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Effects of Ti oxidation state on ethylene, 1-hexene comonomer polymerization by $MgCl_2$-supported Ziegler–Natta catalysts

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Abstract In this study, the influences of the Ti oxidation state on the catalytic properties of $MgCl_2$-supported Ziegler–Natta catalysts in ethylene homo- and co-polymerization with 1-hexene were investigated. Three catalysts having different Ti oxidation states were synthesized by milling $TiCl_4$, $TiCl_3$, or $TiCl_2$ together with $MgCl_2$. With these catalysts having different Ti oxidation states, the polymerization conditions such as the Al concentration, temperature, and 1-hexene concentration were varied to figure out their catalytic abilities in ethylene homo- and co-polymerization. The Ti oxidation state affected the catalyst activity largely, having unique dependences on the polymerization conditions. A higher oxidation state led to a higher activity, slightly larger comonomer incorporation, and lower molecular weight as well as its narrower distribution. However, rough characteristics of copolymers were similar among the different Ti oxidation states.

Keywords Ziegler–Natta catalyst · Titanium oxidation state · Polyethylene · Ethylene/1-hexene copolymerization · Ethylene polymerization

Introduction

Current industrial production of polyethylene and polypropylene still largely depends on $MgCl_2$-supported heterogeneous Ziegler–Natta (ZN) catalysts [1–3]. The mechanical and rheological properties of polyethylene and polypropylene are

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strongly affected by molecular weight (MW) and molecular weight distributions (MWD) [4–6, 8, 9] as well as by chemical composition distribution (CCD) in the case of copolymer. Therefore, it is industrially crucial to control these parameters by catalyst and polymerization technologies.

Homogeneous catalysts represented by metallocene catalysts are generally single-site catalysts so as to give monodisperse MW and chemical composition, and are advantageous in the incorporation of bulky or polar co-monomers. On the other hand, ZN catalysts are multi-sites catalysts and generally lead to broad MWD and CCD, which have been regarded to be advantageous for some polymer properties.

To control the MWD and CCD of polymers with Ziegler–Natta catalysts, the nature of active sites is critically important in a sense that different active sites produce polymers with different MWs and CCs. Several factors are responsible for the nature of active sites such as Ti nucreality [4, 7], dispersion [10], oxidation state [11, 13–19], interaction with $MgCl_2$ support [7, 12], and so on. The oxidation state of Ti species has been regarded as one of the key factors to cause CCD and MWD; Ti species undergo stepwise reduction during polymerization and as a result the Ti oxidation state becomes a mixture of tetravalent (Ti^{4+}), trivalent (Ti^{3+}), and divalent (Ti^{2+}) states [17]. Many researchers have investigated the relationship between Ti oxidation state and polymerization performance. Baulin et al. [13] studied the effects of the Ti oxidation state on the activity of a $TiCl_4$/MgO catalyst by increasing alkylaluminum concentration. A contact of a $TiCl_4$/MgO catalyst with $A1Et_3$ under conditions similar to those of polymerization (A1/Ti of 150-200 for 1 h at 70 °C), more than 90% of Ti^{4+} was reduced (96% to Ti^{3+} and 4% to Ti^{2+}). They were not able to find any quantitative correlation between the degree of Ti reduction and catalytic activity. It was found later that the catalytic activity decreased by precontact between catalyst and alkylaluminum [14, 17]. An even stronger reduction (80% Ti^{2+} and 20% Ti^{3+}) has been reported by Kashiwa et al. [17] for a $TiC1_4$/EB/$MgC1_2$ catalyst after a 2-h reaction with $A1Et_3$ ($A1/Ti = 50$) at 60 °C. They also observed that the catalyst thus obtained was only slightly active for the polymerization of ethylene and completely inactive for propylene polymerization; however, the activity was recovered by re-oxidizing Ti with a chlorinating agent such as *t*-BuCl. It was concluded that a direct relationship exists between the activity and Ti oxidation state. Kissin et al. [20] studied a relationship of the molecular weight and chemical composition with the Ti oxidation state by varying the polymerization time from 5 to 40 min. Based on deconvolution of molecular weight and crystallinity distributions in gel permeation chromatography (GPC) and temperature rising elution fractionation (TREF), they obtained the following conclusions: (i) Ti^{4+} is active for ethylene and propylene homopolymerization and for ethylene/α-olefin copolymerization, and produces polymers with low molecular weights and high comonomer contents (ii) Ti^{3+} is also active for the above mentioned polymerization, producing polymers with moderately high molecular weight (iii) Ti^{2+} is active only for ethylene homopolymerization, giving very high molecular weight polymers. Zakharov et al. [6] have prepared Ti^{2+} (η^6-benzene-$Ti_2Al_2Cl_8$), Ti^{3+} ($TiCl_3 \cdot$*n*-dibutylether), and Ti^{4+} ($TiCl_4$) supported on $MgCl_2$, and investigated behaviors of different Ti oxidation states in ethylene polymerization and ethylene/1-hexene copolymerization. Their results demonstrated that Ti^{2+},

