L. G. ECHEVSKAYA, V. A. ZAKHAROV,
N. V. SEMIKOLENOVA, T. B. MIKENAS
Boreskov Institute of Catalysis
Siberian Branch
Russian Academy of Sciences
Novosibirsk

Copolymerization of ethylene with 1-hexene over supported zirconocene catalysts*)

Summary — Two supported zirconocene catalysts were prepared: (I) $SiO_2/MAO/Me_2Si(Ind)_2ZrCl_2$ (0.1 wt. % Zr, 9.0 wt. % Al) and (II) $MgCl_2/Me_2Si(Ind)_2ZrCl_2$ (0.2 wt. % Zr, 1.6 wt. % Al). Ethylene was homopolymerized and copolymerized with 1-hexene (70—90°C, 6 bar, TIBA as cocatalyst) over (I) and (II). Catalyst (I) incorporated the comonomer as much as did the homogeneous catalyst of the same composition. $MgCl_2$ used as support resulted in reduced copolymerization reactivity of the catalyst. Copolymer crystallinity and catalyst activity were studied in relation to the concentration of 1-hexene.

Key words: supported zirconocene catalysts, ethylene—1-hexene copolymerization, effect of support, silicon dioxide, magnesium dichloride.

One of most promising directions in the research of olefin polymerization over metallocene catalysts is the synthesis and studies on supported metallocene systems keeping the advantages of homogeneous analogs [1—4]. This work is devoted to a study on the ethylene—1-hexene copolymerization initiated by supported zirconocene catalysts differing in support composition: $SiO_2/MAO/Me_2Si(Ind)_2ZrCl_2$ + TIBA (catalyst I) and $MgCl_2/Me_2Si(Ind)_2ZrCl_2$ + TIBA (catalyst II). The resulting data are compared with the respective data obtained with the homogeneous system $Me_2Si(Ind)_2ZrCl_2$ + MAO (polymethylaluminoxane).

EXPERIMENTAL

Preparation of supported catalysts

The support for catalyst (I) was prepared by treatment of SiO_2 sample (Davison 952) dehydroxylated at 400°C with MAO toluene solution (Witco).

Supported catalyst (I) was prepared according to [5] by reacting the SiO_2/MAO support with the toluene solution of zirconocene at 20°C for 30 min. Triple toluene wash was applied to remove the unreacted zirconocene and products unbound to the support. The resulting catalyst (I) contained 0.1 wt. % Zr and 9.0 wt. % Al.

Fine-dispersed $MgCl_2$ obtained by chlorination of magnesium-aluminum complex $MgBu_2 \cdot nAlEt_3$ with carbon tetrachloride at a mole ratio $CCl_4/Mg = 2$ was used as a support for catalyst (II).

To prepare supported catalyst (II), a magnesium chloride sample was treated with a calculated amount of a zirconocene solution in toluene to provide the final *ca.* 0.2 wt. % Zr catalyst. The treatment was performed at 50°C for 1 h and followed by washing with heptane. Catalyst (II) contained 0.2 wt. % Zr and 1.6 wt % Al.

POLYMERIZATION

Ethylene polymerization and ethylene—1-hexene copolymerization over the supported catalysts were performed in a 0.7 L steel autoclave in hexane under intensive stirring, at 70—90°C and a constant pressure of 6 bar. Triisobutylaluminum (TIBA) was used as cocatalyst at a concentration of 5 mmol TIBA/L. Polymerization initiated by the homogeneous complex was performed in toluene as medium, at ethylene pressure of 2.5 bar and with MAO used as cocatalyst. 1-Hexene was introduced into the autoclave once at the beginning of the polymerization run. The time of copolymerization (the

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*) Presented at the 7th Seminar on "Organometallic Complexes as Catalysts of Vinyl Compound Polymerization", Turawa n/Opole, 12—17 September 1999.

yield of a copolymer) was limited so that the change in the concentration of 1-hexene in the reaction medium did not exceed 10—15%.

To determine copolymerization parameter r_1, the experimental data were treated [6] according to the simplified copolymerization equation

$$m_2/m_1 = 1/r_1(M_2/M_1) \qquad (1)$$

where: *r_1 is the reactivity ratio for ethylene, m_2/m_1 is the mole ratio of the units of 1-hexene and ethylene in the copolymer, and M_2/M_1 is the mole ratio of the comonomers concentrations in the reaction medium.*

Analysis of polymers

To determine the 1-hexene content in the copolymers IR spectroscopy was used as described in [7], with the aid of a FTIR BOMEM-MB-102 spectrometer. Crystallinity and melting temperatures of the polymers were analyzed with a Setaram DSC-111 differential scanning calorimeter, heating rate being 1.5°C/min.

