

## CHAPTER IV

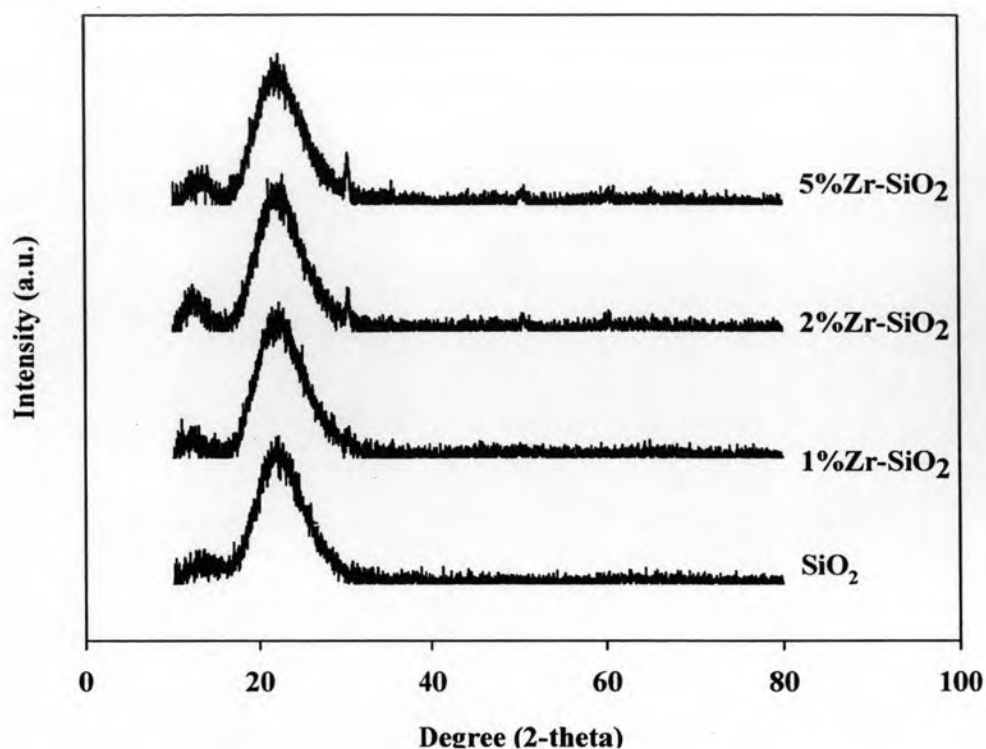
### RESULTS AND DISCUSSIONS

The purpose of this work is to investigate the impact of zirconia modification on silica-supported metallocene catalyst via ethylene/1-octene copolymerization including develop a better understanding on how zirconia modification change the nature of silica-supported metallocene catalyst in terms of activities and properties.

#### 4.1 Characterization of supports and catalyst precursors

##### 4.1.1 Characterization of modified supports with X-ray diffraction (XRD)

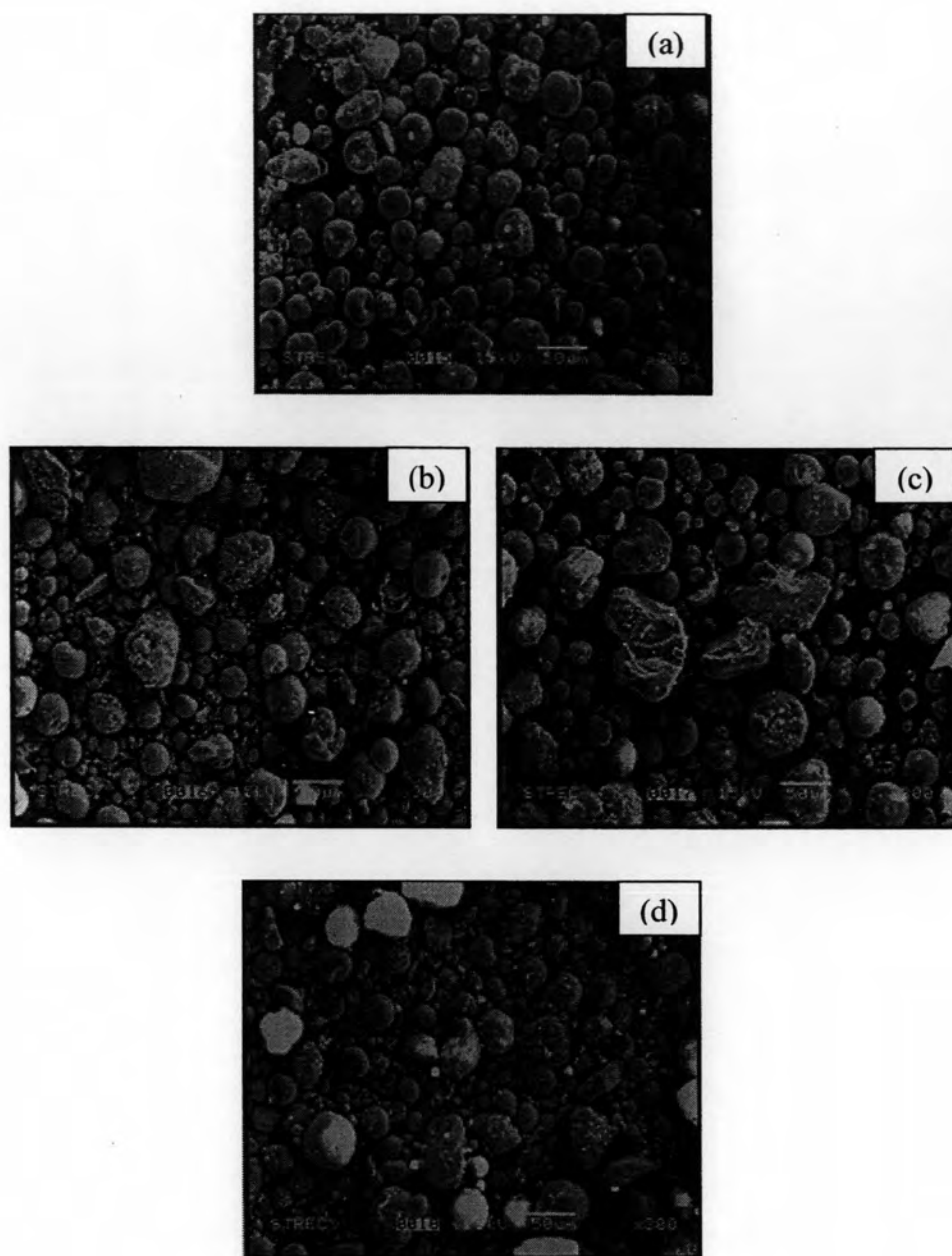
The modified supports containing various amounts of zirconia loading on silica were characterized using XRD measurement . XRD patterns of the silica and Zr-modified supports are shown in Figure 4.1. It was observed that the pure silica exhibited a broad XRD peak at between ca.  $10^{\circ}$  to  $30^{\circ}$  assigning to the conventional amorphous silica. The modified supports with 1%, 2%, and 5%wt of Zr exhibited the similar XRD patterns of pure silica having only a small peak at  $30^{\circ}$  indicating the present of zirconia in the support [67]. This indicated that  $ZrO_2$  was in the highly dispersed form, which was almost invisible by XRD. Furthermore, it can be seen that the intensity of XRD characteristic peaks for the modified supports was changed based on the ratio of  $ZrO_2/SiO_2$  where the characteristic XRD peak of  $ZrO_2$  at  $30^{\circ}$  apparently increased with increasing the amounts of zirconia loading on the silica support.



