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Role of titania in TiO_2–SiO_2 mixed oxides-supported metallocene catalyst during ethylene/1-octene copolymerization

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The present study showed enhanced activities of ethylene/1-octene copolymerization via TiO_2–SiO_2 mixed oxides-supported MAO with a zirconocene catalyst. It was proposed that titania was decorated on silica surface and acted as a spacer to anchor MAO to the silica support resulting in less steric hindrance and less interaction on the support surface.

KEY WORDS: mixed oxides; silica; supported catalyst; titania; zirconocene catalyst.

1. Introduction

Because of the commercial interest of using metallocene catalysts for olefin polymerization, it has led to an extensive effort for utilizing metallocene catalysts more efficiently. It is known that the copolymerization of ethylene with higher 1-olefins is a commercial importance for productions of elastomer and linear low-density polyethylene (LLDPE). Metallocene catalysts with MAO have been studied for such a copolymerization. In fact, zirconocene catalysts along with MAO have been reported for a potential use to polymerize ethylene with 1-olefins [1–2].

However, it was found that homogeneous metallocene catalytic system has two major disadvantages; the lack of morphology control of polymers produced and reactor fouling. Therefore, binding these metallocene catalysts onto inorganic supports can provide a promising way to overcome these drawbacks. It has been reported that many inorganic supports such as SiO_2, Al_2O_3, and $MgCl_2$ have been extensively studied [3–13]. It has been mentioned that silica is perhaps the most widely used support for metallocene catalysts so far. Unfortunately, due to the support effect, it is found that the catalytic activity of catalysts in heterogeneous system is usually lower than the homogeneous one. Therefore, a modification of the support properties is required in order to maintain high activity as in the homogeneous system or even closer. TiO_2–SiO_2 mixed oxide has been considered to be very attractive as catalysts and supports, which have brought much attention in recent years. It was reported that TiO_2–SiO_2mixed materials have been used as catalysts and supports for various reactions [14]. This TiO_2–SiO_2 mixed oxide would lead to robust catalytic supports of metallocene catalysts for olefin polymerization.

In this present study, the ethylene/1-octene copolymerization using TiO_2–SiO_2 mixed oxides supported-MAO with a zirconocene catalyst was investigated for the first time. The ratios of TiO_2/SiO_2 used were varied. The mixed oxide supports and catalyst precursors were prepared, characterized and tested for ethylene/1-octene copolymerization. The role of TiO_2 in the mixed oxide supports was also further discussed.

2. Experimental

All chemicals [TiO_2 (anatase, Ishihara), SiO_2 (Cariact P-10), toluene, rac-ethylenebis (indenyl) zirconium dichloride [$Et(Ind)_2ZrCl_2$], methylaluminoxane (MAO), trimethylaluminum (TMA) and 1-octene] were manipulated under an inert atmosphere using a vacuum glove box and/or Schelenk techniques.

2.1. Materials

2.1.1. Preparation of TiO_2–SiO_2 mixed oxides support

TiO_2–SiO_2 mixed oxide supports [surface areas of $SiO_2 = 300\ m^2\ g^{-1}$ and TiO_2 (anatase form) = $70\ m^2\ g^{-1}$] for MAO were prepared according to the method described by Conway *et al.* [15]. The TiO_2:SiO_2 ratios were varied from 0:1, 2:8, 4:6, 6:4, 8:2, and 1:0. The supports were heated under vacuum at 400 °C for 6 h.

2.2. Preparation of TiO_2–SiO_2 mixed oxides-supported MAO

One gram of the TiO_2–SiO_2 mixed oxide support obtained from 2.1.1 was reacted with the desired amount of MAO at room temperature and stirred for

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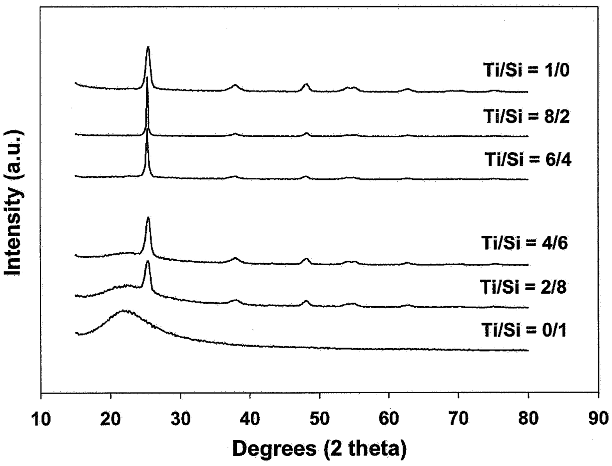


Figure 1. XRD patterns of various TiO_2–SiO_2 mixed oxide supports before MAO impregnation.

