A comparative study of ethylene/α-olefin copolymerization with silane-modified silica-supported MAO using zirconocene catalysts

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Activities of ethylene/α-olefin copolymerization were found to increase with silane-modified silica-supported MAO using ansa-zirconocene catalyst. The increase in activities was less pronounced when higher α-olefins were used. However, silane modification resulted in the narrower molecular weight distribution of polymers. ^{13}C NMR revealed that ethylene incorporation in all systems gave polymers with the similar triad distribution.

KEY WORDS: copolymerization; metallocene catalyst; polyethylene; silica; support.

1. Introduction

Due to the commercial interest of using metallocene catalysts for olefin polymerization, it has led to extensive efforts to utilize matallocene catalysts efficiently. However, it was found that homogeneous metallocene catalysts have two major disadvantages: the lack of morphology control and reactor fouling. Therefore, binding these metallocene catalysts onto inorganic supports as supported metallocene catalysts can overcome those drawbacks. Many inorganic supports such as SiO_2, Al_2O_3, and $MgCl_2$ have been investigated [1–10]. It was reported that silica is perhaps the most attractive support so far. However, the properties of silica itself may not be completely satisfied for all purposes based on the polymers produced. Thus, the modification of silica properties is necessary in order that it can be used efficiently.

It has been reported that a new immobilization method of introducing a spacer group between the support and metallocene resulted in higher catalytic activity [11,12]. However, it should be noted that absorption of MAO on a support prior to immobilizing the metallocene catalysts is one of the possible strategies to form a heterogeneous catalytic system. The use of dimethylsilane-modified silica-supported methylaluminoxane (MAO) with Cp_2ZrCl_2 catalyst for ethylene polymerization was studied by Soga *et al.* [13].

It is known that the copolymerization of ethylene with higher α-olefin is a commercial importance for productions of elastomer and linear low-density polyethylene (LLDPE). Metallocene catalysts have been studied for such a purpose. In our previous study, Chao *et al.* [14] investigated the copolymerization of ethylene and propylene using silane-modified silica-supported MAO with ansa-zirconocene catalyst. It was found that silane modification resulted in an increase in the activity of ethylene/propylene copolymerization.

The main objective of this present study was to further develop a better understanding of silane modification on the copolymerization of ethylene with higher α-olefins such as 1-hexene, 1-octene and 1-decene. The rac-ethylenebis(indenyl) zirconium dichloride [$Et(Ind)_2ZrCl_2$] was used based on the fact that it has been widely studied as the metallocene catalyst system for polymerization of ethylene, propylene, and ethylene with comonomers [15–19].

2. Experimental

2.1. Materials

rac-Ethylenebis(indenyl) zirconium dichloride ($Et[Ind]_2ZrCl_2$) was obtained from Aldrich Chemical Company Inc. Ethylene (polymerization grade) was obtained from National Petrochemical Co., Ltd., Thailand. 1-Hexene (99.8%) was purchased from Fluka Chemie A.G. Switzerland and purified by distilling over sodium/benzophenone under argon atmosphere prior to use. 1-Octene (98%) was purchased from Aldrich Chemical Company Inc. and 1-decene (≥97%) was purchased from Fluka Chemie A.G. Switzerland. Methyl aluminoxane, MAO (2.857 M in toluene) was donated by Tosoh Akzo, Japan. Silica gel (Cariact P-10, surface area 300 m^2/g) from Fuji Silasia Chemical Ltd., Japan was calcined under vacuum at 400 °C for 6 h. $SiCl_4$ was obtained from Aldrich Chemical Company. Sodium hydrogen carbonate was purchase from Fluka Chemie A.G. Switzerland. Toluene was donated from Exxon Chemical Thailand Co., Ltd. It was dried over

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dehydrated $CaCl_2$ and distilled over sodium/benzophenone under an argon atmosphere prior to use. $Al(CH_3)_3$, TMA (2.0 M in toluene) was supplied from Nippon Aluminum Alkyls Ltd., Japan. Ultra high purify (UHP) argon (99.999%) was purchased from Thai Industrial Gas Co., Ltd. and was further purified by passing through molecular sieves 3 Å, BASF catalyst R3-11G, NaOH and phosphorus pentaoxide (P_2O_5) to remove traces of oxygen and moisture.

