 1.78 Å and Al–C = 1.97 Å.

From geometrical considerations, it appears that formation of the five–coordinate structures of types I, II and III, each of which has two surface oxygen atoms attached to each aluminum atom, should be favorable. Five–coordinate structures of types IV, V and VI, in which three oxygen atoms of silica are attached to an individual aluminum atom, would likely be very strained, because the possible positions of the aluminum atom are restricted by three surface Si–O–Al linkages and by the shared–CH_3 linkage. The left part of the picture above simulates the geometry of a type–V structure and the right part of the figure simulates the geometry of a type–VI structure. The C–Al–C angle in the Al–$(CH_3)_2$–Al bridge (right part of the picture) is about 84.4°, which is a strained angle compared to the C–Al–C angle (102°) in the $Al(CH_3)_3$ dimer[25] but this might still be possible to form. On the basis of only the ^{27}Al spectra, all of the above structures (type I through type VI) are possible; we cannot at this time distinguish among them by just a simple ^{27}Al MAS spectrum.

The ^{13}C relaxation results concluded that the surface methyl groups in $Al(CH_3)_n$ moieties are relatively immobile.[26, 27] This characteristic might due to Al–CH_3–Al bridges formed on the surface. Thus, among the five–coordinate aluminum structures proposed above, types II, III, V and VI are likely to be the $Al(CH_3)_n$ species responsible for the most intense signal in ^{13}C spectrum (–12 ppm), and these types of structure manifest the Al–CH_3–Al bridging characteristics.

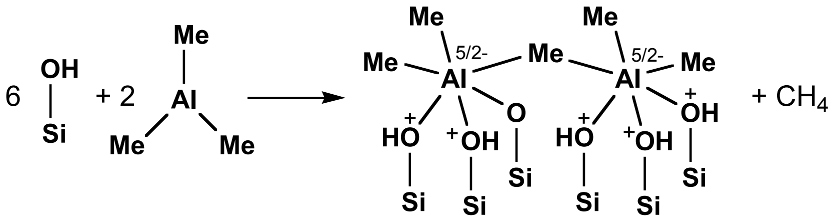
Hypothetical Processes

Formation of Six-Coordinate Aluminum Species.



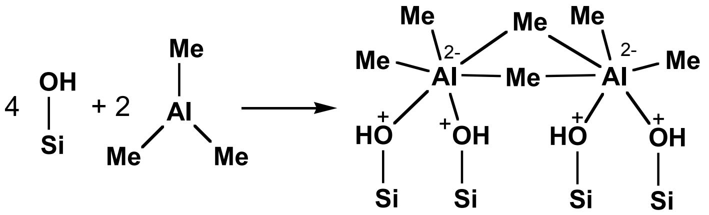
VII

(SI-1)



VIII

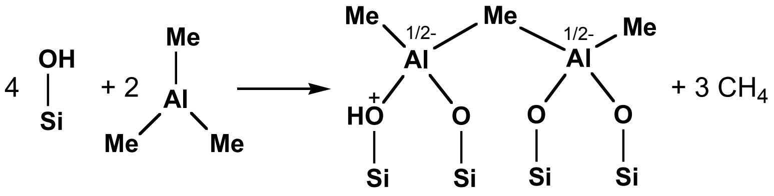
(SI-2)



IX

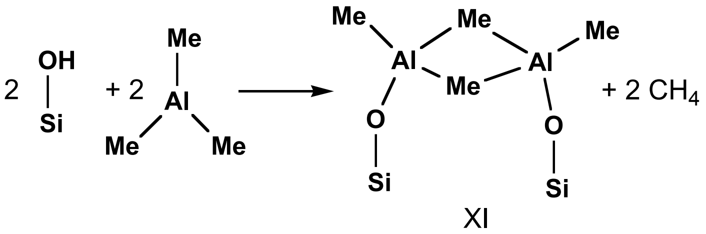
(SI-3)

Formation of Four-Coordinate Aluminum Species.

