ABSTRACT

Ethylene/1-Octene copolymerization over the SiO₂-supported zirconocene/MMAO catalysts was investigated. The silica support was modified by different batches of 1.0 and 0.2 wt% Ga. It was found that Ga was well-dispersed all over the silica granules which cannot be detected by XRD. Based on the EDX measurement, it was revealed that Ga-modification increased the adsorption ability of MMAO on the silica support after impregnation. Thus, Ga-modification showed a promising way to enhance the rate of ethylene/1-octene copolymerization. Based on TGA study, lower interactions between MMAO and support caused by Ga-modification was another reason for increase in catalytic activity. Moreover, the Ga-modification increased Lewis acid centres or active species on the catalytic system. In addition, a comparative study of polymerization was also conducted with in situ and ex situ impregnation methods. It was found that the in situ impregnation method of the MMAO onto silica exhibited remarkable (almost 3 times) activity compared to ex situ method which is attributed to lower deactivation effect of the catalyst. ¹³C NMR analysis, however, indicated that only random copolymers were produced in all systems. These results could be related to the high degree of 1-octene insertion and thus amorphous copolymers were produced in all systems.

INTRODUCTION

Polyethylene (PE) is by volume one of the largest commodity chemicals produced in the world. It is widely used in films, house wares, bottles, containers, pipe, tubing, wire and cable insulations, conduits, and coatings [1-3]. Ziegler-Natta catalysts, metallocene catalysts, and supported metal oxides (Philips process) all are capable of producing linear polyethylene [4]. Metalloocene catalysts activated by methylaluminoxane (MAO) show very high activity in ethylene polymerization and produce polyethylene with a narrow molecular weight distribution of approximately 2.0 [5]. Many metallocene catalysts have been supported on inorganic carriers, typically silica, alumina, and titania [6-9]. The development of supported metallocenes is crucial for industrial application because it enables their use in gas- and slurry-phase processes and prevents reactor-fouling problems. It also enables the formation of uniform particles.
with narrow size distribution and high bulk density. It has been reported that silica is perhaps the most attractive support employed for supported metallocene catalysts, so far. However, the properties of silica itself may not be completely satisfied for all purposes based on the polymerization activity and properties of the obtained polymers. This is because some intrinsic undesirable properties, such as the acidity of various surface OH groups can lead to the formation of multiple active sites [10]. Many efforts have been made in order to generate the active supported metallocene species which are more active and more stable.

In our previous study, the copolymerization of ethylene/1-octene via zirconia modification on the silica-supported metallocene catalyst was also studied [11]. It was found that the zirconia modification on the silica support can result in increased polymerization activity. Besides modification with zirconia, other researchers have focused on catalytic behaviour of acidic metal-modified support [12-14]. In addition, Rahiala et al. [15] found that the presence of acidic Al seems to be advantageous for the formation of active centres and exhibits high polymerization activity level without the use of any pretreatment of the support with MAO. Therefore, the use of support modified with acidic metal including Ga is an interesting alternative for enhancement of catalytic performance and can be further developed for ethylene polymerization.

In addition to support modification, catalyst preparation method is the other important factor that influences the catalytic activity. Two methods used for preparation of supported metallocene are ex situ and in situ impregnations. For ex situ impregnation, it was found that homogeneous system gives higher activity than the supported system [16,17]. However, Campos et al. [18] observed the opposite trend with in situ impregnation. They inferred that the in situ impregnation procedure could be a potential approach for the development of a heterogeneous system.

The main objective of the present study was to further develop a better understanding on how both different impregnation methods of cocatalyst and Ga modifications on the silica support would simultaneously affect the catalytic activity and polymer properties. No such study has been investigated so far. It was found that both Ga modification and different impregnation methods can play important roles on the catalytic activities of the supported metallocene catalysts.

**EXPERIMENTALS**

**Materials**

All chemicals and polymerizations were manipulated under an argon atmosphere, using a glove box and/or Schlenk techniques. Toluene was dried over dehydrated CaCl₂ and distilled over sodium/benzophenone before use. The rac-ethylene bis(indenyl)zirconium dichloride (rac-Et[Ind]₂ZrCl₂) was supplied from Aldrich. Modified methylaluminoxane (MMAO) in hexane was donated by Tosoh (Akso, Japan). Trialkylaluminium (TMA, 2 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 the National Petrochemical Co. Ltd., Thailand. 1-Octene (d = 0.715) was purchased from Aldrich.

