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Reduction of Ti(IV) Alkyls in Cab-O-Sil Surfaces

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$TiCl_4$ was reacted with the surface hydroxyls in two types of Cab-O-Sil. The reaction with annealed-Cab-O-Sil ($n = 1.4$ OH/100 Å^2) evolves 1 HCl/Ti(IV) reacted. This Ti(IV) species was subsequently reacted with various alkyl aluminum compounds to form surface-bound Ti(IV) alkyls. Bimolecular reaction involving pairs of neighboring alkyls resulted in the reduction of Ti(IV) to lower valence species. Alkylation by $Al(i\text{-}C_4H_9)_3$ and subsequent reduction are both rapid and quantitative at −80°. At 25°, even $Al(C_2H_5)Cl_2$ caused complete conversion of surface-bound titanium alkyls to Ti(III) species.

The reaction of $TiCl_4$ with rehydrated-Cab-O-Sil ($n = 4.6$ OH/100 Å^2) liberates 1.5 HCl/Ti(IV) reacted. Subsequent treatment with $Al(i\text{-}C_4H_9)_3$ caused the reduction of only about 45% of the surface-bound Ti(IV) species. These results are interpreted according to the known disposition of silanol groups in the surfaces of these materials.

I. INTRODUCTION

Ziegler-Natta catalysts for olefin-polymerizations are based on transition metal halides and alkyl aluminum halides. As the result of extensive studies during the past decade, the active species have been identified as transition metal alkyls. For α-$TiCl_3$, only those coordinatively unsaturated Ti^{3+} ions in the surface are believed to be active (*1*). The efficiency of this class of catalyst, i.e., grams of polymer produced per gram of catalyst, is quite low. The catalyst residues, unless removed from the polymers, contributes toward corrosion and polymer instability.

In principle, supported catalyst systems can offer higher efficiency since the metal ions are situated only in the surface of the support. The support material, because it is usually chemically innocuous, need not be removed.

The activity of a given catalyst for olefin polymerization depends not only on the initial number of active centers, but also upon how readily the growing chains are terminated and whether the sites are rendered inactive in the termination processes. It has been found (*2*) that there is no significant inactivation of catalytic sites of a $TiCl_3$–alkylaluminum chloride system during polymerization. On the other hand, the activity of a soluble $(\pi\text{-}C_5H_5)_2TiCl_2$–alkylaluminum chloride system decreases rapidly during polymerization. This has been attributed to the reaction (*3*),

$$\begin{aligned}&2CH_3AlCl_2\cdot(\pi\text{-}C_5H_5)_2Ti(Cl)(C_2H_4)_nCH_3 \rightarrow\\&\quad 2CH_3\cdot AlCl_2\cdot(\pi\text{-}C_5H_5)_2TiCl\\&\qquad + CH_3(C_2H_4)_{n-2}CH{=}CH_2\\&\qquad + CH_3(C_2H_4)_{n-1}CH_3. \qquad (1)\end{aligned}$$

It is possible that such reactions could also occur between propagating species supported on a surface. To aid in the design of highly efficient supported catalysts, we undertook a study to delineate those factors which determine the occurrence of this kind of termination.

Two types of Cab-O-Sils were chosen for the investigation because of their well-defined surface structures, because they can be prepared by reproducible procedures, and because they are commonly used as catalyst supports. In this work, the silanol groups in the surface were reacted with $TiCl_4$. The surface-bound Ti(IV) species were subsequently reacted with alkyl aluminum chlorides. The formation of Ti(III) products, presumably by a process analogous to reaction *(1)*, was followed by electron paramagnetic resonance (EPR).

II. EXPERIMENTAL

Materials. Fumed silica was used as a typical catalyst support because much is known about the surface of its various modifications, in particular the so-called annealed and rehydrated materials. To prepare annealed-Cab-O-Sil, Cab-O-Sil M5 contained in a quartz vessel was heated in a muffle furnace to 700° for 48 hr. This substance was refluxed in redistilled water for about 3 hr, then dried at 110°, and broken to ultimate particles by an agate mortar and pestle to give the rehydrated-Cab-O-Sil.

$TiCl_4$ was purchased from Stauffer Chemical Company and distilled immediately before use. The aluminum alkyl and alkyl aluminum chlorides were distributed by Alfa Inorganic Inc. Heptane was purified by repeated treatment with concentrated H_2SO_4, washing, and fractionation. It was stored over molecular sieve under 5 psig of nitrogen.