All chemicals were manipulated under an inert atmosphere using a vacuum glove box and/or Schlenk techniques.

2.2. *Preparation of silane-modified silica*

Silica gel was heated under vacuum at 400 °C for 6 h. Then, the mixture of calcined silica (2 g) and silane (2 mmol) in 20 mL of toluene was refluxed for 7 h while stirring with a magnetic stirrer under an argon atmosphere. The solid part was filtered and washed five times with 40 mL of toluene. Then, the washed solid in 20 mL of toluene was added by 0.038 mL of 1.5 N aqueous solution of sodium bicarbonate ($NaHCO_3$). The mixture was stirred at room temperature for 7 h. The solid was filtered again and washed five times with 40 mL of toluene and dried *in vacuo* at room temperature to obtain the white powder of silane-modified silica support.

2.3. *Preparation of silane-modified silica-supported MAO*

The silane-modified silica was reacted with MAO (34 mmol) in 20 mL at room temperature for 30 min. The solid part was filtered and washed five times with 40 mL of toluene, then dried *in vacuo* at room temperature. The white powder of supported cocatalyst was then obtained.

2.4. *Polymerization reaction*

2.4.1. *Ethylene/α-olefin copolymerization*

Ethylene and α-olefin (hexene, octene and decene) copolymerization was carried out in a 100-mL semi-batch stainless steel autoclave reactor equipped with a magnetic stirrer. A mixture of toluene (30 mL), silica-supported cocatalyst[1] (0.1 g), and α-olefin (3 mL) were added to the reactor in the glove box. $Et[Ind]_2ZrCl_2$ and TMA ($[Al]_{TMA}/Zr = 2500$) were mixed at room temperature for 5-min aging, then injected into the reactor. The reactor was then immersed in liquid nitrogen to freeze the solution and evacuated to remove argon. The reactor was heated to polymerization temperature (70 °C). Feeding ethylene started the reaction. The pressure in the reactor was kept at 50 psi by a continuous ethylene feed. Ethylene consumption at about 18 mmol was fixed to avoid any mass transfer effect and inhomogeneity of copolymer produced, resulting from change comonomer concentration. The reaction time was recorded for the activity calculation. When the desired amount of ethylene was consumed, the reaction was terminated by the addition of acidic methanol (2 mL of 10% HCl in methanol). The product was washed with methanol and dried in an oven at 110 °C for 6 h.

2.5. *Nomenclature*

2.5.1. *Support system*

1. refers to the unmodifed silica-supported MAO system.
2. refers to the silane-modified silica-supported MAO system.

2.5.2. *Copolymerization system*

EH refers to the ethylene/1-hexene (EH) copolymerization.
EO refers to the ethylene/1-octene copolymerization.
ED refers to the ethylene/1-decene copolymerization.

2.6. *Polymer characterization*

2.6.1. *Gel permeation chromatography*

A high temperature GPC (Waters 150-C) equipped with a viscometric detector, differential optical refractometer and four Styragel HT type columns (HT3, HT4, HT5, and HT6) with a 1×10^7 exclusion limit for polysyrene was used to determined the molecular weight (MW) and molecular weight distributions (MWD) of the copolymers produced. The analyses were performed at 135 °C using 1,2,4-trichlorobenzene as the solvent. The columns were calibrated with standard narrow MWD polystyrene and LLDPE.

2.6.2. *^{13}C NMR spectroscopy*

^{13}C NMR spectroscopy was used to determine the comonomer incorporation and polymer microstructure. Chemical shifts were referenced internally to the major backbone methylene resonance (taken at 30 ppm from Me_4Si) and calculated according to the method of Randall [20]. Sample solutions were prepared in *o*-dichlorobenzene and benzene-d_6 (20 vol%) for an internal lock signal. ^{13}C NMR spectra were taken at 80 °C using JEOL JNM-A500 operating at 125 MHz with a flip angle of 70 °C, an acquisition time of 1.5 s, and a delay of 4.0 s [19,21].

