Characterization & Polymerization Studies on Silica-supported Titanium (IV) Complexes

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Polymerization of ethylene using silica-supported [(MeO)3Si(CH2)3C5H4]-TiCl2 catalyst activated with diethylaluminium chloride has been investigated. The rate-time profiles obtained for room temperature polymerizations indicate a decay type behaviour. Although the rates obtained for the supported catalysts are higher than those of the homogeneous analogues, immobilisation of the complex on silica does not offer increased catalyst stability. Characterisation of the supported catalyst has shown that the interaction of [(MeO)3Si(CH2)3C5H4]-TiCl2 with silica can result in two types of supported compounds; one in which the complex anchors to the silica surface with both TiCl2 group and methoxy group and the other in which the methoxy group is anchored to the silica surface.

The use of transition metal complexes supported on silica, alumina or on other inorganic supports has been well known in Ziegler-Natta polymerisation ever since the development of silica supported chromium oxide catalyst for the polymerisation of ethylene1. The use of discrete, well characterized complexes supported on conventional supports offer some exciting possibilities for catalyst development and characterisation, and consequently it was decided to investigate the activity of the complex, [(MeO)3Si(CH2)3C5H4]-TiCl2 supported on silica and activated with dialkylaluminium chloride, for ethylene polymerisation. This dichloro complex2 has proved to be a very active and selective catalyst for terminal olefin hydrogenation, both in the homogeneous and in silica supported state.

Materials and Methods

All manipulations involving air-sensitive materials were performed under nitrogen atmosphere. The complexes, η5-C5H5-TiCl2 (ref. 3), η5-MeC5H5-TiCl2 (ref. 4), η5-C5H4TiCl2 (ref. 5) η5-MeC5H5TiCl3 (ref. 6) and η5-(MeO)3Si(CH2)3-C5H4-TiCl2 (ref. 2), were prepared as previously reported. All solvents were purified and dried by standard procedures.

Far infrared spectra were recorded using a Digilab model FTS-16 FT spectrophotometer. GLC analysis was carried out on a PYE 104 chromatograph using a 2m OV17 column.

Preparation of silica-supported [(MeO)3Si(CH2)3C5H4]-TiCl2

Silica gel [Grace Davison, 929, surface area (BET, N2) 281 m2 g-1] was dried at 300°C for 12 hr in vacuo and cooled in a stream of nitrogen, before adding to degassed toluene (100 ml) which had been stirred with aqueous sodium hydroxide (0.2M, 1 ml). The silica was stirred at 80°C for 1 hr to equilibrate, filtered, washed several times with dried toluene, and dried at 300°C immediately before use. A solution of η5-(MeO)3Si(CH2)3-C5H4-TiCl2 in dried toluene was stirred with the silica at room temperature for 36 hr. Various loadings of the complex on silica were prepared by stirring at room temperature, except in the case of samples C and G, (Table 1) where refluxing was carried out for 16 hr. The silica was filtered, washed with dried diethyl ether, extracted with hot benzene, and dried in vacuo at 50°C.

Electron microprobe

The silica-supported catalysts were made into pellets and subjected to an electron microprobe X-ray fluorescence study for radial distributions titanium and chlorine. Samples D and G were investigated.

Radical profiles for Ti and Cl on the surface of the pellets were determined using an ARL-EMX/SN electron microprobe in the Metallurgy Department, UMIST. The microprobe conditions were as follows: 25 kV accelerating voltage; 0.01 μA sample current; and 1 μm beam width.

Fast atom bombardment mass spectroscopy (FAMBMS)

The silica gel, and samples A, D, and G (Table 1) were analysed as powders. For the fast
atom bombardment the conventional ion source was replaced by an ion atom gun which allowed rapid switching from ion to atom mode and produced a pure mass, filtered particle beam having a current equivalent in the range $10^{-11}$ to $10^{-8}$ cm$^{-2}$.

The mass analyser used was a vacuum generator, MM12-12 quadrupole filter, with a mass range of 1-1200 daltons and unit resolution throughout the range. Secondary ion collection and energy selection was obtained by the modification of some of the optical equipments. A small, plasma discharge, neutral particle source was used for rapid profiling. All the samples were studied using fast argon atom bombardment. There were no problems for obtaining positive or the negative spectra from powders. The spectra were fully reproducible.

