JOURNAL OF CATALYSIS 18, 52-56 (1970)

The Polymerization of Propylene by the $SiO_2/TiCl_4/AlMe_3$ System

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Received September 19, 1969

INTRODUCTION

The present paper is an initial report on the results of an attempt to produce isolated complexes on an insulator oxide by reacting a volatile transition metal halide (viz., $TiCl_4$) with the surface hydroxyl groups of silica, which are covalent in nature and do not exist as hydroxyl ions (*1*), followed by treatment of the product with $AlMe_3$. ESR and IR (*2*) techniques have been used to investigate the reactions that occur, and the structure of the active centers present in the resulting catalytically active material.

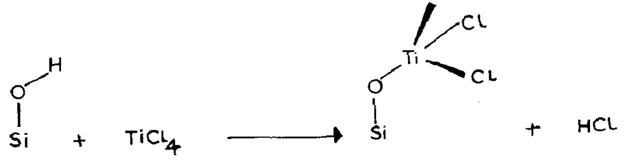
A well characterized (*3, 4*) Aerosil silica surface was chosen as the insulator oxide support. After evacuation at ambient temperatures the surface contains both single (infrared absorption band at 3750 cm^{-1}, see Fig. 1A) and hydrogen bonded hydroxyl groups (infrared absorption band at 3550 cm^{-1}, see Fig. 1A) which provide two distinct reaction sites for the transition metal halide. After calcination at 700°C the silica surface contains only single hydroxyl groups leading to only one coordination of the titanium species.

The self supporting silica discs [RA3/5/700 (*3*)] used in all the experiments described had been calcined at 700°C for a minimum period of 48 hr to virtually eliminate the micropores produced by the pressing process. These were the samples used when surfaces carrying only single hydroxyl groups, were required. For experiments requiring surfaces carrying both types of hydroxyl groups, the calcined discs were immersed in liquid water and evacuated to constant weight at room temperature [RRA3/5/700 (*3*)].

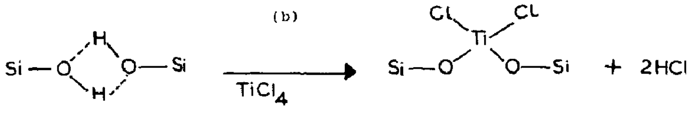
IR STUDIES

(*i*) *Reaction of the Silica Surface with* $TiCl_4$

Treatment of either silica surface with excess $TiCl_4$ vapor at room temperature removed all the surface hydroxyl groups, both isolated and hydrogen bonded (Fig. 1). The infrared spectra and corresponding weight change measurements (*4*) show that the surface hydroxyl groups react as shown below:



Single surface hydroxyls
[Type-A sites (*4*)]



