

Mechanism of Silation of Silica with Hexamethyldisilazane

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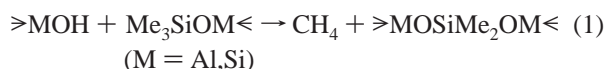
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Received: May 24, 1999; In Final Form: October 20, 1999

The silation of silica with hexamethyldisilazane (HMDS) was examined over the temperature range 150–450 °C. The products and sequence of the reactions at the silica surface were determined. The major products are hexamethyldisiloxane (HMDSO) and ammonia, with lesser amounts of nitrogen and methane. No methane is produced during reactions below 300 °C. Ammonia is the initial product detected, followed by HMDSO. The amount of nitrogen produced increases, and the amount of ammonia and HMDSO produced decreases, with increasing temperature of reaction. A mechanism is proposed. The reaction of HMDS with silica is sequential. Reaction of pendant silyl groups with surface acidic hydroxyls to eliminate methane and the concentration of residual silyl moieties on the silica surface both increase with temperature of reaction.

I. Introduction

We have previously shown that the extent of reaction, the sequence of reaction, and the nature of the gaseous and solid products from silation of dehydroxylated γ -Al₂O₃ with hexamethyldisilazane (HMDS) each depends on the temperature of reaction.¹ We have also shown that silation reactions of SiO₂ and γ -Al₂O₃ with Me₃SiCl are similar in some aspects, but differed in others.^{2–4} The reaction of Me₃SiCl with γ -Al₂O₃ occurs initially with surface coordinatively unsaturated sites (cus) to afford pendant –O–SiMe₃ groups.^{2,3} The inductive effect of the surface bound chloride enhances the acidity of neighboring surface hydroxyls, which subsequently react with the pendant –O–SiMe₃ groups to eliminate methane and form bridging –O–SiMe₃–O– groups.



Differences between the reactions of SiO₂ and Al₂O₃ include the slower and less extensive silation of SiO₂,⁴ the instantaneous formation of methane on reaction of γ -Al₂O₃, even at 200 °C,^{2,3} and the higher amount of methane produced on silation of γ -Al₂O₃.^{2,3} A significant difference is that reaction of Me₃SiCl with surface hydroxyls of SiO₂ also forms HCl,⁴ but this reaction does not occur with γ -Al₂O₃.^{2,3}

HMDS is often used as a silylating agent, especially for silica.^{5–7} A commercial product, Wacker HDK H2000, is a highly porous silica (Wacker HDK N20) silylated with HMDS.⁵ The properties of catalysts such as rhodium complexes on silica silylated with HMDS have been studied.⁷ The electron-transfer capability of titania is reduced when it is silylated with HMDS.⁸ Silation of surfaces of oxides involves reactions of surface hydroxyl groups.^{9–13} The surface of the oxide is rendered less hydrophilic when the surface hydroxyls are replaced or removed by silation.^{14–17} Changing the surface properties in a controlled manner enhances the utility of an oxide for analytical, separation or catalytic processes.^{18–21}

The surface species present on silylated silica have been assumed to be Me₃Si–X– (X = O, NH). Our earlier studies suggest that bridging silyl species may also be formed. The objective of the present study is to determine the nature of silyl species on the surface of silica silylated with HMDS. We have studied the silation of SiO₂ with HMDS at temperatures in the range 150–450 °C and have determined the nature of the gaseous and solid products. We will show that the reaction produces ammonia, hexamethyldisiloxane (HMDSO), and nitrogen at all temperatures, and small amounts of methane when the silation temperature is at least 300 °C. Further, we will show that the extent of reaction and product distribution depend on the temperature of reaction, and that the mechanism involves a sequence of reactions.

II. Experimental Section

Materials. Commercially available silica in granular form (CS2040, PQ Corp.) and HMDS from two commercial suppliers were used. HMDS (Aldrich, 99.9%) was analyzed using GC-MS and was used as received. HMDS (GIC, 98.0%) was double distilled before use. Each sample of HMDS was stored under nitrogen (Matheson, UHP) and transferred to a glass evaporator purged constantly with the inert gas (N₂, He, or Ar) used as carrier in each experiment.

