spectra. In either event, the Raman intensity for the 324-cm^{-1} feature is weak relative to that of the ν_1 band for $Pt(en)_2Cl_2^{2+}$ units, and we conclude that the concentration of $Pt(en)_2ClBr^{2+}$ units in the mixed samples is small.

In earlier studies of pure PtCl,[3f,g] we observed a RR feature at ca. 287 cm^{-1} that gained intensity upon photolysis within the IVCT band. On the basis of agreement between Peierls–Hubbard model calculations and the observed excitation profile, we attributed this feature to the Pt–Cl stretch for a hole polaron. The 294-cm^{-1} band observed in $PtBr_{1-x}Cl_x$ (x = 0.11 and 0.55) exhibits an excitation profile that is similar to that observed for the hole polaron RR vibration in pure PtCl. Accordingly, we attribute this mode to a hole polaron in the PtCl chains in the mixed-halide solids. At other excitation energies, we observe a peak near 260 cm^{-1} that mimics the excitation profile associated with the electron polaron defect mode in pure PtCl (263 cm^{-1}). More detailed spectral studies of local states and their dependences on Cl^- impurities in PtBr will be reported later.

The results obtained here help clarify the origin of the surprising differences between the RR spectra of PtBr and those of PtI and PtCl: $PtBr_{0.99}Cl_{0.01}$ crystals exhibit RR spectral features that are quite similar to those observed for PtI and PtCl.

Conclusions

These results show that the presence of Cl^- ion impurities in PtBr gives rise to the apparent dispersion and fine structure of the ν_1 mode observed in the RR data upon tuning the excitation energy through the IVCT band and that the PtBr ν_1 mode corresponds to the 166-cm^{-1} component. This is consistent with the previously reported sample dependence[3c] on the relative intensities of the 168–, 171–, 174–, and 181-cm^{-1} component bands, since the amount of PtCl present in PtBr will vary according to the method of preparation and purity of starting materials. Simple thermodynamic considerations demonstrate that the coexistence of $Pt(en)_2Cl_2^{2+}$, $Pt(en)_2Br_2^{2+}$, and $Pt(en)_2BrCl^{2+}$ in both solution and the solids is reasonable and expected using the standard preparative route. The polymorphism exhibited by PtBr at room temperature is suggested to result from variations in the relative concentration of Cl^- impurities and the associated change in T_c for the monoclinic to orthorhombic structural phase transformation. That PtCl can coexist with PtBr in these materials and lead to self-doping is an important consideration for future preparation of either pure or mixed-chain materials.

Acknowledgment. We thank Dr. Ed Garcia for important discussions concerning the crystal structures and structural phase transformations. We also acknowledge professor Susumu Kurita for first pointing out to us that PtCl undergoes a phase change near room temperature. This work was performed under the auspices of the U.S. Department of Energy with support from the Materials Science Division of the O.B.E.S. and the Center for Materials Science at LANL.

Registry No. $[Pt(en)_2Br_2][Pt(en)_2](ClO_4)_4$, 62535-08-4.

Thermal Reactivity of Hydrogenosilsesquioxane Gels

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The thermal reactivity under argon, air, and ammonia of the hydrogenosilsesquioxane gels prepared from trichloro- or trialkoxysilane was investigated by using a thermogravimetric analyzer interfaced with a mass spectrometer. Under argon these gels thermally decompose by two different mechanisms: (1) the cleavage of Si–H bonds gives rise to a loss of hydrogen; (2) a redistribution reaction of Si–H and Si–O bonds induces the escape of SiH_4. This second reaction, possibly catalyzed by residual hydroxyl groups, involves the formation of SiH_2 groups as evidenced by IR and solid-state NMR spectroscopies. It accounts for the thermograms obtained under air and ammonia.