Ti^{3+}, and Ti^{4+} were highly active in both of ethylene polymerization and ethylene/1-hexene copolymerization, on the contrary to the results obtained by Kissin et al. [20]. The advantage of their work for the effects of the Ti oxidation state is to have prepared the catalysts from precursors with the corresponding oxidation states. However, not only the oxidation state but also the presence of the extra ligands such as *n*-dibutylether, and η^6-benzene and Al_2Cl_6 might affect the catalytic behavior and polymer properties. In other words, it is not sure if the nature of η^6-benzene-$Ti_2Al_2Cl_8$ is similar to that of $TiCl_2$ formed by reaction of $TiCl_4$ with alkylaluminum. Another research [21] showed that a higher temperature or a larger alkylaluminum/$TiCl_4$ ratio increases the activity until some optimum value for the average oxidation state is achieved, while the activity starts to drop beyond the optimum value. The optimum average oxidation state was $Ti^{2.2+}$ for ethylene polymerization. A similar relation between the catalytic activity and optimum oxidation state was also found for different types of ZN catalysts such as $TiCl_2$, $SiO_2/MgCl_2/THF/TiCl_4$, and $AlCl_3/TiCl_4$ [22–24]. In finding a relationship of the oxidation state with MW and MWD of polyethylene, Zakharov et al. [5] conducted a comprehensive study with systematically varying the Ti oxidation and dispersion states using the above-mentioned three precursors [5, 6]. They found that isolated Ti^{2+} and Ti^{3+} ions supported on $MgCl_2$ were more active than a supported $TiCl_4$ catalyst, which turned into a mixture of isolated and clustered Ti^{3+} after the interaction with alkylaluminum. Moreover, it was shown that produced polyethylene had similar MW and MWD in spite of the sharp distinctions in the Ti oxidation and dispersion states for their catalysts. Thus, the source of MWD was not straightforwardly understood.

From the previous reports mentioned above, the effects of the Ti oxidation state are still controversy on the catalytic activity, polymer molecular weight, and comonomer response in olefin polymerization using Ziegler–Natta catalysts. The co-presence of different Ti oxidation states during polymerization is still an importance problem. In this study, $TiCl_2$, $TiCl_3$, and $TiCl_4$ were directly supported on $MgCl_2$ to get better understanding on the role of the Ti oxidation state in ethylene homopolymerization and ethylene/1-hexene copolymerization. The activity behavior was found to be sensitive to the oxidation state of the $TiCl_x$ precursors, while polymer structures such as MW and CC were basically insensitive, supporting the previously obtained results [5, 6].

Experimental

Materials

Anhydrous $MgCl_2$ and α-$TiCl_3$ (donated by Toho Titanium Co., Ltd.), $TiCl_4$ (Wako Pure Chemical Industries, Ltd.), anhydrous $TiCl_2$ (Aldrich) and $AlEt_3$ (donated by Tosoh Finechem Co.) were used without further purification. Heptane (Wako Pure Chemical Industries, Ltd.) was used after dehydration by passing through a column with molecular sieve 13X, and 1-hexene (Wako Pure Chemical Industries, Ltd.) was distilled with sodium/benzophenone.

