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Effect of Zr-Modified SiO_2-Supported Metallocene/MAO Catalyst on Copolymerization of Ethylene/1-Octene

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Abstract The study revealed enhancement (four to seven times) of catalytic activities for ethylene/1-octene copolymerization via the Zr-modified SiO_2-supported the metallocene/MAO catalyst. Increased activity can be attributed to an increase in absorption ability of MAO on the modified support. In addition, the strong interaction between MAO and the support was also considered.

Keywords Metallocene · Copolymerization · Zirconocene catalyst · Zr modification

1 Introduction

The discovery of metallocene catalyst along with a methylaluminoxane (MAO) cocatalyst essentially led to the development of the highly active for homogeneous polymerization of α-olefin [1, 2]. It is obvious that these active metallocene catalysts can compete with the conventional Ziegler-Natta catalysts. In particular, these catalysts are also capable of producing a variety of polyethylene copolymers, all with different chain compositions and architecture. However, in order to apply metallocene catalysts in the modern gas phase and slurry olefin polymerization processes, they need to be heterogenized on a support.

As known, the homogeneous metallocene catalysts have two major disadvantages; (a) the lack of morphology control and (b) 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 [3–9]. 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 polymerization activity and the properties of obtained polymer. Thus, the modification of silica properties is necessary in order that it can be used more efficiently. It has been reported that the immobilization method of introducing a spacer group between the support and metallocene was found to enhance the catalytic activity [10, 11]. In our previous study, the use of silane-modified silica-supported MAO with $Et[Ind]_2ZrCl_2$ catalyst for ethylene/α-olefin copolymerization was investigated [12]. It was found that silane modification resulted in increased activities for ethylene/1-hexene copolymerization. In addition, the copolymerization of ethylene/α-olefin via mixed TiO_2/SiO_2-supported zirconocene/MAO catalyst was also studied [13, 14]. It was found that mixed TiO_2/SiO_2 supports apparently resulted in increased polymerization activity as well. It was reported that zirconia can be used as a modifier for supports such as silica [15] and alumina [16]. It revealed that some catalytic properties increased with the zirconia modification due to increased dispersion of active species. Therefore, it would be interesting to investigate the impact of zirconia modification on the supported metallocene catalytic systems.

In this work, the impact of zirconia modification on the silica-supported metallocene catalyst was investigated. Experimentally, the Zr-modified silica was prepared by impregnation of a zirconium precursor onto the silica, then subsequently reacted with MAO. The modified support was employed for the copolymerization of ethylene/1-octene.

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The characteristics of the modified support and catalyst precursors were investigated by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), thermal gravimetric analysis (TGA) and N_2 physisorption. The obtained polymers were also further characterized using SEM, differential scanning calorimetry (DSC) and ^{13}C nuclear magnetic resonance (^{13}C NMR).

2 Experimental

All chemicals [zirconium (IV) propoxide, 70 wt.% solution in 1- propanol (Aldrich, St. Louis, MO, USA), silica gel (Fuji Silasia, Cariact P-10), toluene (EXXON), *rac*-ethylenebis(indenyl) zirconium dichloride, *rac*-$Et(Ind)_2ZrCl_2$) (Aldrich), methylaluminoxane, MAO, 2.667 M in toluene (Tosoh Akso), trimethylaluminum, TMA [$Al(CH_3)_3$] 2.0 M in toluene (Nippon Aluminum Alkyls), and 1-octene, 98% (Aldrich)] including the preparation of MAO/supports and polymerization were manipulated under an argon atmosphere using a vacuum glove box and/or Schlenk techniques.

2.1 Materials

2.1.1 Preparation of the Zr-Modified Silica Support

The Zr-modified silica supports were prepared by the sequential impregnation method as referred in [16]. First, Zr was impregnated onto silica using a solution of zirconium (IV) n-propoxide to produce Zr-modified supports having 1, 2, and 5 wt.% of Zr in the support. The mixture was dried in oven at 100 °C overnight.

2.1.2 Preparation of MAO/Modified Support

The modified support was heated under vacuum at 400 °C for 6 h., then, 2 g of the calcined support was reacted with the desired amount of MAO in 10 ml of toluene at room temperature for 30 min. The solid part was separated and washed five times with 20 ml of toluene, followed by drying in vacuum at room temperature to obtain the catalyst support precursor MAO/modified support.