Introduction

Previous papers pointed out that hydrogenosilsesquioxane gels $HSiO_{1.5}$ offer particular properties arising from the Si–H bond.[1-4] Thus these gels are hydrophobic unlike silica gels. Moreover they are reactive toward oxygen, chlorine, and alkenes. The thermal nitridation with ammonia provides an efficient route to silicon oxynitride glasses.[3,4]

However $HSiO_{1.5}$ gels decompose thermally under inert atmosphere. Previous authors reported the liberation of hydrogen and postulated thermal dehydrogenation involving the cleavage of the SiH bond.[1,5]

In this work, pyrolyses under argon, air, or ammonia were monitored by using a thermogravimetric analyzer (TGA/DTA) interfaced with a mass spectrometer. This apparatus allowed the continuous analysis of the gases evolved during thermolysis. The residual solid was studied by IR and solid-state NMR spectroscopies.

Table I. Conditions of Preparation and Characteristics of $HSiO_{1.5}$ Gels

gel	monomer	monomer concn, mol/L	water concn, mol/L	solvt	% H (theor 1.89)
a	$HSi(OEt)_3$	2.38	7.14	ethanol	1.75
b	$HSiCl_3$	0.66	1.32	THF	1.88
c	$HSiCl_3$	0.88	50	ether	1.88

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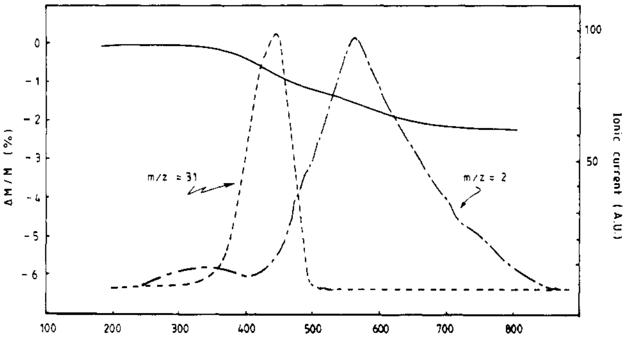

Figure 1. Thermal behavior of gel c under argon (heating rate 10 °C/min): (—) TGA curve; (-•-) H_2 evolution; (---) SiH_4 evolution.

Our results give evidence for another mechanism of dehydrogenation involving the formation of SiH_4[6] that accounts for special features of the thermal analyses under air or ammonia.

Experimental Section

The starting materials trimethoxysilane, triethoxysilane, and trichlorosilane were purchased from Fluka or Aldrich. Aminotrimethoxysilane and hexamethoxydisilazane were prepared according to the literature.[7-9]

Preparation of $HSiO_{1.5}$ Gels. The conditions of preparation and the characteristics of the three samples a–c that were studied are reported in Table I.

Typically compound a was obtained by adding dropwise water (3 equiv) into a stirred solution of $HSi(OC_2H_5)_3$ in ethanol (50% vol/vol) cooled at 0 °C. Gelation occurred after standing for about 15 h at room temperature without stirring. Solvent was evacuated under vacuum, at room temperature for 24 h and then at 150 °C for 24 h. The powder obtained was hydrophobic, and its IR spectrum showed only small absorptions due to hydroxyl groups.[2]

Trichlorosilane was worked up similarly in method b except that water (2 equiv) was diluted in THF before addition and that the solution mixture was stirred 24 h. Before drying, alternative washing procedures were used as shown in Table III.

Method c was described in ref 1.

The hydrogen content was determined by measuring the volume of H_2 gas evolved during alkaline attack of the gels.[2]

Specific surface areas were measured by adsorption/desorption of nitrogen according to the BET method, using a Carlo Erba Sorptomatic apparatus.

Infrared Spectroscopy. Transmission IR spectra were obtained by using KBr pellets on a Perkin-Elmer 298 IR spectrophotometer.

High-Resolution Solid-State NMR Spectroscopy. Proton-decoupled ^{29}Si NMR spectra were obtained on finely ground powders at 7.04 T, corresponding to 59.6-MHz resonance frequency, using a Bruker AM 300 Fourier transform NMR spectrometer and magic angle sample spinning (MASS) technique (spinning frequency was about 4.1 kHz). All spectra were accumulated by using 2K data points, with 0.080-s acquisition time. The usual 90° pulse angle experiment with phase cycling was used.

$^{29}Si\{^1H\}$ cross-polarization (CP) experiments displayed in Figures 7a and 9 were performed with contact times of 5 and 2 ms and repetition times of 60 and 10 s, respectively.

