Modification of γ-Alumina with Chlorotrimethylsilane

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The solid and gaseous products from the silation of partially dehydroxylated γ-alumina with chlorotrimethylsilane have been determined for a wide range of pretreatment and reaction conditions. Unexpectedly and contrary to previous assumptions, in all cases there was no HCl produced. Methane was the only gaseous product detected for silation reactions up to 500 °C. Under very severe conditions a very small amount of higher hydrocarbons was also obtained. The silating reagent is first irreversibly adsorbed by reaction with coordinatively unsaturated aluminum cations and oxygen anions. Subsequent reaction of the silyl methyl group with isolated, highly acidic hydroxyls affords the methane product.

I. Introduction

Alumina continues to be the focus of several investigations, not only because it is widely used as a support in heterogeneous catalysis but also because the nature of its surface is complex and remains incompletely understood.[1] Alumina is an appropriate support for metallic as well as organometallic and oxide catalysts.[2−4] It possesses a defect spinel lattice structure which is terminated by surface hydroxyl groups.[3−7] Numerous investigations have been conducted with the objective of modifying the surface in a controlled manner. The principal approach has been to utilize or modify the surface hydroxyl groups.[8−11] These hydroxyl groups play an important role in determining the surface chemistry of the resulting alumina based materials.[5,12] The removal or modification of surface hydroxyl groups can result in an increase in the hydrophobic nature of the catalyst, especially its capability to resist adsorption of water vapor.[13−15]

Organosilanes have been used effectively as modifying agents to achieve the target characteristics of the substrate surface. Since the abundance of surface hydroxyl groups and the necessity of their removal or modification is a common feature of the most widely used catalyst supports, Al_2O_3 and SiO_2, the application of organosilanes as modifying agents attains wider significance.[13−23] Effective modification of the surface depends in general on two factors: the structure of an organosilicon compound and the types of surface hydroxyl groups.

A large number of organosilicon compounds has been used for this purpose. These organosilanes have hydrolyzable functional groups bonded to the silicon atom that permit covalent bond formation to the surface and, in many cases, cross-linking within the organosilane layer.[15] Chlorotrimethylsilane ($(CH_3)_3$-SiCl) is often used as a modifying agent.

On the alumina surface some hydroxyl groups are not proximate to other hydroxyl groups and are described as "isolated". When two (or more) hydroxyl groups are adjacent, a hydrogen bond is assumed to exist between them, and these are termed "associated" hydroxyl groups. In such pairs only one of the two hydrogen atoms can participate in the hydrogen bond and is termed "hydrogen bonded". The OH bond in this pair which is not directly involved in the hydrogen bonding gives rise to an IR band in the region for "isolated" hydroxyl groups.[26] The silane reacts with both isolated and associated hydroxyl groups at an adsorption temperature of 450 K.[16] The reaction of the isolated hydroxyl groups has been found to quantitatively correlate with the formation of stable alumina-siloxane species on the alumina surface.[16] On both alumina and silica the modification of the surface hydroxyls involves predominantly reaction with isolated hydroxyl groups, which reactions may be followed by reaction of some associated OH species.[14,16] The reaction of hydrogen-bonded hydroxyls is considerably slower than that of the isolated ones.

The surface hydroxyl groups fall into several mutually connected classifications in accordance with different criteria and properties. In his pioneering work on the hydroxyl structure of alumina, Peri[6,25,26] consecutively identified five different infrared (IR) bands which are found in the 3700−3800 cm^{-1} region, showing the presence of five distinct types of OH groups. Knözinger and Ratnasamy[4] have further developed this model for the alumina surface and, according to the coordination number and net electrical charge of the respective alumina sites, have determined five different types of the hydroxyl groups on the ideal alumina surface. The existence of six different surface hydroxyl species has been assumed by Yoshida.[27] In this scheme the surface hydroxyl groups are divided according to steric location and mutual connections into isolated (single) and hydrogen-bonded (associated) ones.[4,25,26] The latter type can be subdivided into weakly hydrogen-bonded and strongly hydrogen-bonded hydroxyls. In the low-temperature region, bands normally assigned to strongly hydrogen-bonded hydroxyls have alternatively been assigned by some researchers to molecules of physically adsorbed water. Peri[26] recognizes three types of hydroxyls which are characterized according to their relative ability to be removed from the original monolayer: removable without defect formation on the alumina surface, approximately 67%; removable with "defects", approximately 25%; and unremovable (or removable with migration), approximately 8%. In another classification the hydroxyl groups have been divided into basic, neutral, and acidic types, based on their apparent pH.[4,26] The coordination number, net electrical charge, and pH character determine whether hydroxyls are effectively negative, neutral, or positive surface sites.[4,26] Each one type of hydroxyl group can be classified simultaneously in each of the five classification systems. The relationships between the types of hydroxyl groups within each classification system and the parameters (*e.g.*, pH, IR band) used to distinguish them have been correlated and related to the local structures about each hydroxyl group.[4,26] For example, the isolated hydroxyl groups which are removable without formation of

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defects on the alumina surface and which have the highest net negative charge are those with the most basic character.

Paul and co-workers[13,16] have thoroughly studied the silation of Al_2O_3 and Rh/Al_2O_3 catalyst for controlling of automotive exhaust emissions. They determined[13] that, surprisingly, the silation of the supported catalysts by extensive exposure to $(CH_3)_3SiCl$ does not result in deactivation of the metallic Rh particles by chlorosilane chemisorption. This finding enabled them to discuss the interaction of $(CH_3)_3SiCl$ with surface hydroxyl groups, while disregarding the presence of the small amount of Rh on the alumina surface. Infrared spectroscopic measurements indicated that an irreversible chemical reaction occurred at an adsorption temperature equal to or greater than about 450 K, between the silane and the surface hydroxyl groups, and that strongly bound aluminasiloxane surface species $(CH_3)_3Si{-}O{-}Al{=}$ were formed. These authors stated that aluminasiloxane compounds were produced as the hydroxyl groups were consumed. At these temperatures the reaction involved the surface hydroxyl groups, and it was assumed that HCl was eliminated. The fate of this HCl was not fully understood; it was proposed that it was either liberated as a gas or adsorbed on the Al_2O_3 surface.[16] It was proposed that the reaction being observed involved, for either isolated and associated OH groups, the elimination of gaseous products as the reaction proceeded according to the following general scheme, in which specific stoichiometry is not implied by eq 1:

$$=\!Al{-}OH + Cl{-}Si{\lessdot} \longrightarrow\ =\!Al{-}O{-}Si{\lessdot} + HCl \qquad (1)$$

