Catalysis Letters, Vol. 117, Nos. 3–4, September 2007 (© 2007)
DOI: 10.1007/s10562-007-9132-7

Observation of bimodal polyethylene derived from TiO_2-supported zirconocene/MAO catalyst during polymerization of ethylene and ethylene/1-hexene

Bunjerd Jongsomjit,* Sutti Ngamposri, and Piyasan Praserthdam

Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

Received 20 April 2007; accepted 23 May 2007

The bimodal polyethylene obtained from TiO_2-supported zirconocene/MAO catalyst was observed during polymerization of ethylene and ethylene/1-hexene. By means of XPS, it revealed that TiO_2 consisted of Ti^{3+} (BE = 462.6 eV) and Ti^{4+} (BE = 464.9 eV). The dual catalytic sites were attributed to the presence of Ti^{3+} and Ti^{4+} in TiO_2.

KEY WORDS: metallocene catalyst; ethylene polymerization; MAO; LLDPE; XPS.

1. Introduction

For years, metallocene catalysts have brought much attention to research in olefin polymerization. As a matter of fact, 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 methylaluminoxane (MAO) have been studied for such a copolymerization. In particular, zirconocene catalysts along with MAO have been reported for a potential use to polymerize ethylene with 1-olefins [1, 2]. Due to lack of morphology control of polymer with homogeneous system, the supported catalytic system has been developed. It has been reported that many inorganic supports such as SiO_2, Al_2O_3 and $MgCl_2$ have been extensively studied. It was found that different supports could alter the catalytic behaviors during reaction as well [3–7].

Basically, for polymer the molecular weight (MW) and molecular weight distribution (MWD) are considered important factors used to determine the mechanical and rheological properties [8]. It is believed that low MW would result in the good flow property whereas the enhancement of melt strength and good mechanical properties can be achieved with the high MW. Hence, the bimodal MW can provide both enhanced rheological and mechanical properties. In general, there are some techniques used to produce the bimodal MW polymer such as; (i) stepwise polymerization [9], (ii) polymerization using a mixture of two catalysts [10–12] for generating the dual sites, and (iii) a sudden variation of reaction conditions [13] for controlling the chain transfer reaction. In this present study, we revealed an alternative way to produce the bimodal PE with TiO_2-supported zirconocene/MAO catalytic system. Here, the LLDPE was synthesized via ethylene/1-hexene copolymerization using SiO_2–, mixed TiO_2–SiO_2–, and TiO_2-supported zirconocene/MAO catalyst. For a comparative study, ethylene polymerization was also conducted based on the similar procedure.

2. Experimental

All chemicals [TiO_2 (pure anatase, JRC-TIO-1, Ishihara), SiO_2 (Cariact P-10, Fuji Silysia), toluene (from Exxon), *rac*-ethylenebis (indenyl) zirconium dichloride [*rac*-Et(Ind)$_2$ZrCl$_2$, Aldrich], methylaluminoxane (MAO, Tosoh Akso), trimethylaluminum (TMA, Nippon Aluminum Alkyl) and 1-hexene (99 + %, Aldrich)] were manipulated under an argon atmosphere using a vacuum glove box and/or Schlenk techniques. The mixed TiO_2–SiO_2 supports [surface areas of SiO_2 = 300 m^2/g and TiO_2 (anatase form) = 70 m^2/g] (TiO_2:SiO_2 = 1:1 by mole) for MAO were prepared by the physical mixing of 1 g of a designed weight ratio of TiO_2–SiO_2 in toluene 20 ml. The mixture was stirred for 30 min, filtered, and then dried under vacuum. The support was heated under vacuum at 673 K for 6 h. In order to prepare the SiO_2–, TiO_2– or mixed TiO_2–SiO_2-supported MAO, 1 g of the support was reacted with the desired amount of MAO in

---

*To whom correspondence should be addressed.
E-mail: bunjerd.j@chula.ac.th

toluene at room temperature and stirred for 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 the supported MAO.

To study the polymerization reaction, the ethylene/1-hexene (EH) 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 ($[Al]_{MAO}/[Zr]_{cat} = 1135$) and 0.018 mole of 1-hexene along with toluene (to make the total volume of 30 ml) were put into the reactor. The desired amount of *rac*-$Et(Ind)_2ZrCl_2$ (5×10^{-5} M) and TMA ($[Al]_{TMA}/[Zr]_{cat} = 2500$) 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 (343 K). Feeding ethylene started the reaction. The pressure in the reactor was kept at 50 psi by a continuous ethylene feed. Ethylene consumption at about 0.018 mole was fixed. The polymerization reaction was stopped and the reaction time used was recorded when 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. For a comparative study, the ethylene polymerization (E) was also conducted with the similar procedure as mentioned before.