Catalyst preparation

Three kinds of $MgCl_2$-supported catalysts with different Ti oxidation states were prepared as follows [10].

(i) $TiCl_2/MgCl_2$: 36 g of $MgCl_2$ and 2.34 g of $TiCl_2$ were put into a 1 L stainless steel pot containing 55 stainless steel balls (25 mm diameter) and then vibration ball-milled under nitrogen for 30 h at RT.
(ii) $TiCl_3/MgCl_2$: 36 g of $MgCl_2$ and 3.1 g of $TiCl_2$ were similarly milled for 30 h at RT.
(iii) $TiCl_4/MgCl_2$: 108 mL of $TiCl_4$, 108 mL of heptane and 36 g of $MgCl_2$ were similarly milled for 30 h at RT, and then the ground product was treated with $TiCl_4$ (200 mL) at 90 °C for 2 h with stirring under nitrogen, followed by washing with heptane repeatedly.

These catalysts, $TiCl_2/MgCl_2$, $TiCl_3/MgCl_2$, and $TiCl_4/MgCl_2$, are designated as Ti2M, Ti3M, and Ti4M. Their titanium contents were 2.36, 2.31, and 1.38 wt%, respectively.

Polymerization

Slurry polymerization in *n*-heptane was performed under constant ethylene pressure of 0.5 MPa at the polymerization temperature from 50 to 70 °C for 1 h. Triethylaluminum (TEA) was used as cocatalyst, whose concentration was 2.0–30.0 mmol/L. The polymerization was initiated by the injection of the catalyst slurry. The catalyst concentration in the polymerization slurry was fixed at 3.5 mg/L. Ethylene/1-hexene copolymerization was carried out under the same polymerization condition and procedure. The 1-hexene concentration was 2.5–10 vol%.

Polymer characterization

^{13}C NMR spectra of copolymers were recorded on a Varian Gemini-300 spectrometer at 120 °C using 1,2,4-trichlorobenzene as a diluent and 1,1,2,2-tetrachloroethane-*d2* as a solvent. MW and MWD of polymers were determined by gel permeation chromatography (GPC, Alliance GPC 2000, Waters), using 1,2,4 trichlorobenzene as a mobile phase.