Reaction of Cab-O-Sil with $TiCl_4$ in slurry. This reaction was performed in a two-necked round bottom flask equipped with a nitrogen sparge tube and a reflux condenser having a water removal attachment. A magnetic stirring bar was also contained in the vessel but was not turned on until after the addition of $TiCl_4$. With a stream of predried nitrogen flushing the reactor, a sample of Cab-O-Sil and a quantity of dry heptane were introduced and refluxed for 1 hr. Typically, 2.5 g of annealed-Cab-O-Sil or 1 g of rehydrated-Cab-O-Sil and 100 ml of dry heptane were used. All molecular water was effectively removed by this procedure. The reaction mixture was allowed to cool and the water-removal attachment was replaced with a scrubber. While the slurry was slowly stirred, 0.75 mole of $TiCl_4$ (10% solution in heptane) was introduced by syringe. The mixture was heated gradually to reflux. The liberated HCl was titrated periodically with 0.5 *N* NaOH until HCl evolution ceased.

Reaction with aluminum alkyls. A slurry sample of Cab-O-Sil with combined titanium and a heptane solution of aluminum alkyl or alkyl aluminum chloride were mixed at —80° in a 25-ml round bottom flask provided with a side arm constructed from 4-mm o.d. quartz tubing. A uniform sample of this reaction mixture was tipped into the side arm at low temperature. The side arm was sealed off and the EPR spectra of the contents were recorded at various temperatures. In other experiments, this reaction was carried out at room temperature. All operations were performed under anaerobic conditions.

III. RESULTS

Stoichiometry of $TiCl_4$ reaction with Cab-O-Sil. Annealed-Cab-O-Sil contains 0.4 mmole of hydroxyl/g. In three separate reactions from 10 to 75% coverage, there was found, on the average, 1.3 mole of HCl evolved/mole of $TiCl_4$ reacted. This stoichiometry ratio is about 30% larger than the ratios found in the reactions of Cab-O-Sil with $TiCl_4$ *(4)* and VCl_4 *(5)* vapor in the absence of diluent.

Rehydrated-Cab-O-Sil contains about 1.3 mmole of hydroxyls/g. When it was reacted with 0.25 to 0.9 mmole g^{-1} of $TiCl_4$; 0.525 to 1.75 mmole g^{-1} of HCl was liberated. The average for four preparations is 2.0 moles of HCl liberated/mole of $TiCl_4$ reacted. The corresponding ratio for reactions performed without diluent for either $TiCl_4$ or VCl_4 *(5)* was 1.55. The slurry procedure again yielded 30% more HCl.

The higher HCl yields could be caused by incomplete removal of all water in the slurry procedures. Azeotropic distillation may not have been sufficiently exhaustive. However, the use of the slurry method is necessary because it was not possible to effect subsequent reductive alkylation in the absence of diluent. The reaction of vapors of aluminum alkyls with dry Ti(IV) which has appended to Cab-O-Sil produced no paramagnetic species. Because of this, the slurry method was used in the $TiCl_4$ reaction even though the HCl yields were somewhat too high.

Reactions of Aluminum Alkyls with Annealed-Cab-O-Sil to which Ti was Appended

A. Low temperature reactions. In these experiments, annealed-Cab-O-Sil, with 75% surface coverage of Ti(IV), **A**, was mixed with a 70-fold excess of an alkyl aluminum compound at —80°. The temperature was raised at a rate of about 0.5° min^{-1} and the EPR spectra were recorded at various temperatures.

The reaction of **A** with $Al(i\text{-}C_4H_9)_3$ resulted in the immediate and nearly quantitative reduction of the surface titaniums. The EPR spectral intensity measurements showed that 3.03 m*M* of the 3.5 m*M* of Ti(IV) initially present was converted to Ti(III). The spectra (Fig. 1) showed only a slight asymmetry ($g = 1.960$; $\Delta H = 86.7$ G). These features were independent of temperature within the range of —130 to 70°. The spectral intensity at —130° is about 2.2 times greater than it is at 70°. This intensity variation is reversible and can be attributed to the temperature dependence of paramagnetism.