30 min. The solvent was then removed from the mixture. About 20 mL of toluene was added into the obtained precipitate, stirred the mixture for 5 min, and then removed the solvent. This procedure was done for 5 times to ensure the removal of impurities. Then, the solid part was dried under vacuum at room temperature to obtain white powder of TiO_2–SiO_2 mixed oxides-supported MAO.

2.3. 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, 0.1 g of the supported MAO ($[Al]_{MAO}/[Zr]$ = 1135) and 0.018 mol 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) and TMA ($[Al]_{TMA}/[Zr]$ = 2500) 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 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 mol ~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

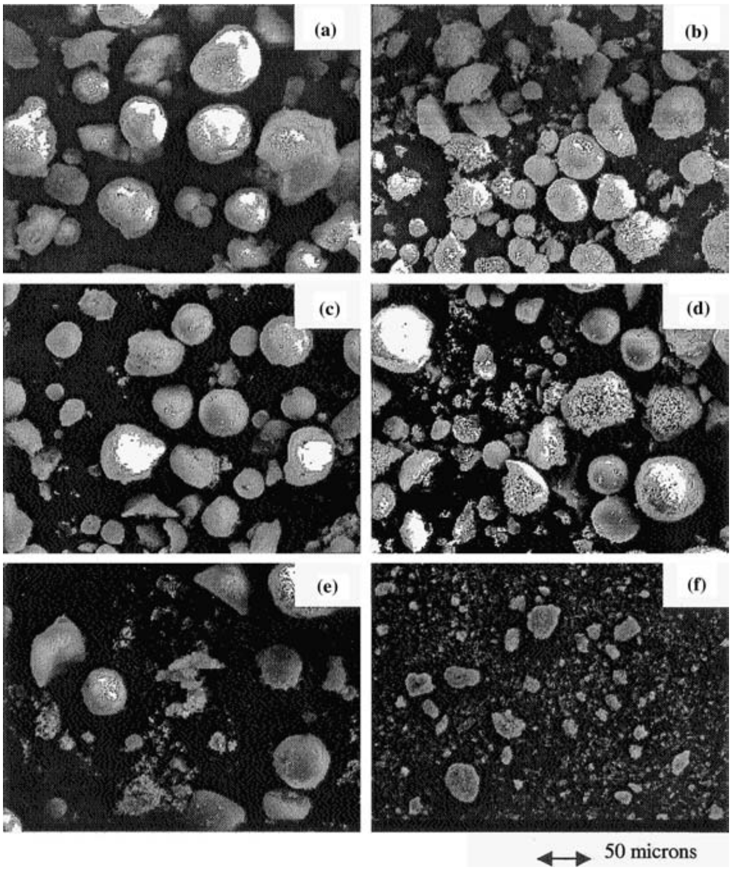


Figure 2. SEM micrographs of various TiO_2–SiO_2 mixed oxide supports before MAO impregnation; (a) Ti/Si = 0/1, (b) Ti/Si = 2/8, (c) Ti/Si = 4/6, (d) Ti/Si = 6/4, (e) Ti/Si = 8/2, (f) Ti/Si = 1/0.