Equipment. The dynamic method and equipment used in this study were the same as described previously.^{1–4}

Experimental Procedure. Silation of SiO₂ with HMDS was examined in the temperature range 150–450 °C. The reactor was dried and charged with dried SiO₂ under a continuous stream of dry N₂ or He. The SiO₂ was dehydroxylated by gradually increasing the temperature to 500 °C for 24 h. The charge of SiO₂ after dehydroxylation (12.0–12.2 g) and the weight of solid product after silation were determined by cooling the reactor slowly to room temperature in a stream of N₂, closing the reactor, and weighing. The BET surface area of the dehydroxylated silica was 452 m²·g^{–1} and the total pore volume was 2.60 cm³·g^{–1}. The reactor was then heated to a selected temperature (150–450 °C). When the temperature had stabilized, the stream of N₂ was switched to the HMDS in N₂ or He feed stream. The concentration of HMDS in the feed stream

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TABLE 1: Amounts of HMDS Consumed and Volatile Products Formed^a

reaction temp (°C)	HMDS consumed (mol × 10 ³)	volatile products							
		NH		N ₂		HMDSO		CH ₄	
		mol × 10 ³	NH ₃ /HMDS	mol × 10 ³	N ₂ /HMDS	mol × 10 ³	HMDSO/HMDS	mol × 10 ³	CH ₄ /HMDS
200	15.5	11.5	0.74	1.1	0.07	8.0	0.52	0	0
300	14.4	9.0	0.62	1.2	0.08	8.1	0.56	0.03	0.002
350	13.4	7.9	0.59	2.3	0.17	5.7	0.42	0.05	0.004
400	13.4	6.1	0.45	3.0	0.22	2.8	0.21	0.06	0.004

^a Duration of consumption of HMDS and production of each product is estimated from GC analyses of the exit stream at 30 min and 1 h intervals.

was varied between 8.5×10^{-4} and 16.8×10^{-4} mol·L⁻¹ (all values are corrected to STP), determined gravimetrically, by changing the temperature of the saturator. A flow rate was selected between 10 and 40 cm³·min⁻¹. The majority of reactions were performed using the same values for HMDS concentration (9.7×10^{-4} mol(HMDS)·L⁻¹) and flow rate (13.65 cm³·min⁻¹), to enable direct comparison of results at different temperatures. HMDS was fed to the reactor in a stream of inert gas (N₂ or He) continuously for 1000–1200 min, until the composition of the exit gas stream showed that no further reaction of HMDS was occurring. The feed stream was switched to N₂ for at least 1 h, and then the reactor was slowly cooled to room temperature. The composition of the exit gas stream was monitored by GC analysis at 30 min intervals and confirmed by IR analysis. The total molar amounts of NH₃, HMDSO, N₂, and CH₄ produced and HMDS consumed during each run were calculated using the reaction profiles in Figures 1–4 (Table 1).

Instrumental Methods. The surface area and pore volume of solid samples were determined by the BET method, nitrogen adsorption–Kelvin condensation at liquid nitrogen temperature, using an Omnisorp 360 sorptometer. Pore size distributions were determined using desorption isotherms.

Gas chromatographic analyses (GC) of the feed and exit gas streams were performed using a Hewlett-Packard 5890 Series II gas chromatograph with a Hewlett-Packard HP3396A integrator. The GC column (5 ft × 1/8 in. o.d.) was packed with Porapak T and operated at 120 °C.

Fourier transform infrared (FTIR) spectroscopic data were collected using a Nicolet 730 FTIR spectrometer. Gas phase samples were collected and analyzed in a 10 cm glass cell (76.4 cm³) with KCl windows.

Elemental analyses (CHN) of solid samples were performed using a Carlo Erba CHNS–O instrument equipped with a GC TCD EA 1108 elemental analyzer.

ESCA determinations of the elemental composition of surfaces of selected solid products were performed using a VG Scientific Escalab Mark II system with a hemispherical analyzer operating in the constant pass energy mode.

III. Results and Discussion

To enable direct comparisons of results of silation of SiO₂ at different temperatures all other conditions were kept constant. Samples were sequentially dehydroxylated at 500 °C for 24 h, cooled and weighed, heated to the selected temperature, and siliated using either HMDS/N₂ or HMDS/He at a concentration of 9.7×10^{-4} mol(HMDS)·L⁻¹ and a flow rate of 13.6(5) cm³·min⁻¹. Thus, the feed rate was 0.13 g(HMDS)·h⁻¹. Runs were performed within the range 150–450 °C. There was no significant difference between silation at 150 and 200 °C, and little difference between silation at 400 and 450 °C. Therefore, only the runs at 200, 300, 350, and 400 °C will be described in detail.

