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Polymerization of propylene over isospecific catalysts immobilized on MAO-pretreated supports with triisobutylaluminum as activator

Summary — The effect of support type on the activity of zirconocene—triisobutylaluminum (TIBA) systems was studied in the polymerization of propylene, and on the properties of the resulting PP. Three zirconocenes were used: $Me_2SiInd_2ZrX_2$ (X = Cl or Me) and $Ph_2CCpFluZrCl_2$; and three supports were used: (i) SiO_2 (spec. area S_{sp} = 300 m^2/g); (ii) SiO_2-*gr*-PAAc [*i.e.* SiO_2 modified with poly(acrylic acid) by radiative grafting]; (iii) PE-*gr*-PAAc (*i.e.* functionalized by radiative grafting, S_{sp} = 4 m^2/g). Propylene was polymerized in the liquid monomer. The supports were made to react with methylaluminoxane (MAO) and the product was used to immobilize a zirconocene compound to produce a supported catalyst. With TIBA as cocatalyst, the resulting PP constituted a replica of catalyst particles; the bulk density of PP was high, up to 0.5 g/cm^3. As the Zr content in the catalyst was increased, the specific productivity (g PP/g catalyst) rose to attain a maximum, characteristic for a given support. Catalyst activity and *M* of PP were studied in relation to TIBA concentration. The type of MAO-modified support had little effect on the PP properties. Modification of the $SiO_2/MAO/Me_2SiInd_2ZrCl_2$ catalyst with a boron compound, $CPh_3B(C_6F_5)_4$, did not affect PP properties but reduced the activity of the catalyst system at $Al_{TIBA}/Zr > 500$.

Key words: methylaluminoxane-modified supports, zirconocenes, propylene polymerization catalyst.

Immobilized metallocene catalysts for synthesis of polyolefins have been amply reported and progress in the field has recently been reviewed [1].

Silica is the support most often used to immobilize metallocene catalysts. There are several approaches to the immobilization of zirconocenes on a support [2]. Immobilization on the support pretreated with a toluene solution of polymethylalumoxane (MAO) is the route more often used. Fixation of zirconocene on immobilized MAO gives rise to fairly active and stable catalytic systems. Additionally, such an approach allows to decrease the MAO consumption and to explore aluminum alkyls as cocatalysts [2]. The active species formed in these immobilized catalytic systems are supposed to be similar to those formed in the corresponding homogeneous zirconocene/MAO systems [3]. We have used the approach to the synthesis of immobilized catalysts anchored to different MAO-pretreated supports to compare the efficiency of the catalysts and to reveal the effect of the support on the properties of the polymer formed.

Three materials were used as supports: (i) SiO_2 (S_{sp} = 300 m^2/g), (ii) SiO_2-*graft*-polyacrylic acid (SiO_2-*gr*-PAAc), and (iii) polyethylene-*grafted*-polyacrylic acid (PR-*gr*-PAAc, S_{sp} = 4 m^2/g). Each support is of special interest as a candidate for the synthesis of immobilized metallocene catalysts. Thus, catalysts of a higher specific productivity expressed in terms of the weight of polymer formed per gram catalyst, were expected to result when porous inorganic materials endowed with high specific surfaces were used. Polymeric supports are of special interest for at least two reasons. First, they will allow to avoid the presence of inorganic components in the resulting polymer; secondly, their operation in the polymerization process at elevated temperatures will direct their catalytic action toward the homogeneous systems owing to the high mobility of the polymer chains carrying zirconocene. SiO_2-*gr*-PAAc was thought to be an intermediate to combine the properties of two other supports together. Prior to the binding of zirconocene complexes as described in the Experimental, each support was treated with an MAO solution.

