Organometallics in ethylene polymerization with a catalyst system $TiCl_4/Al(C_2H_5)_2Cl/Mg(C_6H_5)_2$: 1. Suspension polymerization process

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Suspension polymerization of ethylene with the catalyst system $TiCl_4/Al(C_2H_5)_2Cl/Mg(C_6H_5)_2$, at different molar ratios Mg/Ti and Al/Ti, was studied. The transition metal compounds in the catalyst complex formed in this system were found to consist only of Ti(II) and Ti(III), without free Ti(IV); but even with a Ti(II) content of 30% the catalyst was highly active. The influence of the molar ratio cocatalyst/catalyst (Al/Ti and Mg/Ti) on the catalyst activity and on the polyethylene molecular weight was studied, together with the reduction of $TiCl_4$ by $Al(C_2H_5)_2Cl$ and $Mg(C_6H_5)_2$ in the reduction step. The polymer yield increased to some limiting molar ratio Mg/Ti and to some limit ratio Al/Ti and further increase of organometal concentration in the system has practically no influence on the catalyst productivity. Dependence of the polyethylene molecular weight on the molar ratios Mg/Ti and Al/Ti was observed, proving the presence of chain transfer reactions with organometallics.

INTRODUCTION

A highly active Ziegler–Natta catalyst can be made by reducing titanium tetrachloride with organomaganesium compounds[1]. These catalysts are much more active in the polymerization of ethylene than the well known forms of $TiCl_3$ made by reduction of $TiCl_4$ with organoaluminium compounds. The primary crystal size is apparently very small in these catalysts. Two possible mechanisms whereby these very high catalyst activities are obtained may be considered. Either the intrinsic site activity is enhanced by the incorporation of magnesium halide into the crystal lattice or the number of active and potentially active sites is greatly increased. Both mechanisms could conceivably operate together[2].

Reaction between titanium tetrachloride and organometal cocatalyst play an important role in the preparation of Ziegler–Natta catalyst systems for ethylene polymerization. The nature of these reactions is fairly complicated and has not yet been completely elucidated.

Upon the reaction between titanium tetrachloride and organoaluminium compounds [$Al(C_2H_5)_3$, $Al(C_2H_5)_2Cl$ and $AlC_2H_5Cl_2$] at temperatures up to about 100°C in hydrocarbon solution, brown precipitates were formed. In these reactions Ti(IV) is not reduced beyond Ti(III). The extent of reduction of Ti(IV) to Ti(III) in these reactions is a function of the Al/Ti ratio, the reaction period and the reaction temperature[3].

Magnesium alkyl or aryl compounds reduced Ti(IV) beyond Ti(III). Haward *et al.*[2] reported that as the ratio of reducing alkylmagnesium compounds to $TiCl_4$ was increased, an increase in the divalent titanium content of the catalysts was obtained, but even with a Ti(II) content of 40% the catalyst was highly active.

In our earlier paper[4], we reported the use of the catalyst system titanium tetrachloride–alkylaluminium compound–diphenylmagnesium for the preparation of polyethylene of very high molecular weight. The catalyst system is highly active at reaction temperatures 60°–90°C (suspension polymerization process).

The present paper gives some results of a study of suspension polymerization of ethylene with a catalyst system $TiCl_4/Al(C_2H_5)_2Cl/Mg(C_6H_5)_2$. The influence of the molar ratio cocatalyst/catalyst (Al/Ti and Mg/Ti) on the catalyst activity is studied, together with the reduction of titanium tetrachloride by diethylaluminium chloride and diphenylmagnesium in the reaction step.

EXPERIMENTAL

The ethylene had a minimum purity of 99.9%. The iso-octane used as a reaction medium was a commercial grade, dried and purified by molecular sieve 4A to a water content less than 10 ppm.

Titanium tetrachloride was used as received from Kronos Titangesellschaft. Diethylaluminium chloride from Schering AG was used without further purification. Diphenylmagnesium was prepared in the laboratory and was used as a 2% solution in chlorobenzene.

The catalyst complex was prepared by mixing solutions of $TiCl_4$, $Al(C_2H_5)_2Cl$ and $Mg(C_6H_5)_2$ in a 1 dm^3 glass vessel at 20°C. The catalyst mixture was immediately slurried in iso-octane to 1 dm^3 before being used. Under these conditions the reduction period was very short. The diphenylmagnesium is a more active reduction agent than organoaluminium compounds. $Al(C_2H_5)_2Cl$ reacts with $TiCl_4$ slowly and the reduction process was terminated at 20°C after a long time (4 h)[5]. It is to be expected that in the very short reduction times used for preparation of the catalyst complex, the organoaluminium compound does not take part as an active reduction agent.

