Studies on highly active coordination catalysts for polymerization of α-olefins: 3. Polymerization of propylene with $MgCl_2/TiCl_4/AlEt_3$ or $MgCl_2/PhCOOC_2H_5/TiCl_4/AlEt_3$ systems

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Activity and stereospecificity of the $MgCl_2/TiCl_4$ catalyst in the polymerization of propylene follow curves showing maxima with grinding time of the $MgCl_2$ support. Using $MgCl_2/PhCOOC_2H_5/TiCl_4$ catalysts, no decrease in activity and stereospecificity was observed presumably because of complex formation between $MgCl_2$ support and ethyl benzoate.

Keywords Supported catalyst; electron donors; ethylbenzoate; magnesium chloride; propylene; polymerization; active sites

INTRODUCTION

In Parts 1 and 2 of this series[1,2], a slow equilibrium reaction was demonstrated between the $MgCl_2$ support and the electron donor ethyl benzoate (EB) leading to complex formation. The extent of complexation was influenced by the reaction conditions (such as grinding).

In the present paper, changes in the activity and stereospecificity of catalysts formed in the presence of EB are studied during grinding of the support.

EXPERIMENTAL

Catalysts used for polymerization of propylene were prepared as follows:

$MgCl_2$ alone or together with EB was ground in a ball mill under inert atmosphere for different lengths of time. The milling product was suspended in dried n-heptane and reacted with $AlEt_3$ stirring for 1 h. The support was then washed with n-heptane till free of Al and reacted with $TiCl_4$ by stirring again for 1 h. Unreacted $TiCl_4$ was thoroughly removed by washing with n-heptane and the catalyst was dried *in vacuo.*

Some of the catalysts were prepared another way by treating the ground $MgCl_2$ with EB before addition of $AlEt_3$ and $TiCl_4$.

Initial molar ratios were $AlEt_3/MgCl_2 = 0.71$; $EB/MgCl_2 = 0.17$; and $TiCl_4/MgCl_2 = 0.05$.

Propylene was polymerized in a stainless steel reactor of 1 l under a pressure of propylene of 3 bar at 333K in dried n-heptane for 1 h. Titanium content of the solid catalyst was 0.6–0.9% resulting in 0.02–0.20 mmol dm^{-3} Ti in the polymerization system, in the presence of 7.4 mmol dm^{-3} of $AlEt_3$ cocatalyst and 1.2 mmol dm^{-3} of ethyl anisate. Polymerization activity (A) of the catalyst was expressed as gPP gTi^{-1} h^{-1} bar^{-1}. Isotacticity index (II) of the polymer was determined by extraction with boiling n-heptane. EB and Ti content of the whole catalyst systems was measured by gas chromatography* and EDTA titration[7], respectively.

RESULTS

Activity (A) of the catalyst and isotacticity index (II) of the polymer product followed curves showing maxima as functions of grinding time of $MgCl_2$ support in the absence of EB (*Figures 1* and *2*). The optimum results were obtained after 20 h grinding. Ti content of the catalyst increased monotonically but did not reach 1% (*Figure 3*).

Activity of the catalyst on admixed $MgCl_2$/EB support

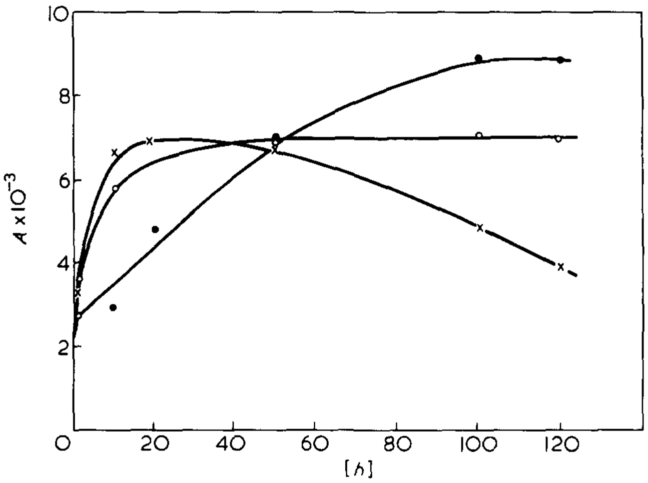

Figure 1 Activity of catalysts of different compositions plotted against grinding time of the support. A = activity in gPP $(gTi)^{-1}$ h^{-1} bar^{-1}. (–x–x–), $MgCl_2/TiCl_4$; (–●–●–), $TiCl_4$ on $MgCl_2$/EB ground together; (–○–○–), $TiCl_4$ on ground $MgCl_2$ + EB

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* EB content was determined by gas chromatography of n-octane extract of acid solution of the whole catalyst on PEGA stationary phase at 150°C using n-butyl benzene as internal standard