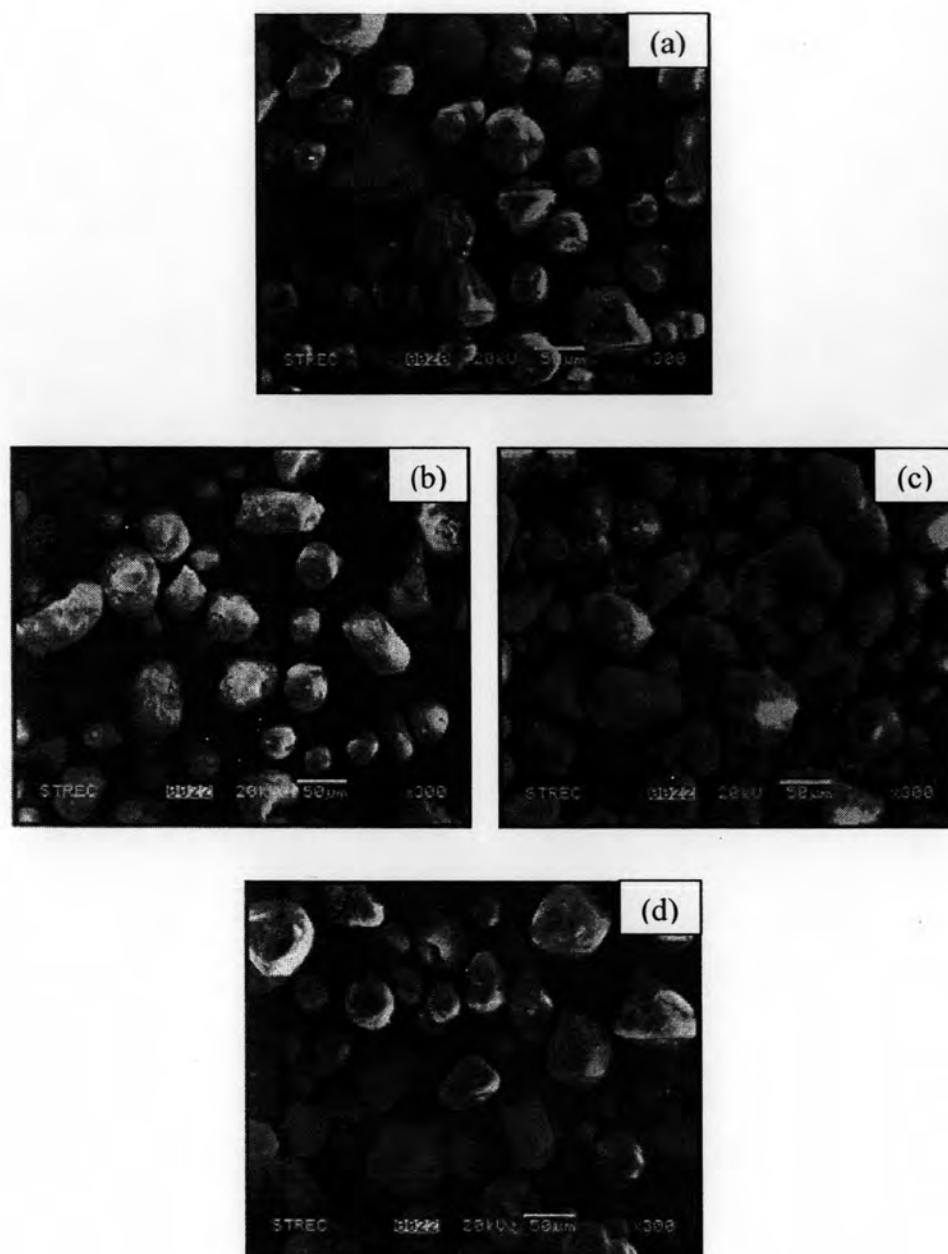
**Figure 4.1** The XRD patterns of various zirconia-modified supports

#### **4.1.2 Characterization of supports and catalyst precursors with scanning electron microscope(SEM) and energy dispersive X-ray spectroscopy (EDX)**

In order to determine the morphologies and elemental distributions of the supports before and after impregnation, SEM and EDX were performed in Figure 4.2, 4.3, respectively. It indicated that zirconia-modified supports having 1, 2, and 5%wt of zirconia was found to decorate on the silica surface as seen in the SEM micrographs. The SEM micrographs of the supports after impregnation with MAO are shown in Figure 4.3 indicating similar results as before the MAO impregnation as seen in Figure 4.2.