Results and discussion

Influence of Al concentration

The alkylaluminum concentration largely affects on the polymerization kinetics through activation and deactivation of Ti species. The deactivation rate was known to be correlated with the rate of reduction of Ti species [17]. Figure 1 shows the effect of the Al concentration on the Ti2M, Ti3M, and Ti4M catalytic activities in ethylene polymerization. The ethylene polymerizations rates for the three catalysts showed different trends with increasing the Al concentration. In the case of Ti2M, it was rather constant, consistent with the previously reported results [23, 25]. This could be explained by the fact that Ti species can not be reduced over Ti^{2+} by alkylaluminum, and the formed active sites are regarded as quite stable with negligible deactivation with alkylaluminum. This conclusion was supported by previous experimental reports [5, 12, 26]. On the other hand, the ethylene polymerization rates for Ti3M and Ti4M increased, and then became nearly constant up to 10 mmol/L of the Al concentration. This trend appeared to be in agreement with the results obtained by Bresadola et al. [25]. They found that the catalytic activity for ethylene polymerization was nearly constant in the range of 50–200 Al/Ti. They observed a slow decrease of Ti^{4+} and Ti^{3+} amount accompanied with a small increase of Ti^{2+}. The total amount of the Ti^{3+} and Ti^{2+} species, both of which are active for ethylene polymerization, was reported to be substantially constant, giving a constant activity. The catalytic activity for Ti4M once reached the maximum, and then gradually dropped over 2.0 mmol/L of the Al concentration, which differed from the constant trends for Ti2M and Ti3M. This could be explained by the fact that $TiCl_4$ easily migrates on $MgCl_2$ in the presence of alkylaluminum to aggregate with each other in the curse of the reduction, leading to the gradual decrease of the active site concentration [10]. $TiCl_2$ and $TiCl_3$, that are originally solids, are bound much more tightly than $TiCl_4$ on $MgCl_2$, to depress the aggregation-induced deactivation. Figure 2 shows the ethylene/1-hexene copolymerization activities with varying the alkylaluminum concentration. The activity of Ti2M was enhanced with the addition of a small amount of 1-hexene, although the activities were the lowest among the three catalysts. Interestingly, copolymers produced with Ti2M had similar composition and sequence distribution to those produced with the other two catalysts, even though the 1-hexene incorporation became lower for higher Al concentrations. These results are in disagreement with the previous explanation [20] that Ti^{2+} is comonomer insensitive and produces homopolyethylene only. In the case of Ti3M and Ti4M, the polymerization rates were drastically increased with the addition of 1-hexene, while the activity variation in terms of the Al concentration obeyed a similar trend for the homopolymerization in Fig. 1. The observed rate enhancement by the addition of 1-hexene is known as a rate enhancement effect by comonomer [27–29]. In the case of ethylene copolymerization with α-olefin, physical explanations seem more plausible, such as the acceleration of monomer diffusion through less crystallizable copolymers [30], and the acceleration of the catalyst fragmentation in copolymerization [29]. The difference in the observed rate enhancements by 1-hexene for the three catalysts might arise from the difference of their incorporation efficiency of 1-hexene.

Table 1 shows sequence distribution of ethylene/1-hexene (E/H) copolymers obtained at different Al concentrations. The copolymers contained 0.37–0.61 mol% of 1-hexene, in which butyl branches existed in an isolated manner without any HHH, HEH, and EHH triad sequences. All of Ti2M, Ti3M, and Ti4M show a similar trend, even though a higher oxidation state tends to lead to larger incorporation: the 1-hexene incorporation is the highest at the lowest Al concentration, and then drops for higher concentrations.

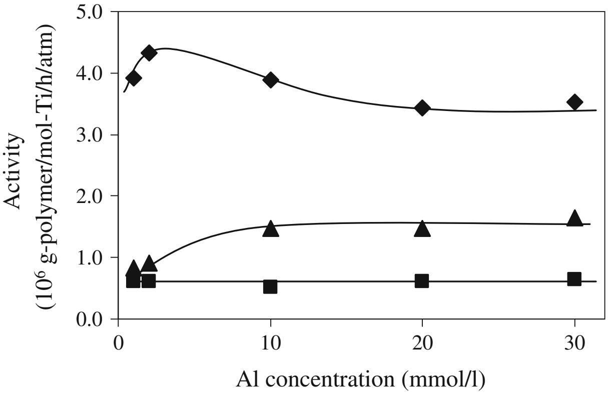

Fig. 1 Influence of the Al concentration on the ethylene homopolymerization activities. The homopolymerization was conducted at 60 °C for 1 h under 0.5 MPa of ethylene. TEA was used as cocatalyst (*filled diamond* Ti4M, *filled circle* Ti3M, and *filled square* Ti2M)

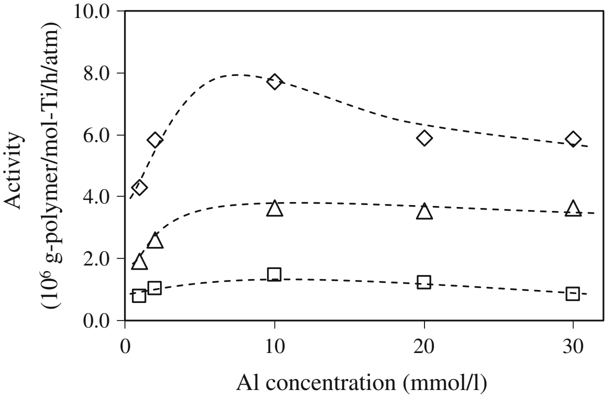

Fig. 2 Influence of the Al concentration on the ethylene copolymerization activities. The copolymerization was conducted at 60 °C for 1 h under 0.5 MPa of ethylene. 10 vol% of 1-hexene was added as the comonomer (*open diamond* Ti4M, *open circle* Ti3M, and *open square* Ti2M)