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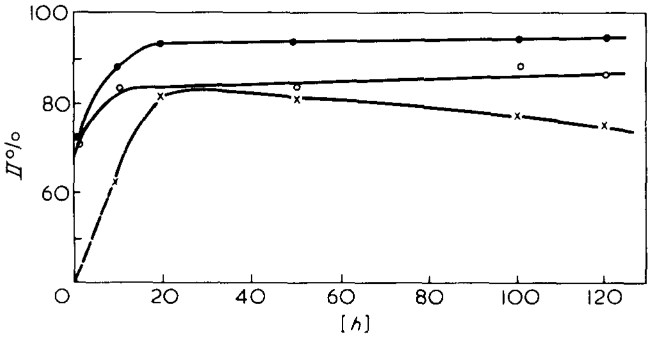

Figure 2 Stereoregularity of polypropylene plotted against grinding time of the support. *II* = isotacticity index. (–x–x–), $MgCl_2/TiCl_4$; (– ● – ● –), $TiCl_4$ on $MgCl_2$/EB ground together; (–o–o–), $TiCl_4$ on ground $MgCl_2$ + EB

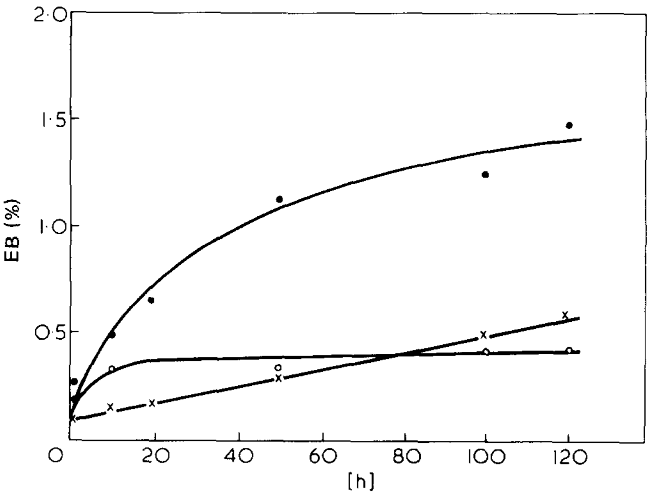

Figure 3 Ti content of the catalyst plotted against grinding time of the support. (–x–x–), $MgCl_2/TiCl_4$; (– ● – ● –), $TiCl_4$ on $MgCl_2$/EB ground together; (–o–o–), $TiCl_4$ on ground $MgCl_2$ + EB

increased continuously as a function of grinding time. After grinding for 50 h, it exceeded the maximum activity of the simple $MgCl_2/TiCl_4$ catalyst (*Figure 1*). No increase in the activity was found beyond 100 h grinding.

The Ti and EB content of the catalyst increased with grinding time, while the molar ratio of EB to Ti remained constant at ~3.2–3.5 (*Figures 3* and *4*). Activity of the ground $MgCl_2$/EB/$TiCl_4$ catalyst was practically unchanged beyond a grinding period of 20 h (*Figure 1*). The Ti and EB content of the catalyst increased slightly with grinding time of the support, while the molar ratio of EB to Ti again remained constant but in the range of ~0.7–0.9 (*Figures 3* and *4*). Isotacticity index of the polymer was not reduced by increasing time of grinding both for ground ($MgCl_2$+EB)/$TiCl_4$ and for ground $MgCl_2$/EB/$TiCl_4$ catalysts (*Figure 2*).

DISCUSSION

Increase in activity and stereospecificity of the $MgCl_2/TiCl_4$ catalyst up to 20 h grinding can be explained by a decrease in crystalline order, an increased number of energetically specific sites[3,4], and enhanced surface area of the support. Thus, the possibility of formation of further active sites exists.

During the grinding of the support, surface sites of different characteristics seem to form on $MgCl_2$ where atactic or isotactic active centres are produced by the adsorption of $TiCl_4$. On the fresh surfaces that arise in the course of grinding, isotactic sites are believed to form at higher frequency. By further grinding, activity of the catalyst decreases in spite of the slight additional reduction in the crystalline particle size of the support[1] simultaneously with an increase in Ti content of the catalyst (*Figure 1*).

This apparent inconsistency can be explained by formation of various $MgCl_2/TiCl_4$ complexes on the surface of the support which are partly inactive with respect to the polymerization of propylene.

Zakharov *et al.*[5] also proposed various surface Ti complexes on $MgCl_2/TiCl_4$ catalysts of different compositions of which only a fraction was found active in the polymerization.

As another factor, the particles of high specific surface area may adhere to each other, when the mechanical effect has ceased, resulting in a drop in number of sites open to formation of active centres, i.e. activity and stereospecificity of the catalyst are reduced. Reducing stereospecificity may be the consequence of the finding that, where the new surface area is forming, the frequency of sotactic centres is growing. By adhering of new surfaces the relative number of isotactic centres also diminishes (*Figure 2*).

It can be concluded that a proportion of $TiCl_4$ is bound on the surface of the support as inactive complexes.