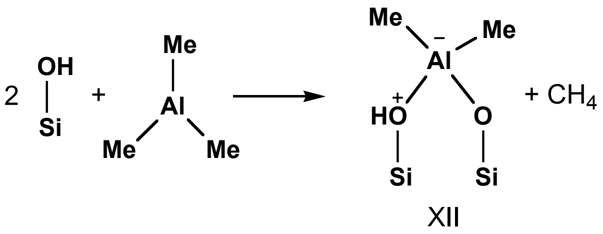


X

(SI-4)

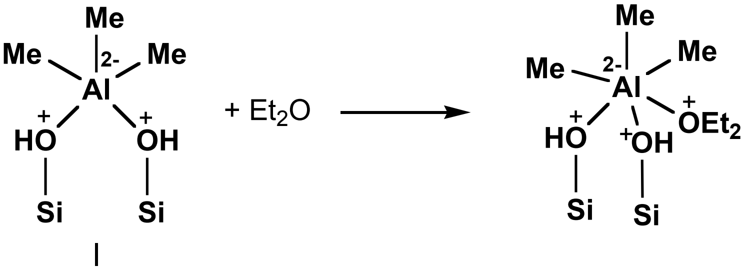


(SI-5)

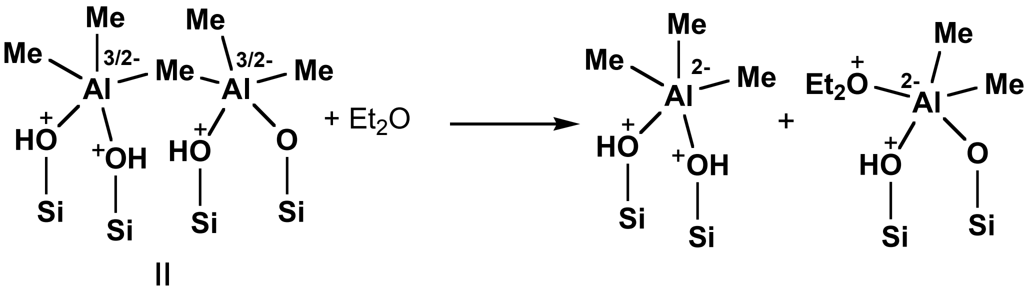


(SI-6)

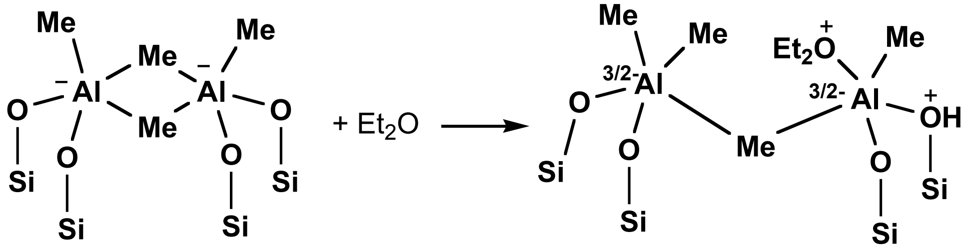
Hypothetical Reactions of Diethyl Ether with Five-Coordinate Aluminum Species.



(SI-7)

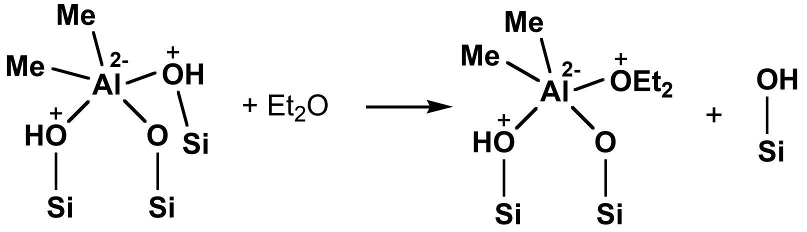


(SI-8)



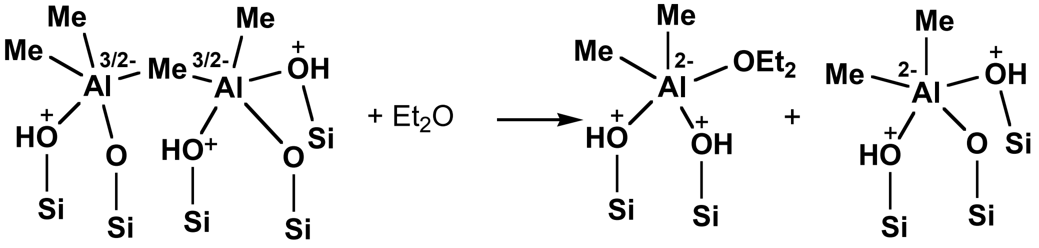
III

(SI-9)