**Polymerization procedure**

In all the cases, the polymerization of ethylene was carried out in a polymerization reactor charged with dried toluene (500 ml), evacuated and purged three times with dried nitrogen. The temperature of the reactor was maintained by water pumped around the reactor from a thermostat bath. The catalyst was dispersed in dried and degassed toluene and carefully added to the reactor. The catalyst-toluene mixture in the reactor was stirred vigorously and ethylene was allowed to saturate the solution to a pressure of 1 atm. Then 2 ml of 15% AIEtCl in dried toluene were added by means of a hypodermic syringe. The solution immediately turned blue and the uptake of ethylene (with time) was recorded by an electronic counter system. The polymerization was allowed to continue for 100 min and was then quenched by the addition of ethanol. The polymer formed was precipitated with a mixture of methanol and HCl, filtered, washed and dried at 80°C in vacuo. The counts obtained were converted into rates using a conversion factor (C) obtained from Eq. (1).

\[
C = \frac{\text{(Total yield of polymer at the end of polymerization)}}{\text{(Total number of counts at the end of the polymerization)}} \quad \ldots (1)
\]

By multiplying this value with the number of counts on the print out, the weight of the polymer at any time in the reactor could be obtained.

**Results and Discussion**

**Characterization of silica-support**

In the present study, silica gel (Grace Davison OFUNNE et al.: POLYMERIZATION OF SILICA-SUPPORTED TITANIUM(IV) COMPLEXES 929) before use was heated at 300°C for 3 hr, and allowed to cool. Adsorption studies (BET) showed the surface area to be 281 m$^2$/g. IR spectrum of a 1 cm thick disc of pre-treated silica exhibited bands in the regions of 3650-3400 and 1300-960 cm$^{-1}$ which are characteristic of surface Si–OH groups. Similarly, when examined with fast atom bombardment spectrometry (FABMS), fragments at $m/z$ 45 and 28, corresponding to [Si–OH]$^+$ and [Si]$^+$ groups respectively, were obtained. Such results are in agreement with those reported by Vickerman et al. when a similar technique was used to analyse glass and zeolite surfaces. Microanalysis of the silica did not detect any organic impurity.

**Immobilization of [(CH$_2$O)$_3$Si(CH$_2$)$_3$C$_5$H$_5$]_2TiCl$_2$**

The synthesis and characterization of [(MeO)$_3$Si-(CH$_2$)$_3$C$_5$H$_5$]$_2$TiCl$_2$ and other complexes have been reported previously. Allum et al. have detailed some possible methods of coupling unstable homogeneous catalysts of this type to silica supports. One possibility is to attach the precursor ligand to silica before complexing the attached ligand with the metal compound (see Eqs 2-4).

\[
\begin{align*}
&\text{(CH$_3$O)$_3$Si(CH$_2$)$_3$C$_5$H$_5$} + \text{Si} - \text{OH} \rightarrow \ldots \ldots (1) \\
&\text{(Sil)} - \text{(CH$_2$)$_3$C$_5$H$_5$} + \text{CH$_3$OH} \ldots \ldots (2) \\
&\text{(Sil)} - \text{(CH$_2$)$_3$C$_5$H$_5$} + \text{Na} \rightarrow \text{(Sil)} - \text{(CH$_2$)$_3$C$_5$H$_5$} \text{Na}^+ \\
&\text{(Sil)} - \text{(CH$_2$)$_3$C$_5$H$_5$} \text{Na}^+ + \text{MCl$_2$} \rightarrow \ldots \ldots (3) \\
&\left[\text{(Sil)} - \text{(CH$_2$)$_3$C$_5$H$_5$}\right]_2\text{MCl$_2$} + \text{NaCl} \\
\end{align*}
\]

However, when using this method, the actual complex anchored to the surface cannot be characterized easily. In the present work, an alternative procedure has been employed. This procedure involves the synthesis of a well characterized discrete complex, and then the anchoring of this complex to a well characterized silica support. [(MeO)$_3$Si-(CH$_2$)$_3$C$_5$H$_5$]$_2$TiCl$_2$ was supported on pretreated silica by stirring in toluene, both at room temperature and also by refluxing at the boiling point of toluene.

In both the cases methanol was detected in the toluene by GLC. However when the reactants were refluxed at the boiling point of toluene HCl was also detected. These observations suggest that the surface silanol, apart from reacting with the methoxy group at reflux temperature, also reacts with the Ti–Cl group, thus displacing chlorine which is evolved as HCl. The possible reactions are illustrated in Eqs 5 and 6.
Table 1—Microanalytical Data for Immobilised Catalysts

