

Exploring Si/Mg Composite Supported Ziegler-Natta Ti-based Catalysts for Propylene Polymerization*

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Abstract A series of (SiO₂/MgO/ID/MgCl₂)·TiCl₄ Ziegler-Natta catalysts for propylene polymerization has been prepared with a new method. These catalysts were synthesized using soluble Mg-compounds as the Mg-source and the preparation progress was relatively simple. The catalyst could copy the spherical shape of the carrier very well. The propylene polymerization results showed that the catalyst revealed the best activity with 9,9-di(methoxymethyl)fluorene (BMMF) as internal donor at 50 °C with the optimal molar ratio Al/Ti = 5, which was much lower than what the industrial polypropylene catalyst used (at least molar ratio Al/Ti = 100), resulting in great cost saving. Additionally, the polymerization kinetics of the catalyst exhibited very stable property after achieving a relatively high value. These catalysts possessed rather high activity and good hydrogen response. The isotactic index (II.) value of the PP products could be higher than 98% in the presence of both internal and external electron donors. Moreover, temperature rising elution fractionation method was used to understand the influence of donors and H₂ on the properties of the PP products.

Keywords Polypropylene; Ziegler-Natta catalyst; External donor; Internal donor; Kinetic curves

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INTRODUCTION

Polypropylene (PP) has been one of the most widely used polyolefin resins over the past decades due to its excellent performance^[1]. The global demand for polymers has reached about 218 million tons and the share of polypropylene in total polymer consumption is about 25% in 2013^[2]. Since Karl Ziegler and Giulio Natta discovered the TiCl₄-AlEt₃ and TiCl₃-AlEt₂Cl catalytic systems which set up the footstone of the industry of polyolefin in early 1950s, the catalyst had made great improvement during the following few decades. Nowadays, the fourth generation Ziegler-Natta catalysts are commonly used in industry, especially in the production of polypropylene. The improvement in supported polyolefin catalysts is crucial to meet growing global demand for polypropylene^[3].

Considerable efforts have been devoted to improve catalyst performance. In recent years, the development of polypropylene catalysts has mainly focused on two aspects: the donors and the support itself. Since the first

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modification of MgCl_2 support with internal electron donor (ID), it has been realized that the ID plays a significant role in the aspect of selectivity and activity of the catalyst. After the discovery of aromatic monoesters (*e.g.*, benzoates) as the first internal donors, lots of new internal donors have been developed such as phthalates^[4], diethers^[5–7], succinates^[8], malonates^[9], glutarates^[10], diketones^[11] and ether^[12].

In terms of the catalyst support, one of the breakthroughs was the discovery of activated MgCl_2 , which opened a new era in the field of Ziegler-Natta catalysts. The first generation of highly active, highly stereospecific carrier catalyst for propylene polymerization was obtained by grinding together MgCl_2 and ethyl benzoate (EB), and successively reacting the grinded product with TiCl_4 ^[13]. Even though MgCl_2 was often considered merely as a support, its role in the formation of the active centers was crucial. Therefore, great attention was paid to the preparation of a suitable MgCl_2 support for Ziegler-Natta catalyst. Böhm^[14] utilized $\text{Mg}(\text{OEt})_2$ as the Mg-source, and then refluxed with TiCl_4 directly to synthesize MgCl_2 support *in situ*, and thus invented another approach of preparing Ti/Mg Ziegler-Natta catalyst support. Kimura *et al.*^[15] prepared a catalyst by heating components of a dialkoxy magnesium, an aromatic carboxylic acid diester and TiCl_4 in the presence or absence of a solvent. This catalyst showed good performance for propylene polymerization. Also, a series of SHAC catalysts for propylene polymerization produced by Dow Chemical Company used dialkoxy magnesium as the catalyst support. Furthermore, magnesium and alcohol were used as raw materials for preparing alkoxy carrier by Toho Titanium company and the resulting THC catalysts had higher activity and lower cost^[16]. Although catalysts prepared with $\text{Mg}(\text{OEt})_2$ showed a higher activity, they had a morphological shortage regarding roundness and particle size distribution as compared with $\text{MgCl}_2 \cdot n\text{ROH}$. In order to adjust the polymer particle size distribution and sphericity, Udoo and Kurausuudeiitaa^[17] combined silica and dialkoxy magnesium as support to synthesize catalyst for propylene polymerization. However, this method had drawbacks of low stereoregularity of PP products and low activity of the catalyst. Nevertheless, few reports of this kind $\text{SiO}_2/\text{MgCl}_2$ composite supported Ziegler-Natta catalysts for propylene polymerization have been published.

