Mechanism of Silation of Alumina with Hexamethyldisilazane

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The silation of γ-Al$_2$O$_3$ with hexamethyldisilazane (HMDS) has been examined over the temperature range 150−450 °C. The products and sequence of the reactions at the alumina surface have been determined, and a mechanism is proposed. At all temperatures and feed rates of HMDS the initial gaseous product is methane. The molar ratio of methane formed to HMDS consumed increases with increasing temperature. As the reaction progresses, hexamethyldisiloxane (HMDSO), ammonia, and nitrogen are formed. The quantity of each of these products decreases with increasing temperature. The proportion of Si and N irreversibly bound to the alumina surface from HMDS consumed increases with increasing temperature. The reaction of HMDS with alumina is sequential. Initially, HMDS reacts with surface sites to generate pendant $-$O$-$SiMe$_3$ and $-$NH$-$SiMe$_3$ moieties. At temperatures over 300 °C the predominant subsequent reaction is elimination of methane by reaction of the pendant silyl groups with acidic surface hydroxyls. At lower temperatures reactions between silyl groups to form HMDSO, protonation of amino groups to form ammonia, and redox reactions to form elemental nitrogen predominate over methane elimination.
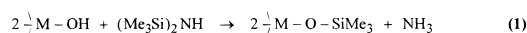
I. Introduction

Organosilanes are frequently used for modification of the surfaces of alumina and other oxide materials. Silation of these surfaces involves reactions of surface hydroxyl groups.[1−5] Chemically replacing or removing some or all of the surface hydroxyl groups renders the surface less hydrophilic.[6−8] The utility of the modified material for use in analytical, separations, or catalytic processes can be changed by changing the surface properties in a controlled manner.[9−11]

Organosilanes that are used to silate surfaces of oxides are usually chloroorganosilanes (R$_n$SiX$_{4−n}$; X = Cl) or alkoxyorganosilanes (X = OR′). The nature and extent of the modification to the silated surface are dependent upon the structure of the silating agent. A number of studies have been conducted in which the properties of silated alumina and silica have been examined in relation to, for example, the number of halogens in a silane R$_n$SiX$_{4−n}$,[11] the length and branching of the organo groups R,[12] or the presence of cyano,[12] amine,[13,14] or other functionality in the organo group of the silating agent.

Hexamethyldisilazane ("HMDS") is also used as a silating agent, especially for silica.[15−17] A commercial product, Wacker HDK H2000, is a highly porous silica (Wacker HDK N20) silated with HMDS.[15] The catalytic properties of rhodium complexes supported on silica silated with HMDS have been compared to related heterogeneous catalysts.[17] The electron-transfer capability of titania is reduced when it is silated with HMDS.[18]

It has been proposed that silation of surfaces with HMDS is effected by the reaction of HMDS with surface hydroxyls to form pendant $-$O$-$SiMe$_3$ groups and liberate ammonia (eq 1).[15−17]

$$2 \tfrac{1}{7} \text{M} - \text{OH} + (\text{Me}_3\text{Si})_2\text{NH} \ \rightarrow \ 2 \tfrac{1}{7} \text{M} - \text{O} - \text{SiMe}_3 + \text{NH}_3 \qquad (1)$$

where M = Al, Si, Ti. Further, it has been suggested that ammonia is then bound wholly or in part in the surface of the silated oxide and acts in a catalytic manner to promote further silation by HMDS. However, the interaction of ammonia or methylamines with dehydroxylated silica provides no evidence for such an effect.[19−22]

Recently, we have shown that Me$_3$SiCl reacts with the surfaces of either alumina or silica to strongly bind chloride and eliminate methane.[23−25] The initial reaction in the sequence is with coordinatively unsaturated ("cus") cationic or anionic sites, respectively, to bind chloride and form $-$O$-$SiMe$_3$ groups. The inductive effect of the bound chloride enhances the acidity of neighboring surface hydroxyls, which then react with $-$O$-$SiMe$_3$ groups to eliminate methane and form $-$O$-$SiMe$_2$$-O-$bridged groups.

We have now studied the reactions of alumina with HMDS to determine the nature of the reactions of HMDS with the surface, and the gaseous products and surface species formed. We will show that the reaction produces ammonia, as expected, and also methane, hexamethyldisiloxane, and nitrogen as volatile products, that the amounts and proportions of the products vary with temperature but not rate of HMDS feed, and that the mechanism involves a sequence of reactions.

II. Experimental Section

Materials. Commercially available granulated alumina (La Roche) was used after dehydroxylation, as previously described.[23,24] The BET surface area was 206 m^2 g^{-1}, as determined, and the total pore volume was 0.386−0.390 cm^3 g^{-1}.

HMDS was obtained from two commercial suppliers. Aldrich HMDS (99.9% purity) was used as received, after the purity was confirmed by GC−MS analysis. GIC HMDS (98.0% purity) was doubly distilled. The distilled HMDS was found (GC−MS) to contain 3.5% hexamethyldisiloxane (HMDSO). Each sample of HMDS was transferred and stored under nitrogen (Matheson, "Ultra High Purity").