The supports (i)—(iii) were used to immobilize isospecific zirconocenes, $Me_2SiInd_2ZrCl_2$ (I). Most propyle-

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ne polymerization experiments were carried out over this immobilized catalyst. The catalytic properties of the immobilized zirconocene dichloride were compared with those of the dimethylated derivative, $Me_2SiInd_2ZrMe_2$ (II). The catalytic performance and the steric action of another stereospecific zirconocene, $Ph_2CCpFluZrCl_2$ (III), giving rise to syndiotactic polypropylene, were examined after the ziconocene had been immobilized on PE-*gr*-PAAc. Co-immobilization of the dichloride complex (I) and of $Ph_3CB(C_6F_5)_4$ (IV) on MAO-covered SiO_2 was carried out to explore the possibility of modifying catalyst performance by introducing perfluorophenyl borate as mentioned in [4].

Both MAO and aluminum trialkyls are used as the cocatalyst of immobilized zirconocenes. Although MAO is the more effective cocatalyst than AlR_3, considerably more leaching of the catalyst has been found to occur in the polymerization with MAO than with AlR_3 [5—7]. Of the AlR_3 (R = Me, Et, i-Bu) usually examined as cocatalysts, $Al(i\text{-}Bu)_3$ (TIBA) is the most active [8]. Additionally, polymer particles of good particle size are formed when TIBA is used as cocatalyst. Therefore, we used TIBA as cocatalyst in each propylene polymerization run.

EXPERIMENTAL

$Me_2SiInd_2ZrCl_2$ and $Ph_2CCpFluZrCl_2$ purchased from Boulder Scientific Co. were used. $Me_2SiInd_2ZrMe_2$ and $Ph_3CB(C_6H_5)_4$ were synthesized according to [9] and [10], respectively.

MAO (Witco's 10% solution in toluene) was used without purification.

Functionalized supports (SiO_2-*gr*-PAAc and PE-*gr*-PAAc) were prepared by a grafting gas-phase polymerization of acrylic acid induced by γ-irradiation from ^{60}Co. Each support [SiO_2 (Devison, S = 300 m^2/g); SiO_2-*gr*-PAAc; PE-*gr*-PAAc (S = 4 m^2/g)] was partially dehydroxylated in vacuum at 90—100°C for 3 h.

General procedure for preparing immobilized catalysts: partially dehydroxylated support (1 g) was suspended in 15 ml toluene and then a MAO solution in toluene was introduced (10 ml of 10% solution per gram SiO_2 and SiO_2-*gr*-PAAc, 3 ml per gram PE-*gr*-PAAc). The mixture was stirred at 30°C for 2 h and filtered. The solid was washed 5 times with 15 ml toluene. A zirconocene solution in toluene was added to the suspension. The mixture was stirred at 30°C for 30 min and filtered. The solid was washed 5 times with 15 ml of toluene, then dried in vacuum. To modify the catalyst with a boron salt, a toluene solution of (IV) was introduced into the immobilized catalyst suspension at a ratio B/Zr = 1 and the suspension was washed with toluene.

The content of zirconium in the supported catalysts was determined by plasma photoelectron element analysis.

For homogeneous polymerization, an amount of (I) was dissolved in toluene with MAO (Al/Zr = 300) and kept for 4 h at 30°C. This preactivated catalyst was used in propylene polymerization with TIBA as cocatalyst.

Propylene was polymerized in a liquid monomer medium at a pressure exceeding that of the propylene saturated vapor pressure at a temperature of 50°C. The reactor volume was 0.25 or 0.42 L. Polymerization was started by introducing the catalyst into the reactor that had been charged with liquid propylene and TIBA.

Molecular weight characteristics was obtained by measuring the viscosity of the polymer solution in decalin at 135°C and by using the Mark-Houwink equation:

$$[\eta] = 4.6 \cdot 10^{-4} M_v^{0.73} \qquad (1)$$

The stereoregularity parameter (macro-isotacticity index) was estimated from IR spectra of the polymers as the ratio of the band intensities at 998 and 973 cm^{-1}.

RESULTS AND DISCUSSION

Propylene polymerizations were conducted over immobilized catalytic systems in the liquid monomer with TIBA as cocatalyst. The main results are summarized in Table 1.