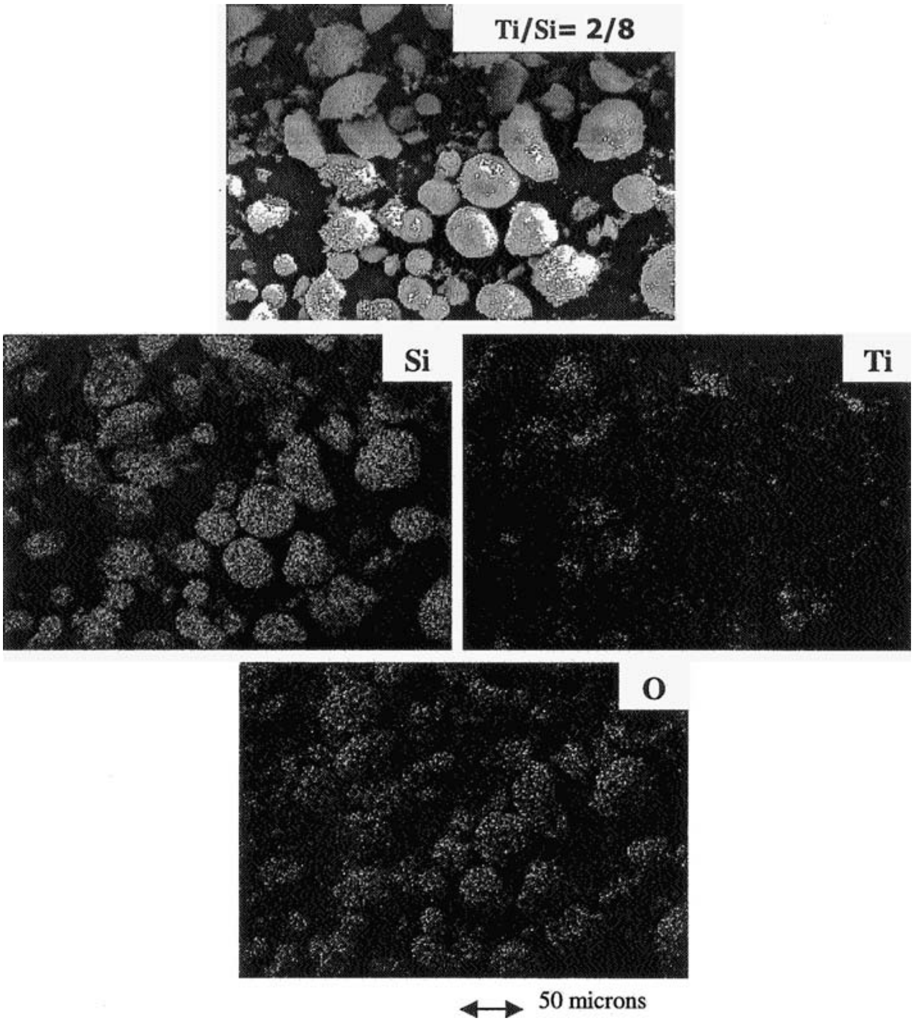


Figure 3. EDX mapping of a typical TiO_2–SiO_2 mixed oxide supports before MAO impregnation.

(0.018 mol) was totally consumed. To start reaction, 0.018 mol of ethylene was fed into the reactor containing the comonomer and catalyst mixtures. 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.

2.4. Characterization

2.4.1. 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 $CuK_\alpha(\lambda = 1.54439$ Å). The spectra were scanned at a rate of 2.4° min^{-1} 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

Table 1
Catalytic activities during ethylene/1-octene copolymerization via TiO_2–SiO_2 mixed oxides supported-MAO with zirconocene catalyst

TiO_2–SiO_2 Weight ratios	wt% of TiO_2 in mixed support	Polymer yield (g)	Polymerization time (s)	Catalytic activity[a] ($\times 10^{-4}$ kg polymer mol^{-1} Zr. h)
Homogeneous	0	1.13	87	3.1
0/100	0	1.19	152	1.9
20/80	20	1.14	116	2.4
40/60	40	1.19	132	2.2
60/40	60	1.18	149	1.9
80/20	80	1.17	157	1.8
100/0	100	1.13	161	1.7

[a] Activities were measured at polymerization temperature of 70 °C, [ethylene] = 0.018 mol, [1-octene] = 0.018 mol, $[Al]_{MAO}/[Zr]$ 1135, $[Al]_{TMA}/[Zr] = 2500$, in toluene with total volume = 30 mL, and $[Zr] = 5 \times 10^{-5}$ M.