Influence of the polymerization temperature

The influence of the polymerization temperature on the activities of homo- and co-polymerization is shown in Fig. 3. The temperature was varied in the range of 50–70 °C. Higher catalyst activities for the ethylene homopolymerization were obtained by increasing the polymerization temperature. Although Ti4M was the most sensitive to the temperature change, the behavior was similar among the different Ti oxidation states. In comparison, the copolymerization activities increased more sharply than the homo-polymerization at 60 °C, but rather dropped at 70 °C, probably because the 1-hexene solubility was decreased upon increasing the reactor temperature.

Table 1 Sequence distribution of ethylene/1-hexene copolymers synthesized using $TiCl_x/MgCl_2$ catalysts ($x = 2$–4) at different Al concentrations

Catalyst	Al conc. (mmol/L)	EHE	EHH	HHH	HEH	EEH	EEE	1-hexene incorporated (mol%)
Ti2M	2.0	0.5	0.0	0.0	0.0	1.1	98.4	0.54
	10.0	0.4	0.0	0.0	0.0	0.7	98.9	0.37
	30.0	0.4	0.0	0.0	0.0	0.8	98.7	0.42
Ti3M	2.0	0.6	0.0	0.0	0.0	1.1	98.3	0.56
	10.0	0.5	0.0	0.0	0.0	1.0	98.5	0.52
	30.0	0.5	0.0	0.0	0.0	1.1	98.4	0.53
Ti4M	2.0	0.6	0.0	0.0	0.0	1.2	98.2	0.61
	10.0	0.6	0.0	0.0	0.0	1.1	98.4	0.55
	30.0	0.6	0.0	0.0	0.0	1.1	98.3	0.57

Polymerization conditions: catalyst amount = 3.5 mg/L, temperature = 60 °C, polymerization time = 1 h, ethylene pressure = 0.5 MPa, 1-hexene concentration = 10 vol%, TEA concentration = 2–30 mmol/L

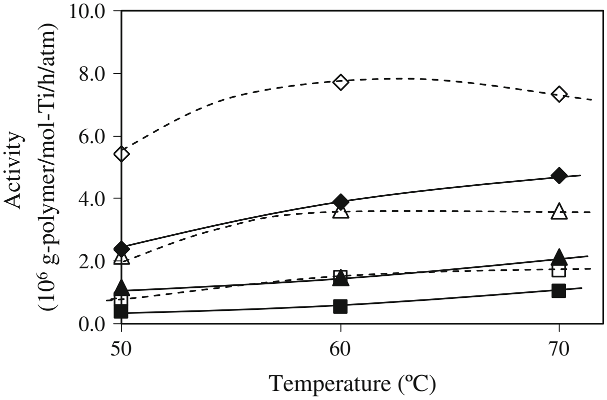

Fig. 3 Influence of the polymerization temperature on the activities of the ethylene homo- and copolymerization. The polymerization was conducted under 0.5 MPa of ethylene for 1 h. 10 mmol/L of TEA was used as cocatalyst. 10 vol% of 1-hexene was added in copolymerization

Influence of the 1-hexene concentration

The effects of the 1-hexene concentration on the polymerization rates and resulting polymer properties were investigated for the different Ti oxidation states. As shown in Fig. 4, all the catalysts activities were linearly increased for the 1-hexene concentration. The sequence distributions of copolymers prepared with the three catalysts are shown in Table 2. The produced copolymers again had similar composition and sequence distribution without sequential 1-hexene insertion. Incorporation of 1-hexene in copolymers was basically increased in correlation with the 1-hexene concentration, but not simply proportional to it. There might be a critical incorporation amount, below which the incorporation efficiency is lower for