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TABLE 1: HMDS Consumed and Gas-Phase Products Formed as a Function of Temperature of Reaction

reacn temp (°C)	HMDS consumed[a] (10^{-3} mol)	products[b]							
		methane		ammonia		nitrogen		HMDSO	
		(10^{-3} mol)	CH_4/HMDS	(10^{-3} mol)	NH_3/HMDS	(10^{-3} mol)	N_2/2HMDS	(10^{-3} mol)	HMDSO/HMDS
200	12.0	0.82	0.07	7.6	0.63	1.4	0.24	8.6	0.72
300	12.2	12.5	1.02	5.8	0.48	1.4	0.23	6.5	0.53
380	7.2	23.3	3.2	2.7	0.37	n.m.	n.m.	0.27	0.04

[a] Feed rate is 0.135 g h^{-1}. Total feed during 20 h of reaction is 2.70 g (16.7×10^{-3} mol). [b] Amounts after 20 h of reaction. n.m. = not measured.

Equipment. Silation of alumina with HMDS was studied using the dynamic method. The equipment was essentially similar to that described previously[23-25] and comprised a gas handling system, a U-shaped glass reactor (100 cm^3) and movable furnace controlled within ±1 °C, and an exit gas control and monitoring system.

Gas samples collected from the feed and exit streams were analyzed using GC and IR spectroscopy. A system of three-way valves and purged connectors was used to prevent contamination of samples by air.

Experimental Procedure. The reactor was dried and then charged with samples of dried γ-alumina. Nitrogen continuously flowed through the reactor. The alumina was then dehydroxylated by gradually increasing the temperature to 500 °C and then holding at 500 °C for 24 h. The reactor was sequentially cooled to room temperature, closed, and then reweighed to determine the weight of the charge (12.02–12.20 g).

The reactor was then reconnected, opened, and heated to the required temperature (150–450 °C). The N$_2$ was then switched to HMDS in an N$_2$ gas mixture feed. The HMDS concentration in the feed was varied by changing the temperature of the saturator and was determined gravimetrically (5.24×10^{-4} to 38.12×10^{-4} mol L^{-1}). The total flow rate was varied between 12 and 50 cm^3 min^{-1} (corrected to STP).

HMDS was fed continuously for 400–1200 min, to completion of each silation reaction as determined by the composition of the exit gases. The composition of the exit gases was monitored by GC and IR spectroscopy throughout each run.

Instrumental Methods. The surface area and pore volume for solid samples were determined using the BET method, by nitrogen adsorption–Kelvin condensation at liquid nitrogen temperature, using an Omnisorp 360 sorptometer. Pore size distributions were determined using desorption isotherms. Gas chromatographic (GC) analyses of the feed or exit gases were performed using a Hewlett-Packard 5890 series II GC with a Hewlett-Packard HP3396A integrator. The GC column (5 ft × $^1/_8$ in. o.d.) was packed with Porapak T and used at 120 °C.

Fourier transform infrared (FTIR) spectroscopic data were collected using a Nicolet 730 FTIR spectrometer. Gas-phase samples were collected and analyzed using a calibrated 10 cm glass cell (76.4 cm^3) with KCl windows.

Elemental analyses (C, H, N) of solid samples were performed using a Carlo Erba CHNS-O instrument equipped with a GC TCD EA 1108 elemental analyzer.

III. Results and Discussion

The silation of 12 g samples of γ-alumina dehydroxylated at 500 °C has been examined over the temperature range 150–450 °C. The feed rates ranged from 0.066 to 0.486 g (HMDS) h^{-1}. The gaseous products of the reaction were methane, ammonia, HMDSO, nitrogen, and small amounts of water vapor.
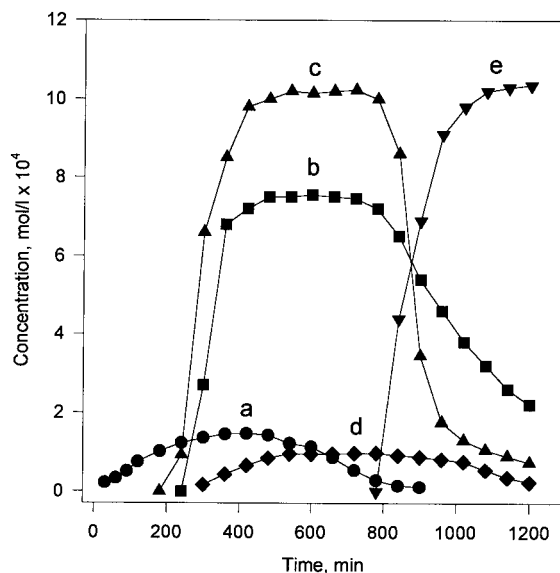

Figure 1. Gas-phase products of silation of γ-alumina with HMDS at 200 °C: (a) CH$_4$; (b) NH$_3$; (c) HMDSO; (d) N$_2$; (e) unreacted HMDS.

The amounts of each gaseous product and the duration, proportions, and sequence of their production depended upon the temperature of silation and the feed rate.

The feed was either 99% purity HMDS, or HMDS containing 3.5% HMDSO, in an inert carrier gas (N$_2$, Ar, or He). It was found that the presence of HMDSO had no detectable effect on the progress or rate of reaction.

The results for each set of reaction conditions will be presented, and the data will be correlated with the changes in reaction parameters. Finally, the implications for the mechanism of the reaction will be presented.