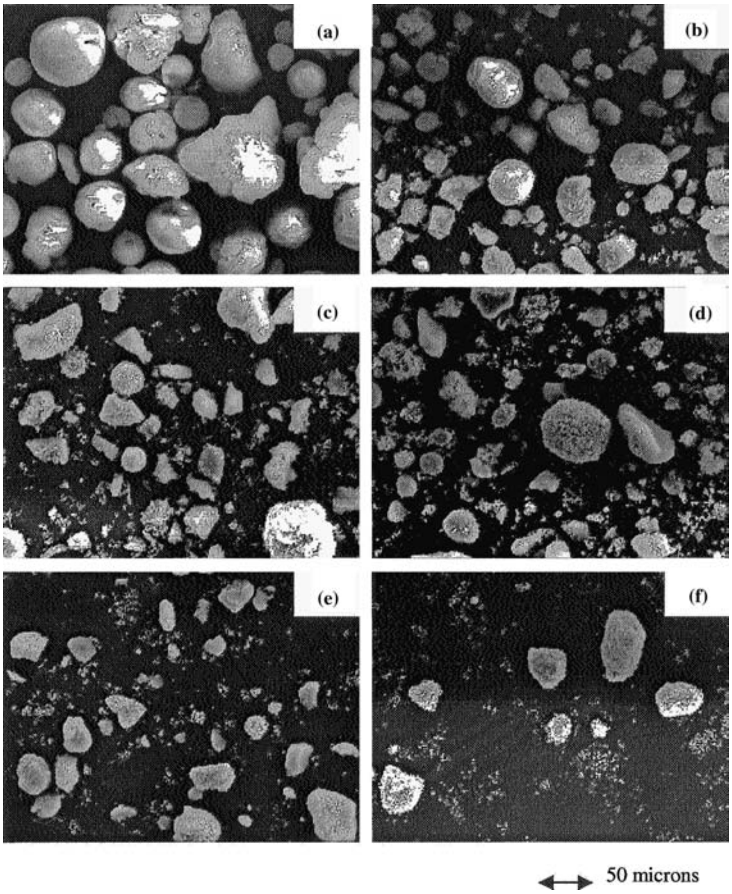


Figure 4. SEM micrographs of various TiO_2–SiO_2 mixed oxide supports after MAO impregnation; (a) Ti/Si = 0/1, (b) Ti/Si = 2/8, (c) Ti/Si = 4/6, (d) Ti/Si = 6/4, (e) Ti/Si = 8/2, (f) Ti/Si = 1/0.

applied. EDX was performed using Link Isis series 300 program.

FTIR spectroscopy: FTIR was conducted on a Perkin-Eelmer series 2000 instruments. The supports (1 mg) were mixed with 100 mg dried KBr. The sample cell was purged with oxygen. About 400 scans were accumulated for each spectrum in transmission with a resolution of 4 cm^{-1}. The spectrum of dried KBr was used as a background subtraction.

2.4.2. Characterization of polymer

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

Gel permeation chromatography (GPC): 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 and molecular weight distributions 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 molecular weight distribution polystyrene and LLDPE.

3. Results and discussion

The present study showed influences of TiO_2–SiO_2 mixed oxide supports on catalytic activities in heterogeneous metallocene catalytic system. The mixed oxide supports containing various amounts of titania and silica were characterized before and after impregnation with MAO. XRD patterns of the supports before impregnation with MAO are shown in figure 1. It was observed that the pure silica exhibited a broad XRD peak assigning to the conventional amorphous silica. Similar to the pure silica, the XRD patterns of the pure titania indicated only the characteristic peaks of anatase titania at 25° (major), 37°, 48°, 55°, 56°, 62°, 71°, and 75°. XRD patterns of the mixed oxide supports containing various amounts of titania and silica revealed the combination of titania and silica supports based on their content. It can be seen that the intensity of XRD characteristic peaks for both supports was changed based on the ratios of TiO_2/SiO_2. After impregnation with MAO, the mixed oxide supports were again identified using