<table>
<thead>
<tr>
<th>Samples</th>
<th>Colour</th>
<th>$\text{Cl}^+$ (%)</th>
<th>$\text{Ti}^2+$ (%)</th>
<th>$\text{Cl}/\text{Ti}$ (Calc.)</th>
<th>$\text{Cl}/\text{Ti}$ (nm$^2$) on surface occupied by each Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Salmon red</td>
<td>3.85(1.08)</td>
<td>2.83(0.59)</td>
<td>2</td>
<td>0.79</td>
</tr>
<tr>
<td>B</td>
<td>Light pink</td>
<td>1.96(0.55)</td>
<td>1.33(0.28)</td>
<td>2</td>
<td>1.96</td>
</tr>
<tr>
<td>C*</td>
<td>Light brown</td>
<td>0.20(0.058)</td>
<td>0.35(0.073)</td>
<td>2</td>
<td>0.76</td>
</tr>
<tr>
<td>D</td>
<td>Salmon red</td>
<td>9.70(2.73)</td>
<td>6.00(1.26)</td>
<td>2</td>
<td>2.18</td>
</tr>
<tr>
<td>E</td>
<td>Dark brown</td>
<td>0.74(0.208)</td>
<td>0.21(0.047)</td>
<td>2</td>
<td>1.22</td>
</tr>
<tr>
<td>F</td>
<td>Salmon red</td>
<td>6.38(1.79)</td>
<td>3.75(0.78)</td>
<td>2</td>
<td>2.30</td>
</tr>
<tr>
<td>G*</td>
<td>Light bridge</td>
<td>0.04(0.004)</td>
<td>0.09(0.018)</td>
<td>2</td>
<td>0.20</td>
</tr>
</tbody>
</table>

*Prepared by refluxing in toluene.

† Values in parentheses are in mmol/g.

$$\text{Si} - \text{OH} + [(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{C}_2\text{H}_4]_2\text{TiCl}_2 \xrightarrow{\text{room temp.}}$$

$$\text{Si} - [(\text{CH}_2)_3\text{C}_2\text{H}_4]_2\text{TiCl}_2 + \text{CH}_3\text{OH} \quad \ldots \quad (5)$$

$$\text{Si} - \text{OH} + [(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{C}_2\text{H}_4]_2\text{TiCl}_2 \xrightarrow{\text{reflux temp.}}$$

$$\text{Si} - \text{Ti}(\text{C}_2\text{H}_4)(\text{CH}_2)_3\text{[Si]} + \text{CH}_3\text{OH} + \text{HCl} \quad \ldots \quad (6)$$

Various loadings of the complex on silica were prepared by stirring in toluene at room temperature, except for sample C, and G for which the mixture was refluxed (see Table 1). This resulted in the evolution of HCl as well as the production of methanol indicating that the surface silanol groups had reacted with the Ti–Cl bonds. This conclusion is further substantiated by microanalyses for samples C and G which show a low Cl to Ti ratio (see Table 1).

**Characterization of supported titanium complexes**

Microanalytical results are summarised in Table 1. It is evident for Ti loadings $>1.30\%$ that chlorine:titanium ratios of about 2.0 are obtained. The data also show that various supported complexes with varying Ti loadings can be prepared depending on the conditions of preparation. Samples D and G have been selected for further studies. Analysis using IR spectroscopy gave bands at 468 ($\nu\text{as Ti–Cl}$), 434 ($\nu\text{as Ti–Cl}$), 190 ($\delta\text{C}_2\text{H}_4\text{–Ti–C}_2\text{H}_4$), 100 ($\delta\text{C}_2\text{H}_4\text{–Ti–Cl}$) and 2900 ($\nu\text{C}–\text{H}$) cm$^{-1}$, for sample D. These bands are characteristic of the presence of a $\text{C}_2\text{H}_4\text{TiCl}_2$ moiety on the surface. Furthermore, IR spectrum of sample G was complex and difficult to interpret. However, bands at 190 and 2900 cm$^{-1}$ were observed.

In order to measure the degree of dispersion of the complex on silica surface, electron microprobe examination was used. Chandrasekharan et al$^8$ have studied the dispersion of a $\text{C}_2\text{H}_4\text{TiCl}_2$ immobilized on polystyrene beads and found a uniform distribution of $\text{C}_2\text{H}_4\text{TiCl}_2$ on the polymer. Similarly, Dawan and Morel$^9$ have studied the dispersion of $\eta^3$-allylnickel(II) on a difluoroacetic terpolymer and reported that the metal atoms were attached to the matrix in such a way that there was a smooth cross-sectional distribution of nickel atoms throughout the polymer. In the present study sample D was examined by an electron microprobe technique and similar counts for titanium and chlorine atoms were obtained across the area studied (see Fig. 1). The intensities of the counts for chlorine, in sample D are about two times those for titanium. In addition the spectrum obtained for sample D is similar to those obtained for samples A and E. These results are consistent with an even distribution of the complex on silica surface. Examination of sample G by this technique, gave very low counts for chlorine, which is inconsistent with the expected Ti:Cl ratio and a uniform distribution on the support surface.