1. Effect of Temperature on Reaction Profile. A series of reactions was performed in which the only parameter that was varied was the temperature at which silation was carried out. In each run the amount of alumina was 12 g, and dehydroxylation was performed at 500 °C. The flow rate of feed gases (corrected to STP) was 13.32 cm^3 min^{-1}, and the feed rate of HMDS was 0.135 g h^{-1}. The runs were conducted at 150, 200, 300, 380, 400, and 450 °C.

In each run the initial product detected was methane, followed by ammonia, HMDSO, and nitrogen. The HMDS consumed and products formed varied in both absolute amounts and relative proportions with the temperature of reaction (Table 1). Further, the order of initial appearance of ammonia, HMDSO, and nitrogen differed. At 200 °C HMDSO was detected before ammonia (Figure 1), but at 300 °C (Figure 2) or 380 °C (Figure 3) ammonia was detected before HMDSO. However, at each temperature, the time during which the steady, maximum rate of both ammonia and HMDSO production occurred was the same.
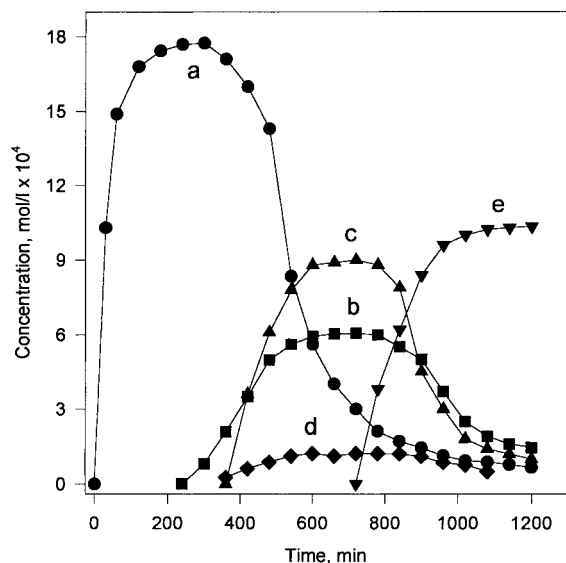
Figure 2. Gas-phase products of silation of γ-alumina with HMDS at 300 °C: (a) CH_4; (b) NH_3; (c) HMDSO; (d) N_2; (e) unreacted HMDS.
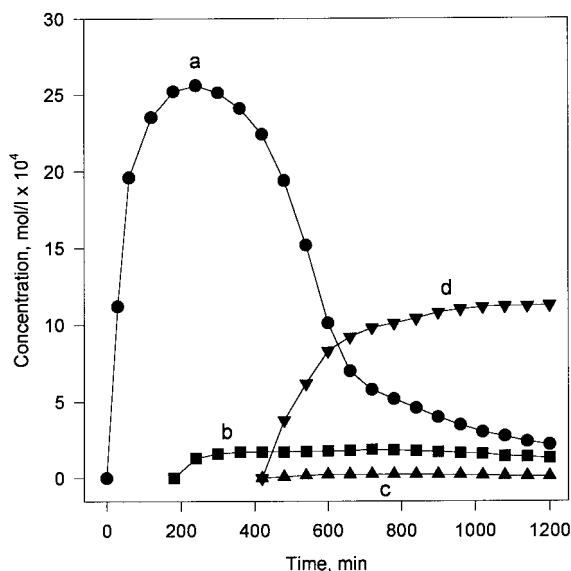

Figure 3. Gas-phase products of silation of γ-alumina with HMDS at 380 °C: (a) CH_4; (b) NH_3; (c) HMDSO; (d) N_2; (e) unreacted HMDS.

1.1. Silation at 200 °C. During the period from very soon after the initiation of silation until after 3 h of reaction, small amounts of methane were the only gaseous product produced. The rate of methane production increased to a maximum after 7 h of reaction and then declined until the concentration of methane in the exit gases was essentially zero, after 14 h.

After 3 h of reaction a small amount of HMDSO was detected in the exit gases, and after 4 h of reaction small amounts of ammonia were also detected. The peak concentration of both ammonia and HMDSO occurred between 6 and 13 h from initiation of the reaction. After 20 h of reaction the concentration of HMDSO in the exit gases had declined to negligible values; however, small but significant amounts of ammonia continued to be produced. The molar amount of ammonia produced was lower than that expected from reaction 1. Unexpectedly, a smaller but measurable molar fraction of the surface nitrogen moieties formed from the HMDS feed was oxidized to elemental nitrogen. The small remaining balance of the nitrogen from HMDS remained bound to the alumina surface (vide infra).

No HMDS was detected in the exit gases during the first 13 h of the reaction. After 13 h the concentration of HMDS in the exit gases increased rapidly, and after 20 h of reaction the concentration of HMDS in the exit gases was the same as its concentration in the feed gas stream, showing that no further HMDS was being consumed.

Significant features of the reaction at 200 °C include the following. The formation of methane occurs throughout the reaction until the breakthrough by HMDS. HMDSO was produced in amounts equivalent to the total of ammonia and nitrogen, and each of these was much larger than for methane. The periods for the maximum rates of production for each of these products terminated as the breakthrough of HMDS occurred. However, although the production of HMDSO fell off rapidly after breakthrough by HMDS, reduced levels of production of ammonia continued, even after 20 h of reaction.