2.2 Polymerization

The ethylene/1-octene copolymerization reaction was carried out in a 100 ml semi-batch stainless steel autoclave reactor equipped with a magnetic stirrer. At first, 0.2 g of the supported MAO ($[Al]_{MAO}/[Zr]_{cat} =$ 2,270) and 0.018 mole of 1-octene along with toluene (to make the total volume of 30 ml) were put into the reactor. The desired amount of $Et(Ind)_2ZrCl_2$ (5×10^{-5} M or 1.5×10^{-6} mole in 30 ml of solution mixture) and TMA (3.75×10^{-3} mole corresponding to $[Al]_{TMA}/[Zr]_{cat} = 2{,}500$) was mixed and stirred for 5 min aging at room temperature, separately, then was injected into the reactor. The reactor was frozen in liquid nitrogen to stop reaction between the catalyst and cocatalyst for 15 min and then the reactor was evacuated to remove argon. The reactor was heated up to polymerization temperature (70 °C). By feeding the fixed amount of ethylene (0.018 mole–6 psi) into the reaction mixtures, the ethylene consumption can be observed corresponding to the ethylene pressure drop. The polymerization reaction was stopped and the reaction time used was recorded when all ethylene (0.018 mole) was totally consumed. After all ethylene was consumed, the reaction was terminated by addition of acidic methanol (0.1% HCl in methanol) and stirred for 30 min. After filtration, the obtained copolymer (white powder) was washed with methanol and dried at room temperature.

2.3 Characterization

2.3.1 Characterization of Supports and Catalyst Precursors

X-ray diffraction. XRD was performed to determine the bulk crystalline phases of samples. It was conducted using a SIEMENS D-5000 X-ray diffractometer with CuK_α ($\lambda = 1.54439$ Å). The spectra were scanned at a rate of 2.4 degree/min in the range $2\theta = 20$–$80°$.

Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy. SEM and EDX were used to determine the sample morphologies and elemental distribution throughout the sample granules, respectively. The SEM of JEOL mode JSM-5800LV was applied. EDX was performed using Link Isis series 300 programs.

Thermal Gravimetric Analysis. TGA was performed to prove the interaction between the $[Al]_{MAO}$ and various supports. It was conducted using TA Instrument SDT Q 600 analyzer. The samples of 10–20 mg and temperature ramping from 50 to 600 °C at 5 °C/min were used in the operation. The carrier gas was N_2 UHP.

N_2 Physisorption. Measurement of BET surface area, average pore diameter and pore size distribution of supports were determined by N_2 physisorption using a Micromeritics ASAP 2000 automated system.

2.3.2 Characterization of Polymer

Scanning Electron Microscopy. Scanning electron microscopy was performed to study morphologies of polymers produced. The same equipment as mentioned above was employed.

Differential Scanning Calorimeter. The melting temperature of ethylene/1-octene copolymer products was determined with a Perkin-Elmer diamond DSC. 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 samples.

Nuclear Magnetic Resonance. ^{13}C NMR spectroscopy was used to determine comonomer incorporation and polymer microstructure. Comparison of the positions of peak in the ^{13}C NMR spectrum of polymer sample with characteristic leads to identification of the sequence of the comonomer incorporation. The ^{13}C NMR spectra were recorded at 100 °C using BRUKER magnet system 400 MHz/54 mm. The copolymer solutions were prepared using 1,2 dichlorobenzene as solvent and benzene-d_6 for an internal lock.

3 Results and Discussion

The present study showed the impact of zirconia modification on silica- supported metallocene catalyst via ethylene/1-octene copolymerization. The modified supports containing various amounts of zirconia loading on silica were characterized using XRD measurement. The XRD patterns of the silica and Zr-modified silica supports are shown in Fig. 1. It was observed that the pure silica exhibited a broad XRD peak between *ca.* 10° and 30° assigning to the conventional amorphous silica. The Zr-modified silica supports having 1, 2, and 5 wt.% of Zr exhibited the similar XRD patterns of pure silica plus a small sharp peak at 30° indicating the presence of zirconia in the tetragonal phase for the Zr-modified support [17]. Furthermore, it can be seen that the intensity of XRD characteristic peaks for the modified supports was changed based on the amounts of zirconia loading where the tetragonal phase peak at 30° apparently increased with increasing the amounts of zirconia in the silica support. In addition, the width of the line is about 0.5° which corresponds to a ZrO_2 crystal size of 15 nm or more. The particles with sizes of 15 nm are not considered to be well dispersed. The surface areas determined by N_2