Polymerization activity and stereospecificity of catalysts on EB-containing supports do not decrease during a longer period of grinding of the support. This suggests that the interaction between EB and $MgCl_2$ hinders the agglomeration of $MgCl_2$ particles, preventing the decrease in number of sites available for the formation of stereospecific active centres.

$MgCl_2$ forms a complex with EB on its surface as a result of a slow equilibrium reaction[2]. Complex formation is thought to occur at the specific sites on the surface of $MgCl_2$ where $TiCl_4$ would, otherwise, produce a surface complex which is inactive in polymerization. In the

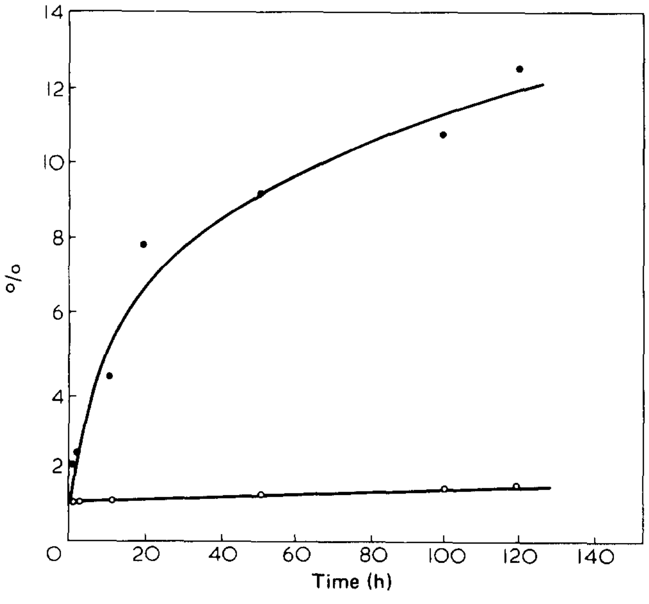

Figure 4 EB content of the catalyst plotted against grinding time of the support. (– ● – ● –), $TiCl_4$ on $MgCl_2$/EB ground together; (–o–o–), $TiCl_4$ on ground $MgCl_2$ + EB

present case, however, $TiCl_4$ may be bound there as an adsorbate oriented by the $EB/MgCl_2$ complex so that the sites inactive in polymerization have been occupied by EB.

$EB/MgCl_2$ complex takes another part in binding $TiCl_4$ since $TiCl_4$, incorporated into the surface defects of the crystal lattice of $MgCl_2$, may also be bonded to EB. This is suggested by the fact that changes in Ti and EB content of the catalyst are parallel both in $EB/MgCl_2$ and $MgCl_2$ treated with EB after grinding. Molar ratio of EB to Ti is 3.2–3.5 and 0.7–0.9, respectively, practically independent of grinding time*.

By i.r. spectroscopic studies of the $MgCl_2/TiCl_4/EB$ system, Keii *et al.*[6] demonstrated a further distortion of $C=O$ bond of EB after incorporation of Ti(IV) into the lattice of $MgCl_2$. They did not report any connection between EB and $MgCl_2$. Zakharov[5] supposed, however, that an exchange occurred between the $TiCl_4/EB$ complex and the $MgCl_2$ support during formation of the active sites. The present experimental results seem to support the assumption that an EB ligand in the active site is bonded both to Ti and to $MgCl_2$.

It should be noted that adsorbed but not complexed EB on the surface of $MgCl_2$, though restricting aggregation of $MgCl_2$ particles, decreases the activity of the catalyst in polymerization since it can form a complex with $TiCl_4$ added in the following step of catalyst preparation. This $TiCl_4/EB$ complex was found to be inactive in polymerization unless it has been ground with $MgCl_2$.

As the grinding time is increased, a greater amount of EB is complexed on the surface of $MgCl_2$ and a lesser proportion remains in the free adsorbed state[2]. In this case, the amount of $TiCl_4$ bonded in the inactive $TiCl_4/EB$ complex is also decreased; in fact, more $TiCl_4$ is capable of forming stereospecific sites by adsorbing on the surface of $MgCl_2$. This is the reason for the continuous increase in the catalytic activity during grinding of $MgCl_2/EB$ support ystem (*Figure 1*).

If the ester is added to $MgCl_2$ after grinding only a relatively small proportion is bonded to the surface of the $MgCl_2$, and furthermore the amount of bonded ester is essentially independent of the grinding time of the $MgCl_2$ (*Figure 4*). Thus the number of active sites and, consequently, the activity of the catalyst remain practically constant after an initial enhancement period.

CONCLUSION

It can be established that activity and stereospecificity of $MgCl_2/TiCl_4$ catalyst formed in the presence of EB are not decreased by increasing the grinding time of the support in contrast to catalysts containing no EB. This phenomenon provides insight into the mechanism of the contribution of EB to the formation of stereospecific active sites in the catalyst. Determination of the exact structure of these active centres requires further investigation.

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[*] It should be noted that a spontaneous $TiCl_4$ uptake by the support is involved in the preparation procedure of catalysts followed by removal of the excess amount of $TiCl_4$.