Further investigations of the catalyst surface were carried out using FABMS analysis. The spectrum of sample D displays fragment ions at $m/z 27[\text{C}_2\text{H}_3]^+$, 41 [$\text{C}_2\text{H}_5]^+$, 65 [$\text{C}_7\text{H}_7]^+$, 77 [$\text{C}_6\text{H}_5]^+$ and 91 [$\text{C}_7\text{H}_7]^+$.

![Fig. 1—X-ray fluorescence analysis of sample D (-----) Ti; (--.--.--.) Cl)
which are thought to have originated from the substituted cyclopentadienyl ring attached to the metal atom. Also, fragments associated with the titanium atom are observed at m/z 115 [C₅H₄TiH]⁺, 119 [TiCl₂]⁺, 127 [CH₃C₅H₄Ti]⁺, 128 [CH₃C₅H₄TiH]⁺, 147 [C₅H₄TiCl]⁺, and 64 [TiO]⁺. The intense peak observed at m/z 119 is a good indication that most of the Ti – Cl groups have not been hydrolysed (see Fig. 2). Sample G afforded a complicated FABMS spectrum and fragments containing – TiCl₂ group were not observed. In addition, the negative ion FABMS spectrum of sample D was studied (see Fig. 3). The main fragments observed were negative ions at m/z 35 [Cl]⁻ and 37 [Cl]⁻ with intense peaks. In contrast the spectrum obtained for sample G showed no significant fragments which could substantiate the existence of – TiCl₂ moieties on the surface.

The results from these analyses therefore indicate that the interaction of the present complex with the silica support can result in two types of supported compounds. In one of these the complex anchors to the silica surface with both the TiCl₂ and MeO-groups, as indicated in the analysis of sample G, while in the other, the methoxy group of the complex is anchored to the silica surface, as illustrated by the analytical observations for sample D.

Polymerization studies: Use of homogeneous catalysts

In order to compare the behaviour of homogeneous and supported polymerization systems, initially polymerization of ethylene was carried out using a number of homogeneous catalysts, viz. (η⁵-C₅H₅)₂TiCl₂; (η⁵-MeC₅H₅)₂TiCl₂; η⁵-C₅H₅TiCl₂; η⁵-MeC₅H₅TiCl₂ and (η⁵-(MeO)₃Si(CH₂)₃C₅H₅)₂TiCl₂. All polymerizations were performed under similar conditions using AlEt₂Cl as cocatalyst at an Al:Ti ratio of 3:64. Typical rate-time profiles are shown in Figs 4 and 5. It is evident from Fig. 6 that the catalyst systems (η⁵-MeC₅H₅)₂TiCl₂ – AlEt₂Cl and [η⁵-(MeO)₃Si(CH₂)₃C₅H₅]₂TiCl₂ – AlEt₂Cl all show settling periods, the maximum rates being attained within the first 15 min of polymerization after which the polymerization rates decrease gradually with time. The catalyst system η⁵-C₅H₅TiCl₂ – AlEt₂Cl and η⁵-MeC₅H₅TiCl₂ – AlEt₂Cl behave somewhat differently with higher maximum rates of polymerization being obtained within 10 min of the start of polymerization but showing a more rapid decrease in rate with time.

These catalyst systems are evidently more active but less stable. The significance of these rate-time profiles has been discussed elsewhere. Values of maximum rates of polymerization together with corresponding rates after 60 min polymerization are presented in Table 2. The order of maximum activities of these homogeneous catalysts is as follows: η⁵-C₅H₅TiCl₂ > η⁵-MeC₅H₅TiCl₂ > η⁵-(MeO)₃Si(CH₂)₃C₅H₅]₂TiCl₂ > (η⁵-C₅H₅)₂TiCl₂ > (η⁵-MeC₅H₅)₂TiCl₂. While it is not easy to explain exactly
Fig. 4 — Rate-time profiles for polymerization of ethylene with homo- 

ogeneous catalysts using AIEtCl as cocatalyst \( \Delta = \{\eta^2\}- 

MeC_5H_5TiCl_2; X = \{\eta^2\}-C_5H_4TiCl_2; \bullet = \eta^5-(MeO)_5Si(CH_2)_3-

C_5H_4TiCl_2. Polymerization condition: Al:Ti = 3.14:1; [Ti] = 0.55 
mol dm\(^{-3}\); C_2H_4 = 1 atm; and temp. = 18°C. \[1\]