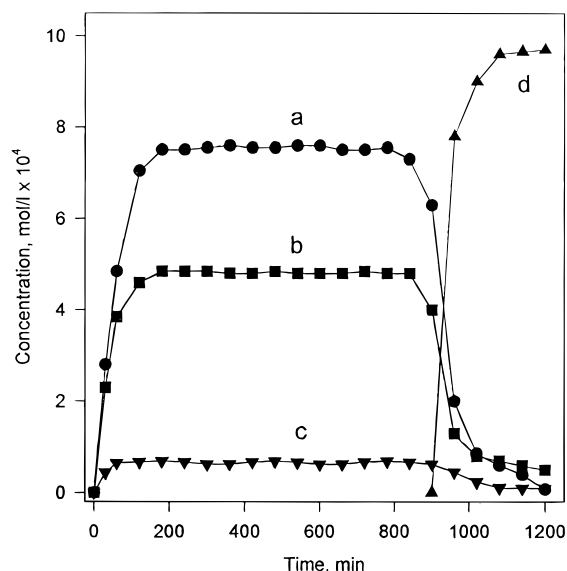


Figure 1. Silation of silica at 200 °C: (a) NH₃; (b) HMDSO; (c) N₂; (d) HMDS.

Runs were also performed at other flow rates in the range 10–40 cm³·min⁻¹, and with feed concentrations in the range $(8.5\text{--}16.8) \times 10^{-4}$ mol(HMDS)·L⁻¹. It was determined that the rate of the reaction varied with the concentration of HMDS in the feed, but that the nature and amounts of each product and the nature of the reaction depend on the temperature of silation and the feed rate.

1. Gaseous Products of Silation Reactions. The reaction products at all temperatures were NH₃, HMDSO, and N₂. CH₄ was produced during silation at temperatures at least 300 °C (Figures 1–4). In all the cases, all HMDS was consumed during an extended period of silation, after which the concentration of HMDS in the exit gas stream increased steadily until it attained the same value as the feed stream concentration. At each temperature the concentration of each gaseous product was initially zero. Then, in some cases after an induction period, the concentration of each product rose until it attained a steady value. Finally, coincident with termination of silation as shown by breakthrough of HMDS, the concentration of gaseous products began to diminish. One or more products continued to be produced even after the concentration of HMDS in the exit stream showed that no further silation was occurring. This shows that these products were being formed in reactions after the initial reaction of HMDS with the surface of SiO₂. The duration of silation was dependent upon the temperature of reaction, as were the absolute and relative amounts of gaseous products formed.

1.1. Silation at 200 °C. HMDS was consumed totally during the first 15 h of reaction (Figure 1). After 16 h reaction the concentration of HMDS in the exit stream rose rapidly to greater

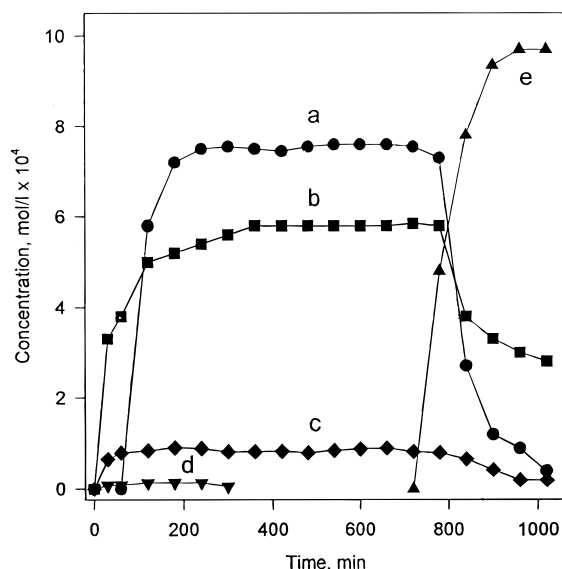


Figure 2. Silation of silica at 300 °C: (a) NH_3 ; (b) HMDSO; (c) N_2 ; (d) CH_4 ; (e) HMDS.

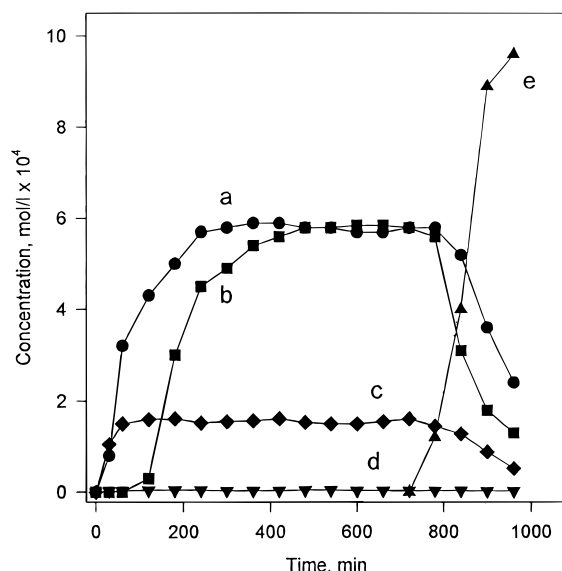


Figure 3. Silation of silica at 350 °C: (a) NH_3 ; (b) HMDSO; (c) N_2 ; (d) CH_4 ; (e) HMDS.