Obviously, it is interesting to compare the catalytic performances of the immobilized and corresponding homogeneous systems both as regards the efficiency and similarity of the active species formed, because these characteristics determine catalyst productivity and properties of propylene. Usually, such a comparison is made by referring the performance of an immobilized catalyst to that of a homogeneous zirconocene/MAO system. The present comparison is not quite correct because it was TIBA rather than MAO that was used as cocatalyst. Therefore, in our experiments, the homogeneous system which was formed in a way similar to that used to prepare the examined immobilized catalysts was used as the reference system. As a first stage, zirconocene was dissolved in MAO solution in toluene (Al/Zr = 300). Thus preactivated, the zirconocene was shown to be effectively activated with TIBA. Table 1 shows the homogeneous system to be highly active, 110 · 10^3 kg PP/(mol Zr h), and to yield PP of molecular weight 60 000. The immobilized catalysts are 5—10 times less active (Nos. 2—11). The molecular weights of PP obtained over the immobilized catalysts are 1.5—2 times lower than the M_v of PP prepared over the homogeneous catalytic system.

Both zirconium content and Al_{TIBA}/Zr ratio are seen to affect the productivity of the immobilized catalysts and the molecular weight of PP. The specific productivity of the immobilized catalyst may be considered in terms of the weight of PP product either per mole Zr or per gram catalyst. One characteristic feature is the efficiency of operation of the active species and another is

T a b l e 1. **Propylene polymerization in liquid propylene (50°C) over various immobilized catalysts**

No.	Catalyst	$[Zr]\cdot 10^5$ mol/g	$Al^{*)}/Zr$	Y_{PP}/P_{cat} g/(g·h)	A, kg PP/ /(mol Zr·h)	M_v	D_{998}/D_{973}	Bulk density, g/cm^3
1	Me_2SiInd_2ZrCl2/MAO (homogeneous)	0.064 (mol)	1050	—	110 000	60 000	0.86	—
2	SiO_2/MAO/$Me_2SiInd_2ZrCl_2$	3	101	140	4700	22 000	0.85	0.4
3	SiO_2/MAO/$Me_2SiInd_2ZrCl_2$	3	170	290	9700	19 000	0.84	0.5
4	SiO_2/MAO/$Me_2SiInd_2ZrCl_2$	3	777	290	9700	30 000	0.85	0.4
5	SiO_2/MAO/$Me_2SiInd_2ZrCl_2$/$Ph_3CB(C_6F_5)_4$	1.5	440	300	22 700	26 000	0.84	0.32
6	SiO_2/MAO/$Me_2SiInd_2ZrCl_2$/$Ph_3CB(C_6F_5)_4$	1.5	560	220	14 500	37 000	0.86	0.46
7	SiO_2/MAO/$Me_2SiInd_2ZrCl_2$/$Ph_3CB(C_6F_5)_4$	1.5	830	130	8000	31 000	0.84	0.42
8	SiO_2/MAO/$Me_2SiInd_2ZrMe_2$	0.4	870	70	17 500	26 000	0.88	0.46
9	SiO_2-*gr*-PAAc/MAO/$Me_2SiInd_2ZrCl_2$	1.5	270	115	7600	13 000	0.85	0.34
10	SiO_2-*gr*-PAAc/MAO/$Me_2SiInd_2ZrCl_2$	1.5	500	200	13 000	17 000	0.86	0.40
11	PE-*gr*-PAAc/MAO/$Me_2SiInd_2ZrCl_2$	0.2	550	32	16 000	35 000	0.86	0.33
12	PE-*gr*-PAAc/MAO/$Ph_2CCpFluZrCl_2$	0.5	860	125	25 000	400 000	—	0.30

*) Aluminum in TIBA-to-zirconium ratio.