The reaction of **A** with $Al(C_3H_5)_2Cl$ was much slower than the one with $Al(i\text{-}C_4H_9)_3$ at the same temperature. After the full —80 to +70° program, 66% of the Ti(IV) was reduced, as judged from the EPR spectra. At room temperature the spectrum has a g-factor of 1.943; its line width and shape are nearly indistinguishable from that shown in Fig. 1. The low temperature EPR spectra are distinctly asymmetric (Fig. 2). Two interpretations are possible. One possibility is that the spin-Hamiltonian is axial at low temperature with $g_\perp = 1.944$ and $g_\parallel = 1.910$; and that the crystal field becomes nearly cubic at elevated temperatures. Alternatively, there may exist two nonequivalent Ti(III) species each with a characteristic g value at —80° which become indistinguishable at higher temperatures because of chemical exchanges. Two arguments seem to favor the second interpretation. From Fig. 2 we calculate that exchange interaction should give an EPR spectrum with an average g-value of 1.940. The observed value at 25° is 1.943. Furthermore, addition of CH_3CN (*vide infra*) shows definitely that there is more than one kind of Ti(III) species.

The reduction of Ti(IV) species in sample **A** by $Al(C_2H_5)Cl_2$ at —80° is about one-sixth as fast as the corresponding reaction with $Al(C_2H_5)_2Cl$. The Ti(III) yield was less than 10% following the —80 to +70° cycle. The g-factor was 1.946; the line width was 98 G. Even though the lineshape was asymmetric, the g-anisotropy must be rather small.

B. Room temperature reactions. This series of experiments parallels the ones above, the only difference being that the reactants were mixed at room temperature.

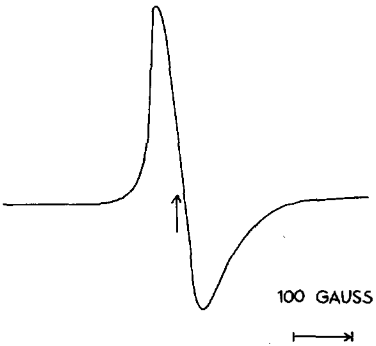


FIG. 1. EPR spectra of Ti(IV) on annealed-Cab-O-Sil formed by the low temperature reaction of $Al(i\text{-}C_4H_9)_3$ with Ti(IV). Marker at 3325 G.

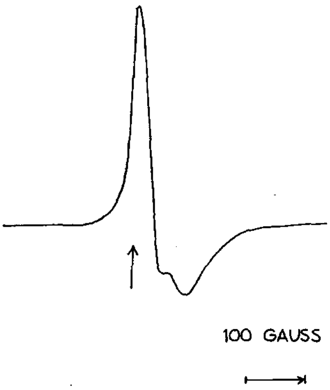


FIG. 2. EPR spectra of Ti(III) on annealed-Cab-O-Sil formed by the low temperature reaction of $Al(C_2H_5)_2Cl$ with Ti(IV). Marker at 3325 G spectra recorded at —80°.

Within 10 min, the transferred sample was cooled to —80° and the EPR spectrum was recorded. The sample was then brought to room temperature; the EPR spectrum was obtained from 25 to 70°.

Mixing of $Al(i\text{-}C_4H_9)_3$ solution with **A** produced a brown supernatant. There was obtained a week EPR spectrum, $g = 1.953$ and $\Delta H = 80$ G. The intensity corresponded to less than 3% of the Ti present. Heating the mixture caused reduction of EPR spectral intensity, which was not recovered by subsequent cooling.

The reaction of **A** with $Al(C_2H_5)_2Cl$ converted about 6% of the Ti(IV) to Ti(III) species. The EPR spectra have the appearance usually attributed to g-anisotropy. However, it can be shown that two different Ti(III) species were formed. Addition of small amounts of acetonitrile greatly reduced the spectral line width. It became possible to resolve two lines completely with g-factors of 1.954 and 1.977 in ratios of 5:1.

Titanium(IV) on annealed Cab-O-Sil can be completely converted to Ti(III) products by room temperature reaction with $Al(C_2H_5)Cl_2$. Two resonances were observed at —80° immediately following mixing at 25°—one with $g = 2.004$, $\Delta H = 110$ G; and one with $g = 1.940$, $\Delta H = 60$ G (Fig. 3a). Warming back to room temperature caused the dissappearance of these signals and the appearance of two new resonances at $g = 1.896$ and 1.860 (Fig. 3e). Figure 3b–d shows the spectra obtained at intermediate temperature. These spectroscopic changes are not reversible.

Reactions of Aluminum Alkyls with Rehydrate-Cab-O-Sil to which Ti was Appended

The experiments reported in this section differed from those with annealed-Cab-O-Sil in only two respects. The sample **B**, had a coverage of only 0.3 mmoles of $TiCl_4$/g of rehydrated Cab-O-Sil corresponding to one titanium for every 4.5 available surface hydroxyl groups. Secondly, only a 25-fold excess of aluminum alkyls was used.