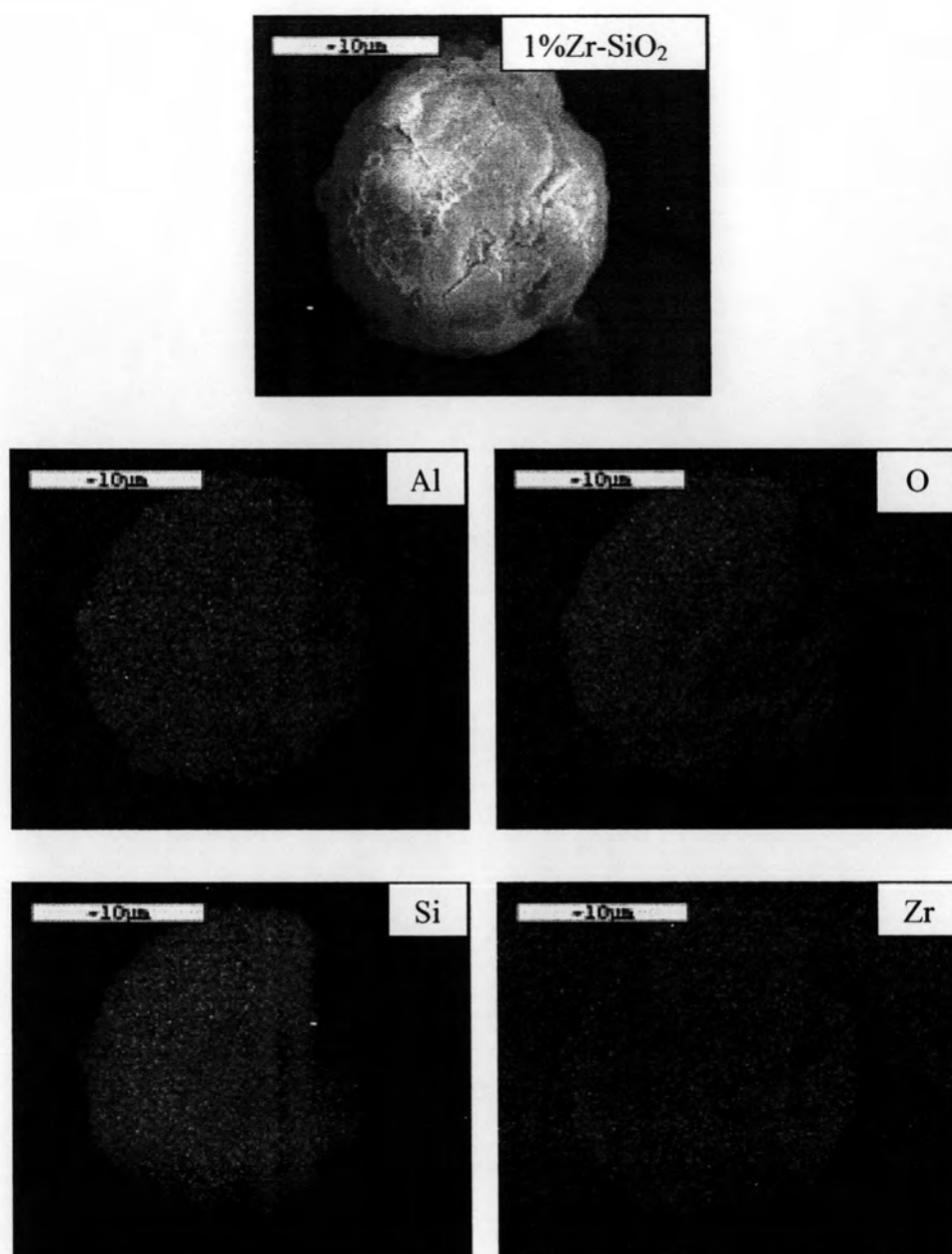


**Figure 4.2** SEM micrographs of various zirconia-modified supports before MAO impregnation; (a)  $\text{SiO}_2$ , (b) 1%Zr- $\text{SiO}_2$ , (c) 2%Zr- $\text{SiO}_2$ , (d) 5%Zr- $\text{SiO}_2$



**Figure 4.3** SEM micrographs of various zirconia-modified supports after MAO impregnation; (a)  $\text{SiO}_2$ , (b) 1%Zr- $\text{SiO}_2$ , (c) 2%Zr- $\text{SiO}_2$ , (d) 5%Zr- $\text{SiO}_2$

The typical EDX mapping images for the Zr-modified  $\text{SiO}_2$  supports after impregnation with MAO are shown in Figure 4.4. The distribution of all elements (Al, O, Si, and Zr) obtained from EDX was similar in all samples. The EDX mapping images of the supports can provide more information about the distribution of MAO as seen for Al distribution mapping on each support. It was found that the MAO was well distributed all over the support granules.