This reaction scheme involving surface hydroxyl groups has been widely published in the area of organosilicon compounds. Although this reaction seemed to occur for both isolated and associated OH groups on the Al_2O_3 surface, it is clear from the sequence of changes in the spectra as the reaction progressed that the isolated OH groups are more reactive since they disappear first. This behavior is observed for pure Al_2O_3 as well as for Rh/Al_2O_3 catalysts.[16]

There exist some commonly found features which characterize all results reported to date concerning silation of aluminas. Very thorough and detailed studies have been made only for the changes in the solid phase, concerning only those aspects of the interaction of the surface hydroxyl groups which are isolated and hydrogen-bonded. In all discussions a complete analogy in the behavior of alumina and silica has been assumed, without any recognition of the significant specific differences in the chemical and surface nature of the two materials. A priori acceptance has been made of the generality of the reaction between chlorosilanes and the surface hydroxyl groups with elimination of hydrogen chloride (HCl), which assumption has unfortunately resulted in a lack of interest in the gas phase products of the reaction. The main method of investigation to date has been IR spectroscopy of the solid phase, in which very small amounts of alumina are examined in reactions with very low concentrations of silane under static conditions, most often in high-vacuum infrared cells. Thus, the data available for this system frequently are not reflective of the macroscopic behaviors of the materials, and interpretations are consequently incomplete.

The purpose of the present work is to study the silation of the γ-alumina surface with $(CH_3)_3SiCl$, paying special attention to (i) carrying out the reaction in dynamic conditions—in a continuous flow fixed bed reactor that allows us to use larger amounts of alumina and $(CH_3)_3SiCl$, permanent control of the gas phase products of the reaction, and variation of the reaction parameters over a wide range—and then (ii) determination of the reaction mechanism, based on complementary data from various methods of investigation. To our knowledge this is the first examination of γ-alumina modification with $(CH_3)_3SiCl$ under dynamic conditions, aiming at characterization of both the solid and gaseous reaction products and the reaction mechanism.

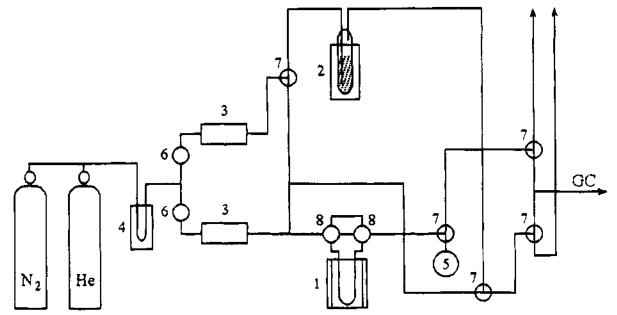


Figure 1. Experimental equipment for treatment of oxide supports with silanes: 1, reactor; 2, saturator; 3, MFC; 4, trap; 5, infrared gas cell sampling device; 6, two-way valve; 7, three-way valve; 8, four-way valve.

II. Experimental Section

Materials. Commercially available granulated alumina (La Roche) was used as received. The supplier reported a BET (Brunauer−Emmett−Teller method) area of 325 $m^2\ g^{-1}$ and the size of granules as 1−3 mm. The BET area for two separate samples as determined in our laboratory using an Omnisorp 360 sorptometer was found to be 206 $m^2\ g^{-1}$, and the total pore volume was 0.386−0.390 $cm^3\ g^{-1}$. Fumed alumina (Alon) with BET area 100.4 $m^2\ g^{-1}$ was also used for comparison purposes.

The alumina was first dried at 120 °C for 3 h and then dehydrated by heating in air at 500 °C for 6 h, followed by storage in an oven at 125 °C.

$(CH_3)_3SiCl$ (Aldrich, purity >99.0%) was double distilled, followed by subsequent vacuum distillation. It was stored under a N_2 atmosphere and transferred to a glass evaporator purged constantly with N_2 gas during use. Both N_2 and He (Matheson, "Ultra High Purity") were obtained in high-pressure cylinders.

Equipment. The dynamic method was used to study the silation of γ-alumina with $(CH_3)_3SiCl$. Experiments were performed in equipment (Figure 1) consisting of three parts: a gas handling system, a reactor, and an exit gas control and monitoring system. For the gas handling system the flow rates and exact proportions of the gases were adjustable; the velocity of the nitrogen stream was regulated by means of two parallel connected Matheson mass flow controllers. The concentration of $(CH_3)_3SiCl$ in the nitrogen−silane gas mixture was controlled through the equilibrium vapor pressure of silane at 0 °C by use of an ice bath and checked by weight measurements. The reaction vessel was a glass U-shaped reactor (100 cm^3) equipped with temperature programmed heating. A system of four-way and three-way valves provided for the distribution and removal of gas phase reaction products. The reactor, connected through two four-way valves, was placed in a movable electrical furnace for which the temperature was controlled within ±1 °C. The temperature profile along the length of the reactor bed was monitored by means of movable thermocouples. A system of three-way valves and connectors necessarily precluded any air contamination when the gas sample was collected in an IR gas cell, since concurrent analyses of gas phase products using gas chromatography (GC; Hewlett-Packard 5890 Series II GC, with HP 3396A integrator) and Fourier transform IR (FTIR; Nicolet 730 instrument) were performed.

Experimental Procedure. The conditions for a series of over 100 experiments of silation of γ-alumina with $(CH_3)_3SiCl$ were varied over a wide range.[1] The dehydration temperatures of γ-alumina varied from 150 to 500 °C and the duration between 24 and 72 h. The silation temperature ranged from 80 to 500 °C.

