Studies on Probing SiO_2 Surface Using BF_3 As Probe and $SiO_2/Al_2Et_3Cl_3/TiCl_4$(PhMgCl) Catalytic System for Copolymerization of Ethylene and Propylene

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ABSTRACT: Using BF_3 as probe, the surface of SiO_2 was probed. The effects of the roast temperature on the SiO_2 surface were investigated and a possible mechanism is suggested. Using SiO_2 as starting material for supports, new supported catalysts for copolymerization of ethylene and propylene were prepared and their possible structures are discussed. It was found that higher polymerization productivity, for instance, 480 kg P/mol_{Ti} h, can be obtained by using a $SiO_2/Al_2Et_3Cl_3/TiCl_4$ catalytic system and addition of PhMgCl to this catalytic system can significantly increase polymerization activity. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1583–1589, 2000

Key words: SiO_2; BF_3 probe; supported Ziegler–Natta catalyst; ethylene and propylene; olefin copolymerization

INTRODUCTION

In recent years, many researchers have discovered and developed new metallocene catalysts for olefin polymerization.[1–7] Due to some serious problems with metallocene catalysts, for example, some resultant polymers prepared by a metallocene catalyst are difficult to process, many researchers still pay much attention to classic titanium-based catalysts suitable for the preparation of polyolefins, particularly for polypropylene, polyethylene, and the copolymer of ethylene and propylene.[8–13] Since most of the conventional

Ziegler–Natta polyolefin industrial plants are designed to use heterogeneous catalysts, fixation of homogeneous catalysts on a solid support is an important but challenging task and has attracted many researchers.[8–16] Various inorganic and organic magnesium compounds such as $MgCl_2$, $Mg(OH)_2$, $Mg(OH)R$, $Mg(OR)_2$, SiO_2, and Al_2O_3 have been used as starting materials to prepare the support. If the catalyst is directly supported, our previous studies showed that the resultant supported catalyst had poor catalytic activity, indicating that the support imposed an extra effect on the active sites and partially made the catalyst decompose. These results agree with those reported by different authors,[17] for example, the 0.002 kg PP/g_{Ti}h ($TiCl_3/SiO_2$ catalytic system)[8] and 11 kg PE/mol_{Zr} h (Cp_2ZrCl_2/SiO_2).[18] Therefore, the probe and modification of the support surface still is one of active research.[19] To determine the reason why polymerization productivity

depends dramatically on the support, probing the surface of and modification of the support have been the objects of many studies in the last decades since the discovery of catalysts for low-pressure polymerization of ethylene by Ziegler and stereospecific polymerization of 1-alkenes by Natta.[11,19,20] $AlEt_3/TiCl_4$/organic magnesium compounds are highly efficient catalytic systems for the polymerization of olefins and have been studied extensively.

In this article, using BF_3 as a probe, the surface of SiO_2 was probed and then modified by $Al_2Et_3Cl_3$. The supported catalytic system $SiO_2/Al_2Et_3Cl_3/TiCl_4(PhMgCl)$ for the copolymerization of olefins was prepared and a possible supporting mechanism is discussed.
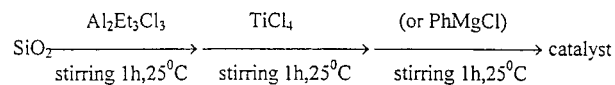
EXPERIMENTAL

Materials

BF_3 was obtained from the Huangyan Synthesis Chemicals Mill (Zhejiang Province, China), and SiO_2, from the Zhejiang Chemicals Mill (Zhejiang Province, China). Before roasting, SiO_2 was pretreated at 200°C for 2 h, then cooled to room temperature and sealed ready for use. The SiO_2 surface hydroxyl content was determined according to the literature.[20] $Al_2Et_3Cl_3$ and $TiCl_4$ were commercially obtained and used without further purification. Hexane was dried by activated molecular sieves under a nitrogen atmosphere. Polymerization-grade ethylene was further purified by passing over 4 Å activated molecular sieves.