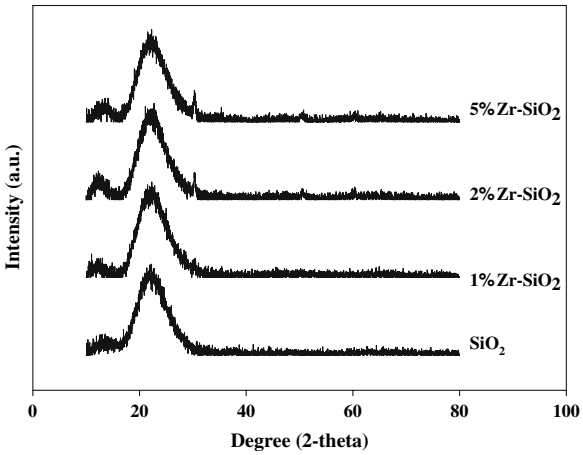


Fig. 1 XRD patterns of various Zr-modified silica supports prior to the MAO impregnation

physisorption of the modified supports decreased from 193 to 160 m^2/g upon increasing the amounts of zirconia loading. The morphologies and elemental distributions of the supports before and after MAO impregnation were determined using SEM and EDX, respectively. The SEM micrographs of the supports prior to MAO impregnation are shown in Fig. 2 indicating similar morphologies of the various supports. After MAO impregnation, the morphologies of the various supports were also determined and shown in Fig. 3. It can be observed that after impregnation with MAO, we obtained the larger size of supports due to the adsorption of MAO on the support. The typical EDX mapping image for Zr-modified silica-supported MAO at the external surface is shown in Fig. 4. The distribution of all elements ($[Al]_{MAO}$, O, Si, and Zr) was similar in all samples indicating well distribution for all elements, especially for the $[Al]_{MAO}$. In order to determine the $[Al]_{MAO}$ distribution inside the support granule, the particle was cut or microtomed, then the EDX mapping was performed at the cross-sectional area as shown in Fig. 5. It also indicated the good distribution of $[Al]_{MAO}$ inside the support granule. In addition, the EDX measurement was also used to determine the concentrations of $[Al]_{MAO}$ present on various supports with the EDX spectrum obtained as seen in Fig. 6. The concentrations of $[Al]_{MAO}$ present on various supports are also listed below. It indicated that the amounts of $[Al]_{MAO}$ apparently increased with zirconia modification from 4.93 to 7.37 wt.% upon increased amounts of zirconia loading. This was suggested that the adsorption of MAO on silica can be enhanced with zirconia modification.

For comparative studies, the catalytic activities toward the copolymerization of ethylene/1-octene upon various supports were measured. The polymerization activities are shown in Table 1. As seen, the polymerization activities were in the order of 1%Zr–SiO_2–2%Zr–SiO_2 > 5%