The molar amounts of ammonia, HMDSO, and nitrogen produced were each less than HMDS consumed (Table 1). Approximately 13% of nitrogen and 28% of the silicon from the HMDS were not converted into volatile products but remained bound to the surface. The methane formed corresponded to 4% of methyl groups initially bound to the surface.

1.2. Silation at 300 °C. The initial gaseous product from the reaction at 300 °C was again methane (Figure 2). The concentrations of methane in the exit gases were an order of magnitude greater than for the reaction at 200 °C. Further, methane production continued, at greatly reduced levels, even after breakthrough of HMDS into the exit gases after 12 h of reaction.

The initial appearances of first ammonia and then nitrogen and HMDSO were later than for reaction at 200 °C, and the periods for maximum concentration of each in the exit gases (9−14 h) were also later and were again coincident.

The amount of methane produced relative to HMDS was much higher than at 200 °C, but the amounts of ammonia, nitrogen, and HMDSO were each significantly reduced (Table 1). Approximately 29% of N and 46% of Si from HMDS remained bound to the surface of the alumina. The amount of ammonia formed was again lower than expected. However, approximately 37% of the methyl groups from the surface-bound silyl moieties reacted further to form methane.

1.3. Silation at 380 °C. Methane was by far the predominant product from the reaction at 380 °C. The methane was produced for the period from initiation for the reaction until well after breakthrough by HMDS into the exit gases after 7 h (Figure 3).

No ammonia was detected in the exit gases during the initial 3 h from initiation of the reaction, and no HMDSO was detected until after 7 h of reaction. The concentrations of ammonia in the exit gases were significantly lower than for the reactions at 200 or 300 °C, and the concentrations of HMDSO and nitrogen remained very low throughout the reaction.

The amounts of HMDS consumed and HMDSO produced show that approximately 96% of Si from the HMDS consumed remained bound to the alumina surface. The amounts of nitrogen in the HMDS feed and in the gas phase and solid products balance within 5%; the nitrogen bound to the surface is approximately 63% of that from the HMDS consumed. The amount of methane produced corresponded to approximately 56% of the Si−Me groups from the silyl moieties initially bound to the surface. Thus, an average of 1.7 methyl groups per bound Me_3Si- moiety have been eliminated as methane, and an average of 2.7 bonds has been formed between Si and surface O or N.

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TABLE 2: Solid Product Analyses

silation temp (°C)	SSA ($m^2 g^{-1}$)	SSA decrease (%)	total pore volume ($mL g^{-1}$)	N (wt %)	C (wt %)	H (wt %)
200	184.86	10.72	0.3954	0.134	1.398	1.161
300	171.34	17.05	0.3922	0.278	2.009	0.982
380	162.38	21.46	0.3577	0.468	1.901	0.874

1.4. Silation at 400 and 450 °C. When the silation reaction was performed at 400 or 450 °C the progress of the reaction was similar to that at 380 °C. The amounts of methane formed were slightly greater than at 380 °C, and the amounts of ammonia, nitrogen, and HMDSO produced were consistently low.

The common characteristics for each of the reactions 200−450 °C are the following: (i) the same products are produced, albeit in different amounts and proportions; (ii) chronologically, methane production is always the first product, and 3−6 h elapses before production occurs for ammonia, HMDSO, and nitrogen; and (iii) the appearance of HMDS in the exit gases coincides with the drop in production of ammonia, HMDSO, and nitrogen, signaling the completion of the reaction of HMDS with surface sites.

1.5. Solid Product Analyses. The surface areas and pore volumes of alumina before and after silation at different temperatures are presented in Table 2. The surface area of the alumina decreases on silation by 10.7% and 21.5% for silation at 200 and 380 °C, respectively. The pore volume decreases by approximately 10% for reaction at 380 °C in a manner similar to that for γ-Al_2O_3 silated using Me_3SiCl.[23,24] Pores of radius 20−30 m^{-10} predominate for all samples.

Elemental analyses (C, H, N) for the solid products were obtained using aliquots from carefully ground and fully mixed samples. In each case the C and N contents of the solid products were low, and there was variance among the samples analyzed. However, the values obtained (Table 3) were in reasonable agreement with the differences between the equivalents of C and N in the feed and product gas streams as follows. The amounts of surface-bound N determined by elemental analyses were similar to the differences between the equivalent amounts of HMDS consumed, and ammonia and nitrogen produced at each temperature. Similarly, the carbon content of the solid products corresponded well to the difference in carbon content between the HMDS consumed (6 C per molecule), and methane (1 C) and HMDSO (6 C) produced.

The amounts of Si bound to the surface were determined from the differences between the HMDS consumed and HMDSO produced. From these data, the C analyses, and the amounts of methane produced, the ratio of residual Si−Me groups remaining bound to surface Si sites has been calculated. The number of methyls per surface silicon decreases from over 2.9 to 0.6 as the temperature of reaction increases from 200 to 450 °C. As the number of Si−Me groups is reduced by methane formation, the number of Si−O bonds formed necessarily increases. This effect is clearly seen in the FT-IR spectra of the solid products. As the temperature of silation increases, the spectra of the resulting solid product show a regular and significant decrease in the relative intensity of the Si−CH_3 stretching vibration close to 840 cm^{-1}, the Si−CH_3 deformation band near 1260 cm^{-1}, and the C−H band near 2960 cm^{-1}. The Si−O band in the region of 1100 cm^{-1} increases in relative intensity with increasing temperature of reaction.