Probing SiO_2 Surface Using BF_3 as Probe

A weighed sample of SiO_2 (1 g) was suspended in toluene (20 mL) and stirred in a two-neck flask. Then, a stoichiometric quantity of BF_3 was introduced to the flask and stirred continually for a fixed period (e.g., 1, 2, 3, 4, 5, and 6 h for different flasks). The slurry was filtered under N_2 and the solid was washed with dry toluene (3 × 10 mL). The resultant solid was then dried in a vacuum. The boron content supported on the SiO_2 surface was determined by chemical titration according to following procedure: One gram SiO_2, after reacting with BF_3, was washed with $0.02M$ NaOH three times. Methyl Red was added to the collected solution. Then, using a dilute HCl solution, the color of the collected solution was adjusted to red. The collected solution was boiled and phenol-

phthalein and 0.4 g mannitol added. The collected solution was titrated using a standard NaOH solution until the collected solution showed an orange–red color. The boron content was determined according to consumed NaOH quantity. IR spectra of the resultant solid were recorded by an IR-470 spectrometer.

Preparation of $SiO_2/Al_2Et_3Cl_3/TiCl_4(PhMgCl)$ Catalyst and Polymerization of Olefins

The preparative procedure of the $SiO_2/Al_2Et_3Cl_3/TiCl_4(PhMgCl)$ catalyst can be described as shown in Scheme 1. The copolymerization was performed at atmospheric pressure in a 200-mL reaction flask provided with a stirrer. In a typical polymerization, 100 mL of anhydrous heptane was introduced into the reactor under nitrogen and thermostated at 20°C. An ethylene–propylene mixture with the appropriate composition (at a mol ratio of ethylene/propylene = 3/1) was rapidly bubbled through the stirred solvent and the catalyst was introduced. The polymerization was terminated by addition of an acidified ethanol solution (adding hydrochloric acid to ethanol to form a $2M$ acidified ethanol solution) and the solution was stirred for another hour. The resultant polymer was washed several times with ethanol and dried in a vacuum oven at 60°C.

Analytical Procedures

The ^{13}C-NMR spectra of the resultant copolymer were recorded with a JEOL FX-90Q spectrometer with hexamethyldisiloxane as the internal standard. The solutions were prepared in o-dichlorobenzene-d up to about 15%. The ESR spectra of the catalyst were recorded at room temperature on a JEOL JES-FEIXG spectrometer under a N_2 atmosphere. The values of the g factor were determined by comparison with those of the Mn^{2+} standard.

RESULTS AND DISCUSSION

Pretreatment of SiO_2 and Probe of SiO_2 Surface Using BF_3

Recent observations suggest that SiO_2 surface hydroxyl is important for loading active species.[20,21]

$$SiO_2 \xrightarrow[\text{stirring 1h,25°C}]{Al_2Et_3Cl_3} \xrightarrow[\text{stirring 1h,25°C}]{TiCl_4} \xrightarrow[\text{stirring 1h,25°C}]{\text{(or PhMgCl)}} \text{catalyst}$$

Scheme 1 Preparation of $SiO_2/Al_2Et_3Cl_3/TiCl_4(PhMgCl)$ catalyst.

Table I Effect of Roast Temperature on the SiO₂ Surface Hydroxyl Content

Content	Roast Temperature (°C)					
	200	300	400	500	600	800
OH (mmol/g_{SiO_2})	1.6	1.1	1.0	0.7	0.57	0.4

Moreover, the population of SiO_2 surface hydroxyl and its control and modification of the SiO_2 surface are key steps for obtaining a highly active catalyst. It was found (Table I) that the population of SiO_2 surface hydroxyl can been controlled by the roast temperature. One can see that, with increasing roast temperature, the SiO_2 surface hydroxyl content decreases quickly. IR spectra of SiO_2 roasted at different temperature are shown in Figure 1(a–c). The range of 3700–3500 cm^{-1} is the absorption of SiO_2 surface hydroxyl. By comparing Figure 1(a–c), it is obvious that, with increasing roast temperature from 300 to 800°C, the absorption at the range of 3700–3500 cm^{-1} disappears gradually, which indicates that surface OH groups are removed gradually.