The molecular weight of polymer was determined using gel permeation chromatography (GPC, PL-GPC-220). Samples were prepared having approximately concentration of 1–2 mg/ml in trichlorobenzene (mobile phase) by using the sample preparation unit (PL-SP 260) with filtration system at a temperature of 423 K. The dissolved and filtered samples were transferred into the GPC instrument at 423 K. The calibration was conducted using the universal calibration curve based on narrow polystyrene standards.

The binding energy (BE) of TiO_2 support was measured by means of X-ray photoelectron spectroscopy (XPS). It was performed using the Shimazu AMICUS with VISION 2-control software. To overcome the charging problem, the sample was coated with a very thin layer of gold sputtering. The energy reference for Ag metal (368.0 eV for $3d_{5/2}$) was used for this study.

3. Results and discussion

In this study, the SiO_2–, mixed TiO_2–SiO_2–, and TiO_2-supported zirconocene/MAO catalysts were employed for ethylene/1-hexene (EH) copolymerization in order to produce the LLDPE. For a comparative study, ethylene (E) polymerization was also conducted using the similar procedure. The catalytic activities of various supports for EH and E polymerization are shown in table 1. For the EH copolymerization, the activity of the homogeneous catalytic system (without the support) was the highest among that obtained from the other supported catalytic systems. This is due to the supporting effect as mentioned by many authors [5, 6]. Considering the various supports, the activities were in the order of TiO_2–SiO_2 > SiO_2 > TiO_2. It was reported that with the presence of TiO_2 on SiO_2, TiO_2 can act as a spacer to anchor MAO to SiO_2 resulting in less steric hindrance and less interaction on the support surface [14]. Thus, the mixed TiO_2–SiO_2 exhibited the highest activity among other supports. It was found that the activity of the catalyst on TiO_2 support was the lowest due to the strong support interaction [15, 16] between MAO and TiO_2. The catalytic activities for E polymerization are also shown in table 1. The similar trend as seen for the EH copolymerization was also evident. However, the activities of the E polymerization were much lower (about 10 times) than those of the EH copolymerization. The comonomer effect on solubility of the catalyst was also the case [2].

The molecular weight (MW) and molecular weight distribution (MWD) obtained from GPC analysis of the various supports are shown in table 2. It can be observed that the homogeneous catalytic system exhibited the slightly higher MW than that of the supported system for both EH and E polymerization. This is because the supported system promotes the chain transfer reaction resulting in lower MW polymer obtained. However, the MW for the various supports was in the same range in regardless of EH and E polymerization. As seen, the effect on chain transfer reaction was more pronounced with the presence of TiO_2. Thus, the low molecular weight based on the number average (M_n) of polymer obtained from the TiO_2, and mixed TiO_2–SiO_2 was observed. Considering the MWD, the homogeneous system, SiO_2– and mixed TiO_2–SiO_2-supported systems apparently exhibited the narrow MWD indicating the single site nature of the catalyst. However, the broad MWD was observed for the TiO_2-supported system suggesting the deviation from the single site nature. This was obvious when compared with what we had seen from the results of SiO_2– and mixed TiO_2–SiO_2-supported systems. In order to clarify this point, the GPC curves of molecular weight distribution are present in figure 1. The typical molecular weight distribution curve obtained from GPC of the homogeneous system, SiO_2 and mixed TiO_2–SiO_2-supported systems for both EH and E polymerization is shown in figure 1 (a) indicating only the unimodal MW PE. This is consistent with the narrow MWD observed. However, the interesting result was found with using the

Table 1
Catalytic activity of ethylene/1-hexene (EH) and ethylene (E) polymerization

Support	Polymerization	Yield (g)	Polymerization time (s)	Catalytic activity[a] (kg of Polym./mol. Zr.h)
No support	EH	1.1325	81	33,555
SiO_2	EH	1.1931	148	19,347
TiO_2–SiO_2	EH	1.1638	109	25,624
TiO_2	EH	1.1578	165	16,840
No support	E	0.4895	436	2,694
SiO_2	E	0.4882	694	1,688
TiO_2–SiO_2	E	0.4960	621	1,917
TiO_2	E	0.4884	902	1,299

[a] Activity were measured at polymerization temperature of 343 K, [ethylene] = 0.018 mole, [1-hexene] = 0.018 mole, $[Al]_{MAO}/[Zr]_{cat}$ = 1135, and $[Al]_{TMA}/[Zr]$ = 2500, in toluene with total volume of 30 mL and $[Zr]_{cat} = 5 \times 10^{-5}$ M.