The concentration of silane in nitrogen−silane (or helium−silane) feed gas varied from 1.5 to 18 mg cm^{-3}, and the velocity of the gas mixture flow was varied from 12 to 60 cm^3 min^{-1} (space velocity from 82 to 252 h^{-1}). The duration of silane treatment was from 30 to 140 min depending on the silane concentration and the space velocity of the mixture. The reactor was normally charged with 12 g of alumina; however, some experiments were also conducted using charges of 10−20 g. When powdered alumina was used, glass beads of 2 mm diameter were mixed with the alumina to ensure uniform contact with reacting agents.

The procedure for the silation of γ-alumina with $(CH_3)_3SiCl$ was as follows. Following dehydration, a sample of granulated γ-alumina was loaded into the reactor which was constantly flushed with nitrogen at a flow rate of 100 cm^3 min^{-1}. The products from the reaction were collected by condensation at liquid nitrogen temperature. The temperature of the reactor was gradually raised to 500 °C and held at this level for 24 h. The reactor was then cooled to room temperature under a N_2 atmosphere. The reactor was disconnected, tightly closed, and weighed on an analytical balance. The reactor was reassembled, and the temperature was raised to 220 °C. The feed gas comprising nitrogen carrier with silane (5.2×10^{-3} g cm^{-3}) was fed (16 N cm^3 min^{-1}) until silane was detected in the gas phase products or 120 min had elapsed. The reactor was again cooled and weighed to obtain the total uptake of silane during the reaction. The reactor was reassembled, and the reaction was repeated, but in the absence of additional fresh silane. A further interaction between the alumina surface and chemisorbed silane was observed at 220 °C with measurable formation of gaseous products for 12−20 h. When the temperature was further increased to 240 or 260 °C, the reaction continued for an additional 12−16 h. In some experiments the temperature was increased gradually to 500 °C. It was found that the reaction continued for 3−5 days over which the gas phase products were continuously monitored. The weight of the solid product was determined periodically, and the amount of silane-derived material left on the surface was calculated from the difference between the weighings.

For comparison, a static method was also used in the second (thermal) stage of some silation procedures. The initial chemisorption of silane on the alumina surface was performed dynamically at 0−60 °C, usually until silane was detected in the reactor outlet stream. The reactor was then closed using two four-way valves, and the second phase of the silation procedure was performed statically at temperatures between 160 and 280 °C, over 12−48 h. No significant difference was found between the products of reactions using dynamic or static procedures.

Silation of Silica. Silation of silica was performed under conditions similar to the above reactions with alumina and literature[14,18,22,24] methods. In each case HCl was immediately and rapidly evolved and was identified by IR spectroscopy.

Instrumental Methods. An Omnisorp 360 sorptometer was used to measure BET area and pore size distribution by nitrogen adsorption. The pore size distribution was obtained from the desorption isotherm. Gas chromatographic analyses were performed using a Hewlett Packard 5890 Series II GC, connected with a HP 3396 A integrator. It was operated at 200 °C using a 1.2 ft, $^1/_8$ in. o.d. column, packed with Porapak Q.

FTIR data in the 4000−400 cm^{-1} region were collected using a Nicolet 730 FTIR spectrometer operating with a liquid nitrogen cooled MCT (mercury−cadmium−telluride) detector. In order to carry out IR transmittance and absorbance measurements for the solid products, the samples were pressed into wafers of suitable thickness and placed in an IR cell connected directly to a vacuum line. The gas phase samples were analyzed using a calibrated 10 cm glass cell with a volume of 76.4 cm^3, equipped with KCl windows.

Mass spectroscopic analyses were performed on either a Varian Vista 6000 GC connected to a VG 7070 E mass spectrometer or a Varian Saturn 3400 GC MS (gas chromatograph−mass spectrometer). Elemental analyses for Al, Si, and Cl in the solid products were carried out using a Cambridge Stereoscan 250 scanning electronic microscope, equipped with a Tracor Northern 5500 energy dispersive X-ray analyzer. Elemental analyses for C and H were performed using a Carlo Erba CHNS-O instrument equipped with GC TCD EA 1108 elemental analyzer. Analyses for Cl were performed by titration.

^1H NMR (nuclear magnetic resonance) spectra were obtained using a Brüker WH 400 instrument, operating at 400.13 MHz, using $SiMe_4$ as the external standard. In all the NMR spectroscopic studies $CDCl_3$ and deuterated cyclohexane (C_6D_{12}) were used as a solvent and as an internal lock. Differential thermal analysis (DTA) and differential thermogravimetric (DTG) analyses were carried out on a Dupont 900 differential thermal analyzer and Dupont 950 GC MS thermogravimetric analyzer, respectively.

III. Results and Discussion

1. Gaseous Products of the Silation Reaction. Since earlier investigations had led to the conclusion (or assumption) that HCl was a product of the silation of alumina, but its fate remained unknown, analyses of the gas phase products were included in our study. However, all of our attempts to establish the formation of HCl were unsuccessful. The major gaseous product of the reaction of $(CH_3)_3SiCl$ with the surface of partially dehydroxylated γ-alumina is methane, CH_4, as determined by infrared and NMR spectroscopy, mass spectrometry, and GC analysis.

Methane is the only detectable gas phase product produced over the course of the reaction.[1] There was no significant difference between the infrared spectra of the gaseous products taken at 10 min intervals throughout the course of the reaction, until silane was detected in the exit gases. In each spectrum there were no bands arising from HCl. In the spectral range 2800−3200 cm^{-1} the bands of CH_4 and HCl are partially superimposed. Consequently, a standard mixture was prepared by adding 0.764 cm^3 of HCl to 76.4 cm^3 of a sample of produced methane, to form a 1 vol % mixture. Although the concentration of HCl in the analyzed mixture was extremely low (0.286×10^{-5} mol cm^{-3}), the appearance of each of the strongest harmonic bands of HCl (2760 and 2711 cm^{-1}) was readily observed.

Competitive analyses were performed using GC. For each sample taken the only gaseous product detected was methane, at a retention time of 0.89 min. The silation reaction was terminated when $(CH_3)_3SiCl$ was identified in the exit gases by detection of a GC peak with the same retention time as that for $(CH_3)_3SiCl$ taken from the inlet of the reactor.