the performance of the immobilized catalyst. Within a certain range of surface concentration of zirconium the two characteristics may be enhanced as the zirconium content is increased. However, at high zirconium contents, not all zirconium species may be active. The specific productivity of the catalyst related to gram catalyst will tend to a constant value, whereas that related to zirconium content will pass through a maximum. Indeed, Figure 1 shows the specific PP yield (per gram catalyst) to increase up to a constant value as the zirconium content is raised. At low zirconium contents, productivities are very close to the value for precatalyst (I) supported on both SiO_2 and PE-*gr*-PAAc. However, at high zirconium loadings, the limiting PP yield depends on the properties of the support carrying zirconocene (Table 2). Thus, the highest value, 300 g PP/g catalyst was reached on a porous, high-specific area SiO_2. Probably, grafting polymerization of acrylic acid gives rise to decreased support porosity and specific surface and thus lowers the specific PP yield to 200 g PP/g catalyst. Consequently, the polymeric support gave the lowest specific PP yield, 130 g PP/g catalyst. The specific catalyst activity per mole immobilized zirconium plotted against zirconium content follows a "bell-like" course (Figure 2). The highest activity occurs at a zirconium content of about 0.5—1 · 10^{-5} mol/g. It is presumably inadvisable to increase the zirconium content above this value because the specific activity will not rise.

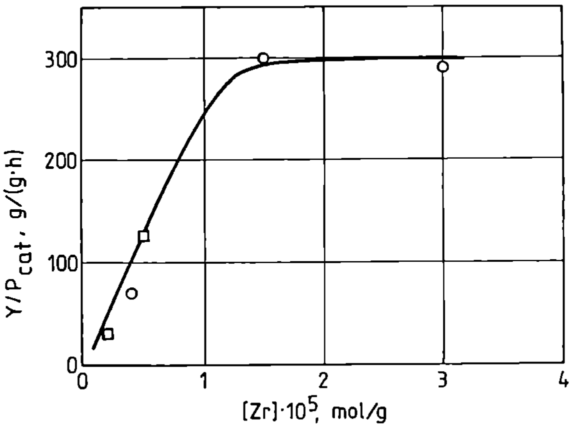

Fig. 1. The specific yield of PP in relation to zirconium content for supported catalysts immobilized on MAO-pretreated supports: (○) — SiO_2 (Nos. 3, 5, 8, Table 1); (□) — PE-gr-PAAc (Nos. 11, 12, Table 1)

T a b l e 2. **Specific yield of polypropylene obtained over catalysts on several supports at surface zirconium contents higher than 10^{-5} mol/g**

Catalyst	Y/P_{cat}, g/(g·h)
SiO_2/MAO/I	300
SiO_2-*gr*-PAAc/MAO/I	200
PE-*gr*-PAAc/MAO/I	130

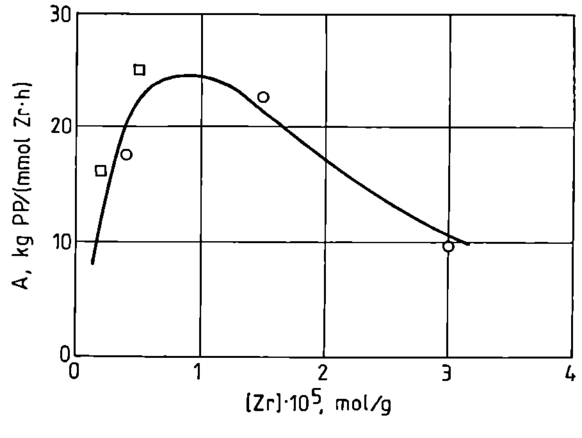

Fig. 2. The activity of supported catalysts in propylene polymerization in relation to zirconium content: (○) — SiO_2-supported catalysts (Nos. 3, 5, 8, Table 1), (□) — PE-gr-PAAc-supported catalysts (Nos. 11, 12, Table 1)

