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Supporting Effects of Silica-Supported Methylaluminoxane (MAO) with Zirconocene Catalyst on Ethylene/1-Olefin Copolymerization Behaviors for Linear Low-Density Polyethylene (LLDPE) Production

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The methylaluminoxane (MAO)/SiO₂ in situ- and ex situ-supported Et(Ind)₂ZrCl₂ catalysts were prepared and studied for ethylene/1-olefin (1-hexene, 1-octene, and 1-decene) copolymerization for linear low-density polyethylene (LLDPE) production. The in situ-supported catalytic system exhibited higher activities than the ex situ-supported catalytic system. Activities continuously increased as the [Al]_(MAO)/[Zr] molar ratio increased up to 1135. The optimum [Al]_(TMA)/[Zr] molar ratio was 2500. The ethylene/1-octene (EO) copolymerization showed the most consistency, in regard to activity, for both catalytic systems. The copolymers produced in both systems were random copolymers.

1. Introduction

Because of the substantially commercial interest of using metallocene catalysts and methylaluminoxane (MAO) as a co-catalyst for the polymerization of olefins, it has led to an extensive effort for utilizing the metallocene catalyst more efficiently. However, it was found that homogeneous metallocene catalytic system has two major disadvantages: the lack of morphology control of the polymers produced and reactor fouling. Therefore, binding these metallocene catalysts onto inorganic carriers can provide a promising way to overcome these drawbacks. As a result, heterogeneous metallocene catalysts offer several additional advantages that are important to industry. They essentially improve product morphologies and the ability to be used in gas-phase and slurry-phase reactors with existing technology. Many supports (such as SiO₂, MCM-41, VPI-5, MgCl₂, and polymer materials) have been studied extensively.^{1–10} It has been reported that silica is the most widely used support for metallocene catalysts so far.

It is known that the copolymerization of ethylene with higher 1-olefins has commercial importance for the production of elastomers and linear low-density polyethylene (LLDPE). Metallocene catalysts with MAO have been studied for such copolymerization. Zirconocene catalysts with MAO have been determined to have the potential to polymerize ethylene with 1-olefins.^{5,11,12} In this present study, supporting effects of MAO/SiO₂ with the in situ- and ex situ-supported zirconocene catalyst on ethylene/1-olefin copolymerization was investigated. The different supported catalytic systems were prepared, characterized, and tested for

ethylene/1-olefin (1-hexene, 1-octene, and 1-decene) copolymerization. The copolymers produced were also further characterized.

2. Experimental Section

2.1. Materials. Silica gel from Fuji Silasia Chemical, Ltd. (Cariact P-10, surface area 300 m²/g) was heated at 400 °C for 6 h under vacuum. Toluene was dried over dehydrated CaCl₂ and distilled over sodium/benzophenone under an argon atmosphere before use. Rac-ethylene bis(indenyl)zirconium dichloride [Et(Ind)₂ZrCl₂] was supplied from Aldrich Chemical Company, Inc. Methylaluminoxane (MAO, concentration of 2.534 M) in toluene was donated by Tosoh (Akso, Japan). Trimethylaluminum (TMA, concentration of 2.0 M) in toluene was supplied by Nippon Aluminum Alkyls, Ltd., Japan. Ultrahigh purity argon was further purified by passing it through columns that were packed with BASF catalyst R3-11G (molecular-sieved to 3 Å), sodium hydroxide (NaOH), and phosphorus pentoxide (P₂O₅), to remove traces of oxygen and moisture. Ethylene gas (99.96% pure) was donated by National Petrochemical Co., Ltd., Thailand. 1-Hexene (99+% pure) and 1-octene were purchased from Aldrich Chemical Company, Inc. 1-Decene was purchased from Fluka Chemie A.G., Switzerland. All chemicals and catalyst preparation were manipulated under an argon atmosphere, using a glovebox and/or Schlenk techniques.

2.2. Catalyst Preparation for In Situ-Supported Catalytic System. Silica gel was heated under vacuum at 400 °C for 6 h. Then, 1 g of the silica was reacted with the desired amount of MAO in 10 mL of toluene at room temperature for 30 min. The solid part was washed twice with toluene, followed by drying under vacuum at room temperature overnight; the white MAO/SiO₂ powder then was obtained.