**Figure 4.4** EDX mapping of various zirconia-modified supports after MAO impregnation

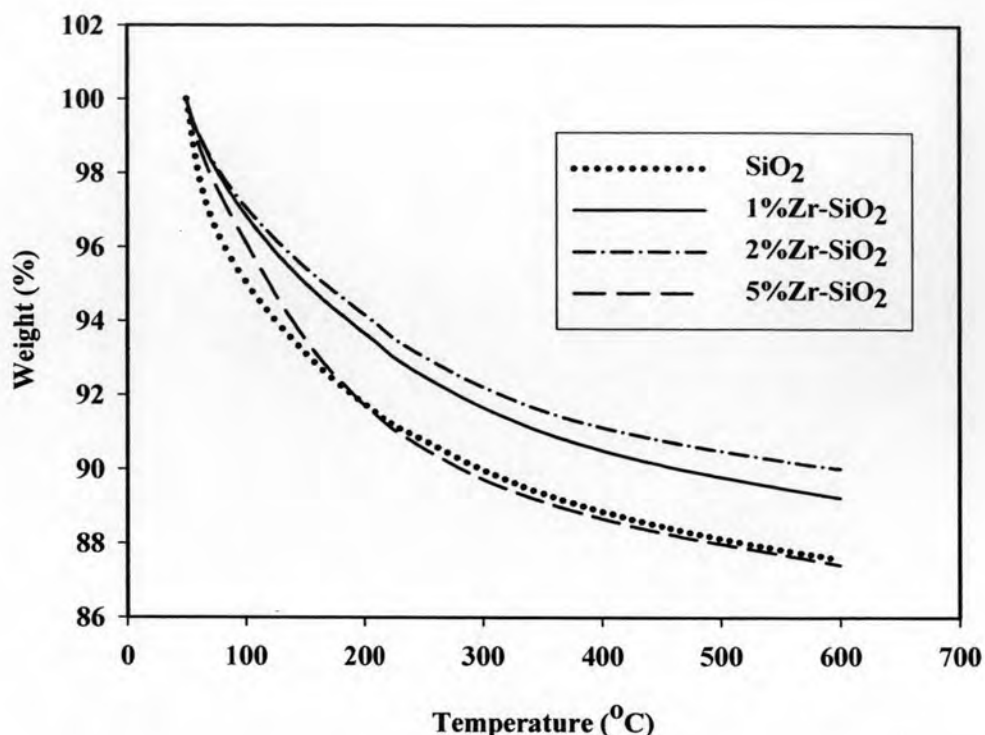
The amounts of  $[Al]_{MAO}$  in the various zirconia-modified supports was determined by the energy dispersive X-ray spectroscopy (EDX) as shown in Table 4.1 and the EDX results of the catalyst precursor are also shown in Appendix A.

**Table 4.1** Average amount of  $[Al]_{MAO}$  in catalyst precursor

Samples	Average wt% of $[Al]_{MAO}$ in catalyst precursor
SiO <sub>2</sub>	4.93
1%Zr-SiO <sub>2</sub>	6.63
2%Zr-SiO <sub>2</sub>	6.78
5%Zr-SiO <sub>2</sub>	7.36

#### 4.1.3 Characterization of supports and catalyst precursors with thermal gravity analysis (TGA)

The TGA measurement was performed to proof the interaction between the  $[Al]_{MAO}$  and various supports. The TGA profiles of  $[Al]_{MAO}$  on various supports are shown in Figure 4.5. It indicated the similar profiles for various supports. It was observed that the weight loss of  $[Al]_{MAO}$  present on various supports was in order of 5%Zr-SiO<sub>2</sub> (12.6%) > SiO<sub>2</sub> (12.4%) > 1%Zr-SiO<sub>2</sub> (10.8%) > 2%Zr-SiO<sub>2</sub> (10.0%). This indicated that  $[Al]_{MAO}$  present on 5%Zr-SiO<sub>2</sub> (12.6%) modified support had the weakest interaction.



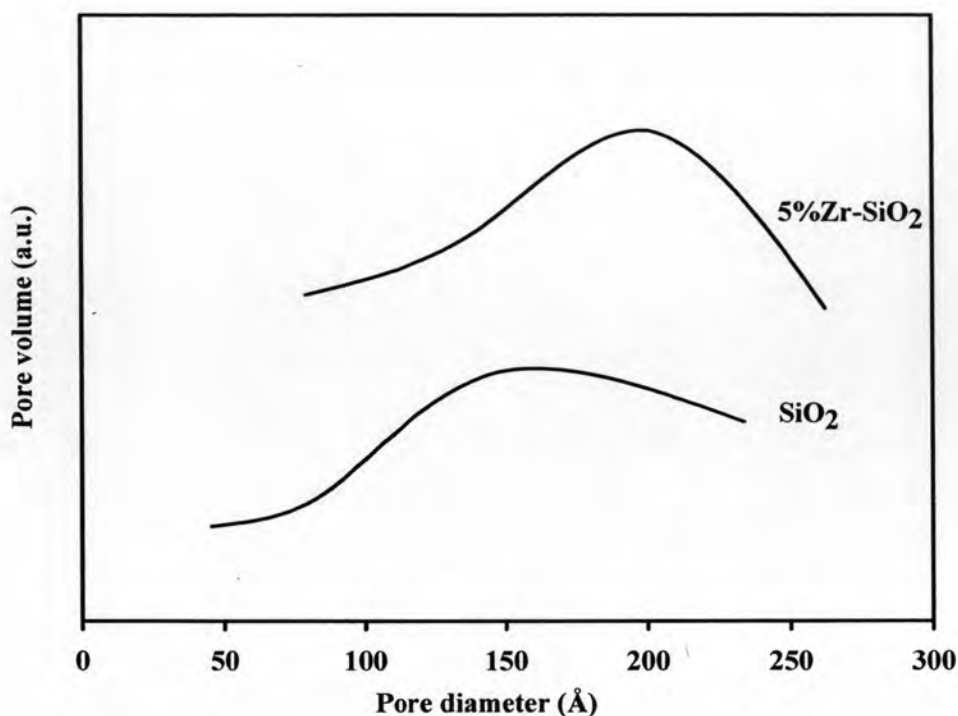
**Figure 4.5** TGA profiles of  $[Al]_{MAO}$  on zirconia-modified supports

#### 4.1.4 Characterization of supports with $N_2$ physisorption

Measurement of BET surface area, average pore diameter and pore size distribution of supports were determined by  $N_2$  physisorption. The BET surface area and average pore diameter of supports are shown in Table 4.2. It was observed that the BET surface area of  $SiO_2$  ( $192.5 \text{ m}^2/\text{g}$ ) was higher than  $5\%Zr-SiO_2$  ( $160.4 \text{ m}^2/\text{g}$ ). It also revealed that the average pore diameter of  $SiO_2$  ( $147.5 \text{ \AA}$ ) was smaller than  $5\%Zr-SiO_2$  ( $159.7 \text{ \AA}$ ). The pore size distribution of supports are shown in Figure 4.6. This indicated that the  $5\%Zr-SiO_2$  support exhibited larger portion of the large pore than the  $SiO_2$  support.

