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Formation of $OGa(CH_3)_2$ and $OGaCl_2$ Groups on Silica Surfaces and Catalysis by the $OGaCl_2$ Group

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Surface-bound products produced at the gas–solid interface by reaction of silica surfaces with BCl_3[1-3], $Al_2(CH_3)_6$,[2,4] Al_2Cl_6,[2] $TiCl_4$,[4] $ClSi(CH_3)_3$,[4] H_2O,[5] and NH_3[5] have been observed from infrared spectra of pressed silica disks obtained before and after reaction.

We have carried out a similar study with the reaction between silica surfaces and $Ga(CH_3)_3$ (TMG). These surfaces were treated with HCl and then used as a catalyst for the reaction of HCl with SiH_4. Fresh Pyrex glass reaction vessels were treated with TMG and then with HCl, also rendering the surfaces catalytic.

The main intent of this investigation was to generate an $OGaCl_2$ moiety bound as the outer monolayer of silica for use as a catalyst.

Results and Discussion

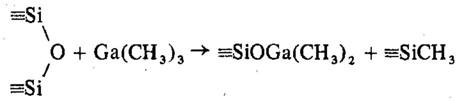
1. Reaction of $Ga(CH_3)_3$ with Silica Surfaces. Infrared spectra of the product surface from reaction of TMG with preheated silica were obtained on thin pressed silica disks while the reaction stoichiometry (ratio of CH_4 produced to TMG consumed) was obtained from reactions with preheated bulk silica. Aerosil silica (Degussa) with an effective surface area of about 200 m^2/g was used.

A. The silica disks were heated to 800 °C in air and then transferred to the combination infrared-reaction cell where the disks were heated at 250 °C under dynamic vacuum. The infrared spectra of these disks in the OH stretching region consisted only of a sharp band at 3747 cm^{-1}. This band is due to non-hydrogen-bonded hydroxyl groups.[6,7] The hydrogen-bonded hydroxyl groups[6,7] absorb strongly at 3550 cm^{-1}. The disks were allowed to react with TMG (40 mmHg) for 20 min at ambient temperature. The infrared spectra after reaction did not contain any absorptions between 4000 and 3400 cm^{-1} (OH region) but did contain absorptions at 3012 (sharp, strong), at 2960 (broad, medium–strong), and at 2915 cm^{-1} (weak). Laboratory air was admitted to the cell. After 2.5 h, the cell was evacuated, and the spectra in the C–H stretching region now contained the absorptions at 2960 and at 2915 cm^{-1}. The band at 3012 cm^{-1} was completely absent.

B. Preheated bulk silica samples (approximately 0.3 g) were allowed to react with TMG at ambient temperature. Typical results from these experiments are listed in Table I.

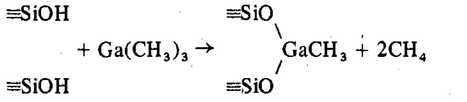
The results from these experiments can be explained by reactions 1 and 2.

$$\equiv SiOH + Ga(CH_3)_3 \rightarrow \equiv SiOGa(CH_3)_2 + CH_4 \qquad (1)$$



$$\equiv Si_2O + Ga(CH_3)_3 \rightarrow \equiv SiOGa(CH_3)_2 + \equiv SiCH_3 \qquad (2)$$

Evidence in favor of reaction 1 and not reaction 3 will be presented in section 2.



$$2\,\equiv SiOH + Ga(CH_3)_3 \rightarrow (\equiv SiO)_2GaCH_3 + 2CH_4 \qquad (3)$$

The results from the infrared spectra show the disappearance of ≡SiOH sites and the appearance of methyl groups on the surface. The absorptions at 3012, 2960, and 2915 cm^{-1} can be assigned to C–H fundamental stretching modes. Since the 3012-cm^{-1} band is lost on exposure to air, it can be assigned to a $Ga–CH_3$ group while the other bands can be assigned to $Si–CH_3$.[8] Similar conclusions were made by Hockey et al.[2] when preheated silica was treated with $Al_2(CH_3)_6$, generating absorptions at 2958, 2938, 2897, and 2830 cm^{-1}. After treatment with H_2O, the only absorptions remaining were at 2958 and 2905 cm^{-1}. It is well-known that alkyl groups bound to aluminum or gallium are very hydrolyzable while alkyl groups bound to silicon are inert.