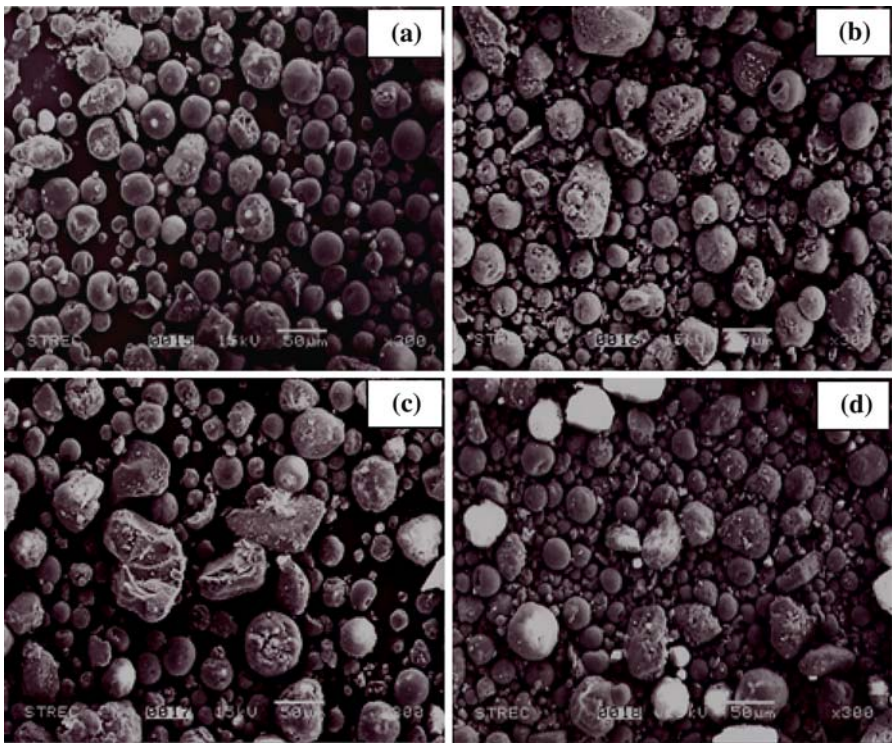


Fig. 2 SEM micrographs of various Zr-modified silica supports prior to the MAO impregnation; (**a**) SiO_2, (**b**) 1%Zr–SiO_2, (**c**) 2%Zr–SiO_2, and (**d**) 5%Zr–SiO_2

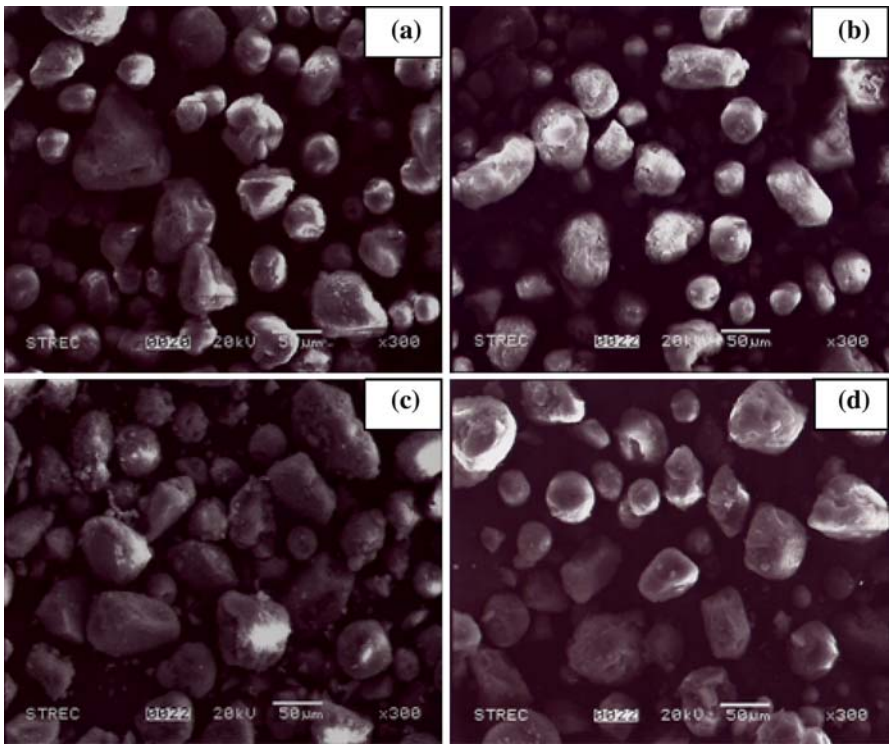


Fig. 3 SEM micrographs of various Zr-modified silica supports after the MAO impregnation; (**a**) SiO_2, (**b**) 1%Zr–SiO_2, (**c**) 2%Zr–SiO_2, and (**d**) 5%Zr–SiO_2

$Zr–SiO_2 > SiO_2$. Apparently, the SiO_2 support exhibited the lowest activity due to the lowest amount of $[Al]_{MAO}$ being present. It was also obvious that the zirconia modification on silica support essentially resulted in increased activities about four to seven times. Considering only the silica supports with zirconia modification, it can be observed that the catalytic activities dramatically decreased with increasing the amounts of zirconia loading, especially