Recently, in our group, a series of novel $(\text{SiO}_2/\text{MgO}/\text{MgCl}_2) \cdot \text{TiCl}_x$ Ziegler-Natta catalysts for ethylene polymerization and ethylene/1-hexene copolymerization were investigated^[18–21]. These series of catalysts were characteristic with much lower cost, simpler preparation process, and high activity. However, propylene polymerization based on these catalysts after introducing internal and external donors has not yet been investigated, and it is important for SiO_2 bi-supported Ziegler-Natta catalyst to develop novel and efficient polypropylene catalysts. So, in this work, a series of Si/Mg composite supported Ziegler-Natta catalysts were prepared by introducing different internal donors and the performance for propylene polymerization was investigated. It was found that 9,9-di(methoxymethyl)fluorene (BMMF) was an excellent internal donor for the polypropylene catalysts. The effects of significant process parameters, such as molar ratio of cocatalyst/Ti, molar ratio of cocatalyst/external donor (ED), with or without hydrogen, were also investigated on the polymerization of propylene and the polymers produced by different conditions were analyzed by temperature rising elution fractionation method.

EXPERIMENTAL

Materials

All the materials and operation steps were performed under dry nitrogen atmosphere using a standard glove box and nitrogen line. The magnesium acetate tetrahydrate (AR grade) and titanium tetrachloride (AR grade) were purchased from LingFeng Chemical Reagent Co., Ltd. Silica gel (Grace Davison 955, surface 261.8 m^2/g , pore volume 1.67 cm^3/g and average pore size 17.4 nm) was donated by Qilu Branch Co., SINOPEC. The high purity nitrogen ($\text{N}_2 \geq 99.999\%$) used in the catalyst preparation, propylene polymerization at atmospheric pressure was further purified by passing through one column of 4 Å molecular sieves (purchased from Sinopharm Chemical Reagent Co., Ltd.) for dehydration and one column of silver molecular sieves (28 wt% of silver(I) oxide on alumina, purchased from Sigma-Aldrich) for deoxidation. And the high purity dry air (total impurity < 1 ppm, dew point of $\text{H}_2\text{O} < -80^\circ\text{C}$) and high purity hydrogen ($\text{H}_2 \geq 99.999\%$) were purchased from Shanghai Wetry

Criterion Gas Co., Ltd. Propylene monomer used for propylene polymerization was purified by subsequently passing through three columns of 4Å molecular sieves, Q-5 reactant catalyst (13 wt% of copper(II) oxide on alumina, purchased from Sigma-Aldrich) and 13X molecular sieves (purchased from Sinopharm Chemical Reagent Co., Ltd.) for dehydration and deoxidation. All the solvents including *n*-hexane (AR grade), *n*-heptane (AR grade) and toluene (AR grade), which were also purchased from Sinopharm Chemical Reagent Co., Ltd., were purged through distillation in the presence of sodium metal slices and diphenyl ketone as indicator until the indicator showed pure blue color before use. Triisobutylaluminium (TIBA, 1.0 mol/L in *n*-heptane) and triethylaluminium (TEA, 1.0 mol/L in *n*-heptane) as cocatalysts were purchased from Alfa Aesar. 9,9-Di(methoxymethyl)fluorene (BMMF, purchased from Sinopharm Chemical Reagent Co., Ltd.), isobutyl phthalate (DIBP), phenetole (PE) and 1,2-diethoxybenzene (DBE) were treated with 4Å molecular sieve and N₂ before use. Dicyclopentyl dimethoxy silane (DCPMS D-donor), which was purchased from Alfa Aesar, was distilled under vacuum before use.

Catalyst Preparation

The catalyst synthesis progress is described in Fig. 1. First, about 7 g of silica gel (calcined at 300 °C) was impregnated with aqueous solution of magnesium acetate at room temperature by stirring for 4 h and then dried at 120 °C for 12 h. After impregnation, the products were calcined at 600 °C under high purity dry air at a flow rate of 600 mL/min for 4 h in a fluidized-bed quartz reactor with a temperature-programmed heating controller. Then it was cooled down to 400 °C under the dry air followed by further cooling down to room temperature under N₂ atmosphere. The obtained SiO₂/MgO sample was transferred into a glovebox for catalyst preparation.

Second, about 2 g of SiO₂/MgO sample and 30 mL of TiCl₄ were charged in a 100 mL 3-necked flask equipped with a magnetic stirrer rotating at 180 r/min under N₂ atmosphere, then the mixture was heated to 140 °C slowly and kept at this refluxing for 1 h. Thereafter, the liquid above was removed and 30 mL of toluene and a certain amount of internal electronic donor (ID/Mg = 0.2) were added to the reactor, followed by refluxing at 120 °C for 2 h. Subsequently, the solid was washed with toluene twice at room temperature and further treated with 30 mL of TiCl₄ at 120 °C for 2 h. Finally, the product was washed with *n*-heptane 7 times to get the final catalyst.