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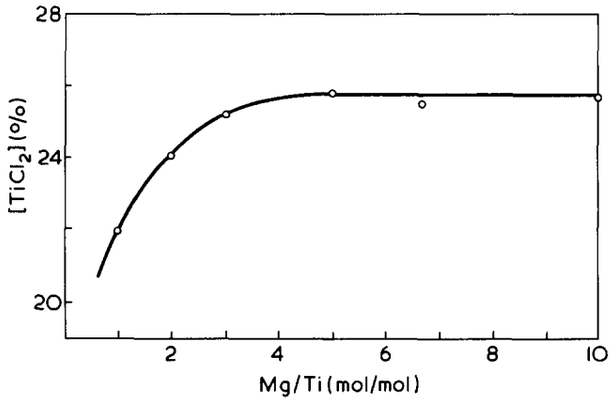

Figure 1 The effect of Mg/Ti molar ratio on the reduction (Al/Ti molar ratio = 10)

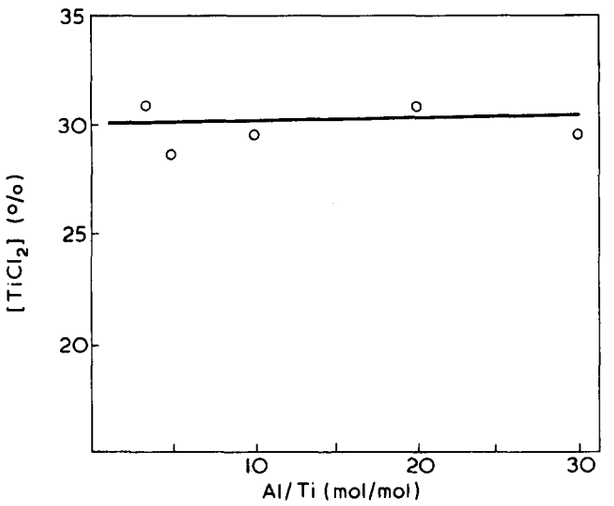

Figure 2 The effect of Al/Ti molar ratio on the reduction (Mg/Ti molar ratio = 3)

The content of chlorobenzene in the catalyst mixture depends on the amount of $Mg(C_6H_5)_2$, introduced in the catalyst complex as a 2% solution in chlorobenzene.

Polymerizations were carried out in a 1.5 dm^3 stainless steel reaction vessel equipped with a stirrer. To obtain some indication of the activity of the catalyst system and the polymer molecular weight at different molar ratios of cocatalyst/catalyst (Al/Ti and Mg/Ti), a series of polymerizations were carried out at the following standard conditions: titanium tetrachloride concentration, 0.05 mmol/dm^3; polymerization time, 15 min; polymerization temperature, 75°C; polymerization medium, 1 dm^3 iso-octane; monomer pressure 5 kg/cm^2.

The percentage of Ti(IV) reduction to Ti(III) and Ti(II) was determined according to the method described in ref 6.

The intrinsic viscosity (limiting viscosity number) was determined at 135°C in decalin in the presence of 0.3% neozon D as an antioxidant.

In view of the extreme reactivity of the titanium tetrachloride towards water and of the organometal compounds towards water and oxygen all experiments have been carried out in an atmosphere of purified nitrogen.

RESULTS AND DISCUSSION

The transition metal compound in the catalyst complex, formed in the system $TiCl_4/Al(C_2H_5)_2Cl/Mg(C_6H_5)_2$, was found to consist only of $TiCl_2$ and $TiCl_3$ without any free $TiCl_4$.

The dependence of the content of $TiCl_2$ on the molar ratio Mg/Ti is shown in *Figure 1*. It is seen that above the ratio Mg/Ti = 3 a constant value is reached for the percentage of $TiCl_2$ in the catalyst complex. It appears from *Figure 2* in the presence of diphenylmagnesium (Mg/Ti = 3) a constant value of $TiCl_2$ is reached in all investigated molar ratios Al/Ti. From this it was concluded that in these conditions (20°C) the presence of diphenylmagnesium in the catalyst system at Mg/Ti molar ratios above 3 is sufficient for the reaction to reach a constant degree of reduction. There is no doubt that organomaganesium compounds are very more active reducing agents than organoaluminium compounds.