**Preparation of Ga-modified Silica Support**

The Ga modification of the silica support was prepared by the incipient-wetness impregnation method according to the procedure described previously [19]. The Ga source in the present case was Ga(NO₃). Ga was impregnated onto silica gel (Cariaq Q-50) by either of 0.2 or 1.0 wt% of Ga. The support was dried in oven at 110°C for 12 h and then calcined in air at 400°C for 2 h.

**Preparation of Dried-MMAO (dMMAO)**

Removal of TMA from MMAO was carried out according to the reported procedure [20]. The toluene solution of MMAO was dried under vacuum for 6 h at room temperature to evaporate the solvent, TMA, and Al(iBu)₃ (TIBA). Then, MMAO was dissolved in 100 mL of heptane and the solution was evaporated...
under vacuum to remove the remaining TMA and TIBA. This procedure was repeated 4 times and the white powder of dried MMAO (dMMAO) was obtained.

**Preparation of Supported MMAO**

**Ex Situ Impregnation Method**

Due to the very low adsorption ability of MMAO onto the silica support, the removal of TMA and TIBA of MMAO to obtain dMMAO was needed prior to impregnation. The silica-supported dMMAO (ex situ) was prepared by reacting 0.1 g of each of thermally treated unmodified and Ga-modified silica supports (at 400°C under vacuum for 4 h) with the desired amount of dMMAO in 10 mL toluene at room temperature for 30 min. The solid part was separated and washed once with 20 mL of toluene and 3 times with 20 mL hexane, followed by drying in vacuum at room temperature. A white powder of supported cocatalyst (dMMAO/SiO2) was then obtained.

**In Situ Impregnation Method and Polymerization**

Samples (0.2 g) of the unmodified and Ga-modified silica supports were allowed in contact with 1.14 mL of MMAO ([Al]/MMAO/[Zr]cat = 1135) for 30 min in a reactor with magnetic stirring. After this period of time, the suspension underwent the clarified liquid test to confirm that all MMAO was immobilized on the support. Then, 1 mL of the clarified liquid test was injected into the polymerization reactor, where a desired amount of zirconocene was already present. By formation of any noticeable amount of polymer it became evident that this clarified liquid still contains MMAO. Therefore, the fixation of cocatalyst onto the support was not completed. To ensure that MMAO was completely impregnated onto the support, the MMAO/support ratio was then reduced until no polymer was formed in the reactor [21].

After this test, the suspension was mixed with desired amounts of rac-Et[Ind]2ZrCl2 and TMA ([Al]/TMA/[Zr]cat = 2500). Then, toluene (to make a total volume of 30 mL) and 0.2 g of dMMAO/SiO2 or dMMAO/Ga-modified SiO2 ([Al]/MMAO/[Zr]cat = 1135) were introduced into the reactor. The mixture of rac-Et[Ind]2ZrCl2 (5×10⁻⁵ M) and TMA (3.75×10⁻³ M corresponding to [Al]/TMA/[Zr]cat = 2500) was mixed in the reactor and stirred for 5 min aging at room temperature, separately, and it was then injected into the reactor. From this point, a similar procedure was performed as described above.

![Scheme I. Diagram of in situ and ex situ impregnation methods.](image-url)
Characterization of Supports and Catalyst Precursors

X-ray Diffraction
A Siemens D-5000 X-ray diffractometer (Germany) with CuKα (λ = 1.54439 Å) was employed to determine the bulk crystalline phases of the samples. The spectra were scanned at a rate of 2.4 degree/min in the range of 2θ = 20-80º.

SEM and Energy Dispersive X-ray Spectroscopy
A Jeol mode JSM-6400 SEM (Japan) was used to determine the morphologies of the sample granules and an EDX with Link Isis series 300 program to observe their complete elemental distribution.