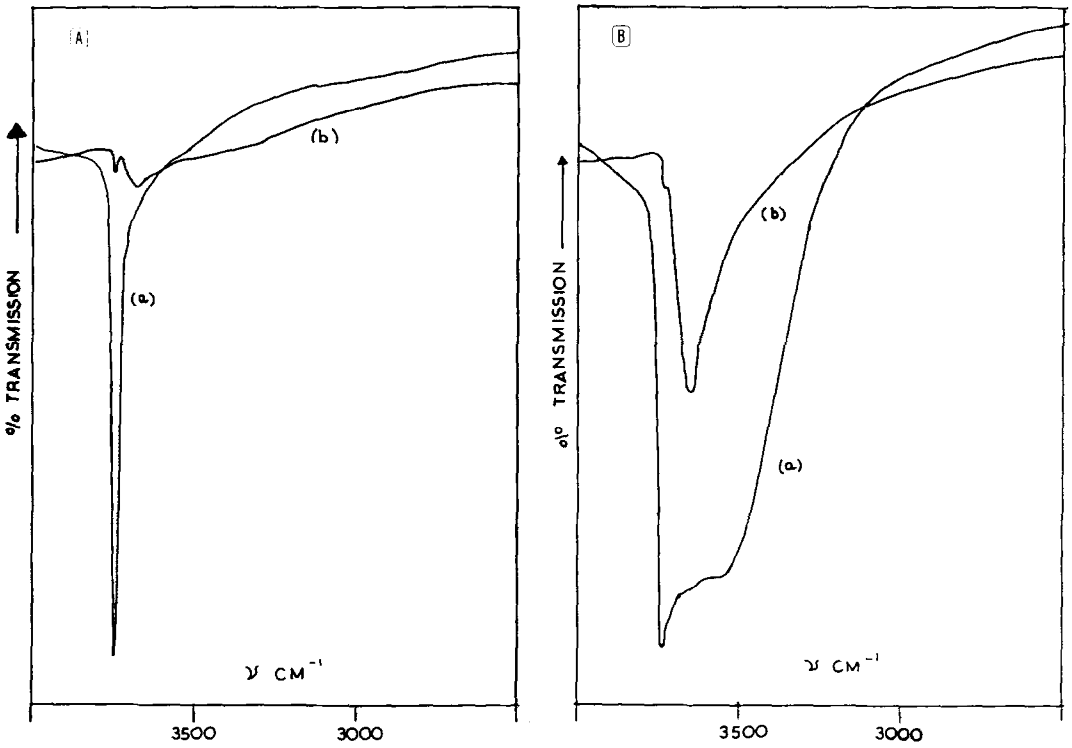


FIG. 1A(a). RA3/5/700 after evacuation at roomtemperature; (b) after reaction at room temperature with $TiCl_4$ vapor followed by evacuation at room temperature; B(a) RRA3/5/700 after evacuation at room temperature; and (b) after reaction at room temperature with $TiCl_4$ vapor followed by evacuation at room temperature.

Interacting surface hydroxyls
[Type-B sites (*4*)]

(*ii*) *Reaction of the $TiCl_4$-Modified Surface*

Treatment of a $TiCl_4$-modified surface with $AlMe_3$ at its SVP at room temperature for 2 min followed by prolonged evacuation of the excess vapor produced a considerable absorption in the C–H stretching region of the infrared spectrum (Fig. 2). The RA3/5/700 and RRA3/5/700 surfaces did not yield the same C–H spectrum as a result of this treatment. The bands in the 2950–2880-cm^{-1} region are typical of the symmetric and asymmetric vibrations of methyl groups. The appearance of the 2885-cm^{-1} band on the RRA3/5/700 surface indicates that some of the methyl groups are in a different environment from the remainder. In one experiment a weak band at 3090 cm^{-1} was observed which, at higher resolution and using ordinate expansion, was found to consist of a series of small peaks corresponding to gas-phase methane—Rodriguez and Gabant (*5*, *6*) have postulated methane formation during the reaction between solid $TiCl_3$ and $AlMe_3$ vapor to form an active Ziegler–Natta catalyst.

Addition of propylene gas (pressure $\simeq$0.1 atm) to samples which had been completely reacted with $TiCl_4$ and then treated with $AlMe_3$ vapor for 2 min produced considerable changes in the IR spectra of the two surfaces (see Fig. 2). The bands at 2955 and 2940 cm^{-1} are attributable to CH_3– and –CH_2– stretching vibrations, respectively. An absorption band at 1660 cm^{-1} was sometimes observed over the silica lattice absorption bands after exposure of a sample to propylene. This is typical of –C–C– multiple bond stretching in unsaturated systems. After exposure to propylene the samples were covered with a "sticky" colorless deposit.