RESULTS AND DISCUSSION

Ethylene homopolymerization

Table 1 presents data on the ethylene homopolymerization initiated by catalysts (I) and (II) at various temperatures, compared with the corresponding data for the homogeneous complex. The supporting of zirconocene on SiO_2/MAO (catalyst I) is seen to result in a noticeably decreased catalyst activity, whereas the MM of PE formed (as inferred from mass-flow rate) increased and polymer morphology essentially improved (Table 1, exps. 1 and 2). The resulting polyethylene samples are uniform powders, consisting of round particles and having a high bulk density. Increasing the polymerization temperature from 70 to 90°C had a slight effect on catalyst activity; the maximum activity was reached at 80°C (Table 1, exps. 2—4). The kinetic curves of ethylene polymerization at these temperatures are stable (*cf.* Fig. 1, curve 1).

Table 1. Data on ethylene homopolymerization over the catalyst under study

Exp. No	Catalyst	*T* °C	$[C_2H_4]$ mol/L	Al/Zr	Activity kg/ mol Zr · h	*MFR* g/ 10 min	B.D. g/cm^3
1	$Me_2Si(Ind)_2ZrCl_2$	70	0.2	26 000	134 000	1.16	0.12
2	I	70	0.4	1000	6400	0.18	0.30
3	I	80	0.36	1300	9800	0.19	0.29
4	I	90	0.36	700	7300	1.50	0.38
5	II	80	0.36	1500	6700	0	0.22

Magnesium chloride used as the support resulted in a still lower mass-flow rate (*MFR*) of PE. The activity of the supported catalyst (I) in the ethylene homopolymerization was slightly higher than that of catalyst (II) (Table 1, exps. 3 and 5). It is important to note that TIBA was used as cocatalyst when the supported catalyst (I) and (II) were used for polymerization, Al/Zr mole ratio being much lower than it was in case of homogeneous catalyst with MAO as cocatalyst. The activity of supported catalyst does not change at the increasing of TIBA/Zr molar ratio.

Copolymerization of ethylene with 1-hexene

The homogeneous catalytic system $Me_2Si(Ind)_2ZrCl_2$/MAO is well known to have a high ability to incorporate comonomers [8—10].

Table 2 and Fig. 1 present data on copolymerization of ethylene with 1-hexene initiated by the supported catalyst SiO_2/MAO/$Me_2Si(Ind)_2ZrCl_2$. Addition of 1-hexene to the reaction mixture is seen to have resulted in a considerably increased catalyst activity. Indeed, as 1-hexene was added at a ratio C_6H_{12}/C_2H_4 = 0.4, the catalyst activity increased 5 times (from 6400 to 32 000

Table 2. Data on ethylene—1-hexene copolymerization*) over the catalyst SiO_2/MAO/$Me_2Si(Ind)_2ZrCl_2$

Exp. No.	$[C_6H_{12}]$ /$[C_2H_4]$	Activity kg/ mol Zr · h	*MFR* g/ 10 min	B.D. g/cm^3	C_6H_{12}**) % mol.	T_m °C	Crystallinity %
1	0	6400	0.18	0.30	0	134.3	53.5
2	0.15	8000	0.8	—	0.8	—	—
3	0.30	12 000	0.5	0.35	1.5	—	—
4	0.4	32 000	0.12	0.34	2.1	114.6	33.8

*) 70°C, Al/Zr = 1000, TIBA. **) The content of 1-hexene in copolymer by FT-IR.

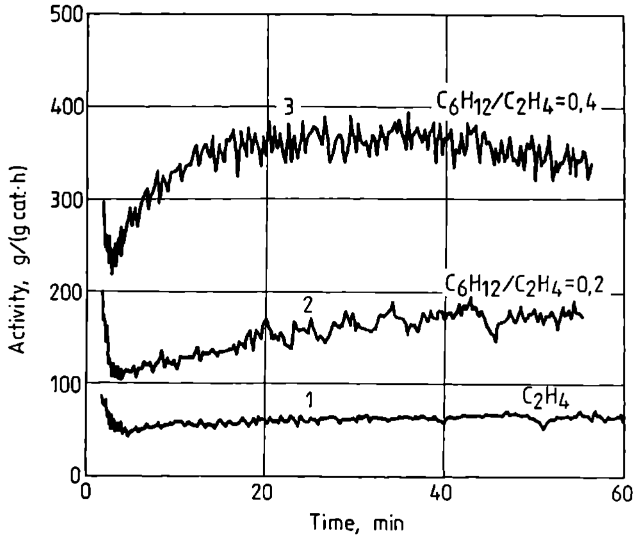

Fig. 1. The kinetic curves of ethylene homopolymerization and ethylene—1-hexene copolymerization at 70°C over the catalyst SiO_2/MAO/$Me_2Si(Ind)_2ZrCl_2$ + TIBA

kg/mol Zr · h; Table 2, exps. 1 and 4); the copolymerization kinetic curves were stable. In experiments 3 and 4 the copolymers retained the homopolymer morphology, the polymer powder constituted round particles and had a high bulk density.