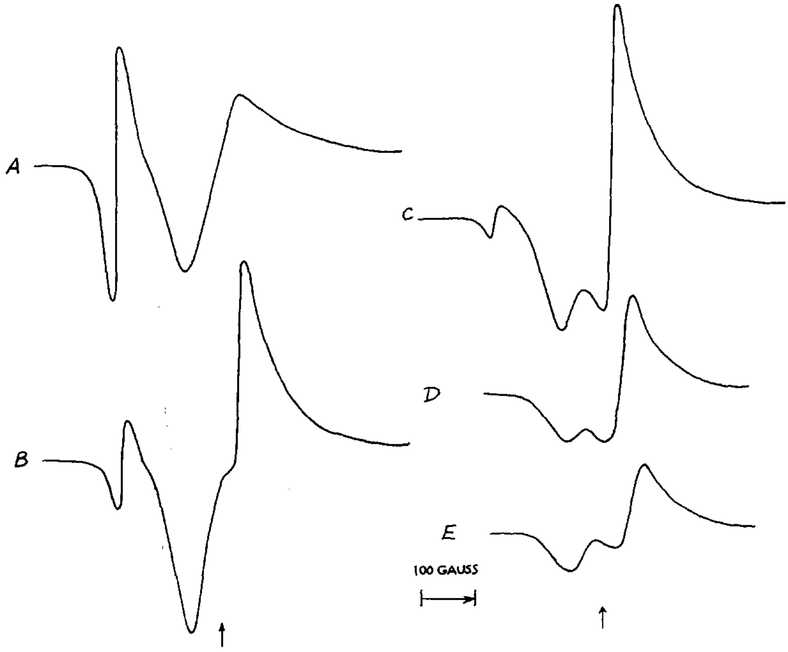


Fig. 3. EPR spectra of Ti(III) on annealed-Cab-O-Sil formed by the room temperature reaction of $Al(C_2H_5)Cl_2$ with Ti(IV). Spectra were recorded at: (a) −80° (1); (b) +25° (0.63); (c) +40° (0.32); (d) +60° (0.1); (e) +70° (0.1) (numbers in parentheses correspond to instrument gain); markers at 3486 G.

A. Low temperature reactions. Reaction of **B** at —80° with $Al(i\text{-}C_4H_9)_3$ resulted in immediate reduction of a portion of the Ti(IV) species on the surface. The EPR spectra accounted for 4.7 m*M* of the 10 m*M* of Ti(IV) on the Cab-O-Sil surface. The spectral parameters are: $g = 1.950$ and $\Delta H = 83$ G. The remaining Ti(IV) resist reduction even at 70°. They are apparently in an unfavorable steric, physical, or chemical situation for reduction.

The $Al(C_2H_5)_2Cl$ reacted much like $Al(i\text{-}C_4H_9)_3$ toward **B.** There was a rapid reaction at —80° which transformed 20% of the Ti(IV) to Ti(III). There was no further reduction detectable by EPR above —50°. The EPR spectra were anisotropic: $g_\perp = 1.960$ and $g_\parallel = 1.927$. Another interpretation could be that two Ti(III) with different *g*-factors are contributing.

Only 10% of the Ti(IV) was reduced by $Al(C_2H_5)Cl_2$ to give EPR spectra having $g = 1.950$ and $\Delta H = 50.8$ G.

The reduction of Ti(IV) by $Al(CH_3)_3$ became significant only above 25°. The —80 to 70° cycle converted 17% of the Ti(IV) to Ti(III). The EPR spectrum is asymmetric: $g = 1.954$ and $\Delta H = 62.7$ G.

B. Reactions at room temperature. Only the reaction with $Al(i\text{-}C_4H_9)_3$ was studied. Reduction of Ti(IV) was rapid. However, the EPR spectral intensity accounted for only 44% of the Ti present. Apparently, the remaining Ti(IV) alkyls are not reduced for steric reasons.

Reaction of $TiCl_4$ with Aluminum Alkyls

The unexpected and apparent ease with which aluminum alkyls are able to reduce those Ti(IV) attached to oxide surfaces prompted a comparison of this reaction with the reactions between $TiCl_4$ and aluminum alkyls in solution. Because soluble Ti(III) species are usually characterized by short spin-lattice relaxation times, a complexing agent such as CH_3CN was introduced in these experiments to increase the relaxation times.