N₂ Physisorption
BET surface area, average pore diameter and pore size distribution were determined by N₂ physisorption method using a Micromeritics ASAP 2000 automated system (USA).

Thermogravimetric Analysis
TGA was performed using a TA Instrument SDT Q 600 analyzer (USA). The samples of 10-20 mg and a temperature range between 30 to 400°C at 2°C min⁻¹ were used in the operation with N₂ UHP carrier gas.

Characterization of Polymer

\(^{13}\)C NMR Spectroscopy
\(^{13}\)C NMR spectroscopy was used to determine the triad distribution and 1-octene insertion indicating the copolymer microstructure. Chemical shifts were referenced internally to the CDCl₃ and calculated according to the method described by Randall [22]. Sample solution was prepared by dissolving 50 mg of copolymer in 1,2,4-trichlorobenzene and CDCl₃. \(^{13}\)C NMR spectra were taken at 60°C using Bruker Avance II 400 (Germany) operating at 100 MHz with an acquisition time of 1.5 s and a delay time of 4 s.

Differential Scanning Calorimetry
The melting temperature of ethylene/1-octene copolymer products was determined with a Perkin-Elmer diamond DSC (USA). The analyses were performed at the heating rate of 20°C/min in the temperature range of 50-150°C. The heating cycle was run twice. In the first scan, samples were heated, and then cooled to room temperature. In the second scan, samples were reheated at the same rate, but only the results of the second scan were reported because the first scan was influenced by the mechanical and thermal history of the samples.

RESULTS AND DISCUSSION

Characteristics of Catalyst Support
In this study, silica was used as a support for the zirconocene/MMAO catalytic system because it has been one of the most widely used supports for metallocene catalysts, so far. However, the properties of silica itself may not be suitable for supporting the metallocene catalysts due to the presence of various functional groups on the surface. Therefore, the modification of silica is important in order to improve the linkage between silica and metallocene catalyst [23]. Here, we used Ga to modify the silica support

Table 1. BET surface areas of unmodified and Ga-modified silica supports.

<table>
<thead>
<tr>
<th>Support</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (mL)</th>
</tr>
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<tbody>
<tr>
<td>SiO₂</td>
<td>70.9</td>
<td>0.26</td>
</tr>
<tr>
<td>SiO₂-Ga-0.2%</td>
<td>70.6</td>
<td>0.25</td>
</tr>
<tr>
<td>SiO₂-Ga-1.0%</td>
<td>68.8</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Figure 1. XRD patterns of different supports.
for that purpose. After modification with Ga loading of 0.2 wt% (SiO$_2$-Ga-0.2%) and 1 wt% (SiO$_2$-Ga-1.0%), the silica and Ga-modified silica supports were characterized by means of N$_2$ physisorption, XRD, and SEM/EDX. As shown in Table 1, it can be observed that the surface areas of the unmodified and Ga-modified silica supports were in the range of 68-71 m$^2$/g which indicate no significant change in the surface area after Ga modification due to its efficient dispersion.

The XRD patterns of the supports are shown in Figure 1. All supports exhibit similar XRD patterns showing only the broad peaks between 20-30$^\circ$ as seen typically for the conventional amorphous silica [19]. No peak of Ga compounds was detected on the modified samples. This was an indication of the crystallite size of Ga being smaller than 3 nm (as in well-dispersed form) [11].

SEM was used in order to determine the morphologies of catalyst supports before and after modification with Ga. SEM images of different supports are shown in Figure 2. It was found that after Ga modification, the support was slightly agglomerated. However, the agglomeration of support would have no effect on other properties as proven by XRD and N$_2$ physisorption.

In the ex situ impregnation method, the cocatalyst, e.g., MMAO has to be deposited on the support. First, the impregnation of MMAO was used. However, it was found that the adsorption ability of MMAO on these specified supports was very low. Therefore, the removal of TMA and TIBA was necessary to obtain the dried MMAO (dMMAO). After impregnation with dMMAO, the different supports were determined by SEM and EDX to study the changes in morphologies and distribution of dMMAO in terms of [Al]$^{dMMAO}$ distribution.