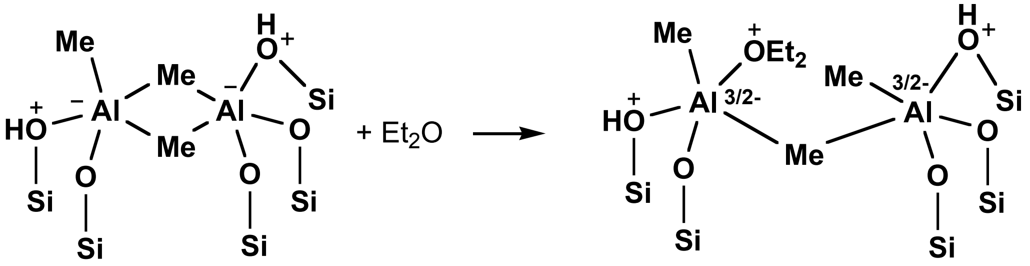
IV

(SI-10)



V

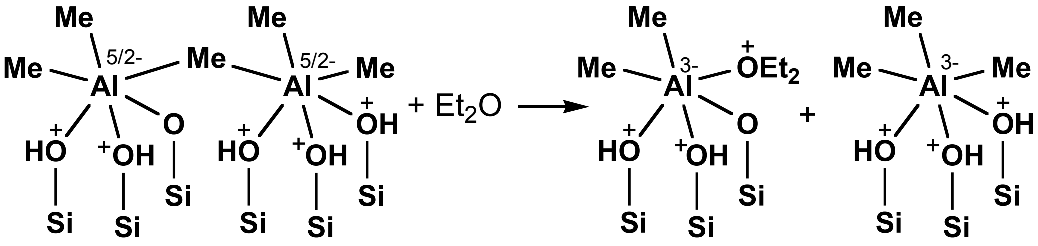
(SI-11)



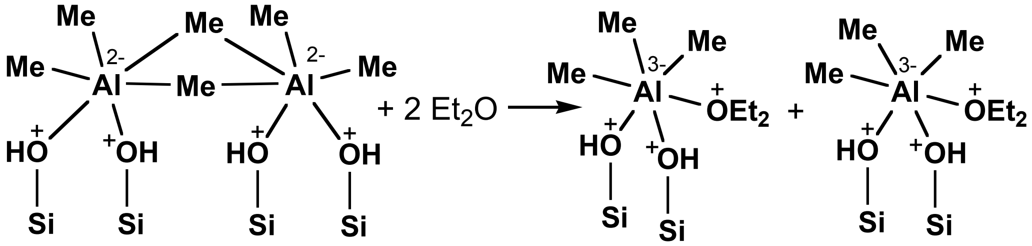
VI

(SI-12)

Hypothetical Reactions of Diethyl Ether with Six-Coordinate Aluminum Species

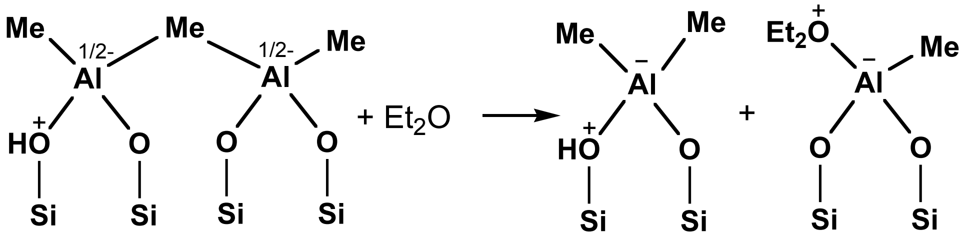


(SI-13)

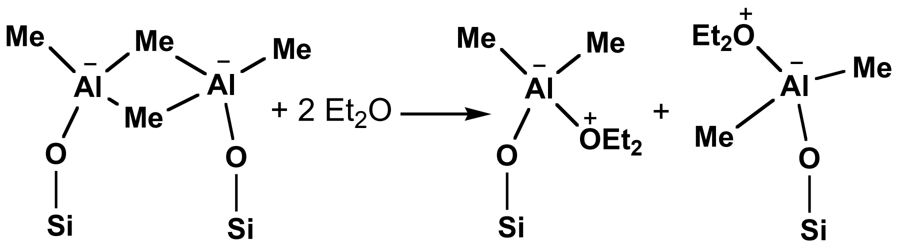


(SI-14)

Hypothetical Reactions of Diethyl Ether with Four-Coordinate Aluminum Species.