2.3. Catalyst Preparation for Ex Situ-Supported Catalytic System. A mixture of the desired amount of

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MAO/SiO₂ prepared as previously described and Et(Ind)₂ZrCl₂ solution in toluene ([Al]_{MAO}/[Zr] molar ratio of 160–1135) was stirred at room temperature for 30 min. The solid part was washed twice with toluene, followed by drying under vacuum at room temperature.

2.4. Polymerization for In Situ-Supported Catalytic System. The ethylene and 1-olefin (1-hexene, 1-octene, and 1-decene) copolymerization reaction was conducted in a 100-mL batch stainless-steel autoclave reactor that was equipped with a magnetic stirrer. To start the reaction, a solution of 0.1 g of MAO/SiO₂ in toluene (total volume of 30 mL) was put into the reactor, and then 0.018 mol of 1-olefin was added. The desired amount of Et(Ind)₂ZrCl₂ (5×10^{-5} M) and TMA ([Al]_{TMA}/[Zr] molar ratios of 1000–4000) were mixed and stirred for 5 min, aging at room temperature, then injected into the reactor. The reactor was frozen in liquid nitrogen to stop reaction, and then the reactor was evacuated to remove argon. The reactor was then heated to polymerization temperature (70 °C). The feeding of a known amount of ethylene (0.018 mol) started the reaction. The reaction was terminated by the addition of acidic methanol. The precipitated copolymer was washed with methanol and dried at room temperature.

2.5. Polymerization for Ex Situ-Supported Catalytic System. Polymerization procedures similar to those previously mentioned for the in situ system were also performed for the ex situ-supported catalytic system, except for the fact that only the desired amount of TMA ([Al]_{TMA}/[Zr] molar ratios of 1000–4000) was injected into the reactor.

2.6. Characterization of Catalysts Precursors. Scanning electron microscopy (SEM) was performed to study the catalyst precursor morphologies. A JEOL model JSM-5800 LV scanning microscope was used. Inductively coupled plasma (ICP) spectroscopy was used to determine the amounts of aluminum and zirconium present in the catalyst precursors, using a Perkin–Elmer Plasma 1000 system.

2.7. Characterization of Copolymers. SEM analysis was conducted to study the morphologies of copolymers that were produced. The equipment used was the same as that previously mentioned. Differential scanning calorimetry (DSC) was used to measure the thermal properties of the copolymers (Netzsch model DSC 200). The analyses were performed at a heating rate of 10 °C/min at temperatures of 30–200 °C. The heating cycle was run twice. In the first scan, samples were heated and cooled at room temperature. In the second, samples were reheated at the same rate, but only the results of the second scan were reported. This is due to the influences of the first scan by the mechanical and thermal history of samples. The molar mass (Mw) and molar mass distribution (MMD) of the copolymers were measured at 135 °C using 1,2-dichlorobenzene as the solvent, via gel permeable chromatography (GPC, Shodex). The GPC instrument was equipped with a viscometric detector, a differential optical refractometer, and three Shodex AT-type columns (AT-803/s, AT-805/s, and AT-807/s) with a 1×10^7 exclusion limit for polystyrene. The columns were calibrated with standard narrow MMD polystyrenes and LLDPE.¹³ Carbon nuclear magnetic resonance (¹³C NMR) was performed to determine the chemical structure of the copolymers (especially, the incorporation of 1-olefins). The ¹³C NMR spectra were recorded at 100 °C, using a JEOL model JMR-A500 apparatus that was operating

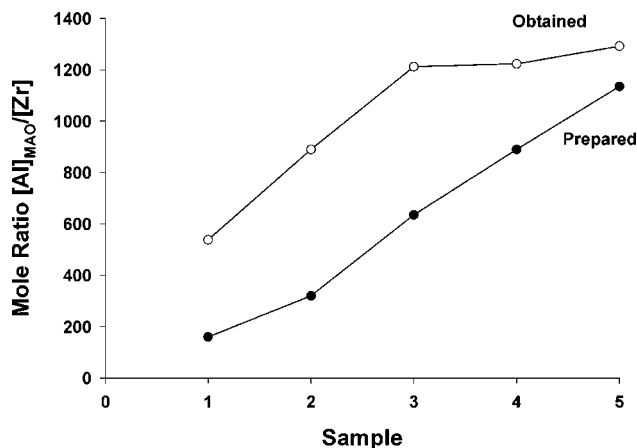


Figure 1. Comparison of the [Al]_{MAO}/[Zr] molar ratios: (●) prepared and (○) obtained.