The catalyst productivity and the polyethylene molecular weight were studied within the range of Mg/Ti ratios of 1 to 10 at constant Al/Ti ratios and within the range of Al/Ti ratios of 5 to 30 at constant Mg/Ti ratios. It is seen from *Figures 3* and *4* that the polymer yield increased to molar

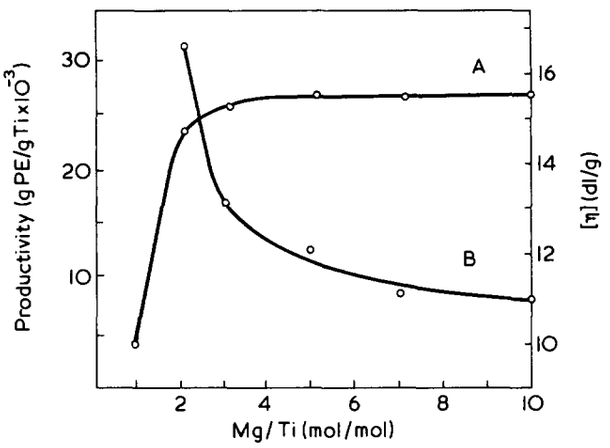

Figure 3 The effect of Mg/Ti molar ratio on A, the catalyst productivity and B, limiting viscosity number. (Al/Ti molar ratio = 10)

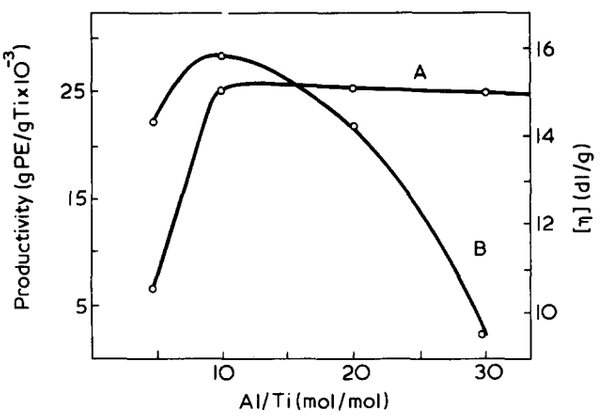

Figure 4 The effect of Al/Ti molar ratio on A, the catalyst productivity and B, limiting viscosity number. (Mg/Ti molar ratio = 3)

ratio Mg/Ti = 3 (*Figure 3*) and to molar ratio Al/Ti = 10 (*Figure 4*). Further increase of the organometal cocatalyst concentration in the catalyst system has practically no influence on the catalyst productivity.

Under these conditions the content of organometallics in the system $TiCl_4/Al(C_2H_5)_2Cl/Mg(C_6H_5)_2$ affected the polymer molecular weight. Using the standard reaction conditions the influence of the molar ratios Mg/Ti and Al/Ti on the polyethylene molecular weight is shown in *Figures 3* and *4*, respectively.

When the results shown in *Figure 1* are compared with the results shown in *Figure 3*, the relationship of degree of reduction to the catalyst productivity is easily demonstrated. Both rise to Mg/Ti molar ratio of 3 and then remain constant.

Above a Mg/Ti ratio the degree of reduction reached a constant value. No further reduction occurred at higher diphenylmagnesium concentrations: therefore the valency state of the transition metal was stabilized. It appears that the nature of the catalyst complex does not change with the increasing ratio of Mg/Ti. Diphenylmagnesium is very active reducing agent. A nearly constant degree of reduction of the tetravalent titanium to the divalent form occurred instantly (after 20 sec) if at least 3 mole of diphenylmagnesium per mole titanium tetrachloride was present. Therefore, the reduction is not responsible for the change of the polymer molecular weight.

The molecular weight of the polyethylene produced is related to the molar ratio cocatalyst/catalyst which produced it[7]. It is seen that in the region of Mg/Ti molar ratios between 1–10 the polyethylene molecular weight decreased. When the Mg/Ti molar ratio increased from 1 to 10 the limiting viscosity number decreased from 16.5 to 11 dl/g. The polymer molecular weight also depends on the Al/Ti molar ratio and shows a maximum at the Al/Ti ratio giving an optimal catalyst productivity. The degree of reduction does not depend on the Al/Ti molar ratio and remains constant, whereas the limiting viscosity number drops with higher ratios.

Dependence of the polyethylene molecular weight on the molar ratio Mg/Ti and on the molar ratio Mg/Ti was observed, proving transfer reactions with diethylaluminium chloride and diphenylmagnesium. Boucher *et al.*[8] also reported that the molecular weight of the polyethylene obtained with similar magnesium-reduced titanium catalysts depends on the concentration of the alkylaluminium compounds in the catalyst system.

In the light of these results it will be clear that organometal compounds act as a chain transfer agent during the polymerization process, but the rate of that reaction is very small. As a result of this the observed change of the polyethylene molecular weight is negligible in the region of Mg/Ti ratios of 1–10 and in the region of Al/Ti ratios of 5–30. The polyethylene obtained is an ultra-high molecular product as shown by its limiting viscosity number.

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