Fig. 5 — Rate-time profile for polymerization of ethylene with homo-

ogeneous catalyst using AIEtCl as catalyst. \( \cdot \), \( \eta^2\)-C_5H_5TiCl_3; X, \( \eta^2\)-MeC_5H_5TiCl_3; Al:Ti = 3.6:1; [Ti] = 0.55 mol \ndm\(^{-3}\); C_2H_4 = 1 atm and temp. = 18°C. \[2\]

Fig. 6 — Rate-time profile for polymerization of ethylene with hom-

ogeneous catalyst using AIEtCl as cocatalyst and with added wa-

ter. \( \cdot \), \( \eta^2\)-C_5H_5TiCl_2 + H_2O; \( \cdot \), \( \eta^5\)-MeC_5H_4TiCl_2 + H_2O. Polymeri-

zation conditions: Al:Ti = 3.61:1; [Ti] = mmol dm\(^{-3}\); C_2H_4 = 1 
atm.; and temp. = 18°C. \[3\]

Fig. 7 — Rate-time profile for polymerization of ethylene with sup-

ported catalysts and using AIEtCl as cocatalyst \( \Delta \), sample D at 60°C; \( \bullet \), sample A at 60°C; \( \Delta \), sample D at 18°C; \( \bigcirc \), sample A at 18°C. Polymerization condition: Al:Ti = 3.64:1; [Ti] = 0.55 mmol/ 
dm\(^{-3}\); and C_2H_4 = 1 atm. \[4\]
Polymers were performed under conditions similar to those reported for the homogeneous systems. AlEt₂Cl was used as cocatalyst and the Al:Ti ratio was maintained at 3.64:1. While samples A and D polymerized ethylene the low loading samples proved to be inactive. Typical rate-time profiles are shown in Fig. 7, and demonstrate that these polymerizations are basically of the decay type\(^3\), in which the rate either shows a maximum initial value or increases quickly to reach a maximum value, and then decreases rapidly with time. This type of rate-time behaviour has been reported previously for many polymerization systems, including highly active supported catalysts MgCl₂/EB/TiCl₄ – AlEt₃ \((\text{ref. 13})\). It has also been observed in the polymerization of ethylene by catalyst systems derived from TiCl₄ and AlEt₃ \(^{14,15}\), and the homogeneous catalyst systems \(^{16}\) such as \((\eta^5\text{-C}_5\text{H}_5\text{TiCl}_2 - \text{AlEtCl})\). Additionally some modified catalyst systems, e.g. VOCl₂/2THF – AlR₃, in vinyl chloride polymerization, behave in the same way\(^1\). All of the supported systems studied show maximum initial rates within 10 min of the start of polymerization, and these rates are higher than those for the corresponding soluble systems (see Tables 2 and 3). In all the cases the rates decrease significantly with time, showing that although these supported catalyst systems are more active than the corresponding homogeneous analogues, these are nevertheless somewhat unstable indicating that supporting the catalyst on an insoluble matrix has not achieved increased stability. And as in the case with the rates of many highly active MgCl₂/EB/TiCl₄ – AlR₃ catalyst systems the rate decay with time could be fitted to a second order decay pattern. Nevertheless it should not be concluded on the grounds of this evidence alone that the decay process is bimolecular, since the decay in the rate of polymerization of many highly active catalyst systems can be represented better by a modified multi-centre first order decay model\(^2\).

### References


### Table 3—Rates of Ethylene Polymerization Using Support-ed Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp. °C</th>
<th>10 Rate/g (Polymer)</th>
<th>(mmol Ti)⁻¹.hr⁻¹.atm⁻¹</th>
<th>Maximum At 80 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample D – AlEt₂Cl</td>
<td>18</td>
<td>1855</td>
<td>272</td>
<td></td>
</tr>
<tr>
<td>Sample D – AlEt₂Cl</td>
<td>60</td>
<td>1852</td>
<td>157</td>
<td></td>
</tr>
<tr>
<td>Sample A – AlEt₂Cl</td>
<td>18</td>
<td>1403</td>
<td>145</td>
<td></td>
</tr>
<tr>
<td>Sample A – AlEt₂Cl</td>
<td>60</td>
<td>1297</td>
<td>436</td>
<td></td>
</tr>
</tbody>
</table>

Polymerization condition: [Ti] = 0.55 mmol/dm³; Al:Ti = 3.64:1; C₂H₄ = 1 atm; [H₂] = 0.01 mol/dm³; temp = 18°C

Use of supported complexes

Ethylene was polymerized using silica-supported silylated titanocene dichloride complexes. Three samples, A, D and G, of differing Ti loadings were studied.