at 125 MHz. Copolymer solutions were prepared using 1,2,4-trichlorobenzene as the solvent and benzene-*d*₆ for an internal lock. The triad distribution was calculated based on the methodology given in ref 13.

3. Results and Discussion

3.1. Characteristics of the Catalyst Precursors. Morphologies obtained from SEM analysis of SiO₂, MAO/SiO₂, and MAO/SiO₂-supported Et(Ind)₂ZrCl₂ were similar (not shown). The elemental analysis of the samples, as shown in Figure 1, indicated that the amounts of zirconium present on the support decreased as the amounts of MAO increased, in terms of the [Al]_{MAO}/[Zr] molar ratio. The decreased amounts of Zr species resulted in higher molar ratios of [Al]_{MAO}/[Zr] present in the ex situ system, compared to the in situ system. The deposition of Zr species onto MAO/SiO₂ was limited, probably because of two reasons: (i) the absorption ability of SiO₂ was limited by the amounts of MAO impregnated prior to the sequential impregnation of Et(Ind)₂ZrCl₂, and (ii) a loss of weakly adsorbed Et(Ind)₂ZrCl₂ species during preparation.

3.2. Polymerization Activities. 3.2.1. Effect of [Al]_{MAO}/[Zr] Molar Ratios. The effect of [Al]_{MAO}/[Zr] molar ratios of 160–1135 on the polymerization was investigated. Both in situ and ex situ catalytic systems were observed to exhibit increases in activity continuously with increasing [Al]_{MAO}/[Zr] molar ratios, up to 1135, as shown in Figures 2, 3, and 4 for the copolymerization of EH, EO, and ED, respectively. This indicated that greater amounts of MAO resulted in more active species being present during polymerization. It was proposed that MAO possibly had many functions, such as an alkylating agent, a stabilizer for a cationic metallocene alkyl and/or counterion, an ionizing and/or reducing agent for the transition element, and a scavenger for the metallocene catalytic system. However, one of the most important roles of MAO is apparently to prevent the formation of ZrCH₂CH₂Zr species, which is formed via a bimolecular process.¹⁴ Considering activities for both catalytic systems, it was found that the ex situ catalytic system exhibited lower activities with the same amounts of zirconium loading, indicating the presence of less active species in the system. This suggested that not all Zr species that are present on the support for the ex situ system were active for polymerization, indicating nonuniform Zr species on the surface. To study the effect of chain-size insertion,

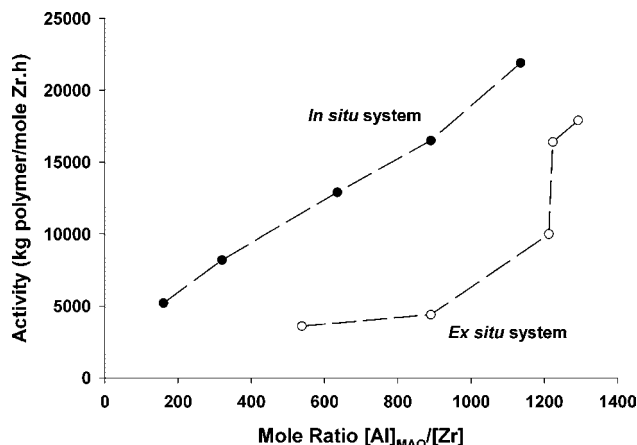


Figure 2. Comparison of the activity of EH in both the (●) in situ and (○) ex situ system; the polymerization temperature is 70 °C, and the $[Al]_{TMA}/[Zr]$ molar ratio is 2500.