The main reason for the observed limitation of immobilized catalysts specific productivity is difficult to define. First, the effect may be caused by the lower efficiency of active species formation at a high surface density of immobilized zirconocene. The second reason may lie in the diffusion limitation of the polymerization reaction originating due to fast formation of a propylene covering which encapsulates the active sites even at low zirconocene contents in the immobilized catalyst. A comparison of the catalytic activities of different stereospecific zirconocenes, I and III, with low surface zirconium contents, showed the specific productivities of these catalysts to follow the same courses (Figs. 1, 2). However, the resulting polypropylenes have different properties. Syndiospecific catalyst III gave rise to a PP of a considerably higher molecular weight (No. 12, Table 1). The similar relationship between the specific PP yield and the zirconium content observed with different immobilized zirconocenes indicates that diffusion of the monomer to encapsulated active centers is most likely the productivity-controlling factor of immobilized catalysts anchored to the MAO-pretreated supports. As may be seen from Fig. 3, the propylene consumption rate *vs.* time resolved profiles are very similar for homogeneous (curve 1) and for a low-zirconium ([Zr] = 2 · 10^{-6} mol/g) immobilized catalyst (curve 2). For the immobilized catalyst, the initial polymerization rate per mole zirconium is only 4 times lower. However, a higher-zirconium catalyst ([Zr] = 3 · 10^{-5} mol/g) demonstrated a considerably lower initial polymerization rate (curve 3) but a more stable action. The progressive decrease of the polymerization rate (curve 2) may be caused either by progressive catalyst deactivation as in the homogeneous system (curve 1) or by diffusion limitation caused by blocking of catalyst particles by polypropylene (curve 3).

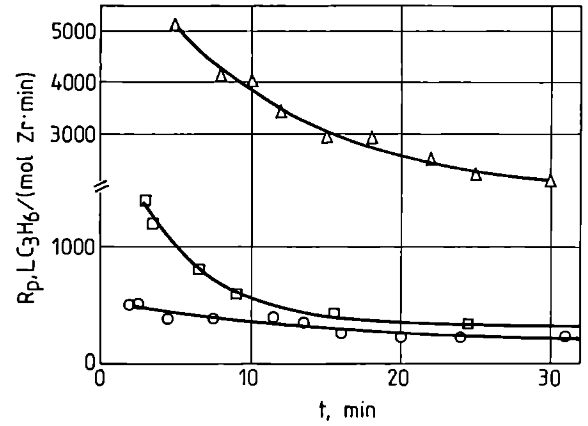

Fig. 3. Propylene consumption rate-time profiles for polymerization over (△) homogeneous (No. 1, Table 1) and (□,○) supported catalysts; immobilized catalysts: (□) — PE-gr-PAAc-supported catalyst (No 11, Table 1), (○) — SiO_2-supported catalyst (No. 4, Table 1)

With TIBA used so far in the catalytic systems, it was necessary to clear up the effect of TIBA concentration on both the catalyst productivity and molecular weight of the resulting PP. In Fig. 4, the specific PP yield is plotted against the Al_{TIBA}/Zr ratio for a SiO_2-immobilized pre-catalyst (I). The specific catalyst productivity is seen to increase as the Al_{TIBA}/Zr ratio is increased and to reach a constant value at Al_{TIBA}/Zr = 200. The molecular weight of PP also increases as the Al_{TIBA}/Zr ratio is raised (Fig. 5). On going from Al/Zr = 100 to Al/Zr = 600, the *M* rose nearly twice, a fact indicating that, in these catalytic systems, TIBA operates as a cocatalyst and does not act as a chain transfer agent.

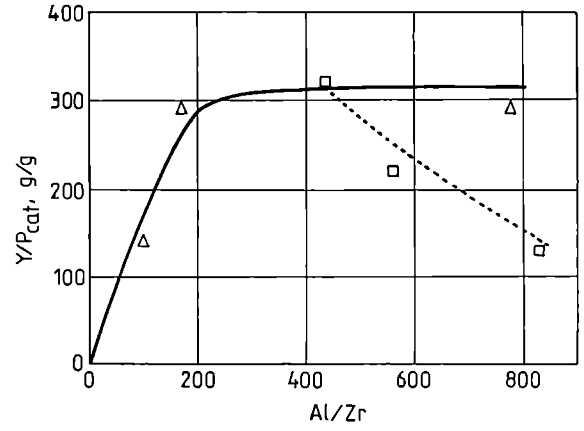

Fig. 4. The specific PP yield in relation to Al_{TIBA}/Zr ratio in SiO_2 supported catalysts: (△) — non-modified (Nos. 2, 3, 4, Table 1), (□) — modified with boron salt IV (Nos. 5, 6, 7, Table 1)