Upon mixing a 20 m*M* $TiCl_4$ solution and an equal volume of a 0.1 *M* $Al(C_2H_5)_3$ solution at —80°, both in heptane, a weak EPR signal was produced (Fig. 4a). This signal represented a mere 2.5% of the Ti(IV) present. The intensity increased slightly and the spectrum became more complex as the temperature was raised

FIG. 4. EPR spectra of a mixture of $TiCl_4$ and $Al(C_2H_5)_3$ recorded at: (a) −130° (1); (b) −50° (1); (c) +70° (1); (d) CH_3CN added, +25° (0.4); markers at 3325 G (numbers in parentheses correspond to instrument gain).

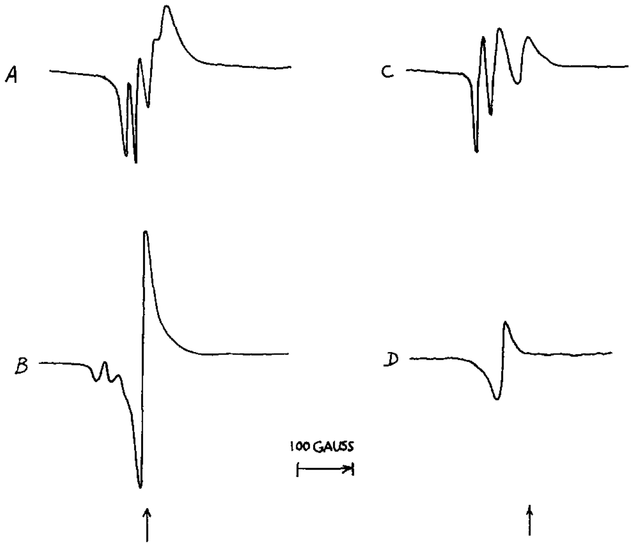


FIG. 5. EPR spectra of a mixture of $TiCl_4$ and $Al(C_2H_5)_2Cl$ recorded at: (a) −50° (1.6); (b) +25° (0.4); (c) +40° (0.4); (d) +70° (0.4); markers at 3325 G (numbers in parentheses correspond to instrument gain).

(Fig. 4b) but also progressively weaker at still higher temperature (Fig. 4c). Introduction of CH_3CN brought out the spectra of several Ti(III) species (Fig. 4d). The overall reduction under these conditions was estimated to be about 15%.

The reduction of $TiCl_4$ by $Al(C_2H_5)_2Cl$ was insignificant below —50°. Many paramagnetic products were formed above that temperature. The total spectral intensity reached a maximum at 25° which represents 10 to 20% of the $TiCl_4$ present (Fig. 5).

No Ti(III) was detected by EPR when solutions of $TiCl_4$ and $Al(C_2H_5)Cl_2$ were mixed until the temperature was brought up to 25°. Above 25°, there was a single symmetric signal ($g = 1.902$; $\Delta H = 38.2$ G) whose intensity increased with the increase of temperature. At 70°, the amount of Ti(III) estimated from its spectrum corresponded to 8% of the $TiCl_4$ in the system initially. Addition of CH_3CN caused a slight shift of g-factor to 1.921 and a reduction of line width to 11 G. Only 1 Ti(III) species was formed and present at any time in this system.

IV. DISCUSSION OF RESULTS

Bimolecular reduction of Ti(IV) alkyls. The reduction of $TiCl_4$ to $TiCl_3$ by aluminum alkyl halides is believed to proceed via titanium alkyls as intermediates. A number of such compounds have been synthesized and characterized (*6–10*). Whereas homolysis of the Ti–C bond had been suggested by some, these studies showed that the principal process is:

$$2Cl_3TiC_2H_5 \rightarrow 2TiCl_3 + C_2H_4 + C_2H_6. \quad (2)$$

The relative stability of methyl titanium trichloride and neopentyl titanium trichloride also follows naturally from this mechanism. Even the decomposition of CH_3TiCl_3 was proven to involve successive bimolecular processes. The overall reaction can be represented by

$$nCH_3TiCl_3 \rightarrow nTiCl_3 + \text{hydrocarbons}. \quad (3)$$

The bimolecular pathway in the presence of $TiCl_4$ is

$$CH_3TiCl_3 + TiCl_4 \rightarrow CH_3Cl + 2TiCl_3. \quad (4)$$

For a catalyst to be highly efficient in olefin polymerization, it is obvious that the metal attached to the support should not easily undergo these bimolecular terminations.