2.6.3. *Temperature-rising elution fractionation (TREF)*

TREF was used to analyze the chemical composition distribution of copolymers. Details of TREF procedure

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[1] Copolymerzation was carried out using both the silica-supported cocatalyst with and without silane modification for the comparative study.

and the method of data analysis were described elsewhere [22].

3. Results and discussion

The results of activities, MW and MWD are shown in table 1. For EH copolymerization, it can be seen that the activity increased about four times with the silane modification on the support. It is suggested that silane modification could result in less steric hindrance on the support surface. However, the MW of polymer produced decreased about a half (decreased from 85,000 to 44,000 g/mol) with silane modification suggesting the occurrence of chain transfer reaction. It was proposed that most likely β-hydrogen elimination is more prevalent when the support surface was treated with silane [14]. The narrower MWD can be observed in EH copolymerization with silane modification support indicating more single catalytic sites present on this system. However, in the copolymerization of ethylene/1-octene (EO), the silane modification resulted in only a slight increase in activity. The MW of polymer produced decreased with a lesser degree compared to that in the EH copolymerization suggesting a lesser degree of chain transfer reaction. The MWD was also found to be narrower with silane modification support. The polymerization behaviors of ethylene/1-decene (ED) copolymerization were also similar to those of EO copolymerization.

Based on the increased activities upon silane modification, it is suggested that silane acts as a spacer group on the surface of silica as reported by Soga *et al.* [13]. Thus, more active species can be adsorbed on the support resulting in an enhancement of activities. It should be noted that this is probably only true for the copolymerization of ethylene with lower α-olefins such as propylene [14] and 1-hexene. However, when higher α-olefins such as 1-octene and 1-decene were used as copolymers the effect on activities of silane modification became less pronounced. This is probably due to the steric effect of comonomer insertion resulted from higher olefins used.

Considering the MW of polymer produced, it can be seen that silane modification resulted in a decrease in MW of polymer, especially in EH copolymerization system. The decrease in MW was due to the chain transfer reaction resulted from the silane modification. However, only a slight decrease in MW was found in the EO and ED copolymerization with silane modification. This indicated that the effect of silane modification on MW was diminished by a longer chain insertion. It should be noted that the MW of copolymers produced by the silane modification system were about the same as the ones produced by homogeneous system [14] suggesting that the silane modification system can result in more homogeneous-like with less effect of the support. The silane modification system also exhibited narrower MWD compared to the unmodified one as shown in table 1 in all cases. Hence, a narrow MWD can be achieved when silane is present as a silica-support modifier. This indicates that more uniform catalytic sites can be achieved though silane modification.

The characteristics of ^{13}C NMR spectra (not shown) for all copolymers were similar. The triad distribution for all copolymers obtained from ^{13}C NMR is shown in table 2. Ethylene incorporation in all systems gave copolymers with similar triad distribution regardless of silane modification. No significant change was found. It was also shown a little probability to produce the blocks of HH, OO, and DD, which is the characteristic of this zirconocene in homogeneous system. Only random copolymers can be produced with this system regardless of silane modification.

TREF profiles for all systems are shown in figure 1. It indicated that EH copolymers for silane-modified silica-supported MAO and unmodified silica-supported MAO systems gave only one sharp peak, however, with a shift to lower temperature when silane was present. The EO and ED with unmodified silica-support system exhibit a different result due to effects of the longer chain insertion as mentioned before. Thus, two distinct peaks of TREF profiles can be observed when 1-octene and 1-decene were used indicating the presence of two or more types of catalytic sites in the unmodified silica-supported MAO system. However, when silane was present, only one distinct peak can be observed for EO and ED

Table 1
Activity, molecular weight, and molecular weight distribution of copolymers produced

System	Reaction time (min)	Activity (kg polymer/mol. Zr h)	M_w (g/mol)	MWD
EH1	8.6	2539	85,000	2.7
EH2	2.0	11,034	44,000	1.9
EO1	2.7	15,376	23,904	2.6
EO2	2.5	15,751	18,897	2.3
ED1	2.8	14,726	24,728	3.0
ED2	2.6	15,413	18,407	2.3

Reaction conditions: [Zr] = 5×10^{-5} M, T = 70 °C, P = 50 psi, catalyst precursor = 0.1 g, and $[\mathrm{Al}]_{\mathrm{TMA}}/[\mathrm{Zr}]$ = 2500.