Experiments without cross polarization (Figure 7b) were performed using 600-s repetition time to deal with long spin–lattice relaxation times of nuclei.

All chemical shifts are given in ppm relative to TMS.

Thermal Analysis. Thermogravimetric analysis and differential thermal analysis were performed on a Netzsch STA 409 thermobalance coupled with a Kenos KSM 200 (EI 70 eV) mass spectrometer.

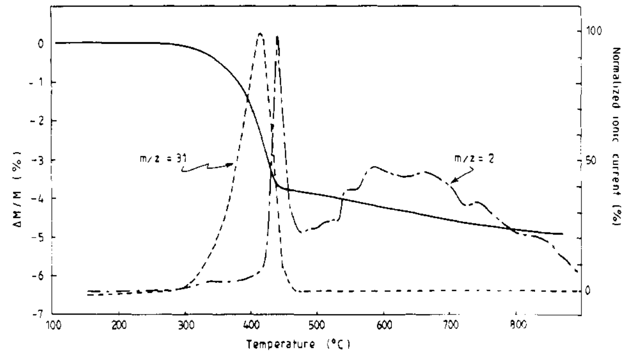

Figure 2. Thermal behavior of gel a under argon (heating rate 10 °C/min): (—) TGA curve; (-•-) H_2 evolution; (---) SiH_4 evolution.

Table II. Specific Surface Area and Loss of SiH_4, Expressed in wt % of the Starting Gel

gel	specific surf. area, m^2/g	% SiH_4 (w/w)
a	300–700	2–6
b	400–900	0–2
c	100–300	2–5

Table III. Influence of the Washing Conditions on the Release of SiH_4, Expressed in wt % of the Starting Gel (Preparation b)[a]

washing conditions	% SiH_4 (w/w)
no washing	2
washed with acetone, then diethyl ether	2
washed with water, then acetone and ether	6.3
heated 15 h at 80 °C, then washed with acetone and ether	0.9

[a] Drying procedure: 24 h at room temperature and then 24 h at 150 °C under vacuum.

Results and Discussion

Thermogravimetry: Evolved Gas Analysis. (a) Under Argon. Thermograms of dried $HSiO_{1.5}$ gels heated under argon usually show a two-step weight loss (Figures 1 and 2).

Analysis by mass spectroscopy of the gases evolved during the pyrolysis shows that the first step (between 300 and 500 °C) corresponds to an escape of SiH_4 (*m/z* 28 to 32 in the mass spectrum). This assignment was further confirmed by the IR spectrum of the trapped pyrolysis gases (characteristic stretching absorption at 2187 cm^{-1}[10]).

The amount of silane evolved varies from less than 0.5% (w/w) to more than 6% (w/w) depending on the preparative procedure of the gel (Table II). However general trends can be drawn:

(a) The SiH_4 escape is observed for gels prepared from alkoxysilanes as well as from chlorosilanes.

(b) The amount of SiH_4 is not correlated to the specific surface area of the gels, which varied from 200 to 900 m^2/g (Table II).

(c) The lowest losses of SiH_4 correspond to gels prepared by using a low (or no) excess of water, and a weakly nucleophilic solvent miscible with water such as THF (preparation b).

(d) The washing and drying procedures of the gel are of considerable importance; thus, washing of a sample with water and then with acetone and ether increases the silane

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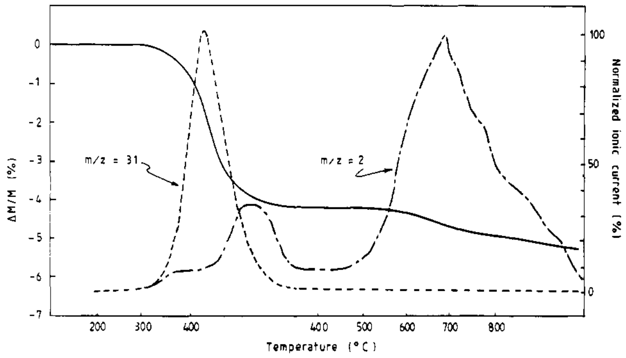

Figure 3. Thermal behavior of gel a under argon; heating schedule: +10 °C/min from 180 to 410 °C; 30 min at 410 °C; +10 °C/min from 410 to 900 °C: (—) TGA curve; (-·-) H_2 evolution; (---) SiH_4 evolution.

escape by a factor of 3 (Table III).