The reduction of $TiCl_4$ by alkyl aluminum chlorides *in solution* is a function of both the alkylating power of the latter and the concentrations of the reactants. In dilute solutions and below ambient temperatures, the reduction is slow with $Al(i\text{-}C_4H_9)_3$ and negligible with Al-

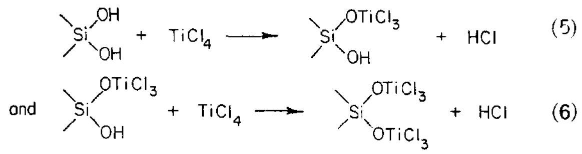
$(C_2H_5)_2Cl$. Therefore, it is most remarkable that the Ti(IV) species in the Cab-O-Sil surface were readily reduced by $Al(i\text{-}C_4H_9)_3$ at −80° and even by $Al(C_2H_5)Cl_2$ at 25°. If Eqs. (2–4) correctly represent the reduction processes, the Ti(IV) species must be situated in close proximity to one another.

Distribution of surface silanol groups in Cab-O-Sil. We give a brief review here about the distribution of surface silanol groups in Cab-O-Sil. Dried hydrogel of silica usually holds 7.85 hydroxyls/100 Å^2. Ibers (*11*) believed that the surface of this material resembles the [100] face of β-cristobalite. DeBoer and Vleeskens (*12*) discovered a rehydrated material, which can be prepared by first annealing silica gel at 500°, or above; and subsequently boiled in water, filtered, and dried at 100°; the product has a constant $n = 4.6$. All fumed silicas, similarly treated, hold this amount of surface OH groups. The authors ascribed the surface to the octahedral faces of β-cristobalite or to the [0001] face of β-tridymite. Other workers (*3, 4*) found that there exist on silica surfaces many neighboring OH groups ("vicinal" hydroxyls) which react in pairs with reagents such as $(CH_3)_2SiCl_2$, CH_3SiCl_3, Al_2Cl_6, $SiCl_4$, etc. Peri and Hensley (*14*) proposed that the surface of silica gel is that of [100] face of β-cristobalite as first postulated by Iber. Annealing of such a surface leaves vicinal and geminal hydroxyls behind. Only 1.2 geminal hydroxyls/100 Å^2 remained when the material is fully dehydrated, i.e., the annealed-Cab-O-Sil.

Recently, we determined the local concentrations of the various types of silanol groups in annealed- and rehydrated-Cab-O-Sils (*5*). In this method, VCl_4 was reacted with Cab-O-Sil and the EPR spectra of the surface-bound vanadiums were obtained for a range of fractional monolayer coverages at −195 and 25°. The interpretation of the data relied mostly on two EPR phenomena. When the distance separating two vanadium atoms is less than 8.3 Å, exchange broadening can obliviate the ^{57}V hyperfine splittings. If two vanadium atoms are bonded to the two OH groups of the same geminal pair, their resonances become too broad to be discerned from the base line because of exchange interaction and modulation of zero-field splitting.

The results of that study (*5*) showed that the model of Peri and Hensley (*14*) is almost correct. Rehydrated-Cab-O-Sil contains about equal proportion of vicinal and geminal pairs. Annealed-Cab-O-Sil contains mostly geminal hydroxyl groups in clusters of about 2.6 pairs/100 Å^2. Peri and Hensley had proposed a random distribution of only 0.7 pairs/100 Å^2.

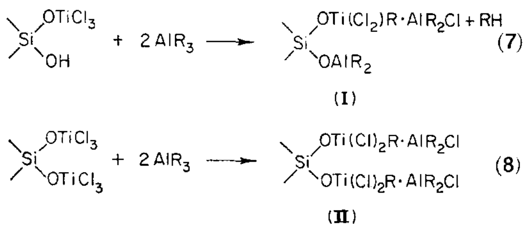
Annealed-Cab-O-Sil. Two types of Ti(IV) species are probably formed when annealed-Cab-O-Sil reacts with $TiCl_4$.



$$\equiv Si(OH)_2 + TiCl_4 \longrightarrow \equiv Si(OTiCl_3)(OH) + HCl \quad (5)$$

$$\text{and}\quad \equiv Si(OTiCl_3)(OH) + TiCl_4 \longrightarrow \equiv Si(OTiCl_3)_2 + HCl \quad (6)$$

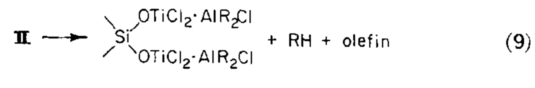
Subsequent reaction with AlR_3 gives



$$\equiv Si(OTiCl_3)(OH) + 2AlR_3 \longrightarrow \equiv Si(OTi(Cl_2)R\cdot AlR_2Cl)(OAlR_2) + RH \quad (7)$$

$$\equiv Si(OTiCl_3)_2 + 2AlR_3 \longrightarrow \equiv Si(OTi(Cl)_2R\cdot AlR_2Cl)_2 \quad (8)$$