Table 2
Triad distribution of copolymers prepared with different supports

System	EEE	CEE + EEC	CEC	ECE	CCE + ECC	CCC
EH1	0.545	0.189	–	0.148	0.236	–
EH2	0.539	0.224	–	0.149	0.177	–
EO1	0.605	0.269	–	0.126	–	–
EO2	0.589	0.291	–	0.120	–	–
ED1	0.569	0.290	–	0.141	–	–
ED2	0.610	0.255	–	0.134	–	–

E refers to ethylene and C refers to corresponding comonomers: 1-hexene, 1-octene, or 1-decene.

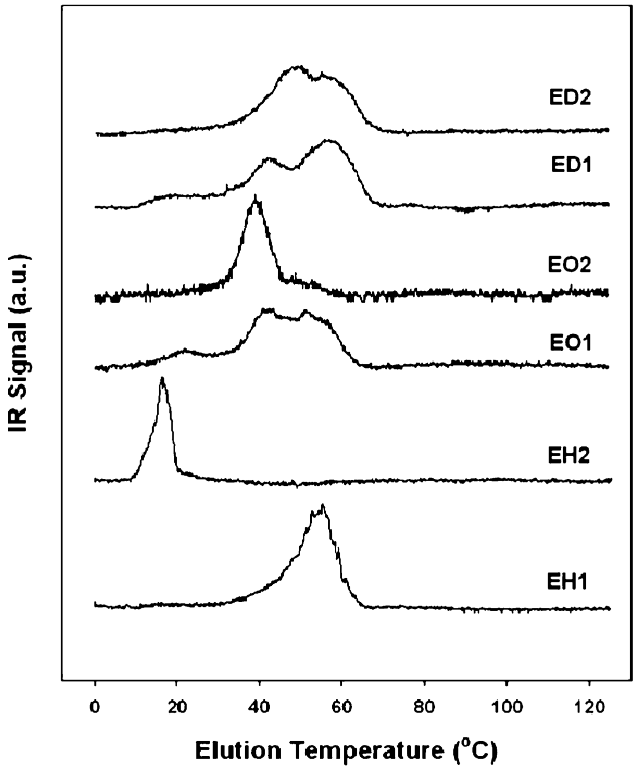

Figure 1. TREF profiles of ethylene/1-olefin copolymers produced with different catalyst systems.

copolymers (the minimum and maximum in the pattern for ED at about 55 °C is probably not a separate peak; such small variations in the IR signal occur in TREF analysis). The TREF peak for EO is very narrow with silane modification (EO1) indicating a very narrow branching distribution. This suggests that silane modification can result in a narrow branching distribution for ethylene copolymerization, especially with longer chain olefin comonomers. However, the effect of silane modification on the narrow branching distribution was slightly pronounced when 1-decene was used as comonomer.

4. Conclusions

The activities of ethylene copolymerization with α-olefins such as 1-hexene, 1-octene, and 1-decene increased by using silane-modified silica-supported MAO system along with zirconocene catalyst. However, the effect of silane on activities was less pronounced with ethylene/higher α-olefin (1-octene and 1-decene) copolymerization. This is probably due to steric effect of the longer chain insertion. The MWs of copolymers decrease with silane modification suggesting that the system is more homogeneous-like. It should be noted that the differences in MW are not as much when higher α-olefins were used. Silane modification also resulted in narrower molecular weight distribution indicating more uniform catalytic sites present. It was found that ethylene incorporation in all systems gave copolymers with similar triad distribution indicating only random copolymers produced. Silane modification also results in a narrow branching distribution for ethylene copolymerizaion even when higher α-olefins were used.

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