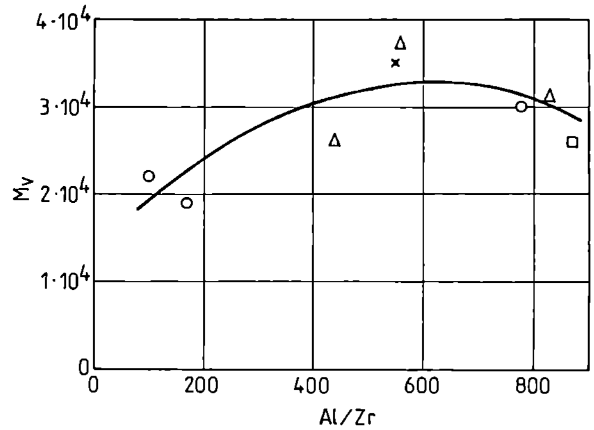

Fig. 5. The molecular weight of PP in relation to Al_{TIBA}/Zr ratio for immobilized catalysts: (○) — nonmodified SiO_2-supported catalyst (Nos. 2, 3, 4, Table 1); (△) — modified SiO_2-supported catalyst (Nos. 5, 6, 7, Table 1); (□) — SiO_2-supported catalyst (No. 8, Table 1), (x) — PE-gr-PAAc-supported catalyst (No. 11, Table 1)

We have examined the possibility of modifying the immobilized catalyst by introducing perfluorophenyl borate into the catalytic system by co-immobilizing zirconocene and the borate at B/Zr = 1. The borate was found to produce no integral modification of the catalytic performance. Neither the catalyst productivity nor the molecular weight of PP were affected (Nos. 4, 5 in Table 1, Fig. 5). However, as the TIBA/zirconocene ratio was raised from 400 to 800, the specific catalyst productivity fell (Fig. 4). Such a behavior may be attributed to deactivation of the active species in a side-reaction of $CPh_3B(C_6F_5)_4$, TIBA, and cationic zirconocene. Some reactions have been reported [11] for homogeneous catalytic systems.

With chloride ligands in the pre-catalyst replaced by methyl ligands, the immobilized catalyst exhibited similar catalytic properties, both in terms of catalyst productivity (Nos. 8, 11, Table 1) and molecular weight of PP (Fig. 5). The isotacticity index rose in the PP prepared over the immobilized dimethylated derivative. Dialkylation of zirconocene dichloride is thus seen to accompany its immobilization on the MAO pretreated support. The resulting active species are identical both with the immobilized dichloride and the dimethylated zirconocene.

These results allow to conclude what follows: The stereospecific zirconocenes immobilized on MAO-pretreated TIBA-activated inorganic and polymeric supports have shown a reasonably high activity in propylene polymerization in the medium of the liquid monomer. The specific productivity of the TIBA-activated immobilized catalysts (per mol Zr) is 5—10 times lower than that of the corresponding homogeneous systems pre-activated with MAO with following their activation with TIBA. When used as activator, TIBA allows to produce PP of considerably higher bulk density than that of the polymers obtained with MAO as cocatalyst. Catalyst productivity and molecular weight of PP have increased as the Al_{TIBA}/Zr ratio is increased over the range of 100—800 mol/mol, whereby TIBA is seen to act as cocatalyst in the catalytic systems. The molecular weight of the PP prepared over the immobilized catalysts is about one-half that produced by the corresponding homogeneous systems. The isotacticity indices of the PP generated by both the homogeneous and the immobilized catalytic systems are similar. The limiting specific yields of PP in terms of grams PP/gram catalyst can be arranged in the following ascending order: PE-*gr*-PAAc (130 g/g) < SiO_2-*gr*-PAAc (200 g/g) < SiO_2 (300 g/g). PP properties are not influenced by the nature of the support. Modification of MAO-pretreated immobilized catalyst by co-immobilization with $CPh_3B(C_6F_5)_4$ followed by activation with TIBA, does not influence the characteristics of the PP formed and leads to decreased catalyst specific productivities at $Al_{TIBA}/Zr > 500$, thus showing the immobilized borate to interact with TIBA accompanied with active species deactivation.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 97-03-32243).

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