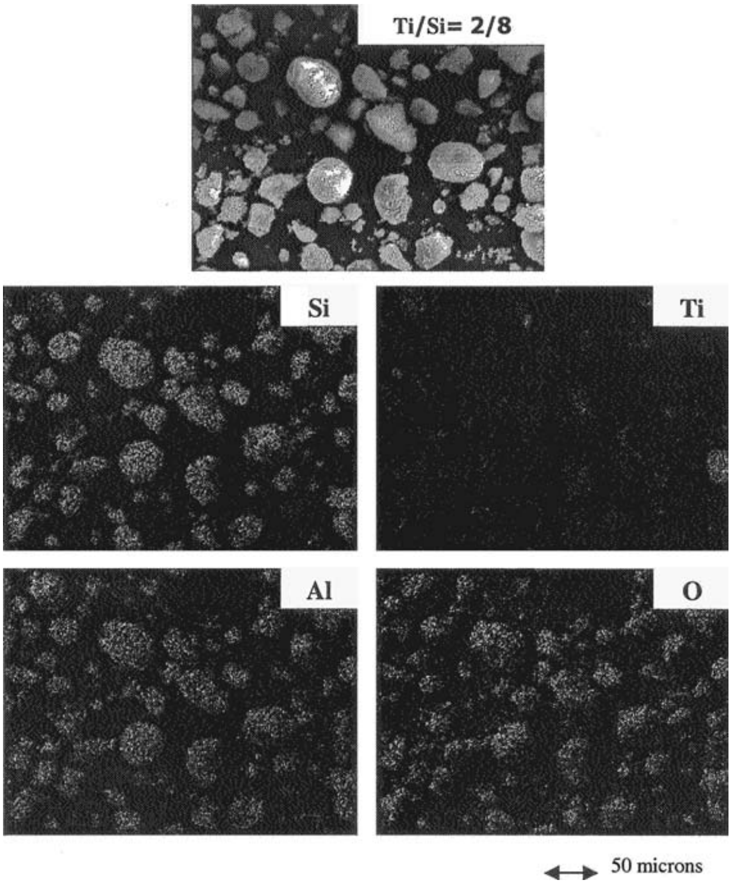


Figure 5. EDX mapping of a typical TiO_2–SiO_2 mixed oxide supports after MAO impregnation.

XRD. It was found that XRD patterns for the supports after impregnation with MAO were identical with those before impregnation with MAO indicating highly dispersed MAO species. In order to determine the morphologies and elemental distributions of the supports before and after impregnation, SEM and EDX were performed, respectively. The SEM micrographs of the supports before impregnation with MAO were shown in figure 2. It showed that silica was appeared in larger particles than titania. It also indicated that at the low content of titania ranged between 20 and 60%, titania was found to decorate on the silica surface as seen in the SEM micrographs. However, at high content of titania, it revealed that titania, essentially isolated from the silica surface. This was probably because the adsorption ability of silica surface with titania was limited by the titania contents in the mixed oxide supports. The distribution of all elements (Si, Ti, and O) obtained from EDX was similar in all samples. The typical EDX mapping images for the mixed oxide support are shown in figure 3 indicating titania located on the silica outer surface. After impregnation with MAO, SEM and EDX of the supports were also conducted. The SEM micrographs of the supports after impregnation with MAO are shown in figure 4 indicating similar results as seen in figure 2. 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 MAO was well distributed all over the support granules. The typical EDX mapping images for the mixed oxide supports after impregnation with MAO are shown in figure 5. Figure 6 apparently shows SEM and EDX mapping of titania located on the outer surface of silica support. IR spectroscopy was also performed in order to identify chemical species and bonding of the mixed oxide supports. The IR spectra of samples are shown in figure 7. It revealed that at low concentrations of titania, the IR band at ca. 980 cm^{-1} assigning to Si–O–Ti connectivity was observed as also reported by Dutoit *et al.* [16]. The strong IR bands were also seen at ca. 1100 cm^{-1} assigning to asymetric Si–O–Si stretching vibration. Then, the various TiO_2–SiO_2 mixed oxide supports after impregnation with MAO were used and investigated for catalytic activities. Copolymerization of ethylene/1-octene via various TiO_2–SiO_2 mixed oxides-supported MAO with zirconocene catalyst was performed in order to determine the catalytic activities influenced by the various supports. The resulted reaction study is shown in table 1 and figure 8. The activities of the supported system were much