than 80% of the value for the feed stream. The concentrations of HMDS in the feed and exit streams were the same after 18 h, showing that silation of SiO_2 was complete. The concentrations of NH_3 , HMDSO, and N_2 in the exit gas rose steadily during the first 3 h of the run, and then remained essentially constant during a further 11 h. No methane was detected throughout the run. The molar concentrations of NH_3 , HMDSO, and N_2 during this steady period of the reaction were the maximum values found. These values were approximately 80%, 50%, and 10%, respectively, of the molar concentration of HMDS ($9.7 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$) in the feed stream. The concentrations of each gaseous product then declined during the final 6 h of the run, until these concentrations became very small after completion of the 20 h run. Essentially all N from the HMDS consumed was found in the gaseous products NH_3 and N_2 (Table 1). Approximately 50% of SiMe_3 groups formed HMDSO. The remaining 50% of $-\text{SiMe}_3$ groups thus remained as pendant $-\text{O}-\text{SiMe}_3$ groups on the surface of the siled SiO_2 , as confirmed by elemental (C, H, N) and ESCA analyses (vide infra).

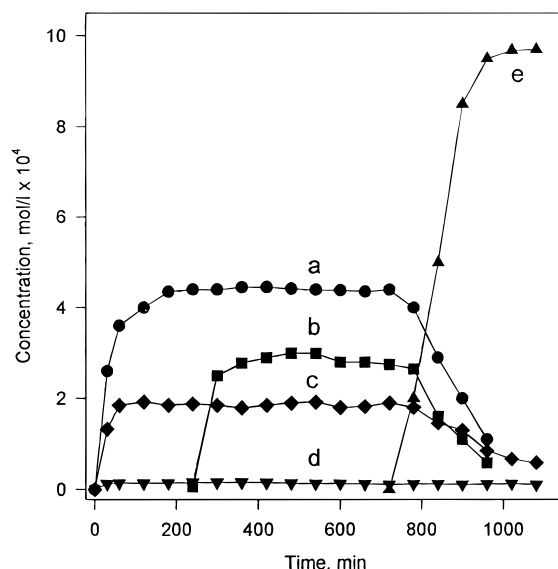


Figure 4. Silation of silica at 400 °C: (a) NH_3 ; (b) HMDSO; (c) N_2 ; (d) CH_4 ; (e) HMDS.

1.2. Silation at 300 °C. Less HMDS was consumed in the reaction at 300 °C than was consumed at 200 or 350 °C. Breakthrough of HMDS into the exit stream occurred after 12 h (Figure 2), and the concentration of HMDS rose steadily until 16 h reaction, after which the concentrations of HMDS in the feed and exit streams were identical.

No NH_3 was detected until after 1 h reaction, but HMDSO, N_2 , and traces of CH_4 were detected 30 min after the start of HMDS feed. The maximum, steady concentration of NH_3 in the exit stream was approximately 80% of the value for HMDS in the feed, and lasted from 4 to 13 h after the initiation of HMDS feed. The decline in NH_3 concentration commenced 1 h after the breakthrough of HMDS into the exit stream and that concentration became very low after 17 h reaction.

The concentration of HMDSO rose steadily during the first 6 h reaction until it reached a maximum value approximately 60% of that of HMDS in the feed stream. The maximum concentration of HMDSO then remained constant for 7 h, after which it declined gradually to a value of approximately 30% over a further 4 h. The run was terminated when the HMDS concentration in the exit stream showed that silation was complete after 17 h total reaction time. The concentrations of NH_3 and N_2 were essentially zero. However, in repeated experiments it was shown that a small exit concentration of HMDSO was detectable in the exit stream even after shutting off the supply of HMDS and flushing the reactor with pure N_2 or He. The small amount of HMDSO generated after shutting of the supply of HMDS has been included in the results (Table 1).

The molar concentration of N_2 rose to a maximum, steady value close to 10% of the concentration of HMDS in the feed stream. Essentially all N from HMDS formed NH_3 or N_2 , and no significant amounts (elemental analysis, ESCA) remained on the surface of siled SiO_2 (vide infra).

Very small amounts of CH_4 were produced during the initial 5 h reaction, but no CH_4 was detected in the exit stream after that time.

1.3. Silation at 350 °C. All HMDS feed was consumed up to 13 h reaction time, after which time the concentration of HMDS in the exit stream rose during the next 3 h to the same value as the feed (Figure 3).