2. Effect of Feed Rate. The rate of formation of the gas-phase products, methane, ammonia, HMDSO, and nitrogen, has been determined at four temperatures (200, 300, 380, and 450

°C), for two or more different rates of addition of HMDS at each temperature (0.066, 0.135, 0.237, 0.486 g (HMDS) h^{-1}). The common characteristic for each set of reactions at the different temperatures was that the reaction profiles varied in a similar manner for each temperature and for each product. In each case the initial rate, the rise in rate with time of reaction, and the maximum rate of production of methane, ammonia, HMDSO, and nitrogen each increased with an increase in HMDS feed rate.

In each case methane was produced immediately after initiation of the reaction, showing that the formation of methane involved a very rapid reaction or sequence of reactions. In each case, the rate initially increased with time of reaction for several hours to a maximum value that was then maintained for a period (Figure 4). The rate then declined to an insignificantly small value at or soon after the breakthrough of HMDS into the product gas stream. An inverse relationship exists between HMDS feed rate and the elapsed times for both the start of the decline in methane production and the completion of the reactions to produce methane. However, for a given temperature the total amount of HMDS reacted and the total amount of methane produced were independent of the HMDS feed rate.

Thus, the rate of methane production is dependent upon both the feed rate of HMDS and the temperature of reaction, but the extent of the methane production reaction is dependent only upon the temperature of the reaction.

3. Effect of Temperature on Product Distribution. The dependence upon temperature of reaction of the time average amount of methane produced during silation of γ-Al_2O_3 by HMDS at 150−450 °C is shown in Figure 5. At temperatures up to 200 °C the concentration of methane was insignificant. Therefore, at temperatures up to 200 °C, the reaction of HMDS with the surface of γ-Al_2O_3 either is slower than that with Me_3SiCl[24] or is reversible.

As the temperature of the reaction is increased, the concentration of methane in the exit gases increases as well as the total amount of methane produced. The efficiency in consumption of HMDS increases, and no HMDS is detected in the exit gases until 780 min (200 °C), 720 min (300 °C), or 300−330 min (450 °C). Thereafter, the concentration of HMDS in the exit gases increases in a manner similar to that for the low-temperature reactions.

The total amounts of methane produced at each temperature, expressed as an average concentration in the exit gases, and the peak concentration measured are both compared in Figure 6. In each case the average concentration over the reaction period is in the range 61−67% of the peak value. This consistency indicates that the rate of reaction is temperature-dependent but that the mechanism is essentially similar at all temperatures.

As the temperature of the reaction is increased, an increasing number of the six available Si−Me groups per HMDS molecule consumed reacts to form methane. The molar ratio increases from 0.07 at 200 °C to 3.2 at 380 °C and 4.4 at 450 °C. Thus, approximately 2.2 silicon−methyl bonds per silicon atom can be replaced by surface Si−O links by reaction with acidic hydroxyls at high temperatures (Figure 7). This value is very similar to the result for silation of γ-Al_2O_3 using Me_3SiCl at 360 °C, for which 2.6 mol of methane were produced per mole of Me_3SiCl consumed.[24]

3.1. Thermal Treatment of Silated Alumina. A sample of γ-Al_2O_3 was silated at 200 °C. The product was held at 200 °C for 24 h, during which gas-phase analysis showed that negligibly small amounts of methane, ammonia, and HMDSO

Silation of Alumina

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TABLE 3: Calculated versus Measured Mass Balance Values for the Solid Product

reacn temp (°C)	mass increase (g)		N (g atom)		C (g atom)		Si (g atom)
	from elemental analysis by weight	calcd[a]	from elemental analysis	calcd[a]	from elemental analysis	calcd[b]	calcd[a]
200	0.51	0.42	1.20	1.60	14.93	20.0	7.16
300	0.68	0.60	2.54	3.50	21.46	21.6	11.36
380	0.78	0.70	4.30	4.56	20.38	18.3	13.85

[a] Based on the difference between HMDS consumed and gas-phase products formed.