The observed morphologies and [Al]$^{dMMAO}$ distribution are shown in Figure 3. Based on the EDX mapping, it is revealed that different supports exhibit good distribution all over the support granules. Besides, EDX was also used to measure the amount of [Al]$^{dMMAO}$ present on different supports as the typical EDX spectrum of dMMAO/ support is shown in Figure 4. The amounts of [Al]$^{dMMAO}$ present in different supports is presented in Table 2. It was found that the average amounts of [Al]$^{dMMAO}$ on

![Figure 2. SEM micrographs of different supports before dMMAO impregnation: (a) SiO$_2$, (b) SiO$_2$-Ga -0.2%, and (c) SiO$_2$ -Ga -1.0%.](image-url)
SiO\textsubscript{2}, SiO\textsubscript{2}-Ga-0.2\%, and SiO\textsubscript{2}-Ga-1.0\% were 13.1, 15.2, and 17.7 wt\%, respectively. Apparently, Ga modification on silica can result in increased amounts of [Al\textsubscript{dMMAO} present on the Ga modified support. This can be attributed to the increased adsorption ability of [Al\textsubscript{dMMAO} and silica by Ga modification. Then, the different supports with and without Ga modification having the dMMAO impregnation were used for polymerization (ex situ impregnation method). In order to compare the catalytic activity, the in situ impregnation of supports with and without Ga modification (without dMMAO impregnation) was also conducted further.

**Catalytic Activity**

The catalytic activities for all different supports and impregnation systems are listed in Table 3. Considering the homogeneous (run 1) and ex situ impregnation system (runs 3, 5, and 7) it can be seen that the supported system exhibited lower activities due to supporting effect as mentioned elsewhere [7,11,24]. However, for the supported system, it was found that activities increased with Ga modification. In general, increased activities can be attributed to

<table>
<thead>
<tr>
<th>Catalyst precursor</th>
<th>[Al\textsubscript{dMMAO} on the support (wt%)</th>
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</thead>
<tbody>
<tr>
<td>dMMAO/SiO\textsubscript{2}</td>
<td>13.1</td>
</tr>
<tr>
<td>dMMAO/SiO\textsubscript{2}-Ga-0.2%</td>
<td>15.2</td>
</tr>
<tr>
<td>dMMAO/SiO\textsubscript{2}-Ga-1.0%</td>
<td>17.7</td>
</tr>
</tbody>
</table>
increased amount of [Al]dMMAO present on different support and the interaction of [Al]dMMAO and support. The former factor can be eliminated by using the same ratios of [Al]dMMAO/[Zr]cat = 1135 in each run. As determined by EDX, the amounts of [Al]dMMAO present on different supports were unequal due to the different adsorption ability of each support. As a result, changes in activity did not cause by the different amounts of [Al]dMMAO. Hence, the effect of interaction would be the case here. In order to prove the interaction between the dMMAO and support, TGA measurement was performed. As known, the connection of the support and cocatalyst occurred via the O support-Alcocatalyst linkage [25].

The TGA can provide the useful information on the degree of interaction for dMMAO bound to silica in terms of weight loss and removal temperature [26-30]. Thus, too strong interaction can result in it, makes it more difficult for dMMAO bound to be supported to react with the zirconocene catalyst during the deactivation process. It was then lead to lower catalytic activity for polymerization. The TGA profiles of [Al]dMMAO on various supports are shown in Figure 5. It was observed that the weight loss of [Al]dMMAO present on various supports were in the order of SiO2 (9%) < SiO2-Ga-0.2% (15%) < SiO2-Ga-1.0% (16%). It also corresponds to the decomposition temperature at 10% weight loss (Td10%) of 420, 205 and 178ºC, respectively. This indicates that [Al]dMMAO present on SiO2 exhibited the strongest interaction among other supports, resulted in the lowest activity obtained.

