Polymerization of propene over a MgCl₂-supported dichlorosilylenebisindenylzirconium dichloride catalyst combined with methylalumoxane

Kazuo Soga*, Takashi Arai and Toshiya Uozumi

School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Tatsunokuchi-cho, Nomi-gun, Ishikawa 923-12, Japan
(Received 25 November 1996; revised 6 January 1997)

An isospecific heterogeneous zirconocene catalyst was prepared by supporting rac-Cl₂SiInd₂ZrCl₂ on MgCl₂ using an impregnation method. Polymerization of propene was conducted over this combined with methylalumoxane as co-catalyst. It was found that the catalyst displayed a fairly high activity to give highly isotactic polypropene at 40°C. With an increase in the polymerization temperature from 40 to 100°C, the activity increased monotonically accompanied by a decrease in isospecificity. © 1997 Elsevier Science Ltd.

(Keywords: metallocene catalyst; propene polymerization; methylalumoxane)

Introduction

Since the discovery of metallocene catalysts by Sinn and Kaminsky[1], a variety of supported-type metallocene catalysts have been prepared. Among them, those prepared by contacting metallocenes with methyl-alumoxane (MAO)-fixed carriers exhibit very high activities compared to the homogeneous analogues[2-7]. The direct reactions of metallocenes with silica gel generally yield less active catalysts due to decomposition of the metallocene compounds[8]. We have recently reported that the catalysts prepared by the reaction of ZrCl₄ and polysiloxanes substituted with methyl-indenyl or two indenyl groups show very high activities for ethene, but not propene polymerizations when MAO is used as co-catalyst[9]. However, the catalysts contain inseparable *meso* and *racemic* diastereomers and consequently give a mixture of isotactic and atactic polypropene.

More recently, we have prepared a variety of MgCl₂ supported half titanocene and dichlorobis(β-diketonato) titanium catalysts and tested them for propene polymerization. Those catalysts were found to be very active even using ordinary alkylaluminiums as co-catalyst[10]. On the other hand, Diamond and Jordan have established a beautiful methodology to obtain chiral ansa-zirconocenes[11]. Utilizing these methods, we have synthesized an isospecific heterogeneous zirconocene catalyst, rac-Cl₂SiInd₂ZrCl₂/MgCl₂.

This communication reports the synthesis of the catalyst, together with preliminary results of propene polymerization over it.

Experimental

Materials. MgCl₂ (surface area measured by BET method = 80 m² g⁻¹) donated by Toho Titanium Co., Japan, and alkylaluminiums (triethylaluminium, TEA; triisobutylaluminium, TIBA; MAO) donated by Tosoh

Akzo Co., Japan, were used without further purification. Tetrachlorosilane commercially obtained from Kanto Chemicals Co., Japan, was purified by distillation under nitrogen atmosphere. Toluene and n-heptane commercially obtained from Kanto Chemicals Co. were purified according to the usual procedures. Propene donated by Mitsui Petrochemical Co., Japan, was further purified by passing through NaOH and P₂O₅ columns.

Synthesis of organosilanes. Ind₂SiCl₂. Tetrachlorosilane (12.2 ml, 107 mmol) was added dropwise to a slurry of indenylmagnesium bromide (214 mmol) in 330 ml of diethyl ether at −20°C[12]. The mixture was refluxed for 10 h. After the reaction, diethyl ether was evaporated to dryness *in vacuo*. Pentane was then added to separate the lithium salt, and bisindenyldichlorosilane was obtained as a pale-yellow powder by recrystallization in pentane at −30°C (18.5 g, 52.9%).