(e) On the other hand, heating of the gel at 60 °C for 24 h to complete the hydrolysis and condensation reactions decreases the release of SiH_4 to below 1%.

In the case of gels yielding high amounts of silane, we observed a very steep decrease in the SiH_4 evolution above 450 °C, connected with a sharp peak for hydrogen (with heating rates ranging from 5 to 10 °C/min, Figure 2). This is ascribable to the thermal decomposition of the silane in the gaseous phase, which is very fast at this temperature:[11]

$$SiH_4 \rightarrow Si + 2H_2$$

As shown in Figure 3 this phenomenon is no longer observed after a short isothermal treatment at 410 °C. The silane amount is more accurately evaluated under these conditions as the weight loss between 280 and 410 °C. The theoretical weight loss for a complete reaction would be 15.1% according to

$$4HSiO_{1.5} \rightarrow 3SiO_2 + SiH_4$$

The experiment described in Figure 3 indicates that, even under isothermal conditions, the dehydrogenation of $HSiO_{1.5}$ gels via SiH_4 formation is limited. In this case, the 4.2 wt % of silane evolved corresponds to 28% of the hydrogen atoms initially present in the gel.

Figures 1–3 clearly indicate that the second step of the thermal dehydrogenation (between 450 and 900 °C) corresponds to an escape of hydrogen (m/z 2). It arises from the cleavage of the Si–H bond in the $HSiO_{1.5}$ units, which is expected in this temperature range.[12] As observed by IR spectroscopy the dehydrogenation was complete at 900 °C.

(b) Under Air. The thermal behavior of $HSiO_{1.5}$ gels under argon helps explain their thermal behavior under air and the DTA patterns observed.[2]

Thus Figures 1 and 4 show the thermal analyses of the same gel under argon and air, respectively. The oxidation of the gel is a very exothermic reaction, which leads to a weight increase of nearly 10% between 300 and 550 °C, accompanied by a strong water escape. The dissymetrical shapes of the DTA curve and the water peak in Figure 4 suggest two steps:

(1) The first step, around 300–350 °C, is very exothermic; it may be related to the oxidation of silane, according to the reaction[13]

$$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$$

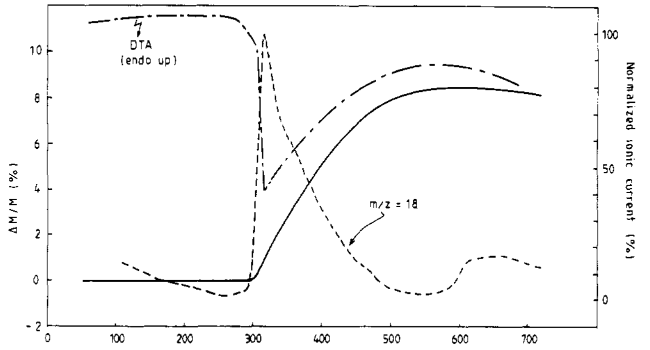

Figure 4. Thermal behavior of gel c under air (heating rate 10 °C/min): (—) TGA curve; (-·-) DTA curve (scale 300 μV/mg); (---) H_2O evolution.

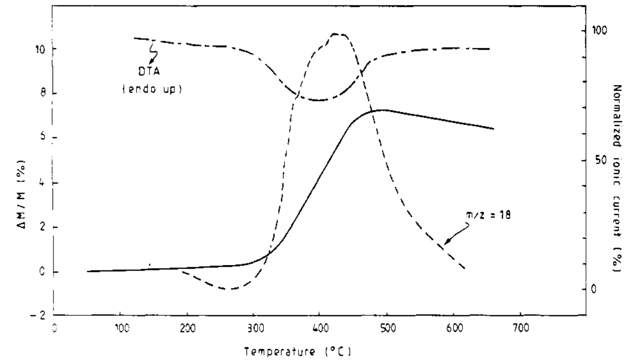

Figure 5. Thermal behavior under air of gel a preheated at 350 °C for 10 h under argon: (—) TGA curve; (-·-) DTA curve (scale 300 μV/mg); (---) H_2O evolution.