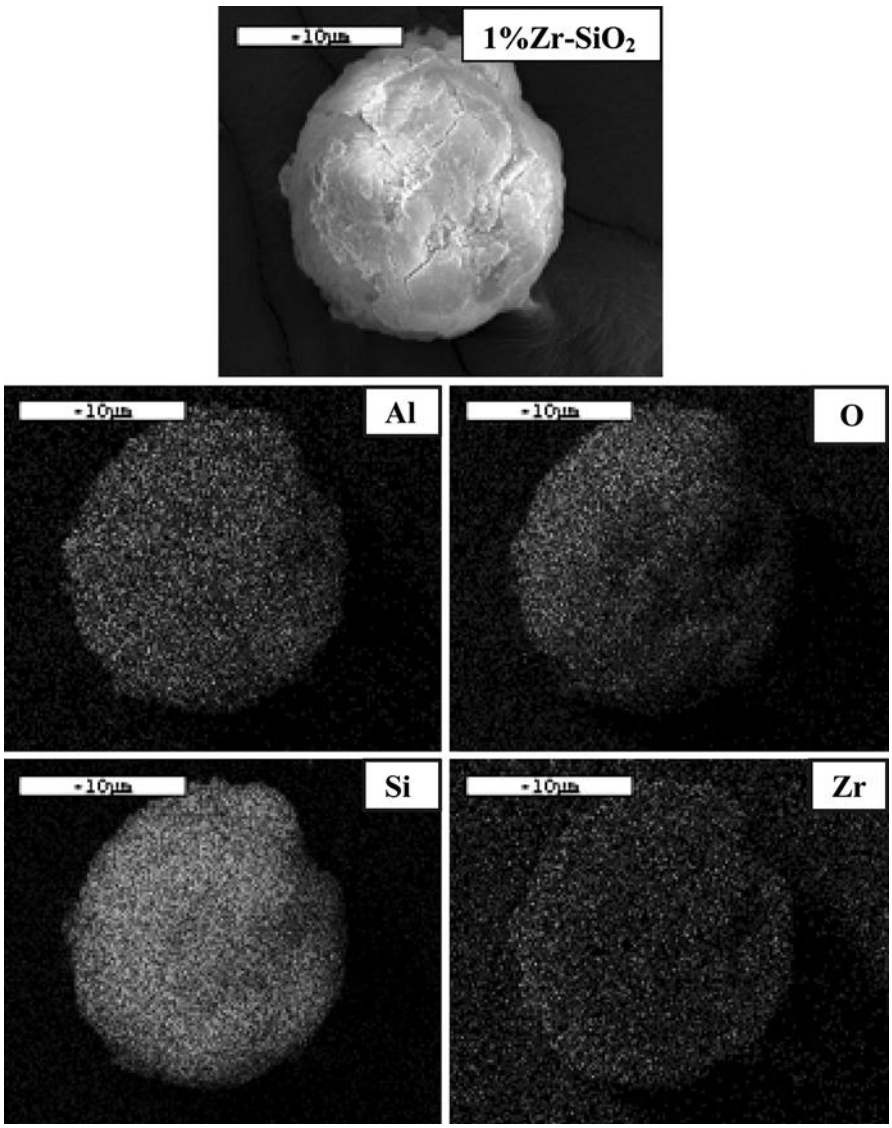


Fig. 4 A typical SEM/EDX mapping (external surface) of Zr-modified silica supports after the MAO impregnation

up to 5 wt.% of Zr. From the EDX measurement as mentioned before, the amount of $[Al]_{MAO}$ (7.37 wt.%) for the 5%Zr–SiO_2 support was the highest among other supports. Thus, based on the amount of $[Al]_{MAO}$ present in the support, one might argue that the polymerization activity for the 5%Zr–SiO_2 support should be the highest due to the largest amount of $[Al]_{MAO}$ adsorbed. This indicated that besides the concentrations of $[Al]_{MAO}$, the interactions between $[Al]_{MAO}$ and the support were very important. Based on this study, $[Al]_{MAO}$ was dispersed by impregnation onto the various supports prior to polymerization. The degree of interaction between the support and $[Al]_{MAO}$ can be determined by the TGA measurement [18]. In order to give a better understanding, we propose the interaction of support and $[Al]_{MAO}$ based on the review paper by Severn et al. [19]. They explained that the connection of the support and cocatalyst occurred via the $O_{support}$–$Al_{cocatalyst}$ linkage. In particular, the TGA can only provide useful information on the degree of interaction for the $[Al]_{MAO}$ bound to the support in terms of weight loss and removal temperature. As a matter of fact, too strong interaction can result in it being more difficult for the $[Al]_{MAO}$ bound to the support to react with the metallocene catalyst during activation processes, leading to low activity for polymerization. Conversely, the leaching of $[Al]_{MAO}$ can occur due to very weak interaction resulting in low activity as well. Therefore, the optimum interaction between the $O_{support}$–$Al_{cocatalyst}$ linkage is necessary. Here, the TGA measurement was performed to prove the interaction between the $[Al]_{MAO}$ and various supports. The TGA profiles of $[Al]_{MAO}$ on various supports are shown in Fig. 7 indicating similar profiles for various supports. We observed that the