In order to compare the different impregnation method, the in situ impregnation of MMAO as shown in Scheme I was also conducted. The catalytic activities of supports with and without Ga modifications (run 4, 6, and 8) were also shown in Table 2. Considering the support with Ga modification, it was found that its effect on the catalytic activities was in similar trend as seen for those of the ex situ impregnation method as mentioned before. Hence, it was confirmed that Ga modification apparently resulted in increased activity. In addition,
the effect of Ga in polymerization activity can be also explained based on the work reported by Campos et al. [18]. They revealed that the introduction of Ga, even in small amount, strongly improves the ability of the MCM-41 supports to immobilize metallocene catalysts. Based on our present study, for the in situ impregnation, the activities increased about 1.5 times with Ga modification of SiO2. However, with the Ga modification on MCM-41 support, activities reported by Campos et al. [18] increased almost 2.5 times. It should be mentioned that different increased activities were attributed to different types of metallocene, cocatalyst and metallocene ratios employed.

From FTIR analysis [17], there are the characteristic peaks of Lewis acid centre at 1457, 1492 and 1621 cm⁻¹ in the case of Ga-MCM-41, while MCM-41 does not exhibit these peaks. This result suggested that the interaction between zirconocene and the Lewis acid centers derived from the introduction of Ga in the support seems to play an important role in the formation of the active species and the optimization of Ga of the MCM-41 support.

When compared the catalytic activities of the ex situ and in situ impregnation methods (runs 3 and 4, runs 5 and 6, and runs 7 and 8), it was found that the in situ impregnation exhibited remarkable activities compared to the ex situ impregnation. This can be attributed to the partial entering of MMAO into the pores of the support leading to the loss of active species for the ex situ impregnation method, whereas most of the MMAO is present on the external surface of the support in case of in situ impregnation method. In addition, the multiple steps for the ex situ impregnation method would also be the cause for deactivation of active sites.

It is worth noting that based on the in situ impregnation method, the heterogeneous system surprisingly exhibited higher catalytic activity than the homogeneous one (runs 2 and 4). However, based on the work done by Jungling et al. [31] a good bulk density can improve the distribution of active site. In addition, it can reduce reactor fouling which is resulted from the adhesion of polymer to the reactor. Here, the heterogeneous system has exhibited higher bulk density than the homogeneous system under this specified reaction condition. Meanwhile, it can be proposed that the SiO₂ support might inhibit the formation of ZrCH₂CH₂Zr species [32,33] which are formed via a bimolecular process as it minimizes the steric hindrance effect of the system.

**Polymer Characteristics**

The melting temperatures \((T_m)\) of copolymer evaluated by differential scanning calorimeter (DSC) cannot be observed for all polymer samples, which indicate that non-crystalline polymers are produced in this specified polymerization system. The non-crystalline polymers were attributed to the high degree of 1-octene insertion, which can be confirmed by \(^{13}\text{C}\) NMR. The quantitative analysis of triad distribution for all copolymers was conducted on the assignment of the \(^{13}\text{C}\) NMR spectra of ethylene/1-octene (EO) copolymer which was calculated according to the method of Randall [22]. The typical characteristics of \(^{13}\text{C}\) NMR spectra for all copolymers as shown in Figure 6 were similar indicating the formation of ethylene/1-octene copolymer. The EO triad distribution of all polymers is shown in Table 4. Ethylene incorporation in all systems gave copolymers with similar triad distribution. Thus, only the random copolymers can be produced in all systems. It is shown that Ga modification tended to increase the 1-octene incorporation to a small extent.

![Typical \(^{13}\text{C}\) NMR spectra of ethylene/1-octene copolymers obtained with (a) SiO₂ and (b) SiO₂-Ga-1.0% support.](image-url)
The densities of copolymer were also measured using densitometer. They were in the range of 0.891-0.901 g/cm³. Thus, no significant change in density was found upon Ga modification.

**CONCLUSION**

In summary, the catalytic activities of ethylene/1-octene copolymerization with silica-supported zirconocene/MMAO catalyst can be enhanced with Ga modification on the silica support. It was proposed based on TGA measurement that Ga modification can result in lower interaction between the Osupport-Alcocatalyst linkages. By comparing different impregnation methods, we found that in situ impregnation exhibited remarkably higher catalytic activities compared to ex situ impregnation, which is due to increased bulk density of the polymerization system resulting in high dispersion of active sites and decreased reactor fouling. The microstructure of copolymers was of a random type for both in situ and ex situ impregnation systems showing that these two immobilized systems did not affect on the copolymer microstructure as confirmed by 13C NMR.

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