**Table 4.2** BET surface area and average pore diameter of supports

Supports	BET surface area ( $\text{m}^2/\text{g}$ )	Average pore diameter ( $\text{\AA}$ )
$SiO_2$	192.5	147.5
$5\%Zr-SiO_2$	160.4	159.7



**Figure 4.6** Pore size distribution of  $\text{SiO}_2$  and  $5\%\text{Zr-SiO}_2$  supports

## 4.2 Effect of zirconia-modified supports in ethylene/1-octene copolymerization system

### 4.2.1 The effect of zirconia-modified supports on the catalytic activity

Then, the various zirconia-modified supports after impregnation with MAO were used and investigated for catalytic activities. Copolymerization of ethylene/1-octene via various zirconia-modified supports with zirconocene catalyst was performed in order to determine the catalytic activities influenced by the various supports. Methylaluminoxane (MAO) was used as cocatalyst which the molar ratio of  $\text{Al}_{(\text{MAO})}/\text{Zr}_{(\text{cat})}$  was 2270. The copolymerization was performed in toluene solvent at  $70^\circ\text{C}$  using ethylene consumption of 0.018 mol (pressure in reactor 50 psi), 0.018 mol ( $\approx 3$  ml) of 1-octene, 200 mg of catalyst precursor and zirconium concentration  $5.0 \times 10^{-5}$  M with total solution volume of 30 ml. The resulted reaction study is shown in Table 4.3.



**Table 4.3** Catalytic activity of various zirconia-modified supports in ethylene/1-octene

Samples	Yield (g)	Polymerization Time (sec)	Catalytic Activity <sup>a</sup> (kgCopolymer/molZr.h)
SiO <sub>2</sub>	0.6348	384	3968
1%Zr-SiO <sub>2</sub>	1.7586	156	27055
2%Zr-SiO <sub>2</sub>	1.7757	167	25519
5%Zr-SiO <sub>2</sub>	1.0644	180	14192

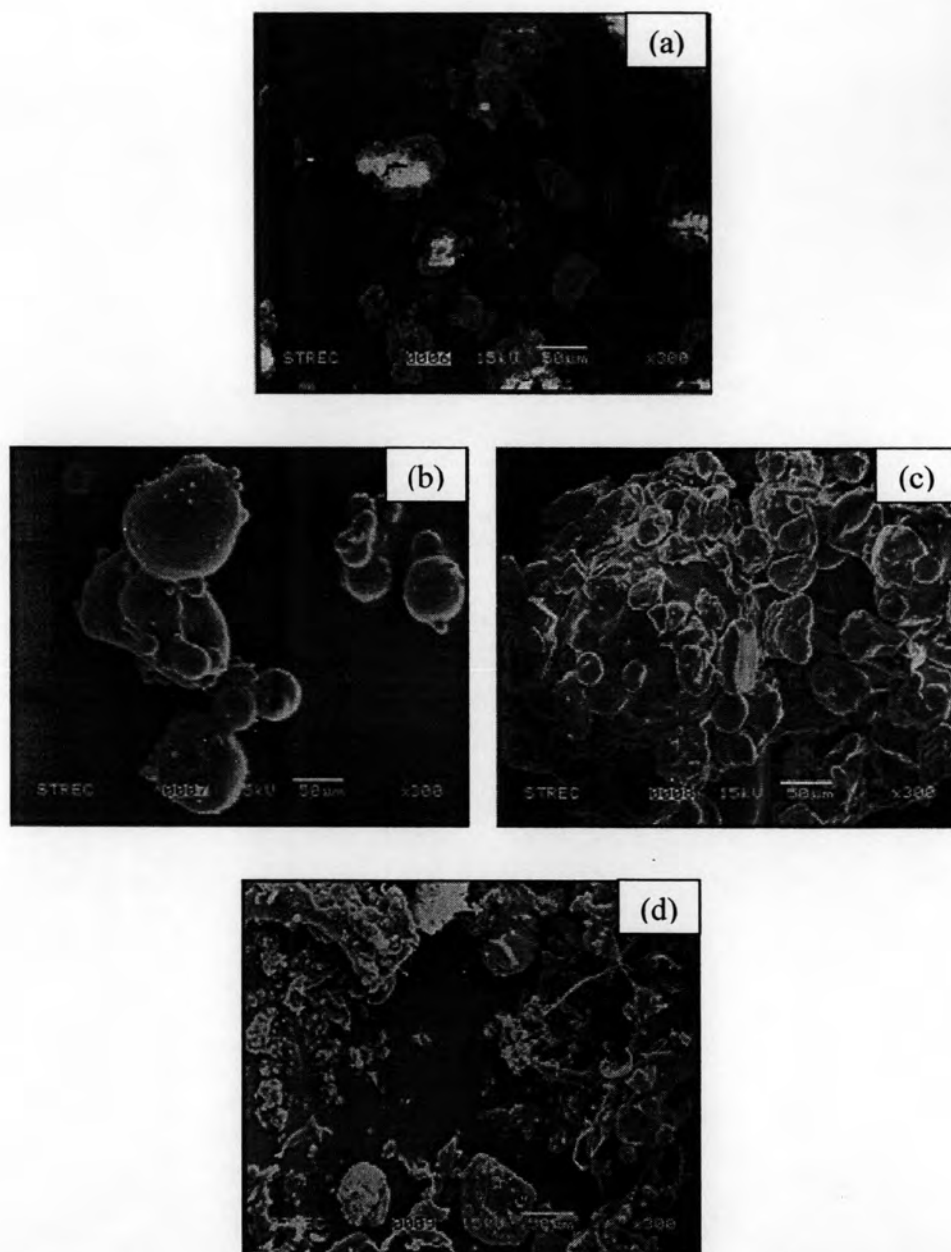
<sup>a</sup>copolymerization conditions:  $Al_{(MAO)}/Zr_{(cat)} = 2270$ ,  $Al_{(TMA)}/Zr_{(cat)} = 2500$ , precursor = 200 mg, reaction temperature 70°C, 0.018 mol of ethylene consumption, 0.018 mol of 1-octene, total volume = 30 ml, and  $[Zr]_{cat} = 5 \times 10^{-5}$  M.