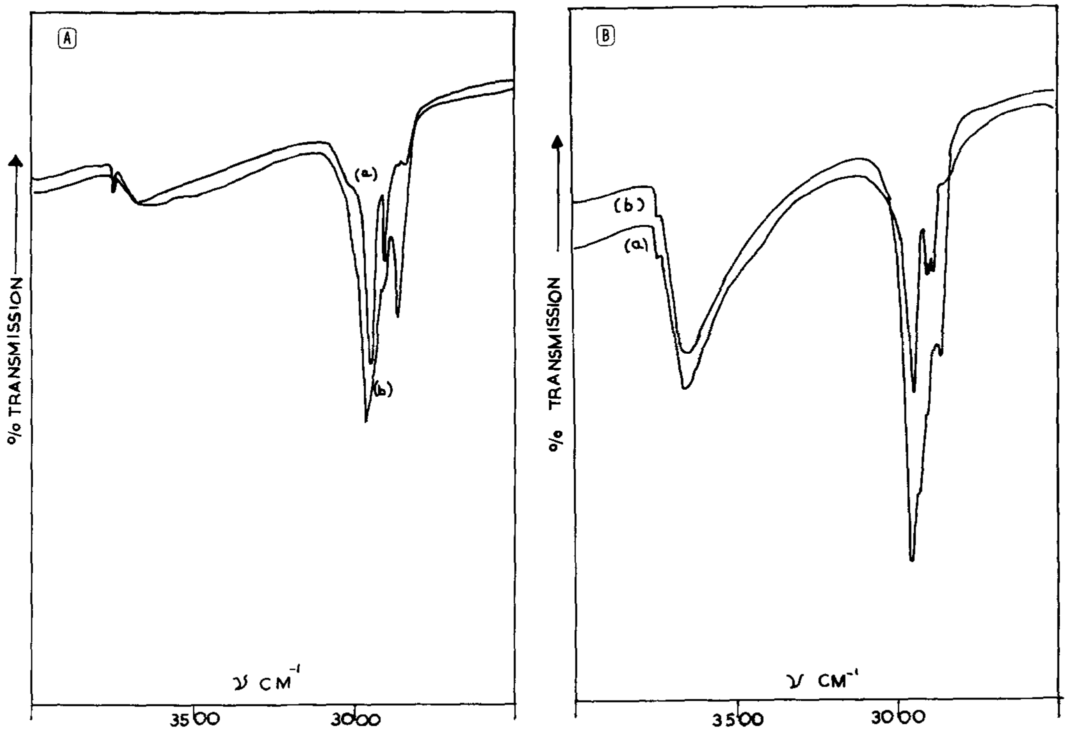


FIG. 2A(a). Sample as in Fig. 1Ab treated with $AlMe_3$ vapor at room temperature followed by evacuation; (b) after exposure to propylene gas (0.1 atm) overnight at room temperature followed by evacuation; (Ba) sample as in Fig. 1B(b) treated with $AlMe_3$ vapor at room temperature followed by evacuation; and (b) after exposure to propylene gas (0.1 atm) for 20 min at room temperature followed by evacuation.

The IR data indicate that the propylene has reacted with the $TiCl_4/AlMe_3$ system at the silica surface. The production of $-CH_2-$ groups and unsaturation on the surface may be due to the chemisorption of propylene but the appearance of the sample and gravimetric measurements confirm that polymer formation has occurred. Indeed the C–H region of the IR spectrum of the propylene-treated discs is similar to that of amorphous polypropylene (*7*).

ESR STUDIES OF THE CATALYTICALLY ACTIVE SURFACE

As expected none of the samples showed any ESR absorption either before or after reaction with $TiCl_4$. Admission of $AlMe_3$ vapor to a titanium tetrachloride-modified sample, which was in a quartz tube situated in the ESR spectrometer cavity, *immediately* produced a narrow, asymmetric absorption at $g = 1.94$ (Fig. 3). With the aluminum trimethyl vapor present, the signal intensity increased steadily with contact time until it reached a steady level. Evacuation of the gas-phase reactant and any products before the signal had reached its maximum value reduced the growth rate of the asymmetric signal but did not stop it completely.

This latter result suggests perhaps that the ESR signal arises as the result of the rearrangment or (more likely) decomposition of an initially formed surface complex, rather than as a result of the direct reaction of $AlMe_3$ with the $SiO_2/TiCl_4$ system. The reduction of Ti(IV) to Ti(III) yields a $3d^1$ system whose unpaired electron would give a single resonance line similar to the one observed and at the same g value (*8*). The results of recent investigations have shown that the active site in most Ziegler–Natta catalysts is the transition metal

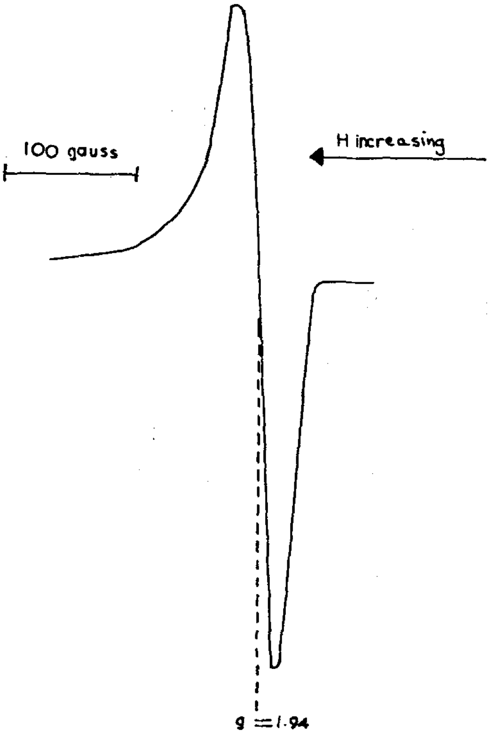


FIG. 3. ESR signal observed after treatment of a $TiCl_4$-modified silica with $AlMe_3$ vapor.

atom. Systems prepared using Ti(IV), as in this case, are only catalytically active when a reduction occurs *in situ* and Ti(III) is produced (*8*, *10*).

Figure 3 shows the ESR signal of a catalytically active sample. Admission of propylene (~10 cm Hg pressure) to such a sample at room temperature decreases the signal intensity but has no apparent effect on its width or symmetry.

Aluminum trimethyl also reacts with the surface hydroxyl groups of silica as follows (Fig. 5).

An RRA3/5/700 surface which had been completely reacted with $AlMe_3$ vapor followed by evacuation produced no ESR absorption. Admission of $TiCl_4$ vapor to this system produced a relatively smaller signal at $g \simeq 1.94$ (see Fig. 4). This signal was much more asymmetric than that produced by the samples prepared using the "normal" procedure, and showed no change in intensity with time after removal of the $TiCl_4$ vapor.