It is known that the reaction among halogenate, boron, and SiO_2 surface hydroxyl mainly is in the manner by which surface OH groups are removed and —OBX_2-containing groups are produced.[22] The main reaction may be denoted as follows:
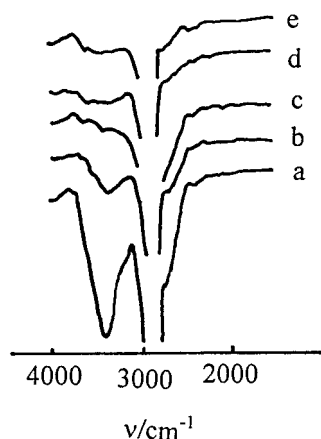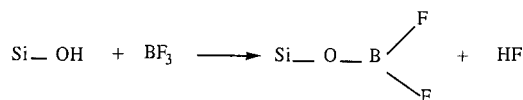
$$Si\!-\!OH \ + \ BF_3 \ \longrightarrow \ Si\!-\!O\!-\!B\!\!\begin{array}{c}{\diagup F}\\{\diagdown F}\end{array} \ + \ HF$$

Figure 1 IR spectra of SiO_2 before and after the modification of BF_3: (a) SiO_2 roasted at 300°C; (b) SiO_2 roasted at 500°C; (c) SiO_2 roasted at 800°C; (d) SiO_2 roasted at 300°C, then modified by using BF_3; (e) SiO_2 roasted at 500°C, then modified by using BF_3.

**Table II Effect of BF₃-added Content for Boron-loaded Content on the SiO₂ Surface**

Boron Content	Added BF₃ (mmol/20 mL toluene)				
	0.8	1.5	2.2	3	5
B (mmol/g_{SiO_2})	0.6	1.0	1.77	1.79	1.75

SiO_2: pretreated at 200°C; reaction time: 2 h.

Therefore, important information on the SiO_2 surface can be obtained through a reaction between —OH on SiO_2 and BF_3 using BF_3 as a probe. It was found that, while adding BF_3 at a constant content, with increasing reaction time, the B-loaded content on the SiO_2 surface first increases quickly (1.8 mmol/g_{SiO_2}), then slowly trends to a stable value. This result suggests that BF_3 diffuses first to the SiO_2 surface, contacts and reacts with OH groups quickly, then trends to a saturation boron-loaded content. Table II shows the effect of increasing BF_3 content on the boron-loaded content on SiO_2. The effect is apparent when the BF_3-added content is lower. It is worth mentioning that the saturation boron-loaded content (1.8 mmol/g) is higher than the SiO_2 surface hydroxyl content (1.6 mmol/g). The IR spectra of SiO_2 before and after modification with BF_3 are shown in Figure 1. In comparison with Figure 1(d,e), the absence of absorption in the range of 3700–3500 cm^{-1} is found for SiO_2 roasted at 300 and at 500°C and then reacted with BF_3 (at a ratio of boron-added mol : surface OH mol = 1 : 1), which also indicates that the following reaction takes place: $\equiv Si\!-\!O\!-\!H + BF_3 \rightarrow \ \equiv Si\!-\!O\!-\!BF_2 + HF$. One may come to the conclusion that, through chemical reaction between BF_3 and OH,

Table III Effect of Roast Temperature for Boron-loaded Content on SiO₂ Surface

Boron Loaded	Roast Temperature (°C)					
	200	300	400	500	600	800
Total boron loaded (mmol/g_{SiO_2})	1.84	1.7	1.8	1.65	1.6	1.58
Boron loaded chemically (mmol/g_{SiO_2})	1.6	1.2	0.95	0.7	0.55	0.35
Boron loaded physically (mmol/g_{SiO_2})	0.24	0.5	0.85	0.95	1.05	1.23
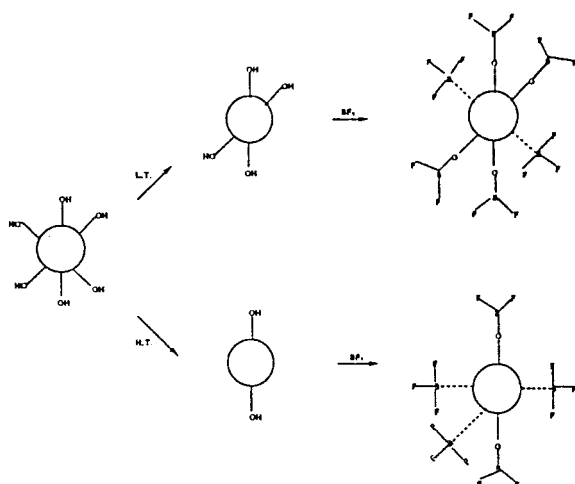
Scheme 2   Dehydroxylation of SiO_2 and the reaction between SiO_2 and BF_3.

the removal of surface OH groups can be complete and, moreover, preferred. The saturation boron-loaded content (1.8 mmol/g) is higher than the SiO_2 surface hydroxyl content (1.6 mmol/g), which may suggest that, except for the chemical reaction between surface OH and BF_3, BF_3 is partially absorbed on the bare surface of SiO_2 physically due to the presence of the partially bare surface on SiO_2. Usually, it is claimed that surface OH groups make the catalyst decompose.[17] The complete removal of surface OH is important to obtain a high active catalyst.