The GC MS spectra of exit gases for a variety of conditions showed only peaks arising from methane and the carrier gas. The peak at *m/e* 14 was considerably higher than the one from a sample of standard methane because of superposition of N^+,

and peaks at 28 (N_2^+) and 29 ($^{14}N^{15}N^+$) were also from N_2, since the reaction was carried out in nitrogen flow. The peak at *m/e* 17 is slightly larger than for the methane standard and arises from traces of OH^+. A peak at *m/e* 18 showed the presence of traces of OH_2^+. Peaks at *m/e* 32 and 40 were due to trace amounts of oxygen and argon impurities, respectively.

The presence of methane was also confirmed by analyses using NMR. The separated gas phase methane from the outlet of the reactor was collected and dissolved in either $CDCl_3$ (NMR at −58 °C) or C_6D_{12} (NMR at 6 °C). The results of analyses in each solvent showed the presence of only methane and for high temperature (300−500 °C) reactions (vide infra) trace amounts of higher hydrocarbons.

The absence of detectable amounts of HCl in the gas phase product was further established by means of sensitive qualitative contact reactions with pH paper and a fresh solution of NH_4OH. The eliminated methane was captured at liquid nitrogen temperature in a glass trap, quantified, and identified as above.

2. Solid Phase Studies. After dehydroxylation of alumina in the temperature range 400−500 °C, the concentration of isolated OH groups left on the surface is between 6.4×10^{14} and 8.2×10^{14} OH groups/cm^2, based on DTG analysis. The number of hydroxyl groups on partially dehydroxylated alumina depends on the source, its chemical purity, BET area, and the experimental conditions for dehydroxylation. Dehydration studies are usually carried out in vacuum. The concentration of hydroxyl groups has been reported to be between 3 and 9 OH/100 Å^2 ($(3-9) \times 10^{14}$ OH/cm^2).[28−30] In our experiments the dehydration was carried out in flowing nitrogen, which apparently results in a higher number of hydroxyls left on the surface after continuous treatment for 24 h at 500 °C.

The degree of silation for either granulated or pulverized alumina was the same. Decreases in the BET area (7−13%) and pore volume (16−20%), as well as the amount of supported silane on the surface of granulated and pulverized alumina, were essentially the same for each sample. Thus, pulverization does not influence the nature or affect the concentration of available reaction sites. The peak value of surface concentration of $(CH_3)_3SiCl$ adsorbed on partially dehyroxylated alumina was determined gravimetrically. Depending on the silation temperature, a concentration of $(1.92-2.25) \times 10^{14}$ molecules/cm^2 was obtained. The ratio of adsorbed silane molecules to residual hydroxyl groups is between 1:2 and 1:4. Therefore, there exist sufficient residual hydroxyls to effect the formation of the methane produced as the only gaseous product.

The calculations based on DTG analyses showed that the number of pairs of coordinatively unsaturated Al^{3+} and O^{2-} is 1.6−2.0 times higher than the number of surface hydroxyls. This result is in agreement with Peri's model,[25,26] which suggests that about 67% of the surface hydroxyls are removed during dehydration at 500 °C. The disparity between the higher number of vacancies (coordinatively unsaturated sites) and the smaller number of chemisorbed silane molecules may be a consequence of steric factors at specific sites. The optimum number of non-mutually interfering silane molecules that could be located on an area of 100 Å^2, under the conditions of our experiment, is approximately two (2×10^{14} molecules/cm^2).

The concentrations of silane molecules per unit alumina surface area calculated from the gravimetric analyses and the elemental analyses for silicon and chlorine are very consistent. The chlorine content has been determined using two different methods.[1] However, between different minute fragments of a single finely crushed pellet, the ratio of analyses for Si and Cl varied between 1.66:1.45 and 1.42:1.68 mol %. This variation

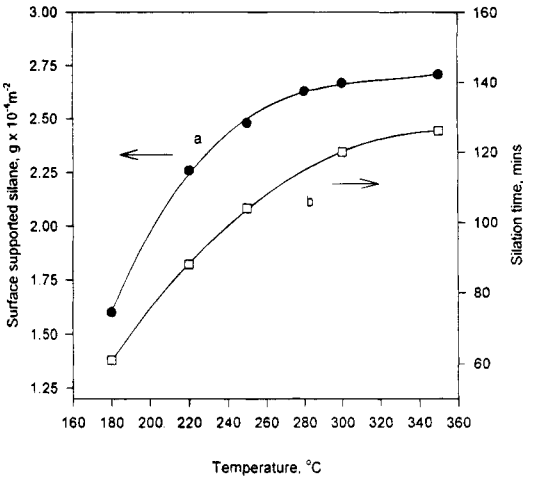
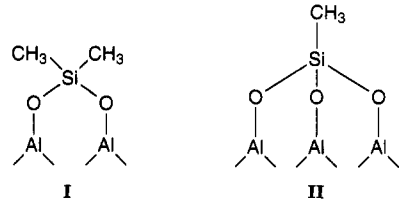


Figure 2. Effect of the silation stage A temperature upon the chemisorption of silane: (a) surface concentration of absorbed silane; (b) elapsed silation time until appearance of silane in the gas phase products.

in the ratio suggests that some segregation of chloride and silyl fragments may have occurred.

The amount of silane which is adsorbed on the surface of alumina is dependent upon the temperature of silation, as shown in Figure 2. As the temperature is increased, the amount of silane adsorbed increased (curve a). Consistent with this result, the elapsed time until detection of silane in the exit gas also increased (curve b). The temperature dependence of the number of reacted CH_3 groups per molecule of silane during silation A is shown in Figure 3. The number of reacted CH_3 groups has been determined by elemental analysis of carbon. The results of elemental analyses for hydrogen are consistent with the analyses for carbon and show that hydrogen content continuously decreases with increasing temperature. In the temperature range from 140 to 250 °C the number of reacted CH_3 groups per molecule of silane is between 1.0 and 1.8. When the temperature is increased to 300 °C and higher, the ratio of reacted methyl groups per molecule of silane is greater than two. The data show that the number of reacted CH_3 groups per molecule of silane is close to 2.5 for samples heated to 500 °C over 3−5 days. In these cases oxidative pyrolysis also probably takes place. The location of the silane moiety on the alumina surface could be presented as **I** for the silation temperatures to 160 °C and as **II** for temperatures over 200 °C.



