

case of TMC-C than for the catalyst TMC-A. The PP obtained using catalyst TMC-C has a lower content of atactic fractions. This is probably due to the higher DBP/Ti ratio in TMC-C than in TMC-A after the treatment with AlEt_3 (Table 1, entries 4, 11).

Pretreatment of TMC-A and TMC-C catalysts with PTMS leads to a sharp activity decrease, by a factor of about 25 (Table 2, runs.1 and 2, 5 and 6). These data indicate that pretreatment of the catalyst with PTMS results in deactivation of active sites, probably by adsorption of PTMS to Ti ions. Our chemical analysis data show indeed that the high contents of PTMS and of total PTMS+DBP+Ti components can be explained only by an adsorption of PTMS on Ti centers of the catalyst (Table 1, runs.3, 10).

We carried out additional experiments, in which catalysts TMC-A and TMC-C were treated with PTMS directly in the reactor at 70°C for 1h, before starting the propylene polymerization (Table 2, entries 1 and 3, 5 and 7).

In this case, the activity of the catalysts was also found to be reduced, but to a lesser extent, while the fraction of atactic polypropene (APP) decreased approximately twice. This means that PTMS is absorbed mainly on non-stereospecific catalyst sites and deactivates them.

Further experiments were carried out with catalysts TMC-A and TMC-C under conditions typical for the stereospecific polymerization of propylene. In this case, a heptane solution of AlEt_3 and PTMS (molar ratio $\text{Al/Si} = 20$) was injected into the reactor before starting the polymerization (Table 2, entries 1 and 4, 5 and 8). The activity of both catalysts decreased slightly and the yield of atactic PP was greatly reduced in this case.

Thus, the conditions of interaction of an external donor (PTMS) with TMCs significantly affect the composition of these catalyst systems and their properties in propylene polymerization. The presence of the AlEt_3 cocatalyst in the reaction system is the most important factor controlling the interaction of a TMC with the external donor (PTMS). If the AlEt_3 cocatalyst is absent in the reaction system, the external donor PTMS partially replaces DBP on the surface of MgCl_2 and is mainly adsorbed on coordinatively unsaturated Ti ions; this leads to deactivation of active sites and,

hence, to a great decrease in activity. In the presence of AlEt_3 , however, reaction between AlEt_3 and an ID such as DBP results in freeing LAS on the surface of MgCl_2 . As a consequence, the external donor PTMS is mainly adsorbed onto free acidic sites of MgCl_2 and on coordinatively unsaturated Ti ions, predominantly on non-stereospecific active sites, thus resulting in some decrease of activity and in a marked increase in stereospecificity.

So polymerization data show:

- The activity of both catalysts was found to decrease sharply (5-6 fold) after a pretreatment with PTMS. Probably, PTMS is firmly adsorbed on the titanium ions, leading to a sharp decrease in the activity;
- When treated only with the cocatalyst AlEt_3 , the catalysts showed high activity and low stereospecificity. Reduced stereospecificity is in this case related to the removal of DBP from the catalysts;
- Their activity decreases only slightly if polymerization proceeds with a mixture $\text{AlEt}_3/\text{PTMS}$, but in this case the amount of atactic PP decreases;
- The differences in activity and stereospecificity of the TMC-A and TMC-C catalysts are probably due to different ratios of the individual components (Ti, DBP, PTMS, Al) in the initial state of these catalysts and after the reaction with a mixture of $\text{AlEt}_3/\text{PTMS}$.

CONCLUSION

Three types of TMC were used in this study. Catalysts TMC-A and TMC-B were prepared using an MgCl_2 carrier obtained by reacting Mg with BuCl in heptane in the absence of electron donor compounds, and consecutive treatment of this MgCl_2 carrier with DBP and TiCl_4 and with $(\text{DBP}\cdot\text{TiCl}_4)$ complex, respectively. Catalyst TMC-C was synthesized by reacting TiCl_4 and DBP with $\text{Mg}(\text{OEt})_2$ in chlorobenzene. The interaction of TMCs prepared by different procedures with the external donor PTMS, AlEt_3 and a mixture of $\text{PTMS}/\text{AlEt}_3$ was studied by chemical analysis and infrared diffuse reflectance spectroscopy (DRIFTS).

It was found the amount of DBP and TiCl_4 removed from the catalysts after a treatment with PTMS or a mixture $\text{PTMS}/\text{AlEt}_3$ depended on: (i) a method of the catalyst preparation; (ii) a chemical composition and

textural parameters of the initial TMC; (iii) a presence of AlEt_3 at the interaction of TMC with an external donor.

DRIFTS and chemical composition data showed that PTMS could substitute both TiCl_4 and DBP. DRIFTS data evidenced also selective substitution of DBP by PTMS. One type of adsorbed DBP remained mainly after treatment of TMC with PTMS/ AlEt_3 mixture.

The presence of AlEt_3 in the PTMS/ AlEt_3 mixture played a key role on the chemical composition of the catalysts (content and DBP/ TiCl_4 ratio). The treatment of the catalysts with PTMS alone before polymerization led to a sharp decrease of activity due to its adsorption on titanium species, while the interaction of the catalysts with the PTMS/ AlEt_3 mixture led only to a slight decrease of activity, probably due to a deactivation of non-stereospecific active species.

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