No HMDSO was detected in the exit gases until 2 h following initiation of HMDS feed. The concentration of HMDSO then

rose slowly over the next 6 h to a maximum, steady concentration approximately 60% of that for HMDS in the feed stream. The maximum concentration of HMDSO was sustained for a further 5 h, after which it declined rapidly to approximately 15% when the run was terminated after 16 h. The decline in HMDSO concentration coincided with the breakthrough of HMDS into the exit stream.

A small concentration of NH_3 appeared in the exit stream 30 min after initiation of HMDS feed. The concentration of NH_3 then rose steadily over the next 4.5 h to a maximum value close to 60% of the concentration of HMDS in the feed. The maximum value was sustained during the following 8 h, and then slowly declined, coincidentally with breakthrough of HMDS into the exit stream, to approximately 30% at the termination of the run (16 h).

The concentration of N_2 in the exit stream rose immediately after initiation of the reaction, attaining a maximum value after 1 h which was slightly lower than 20% of the concentration of HMDS in the feed. The maximum concentration of N_2 was then sustained for a further 12 h. The concentration of N_2 declined following breakthrough of HMDS into the exit stream, to a value less than half the maximum value after 16 h reaction.

Methane was detected, at low concentrations, in the exit stream, throughout the 16 h run. The total molar amount of methane corresponded to less than 1% of the molar amount of HMDS consumed (Table 1).

1.4. Silation at 400 °C. HMDS breakthrough into the exit stream occurred after 12 h reaction time (Figure 4). The concentration of HMDS then rose steadily over the next 5 h, until the concentrations of HMDS in the feed and exit streams were identical.

No HMDSO was detected in the exit stream until 5 h reaction time. The concentration of HMDSO then rose rapidly and was sustained at values between 25% and 30% of the concentration of HMDS in the feed for the next 8 h. The concentration of HMDSO declined following breakthrough of HMDS into the exit stream, and no HMDSO was detected in the exit stream after 17 h total reaction time.

The concentration of NH_3 in the exit stream rose rapidly following initiation of HMDS feed, attaining a maximum value after 3 h reaction time. The maximum value was sustained during the next 9 h, at a value approximately 45% of the concentration of HMDS in the feed stream. The concentration of NH_3 declined coincidentally with the breakthrough of HMDS into the feed stream. No further NH_3 was detected after 17 h total reaction time.

A small concentration of CH_4 was detected in the exit stream throughout the duration of the 18 h run. The molar amount of CH_4 was less than 1% of the molar amount of HMDS consumed.

1.5. Thermolysis of Silated SiO_2 . A sample of SiO_2 silated at 200 °C, as above (section 1.1), was heated in steps to 260, 320, and 380 °C. At each increase in temperature small but significant amounts of CH_4 were eliminated (Figure 5). The incremental amount of CH_4 eliminated increased with increasing temperature. These data suggest that increasingly higher numbers of surface hydroxyl groups are being thermally activated with increasing temperature,³ enabling reaction between neighboring surface hydroxyl and pendant $-\text{O}-\text{SiMe}_3$ groups (section 4, below).¹⁻⁴

2. Solid Products of Silation Reactions. Each sample of silated SiO_2 was weighed in the reactor in which silation had been performed. The expected increase in mass of the sample was calculated from the difference between the mass of HMDS consumed and the sum of the masses of the gaseous products.

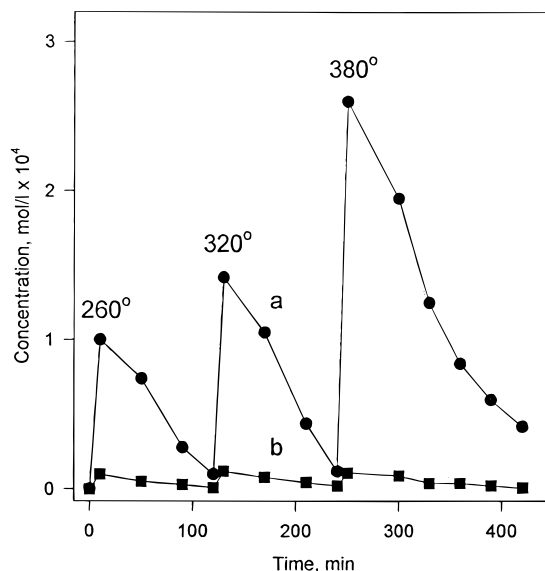


Figure 5. Evolution of CH_4 (a) and HMDSO (b) on heating SiO_2 silated at 200 °C.

In each case the mass increase determined by weighing (Table 2) was greater than the difference in mass between the feed consumed and gaseous products. The accuracy of the mass balance, as determined by weighing the SiO_2 charge and silated SiO_2 within the reactor, may have been compromised by the much greater mass of the reactor. The impact of this discrepancy on the overall C and N mass balance is not significant, as will be discussed below.