In the FTIR spectrum of silated alumina bands are observed which are not present in the spectrum of alumina, including a weak band at 1274 cm^{-1}, which may be a CH_3 symmetric deformation mode, and a broad feature, centered at 1100 cm^{-1}, which is assigned to the asymmetric Si−O stretching vibration mode.

The nature of the Al^{3+} sites involved in the silation reaction is shown to be the coordinatively unsaturated "tetrahedral" Al^{3+} sites by the following diagnostic reaction. When the silated alumina was exposed to 20 Torr of CO, the CO was readily adsorbed, as shown by its IR spectrum. The silated alumina was sequentially evacuated at 250 °C for 6 h, at 350 °C for 4

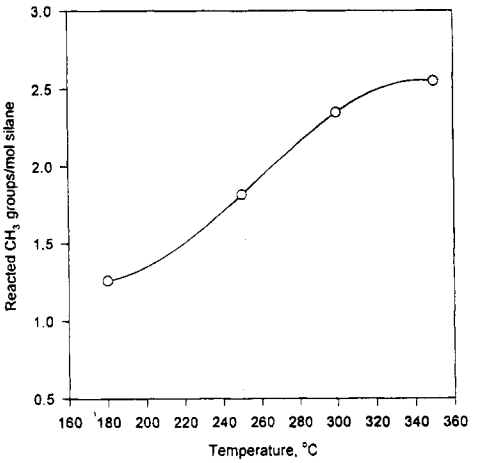


Figure 3. Methyl groups reacted per mole of silane chemisorped as a function of the silation temperature.

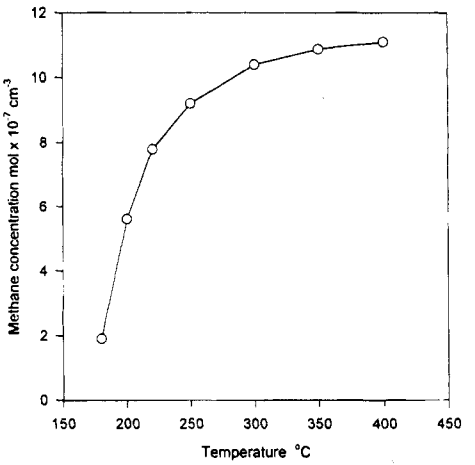


Figure 4. Methane concentration in the gas phase as a function of the temperature of silation stage A.

h, and finally at 500 °C for 1 h, before exposure to CO. The position of the CO infrared spectral band, 2208 cm^{-1}, shows that the CO coordinated at only the coordinative unsaturated "octahedral" Al^{3+} sites on the alumina surface and not at the tetrahedral Al^{3+} sites, for which a band at 2235 cm^{-1} would have been expected for coordinated CO.[32] Thus, the tetrahedral sites, which are normally considered to be the more active Al^{3+} sites, must already have been occupied in the silated alumina.

The analytical data for the solid products are consistent with the CO coordination reaction. All chloride from the silating agent remains firmly bound to the silated alumina.[1] It is therefore highly probable that the silating agent reacts with available tetrahedral Al^{3+} sites and that the chloride binds irreversibly to these sites.

3. Influence of the Temperature. The degree of reaction and the nature of the silated alumina are each affected by the temperature of each of the three different stages of γ-alumina surface silation: the degree of preliminary dehydration of surface, the process of active silation in the presence of silane (silation A), and the subsequent reaction resulting from thermal treatment only, in the absence of additional silane (silation B). The temperature for the reaction of $(CH_3)_3SiCl$ with the γ-alumina surface influences the degree of silane chemisorption at the surface (the amount of supported silane molecules), the amount of eliminated methane, and the rate of the silation process. Our test results cover the temperature range reported by Paul et al. for the silation of γ-alumina.[13,16]

The degree of preliminary dehydration of the surface determines whether the reaction is carried out with or without change of the surface hydroxyl group number. When alumina has been partially dehydrated at 220 °C (or lower), further separation of water occurs upon silation, even when the silation temperature is 30–60 °C lower than the dehydration temperature. The formation of water is usually observed between 30 and 50 min following the start of reaction and is independent of the silane concentration in the nitrogen–silane feed. Similar additional low-temperature dehydration is also observed during the treatment of partially dehydrated alumina surface with HCl. Therefore, it is conceivable that for these systems the chloride anions displace OH groups, which then react further and condense as water. DeCanio et al.[5,31] observed a similar decrease of the surface concentration of hydroxyl groups on alumina as a result of fluorination of the surface.

During the silation of alumina with $(CH_3)_3SiCl$ (silation A) over the temperature range from 100 to 400 °C, methane is the only gaseous product. The FTIR spectrum of the gaseous products from silation in the temperature range 100–160 °C showed only bands arising from methane and that the amount of methane increased with increasing temperature, as determined by the increase in absorbance of the bands at 1302 and 3013 cm^{-1}. Over the temperature range 180–250 °C the rate and amount of methane formation are highly temperature dependent but are essentially similar in the range from 300 to 400 °C, as determined by the concentration of methane in the exit gas stream (Figure 4).

The rate of reaction of $(CH_3)_3SiCl$ with the surface of γ-alumina is characteristically low. The temperature at which silation is performed is a key parameter in determining the extent and nature of the reaction. A pattern of increased methane formation was observed on heating the solid product of silation in the absence of additional $(CH_3)_3SiCl$ (silation B). A sample of alumina was silated at 220 °C for 100 min, using a nitrogen–silane mixture at a flow rate of 23.14 N cm^3 min^{-1}. The silane adsorbed was 0.66 g (Table 1). As the silated alumina was successively heated to temperatures from 220 to 440 °C in a stream of nitrogen, and held for periods of hours at each temperature, the weight of the sample (Table 1) and the amount of methane produced (Figure 5) were each monitored. A series of infrared spectra of the gaseous product were obtained as a sample of silated alumina was heated to successively higher temperatures over a period of 6 days. Initially the sample was heated and then held at 180 °C. The methane was initially produced in high amounts, which decreased until the reaction was essentially complete after 20 h. The solid was then heated to 220 °C, and the production of methane immediately resumed, and then again decayed over 6 h. When the temperature was further increased successively to 260 °C and then 300 °C, the same pattern of behavior was observed. After the sample had been held at 260 °C for 2 days, there was very little methane detected in the exit gases. The sample was then successively heated to 400 °C, held for 6 h, and after a further 20 h heated to 440 °C. In each case, an increase in temperature caused further rapid reaction and production of additional methane, but no other gaseous product. For each increment in temperature an initial rapid increase in concentration of methane in the exit gases was observed, followed by an initially rapid decline in methane production and then continued methane production at a very low rate. The initial increase in methane concentration was similar for each 40 °C increase in temperature. The amount of methane produced at each temperature can be determined by integration of the area under the respective peaks.