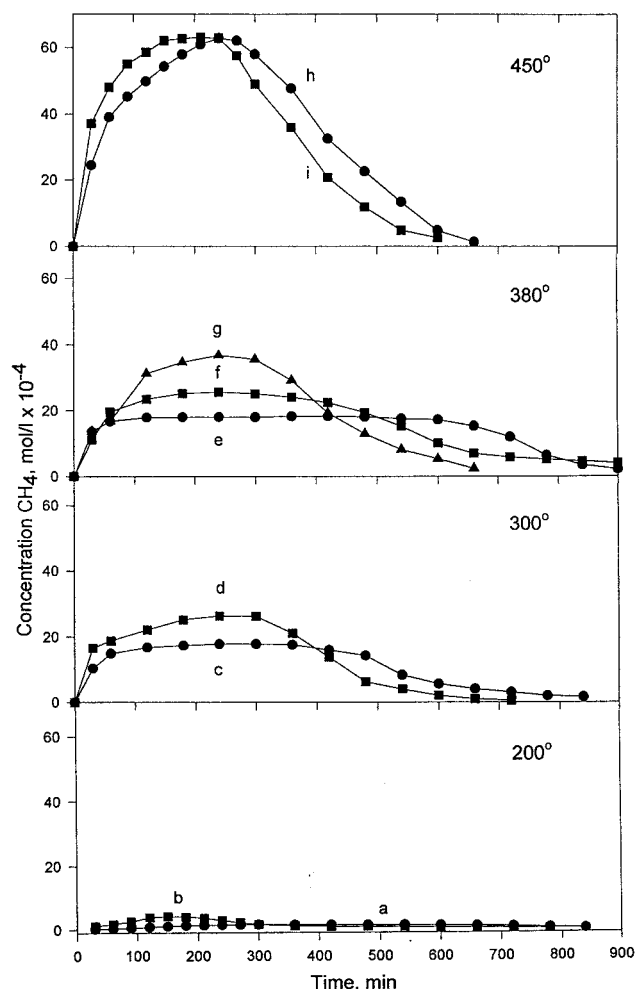**Figure 4.** Effect of HMDS feed rate on CH_4 production at different temperatures: (a, c, f, h) 0.135 g (HMDS) h^{-1}; (b, d, g, i) 0.237 g (HMDS) h^{-1}; (e) 0.066 g (HMDS) h^{-1}.

Figure 5. Effect of reaction temperature on methane production in the temperature range 150−450 °C.
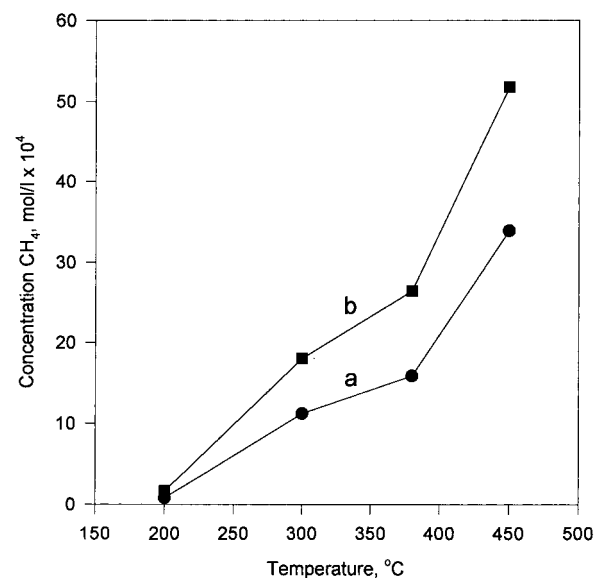
Figure 6. Temperature dependence of (a) time average and (b) peak concentration of CH_4 produced.

were produced. The sample was then heated in 60 °C stages and held at each incremental temperature for 2 h. The major product during each stage of heating was methane (Figure 8). Heating to 260 °C also produced smaller amounts of HMDSO and ammonia. At 320 and 380 °C small amounts of ammonia and HMDSO were produced, but the predominant product was still methane. The total amount of methane produced thus increased as the temperature increased, in a manner parallel to the increase in production of methane with an increase in temperature of the silane reaction. At the highest temperatures the majority of the methane was produced very rapidly over a shorter reaction period.

The results from this experiment lead to a series of conclusions. First, chemisorption of HMDS at the γ-Al_2O_3 is the initial reaction in the mechanism, and only a small fraction of HMDS molecules are reversible chemisorbed. Second, the reaction of Si−Me groups with surface hydroxyls to produce methane is a subsequent step. Third, the low amount of methane produced

at 200 °C and the much higher amounts produced as the temperature is increased show that there is a high activation energy for the methane elimination reaction. Fourth, the production of only very small amounts of ammonia and HMDSO as the temperature is increased shows that these reactions are not thermally promoted in the same manner as methane production.

3.2. Relationship of Ammonia and Nitrogen Production to HMDSO Production. The profiles for the production of ammonia, nitrogen, and HMDSO are similar for each reaction temperature (Figures 1−3), and the quantity of HMDSO

Figure 7. Methane molecules produced per Me_3Si- group as a function of temperature.

Figure 9. Temperature dependence of (a) consumed HMDS and produced (b) CH_4, (c) NH_3, (d) HMDSO, and (e) N_2.

more steps in the mechanism by which the other volatile products are formed.

4. Mechanism of the Reaction of HMDS with γ-Al$_2$O$_3$. The results illustrated in Figures 1−4 are of consistent character but are quantitatively distinct. In each case the reaction shows the following characteristics. The major gas-phase products are methane, ammonia, and HMDSO with lesser amounts of nitrogen, and the amount of each produced increases with time of reaction to a maximum value, then decreases sharply. The time to maximum concentration of methane in the exit gases is inversely dependent upon concentration of HMDS in the feed, but the total amount of methane is independent of feed rate. The total amount of methane formed increases with increasing temperature. At the beginning of each reaction little or no HMDS is observed in the exit gas stream. HMDS is detected after the rate of methane formation has passed through its maximum value, e.g., after 780 min at 200 °C, and the concentration of HMDS in the exit gases increases as the reaction proceeds toward completion. These data show that reaction of HMDS with the surface is the primary reaction and that methane formation is a subsequent and not a coincident step.