Elemental analyses (C, H, N) of ground samples of all solid products, and ESCA analyses of the surfaces of selected samples, were performed to determine the composition of the solid products from silation at different temperatures. The small masses of N and C in the solid products, calculated using elemental analyses and the weighed mass of silated SiO_2 , are also presented in Table 2.

The concentration of silyl groups arising from HMDS was small compared to the concentration of Si from silica. Consequently, ^{29}Si could not be used to determine concentrations of the different silyl species present at the surface. Bands in the IR due to the environment of CH_3 are at similar values close to 2965 (s) and 2907 (w) cm^{-1} . Bands due to $(\text{CH}_3)_3\text{Si}$, close to 1260 cm^{-1} , are masked by SiO_2 lattice vibrations. The intensity of the hydroxyl bands decreases with increasing temperature of reaction, which is consistent with the proposed reaction scheme. In particular, a sharp band at 3741 cm^{-1} in the spectrum of silica is absent from the spectra of the silated silica. This shows that isolated acidic hydroxyls react readily with HMDS. Further discussion of the IR spectra of silated alumina and silica will be presented in a subsequent paper.

3. Mass Closure. The C and N contents for the silated SiO_2 were determined by crushing multiple samples of each solid product and then performing elemental analyses. The values for N were essentially zero for products of runs at 200 and 300 °C, and very low for products of runs at 350 and 400 °C. The values for C and N varied from sample to sample of the same product, showing that silation had not occurred evenly throughout the bulk of each product. This suggests that there was restricted mass transfer to the interior of each particle. Averaged values for analyses from multiple samples are reported in Table 2, and so there remains some degree of uncertainty in the C and N values for solid products. Nevertheless, it is readily seen from inspection of the data in Table 2 that a reasonable C and

TABLE 2: Mass Balance

reaction temp (°C)	solid product mass increase (g)	nitrogen content $\times 10^3$ (g·atom)			carbon content $\times 10^3$ (g·atom)		
		MHDS consumed ^a	volatile products ^a	solid products ^b	HMDS consumed ^a	volatile products ^a	solid products ^b
200	1.38	15.5	13.5	trace	93.0	48.0	54.8
300	1.39	14.4	11.4	trace	86.4	48.6	48.6
350	1.44	13.4	12.5	0.7	80.4	34.25	52.7
400	1.87	13.4	12.1	0.75	80.4	16.9	59.0

^a GC and FTIR analyses of feed and exit streams. ^b Averaged elemental analyses of ground samples of solid products.

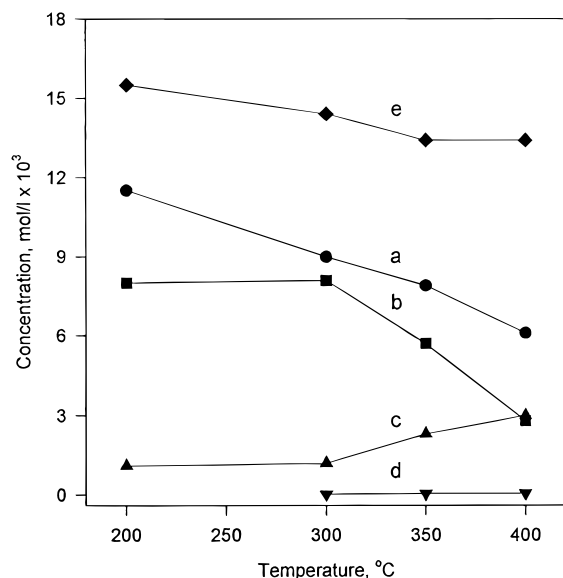


Figure 6. HMDS (e) consumed, and NH_3 (a), HMDSO (b), N_2 (c), and CH_4 (d) formed during silation of SiO_2 , as a function of temperature.

N mass balance has been achieved. The amount of C and N in the solid product is consistent with the difference between HMDS consumed and the volatile products determined from analyses of the exit stream.

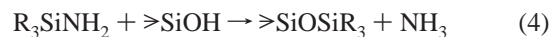
The total amounts of C and N in the gaseous and solid products have been calculated using both the weighed and calculated increase in mass of the solid products. The difference between the weighed mass of the solid products and the calculated mass is in all cases below 4%. Thus, the error in total mass of either C or N arising from an error in determining the mass of the solid product is lower than the differences found between analyses of different samples of the solid product, and any error in calculated C or N mass in the solid product does not significantly affect the total C and N mass balance calculated (Table 2).