The total boron content, the boron content resulting from chemical reaction, and the boron content physically absorbed on SiO_2 roasted at different temperatures are summarized in Table III. A drastic phenomenon is found from the results shown in Table III. It is apparent that the total boron content loaded is always higher than boron content resulting from chemical reaction. What is surprising is that, with increasing roast temperature at which SiO_2 was roasted, the boron content resulting from chemical reaction decreases and that resulting from physical absorption increases. Due to the latter being easy to remove during the polymerization, the implication of the above results is that the roast temperature is

critical both for controlling the surface hydroxyl content and even for chemically anchoring the catalytic active center on the surface. These results agree with those reported by different authors and our previous work.[20] The dehydroxylation of SiO_2 and the reaction between SiO_2 and BF_3 are shown conceptually in Scheme 2.

**Preparation of $SiO_2/Al_2Et_3Cl_3/TiCl_4$(PhMgCl) Catalytic System and Polymerization**

Our previous work showed that the supported catalysts, using SiO_2 with medium anchor points as starting materials of supports, are highly active. From the above results with BF_3 probing, selecting SiO_2 with a medium OH content (roasted at 600°C) as starting materials of supports, a $SiO_2/Al_2Et_3Cl_3/TiCl_4$(PhMgCl) catalytic system was prepared. The preparation procedure for the $SiO_2/Al_2Et_3Cl_3/TiCl_4$(PhMgCl) catalytic system can be divided into three steps:

1. Interaction of $Al_2Et_3Cl_3$ with OH on SiO_2 to form Intermediate 1;
2. Interaction of Intermediate 1 with $TiCl_4$ to form catalyst B;
3. Interaction of catalyst B with PhMgCl to form catalyst C.

The interaction between SiO_2 and $Al_2Et_3Cl_3$ can be described simply as shown in Scheme 3,[10,12] which was supported by trapped ethane.

It was found that the number of surplus surface hydroxyl groups of SiO_2 is ~ 0.6 mmol $OH/gSiO_2$. The —$OAlCl_2$ and —$OAlClEt$ anchor points in Intermediate 1 makes supported Ti sepsis become so far removed from each other that the interaction between Ti and Ti becomes weaker and Ti^{3+} fundamentally is observable by ESR. Therefore, the ESR technique could be a logical research tool to aid in elucidating the structure of the active sites, due to Ti^{3+} being an active species for the copolymerization of ethylene and propylene.

As shown in Figure 2(a–c), no ESR signal was detected from the starting materials of the cata-
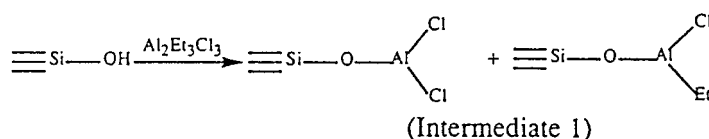
(Intermediate 1)

Scheme 3   Interaction between SiO_2 and $Al_2Et_3Cl_3$ to form Intermediate 1.

Mn^{2+} standard

5mT
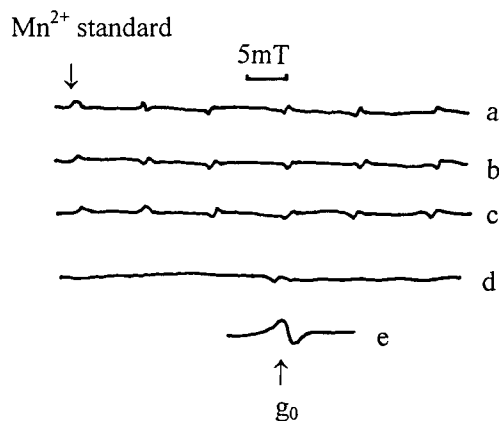
Figure 2 ESR spectra of (a) SiO$_2$, (b) Al$_2$Et$_3$Cl$_3$, (c) TiCl$_4$, (d) SiO$_2$ reacted with Al$_2$Et$_3$Cl$_3$ (amplification: 79), and (e) SiO$_2$ reacted with Al$_2$Et$_3$Cl$_3$ (amplification: 630).

lyst: SiO$_2$, Al$_2$Et$_3$Cl$_3$, and TiCl$_4$. However, after SiO$_2$ reacted with Al$_2$Et$_3$Cl$_3$, immediately an ESR signal (g_0 = 2.0035), corresponding to the free-electron resonance, was detected [Fig. 2(d,e)].