Table 2
Molecular weight and molecular weight distribution

Support	Polymerization	GPC Analysis[a] (g/mol)		
		M_w	M_n	MWD
No support	EH	28,500	13,900	2.1
SiO_2	EH	24,900	19,400	1.4
TiO_2-SiO_2	EH	19,100	9,220	2.2
TiO_2	EH	26,700	5,400	5.0
No support	E	38,000	10,300	3.7
SiO_2	E	32,000	12,300	2.6
TiO_2-SiO_2	E	25,200	10,200	2.5
TiO_2	E	26,200	4,700	5.5

[a] MWD was calculated from M_w/M_n

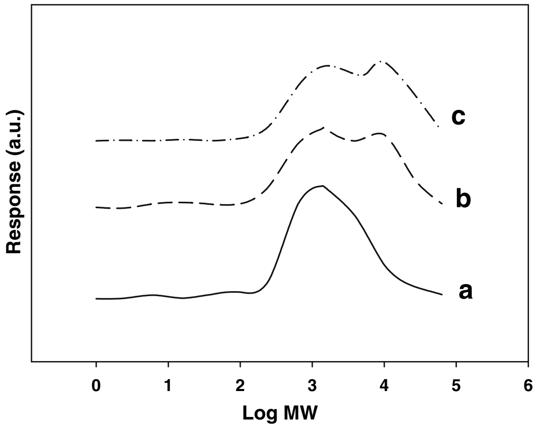

Figure 1. Typical molecular weight distribution of polymer; (**a**) unimodal for PE and LLDPE derived from homogeneous, SiO_2– and TiO_2–SiO_2-supported system, (**b**) bimodal for LLDPE (EH copolymerization) derived from TiO_2-supported system, and (**c**) bimodal for PE (ethylene polymerization) derived from TiO_2-supported system.

TiO_2-supported system revealing the bimodal MW PE as shown in figure 1 (b) for EH copolymerization. In order to confirm this dramatic result, the molecular weight distribution of the E polymerization was also determined and the GPC curve is shown in figure 1 (c) indicating the similar bimodal PE. It should be mentioned that the bimodal PE can be obtained using the TiO_2 support for both EH and E polymerization. As mentioned earlier, some techniques have been used to produce bimodal polymer. They can be categorized upon on the modification of reactors used, adjusting the process conditions, and use of the mixed catalysts. Based on the catalysis point of view, the mixing of two types of catalysts can generate the dual sites for them where one catalytic site responds for the low MW and the another site is for the high MW. Thus, it is the key point to create the dual catalytic sites by any means in order to achieve the bimodal polymer. First, one might think that if a catalyst is located onto two different supports the dual catalytic sites could be generated or not. Here, we showed that the zirconocene/MAO catalyst present on the mixed TiO_2–SiO_2 did not render the dual catalytic sites having only unimodal PE. After mixing, the supports exhibited the uniform structure, then acted as a sole support resulting in a single site catalyst. This was also suggested that all MAO might be adsorbed only on the silica support due to higher surface area. In addition, we also varied the ratios of TiO_2:SiO_2 mixtures (not shown), however, the similar trend was still observed. It indicated that the mixed TiO_2–SiO_2 support exhibited only a single site catalyst (confirmed by narrow MWD) as seen in the sole SiO_2 support.

Surprisingly, only the sole TiO_2 support apparently generated the dual sites in the catalyst (confirmed by broad MWD). Thus, it was interesting to figure out how the TiO_2 support rendered the bimodal PE. In order to give a better understanding, the XPS analysis on the TiO_2 support was performed to determine the binding energy (BE). The XPS profile after deconvolution is shown in figure 2. It indicated that the TiO_2 employed in this work consisted of Ti^{3+} (BE = 462.6 eV for Ti $2p_{3/2}$) and Ti^{4+} (BE = 464.9 eV for Ti $2p_{3/2}$). The presence of lower valences Ti^{3+} along with the Ti^{4+} by the red shift of ~ 2.2 eV (Ti $2p_{3/2}$) was also reported by Wu et al. [17]. This is consistent with the electron spin resonance (ESR) analysis by Serwicka [18], who detected the presence of Ti^{3+} on vacuum-reduced TiO_2 at 400–773 K. The details of XPS results of the TiO_2– and