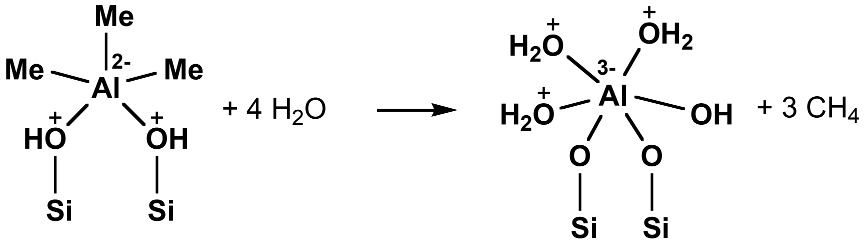


(SI-15)

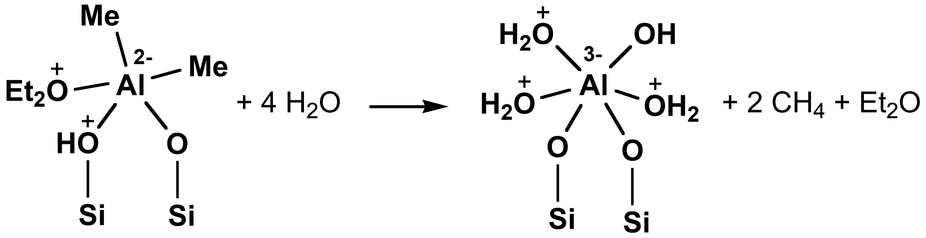


(SI-16)

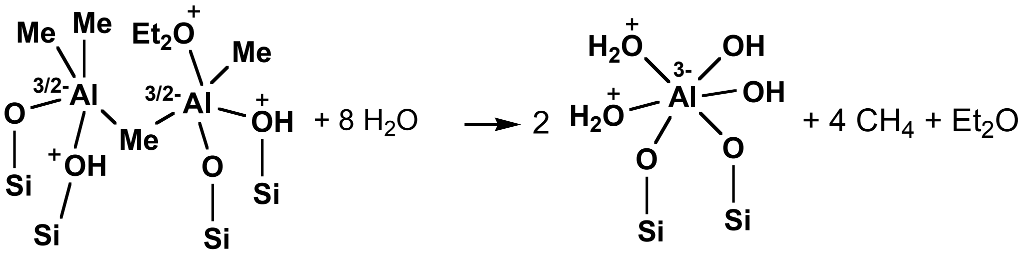
Hypothetical Reactions of Water with Five-Coordinate Aluminum Species.



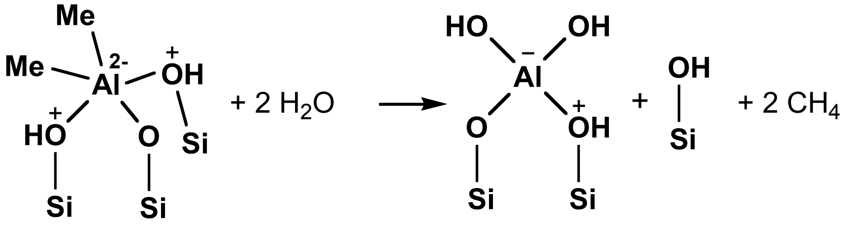
(SI-17)



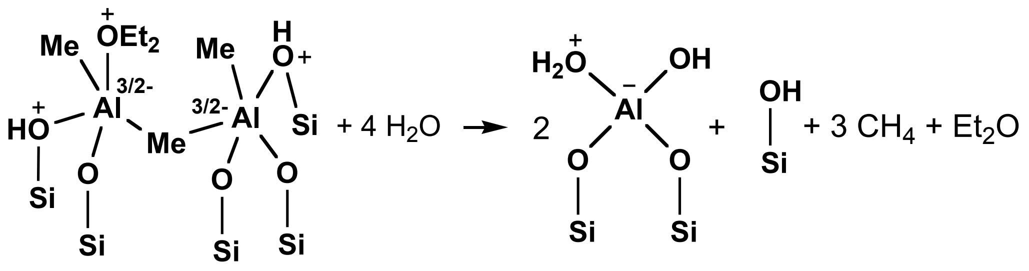
(SI-18)