After Intermediate 1 was reacted with TiCl$_4$ at the ratio of Al/Ti $\sim$ 1/0.53 to form catalyst B, the ESR spectrum was recorded immediately to give Figure 3(a) characterized by three resonances: g_2 = 1.920, g_1 = 1.950, and g_0 = 2.0035. The last signal corresponds to the free-electron resonance. It is reasonable that the signals of g_2 and g_1 can
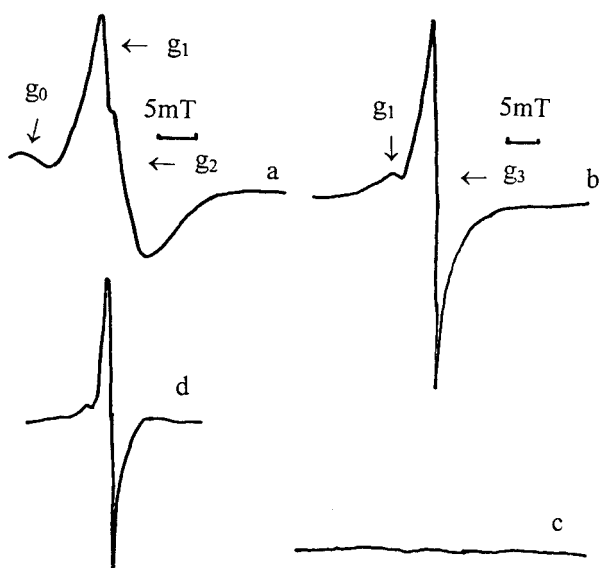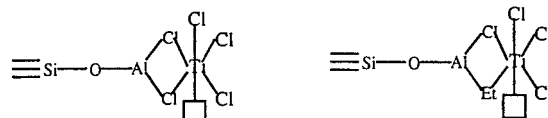

Figure 3 ESR spectra of Intermediate 1 reacted with TiCl$_4$: (a) Al = OH, at Al/Ti $\sim$ 1 : 0.53; (b) Al > OH, at Al/Ti $\sim$ 1 : 0.53 (solid phase); (c) Al > OH, at Al/Ti $\sim$ 1 : 0.53 (liquid phase); (d) simulating spectrum of b.

Scheme 4 Interaction between —OAlCl$_2$ and —OAlClEt and TiCl$_4$ to form catalyst B.

be, respectively, assigned to two paramagnetic species as shown in Scheme 4.

At Al : Ti = 1 : 0.53, with an increasing added amount of Al$_2$Et$_3$Cl$_3$ and TiCl$_4$, a new symmetric signal of g_3 = 1.930, obviously originating from mobile Ti^{3+} species, appears as shown in Figure 3(b). Moreover, there is no ESR signal for the liquid phase of catalyst B slurry [Fig. 3(c)], which indicates that mobile Ti^{3+} species are present in the microliquid phase on the solid surface owing to fewer —OAlCl$_2$ and —OAlClEt anchoring points than those of the Ti^{3+} species and the presence of a bare surface on SiO$_2$. The result confirms the coexisting possibility of multiple active species on the catalyst B system. To confirm the above assignment of three Ti^{3+} sepsis, an experimental ESR spectrum was simulated on a computer by the following equation[9]:

$$I'(H) = \frac{dI(H)}{dH}$$

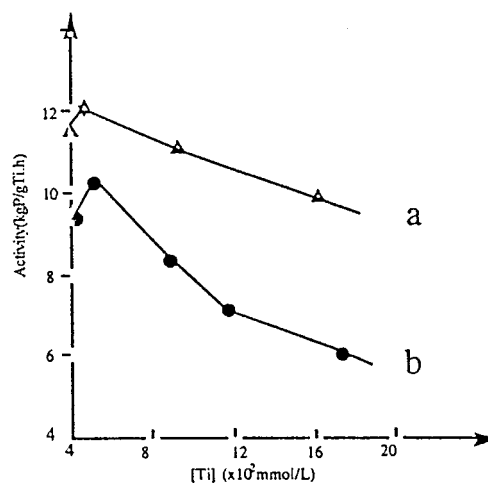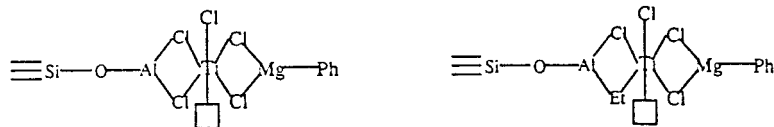$$= \sum_{n=1}^{N} \int_0^{2\pi} \int_0^{\pi} \frac{\delta/\pi(H - H_R)}{[\delta^2 + (H - H_R)^2]^2} P d \cos \theta \, d\phi$$

Figure 4 [Ti] dependence of polymerization activity: (a) SiO$_2$/Al$_2$Et$_3$Cl$_3$/TiCl$_4$/PhMgCl; (b) SiO$_2$/Al$_2$Et$_3$Cl$_3$/TiCl$_4$; E/P = 3; T_p = 50°C; t = 1 h.

Scheme 5   Active species of higher activity in $SiO_2/Al_2Et_3Cl_3/TiCl_4$ (PhMgCl) catalytic system (catalyst C).

It can be found that the ESR spectrum obtained by computer simulation [Fig. 3(d)] is consistent with that obtained experimentally [Fig. 3(b)], which shows that the assignment of three Ti^{3+} species —$OAlCl_2Ti$, —$OAlClEtTi$, and mobile Ti is reasonable. However, polymerization results indicate that the mobile Ti^{3+} species has low activity for the copolymerization of ethylene and propylene.[10] Therefore, it should be noted that it is important to select an appropriate OH/Al/Ti ratio in order to obtain a catalyst with high activity.

The influences of [Ti] on polymerization activity are summarized in Figure 4. It was observed that, first, polymerization productivity rises to a maximum value, then decreases with [Ti] increasing [as shown in Fig. 4(b)]. The polymerization productivity increases after adding internal PhMgCl to the $SiO_2/Al_2Et_3Cl_3/TiCl_4$ catalytic system as shown in Figure 4(a).

Ligands around active species are believed to exert considerable influence on polymerization activity. A possible reason may be that internal PhMgCl can coordinate with active species and form the active species of higher activity, mainly owing to its stronger π-electron-donating capability of benzene. The active species of higher activity in the $SiO_2/Al_2Et_3Cl_3/TiCl_4$ (PhMgCl) catalytic system (catalyst C) may be as shown in Scheme 5.[12] The ^{13}C-NMR spectrum indicates that the resultant polymer is a typical copolymer of ethylene and propylene (see Fig. 5).
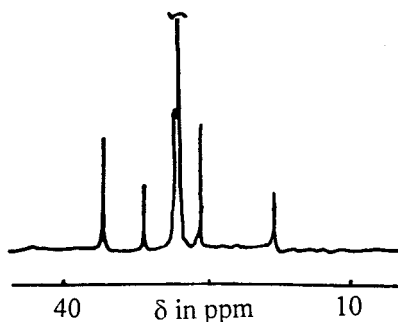
The following conclusions can be drawn from the above research results:

1. A new method using BF_3 as a probe in order to study the support surface and to select the support with an appropriate OH population was developed.
2. A new preparative method, as depicted in following scheme, gives a well-performing catalyst:

$$SiO_2 \xrightarrow{Al_2Et_3Cl_3} \text{intermediate 1} \xrightarrow{TiCl_4}$$

$$\text{catalyst B} \xrightarrow{\text{(or PhMgCl)}} \text{catalyst C}$$
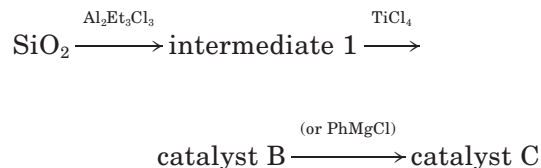
3. Multiple active species, including one mobile species on the microliquid phase of a solid, were discovered.
4. The addition of PhMgCl to $SiO_2/Al_2Et_3Cl_3/TiCl_4$ can increase polymerization productivity, maybe due to the Ph electron-donating capability.

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Figure 5 ^{13}C-NMR spectrum of resultant polymer.

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