The activities of the zirconia-modified supports were much higher (almost 7 times) than that of the silica support. This can be attributed to the larger amounts of MAO present on the zirconia-modified SiO<sub>2</sub> as seen from EDX (Table 4.1). This was suggested that Zr modification can increase the adsorption ability of MAO on the SiO<sub>2</sub> supported resulting in larger amounts of MAO on the modified support. However, considering only zirconia-modified support, it was found that at low content of zirconia in the modified supports (1 and 2%wt) the activities were much higher than that of the 5%wt of zirconia-modified support. This can be attributed to stronger interaction between MAO and support as seen by TGA results (Figure 4.5). It should be noted that weaker interaction can possibly resulted in loss of MAO during reaction due to leaching of MAO to the reaction medium.

#### 4.2.2 The effect of zirconia-modified supports on the morphologies of copolymers

Morphologies of polymers produced via various supports were also investigated. SEM micrographs of copolymers have shown in Figure 4.7. It indicated

that there was no significant change in polymer morphologies upon various zirconia-modified supports used.



**Figure 4.7** SEM micrographs of ethylene/1-octene copolymers obtained with various zirconia-modified supports ; (a)  $\text{SiO}_2$ , (b) 1%Zr- $\text{SiO}_2$ , (c) 2%Zr- $\text{SiO}_2$ , (d) 5%Zr- $\text{SiO}_2$

### 4.2.3 The effect of zirconia-modified supports on the melting temperatures of copolymers

The melting temperatures ( $T_m$ ) of copolymer were evaluated by differential scanning calorimeter (DSC) as shown in Table 4.4. DSC curves of the copolymer are also shown in Appendix B.

**Table 4.4** Melting temperatures of various zirconia-modified supports in ethylene/1-octene

Polymer Samples	$T_m$ ( $^{\circ}\text{C}$ )	% crystallinity
$\text{SiO}_2$	97	13.79
1%Zr- $\text{SiO}_2$	86	4.56
2%Zr- $\text{SiO}_2$	88	7.76
5%Zr- $\text{SiO}_2$	94	8.68

Based on the DSC measurement of copolymer as seen in Table 4.4, it revealed that the melting temperatures ( $T_m$ ) of copolymer decreased with using the Zr-modified silica support. Decreased  $T_m$  was less pronounced at high loading of zirconia. %crystallinity of copolymers was calculated according to Liu, S. and *et al.* [68]. One effect of the higher degree of comonomer (i.e. 1-octene) incorporation is a decrease in crystallinity as also seen in Table 4.4. As a result, polymers with a lower melting point and density, and an increased flexibility and processibility are obtained [69].

#### 4.2.4 The effect of zirconia-modified support on the incorporation of polymers determined by means of $^{13}\text{C}$ NMR

**Table 4.5** Incorporation of various zirconia-modified supports in ethylene/1-octene copolymer

Polymer Samples	Comonomer Insertion (%)
SiO <sub>2</sub>	4.3
1%Zr-SiO <sub>2</sub>	7.8
2%Zr-SiO <sub>2</sub>	12.8
5%Zr-SiO <sub>2</sub>	10.4

**Table 4.6** Triad distribution of ethylene /1-octene

Polymer Samples	OOO	EOO	EOE	EEE	OEE	OEO
SiO <sub>2</sub>	0.000	0.000	0.043	0.855	0.102	0.000
1%Zr-SiO <sub>2</sub>	0.000	0.000	0.078	0.719	0.201	0.002
2%Zr-SiO <sub>2</sub>	0.003	0.000	0.125	0.612	0.234	0.026
5%Zr-SiO <sub>2</sub>	0.000	0.000	0.104	0.683	0.198	0.015

**E** refers to ethylene and **O** refers to corresponding comonomers: 1-octene

$^{13}\text{C}$  NMR spectroscopy was used to determine comonomer incorporation and polymer microstructure. Chemical shift were referred internally to the major backbone methylene resonance and calculated according to ref. reported by J.C. Randall [70]. The result obtained for the triad sequence distribution of copolymer is shown in Table 4.6. The result suggested that the copolymer had a random distribution of comonomer insertion with very low amount of comonomer triad in the polymer chain. Comonomer incorporation increased with the zirconia modification.