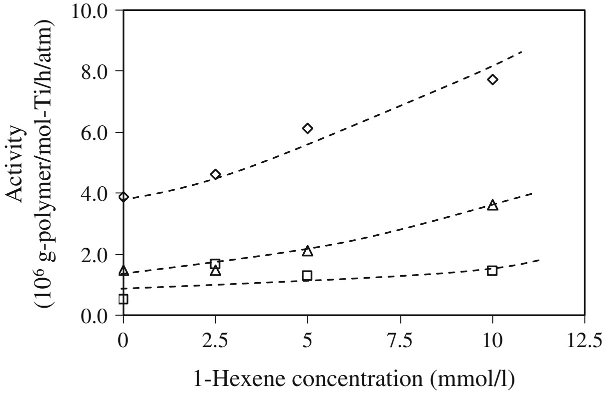

Fig. 4 Relationship between the 1-hexene concentration and catalytic activity. The copolymerization was conducted at 60 °C for 1 h under 0.5 MPa of ethylene. 10 mmol/L of TEA was used as the cocatalyst (*open diamond* Ti4M, *open circle* Ti3M, and *open square* Ti2M)

Table 2 Sequence distribution of ethylene/1-hexene copolymers synthesized using $TiCl_x/MgCl_2$ catalysts ($x = 2$–4) at different 1-hexene concentrations

Catalyst	1-Hexene injected (vol%)	EHE	EHH	HHH	HEH	EEH	EEE	1-Hexene incorporated (mol%)
Ti2M	2.5	0.2	0.0	0.0	0.0	0.4	99.4	0.20
	5.0	0.2	0.0	0.0	0.0	0.5	99.3	0.24
	10	0.4	0.0	0.0	0.0	0.8	98.8	0.42
Ti3M	2.5	0.3	0.0	0.0	0.0	0.6	99.1	0.32
	5.0	0.4	0.0	0.0	0.0	0.7	98.9	0.37
	10	0.5	0.0	0.0	0.0	1.0	98.5	0.52
Ti4M	2.5	0.3	0.0	0.0	0.0	0.6	99.1	0.30
	5.0	0.6	0.0	0.0	0.0	1.2	98.2	0.58
	10	0.6	0.0	0.0	0.0	1.1	98.4	0.55

Polymerization conditions: catalyst amount = 3.5 mg/L, temperature = 60 °C, polymerization time = 1 h, ethylene pressure = 0.5 MPa, 1-hexene concentration = 2.5–10 vol%, TEA concentration = 10 mmol/L

the 1-hexene concentration, and above which the incorporation efficiency discontinuously increases and then becomes stable. This might be related to some discontinuous change in the monomer diffusivity, in lowering the crystallinity by incorporation of 1-hexene. It is notable that a higher oxidation sate led to higher incorporation efficiency, even with the similar response to the 1-hexene concentration. The molecular weights and their distributions of copolymers synthesized with the three catalysts are summarized in Table 3. Ti2M produced a copolymer with the broadest MWD as compared with those obtained by Ti3M and Ti4M. The broadness of MWD for Ti2M arose mainly from the formation of a high-molecular weight tail, as indicated in the highest M_w. The lowest incorporation of 1-hexene and the highest molecular weight partly agrees with the previous proposal by Kissin

Table 3 Molecular weight and their distribution of copolymers synthesized using $TiCl_x/MgCl_2$ catalysts ($x = 2–4$)

Catalyst	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$	M_w/M_n
Ti2M	3.6	14	4.0
Ti3M	3.2	12	3.7
Ti4M	3.7	12	3.2

Polymerization conditions: catalyst amount = 3.5 mg/L, temperature = 60 °C, polymerization time = 1 h, ethylene pressure = 0.5 MPa, 1-hexene concentration = 10 vol%, TEA concentration = 10 mmol/L

et al. [20]. However, it should be stressed that the obtained copolymers had roughly similar characteristics in CC and MW, in agreement with the results by Zakharov et al. [5, 6].