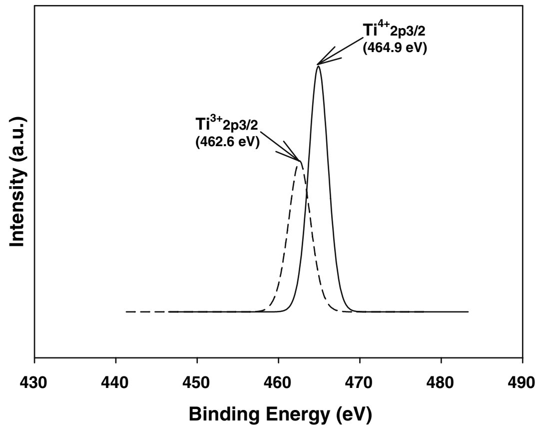

Figure 2. XPS profile indicating the binding energy (BE) of Ti^{3+} and Ti^{4+} species.

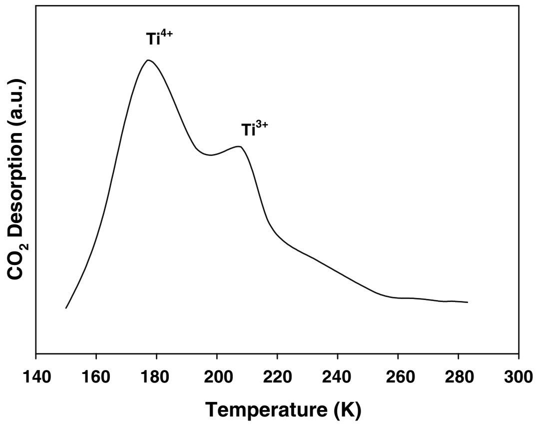

Figure 3. CO_2 TPD profile of TiO_2 indicating the presence of Ti^{3+} and Ti^{4+} species.

TiO_2–SiO_2-supported MAO are also shown in table 3. The presence of only small amount of the Ti^{3+} and Ti^{4+} in the mixed TiO_2–SiO_2 support was detected as shown in table 3. However, it did not exhibit the catalytic dual sites because the effect of SiO_2 was more pronounced resulting in the unimodal PE obtained as mentioned above. The temperature programmed desorption (TPD) using CO_2 as a probe molecule was also performed to determine the Ti^{3+} and Ti^{4+} on TiO_2. It was carried out using 1 g of sample. The sample was dosed by 1% CO_2 in He for 1 h in liquid nitrogen and then desorbed in a range of temperature from 123 to 253 K. A Gow-Mac (series 150) gas chromatography equipped with a thermal conductivity detector was used to analyze CO_2. The CO_2-TPD profile is shown in figure 3. It revealed two desorption peaks at temperature ca. 175 and 200 K. Thomson et al. [19] reported that surface of TiO_2 incorporates fivefold-coordinated Ti^{4+} sites and fourfold-coordinated Ti^{3+} sites. Based on their study, it was confirmed that the peak at ca. 170 K was attributed to CO_2 bound to the Ti^{4+} site. The second peak at ca. 200 K was considered as the CO_2 molecules bound to the Ti^{3+} site.

In order to determine the nature of cocatalyst on various supports, XPS measurement was performed as shown in table 3. The samples were mounted on an adhesive carbon tape as pellets. They were prepared in a glove box and transferred under inert atmosphere. It was found that the binding energy for Al 2p core-level of the cocatalyst was about 74.7–74.8 eV for all supports employed. This was suggested that any differences in catalytic sites probably occurred during the activation of catalyst by the cocatalyst or during polymerization. Hence, the dual catalytic sites generated by the TiO_2 support could be due to the presence of Ti^{3+} and Ti^{4+} species. It was proposed that the nature of zirconocene/MAO present on the Ti^{3+} and Ti^{4+} was different, then resulting in the low MW PE on one site and higher MW PE on another site. This was also consistent with the broad MWD (~ 5) as seen for PE obtained from the TiO_2 support. However, for further investigation according to the catalyst design, we will need to determine the functionality for each Ti^{3+} and Ti^{4+} species on the molecular weight of PE obtained. By varying the ratios of Ti^{3+} and Ti^{4+} species, the MWD of polymer can be altered. To create various ratios of Ti^{3+} and