rac-Cl₂SiInd₂ZrCl₂. This was synthesized according to the method reported by Diamond and Jordan[13]. A 100 ml Schlenk vessel was charged with Zr(NMe₂)₄ (1.0 g, 3.7 mmol), Ind₂SiCl₂ (1.2 g, 3.7 mmol) and toluene (20 ml). The reaction mixture was heated to 100°C with stirring for 17 h. After the solid products were removed by filtration, the residual solution was concentrated under reduced pressure and cooled down to −20°C. The solid fraction was separated by filtration to obtain Cl₂Si Ind₂Zr(NMe₂)₂ as an orange powder in 49% yield (1.2 g). A solution of Me₂NH.HCl (0.4 g, 4.7 mmol) in CH₂Cl₂ (20 ml) was then added dropwise to the solution of Cl₂SiInd₂Zr(NMe₂)₂ (1.2 g, 1.8 mmol) in CH₂Cl₂ (20 ml) with stirring at −78°C. The clear, yellow solution was warmed to room temperature and kept standing for 30 min. After the solvent was removed by evaporation, the residue was adequately washed with hexane and extracted with toluene, followed by evaporating to dryness to obtain rac-Cl₂SiInd₂ZrCl₂ as a yellow solid (0.6 g, yield 28%).

*To whom correspondence should be addressed

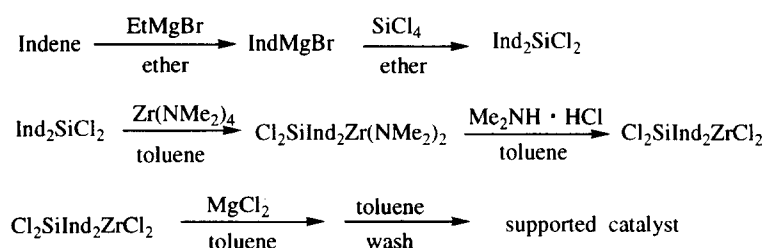*Me$_2$SiInd$_2$ZrCl$_2$ (diastereomer).* A solution of Me$_2$Si(IndH)$_2$ (10 mmol) in tetrahydrofuran (30 ml) was added to a solution of butyllithium (22 mmol) in n-hexane (13.4 ml) at 25°C, and the mixture was stirred for 15 h. After removing the solvents, a suspension of ZrCl$_4$ (10 mmol) in CH$_2$Cl$_2$ (50 ml) was added at −78°C. The mixture was allowed to warm to react at 25°C for 15 h, followed by evaporation to yield a 1/1 mixture of the *racemic* and *meso* isomers. The mixture was then extracted with toluene, and the racemate (an orange–yellow crystalline powder) was recovered from the extract by recrystallization (−35°C); further recrystallization from CH$_2$Cl$_2$ afforded rac-Me$_2$SiInd$_2$ZrCl$_2$ in 10–25% yield.

Preparation of the rac-Cl$_2$SiInd$_2$ZrCl$_2$/MgCl$_2$ catalysts. All the reactions were performed under nitrogen atmosphere using a standard Schlenk technique. The supported catalyst was prepared by allowing rac-Cl$_2$SiInd$_2$ZrCl$_2$ (0.8 mmol), prepared as above, to react with MgCl$_2$ (7.5 g) in toluene (50 ml) at room temperature overnight. The solid product was washed with 1 l of toluene at room temperature, followed by drying *in vacuo* to obtain the catalyst (Cat-A). For reference, the Me$_2$SiInd$_2$ZrCl$_2$/MgCl$_2$ catalyst (Cat-B) was also prepared by a similar procedure. The contents of Zr in the supported catalysts were analysed by an inductively coupled plasma atomic emission spectrometer (Seiko Instruments SPS7700).

Polymerization and analytical procedures. To a 100 ml stainless steel reactor equipped with a magnetic stirrer were introduced the measured amounts of toluene, co-catalyst and catalyst in this order under a nitrogen atmosphere at room temperature. The reactor was degassed, followed by introduction of 7 l (*ca* 0.3 mol) of propene. Polymerization was conducted at 0–120°C for several hours and terminated by adding acidic methanol. The precipitated polymer was adequately washed with methanol and dried *in vacuo* at 60°C for 6 h. The molecular weight and molecular weight distribution of the polymer were measured at 145°C by gel permeation chromatography (Senshu Scientific, SSC7100) using *o*-dichlorobenzene as the solvent. Differential scanning calorimetry measurements were made using a Seiko DSC220C at a heating rate of 10°C min^{-1}. The ^{13}C nuclear magnetic resonance spectra of the polymers were recorded at 140°C using a Varian GEM-300 spectrometer operating at 75 MHz.