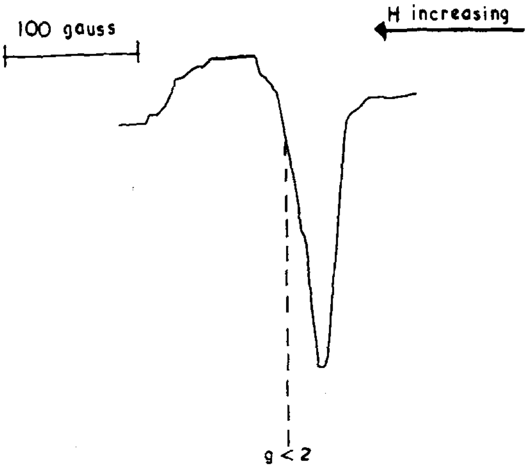


FIG. 4. ESR signal observed after treatment of an $AlMe_3$-modified silica with $TiCl_4$ vapor.

Samples prepared by this "reversed" methylation procedure displayed a comparable catalytic activity to those prepared by the "normal" route (i.e., $TiCl_4$ treatment followed by $AlMe_3$). The catalytically active samples prepared by the "reversed" route are "pale straw" color, with the intensity of the coloration depending on the length of the $TiCl_4$ treatment up to a total treatment time of 2 min.

The cessation in growth of the Ti^{3+} signal on removal of the $TiCl_4$ vapor in the "reversed" methylation procedure together with the absence of any black discoloration is interesting. Our other studies on similar systems involving $AlMe_3$ show that it is quite likely that this reagent is capable of attacking the $Si–O–TiCl_3$ and $(Si–O–)_2TiCl_2$ surface structures at the oxygen atom forming the more stable Si–O–Al system, and so displaces the $–TiCl_x$ species from their initially discrete surface sites with the resulting possibility of further complicated surface rearrangements of both a physical and chemical nature. Under "reversed" methylation conditions such displacement reactions involving the rupture of Si–O–Al bonds by $TiCl_4$ are, of course, unlikely. In consequence, the catalyst prepared by "reversed" methylation may well, in practice, correspond more closely to the ideal situation of discrete, catalytically active surface sites of a determinable structure.

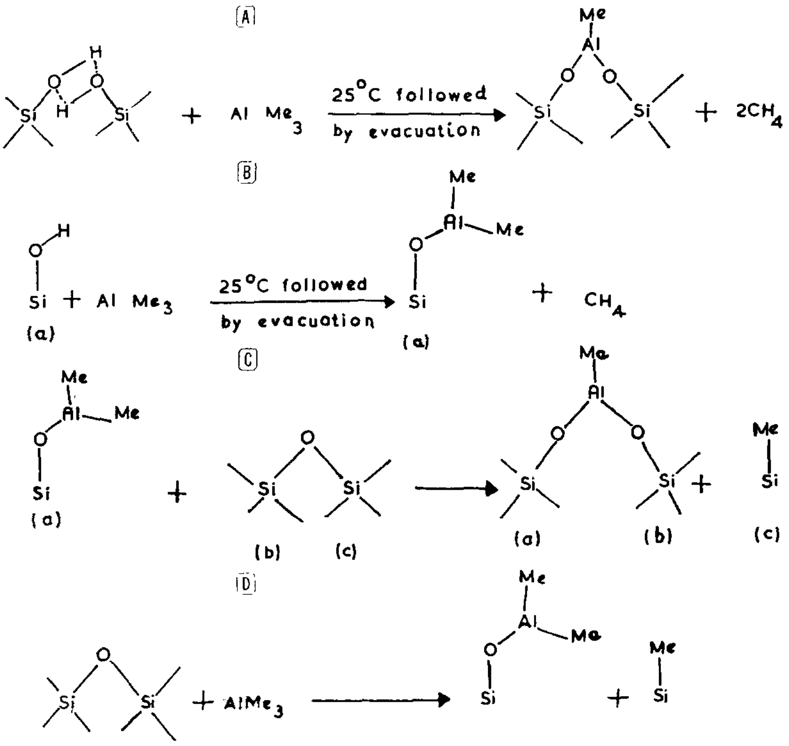


FIG. 5. Reaction of the silica surface with AlMe$_3$ vapor: (A) reaction of hydrogen bonded surface hydroxyl groups; (B) reaction of single-surface hydroxyl groups; (C) reaction of the product from (B) with neighboring surface oxygen atoms (*11*, *12*); and (D) direct reaction with surface oxygen atoms.

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