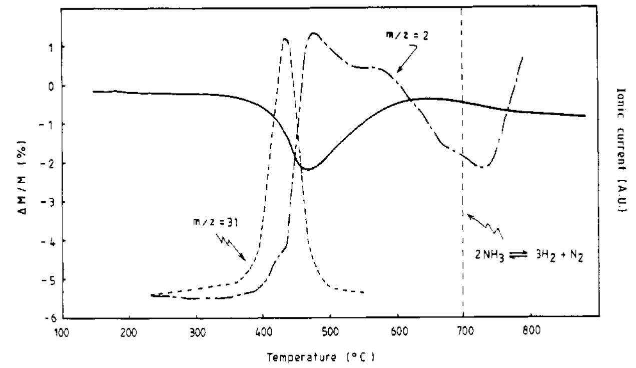

Figure 6. Thermal behavior under NH_3 of gel b: (—) TGA curve; (-·-) H_2 evolution; (---) SiH_4 evolution.

However the weight gain observed suggests either that the oxidized SiH_4 is somehow trapped in the gel or that the intermediates normally leading to SiH_4 under argon (viz., sites SiH_2O and $SiH_3O_{0.5}$) are first oxidized.

(2) The second step, less violent, between 350 and 550 °C, corresponds to the oxidation of the remaining SiH bonds into silanol groups, which are then condensed into siloxane linkages, as shown in ref 2 by IR spectroscopy:

$$2{\equiv}SiH + O_2 \rightarrow 2{\equiv}SiOH \rightarrow {\equiv}SiOSi{\equiv} + H_2O$$

Accordingly when the gel was preheated under argon to eliminate SiH_4, the oxidation reaction proceeded more slowly, by the second reaction, as shown in Figure 5.

(c) Under Ammonia. The pyrolysis under ammonia takes place in three steps (Figure 6): (1) Between 350 and 450 °C the weight loss corresponds to the escape of

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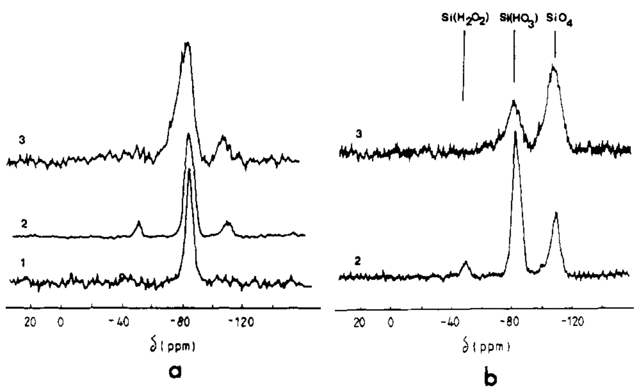

Figure 7. Solid-state MAS ^{29}Si NMR spectra of gel c: 1, not heated; 2, heated for 20 min at 405 °C under argon; 3, heated for 20 min at 565 °C under argon; (a) with ^{29}Si{^{1}H} cross polarization; (b) without cross polarization.

silane. (2) In the range 450–600 °C the weight gain connected with an evolution of hydrogen is ascribed to the following reaction:[4]

$$\equiv SiH + NH_3 \rightarrow \equiv SiNH_2 + H_2$$

(3) Over 600 °C a slight weight loss occurs while no gas is detected; it is related to the condensation of the above amino groups into silazane linkages[4] (under ammonia it is of course impossible to detect this gas):

$$2\equiv SiNH_2 \rightarrow \equiv SiNHSi\equiv + NH_3$$

IR and NMR Spectroscopies. The spectral characteristics of $HSiO_{1.5}$ gels were independent of the mode of preparation. Their thermal evolution under argon was investigated by ^{29}Si MASS NMR spectroscopy (Figure 7). The ^{29}Si chemical shift (−85 ppm) assigned to the $HSiO_3$ unit in the starting gels (Figure 7a1) corresponds to the value reported for soluble siloxanes.[14] After heating at 400 °C, peaks centered at −50 and −110 ppm appear, which are assigned respectively to the tetrahedral units H_2SiO_2[15] and SiO_4.[16] On heating at higher temperature (typically up to 570 °C), the structural units H_2SiO_2 disappear and more silica forms. Moreover the peak at −85 ppm broadens downfield, indicating new resonances between −60 and −80 ppm. This points out some new arrangements around silicon atoms, such as the formation of SiSi bonds by dehydrogenation of SiH bonds (similar resonances around −70 ppm were reported for powder SiO samples[17]). Actually the formation of silicon sesquioxide (composed of $Si(SiO_3)$ units) from $HSiO_{1.5}$ was postulated in ref 1:

$$2HSiO_{1.5} \rightarrow 2SiO_{1.5} + H_2$$

The ^{29}Si solid-state NMR spectra in Figure 7b were recorded without cross polarization (CP) from proton to silicon and with a large relaxation delay (600 s). They clearly indicate that the relative abundance of the nonprotonated sites such as SiO_2 are underevaluated in the CP experiments. However a quantitative MASS NMR study would require a longer repetition time (or a shorter pulse time) because of the long spin–lattice relaxation time of silica.[18]

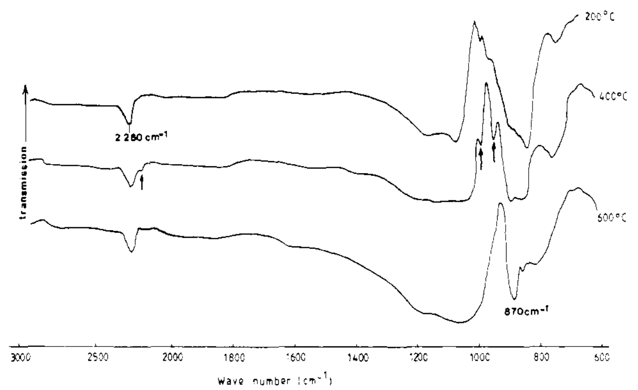

Figure 8. Infrared spectra of gel a (in KBR pellets): 1, heated for 1 h at 200 °C under argon; 2, heated for 1 h at 400 °C under argon; 3, heated for 1 h at 600 °C under argon. Arrows indicate the characteristic bands of H_2SiO_2 units.[15]

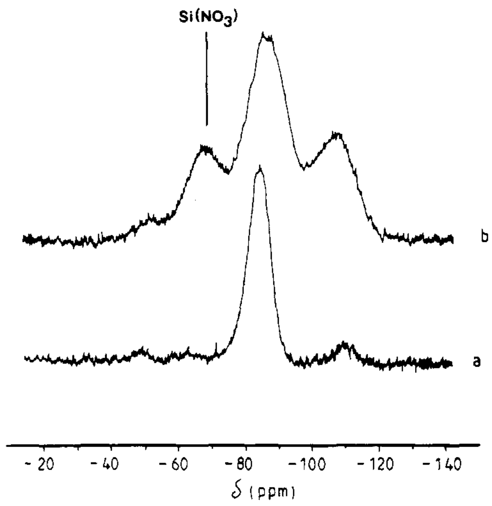

Figure 9. Solid-state CP MAS ^{29}Si NMR spectra of gel c treated with NH_3: a, for 2 h at 350 °C; b, for 2 h at 500 °C.

IR spectroscopy confirms the formation of units H_2SiO_2 near 400 °C, characterized by the weak stretching band at 2200 cm^{-1} and the sharp bending bands at 970 and 940 cm^{-1}[15] (Figure 8). These bands disappear above 500 °C, whereas new absorptions appear in the region of bending vibrations of SiOSi bonds:[19] the first at 800 cm^{-1} corresponds to the formation of SiO_2; the second at 870 cm^{-1} is likely related to distortions due to the formation of SiSi bonds.[20]