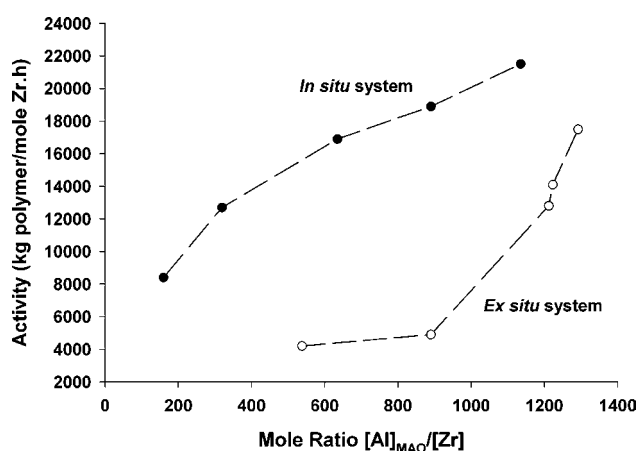


Figure 3. Comparison of the activity of EO in both the (●) in situ and (○) ex situ system; the polymerization temperature is 70 °C, and the $[Al]_{TMA}/[Zr]$ molar ratio is 2500.

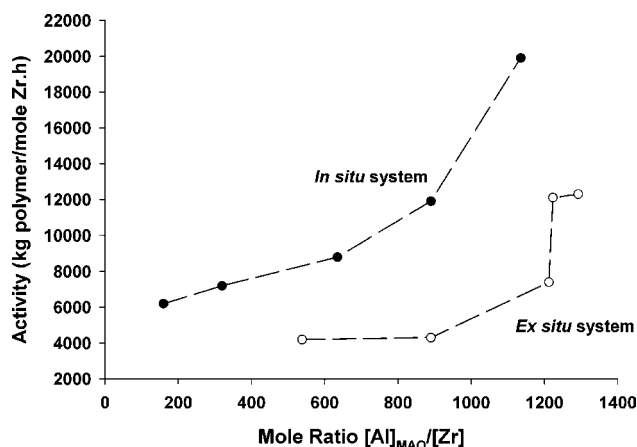


Figure 4. Comparison of the activity of ED in both the (●) in situ and (○) ex situ system; the polymerization temperature is 70 °C, and the $[Al]_{TMA}/[Zr]$ molar ratio is 2500.

different 1-olefins (such as 1-hexene, 1-octene, and 1-decene), to be used as a co-monomer, were varied during polymerization. This procedure showed that, for the in situ catalytic system, the copolymerization of ethylene with 1-octene (EO) resulted in the highest activities under the polymerization conditions used, suggesting that the optimum chain-size insertion was required. However, this phenomenon was not distinct

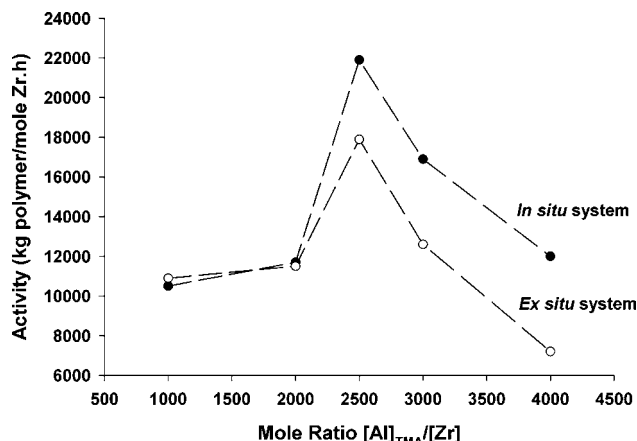


Figure 5. Comparison of the activity of EH in both the (●) in situ and (○) ex situ system; the polymerization temperature is 70 °C, and the $[Al]_{MAO}/[Zr]$ molar ratio is 1135.