Conclusion

We have investigated the influences of the oxidation state on ethylene homo- and co-polymerization using $MgCl_2$-based Ziegler–Natta catalysts made directly from $TiCl_4$, $TiCl_3$, and $TiCl_2$ precursors. The Ti oxidation state had large effects on the catalytic activity in both of ethylene homo- and co-polymerization with 1-hexene. Especially, $TiCl_2/MgCl_2$ had a unique response that was very different from $TiCl_4/MgCl_2$ and $TiCl_3/MgCl_2$ upon varying the Al concentration and 1-hexene concentration. All the copolymers produced by the catalysts had similar sequence distribution, even though the increase of the oxidation state caused a slight enhancement of 1-hexene incorporation. Similarly, molecular weights and their distributions of the copolymers were not largely dependent on the Ti oxidation state. It is worth noting that these results are in accordance with those from Zakharov et al. [5, 6] even through the catalyst precursors to obtain the different oxidation states of Ti were different. Thus, it was concluded that the oxidation state was not important for the copolymer characteristics, while it played a major role in the catalytic activity.

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References

1. Lynch DT, Jejelowo MO, Wanke SE (1991) The influence of aluminum alkyls on the polymerization of ethylene with silica/magnesium chloride-supported titanium tetrachloride catalysts. Can J Chem Eng 69:657–664
2. Piotr S (1989) The role of magnesium chloride as supporter for the new generation of olefin polymerization catalysts. Polym Plast Tech Eng 28:493–510
3. Chadwick JC, Miedema A, Ruisch BJ, Sudmeijer O (1992) Effects of procatalyst composition on the stereospecificity of a Ziegler–Natta catalyst system. Makromol Chem 193:1463–1468
4. Echevskaya LG, Matsko MA, Mikenas TB, Nikitin VE, Zakharov VA (2006) Supported titanium-magnesium catalysts with different titanium content: kinetic peculiarities at ethylene homopolymerization and copolymerization and molecular weight characteristics of polyethylene. J of Appl Polym Sci 102:5436–5442