Several authors observed the effect of activity increase (so called "comonomer effect") in copolymerizations initiated by different catalytic systems. In ref. [8] the "comonomer effect" was observed in ethylene—1-hexene copolymerization, initiated by the homogeneous complex $Me_2Si(Ind)_2ZrCl_2/MAO$ in toluene as medium at 25°C; as the mole ratio C_6H_{12}/C_2H_4 was increased from 0 to 1:1, the catalyst activity increased 2.6 times.

We observed a still greater increase in the catalyst I activity (5-fold) already at $C_6H_{12}/C_2H_4 = 0.4$ (Table 2), when powder copolymers, insoluble under the polymerization conditions, were produced. Ethylene—propylene and ethylene—1-hexene copolymerization run over a supported catalytic system $SiO_2/MAO/Et[IndH_4]_2ZrCl_2$ revealed a more profound "comonomer effect" as compared with that observed for the corresponding homogeneous analog [11].

The data of Table 2 show the introduction of 1-hexene to give rise to increased catalyst activity simultaneously with a decreased crystallinity of the final polymer.

T a b l e 3. Data on ethylene—1-hexene copolymerization*) over the catalyst $MgCl_2/Me_2Si(Ind)_2ZrCl_2$

No exp.	$[C_6H_{12}]/[C_2H_4]$	Activity kg/ mol Zr · h	*MFR* (21) g/10 min	C_6H_{12}**) mol %	T_m, °C	Crystallinity, %
1	0	6700	0	0	136.1	72.1
2	1.1	2000	0	0.8	—	—
3	3.3	810	0	2.4	128.7	52.4

*) 80°C, Al/Zr = 1500, TIBA, heptane as a solvent. **) The content of 1-hexene in copolymer by FT-IR.

Table 3 contains the data on ethylene—1-hexene copolymerization initiated by the catalyst (II), where $MgCl_2$ was used as a support. In this case, as 1-hexene concentration was increased, the activity of the supported catalyst decreased.

The data on the ethylene—1-hexene copolymerization run over supported catalysts (I) and (II), were used to calculate the copolymerization parameter r_1 from equation (1). Table 4 presents results together with the literature data for the homogeneous catalyst $Me_2Si(Ind)_2ZrCl_2/MAO$ [9] and the data we have obtained earlier for the supported Ziegler type systems of various compositions. The supported catalyst (I) and the respective homogeneous system are seen to show similar high comonomer response (Table 4). Thus, supporting of the complex $Me_2Si(Ind)_2ZrCl_2$ on a SiO_2/MAO support produces no effect on its high activity to incorporate 1-hexene. However, when $MgCl_2$ is used as a support, the situation changes dramatically: the r_1 value sharply increases, and the resulting catalyst shows the poorest copolymerizing reactivity of all the systems examined (Table 4).

T a b l e 4. Values of r_1 for ethylene—1-hexene copolymerization*) over catalysts of different compositions

Catalyst	r_1	Reference
$Me_2Si(Ind)_2ZrCl_2$ + MAO	25 (60°C)	[9]
(I) $SiO_2/MAO/Me_2Si(Ind)_2ZrCl_2$ + TIBA	19	this work
(II) $MgCl_2/Me_2Si(Ind)_2ZrCl_2$ + TIBA	130	this work
$MgCl_2/TiCl_4$ + TIBA	100	[6]
$MgCl_2/VCl_4(VOCl_3)$ + TIBA	23	[6]

*) Copolymerization temperature, 70°C.

A similar effect of support composition on the catalyst activity and comonomer incorporation has been observed [11] in the ethylene—propene and ethylene—1-hexene copolymerizations initiated by $Et[IndH_4]_2ZrCl_2$ supported on SiO_2/MAO, Al_2O_3 or $MgCl_2$. The SiO_2/MAO supported catalyst showed the highest activity and comonomer response. With Al_2O_3 used as the support, the catalyst activity fell, and the effect on the comonomer incorporation was nil. Supporting of zirconocene on the $MgCl_2$ surface resulted in both the catalyst activity and comonomer response (doubled r_1) reduced. In our experiments with $Me_2Si(Ind)_2ZrCl_2$ used as the active component, the difference in comonomer reactivity ratios was even more profound (Table 4, catalyst I and II). This may be attributed to the fact that we used TIBA as cocatalyst, whereas in [11] it was $AlMe_3$.