The most important difference between silation A and silation B is exhibited at temperatures 280 °C and higher. In this temperature range silation A shows a progressive generation

TABLE 1: Weights of Solid Product at Stages during the Silation Procedure[a]

stage	initial silation	sequential thermal treatment						
temp of treatment stage (°C)	220	220	260	300	320	360	400	440
duration of treatment (h)	0	4	44	25	5	17	6	17
weight of sample (g)	12.46	12.44	12.38	12.34	12.34	12.28	12.26	12.22
change in sample weight during stage[c] (g)	+0.62[b]	−0.02	−0.06	−0.04	0.00	−0.06	−0.02	−0.04

[a] Weight of reactor, 264.13 g; weight of alumina before silation, 11.84 g. [b] Equivalent to weight of silane chemisorped. [c] Corresponds to cumulative formation of 0.24 g of CH_4.

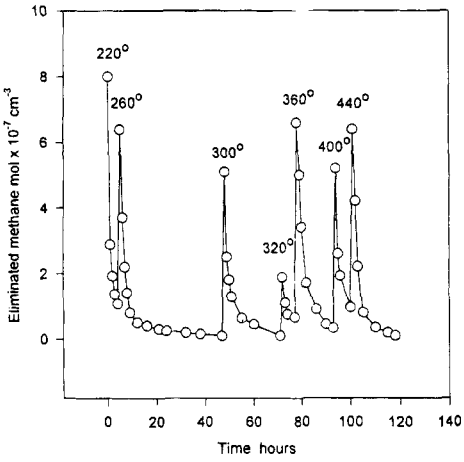


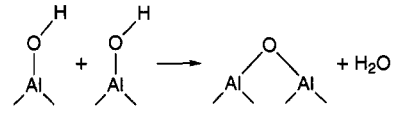
Figure 5. Effect of the temperature and duration of silation stage B on the concentration of methane in the gas phase.

of other reaction products, notably higher hydrocarbons, after 25−30 min from the initiation of the reaction. The amount of higher hydrocarbons increases as the temperature of silation A is increased from 300 to 350 °C. In the case of silation B, the only reaction product at all temperatures is methane. Thus, methane is the only product in the absence of fresh gas phase silane at higher temperatures, whereas higher hydrocarbons only form at high temperatures and in the presence of vapor phase $(CH_3)_3SiCl$.

4. Mechanism of Silation. The reaction of $(CH_3)_3SiCl$ with silica is known to occur by direct reaction with the residual surface hydroxyl groups and consequent elimination of HCl and formation of "umbrella structure" pendant groups: surface−$O-Si(CH_3)_3$.[14,18,22,24] The formation of HCl has been determined and quantified by these authors, and our data are in agreement with these results. The formation of HCl by the reaction with silica is both immediate and rapid upon exposure of the silica surface to $(CH_3)_3SiCl$. The above data on the volatile products from the reactions of partially dehydroxylated alumina with the same silating reagent preclude any similar reaction for alumina. No HCl is detected in the gaseous products, even though molar amounts as low as 10^{-3} times the methane generated would have been easily detectable and quantifiable (see section 1). Even if HCl had been initially generated and then reacted with other surface sites, it is difficult to envisage such a reaction trapping all HCl with such high efficiency throughout the reaction as to totally remove it from the gas stream in a dynamic system. Further, the chlorine from the silating reagent remains firmly bound to the silated alumina.[1] Thus, it is concluded that HCl is not generated as either a product or an intermediate.

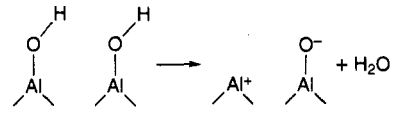
The silation does, however, cause a reduction in intensity of the IR bands associated with the surface hydroxyls (see section 2). Thus, it is clear that the mechanism requires the participation of more than one kind of surface site on the alumina, including the hydroxyls.

Of primary importance with respect to the surface chemistry of oxide supports, and in particular of alumina, is the presence on the surface of exposed aluminum cations, oxide anions, and very often hydroxyl groups.[3,4] The creation of these coordinatively unsaturated sites (CUS) is caused most often by preliminary dehydration of surface. These ions seem to be directly involved in sites for both chemisorption and catalytic activity. Dehydration of the alumina surface has been postulated to generated "strained oxide linkages":[32,33] a reaction which may be depicted as follows.



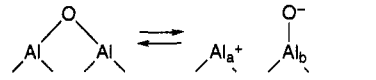
(2)

However, it is now agreed[26,33,34] that the dehydroxylation process leaves coordinatively unsaturated oxygen anions in the outermost surface layer and exposed, incompletely coordinated, aluminum cations in the next lowest layer, shown schematically as follows.



(3)

Exposed or coordinatively unsaturated metal ions act as Lewis acid sites and can thus provide interaction points for Lewis bases, such as electron donor ligands. Surface anions possess Lewis base properties and can effect nucleophilic attack at appropriate centers of supported molecules.[3,35,36] In this sense the "strained oxide linkages" could be treated as coordinatively unsaturated sites as well, if we accept that the CUS aluminum atom (Al_a) is a Lewis acid center and the CUS oxygen bonded to the other one (Al_b) is a Lewis base center.