(SI-19)

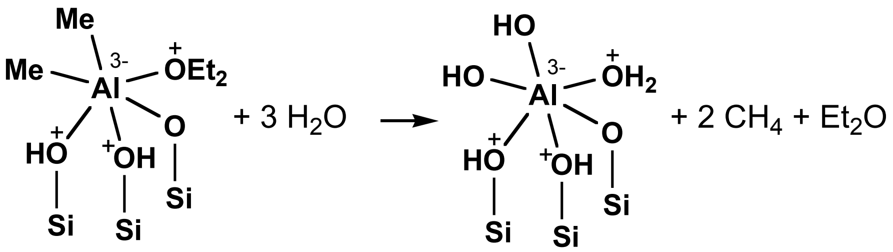


(SI-20)

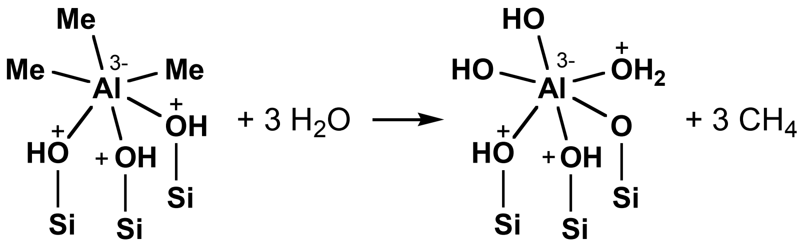


(SI-21)

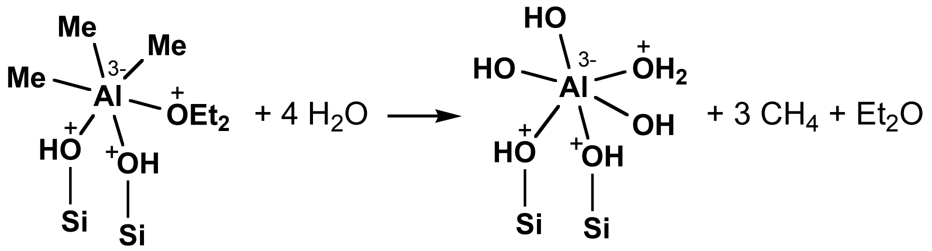
Hypothetical Reactions of Water with Six-Coordinate Aluminum Species.



(SI-22)

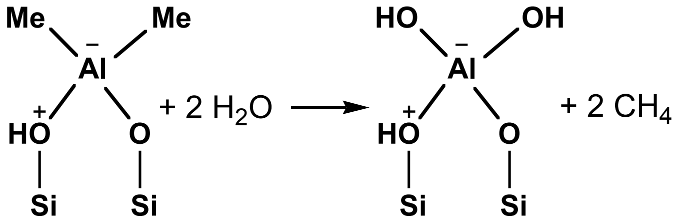


(SI-23)

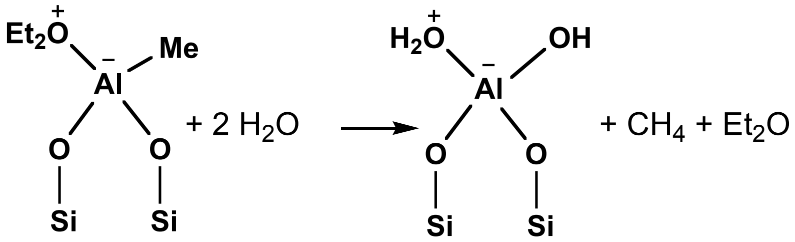


(SI-24)

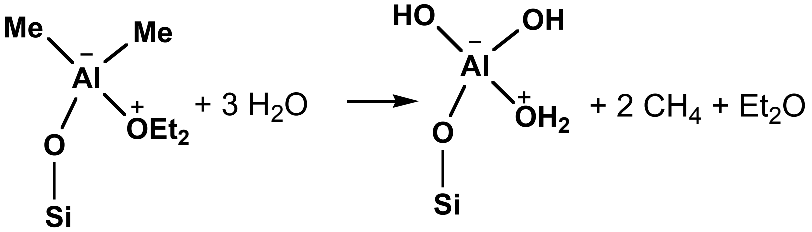
Hypothetical Reactions of Water with Four-Coordinate Aluminum Species.