Product **II** is rapidly reduced,

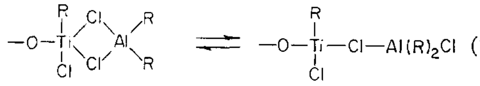


$$\textbf{II} \longrightarrow \equiv Si(OTiCl_2\cdot AlR_2Cl)_2 + RH + \text{olefin} \quad (9)$$

Similar reduction of **I** can occur when it reacts with another **I** or **II** species. The fact that the surface initially contains predominantly clusters of geminal hydroxyl pairs and the observation that all the surface-bound Ti(IV) species can be reduced even by $Al(C_2H_5)Cl_2$ implies that **I** is situated close to either another **I** or **II** species. The complete conversion of Ti(IV) to Ti(III) by $Al(i\text{-}C_4H_9)_3$ at —80° can be similarly explained.

Several other observations require comments. The first is the fact that at —80° $Al(C_2H_5)_2Cl$ and $Al(C_2H_5)Cl_2$ reduced only a portion of Ti(IV) to Ti(III) species as judged from the EPR spectral intensities. There can be two possible explanations. The first possibility is that reduction did take place but the resulting Ti(III) have very short relaxation times, because if the spin-Hamiltonian is octahedral, the ground state is orbitally degenerate. An example is aquated Ti(III) which displays EPR absorption only at liquid He temperature. On the other hand, if the spin-Hamiltonian has much lower symmetry, the degeneracy is lifted. Ti(III) compounds of this type are known to possess EPR spectra. The best known examples are the aluminum alkyl and aluminum chloride complexes of bis(cyclopentadienyl)titanium chlorides (*15–17*). Alternatively, ligand-field distortion may be imparted by complexing with a Lewis base. For example, $TiCl_3 \cdot 2CH_3CN$ shows an EPR spectrum at room temperature (*18*). That this possibility is untenable here is shown by the absence of any effect on the EPR spectra when CH_3CN was added to the reaction mixture.

A second possibility is that the Ti(IV) species are incompletely reduced by $Al(C_2H_5)_2Cl$ and $Al(C_2H_5)Cl_2$ because they are stronger Lewis acids and weaker alkylating agents than $Al(i\text{-}C_4H_9)_3$. Consequently, the Ti(IV) species are alkylated only slowly by the former reagents. Once alkylated, the electron-deficient Cl-bridges between Ti and Al are strong. These strong Cl-bridging bonds could retard the reduction of Ti(IV) if the formation of the transition state requires the disruption of one of the Cl-bridging bonds, i.e.,


(10)

Equilibrium 10 is more favored in the forward direction with $Al(i\text{-}C_4H_9)_3$ than it is for either $Al(C_2H_5)Cl_2$ or $Al(C_2H_5)_2Cl$. Finally, in a closed system, another back reaction 11 (*19*) can also occur between alkylated titanium and HCl.

$$\text{—O—Ti}(C_2H_5)Cl_2 + HCl \longrightarrow \text{—O—TiCl}_3 + C_2H_6 \qquad (11)$$

This reaction is prevented by $Al(i\text{-}C_4H_9)_3$ which could react with HCl, whereas the alkyl aluminum chlorides do not. Furthermore, with $Al(i\text{-}C_4H_9)_3$ reduction is probably too fast for the back reaction (*7*) to compete effectively.

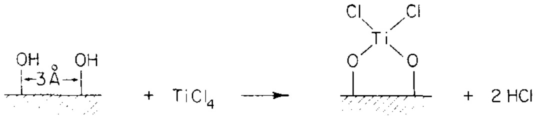
Figure 3 shows that in the reaction with $Al(C_2H_5)Cl_2$, at least two different Ti(III) species were produced at the outset (see the spectrum recorded at —80° immediately after initial mixing at 25°). As the temperature was increased, the low-field signal decreased in intensity. In its place a new signal appeared at high field (Fig. 3b). At 70°, the spectrum (Fig. 3e) is the resonance of two Ti(III) species, the *g*-values of which are different from those of the initial species (*vide supra*). Some candidates for these species are: $\text{-OTiCl}_2 \cdot Al(C_2H_5)Cl_2$, $\text{-OTiCl}_2 \cdot AlCl_3$, $\text{-O-Ti}(C_2H_5)Cl \cdot Al(C_2H_5)Cl_2$, and $\text{-OTi}(C_2H_5)Cl \cdot AlCl_3$.