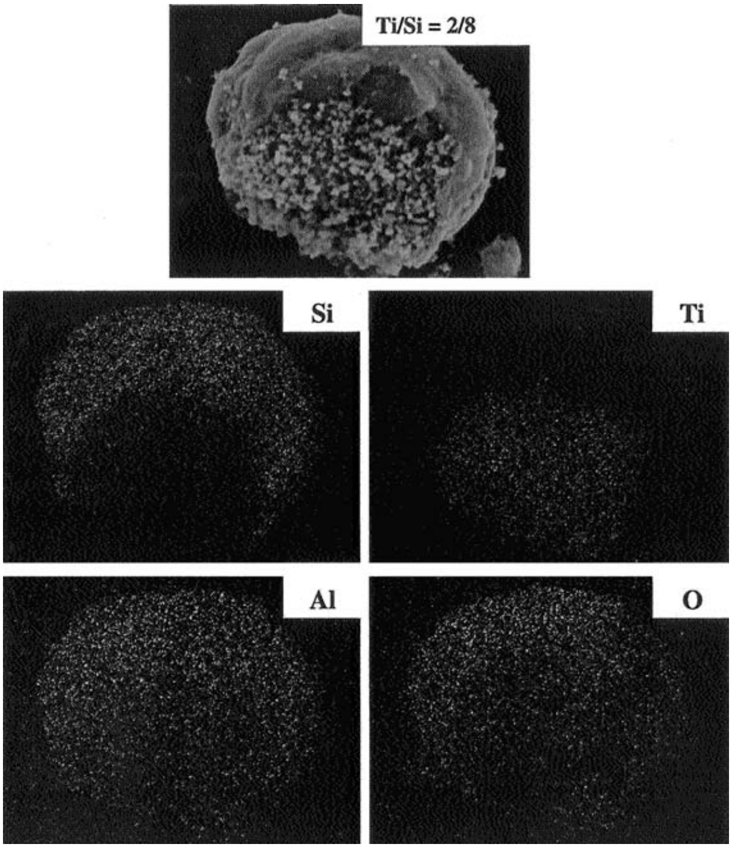


Figure 6. SEM and EDX mapping of titania located on the mixed support granule.

lower than the homogeneous one as expected. However, considering only the supported system, it was found that activities dramatically increased with increasing the amounts of titania up to 60% in the supports compared with those for the pure silica support. The maximum activity can be obtained with the presence of 20% titania in the mixed support. However, with increasing the amounts of titania more than 60% resulted in lower activities compared to the pure silica. It was also found that the activity for the pure titania is the lowest because the strong support interaction [17] between MAO and titania was more pronounced. Based on the resulted activities, the role of titania in TiO_2–SiO_2 mixed oxide supports can be proposed. In order to give a better understanding for the role of titania, a conceptual model for titania effect is illustrated in Scheme 1. As known,

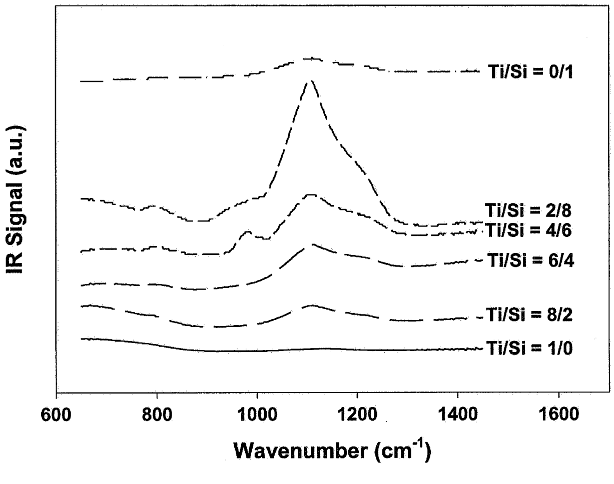


Figure 7. IR spectra of various mixed oxide supports.

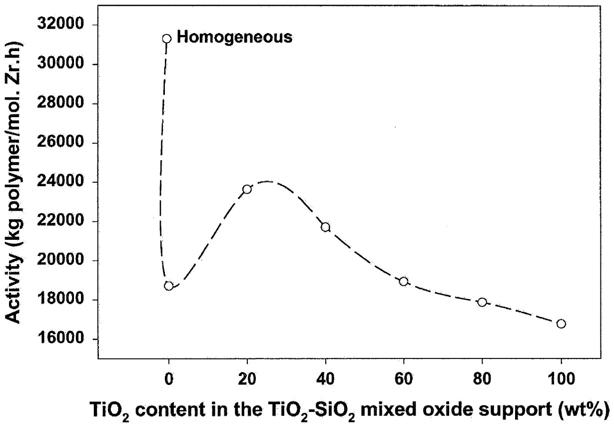
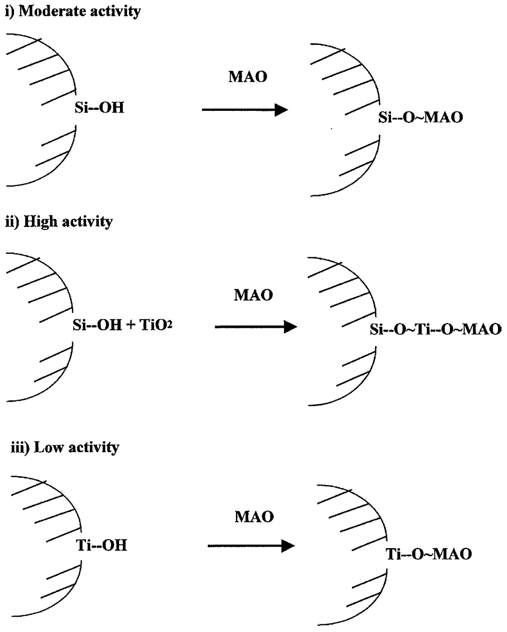


Figure 8. Activities of ethylene/1-octene copolymerization via various TiO_2–SiO_2 mixed oxides-supported MAO with a zirconocene catalyst.