In a previous investigation of the nitridation of $HSiO_{1.5}$ gels by ammonia,[3,4] IR spectroscopy showed that $SiNH_2$ groups form at about 450 °C and then convert into silazane linkages above 650 °C. Complementary information is given in Figure 9 by solid-state ^{29}Si NMR spectroscopy, which was performed on samples heated for 2 h under ammonia at 350 and 500 °C (using CP MASS, viz., nonquantitative, technique). Besides the signals described above, a new peak centered at −65 ppm begins to appear at 500 °C, which is ascribed to silanamine groups. The chemical shifts measured in solution for $(MeO)_3SiNH_2$ and $(MeO)_3SiNHSi(OMe)_3$ are surprisingly in the same range (−62.0 and −64.7 ppm, respectively), although the siloxane linkages would be expected to induce an upfield effect (e.g. −110 ppm for SiO_2 vs −78.5 ppm for $(MeO)_4Si$). Never-

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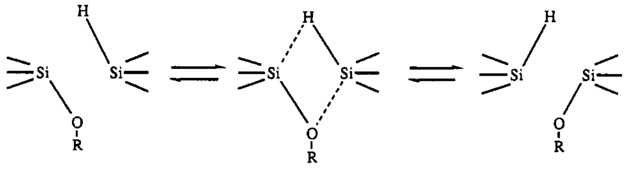

Figure 10. Probable four-centered intermediate occurring in exchange reactions.

theless the close values observed show that it is difficult to distinguish between sites O_3SiNH_2 or $O_3SiNHSi$.

Conclusions

Our spectroscopic results suggest that the silane evolution arises from a redistribution reaction of the SiH and SiO bonds proceeding via the formation of H_2SiO_2 units. Although they are not detected (probably because of their lability[21]), $H_3SiO_{0.5}$ groups are likely involved too, according to the following scheme:

$$2HSiO_{1.5} \rightleftarrows SiO_2 + H_2SiO$$

$$H_2SiO + HSiO_{1.5} \rightleftarrows SiO_2 + H_3SiO_{0.5}$$

$$H_3SiO_{0.5} + HSiO_{1.5} \rightleftarrows SiO_2 + SiH_4\uparrow$$

Such successive equilibria are involved in the redistribution reactions in solution, which are well documented.[22] In many cases the exchange of substituents attached to silicon occurs quite readily under relatively mild conditions (usually acidic or basic catalysis). Moreover the exchange of SiH and SiO bonds involves the formation of gaseous SiH_4; this displaces the equilibrium as an effect of Le Chatelier's principle. Thus mono- and dialkoxysilanes disproportionate rapidly at room temperature,[21] and the redistribution of triethoxysilane occurs by refluxing in the presence of metallic sodium:[22]

$$4HSi(OC_2H_5)_3 \rightarrow SiH_4 + 3Si(OC_2H_5)_4$$

With regard to the influence of the preparative conditions on the amount of SiH_4 evolved, a basic (or nucleophilic[23]) catalysis pathway may provide an explanation. Here catalysis might be provided by traces of water, as well as remaining hydroxyl (or alkoxy) groups. Thus, washing with water likely induces the hydrolysis of residual SiCl bonds and/or the adsorption of water on the hydroxyl groups.

The limited mobility of the atoms in the solid state prevents distant sites from forming the probable four-centered intermediates[22] featured in Figure 10. Moreover the catalytic sites such as the hydroxyl groups undergo thermal dehydration. Accordingly the silane evolution does not go to completion, even after annealing at 410 °C as mentioned above.

Nevertheless the main reaction under argon is the cleavage of the SiH bonds above 450 °C. Furthermore the TGA and NMR data support our previous assertion[4] that the nitridation of $HSiO_{1.5}$ gels with ammonia originates from the SiH functions. Actually ammonolysis begins near 500 °C and clearly corresponds to the cleavage of the SiH bonds. It was previously suggested by Kamiya and coworkers that such SiH groups are involved in the ammonolysis of $CH_3SiO_{1.5}$ gels.[24] In our case a nitrogen content of 5% (against 8% theoretically expected) was obtained by treatment at 700 °C for 1 h under ammonia.[4] However this study demonstrates that minimization of silane release should improve nitrogen incorporation. It is noteworthy that the nitridation occurs significantly below the decomposition temperature of ammonia, which our TG-MS experiments place near 695 °C under the conditions employed.

Registry No. $HSiO_{1.5}$, 44234-98-2; NH_3, 7664-41-7; Ar, 7440-37-1; $HSi(OEt)_3$, 998-30-1; $HSiCl_3$, 10025-78-2; SiH_4, 7803-62-5.

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