It is important to note that supported catalyst (II) differs from catalyst (I) by several kinetic parameters. In particular, catalyst (II) initiates formation of PE with essentially higher MM compared with PE formed in the presence of catalyst (I) (Table 1, exps. 3 and 5, Fig. 2). In the case of catalyst (II), no "comonomer effect" is observed; the activity of catalyst (II) decreased as 1-hexene was added up until the ratio $[C_6H_{12}]/[C_2H_4]$ was 3.3. The PE produced with catalyst (I) shows an essentially

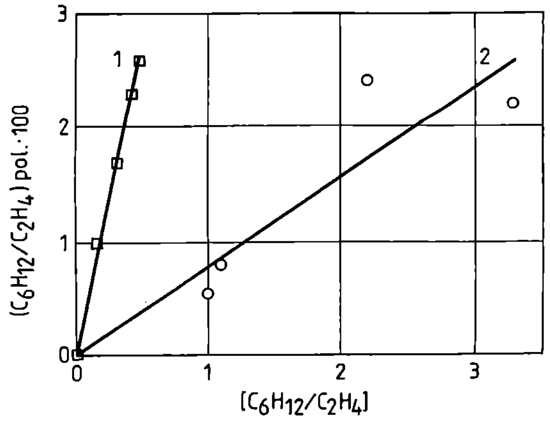

Fig. 2. Data on ethylene—1-hexene copolymerization over the catalyst $SiO_2/MAO/Me_2Si(Ind)_2ZrCl_2$ (1) and $MgCl_2/Me_2Si(Ind)_2ZrCl_2$ (2) plotted in the coordinates of equation (1)

lower crystallinity than the PE produced with catalyst (II) (Table 2, exp. 1 and Table 3, exp. 1).

Thus, the reactivity of active centers of supported metallocene catalysts depends on the nature of the support. The catalyst supported on SiO_2/MAO is most similar to the respective homogeneous analog in terms of catalytic performance. Most likely, the different nature of the acidic sites in MAO and in the supporting $MgCl_2$ is responsible for the formation of active centers of different types in the supported catalysts SiO_2/MAO/zirconocene and $MgCl_2$/zirconocene.

It is interesting to compare the copolymerization parameters for zirconocene catalysts discussed above with that for the supported Ziegler type systems we have studied [6] (Table 4). The supported zirconocene catalyst (I) and supported vanadium-magnesium catalysts have almost similar r_1 values. The copolymerizing reactivity of the supported zirconocene catalyst $MgCl_2$/ $Me_2Si(Ind)_2ZrCl_2$ is much lower than that of V-Mg and Ti-Mg catalysts (higher r_1 value).

ACKNOWLEDGMENTS

The Authors are grateful to E. B. Burgina for the IR spectra and to V. A. Drebuschak for the DSC measurements.

This research was supported by the Russian Fund of Basic Research, Grant No. 97-03-32546a.

REFERENCES

1. Ribero M. R., Deffleux A., Portela M. F.: *Ind. Eng. Chem. Res.* 1997, **36**, 1224.
2. Harrison D., Coulter I., Wang S.: *J. Mol. Cat. A* 1998, **128**, 652.
3. Chien J. C. W.: *Topics in Catalysis* 1999, **7**, 23.
4. Nowakowska M., Ochędzan-Siodłak W., Kordowska M.: *Polimery* 2000, **45**, 323.
5. Semikolenova N. V., Zakharov V. A.: *Macromol. Chem. Phys.* 1997, **198**, 2889.
6. Zakharov V. A., Echevskaya L. G.: *Polym. Sci. Ser. B* 1997, **39**, 291.
7. Echevskaya L. G., Zakharov V. A., Golovin A. V., Mikenas T. B.: *Macromol. Chem. Phys.* 1999, **200**, 1434.
8. Herfert N., Montag P., Fink G.: *Macromol. Chem. Phys.* 1993, **194**, 3167.
9. Kaminsky W.: *Macromol. Chem. Phys.* 1996, **197**, 1907.
10. Lehmus P., Harkki O., Leino R. et al.: *Macromol. Chem. Phys.* 1998, **199**, 1965.
11. Soga K., Kaminaka K.: *Macromol. Chem. Phys.* 1994, **195**, 1369.