Scheme 1. A conceptual model for evaluation of activities via various TiO_2–SiO_2 mixed oxide supports.

when the heterogeneous system was conducted, activities decreased significantly compared to the homogeneous one as also seen in figure 8. This should be due to a loss of active species by support interaction and/or the steric hindrance arising from the support. Considering Scheme 1, activities on the heterogeneous system can be divided into three levels; (i) moderate activity with the conventional pure silica support, (ii) high activity with the certain amounts of titania present in the mixed oxide support, (iii) low activity with the pure titania support (due to strong support interaction [17]). In Scheme 1 (ii), it showed that the presence of certain amounts (20–60 wt%) of titania dramatically enhanced activities. The contribution of titania can be drawn as MAO anchored on silica with titania as a spacer group. It can be also seen from SEM and EDX that at low content of titania, it was apparently decorated on silica surface and acted as a spacer to anchor MAO to the silica support. Thus, activities increased about 15–25% with the presence of titania between 20 and 40% in the mixed oxide supports. It should be mentioned that increased activities with the presence of titania as a spacer were observed because of less steric hindrance and less interaction on the support surface when a spacer was introduced. Thus, this was suggested to be more homogeneous-like system. Investigation of a spacer such as silane in copolymerization of ethylene/1-olefins was also reported [18,19]. However, when high amounts of titania were added, activities decreased because the strong support interaction as seen in Scheme 1 (iii) can occurred resulting in a combination

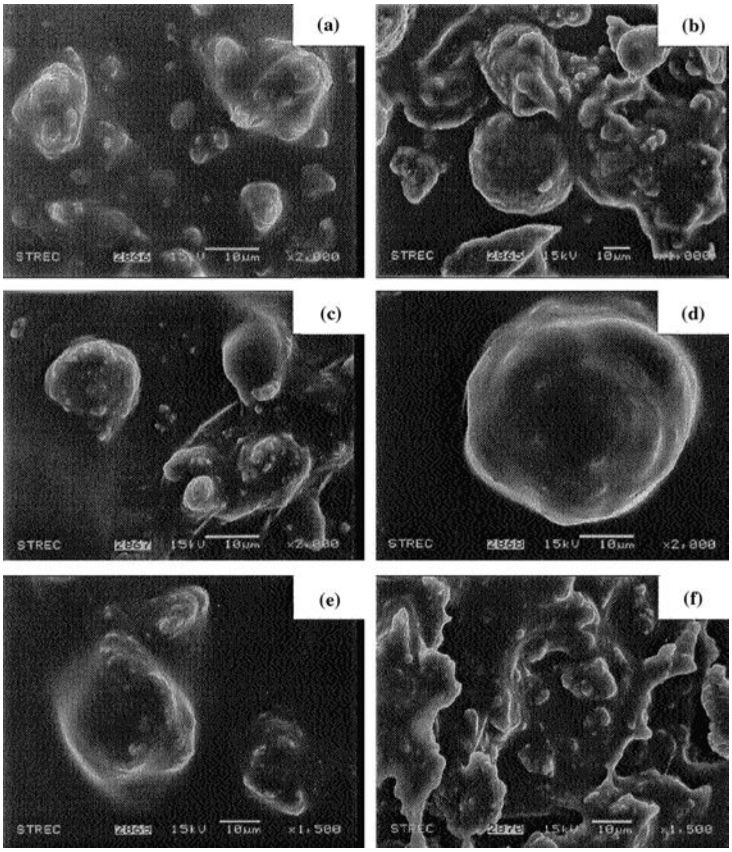


Figure 9. SEM micrographs of polymers obtained with various TiO_2–SiO_2 mixed oxide supports; (a) Ti/Si = 0/1, (b) Ti/Si = 2/8, (c) Ti/Si = 4/6, (d) Ti/Si = 6/4, (e) Ti/Si = 8/2, (f) Ti/Si = 1/0.