Table I. Reactions of TMG with Bulk Silica Samples

surface	time, h	mmol of TMG added	mmol of TMG consumed	mmol of CH_4 produced	CH_4 (produced)/TMG (consumed)
1[a]	2.6	0.42	0.39	0.23	0.59
2[b]	3.4	0.29	0.17	0.065	0.38
3[b]	1.8	0.28	0.09	0.027	0.31
4[a]	2.0	0.38	0.35	0.29	0.83
5[b]	2.5	0.18	0.13	0.056	0.43
6[a]	3.0	0.61	0.45	0.28	0.62
7[b]	2.5	0.22	0.072	0.018	0.26
8[a,c]	2.2	0.24	0.20	0.12	0.60
9[b]	2.2	0.24	0.043	0.0094	0.22

[a] Surface heated to 800 °C in air for 16 h and then heated under dynamic vacuum at 250 °C. [b] These surfaces were those from the previous reaction. [c] Surface heated to 800 °C under dynamic vacuum for 16 h after initial heating in air at 800 °C.

Table II. Preparation of Catalytic Surfaces ($\equiv SiOGaCl_2$)

surface[a]	amt, mmol TMG consumed	amt, mmol CH_4 formed	amt, mmol HCl consumed	amt, mmol CH_4 formed
1[b]	0.43	0.31	0.54	0.31
2[c]	0.76	0.28	0.98	
3[b]	0.45	0.19	0.40	0.25

[a] The silica (about 0.3 g) was heated in air at 800 °C overnight and then at 800 °C under vacuum overnight and transferred in air when cool. [b] The TMG was added in one dose. [c] The TMG was added in two doses.

The results listed in Table I indicate that reaction 1 was favored over reaction 2 for fresh surfaces, with reaction 2 becoming more important as ≡SiOH sites were consumed. These results differ from those of Hockey[2,3] et al. (for the $Al_2(CH_3)_6–SiO_2$ system) in that the analogous reaction 1 was not observed. In the study with $Al_2(CH_3)_6$, the intensity of the 3747-cm^{-1} band remained constant during reaction.

2. Reactions of Silica-Bound $\equiv SiOGa(CH_3)_2$ with HCl. Bulk silica surfaces heated under dynamic vacuum at 800 °C were allowed to react with TMG as described in section 1. In a typical experiment, 0.116 mmol of TMG was "lost" to the silica surface. This surface was then repetitively exposed to HCl at ambient temperature until CH_4 was no longer generated. At this time, 0.241 mmol of CH_4 was formed while 0.826 mmol of HCl was lost to the surface. The ratio of CH_4 generated after reaction with HCl to TMG originally "lost" to this surface was 2.08. This result is consistent with eq 4 and suggests that the major bound gallium species from reaction of TMG with preheated silica was $\equiv SiOGa(CH_3)_2$.

$$\equiv SiOGa(CH_3)_2 + 2HCl \rightarrow \equiv SiOGaCl_2 + 2CH_4 \qquad (4)$$

3. Catalysis with $\equiv SiOGaCl_2$ on Silica. Silica surfaces containing ≡$SiOGaCl_2$ moieties bound to the surface were used to catalyze the ambient-temperature reaction of HCl with SiH_4 to form chlorosilanes. The results of these reactions are listed in Table III. The catalytic surfaces were prepared as described in Table II where treatment with HCl was not carried out to the completion of reaction 4. They were prepared, stored

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Table III. Reaction[a,b] of SiH_4 with HCl over Surfaces from Table II

surface (Table II)	amt, mmol			
	reactants consumed		products[c]	
	SiH_4	HCl	H_2	others
1	0.2	0.3	0.39	none
	0.2[d]	0.3	0.37	0.1, $ClSiH_3$[e] 0.1, Cl_2SiH_2
2	0.15	0.4	0.38	0.1, $ClSiH_3$[e]
3	0.3	0.35		0.1, $ClSiH_3$[e]

[a] Reactions carried out for 1 h at ambient temperature. [b] Typically, 0.4 mmol of SiH_4 and 0.4 mmol of HCl were added to the reaction vessel (~200 mL). [c] Volatile products distilled from reaction vessel. [d] Second reaction over surface 1. [e] A small quantity of SiH_3OSiH_3 was also obtained.

overnight under vacuum, and then used in the same reaction vessel the next day.

The results listed in Table III demonstrate that SiH_3Cl is formed when SiH_4 and HCl react over the prepared ($\equiv SiOGaCl_2$) surface at room temperature. In a control experiment, a silica surface was treated as generally described in Table II except that the TMG treatment was omitted. This surface did not catalyze the SiH_4–HCl reaction (i.e., no H_2 or SiH_3Cl was produced).

The first reaction over surface 1 presumably generated $ClSiH_3$ (H_2 was formed) which was consumed by the surface. The second reaction was then successful in generating free chlorosilanes. The much larger quantity of TMG used for surface 2 presumably destroyed the sites which "retained" the product $ClSiH_3$.