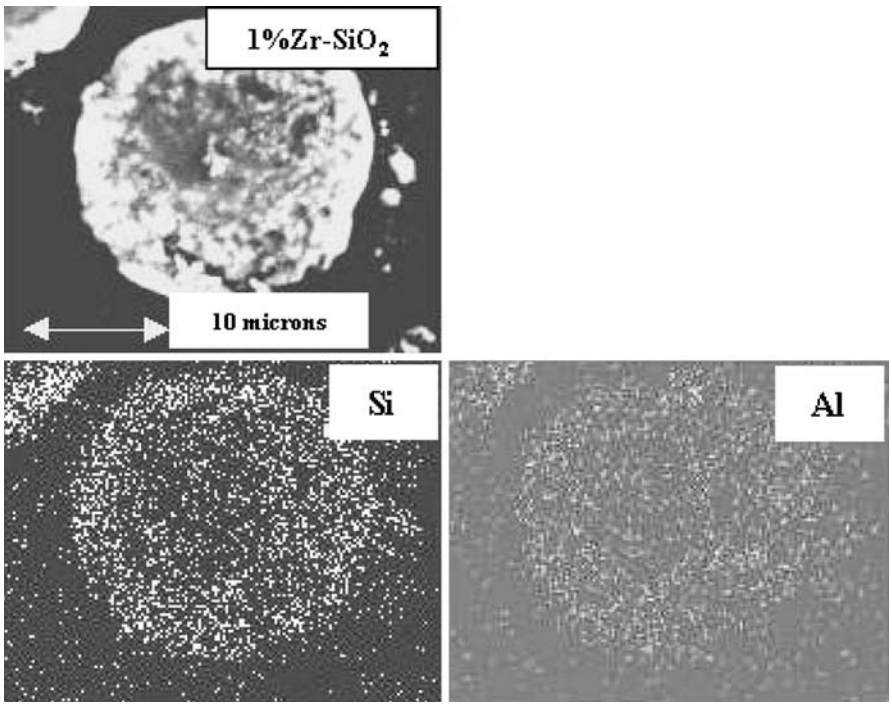
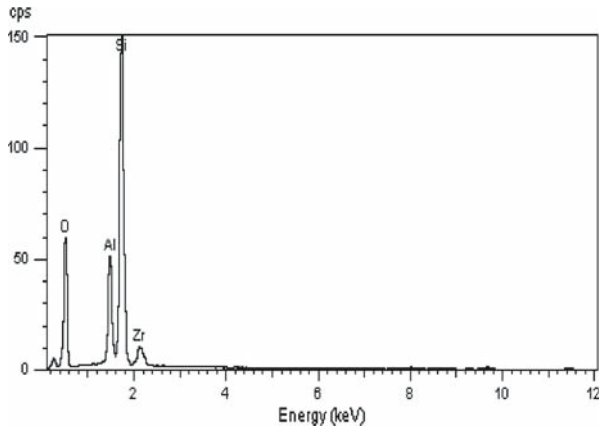


Fig. 5 A typical SEM/EDX mapping of (cross-sectional area) of Zr-modified silica supports after the MAO impregnation



Supported MAO	$[Al]_{MAO}$ (wt%) on the support
MAO/SiO_2	4.93
$MAO/1\%Zr\text{-}SiO_2$	6.63
$MAO/2\%Zr\text{-}SiO_2$	6.78
$MAO/5\%Zr\text{-}SiO_2$	7.36