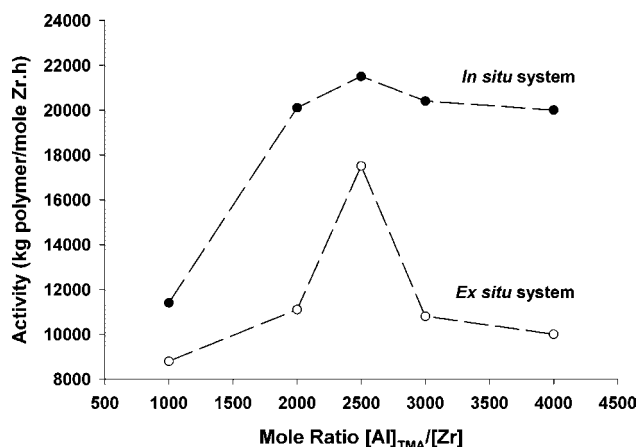


Figure 6. Comparison of the activity of EO in both the (●) in situ and (○) ex situ system; the polymerization temperature is 70 °C, and the $[Al]_{MAO}/[Zr]$ molar ratio is 1135.

for the ex situ catalytic system. Copolymerization of ethylene with 1-decene (ED) exhibited the lowest activities, compared to the other 1-olefins, for both catalytic systems.

3.2.2. Effect of $[Al]_{(TMA)}/[Zr]$ Molar Ratios. TMA was added in the polymerization process as a scavenger, to remove impurities and regenerate active sites. Thus, the effect of the $[Al]_{(TMA)}/[Zr]$ molar ratio was also investigated. It was observed that the optimum molar ratio of $[Al]_{(TMA)}/[Zr] = 2500$ was observed for both in situ and ex situ catalytic systems, as shown in Figures 5, 6, and 7 for the copolymerization of EH, EO, and ED, respectively. Increases in the $[Al]_{(TMA)}/[Zr]$ molar ratios (to > 2500) resulted in decreased activities. This was due to the inhibition of MAO functionality by the larger amounts of TMA that were used. On the other hand, TMA is a stronger alkylating and reducing agent than MAO; thus, the metallocene complex can be easily reduced by TMA, leading to catalyst deactivation. Moreover, an addition of TMA could reduce the degree of oligomerization of MAO and its overall effectiveness.¹⁴ Therefore, the addition of TMA can result in both advantages and disadvantages to the catalyst activity. Also note that the in situ catalytic system also showed higher activities at the same amounts of zirconium loading. When $Et[Ind]_2ZrCl_2$ was supported on MAO/ SiO_2 (ex situ), instead of being injected separately (in situ) into the reactor, TMA had a greater influence on

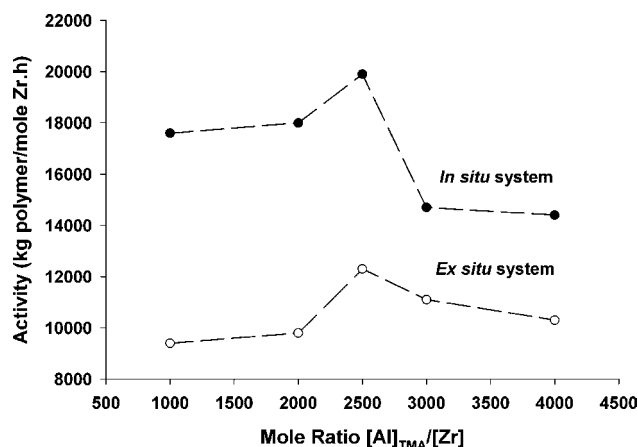


Figure 7. Comparison of the activity of ED in both the (●) in situ and (○) ex situ system; the polymerization temperature is 70 °C, and the $[Al]_{MAO}/[Zr]$ molar ratio is 1135.

Table 1. Characteristics of Copolymers Produced by the In Situ- and Ex Situ-Supported Catalytic Systems

copolymer ^a	Mw ($\times 10^{-4}$ g/mol) ^b	Mn ($\times 10^{-4}$ g/mol) ^c	MMD ^d	T_m (°C) ^e
In Situ Catalytic System				
EH	2.8	1.2	2.3	
EO	2.3	1.0	2.3	
ED	2.5	1.0	2.5	
Ex Situ Catalytic System				
EH	2.7	1.2	2.3	
EO	3.2	1.3	2.5	
ED	4.7	1.5	3.1	97