Results and discussion

The reaction scheme for the synthesis of Cat-A is shown in *Scheme 1*. The contents of Zr in Cat-A and Cat-B were estimated to be 0.021 and 0.012 mmol g-cat^{-1}, respectively. Polymerization of propene was first conducted at 40°C for 6 h over the two catalysts combined with MAO as co-catalyst. From the polymerization tests separately using the solution and solid fractions, it was confirmed that the solution part did not display any

Indene $\xrightarrow[\text{ether}]{\text{EtMgBr}}$ IndMgBr $\xrightarrow[\text{ether}]{\text{SiCl}_4}$ Ind$_2$SiCl$_2$

Ind$_2$SiCl$_2$ $\xrightarrow[\text{toluene}]{\text{Zr(NMe}_2)_4}$ Cl$_2$SiInd$_2$Zr(NMe$_2$)$_2$ $\xrightarrow[\text{toluene}]{\text{Me}_2\text{NH} \cdot \text{HCl}}$ Cl$_2$SiInd$_2$ZrCl$_2$

Cl$_2$SiInd$_2$ZrCl$_2$ $\xrightarrow[\text{toluene}]{\text{MgCl}_2}$ $\xrightarrow{\text{toluene wash}}$ supported catalyst

Scheme 1

Table 1 Results of propene polymerization with MgCl$_2$-supported zirconocene catalysts

Catalyst	Co-catalyst	Al/Zr ratio (mol mol^{-1})	T_p (°C)	Activity kg PP/mol-Zr · h^{-1}	I.I. (C5) (%)	M_w (10^3)	M_w/M_n	T_m (°C)	mmmm (%)
Cat-A	MAO	10 000	40	329	85.6	24	2.7	143.7	—
	MAO	5000	40	226	91.9	24	2.7	142.9	91.8
	MAO	5000	40^a	86.6	78.2	25	2.6	142.5	—
	Ph$_3$C · B(C$_6$F$_5$)$_4$	1	40	108	97.6	47	2.8	146.5	92.7
	MAO	5000	0	2	—	—	—	—	—
	MAO	5000	80	233	57.9	17	2.7	132.6	—
	MAO	5000	100	361	39.4	12	2.9	131.4	77.3
Cat-B	MAO	10 000	40	1.4	—	18	4.2	—	—
	MAO	5000	40	5.5	—	—	—	—	—
Cat-A	TIBA	1000	40	1.8	—	32	5.5	147.6	—
	TEA	1000	40	trace	—	—	—	—	—
Cat-B	TIBA	1000	40	2.3	—	54	6.3	140.9	—
	TEA	1000	40	0.9	—	49	4.1	148.9	—
Me$_2$SiInd$_2$ZrCl$_2$	MAO	5000	40	37 500	—	119	1.8	142.0	89.0
	MAO	5000	100	36 100	53.7	12	2.4	129.7	83.0

Polymerization conditions: catalyst = 0.0005 mmol; toluene = 30 ml, propene = 7 (*ca* 0.3 mol); polymn time = 6 h
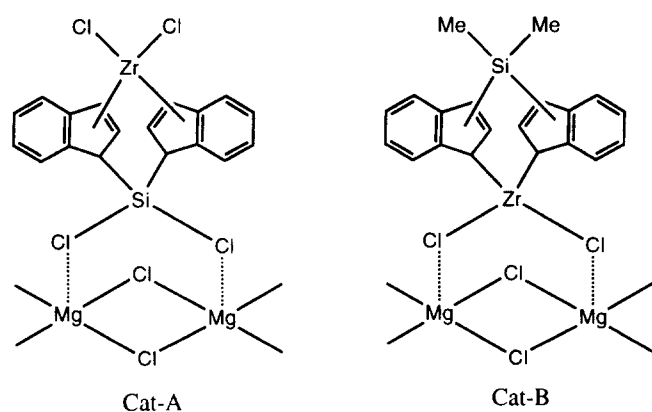^{a} Cat-A was aged at 100°C for 2 h

Figure 1 Plausible structures of active species

activity. It may be considered, therefore, that the zirconocene compounds once anchored to the $MgCl_2$ surface are not extracted under the reaction conditions.