### 4.3 Effect of zirconia-modified supports with different comonomers

#### 4.3.1 The Effect of zirconia-modified supports with different comonomers on the catalytic activity

Then, the various zirconia-modified supports after impregnation with MAO were used and investigated for catalytic activities. Copolymerization of ethylene/1-hexene and ethylene/1-decene via various zirconia-modified silica-supported MAO with zirconocene catalyst was performed in order to determine the catalytic activities influenced by the various supports and comonomers. Methylaluminoxane (MAO) was used as cocatalyst which the molar ratio of  $Al_{(MAO)}/Zr_{(cat)} = 2270$ . The copolymerizations were performed in toluene solvent at  $70^{\circ}C$  using ethylene consumption of 0.018 mol, 6 psi (pressure in reactor 50 psi), 0.018 mol ( $\approx 3$  ml) of  $\alpha$ -olefin, 200 mg of catalyst precursor and zirconium concentration  $5.0 \times 10^{-5}$  M with total solution volume of 30 ml. The resulted reaction study is shown in Table 4.7- 4.8.

**Table 4.7** Catalytic activity of various zirconia-modified supports in ethylene/1-hexene

Samples	Yield (g)	Polymerization Time (sec)	Catalytic Activity <sup>a</sup> (kgCopolymer/molZr.h)
SiO <sub>2</sub>	0.5407	848	1530
1%Zr-SiO <sub>2</sub>	0.9262	202	11004
2%Zr-SiO <sub>2</sub>	0.8790	346	6097
5%Zr-SiO <sub>2</sub>	0.6620	695	2286

<sup>a</sup>copolymerization conditions:  $Al_{(MAO)}/Zr_{(cat)} = 2270$ ,  $Al_{(TMA)}/Zr_{(cat)} = 2500$ , precursor = 200 mg, reaction temperature  $70^{\circ}C$ , 0.018 mol of ethylene consumption, 0.018 mol of 1-hexene, total volume = 30 ml, and  $[Zr]_{cat} = 5 \times 10^{-5}$  M.

**Table 4.8** Catalytic activity of various zirconia-modified supports in ethylene/1-decene

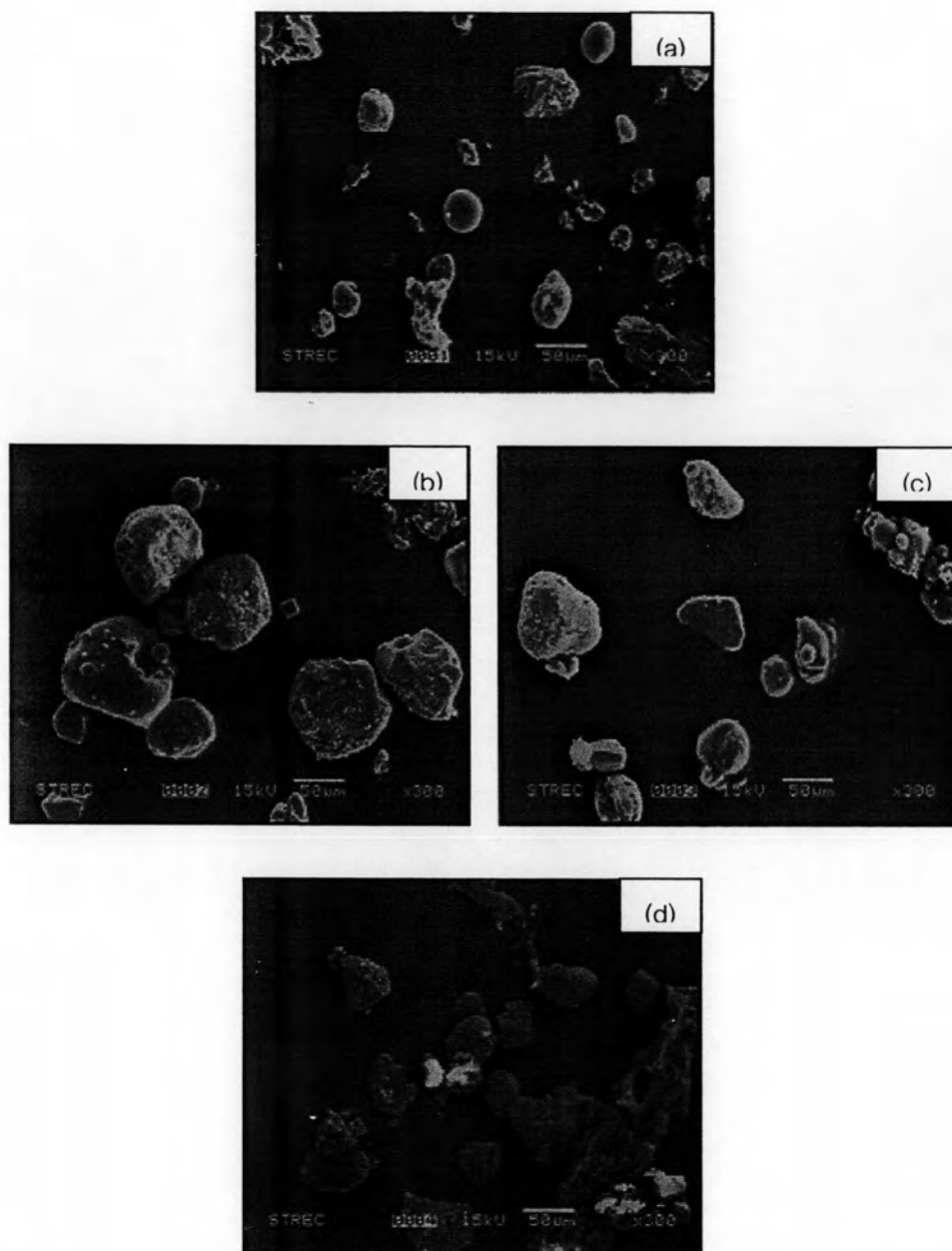
Samples	Yield (g)	Polymerization Time (sec)	Catalytic Activity <sup>a</sup> (kgCopolymer/molZr.h)
SiO <sub>2</sub>	0.8197	798	2465
1%Zr-SiO <sub>2</sub>	1.2636	164	18491
2%Zr-SiO <sub>2</sub>	1.0965	384	6853
5%Zr-SiO <sub>2</sub>	1.1168	419	6397

<sup>a</sup>copolymerization conditions:  $Al_{(MAO)}/Zr_{(cat)} = 2270$ ,  $Al_{(TMA)}/Zr_{(cat)} = 2500$ , precursor = 200 mg, reaction temperature 70°C, 0.018 mol of ethylene consumption, 0.018 mol of 1-decene, total volume = 30 ml, and  $[Zr]_{cat} = 5 \times 10^{-5}$  M.