Fig. 6 A typical spectrum of the supported MAO from EDX analysis used to measure the average $[Al]_{MAO}$ concentration on various supports

weight loss of $[Al]_{MAO}$ present on various supports was in order of $5\%Zr\text{–}SiO_2$ (12.6%)–SiO_2 (12.4%) > $1\%Zr\text{–}SiO_2$ (10.8%) > $2\%Zr\text{–}SiO_2$ (10.0%). This indicated that $[Al]_{MAO}$ present on $5\%Zr\text{–}SiO_2$ support had the weakest interaction among other supports. Although it had the highest amount of $[Al]_{MAO}$ among other Zr-modified supports, it exhibited the lower activity. This should be due to the weak interaction as mentioned before. Based on the observed polymerization activities, it is worth noting that

Table 1 Polymerization activities[a]

Samples	Yield (g)	Polymerization Time (sec)	Catalytic Activity (kg of polymer/molZr h)
SiO_2	0.6348	384	3,968
$1\%Zr\text{–}SiO_2$	1.7586	156	27,055
$2\%Zr\text{–}SiO_2$	1.7757	167	25,519
$5\%Zr\text{–}SiO_2$	1.0644	180	14,192

[a] Activities were measured at polymerization temperature of 70 °C, [ethylene] = 0.018 mole, [1-octene] = 0.018 mole, $[Al]_{MAO}/[Zr]_{cat}$ 2,270, $[Al]_{TMA}/[Zr]_{cat} = 2{,}500$, in toluene with total volume = 30 ml, and $[Zr]_{cat} = 5 \times 10^{-5}$ M

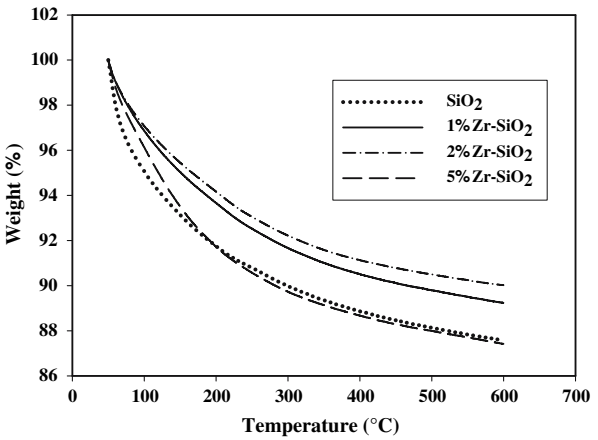


Fig. 7 TGA profiles of $[Al]_{MAO}$ on various Zr-modified silica supports

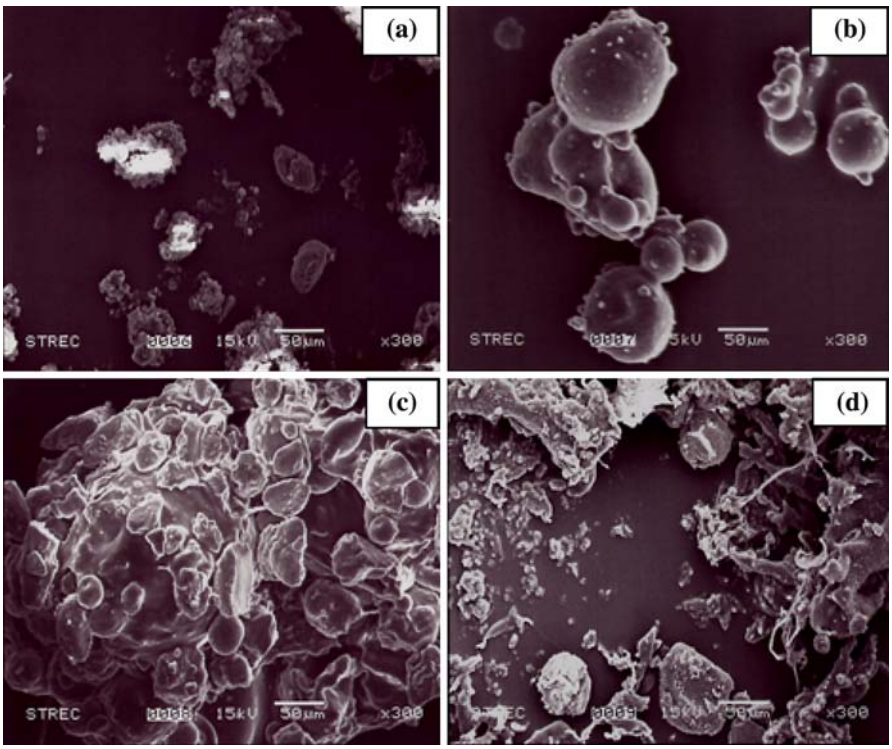


Fig. 8 SEM micrographs of ethylene/1-octene copolymers obtained from various Zr-modified silica supports; (**a**) SiO_2, (**b**) 1%Zr–SiO_2, (**c**) 2%Zr–SiO_2, and (**d**) 5%Zr–SiO_2