Table 2
Molar weight and molecular weight distribution of polymers obtained via TiO_2–SiO_2 mixed oxides supported-MAO with zirconocene catalyst

TiO_2–SiO_2 weight ratios	wt% of TiO_2 in mixed support	M_w^a ($\times 10^{-4}$ g mol^{-1})	M_n^a ($\times 10^{-4}$ g mol^{-1})	MWD[a]
0/100	0	3.61	1.06	3.4
20/80	20	3.42	1.08	3.2
40/60	40	2.91	1.13	2.6
60/40	60	2.60	0.96	2.7
80/20	80	2.65	0.93	2.8
100/0	100	2.41	0.59	4.1

[a] Obtained from GPC and MWD was calculated from M_w/M_n.

between Scheme 1 (i) and (iii) where titania started to isolate from silica as segregated titania. Morphologies of polymers produced via various supports were also investigated. The SEM micrographs of polymers are shown in figure 9. It indicated that there was no significant change in polymer morphologies upon various mixed oxide supports used. The molecular weight based on weight average (M_w) and based on number average (M_n), and molecular weight distribution (MWD) of polymers obtained are shown in table 2. It indicated that the addition of TiO_2 resulted in decreased molecular weights of polymers compared to those of pure SiO_2. However, the narrower molecular weight distribution was observed with the addition of TiO_2 except for the one with pure TiO_2.

4. Conclusions

The present study revealed influence of various TiO_2–SiO_2 mixed oxides supported-MAO on the catalytic activities during copolymerization of ethylene/1-octene. It was found that at certain contents of titania ranged between 20 and 60 wt% in the mixed oxide support, activities dramatically increased by 15–25% compared to those with the conventional pure silica support. It was proposed that titania added acted as a spacer to anchor MAO to the silica support resulting in less steric hindrance and less interaction on the support surface. However, larger amounts of titania resulted in lower activities because the strong support interaction between titania and MAO was more pronounced. The molecular weights of polymers were found to decrease with the addition of TiO_2 whereas narrower molecular weight distribution can be observed in the mixed TiO_2–SiO_2 supports.

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References

[1] C.L.P Shan, J.B.P Soares and A Penlidis, Polym. Chem. 40 (2002) 4426.

[2] K.J Chu, C.L.P Shan, A Soares and J.B.P Penlidis, Macromol. Chem. Phys. 200 (1999) 2372.

[3] A.M Uusitalo, T.T Pakkanen and E.I Iskola, J. Mol. Catal. A: Chem. 177 (2002) 179.

[4] K Soga and M Kaminaka, Makromol. Chem. 194 (1993) 1745.

[5] Y.S Ko, T.K Han, J.W Park and S.I Woo, Macromol. Rapid Commun. 17 (1996) 749.

[6] T. Sugano and K. Yamamoto *Eur. Pat. Appl.* 728773 (1996).

[7] M Margue and A Conte, J. Appl. Polm. Sci. 86 (2002) 2054.

[8] S Sensarma and S Sivaram, Polym. Inter. 51 (2002) 417.

[9] P.G Belelli, M.L Ferreira and D.E Damiani, Appl.Catal. A: Gen. 228 (2002) 189.

[10] J.T Xu, Y.B Zhu, Z.Q Fan and L.X Feng, J. Polym. Sci. Part A: Polym. Chem. 39 (2001) 3294.

[11] L Korach and K Czaja, Polym. Bull. 46 (2001) 67.

[12] A Koppl and H.G Alt, J. Mol. Catal. A: Chem. 165 (2001) 23.

[13] B Jongsomjit, P Praserthdam and P Kaewkrajang, Mater. Chem. Phys. 86 (2004) 243.

[14] X Gao and I.E Wachs, Catal. Today 51 (1999) 233.

[15] S.J Conway, J.W Falconer and C.H Rochester, J. Chem. Soc. Faraday Trans. 185 (1989) 71.

[16] D.C.M Dutoit, M Schneider and J Baiker A., J. Catal. 153 (1995) 165.

[17] R Riva, H Miessuer, R Vitali and G Del Piero, Appl. Catal. A 196 (2000) 111.

[18] C Chao, W Pratchayawutthirat, P Praserthdam Shiono and T Rempel, Macromol. Rapid Commun. 23 (2002) 672.

[19] B Jongsomjit, P Kaewkrajang, S.E Wanke and P Praserthdam, Catal. Lett. 94 (2004) 205.