In an effort to ensure that the catalysis was due to $\equiv SiOGaCl_2$ bound to silica we carried out the experiments described in section 4.

4. Catalysis with Modified ($\equiv SiOGaCl_2$?) Pyrex Glass. Results similar to those described in section 3 were obtained in the same reaction vessel when the 0.3 g of silica was not present.

In addition, a new reaction vessel (50 mL) was treated as follows: (i) cleaned with alcoholic KOH, HNO_3, and distilled water and dried; (ii) treated with 0.20 mmol of TMG (20 min) (the TMG was consumed with the formation of 0.09 mmol of CH_4); (iii) treated with 0.72 mmol of HCl in two doses. Methane (0.14 mmol) was produced while 0.37 mmol of HCl was consumed. Silane (0.43 mmol) and HCl (0.39 mmol) were allowed to react in this vessel for 1 h at ambient temperature, yielding 0.46 mmol of H_2 and 0.26 mmol of SiH_3Cl (with a small quantity of SiH_3OSiH_3 present). It would appear that $\equiv SiOGaCl_2$ (or possibly $=BOGaCl_2$) was also generated on the Pyrex glass surface. When this vessel was exposed to laboratory air and then evacuated, the SiH_4–HCl reaction produced only a small amount of H_2 and no chlorosilanes. To our surprise, the treated Pyrex reaction vessel with a very small effective surface area compared to that of the silica (about 70 m^2) was as effective as the treated silica.

5. Catalysis with Al_2Cl_6. In an effort to compare the effectiveness of the "$\equiv SiOGaCl_2$" catalytic surface to that of Al_2Cl_6, we examined the HCl–SiH_4 reaction over Al_2Cl_6.

The Al_2Cl_6[9] catalysis of the HCl–SiH_4 reaction is reported to require 100 °C while it is now known that SiH_4 reacts with HI over Al_2I_6[10] at −45 °C. We have now observed that the HCl–SiH_4 reaction is catalyzed by freshly sublimed Al_2Cl_6 at 25 °C and also at −45 °C. However, it is difficult to compare these catalysts without having more carefully defined surfaces. We have also observed formation of chlorosilanes (no iodosilanes) from reaction of SiH_4 with HCl over Al_2I_6 at 25 °C. The equilibrium[11] of SiH_3I with HCl lies toward SiH_3Cl and HI so this latter result could be from either initial SiH_3I or initial SiH_3Cl formation.

Experimental Section

All experiments were carried out in standard high-vacuum Pyrex glass systems. Starting materials and products were examined for purity and identified by infrared and mass spectral analysis. Methane–H_2 mixtures were Toepler-pumped into a calibrated volume to determine their total quantity while their ratio was determined from mass spectra by using known mixtures to calibrate the mass spectrometer. Separations of products were made by trap to trap distillations.

Silica samples were preheated to 800 °C in air prior to use for bulk reactions and prior to being pressed into disks. Silica disks of 2.5-cm diameter were prepared from about 25-mg of silica pressed in a stainless steel die at 2000 lb/in^2. The infrared cell was similar in design to that described by Morrow and Ramamurthy.[12]

The infrared spectra were obtained on a Perkin-Elmer Model 625 spectrometer with the reference beam intensity decreased by a standard screen. Typical scan times to cover 600 cm^{-1} were 16 h with a very slow pen response.

Registry No. Silica, 7631-86-9; TMG, 1445-79-0; HCl, 7647-01-0; SiH_4, 7803-62-5.

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Deuterated Sodium Octahydrotriborate(1−)

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Deuterated octahydrotriborate(1−) ($B_3H_8^-$) can be obtained by the known methods for the preparation of $B_3H_8^-$ by using deuterated borane species. Some of the reactions that may be used are

$$2B_2H_6 + 2Na/Hg \rightarrow NaB_3H_8 + NaBH_4{}^{1}$$

$$B_2H_6 + NaBH_4 \rightarrow NaB_3H_8 + H_2{}^{2}$$

$$B_4H_{10} + NaBH_4 \rightarrow NaB_3H_8 + B_2H_6{}^{3}$$

$$3NaBH_4 + I_2 \rightarrow NaB_3H_8 + 2NaI + 2H_2{}^{4}$$

Alcoholyses of B_5H_9[5] and $(CH_3)_4NB_9H_{12}$[6] are also known to give $B_3H_8^-$ ion.

Recently a method using anhydrous deuterium chloride for the deuteration of tetrahydrofuran–triborane(7) ($THF{\cdot}B_3H_7$) was reported.[7] Meanwhile, treatment of $THF{\cdot}B_3H_7$ with sodium hydride under appropriate conditions should give NaB_3H_8. Combination of the above two processes, therefore, would