The effect of zirconia-modified supports with different comonomers on the catalytic activity are shown in Table 4.7 and 4.8. It was observed that the catalytic activity on various supports was in order of 1%Zr-SiO<sub>2</sub> > 2%Zr-SiO<sub>2</sub> > 5%Zr-SiO<sub>2</sub> > SiO<sub>2</sub>. This indicated that catalytic activity was increased with zirconia-modified silica-supported in the copolymerization of ethylene with 1-olefin by metallocene catalysis.

#### 4.3.2 The effect of zirconia-modified supports on the morphologies of copolymers

Morphologies of polymers produced via various supports were also investigated. It indicated that there was no significant change in polymer morphologies upon various zirconia-modified supports used. The copolymerization of ethylene with three different comonomers gave copolymers having similar morphologies as shown in Figure 4.8. Besides, SEM micrographs of all copolymers are shown in Appendix A.



**Figure 4.8** SEM micrographs of ethylene/1-hexene copolymers obtained with various zirconia-modified supports;(a) SiO<sub>2</sub>, (b) 1%Zr-SiO<sub>2</sub>, (c) 2%Zr-SiO<sub>2</sub>, (d) 5%Zr-SiO<sub>2</sub>

### 4.3.3 The effect of zirconia-modified supports on the melting temperatures of copolymers with different comonomers

The melting temperatures ( $T_m$ ) of copolymer were evaluated by differential scanning calorimeter (DSC) as shown in Table 4.9 and Table 4.10. DSC curves of the copolymer are also shown in Appendix B.

**Table 4.9** Melting temperatures of various zirconia-modified supports in ethylene/1-hexene

Polymer Samples	$T_m(^{\circ}\text{C})$	% crystallinity
SiO <sub>2</sub>	89	9.89
1%Zr-SiO <sub>2</sub>	82	3.33
2%Zr-SiO <sub>2</sub>	83	4.17
5%Zr-SiO <sub>2</sub>	88	7.91

**Table 4.10** Melting temperatures of various zirconia-modified supports in ethylene/1-decene

Polymer Samples	$T_m(^{\circ}\text{C})$	% crystallinity
SiO <sub>2</sub>	92	8.40
1%Zr-SiO <sub>2</sub>	77	0.90
2%Zr-SiO <sub>2</sub>	82	2.49
5%Zr-SiO <sub>2</sub>	84	2.86

Based on the DSC measurement of copolymer as seen in Table 4.9 and 4.10, it revealed that the melting temperatures ( $T_m$ ) of copolymers decreased with using the Zr-modified silica support as mentioned before. Decreased  $T_m$  was less pronounced at high loading of zirconia. One effect of the higher degree of comonomer incorporation is a decrease in crystallinity as also seen in Table 4.9 and 4.10. As a result, polymers with a lower melting point and density, and an increased flexibility and processibility are obtained [70].



#### 4.3.4 The effect of zirconia-modified supports on the incorporation of polymers determined by means of $^{13}\text{C}$ NMR

**Table 4.11** Incorporation of various zirconia-modified supports in ethylene/1-hexene copolymer

Polymer Samples	Comonomer Insertion (%)
$\text{SiO}_2$	10.6
1%Zr- $\text{SiO}_2$	33.1
2%Zr- $\text{SiO}_2$	10.5
5%Zr- $\text{SiO}_2$	9.2

**Table 4.12** Triad distribution of ethylene /1-hexene

Polymer Samples	HHH	EHH	EHE	EEE	HEE	HEH
$\text{SiO}_2$	0.039	0.000	0.067	0.816	0.078	0.000
1%Zr- $\text{SiO}_2$	0.000	0.250	0.081	0.520	0.141	0.008
2%Zr- $\text{SiO}_2$	0.005	0.000	0.100	0.699	0.181	0.015
5%Zr- $\text{SiO}_2$	0.000	0.014	0.078	0.762	0.142	0.004

E refers to ethylene and H refers to corresponding comonomers: 1-hexene

**Table 4.13** Incorporation of various zirconia-modified supports in ethylene/1-decene copolymer

Polymer Samples	Comonomer Insertion (%)
$\text{SiO}_2$	6.1
1%Zr- $\text{SiO}_2$	8.6
2%Zr- $\text{SiO}_2$	7.8
5%Zr- $\text{SiO}_2$	9.2

**Table 4.14** Triad distribution of ethylene /1-decene

<b>Polymer Samples</b>	<b>DDD</b>	<b>EDD</b>	<b>EDE</b>	<b>EEE</b>	<b>DEE</b>	<b>DED</b>
SiO <sub>2</sub>	0.000	0.000	0.061	0.803	0.136	0.000
1%Zr-SiO <sub>2</sub>	0.000	0.000	0.086	0.697	0.211	0.006
2%Zr-SiO <sub>2</sub>	0.000	0.000	0.078	0.678	0.239	0.005
5%Zr-SiO <sub>2</sub>	0.000	0.000	0.092	0.686	0.216	0.006

**E** refers to ethylene and **D** refers to corresponding comonomers: 1-decene

The result suggested that the copolymer had a random distribution of comonomer insertion with very low amount of comonomer triad in the polymer chain. Comonomer incorporation increased with the zirconia modification. Furthermore, zirconia modification also resulted in the changes physical properties of copolymers due to the change of  $Al_{(MAO)}/Zr_{(cat)}$  ratios in the support.