At room temperature, the reaction with $Al(i\text{-}C_4H_9)_3$ produced only a weak Ti(III) resonance even though all the Ti(IV) atoms were reduced to Ti(III) species at —80°. Most probably the Ti(III) were reduced further to Ti(II) species. Low spin Ti(II) complexes are diamagnetic. Even high spin Ti(II) complexes could have resonances excessively broadened by modulation of zero-field splittings. It was found (*20*) in solution reactions that at an $AlR_3/TiCl_4$ ratio of 3:1, the average valence of

Ti after reaction is 1.5; it is even lower at higher ratios.

Rehydrated-Cab-O-Sil. The observations made concerning annealed Cab-O-Sil are largely applicable to this material as well. The most significant departures are the following: Low temperature reactions with Al(i-C_4H_9)$_3$ were complete when the substrate was annealed-Cab-O-Sil; it was only 47% complete for rehydrated-Cab-O-Sil. Whereas the same reaction at room temperature caused over-reduction of the titanium supported on annealed Cab-O-Sil, 44% of the titanium remained in the trivalent state when the substrate was rehydrated-Cab-O-Sil.

These differences can be attributed to the fact that in addition to singly-attached Ti(IV) species (**I** and **II**), there is also produced doubly-attached species (**III**), by the reaction of $TiCl_4$ with both hydroxyl groups of a vicinal pair.



III

(12)

Roughly 50% of the surface-bound Ti(IV) species on rehydrated Cab-O-Sil belongs to this type as judged from the fact that this reaction liberates about 1.5 $HCl/TiCl_4$ reacted.

Doubly-attached Ti(IV), (**III**), are completely immobile (*5*). They are probably not free to assume whatever stereochemical configuration is needed to form a transition state complex with a neighboring Ti(IV) species for the reduction to proceed. The results are quantitatively consistent with an hypothesis that only those singly-attached Ti(IV) species, i.e., **I** or **II** are reduced.

Some comments on the EPR spectra. Table 1 summarizes the spectral features of the Ti(III) species in the Cab-O-Sil surface. The line widths range from 50 to 100 G and are temperature independent. This is to be compared with a much narrower line width of 20 G for $TiCl_3 \cdot 2CH_3CN$. Two line-broadening processes are probable: unresolved hyperfine interaction with the complexed aluminum nuclei and exchange interaction with a neighboring

TABLE 1
Ti(III) SPIN-LABEL SPECTRA

Spin-label		Temp of reaction (°C)	ΔH (G)	g
Ti(IV) on	alkyl			
Annealed Cab-O-Sil	Al(i-C_4H_9)$_3$	−80	86.7	1.960
	Al$(C_2H_5)_2$Cl	−80	86.7	1.944, 1.910
	Al$(C_2H_5)Cl_2$	−80	98	1.946
	Al$(CH_3)_3$	−80	57.5	1.956
	Al(i-C_4H_9)$_3$	25	80	1.953
	Al$(C_2H_5)_2$Cl	25		1.954, 1.977
	Al$(C_2H_5)Cl_2$	25	14, 60	2.004, 1.940 initial 1.8956, 1.8603 final
Rehydrated Cab-O-Sil	Al(i-C_4H_9)$_3$	−80	83	1.950
	Al$(C_2H_5)_2$Cl	−80		1.960, 1.927
	Al$(C_2H_5)Cl_2$	−80	50.8	1.950
	Al$(CH_3)_3$	−80	62.7	1.954
	Al(i-C_4H_9)$_3$	25		

Ti(III) atom. When CH_3CN was added to the sample the line width was reduced to about 15 G. Therefore, either CH_3CN replaces the complexed aluminum alkyl chloride to eliminate the hyperfine interaction, or the additional complexing with CH_3CN reduces the exchange interaction.

V. Conclusions

On the surfaces of Cab-O-Sils, almost every titanium atom incorporated by the reaction between $TiCl_4$ and the silanol groups is sufficiently close to another titanium so that once they are alkylated, reduction followed readily under conditions normally encountered in olefin polymerizations. This statement is probably also applicable to most other metal oxide supports as long as the transition metal ions are attached to the surface by a single linkage. This reduction is prevented when two bonds link the transition metal ion to the surface.

It is understandable that termination of the kind discussed here is not a problem with most of the commercial olefin polymerization catalysts. In the case of the $TiCl_3$–aluminum alkyl chloride system, the Ti(III) ions are imbedded in the matrix of the $TiCl_3$ crystal. In the case of the Phillips catalyst system, the chromium ions are definitely multiply bonded to the silica-alumina support (*18*).

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