4.1. Chemisorption. No HMDS is detected in the exit gases until after termination of the reaction, at each temperature. Therefore, the initial reaction is a direct interaction of HMDS with the available surface sites. The molar amount of silyl groups retained on the surface of γ-Al$_2$O$_3$ is similar to the molar amount of Me$_3$SiCl, which reacts irreversibly with γ-Al$_2$O$_3$.[23,24] It is therefore proposed that the initial reaction of HMDS with γ-Al$_2$O$_3$ is dissociative chemisorption by reaction with coordinatively unsaturated $>$Al$^+$ and $-$O$^-$ sites (eq 2).

$$(2)$$

Chemisorption of HMDS is not reversible. When a sample of γ-Al$_2$O$_3$, which has been previously silated using HMDS at 200 °C, is then heated to higher temperatures, the major product is methane and minor products are ammonia and HMDSO. The correspondence of the amount of HMDS adsorbed with that of

Figure 8. Gas-phase products from the subsequent thermal treatment of γ-alumina silated at 200 °C: (a) CH$_4$; (b) NH$_3$; (c) HMDSO.

produced is approximately the same as the equivalents of ammonia and nitrogen produced. Thus, there exists a connection between these products in one aspect of the reaction mechanism. However, the temperature dependence of the amount produced of each of these products differs (Figure 9). The amount of ammonia produced at 380 °C is approximately one-third that produced at 200 °C. The amount of HMDSO produced is reduced by 2 orders of magnitude over the same range of conditions. The sharp drop in HMDSO production is accounted for by the increased amounts of methane produced; silyl moieties that have lost pendant methyl groups can no longer form HMDSO but must remain bound to the surface.

The most noteworthy feature of the dependence of the distribution of products on temperature of reaction is that the effect on methane production is opposite the effect on all other volatile products (Figure 9). Total methane production increases dramatically with increasing temperature of reaction. Total amounts of ammonia, HMDSO, and nitrogen each decrease with increasing temperature. Thus, the step in the reaction mechanism by which methane is formed must be distinct from one or

Me_3SiCl, which can be irreversibly adsorbed, and thus with the number of available cus Al^+ and O^- sites suggests that the HMDS is predominantly chemisorbed by a dissociative mechanism, as illustrated by reaction 2.

4.2. Methane Formation. The amount of methane produced increases dramatically with increasing temperature of reaction. Also, when γ-Al_2O_3 first reacts with HMDS at 200 °C and the product is then heated to higher temperatures, the amount of methane produced again increases with increasing temperature. This behavior directly parallels the reaction of γ-Al_2O_3 with Me_3SiCl.[23,24] However, there are two significant differences between the reactions of γ-Al_2O_3 with Me_3SiCl and HMDS. In the former reaction the generation of methane occurs rapidly upon the interaction of Me_3SiCl with the surface of γ-Al_2O_3. In the latter reaction the major production of methane does not occur until after a significant amount of time has elapsed, which is a function of temperature. Second, the maximum number of methane molecules formed per HMDS molecule consumed is attained at a much higher temperature than for Me_3SiCl. These differences in behavior are attributed to the difference in inductive power between the $-Cl$ and $-NHSiMe_3$ moieties, which bind to the aluminum cus. The strong inductive effect of Cl increases the Brønsted acidity of neighboring hydroxyls and thus promotes the reaction of proximate hydroxyl and $-OSiMe_3$ groups to eliminate methane and form bridging $-OSiMe_2O-$ groups.[23,24] The $-NHSiMe_3$ groups have a lesser inductive effect. Consequently, the nearby hydroxyls will be less acidic than in the previous case, and the reaction to form methane does not occur until after a significant number of $-OSiMe_3$ and $-NHSiMe_3$ are present on the surface (eq 3).


(3)
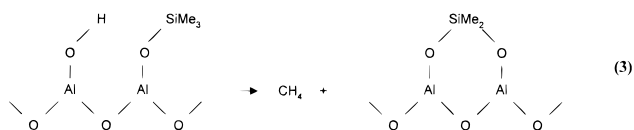
The increase in the amount of methane produced with increasing temperature of reaction, or subsequent thermal treatment, is consistent with reaction 3. The number of hydroxyl groups that become sufficiently active to react with $-OSiMe_3$ groups will increase with increasing temperature, and so more methane will be formed.

The molar amount of methane produced at temperatures greater than 300 °C exceeds the molar amount of HMDS reacted. Thus, more than one $Si-Me$ bond is cleaved per mole of HMDS. This, too, parallels the reactions of Me_3SiCl with γ-Al_2O_3.[24] or SiO_2.[25] The total methane produced per mole of HMDS reacted is lower than that for the corresponding reaction with Me_3SiCl at each temperature. This observation is also consistent with the proposed mechanism. The acidity of surface hydroxyls is lower on γ-Al_2O_3 treated with HMDS than on γ-Al_2O_3 treated with Me_3SiCl, and so the extent of reaction 3 is also lower. At temperatures greater than 380 °C the amount of methane liberated exceeds four moles of methane per mole of HMDS reacted. The majority of the silicon is retained at the surface at temperatures over 300 °C. Thus, the process of methane elimination has the effect of irreversibly binding the silyl groups to the surface. Further, since the amount of nitrogen irreversibly bound is smaller than the amount of silicon (section 4.4 below), the silyl groups are largely present as surface $-O_{4-x}$-$SiMe_x$ groups and less as $-NHSiMe_3$ or derived groups.