4. Mechanism of Silation. The relative amounts of HMDS consumed and NH_3 , HMDSO, N_2 , and CH_4 produced depend on the temperature of silation (Figure 6). The amount of HMDS consumed varies only slightly with temperature, indicating that the extent of the initial reaction of HMDS with the surface of SiO_2 depends only on the number of available and active hydroxyl sites.

The amounts of NH_3 , HMDSO, N_2 , and CH_4 produced vary greatly with temperature of silation. The amounts of NH_3 and HMDSO decrease with increasing temperature of reaction. The amount of N_2 increases slightly with temperature, as does the small amounts of CH_4 produced in reactions at 300 °C or higher temperatures. These data indicate that the surface moieties formed in the initial reaction of HMDS with the surface of SiO_2 then react further by at least two competing pathways.

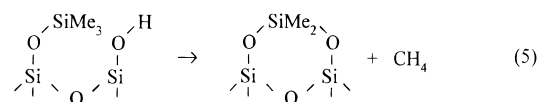
In our previous reports we have shown that HMDS reacts with the surface coordinatively unsaturated sites (cus) of $\gamma\text{-Al}_2\text{O}_3$

to form surface $-\text{O}-\text{SiMe}_3$ and $-\text{NH}-\text{SiMe}_3$ moieties.¹ There are two subsequent reactions. Reaction between neighboring pendant silyl groups forms HMDSO.¹ Neighboring acidic hydroxyls react with silyl groups to eliminate CH_4 and form $-\text{O}-\text{SiMe}_2-\text{X}-$ ($\text{X} = \text{O}, \text{NH}$) groups.¹⁻⁴ In contrast to $\gamma\text{-Al}_2\text{O}_3$, SiO_2 has relatively few cus, and so silation occurs predominantly by reaction with surface hydroxyls.³ An initial reaction of HMDS, either preadsorbed or from the gas phase, with the surface of SiO_2 results in formation of pendant $-\text{O}-\text{SiMe}_3$ groups (eq 2). However, any Me_3SiNH_2 so formed is then rapidly consumed by either of two rapid reactions. It is known that sterically unhindered aminosilanes, R_3SiNH_2 , are inherently unstable to disproportionation (eq 3), and also react readily with protonic reagents, which will include surface hydroxyls, to liberate NH_3 (eq 4).²² Thus, as we have found, no Me_3SiNH_2 appears in the exit stream, but copious amounts of ammonia are formed immediately after initiation of silation with HMDS (Figures 1-4).



HMDSO is a major product of silation of SiO_2 with HMDS at all temperatures studied. However, the onset of formation of HMDSO varies with temperature. At 200 °C, HMDSO is formed essentially from the initiation of silation (Figure 1). At 400 °C, HMDSO is not formed until 4 h after initiation of silation (Figure 4). Further, the amount of HMDSO formed decreases with increasing the temperature of silation (Figure 6). Thus, the reaction by which HMDSO is formed is not an initial reaction, and is not thermally promoted in a direct manner. It is also unlikely that HMDSO is formed by reaction of HMDS with pendant $-\text{O}-\text{SiMe}_3$ groups, as both are present from initiation of silation but HMDSO is not formed immediately for reactions at temperatures of at least 300 °C. It is noteworthy that the delay in formation of HMDSO coincides with the formation of small amounts of CH_4 , and the length of the delay increases with the amount of CH_4 formed. These data suggest that a competitive reaction is occurring.

We have shown that acidic hydroxyls at the surface of oxides react with pendant $-\text{O}-\text{SiMe}_3$ groups to liberate CH_4 and form bridging $-\text{O}-\text{SiMe}_2-\text{O}-$ groups (e.g., eq 5).¹⁻⁴



The rate and extent of reaction 5 increases with increasing temperature. Any silyl group that no longer be available to form HMDSO. These data suggest that, at temperatures of 300 °C or higher, acidic hydroxyls on the surface of

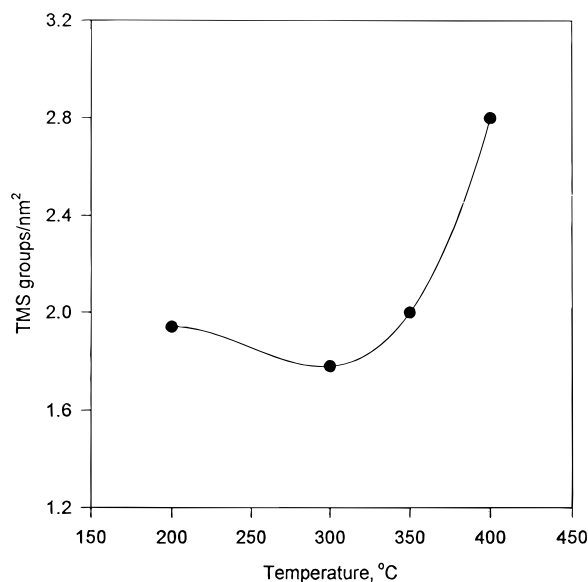
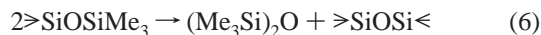