Table 1 shows the results of propene polymerization, together with some analytical data for polymers, where those with the corresponding homogeneous system are also attached for reference. Cat-A displayed a fairly high activity, although the relative productivity as compared to the homogeneous system was still far less. The molecular weights of the resulting polymers were found to be not so high, the reason for which is open to discussion at the moment, whereas Cat-B showed almost no activity. The active species formed in Cat-A and Cat-B may be assumed as illustrated in *Figure 1*, which suggests that Cat-B in such a form cannot be activated by MAO. Considering that the polydispersity (M_w/M_n) of the polymer produced with Cat-B is broader, the poor activity might result from some decomposed species. The polymers obtained were fractionated by boiling pentane. The insoluble fraction (I.I.) reached as high as 97.6 wt% when $Ph_3C.B(C_6F_5)_4$ was employed as co-catalyst, indicating that the majority of rac-$Cl_2SiInd_2ZrCl_2$ anchored to the $MgCl_2$ surface remained unisomerized.

Propene polymerization was then conducted with Cat-A at different temperatures to check the stability of active species (*Table 1*). The activity was found to increase monotonically up to 100°C.

It is considered, therefore, that the active species formed in Cat-A is quite stable. However, the boiling pentane insoluble fraction (I.I.) of the polymer obtained at 100°C was as low as 39.4 wt%.

The [mmmm] pentad of the insoluble fraction was also

decreased to a great extent. On the other hand that of the soluble fraction slightly increased. These results suggest that such a marked decrease in I.I. is caused by the isomerization of active species and the decrease in M_n of isotactic polypropene as well. The assumption was confirmed to be valid from the polymerization conducted at 40°C using the Cat-A, which had been subjected to MAO at 100°C for 2 h. Namely, I.I. of the resulting polymer was greatly reduced (from 91.9 to 78.2 wt %).

Finally, the polymerization of propene was briefly checked over Cat-A and Cat-B using ordinary alkyl-aluminiums as co-catalyst, the results of which are shown at the bottom of *Table 1*. Both the catalysts gave only trace amounts of polypropene with broad polydispersities (M_w/M_n), suggesting that polymerization is initiated by some decomposition species.

In conclusion, we have prepared a heterogeneous isospecific metallocene catalyst by supporting rac-$Cl_2SiInd_2ZrCl_2$ on $MgCl_2$. Further studies are of course necessary to improve the activity as well as to characterize the catalysts. We hope, however, the preparation method for the catalyst described here will be of use for the development of novel supported-type metallocene catalysts.

References
1. Sinn, H. and Kaminsky, W., *Adv. Organomet. Chem.*, 1980, **18**, 99.
2. Soga, K. and Kaminaka, M., *Makromol. Chem.*, 1993, **194**, 1745.
3. Soga, K., Kim, H. J. and Shiono, T., *Macromol. Chem., Rapid Commun.*, 1994, **15**, 139.
4. Lee, D. H. and Yoon, K. B., *Macromol. Chem., Rapid Commun.*, 1994, **15**, 841.
5. Hsu, J. C., Sun, L., Xie, T., Bacon, D. W. and McAuley, K. B., *Proceedings of MetCon '95*, 17–19 May, 1995, Houston, TX. Catalysts Consultants Inc.
6. Chien, J. C. W. and He, D., *J. Polym. Sci., Part A: Polym. Chem.*, 1991, **29**, 1603.
7. Kaminsky, W. and Renner, F., *Makromol. Chem., Rapid Commun.*, 1993, **14**, 239.
8. Soga, K. and Kaminaka, M., *Makromol. Chem.*, 1994, **195**, 1369.
9. Arai, T., Hoang, T. B., Uozumi, T. and Soga, K., *Macromol. Chem. Phys.*, 1997, **198**, 229.
10. Soga, K., Kaji, E. and Uozumi, T., *J. Polym. Sci., Part A: Polym. Chem.*, 1997, **35**, 823.
11. Diamond, G. M. and Jordan, R. F., *J. Am. Chem. Soc.*, 1996, **118**, 8024.
12. Chen, Y. X., Raush, M. D. and Chien, J. C. W., *Organometallics*, 1993, **12**, 4607.
13. Diamond, G. M. and Jordan, R. F., *Organometallics*, 1996, **15**, 4030.