4.3. Formation of HMDSO. The reaction of γ-Al_2O_3 with HMDS had previously been assumed to be a metathetical reaction to form surface $-OSiMe_3$ groups and ammonia.[15-17] We have now shown for the first time that significant amounts

of HMDSO and small amounts of nitrogen are formed, especially at temperatures below 380 °C. To form HMDSO, a silyl group must be transferred to an existing $-OSiMe_3$ moiety from another source, Me_3SiX. The nature of the group X cannot be determined unambiguously from the available evidence, but the amount, rate, and timing of formation of HMDSO are consistent with reaction of neighboring surface $-SiMe_3$ groups (eq 4).

(X = O, NH)
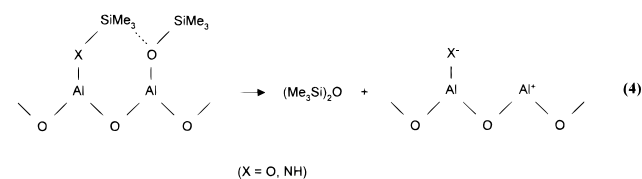
However, the possibility of some reaction of surface $-OSiMe_3$ groups with gas-phase HMDS cannot be discounted.

The amount of HMDSO produced is inversely dependent upon the temperature of reaction. This observation is consistent with reactions 3 and 4. As the rate of reaction 3 increases, more $-OSiMe_3$ groups are rapidly consumed to form silyl groups multiply bound to the surface and are therefore no longer available for reaction 4. This effect is especially important when X is O.

4.4. Formation of Ammonia and Nitrogen. Dissociative chemisorption of HMDS on the surface of γ-Al_2O_3 will afford surface $-NHSiMe_3$ groups (eq 2). The formation of ammonia from a surface $-NHSiMe_3$ group, or HMDS, requires the transfer of two hydrogen atoms to the nitrogen center, as in eq 1. The $Al-N$ bond is thermally strong but chemically labile.[26] Thus, the severance of this bond by reaction with a Brønsted acid will be facile. The $Si-N$ bond is also thermally strong and is less readily cleaved by acid than is an $Al-N$ bond.[26] We have seen that HMDSO and NH_3 are formed during essentially the same period of reaction at all temperatures (Figures 1−3). This observation suggests that amido groups from which the silyl group has been removed, as in eq 4 (X = NH), are readily converted to ammonia and liberated from the surface.

It is noteworthy that the amount of nitrogen that is retained in the solid products after the reaction is consistently lower than the amount of silicon retained as pendant or bridging silyl moieties (Table 3). These data show that the number of pendant $-NHSiMe_3$ groups retained at the surface is lower than the number of $-OSiMe_3$ groups, or corresponding bridging groups.

The total nitrogen in the solid product and the ammonia in the exit gases is less than the total nitrogen in the HMDS consumed. No other amine product is detected. The discrepancy between these amounts of nitrogen is attributed to oxidation of a portion of the nitrogen compounds to form elemental nitrogen. To test this proposal, a series of reactions of γ-Al_2O_3 with HMDS was conducted at different temperatures using each of argon and helium as the carrier instead of nitrogen. Molecular nitrogen was detected in the exit gases in molar quantities approximately corresponding to the difference between the HMDS consumed and other nitrogen-containing products, thus accounting for the above discrepancy. The oxidation of nitrogen compounds to elemental nitrogen by alumina was unexpected, but oxidative reactions at the alumina surface are precedented. When H_2S is passed over γ-Al_2O_3, initially a fraction of the H_2S is oxidized to elemental sulfur by surface oxide species, which cannot be readily removed using common methods.[28]

Thus, the reaction of HMDS with γ-Al_2O_3 is distinct from that of Me_3SiCl. For the latter, the methane formation reaction occurs readily and rapidly, and formation of methane im-

mediately parallels uptake of Me_3SiCl.[23,24] This effect is attributed to the inductive effect of chloride, which effects an increase in the Brønsted acidity of the neighboring Al−OH groups. The inductive effect of a surface Al−NHSiMe₃ group will be much less than that for chloride.

IV. Conclusions

The gaseous products from the reactions of HMDS with dehydroxylated alumina include not only ammonia and traces of water but also methane, hexamethyldisiloxane, and nitrogen. The initial reaction in each case involves the formation of pendant −O−SiMe₃ and −NH−SiMe₃ groups. The subsequent reaction of these pendant groups with residual surface hydroxyls to form methane and siloxane bridging groups does not occur to a significant extent up to 200 °C. The amount of methane generated, which increases with increasing temperature up to 450 °C, is less than that formed when the same oxides are silated using Me_3SiCl. This effect is attributed to the higher inductive effect of surface chloride compared with surface amido groups and the consequent lack of strongly acidic surface hydroxyl groups in the latter case.

After most of the coordinatively unsaturated sites have reacted with HMDS, further reaction occurs between HMDS and surface hydroxyls to eliminate methane, ammonia, nitrogen, and hexamethyldisiloxane.

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