Figure 7. Concentration of surface silyl groups as a function of temperature of silation reaction.

silated SiO_2 initially react rapidly with neighboring pendant $-\text{O}-\text{SiMe}_3$ groups to liberate CH_4 . Thereafter, the concentration of intact $-\text{O}-\text{SiMe}_3$ groups begins to increase, and neighboring $-\text{O}-\text{SiMe}_3$ groups are then able to react to form HMDSO (eq 6).



No CH_4 is produced during silation of SiO_2 by HMDS at 200 °C, and so HMDSO is produced by reaction 6 immediately after initiation of silation (Figure 1). At 300 °C, after formation of HMDSO has commenced, HMDSO and CH_4 are produced concurrently for a short time (Figure 2). HMDSO and CH_4 are produced concurrently for an extended period at 350 °C (Figure 3) and 400 °C (Figure 4). The rates of formation of CH_4 and HMDSO at 350 and 400 °C decline coincidentally with the decline in rate of consumption of HMDS (Figures 3,4). These data suggest that reactions 5 and 6 continue, in a competitive manner, at these temperatures until silation of SiO_2 by HMDS is completed.

The net effect is that the amount of HMDSO formed, as a proportion of HMDS consumed, decreases with increasing temperature (Table 1), and the number of surface-bound silyl groups increases with increasing temperature (Figure 7). The surface silyl groups include both pendant $-\text{O}-\text{SiMe}_3$ groups, and bridging groups from which methyl groups have been removed by elimination of methane.

The concentration of residual hydroxyl groups on the surface of silica dehydroxylated at 500 °C is 3–4 OH/100 Å². The hydroxyl groups include both isolated and proximate hydroxyls, and hydrogen-bonded adjacent hydroxyls.²³ The acidity of each type of hydroxyl depends on the nature of the site at which it is bonded and on the inductive influence of neighboring moieties. We have shown that elimination of CH_4 requires the reaction of a pendant $\text{Me}_3\text{Si}-\text{O}-$ group with an adjacent acidic hydroxyl.^{1–4} The low levels of CH_4 produced during silation of silica with HMDS show that the concentration of acidic hydroxyls adjacent silyl groups from silation of silica with HMDS is very low. In turn, this suggests that a high proportion of the most acidic hydroxyls are consumed in the initial reaction of HMDS and in the subsequent reaction to form ammonia (vide supra).

The predominant nitrogen-containing product at all temperatures is NH_3 (Figure 6). The majority of the remaining N from HMDS forms N_2 , and a small amount of N remains bound to the surface after silation at temperatures 300 °C or higher. We had earlier found that N_2 was also formed during silation of $\gamma\text{-Al}_2\text{O}_3$ with HMDS,¹ in a manner similar to formation of limited amounts of elemental sulfur when H_2S is passed over alumina.²⁴ Thus, an oxidation reaction in which N_2 is formed, although unexpected, is preceded. The oxidative reaction to form N_2 involves surface oxide species, possible formed during calcination or dehydroxylation at 500 °C, which are not readily removed by thermal desorption or decomposition.

IV. Conclusions

The gaseous products from silation of SiO_2 with HMDS include NH_3 , HMDSO, and N_2 at all temperatures in the range 150–450 °C, and minor amounts of CH_4 at temperatures 300 °C or higher. The reaction is sequential. The initial reaction forms NH_3 and pendant $-\text{O}-\text{SiMe}_3$ groups. The major subsequent reaction is the reaction of neighboring pairs of $-\text{O}-\text{SiMe}_3$ groups to form HMDSO, at all temperatures 150–450 °C. A second, minor, competing subsequent reaction is the reaction of neighboring hydroxyl and $-\text{O}-\text{SiMe}_3$ groups to eliminate CH_4 and form bridging $-\text{O}-\text{SiMe}_2-\text{O}-$ groups, at temperatures 300 °C or higher. When a sample of SiO_2 that has been silated at 200 °C is subsequently heated in steps to higher temperatures, further amounts of CH_4 are eliminated as additional acidic hydroxyls are thermally activated.

Acknowledgment. This project was supported by The Research Grant from Natural Sciences and Engineering Research Council of Canada. ESCA surface analyses were performed by Dr. A. Adnot and Professor F. Larachi, Université Laval, to whom we are grateful.

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