Table 2 Triad distribution of EO copolymers[a] and their melting temperature (T_m)[b]

Polymer samples obtained from	OOO	EOO	EOE	EEE	OEE	OEO	Mol. %O insertion	T_m (°C)
SiO_2	0.000	0.000	0.043	0.855	0.102	0.000	4.3	97
1%Zr–SiO_2	0.000	0.000	0.078	0.719	0.201	0.002	7.8	86
2%Zr–SiO_2	0.000	0.000	0.125	0.615	0.234	0.026	12.8	88
5%Zr–SiO_2	0.000	0.000	0.104	0.683	0.198	0.015	10.4	94

[a] Obtained from ^{13}C NMR

[b] Obtained from DSC

in order to obtain the high polymerization activity, one needs to consider on both high concentration of $[Al]_{MAO}$ present and the interaction between the $O_{support}$–$Al_{cocatalyst}$ linkage. A wide range of variables including the concentration of $[Al]_{MAO}$ and support interaction between the $O_{support}$–$Al_{cocatalyst}$ linkage can affect the polymerization activity. These effects of both $[Al]_{MAO}$ concentration and interaction of $O_{support}$–$Al_{cocatalyst}$ linkage can be superimposed on each other. Thus, an increase in the amount of $[Al]_{MAO}$ can result in weaker interaction (as seen for the 5%Zr–SiO_2 support) leading to lower polymerization activity compared to other Zr-modified supports.

The obtained copolymers were further characterized using SEM, ^{13}C NMR and DSC measurements. The SEM micrographs of polymers are shown in Fig. 8 indicating the typical morphologies of copolymers obtained from this catalytic system [9, 14]. There was no significant change in copolymer morphologies upon various supports employed. The quantitative analysis of triad distribution for all copolymers was conducted on the basic assignment of the ^{13}C NMR spectra [20]. The triad distribution for all copolymers is shown in Table 2. All copolymers produced from different supports exhibited the similar triad distribution having the majority triad of EEE without the triad of OOO. Based on ^{13}C NMR, it was suggested that the zirconia modification did not affect the microstructure of copolymers. However, considering the insertion of 1-octene (Table 2), it was found that zirconia modification resulted in an increase in 1-octene insertion. This was probably due to decreased steric hindrance in Zr-modified silica supports. It should be mentioned that the amounts of polyethylene products which should have been produced based on the 1-octene insertion (4.3–12.8 mol.%) obtained from the ^{13}C NMR

results as listed in Table 2 is about 0.6–0.8 g. However, the obtained polymer yields as seen in Table 1 are higher. This should be probably due to the presence of high MW polyoctene or some impurities, which cannot be dissolved using the 1,2 dichlorobenzene prior to the ^{13}C NMR measurement. Therefore, the degree of 1-octene insertion obtained from ^{13}C NMR was less than that calculated from the polymer yield obtained. In addition, the melting temperatures (T_m) of copolymers were evaluated using DSC as also shown in Table 2. It revealed that T_m of copolymers trended to decrease with zirconia modification on the support. The decreased T_m of copolymers can be attributed to the increased degree of 1-octene insertion, which can be confirmed by ^{13}C NMR as mentioned before.

4 Conclusions

The zirconia modification on the silica support was found to enhance the catalytic activity for ethylene/1-octene copolymerization using the zirconocene/MAO catalyst. The increased activities can be attributed to the larger amounts of $[Al]_{MAO}$ present on the modified support coupled with stronger interaction between the $O_{support}$–$Al_{cocatalyst}$ linkage. The zirconia modification can also increase the degree of 1-octene insertion without any significant change in polymer microstructure. Increased degree of 1-octene insertion consequently resulted in decreased T_m of copolymers obtained.

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