Table 3
XPS results of TiO_2– and TiO_2–SiO_2-supported MAO

Support	Element	BE (eV)	FWHM (eV)	Atomic Conc. (%)	Mass Conc. (%)
TiO_2	O 1s1	532.26	2.96	57.61	44.74
	O 1s2	529.15	1.73	1.44	1.12
	Ti 2p1	464.90	1.73	0.33	0.78
	Ti 2p2	462.62	2.36	0.17	0.39
	Al 2s	119.58	2.46	19.73	25.84
	Al 2p	74.71	1.99	20.72	27.13
TiO_2–SiO_2	O 1s1	532.42	3.06	56.39	43.76
	O 1s2	529.31	2.17	2.23	1.73
	Ti 2p1	464.94	2.01	0.15	0.34
	Ti 2p2	462.65	3.49	0.06	0.14
	Al 2s	119.65	2.68	18.62	24.36
	Al 2p	74.80	2.29	19.53	25.56
	Si 2p	103.08	2.55	3.02	4.11

Ti^{4+}, it can be done with varying the preparation conditions and calcination at different atmospheres [20].

4. Summary

In the present study, we revealed an alternative way to produce a bimodal PE using the TiO_2-supported zirconocene/MAO catalyst. The obtained polymer exhibited the bimodal PE for both ethylene homopolymerization and ethylene/1-hexene copolymerization. It was proposed that the presence of Ti^{3+} and Ti^{4+} in TiO_2 support possibly was the cause of the dual catalytic sites. The observation of broad MWD found in the TiO_2-supported system was also evident.

Acknowledgments

The authors thank the Thailand Research Fund (TRF) for the financial support of this work. We also extend our thankful for P. Supphasrirongjareon for the XPS analysis and the research and development department, Thai Petrochemical Industry Public Company Limited for the GPC analysis.

References

[1] C.L.P. Shan, J.B.P. Soares and A. Penlidis, J. Polym. Sci.,Part A: Polym. Chem. 40 (2002) 4426.
[2] K.L. Chu, C.L.P. Shan, J.B.P. Soares and A. 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] Y.S. Ko, T.K. Han, J.W. Park and S.I. Woo, Macromol. Rapid Commun. 17 (1996) 749.
[5] B. Jongsomjit, S. Ngamposri and P. Praserthdam, Catal. Lett. 100 (2005) 139.
[6] M.D.V. Margues and A. Conte, J. Appl. Polm. Sci. 86 (2002) 2054.
[7] B. Jongsomjit, J. Panpranot and J.G. Goodwin Jr., J. Catal. 204 (2001) 98.
[8] Q. Wang, L. Li and Z. Fan, Euro. Polym. J. 40 (2004) 1881.
[9] F.P. Alt, L.L. Bohm, H.F. Enderle and J. Berhold, J. Macromol. Symp. 163 (2001) 135.
[10] J.B.P. Soares and J.D. Kim, J. Polym. Sci. Polym. Chem. 38 (2000) 1408.
[11] C.L.P. Shan, K.J. Chu, J.B.P. Soares and A. Penlidis, Macromol. Chem. Phys. 201 (2000) 2195.
[12] Y. Kim, Y. Han, M.H. Lee, S.W. Yoon, K.H. Choi and B.G. Song, Macromol. Rapid Commun. 22 (2001) 573.
[13] T.K. Han, H.K. Choi, D.W. Jeung, Y.S. Ko and S.I. Woo, Macromol. Chem. Phys. 196 (1995) 2637.
[14] B. Jongsomjit, S. Ngamposri and P. Praserthdam, Ind. Eng. Chem. Res. 44 (2005) 9059.
[15] R. Riva, H. Miessuer, R. Vitali and G. Del Piego, Appl. Catal. A. 196 (2000) 111.
[16] B. Jongsomjit, C. Sakdamnuson, J.G. Goodwin Jr. and P. Praserthdam, Catal. Lett. 94 (2004) 209.
[17] N.L. Wu, M.S. Lee, Z.J. Pon and J.Z. Hsu, J. Photochem. Photobio. A.: Chem. 163 (2004) 277.
[18] E. Serwicka, Colloids Surf. 13 (1985) 287.
[19] T.L. Thompson, O. Diwald and J.T. Yates Jr., J. Phys. Chem. B. 107 (2003) 11700.
[20] K. Suriye, P. Praserthdam and B. Jongsomjit, Ind. Eng. Chem. Res. 44 (2005) 6599.