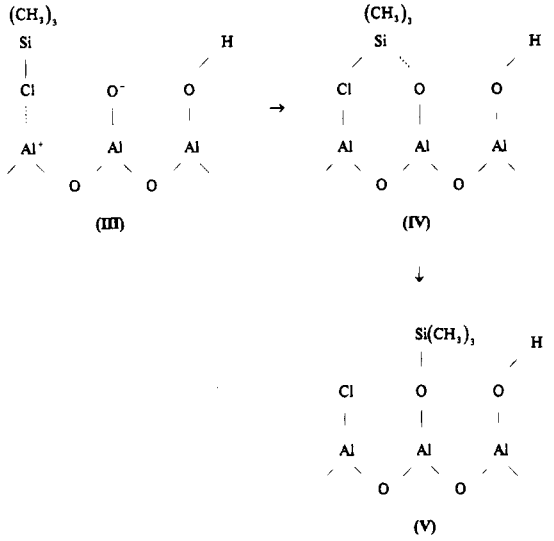


(4)

The Si−Cl bond in organosilicon compounds has significant polarity due to the great difference between the Pauling electronegativities of silicon (1.8) and chlorine (3.0). This is why the Si−Cl bond normally undergoes heterolytic rather than homolytic fission. On the other hand, the Si−Cl bond is easily cleaved by means of nucleophilic ionic agents which attack the silicon atom.[37] Thus, the first stage of interaction of $(CH_3)_3$-SiCl with the γ-alumina surface can be understood as the dissociative chemisorption of the silane molecule (Scheme 1).

The ionic character of the Si−Cl bond and the presence of three available unshared electron pairs in sp^3 orbitals cause the chlorine to behave as a Lewis base. The silane molecule coordinates via the chlorine center to the coordinatively unsaturated Al^{3+} cation, which is a Lewis acid center (**III**). Nucleophilic attack by an adjacent oxygen anion then occurs at the silicon atom (**IV**), resulting in formation of a surface alumina-siloxane compound (**V**).[37]

SCHEME 1: Interaction of Chlorotrimethylsilane with Lewis Acid and Base Sites on the Alumina Surface



The dissociative adsorption and aluminasiloxane species formation are consistent with the known chemistry of both alumina surfaces and organosilicon compounds. The reaction is readily conceptualized as resulting from the action of both the Lewis acid and base centers in adjacent positions on the surface with the corresponding Lewis base and Lewis acid sites of the organosilicon compound.

Although the existing evidence does not permit distinction between possible concerted or sequential interactions between the pertinent pairs of Lewis acids and bases, a concerted mechanism is considered the most probable. In a concerted mechanism there is no need to invoke free silyl cations, and the actions of the surface Lewis acid and base sites will effect cleavage of the Si−Cl bond in a synergistic manner.

In discussion of the role of polarity and ionic character of the Si−Cl bond concerning dissociative chemisorption of silane and formation of surface aluminasiloxane species, a characteristic of this bond should be noted. From the earlier work it has been shown that the polarity of the Si−halogen bond is lower than that expected from the theoretical value, due to the partial back (π) bond formation between the available electron pairs of the chlorine atom and the vacant silicon atom (3d) orbitals. This effect, however, is evinced mainly in low dipole moments of organosilyl halides.[37]

The stability of the Si−C bonds toward homolytic fission parallels that of the C−C bonds, and there is only a small difference between the bond energies. In accordance with the difference in the electronegativities, the Si−C bond is generally polarized as Si^+ and C^- and consequently can react through simultaneous nucleophilic attack on silicon and an electrophilic attack on carbon.[37,38] Based on the above data, the mechanism we propose for methane formation during the interaction of $(CH_3)_3SiCl$ with γ-alumina surface includes participation of surface CUS oxide, located proximate to a coordinatively unsaturated aluminum cation Al^{3+} and an isolated OH group that is capable of supplying the proton necessary for methane formation. The elimination of the CH_4 molecule is accompanied by formation of a surface aluminasiloxane-bridged structure.

The key point of methane molecule formation in the reaction of $(CH_3)_3SiCl$ with γ-alumina surface is the incorporation of the proton from surface hydroxyl and the methyl group from the silane. The source of protons is hydroxyl groups left on the surface after partial dehydration. According to Peri,[26] the most negative hydroxyls, having four oxide ions as nearest neighbors, would be associated with the highest overall negative charge, and their chemical behavior would be most basic. The least negative hydroxyl groups, located among four immediately adjacent vacant sites, would be most acidic. The other hydroxyl groups would fall between these limits. The five isolated hydroxyl bands observed in the range 3700−3800 cm^{-1} are tentatively assigned to these hydroxyl ions, with the most acidic ones located near 3700 cm^{-1} and the most basic centered near 3800 cm^{-1}. The surface of γ-alumina is dominated by basic acidic hydroxyl groups; the concentration of both neutral and weakly acidic hydroxyls is significantly smaller. The suggested mechanism needs participation of hydroxyl groups with acidic character, *i.e.*, those in which the OH hydrogens show a stronger proton-donor character and which are adjacent to vacant sites. The IR studies of irreversible reaction of surface hydroxyl groups with $(CH_3)_3SiCl$[13,16] show that the most acidic surface hydroxyls predominantly participate in the reaction. It has been observed[16] that the isolated OH modes at 3716 and 3670 cm^{-1} gradually disappear. These isolated OH species react first, followed by reaction of some of the associated OH species. Our results are consistent with the established quantitative relationship by Paul et al.[16] for the reaction of isolated hydroxyl groups and the production of irreversibly chemisorbed $(CH_3)_3Si-O-Al=$ groups.

The adjustment of surface acidity is of significant importance to the silation of γ-alumina and the resulting formation of methane. The overall acidity of the surface is determined by the number of Lewis and Brønsted acid sites. Whereas the Lewis acidity of the Al_2O_3 surface is considered well established, the existence of intrinsic Brønsted acid sites is controversial. The existence of weak Brønsted acid sites has been inferred from spectroscopic studies[39,40] and model reactions.[41,42] Pure alumina exhibits little or no Brønsted acidity;[31] in a sense, the surface acidity of alumina is "relative", depending on the relative basicity of probe molecules.[42] The incorporation of fluoride into Al_2O_3, however, creates some Brønsted acid sites, as has been proved by protonation of pyridine.[31] Thus, it is known that one of the major effects of incorporating fluoride into Al_2O_3 is the increase of the overall acidity of the Al_2O_3 surface.[31,43,44] The increase in the strength of Brønsted acidity is thought to be due to the electronegativity of fluorine, which makes the OH hydrogens more protonic.[43] This inductive effect might also be expected to increase the strength of Lewis acid sites. However, DeCanio et al.[31] concluded that the effect of added fluoride is to decrease the number of Lewis sites, whether or not they are more strongly acidic, and to increase the number of Brønsted acid sites. The latter effect is more prevalent than the former, so the composite trend is toward increased acidity and toward increased Brønsted character of the acidic sites.