(SI-25)



(SI-26)



(SI-27)

Supporting Information References

1. Pines, A.; Gibby, M. G.; Waugh, J. S., *Chem. Phys. Lett.* **1972,** *15*, 373.
2. Maciel, G. E.; Sindorf, D. W., *J. Am. Chem. Soc.* **1980,** *102*, 7606.
3. Sindorf, D. W.; Maciel, G. E., *J. Am. Chem. Soc.* **1981,** *103*, 4263.
4. Sindorf, D. W.; Maciel, G. E., *J. Am. Chem. Soc.* **1983,** *105*, 3767.
5. Chuang, I. S.; Kinney, D. R.; Maciel, G. E., *J. Am. Chem. Soc.* **1993,** *115*, 8695.
6. Chuang, I. S.; Maciel, G. E., *J. Am. Chem. Soc.* **1996,** *118*, 401.
7. Maciel, G. E.; Chuang, I. S., *Surfactant Science Series* **2006,** *131*, 425.
8. Gore, K. U.; Abraham, A.; Hegde, S. G.; Kumar, R.; Amoureux, J.-P.; Ganapathy, S., *J. Phys. Chem. B* **2002,** *106*, 6115.
9. Samoson, A.; Lippmaa, E., *Physical Review B: Condensed Matter and Materials Physics* **1983,** *28*, 6567.
10. Liu, C. C.; Maciel, G. E., *J. Am. Chem. Soc.* **1996,** *118*, 5103.
11. Wang, X.; Coleman, J.; Jia, X.; White, J. L., *J. Phys. Chem. B* **2002,** *106*, 4941.
12. Breitmaier, E.; Voelter, W., *^{13}C NMR spectroscopy: methods and applications*. Verlag Chemie: Weinheim, Bergstr., 1974; p 51.
13. Ganapathy, S.; Schramm, S.; Oldfield, E., *J. Chem. Phys.* **1982,** *77*, 4360.
14. Stejskal, E. O.; Memory, J. D., *High resolution NMR in the solid state: fundamentals of CP/MAS*. Oxford University Press: New York, 1994; Vol. I Introduction to NMR Principles 3, p 111.
15. Wiberg, N.; Amelunxen, K.; Blank, T.; Nöth, H.; Knizek, J., *Organometallics* **1998,** *17*, 5431.
16. Chuang, I. S.; Maciel, G. E., *J. Phys. Chem. B* **1997,** *101*, 3052.
17. Atwood, J. L.; Hunter, W. E.; Crissinger, K. D., *J. Organomet. Chem.* **1977,** *127*, 403.
18. Hobbs, J. D.; Cygan, R. T.; Nagy, K. L.; Schultz, P. A.; Sears, M. P., *Am. Mineral.* **1997,** *82*, 657.
19. Liu, W.; Hassan, A.; Wang, S., *Organometallics* **1997,** *16*, 4257.
20. Thomson, K. T.; Wentzcovitch, R. M.; McCormick, A.; Davis, H. T., *Chem. Phys. Lett.* **1998,** *283*, 39.
21. Gutierrez, G.; Johansson, B., *Physical Review B: Condensed Matter and Materials Physics* **2002,** *65*, 104202/1.

22. Turney, J. M.; Sari, L.; Yamaguchi, Y.; Schaefer, H. F., III, *J. Chem. Phys.* **2005,** *122*, 094304/1.

23. Baur, W. H., *Acta Crystallographica, Section B: Structural Crystallography and Crystal Chemistry* **1977,** *B33*, 2615.

24. Dove, M. T.; Keen, D. A.; Hannon, A. C.; Swainson, I. P., *Phys. Chem. Miner.* **1997,** *24*, 311.

25. Nyfeler, D.; Armbruster, T., *Am. Mineral.* **1998,** *83*, 119.

26. DiVerdi, J. A.; Li, J.; Maciel, G. E., *J. Phys. Chem.*To be submitted. **2006**.

27. Li, J. *M.S. Thesis*, Colorado State University, Fort Collins, Colorado, 2006.