5. Tregubov AA, Zakharov VA, Mikenas TB (2009) Supported titanium-magnesium catalysts for ethylene polymerization: a comparative study of catalysts containing isolated and clustered titanium ions in different oxidation states. J Polym Sci Part A Polym Chem 47:6362–6372
6. Mikenas TB, Tregubov AA, Zakharov VA, Echevskaya LG, Matsko MA (2008) Titanium-magnesium catalysts for olefin polymerization—effect of titanium oxidation state on catalyst performance. Polimery 53:353–357
7. Potapov AG, Kriventsov VV, Kochubey DI, Bukatov GD, Zakharov VA (1997) EXAFS study of supported TiCl4/MgCl2 catalyst. Macromol Chem Phy 198:3477–3484
8. Czaja K, Bialek M (2000) Effect of hydrogen on the ethylene polymerization process over Ziegler–Natta catalysts supported on MgCl2(THF)2 I studies of the chain-transfer reaction. J of Appl Polym Sci 79:356–360
9. Giuliano C, Giampiero M, Anteo P (2001) Polypropene product innovation by reactor granule technology. Macromol Symp 173:195–209
10. Wada T, Taniike T, Kouzai I, Takahashi S, Terano M (2009) Propylene polymerization performance of isolated and aggregated Ti species studied using a well-designed TiCl3/MgCl2 Ziegler–Natta model catalyst. Macromol Rapid Commun 30:887–891
11. Mori H, Hasebe K, Terano M (1998) Variation in oxidation state of titanium species on MgCl2-supported Ziegler catalyst and its correlation with kinetic behavior for propylene polymerization. Polymer 40:1389–1394
12. Taniike T, Terano M (2008) Reductive formation of isospecific Ti dinuclear species on a $MgCl_2$ (110) surface in heterogeneous Ziegler–Natta catalysts. Macromol Rapid Commun 29:1472–1476
13. Baulin AA, Novikova EI, Mal'kova GYa, Maksimov VL, Vyshinskaya LI, Ivanchev SS (1980) Correlation between the reduction of titanium in supported Ziegler catalysts and their activity in the polymerization of ethylene. Vysokomol Soed A 22:181–188
14. Soga K, Chen SI, Ohnishi R (1982) Correlation between the oxidation states of titanium and the polymerization activities for higher α-olefins and diene compounds. Polym Bull 8:473–478
15. Soga K, Shiono T, Doi Y (1983) Titanium (IV) chloride/magnesium chloride catalytic systems. Polym Bull 10:168–174
16. Soga K, Uozumi T, Park JR (1990) Effect of catalyst isospecificity on olefin copolymerization. Makromol Chem 191:2853–2864
17. Kashiwa N, Yoshitake J (1984) The influence of the valence state of titanium in magnesium chloride-supported titanium catalysts on olefin polymerization. Makromol Chem 185:1133–1138
18. Kashiwa N, Yoshitake J, Tsutsui T (1987) Polymerization of styrene with a highly active magnesium dichloride supported titanium tetrachloride catalyst system. Polym Commun 28:292–296
19. Kojoh SI, Kioka M, Kashiwa N (1999) The influences of cocatalyst on propylene polymerization at high temperature with $MgCl_2$-supported $TiCl_4$ catalyst system. Eur Polym J 35:751–755
20. Kissin YV, Mirabella FM, Meverden CC (2005) Multi-center nature of heterogeneous Ziegler–Natta catalysts: TREF confirmation. J Polym Sci Part A Polym Chem 43:4351–4362
21. Ludlum DB, Anderson AW, Ashby CE (1958) Polymerization of ethylene by lower-valent compounds of titanium. J Amer Chem Soci 80:1380–1384
22. Mobarakeh HS, Monfared MF, Vakili M (2006) Gas phase copolymerization of ethylene and 1-butene with prepolymerized MgCl2 supported Ziegler–Natta catalyst: effect of Al/Ti ratio. Iranian Polym J 15:569–575
23. Benning CJ, Wszolek WR, Werber FX (1968) Crystalline titanium dichloride. Active catalyst in ethylene polymerization. II. Polymer structure, polymerization variables, and scope. J Polym Sci Part A-1 Polym Chem 6:755–762
24. Skalli MK, Markovits A, Minot C, Belmajdoub A (2001) A theoretical investigation of the role of AlR_3 as cocatalyst. Catal Lett 76:1–2
25. Fregonese D, Mortara S, Bresadola S (2001) Ziegler–Natta $MgCl_2$-supported catalysts: relationship between titanium oxidation states distribution and activity in olefin polymerization. J Molecular Catal A Chem 172:89–95
26. Ono Y, Keii T (1966) Electron spin resonance studies on Ziegler–Natta type catalyst systems. J Polym Sci Part A-1Polym Chem 4:2441–2446
27. Ko YS, Han TK, Sadatoshi H, Woo SI (1998) Analysis of microstructure of ethylene–1-hexene copolymer prepared over thermally pretreated $MgCl_2$/THF/$TiCl_4$ bimetallic catalyst. J Polym Sci Part A Polym Chem 36:291–300

28. Kim I, Kim JH, Choi HK, Chung MC, Woo SI (1993) Comonomer enhancement effect of 1-hexene in ethylene copolymerization catalyzed over $MgCl_2$/THF/$TiCl_4$ catalysts. J Appl Polym Sci Part A Polym Chem 48:721–730
29. Chien JCW, Nozaki T (1993) Ethylene/hexene copolymerization by heterogeneous and homogeneous Ziegler–Natta catalysts, and the comonomer effect. J Polym Sci 31:227–237
30. Floyd S, Choi KY, Taylor TW, Ray WH (1986) Polymerization of olefins through heterogeneous catalysis. III. Polymer particle modelling with an analysis of intraparticle heat and mass transfer effects. J Appl Polym Sci 32:2935–2960