^a Copolymers were obtained in toluene, with the total volume of 30 mL, under the following conditions: polymerization temperature, 70 °C; [ethylene]/[1-olefin] molar ratio, 1:1; $[Zr] = 5 \times 10^{-5}$ M; $[Al]_{MAO}/[Zr]$ ratio, 1135; and $[Al]_{TMA}/[Zr]$ ratio, 2500. ^b Molar mass, obtained using gel permeation chromatography (GPC). ^c Obtained using gel permeation chromatography (GPC). ^d Molar mass distribution (MMD = Mw/Mn). ^e Melting point, obtained using differential scanning calorimetry (DSC).

the activity at higher $[Al]_{TMA}/[Zr]$ molar ratios. Because the activities of the in situ catalytic system were higher, these might have resulted from the exposure and activation of new sites formed after catalyst fragmentation, which can be easier to reach by a monomer for the in situ catalytic system than the ex situ catalytic system. Moreover, the impregnation of $Et[Ind]_2ZrCl_2$ on the MAO/SiO₂ support may cause $Et[Ind]_2ZrCl_2$ and MAO to react with each other and then deactivate, to some extent, prior to the polymerization process, leading to low activities. The effect of the $[Al]_{TMA}/[Zr]$ molar ratio was more pronounced in the case of the in situ catalytic system for ethylene/1-olefin copolymerization. For the in situ catalytic system, the copolymerization of EO (Figure 6) apparently exhibited great consistency in regard to catalytic activity when the $[Al]_{TMA}/[Zr]$ molar ratios were increased, whereas the copolymerization of EH (Figure 5) and ED (Figure 7) showed the lower activities. It is likely that the 1-octene-coordinated active sites produce the copolymerization with a different reactivity than the others. The similar behavior of EO copolymerization cannot be observed for the ex situ catalytic system.

3.2.3. Characteristics of Copolymers. The characteristics of copolymers produced by the in situ and ex situ catalytic systems are shown in Table 1. Generally, the molar mass (Mw) of the copolymers produced by both in situ- and ex situ-supported catalytic systems was

Table 2. Triad Distribution of Copolymers Obtained Using ¹³C NMR^a

copolymer	EEE	CEE + EEC	CEC	ECE	CCE + ECC	CCC
In Situ Catalytic System						
EH	0.62	0.21		0.17		
EO	0.82	0.10		0.08		
ED	0.75	0.17		0.08		
Ex Situ Catalytic System						
EH	0.54	0.19				0.27
EO	0.61	0.27				0.12
ED	0.57	0.29				0.14

^a E refers to ethylene monomer and C refers to the corresponding co-monomers (1-hexene, 1-octene, and 1-decene).

similar. However, only a slight increase in Mw was observed for ED under the ex situ system. All of the copolymers produced were amorphous for both catalytic systems. Only the ED copolymer with the ex situ system exhibited a melting point ($T_m \approx 97$ °C). The MMDs of the copolymers produced were also similar for both catalytic systems.

¹³C NMR spectroscopy was performed to determine the co-monomer incorporation and polymer microstructure. The characteristics of the ¹³C NMR spectra for all copolymers (not shown) were essentially similar. The triad distribution for all copolymers produced from both catalytic systems is shown in Table 2. No significant change for insertion of co-monomers in both catalytic systems was observed. Generally, ethylene incorporation in both catalytic systems gave copolymers with similar triad distribution. There was no significant change in copolymer morphologies in both catalytic systems (not shown).

4. Summary

The supporting effects of different MAO/SiO₂ in situ- and ex situ-supported $Et(Ind)_2ZrCl_2$ catalysts for ethylene/1-olefin (1-hexene, 1-octene, and 1-decene) copolymerization were investigated. This research showed that the activities for both supported catalytic systems increased continuously as the $[Al]_{MAO}/[Zr]$ molar ratios increased. The in situ catalytic system exhibited higher activities than the ex situ system, because more active catalytic species were present. Ethylene/1-octene copolymerization under the in situ catalytic system exhibited more consistency, in regard to catalytic activity, with changing $[Al]_{TMA}/[Zr]$ molar ratios, indicating that the optimum chain-size insertion was required. Generally, random copolymers were essentially produced in both systems. Similar morphologies of the copolymers were obtained for both catalytic systems.

Acknowledgment

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Nomenclature

EH = ethylene/1-hexene copolymerization
EO = ethylene/1-octene copolymerization
ED = ethylene/1-decene copolymerization

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