A consequence of silation of γ-alumina with $(CH_3)_3SiCl$ is the impregnation of the alumina surface with another strong halide−chloride. The elemental analyses of our silated aluminas show that the average content of chloride on the alumina surface is between 2.4 and 3.0 wt %. Thus, our data are completely commensurable with the amount of fluoride determined elsewhere for other treated aluminas.[31] The specific feature of work described herein is that the alumina surface has not been premodified with the halogen and treated later with a chemisorbing compound, but rather that the halogen modification of the surface has been effected as a consequence of silation. The advantage of this latter course of action is that the chloride is always located in proximity to the silane moiety, which we propose promotes the inductive effect and accelerates the reaction to form the silicon−oxygen bond. The disadvantage is that chlorine has a lower Pauling electronegativity (3.0)

compared with that of fluorine (4.0), and consequently any inductive effect will be more moderate.

It is expected that the impregnation of the alumina surface with chloride will lead to an increase in the overall acidity. Brønsted acidity (as well as Lewis acidity) is associated with formation of an amorphous phase, most probably a chloroaluminum moiety which is not present in sufficient amounts to be detectable using XRD (X-ray diffraction). For fluoride loadings of 2 and 5 wt % only the typical diffraction peaks of γ-alumina are detectable.[31]

The fluorination of the alumina surface leads to a change in the surface concentration of hydroxyl groups. The increase in the strength of Brønsted acid sites is accompanied by a decrease in the density of alumina hydroxyl groups, due to the replacement of OH groups with fluoride anions.[31,43] In our study, the chlorination of the alumina surface is not accompanied by any significant change in the density of OH groups other than through the direct reaction, because of the different chemical nature of the reactant and the greater number of coordinatively unsaturated sites on the surface compared with the number of chloride anions. A change of number of surface hydroxyl groups was observed only in the case of silation of alumina, dehydrated at temperatures of 200 °C and lower, of which the surface is insufficiently dehydrated.

The location of halogen atoms on the alumina surface leads to an increase in the total acidity due to either the through-lattice inductive effect or the electron-withdrawing effect of a proximate halogen, resulting in a reduction of electron density of the neighboring chemical environment. However, the increase in the alumina surface acidity appears to be moderated, since the relatively higher acidity of silica surface does not effect the methane formation reaction to any comparable degree.

The acquired acidity of isolated hydroxyl groups affects the steric orientation of the chemisorbed aluminasiloxane species and formation of the methane molecules. Acid OH groups (as those found on Al_2O_3) can interact with weak basic (B) molecules, giving hydrogen-bonded OH···B species, whereas with strong bases, ionic species are formed by proton transfer,[3] $O^-\cdots HB^+$.

When either γ-alumina or Rh/Al_2O_3 catalysts have been modified by silation using $(CH_3)_3SiCl$, there has been acceptance[13,16] a priori of a mechanism according to eq 1. This reaction involving surface hydroxyl groups has been assumed in the area of organosilicon compounds.[16] However, we have not observed production of HCl, and therefore have found no evidence for the occurrence of the above reaction. The previous interpretation appears to be based upon the erroneous assumption that the behavior of Al_2O_3 and SiO_2 surfaces will be similar. It must be borne in mind that two significant differences exist between the natures of these catalyst supports. The first difference concerns the unsaturated nature of the alumina surface. As a result of dehydration on the alumina surface, a large number of coordinatively unsaturated sites, aluminum cations Al^{3+} and oxygen anions O^-, are created.[3,35,36] In contrast, heating of a silica surface under vacuum progressively eliminates OH groups, which condense to form H_2O and bridged oxides at the surface, Si−O−Si. These oxide bridges are relatively unstrained and consequently homopolar in character.[3] They are not as readily susceptible to either nucleophilic or electrophilic attack. The silica surface does not possess significant numbers of coordinatively unsaturated sites, and relatively few isolated hydroxyls remain. The second distinguishing characteristic concerns the difference in the acid−base character of the surface hydroxyl groups. Pure alumina contains mostly basic and some neutral and weak acidic groups. All hydroxyl groups on the silica surface possess weak acidic character. The isoelectric point of alumina is 8.3 and that of silica is about 2.0, which determines the different charge of the surface; Al_2O_3 has a positively charged surface, and SiO_2 has a negatively charged one. The SiO_2 surface contains OH groups which are less reactive than those of Al_2O_3.[28]

Thus, the initial reaction of alumina is not with surface hydroxyl groups but with coordinatively unsaturated Al^{3+} and O^{2-} centers. The irreversible modification of the surface with chloride increases the effective positive charge of the isolated hydroxyls to an acidity between that of hydroxyl groups on the neutral alumina surface and acidic hydroxyls on the surface of silica. These hydroxyl groups then react with the pendant $-O-Si(CH_3)_3$ groups, formed as intermediates, to eliminate methane as the only gaseous product.

IV. Conclusions

The reaction of $(CH_3)_3SiCl$ with the surface of alumina forms neither HCl nor pendant $-O-Si(CH_3)_3$ groups. Instead, the mechanism is a sequential reaction which affords methane as the only gaseous product. The silane is initially chemisorbed at the coordinatively unsaturated surface sites. This has the effect of modifying the surface by chloride, and the isolated hydroxyl groups are thus made more acidic. The hydroxyl groups then react with CH_3-Si groups to eliminate methane and to form bridging silyl moieties. Methane is the only gaseous product during silation of the alumina surface over the temperature range 140−260 °C as well as during thermal treatment of silated samples in a nitrogen atmosphere up to 500 °C. Methane production increases with each increment in temperature.

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