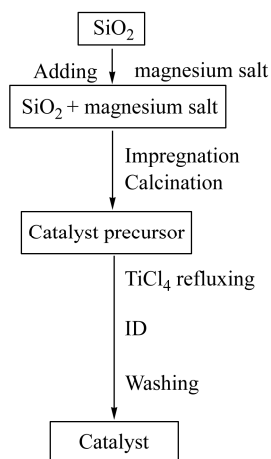


Fig. 1 Novel catalyst preparation method

Propylene Polymerization

Propylene polymerization was performed in a 250 mL three-neck flask equipped with a magnetic stirrer rotating at 350 r/min. One small ampoule tube on the top of 250 mL three-neck flask was used to contain 100 mg of catalyst, which was previously weighed and sealed in the glovebox. The reactor was placed at a thermostatic oil bath and purged by nitrogen for at least three times. Then the propylene was introduced until the pressure was about 0.12 MPa, and 80 mL of *n*-heptane, a certain amount of co-catalyst such as TIBA or TEA, and a certain

amount of DCPMS were introduced into the reactor and the propylene pressure was raised to 0.15 MPa at 50 °C. After the solution was saturated of propylene, 100 mg of catalyst was fed into the reactor to initiate the polymerization. The polymerization was conducted for 60 min with a continuous supply of propylene gas at 0.15 MPa. The polymer was recovered by pouring the reaction slurry into ethanol with dilute HCl. All the obtained polymers were washed with ethanol, and dried under vacuum at 60 °C for at least 6 h before weighing.

Characterization

ICP spectrometer (Varian 710-ES) was used to identify the magnesium loading; the power was 1.10 kW. The flow rates of plasma gas and auxiliary gas were 15.0 and 1.50 L/min, respectively. The titanium content of the synthesized catalysts was determined by Mapada UV-3200 spectrophotometer through hydrogen peroxide colorimetric method. The ID content was determined on a gas chromatograph (Clarus 580), manufactured by PE in the US. Nitrogen adsorption/desorption experiments were conducted on an automatic physisorption analyzer (Micromeritics ASAP 2020, USA) at 77 K to obtain the value of the specific surface area, SBET, calculated based on the BET method; the pore volume V_p and pore size d_m were evaluated using the BJH method. The molecular weight (MW) and molecular weight distribution (MWD) of produced polypropylene were measured by HT-GPC (Agilent PL-220) with two PLgel-Olexis columns at 160 °C and the flow rate of 1.0 mL/min. 1,2,4-Trichlorobenzene (TCB) and polystyrene (PS) were used as solvent and standard sample, respectively. The PP was separated by a homemade TREF system which was mainly composed of a silicone oil bath with thermostat (Huber, POLYTSTAT CC (3 ± 0.02) °C), a 850 mL fractionation bottle filled with quartz sand (AR), a pump (KNF Lab, STEPDOS 08 S) and a rotary evaporator (EYELA). The sample was kept dissolving at 135 °C for 1 h and then cooled down to 40 °C at 1 K/h. After this cooling step, the temperature was raised to the selected temperature and kept for at least 1 h for dissolution of the corresponding fraction. Differential scanning calorimetry (DSC) test was made by DSC analyzer (TA, DSC Q200) at a heating rate of 10 K/min. The isotacticity index of PP was determined by measuring the amount of boiling heptane insoluble fraction percent in the polymer. The X-ray photoelectron spectroscopy (XPS) experiments were carried out on a PerkinElmer Model PhI5000 ESCA spectrometer equipped with a hemispherical electron analyzer working in the constant pass energy mode. A monochromatic Al K α radiation (1486.6 eV) operated at 300 W was used as the X-ray source. All binding energies were referenced to the Si2p peak of silica gel at 103.3 eV for the charging effect correction. The morphology of the support and catalysts was observed on a Nova Nano450 scanning electron microscope. The high vacuum resolution was 3.0 nm and the low vacuum resolution was 4.0 nm. The magnification range was 200–10000.

RESULTS AND DISCUSSION

Exploring the Proper Internal Electronic Donors

Firstly, four kinds of internal electron donors had been explored during the propylene catalysts preparation. The internal electron donors structures are shown in Fig. 2.

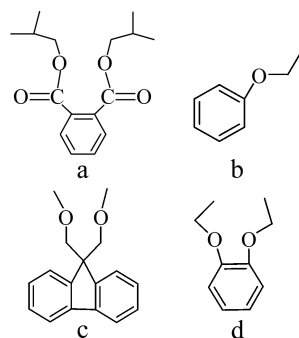


Fig. 2 Four kinds of internal electron donors: (a) isobutyl phthalate (DIBP), (b) phenetole (PE), (c) 9,9-di(methoxymethyl)fluorene (BMMF), (d) diethoxybenzene (DBE)

The four compounds were employed as internal electron donors in the preparation of corresponding catalysts Cat-DIBP, Cat-PE, Cat-BMMF and Cat-DEB. For each type of ID, the concentration was 0.2 molar ratio of ID/Mg, which was a relatively proper concentration according to our experimental results. The performance of these catalysts was evaluated by propylene polymerization without external electron donor, and the polymerization results are presented in Table 1. It can be clearly seen that the structure of internal donors has a significant effect on the polymerization performance. The activity of the catalysts with IDs exhibited the following order: Cat-BMMF > Cat-PE > Cat-DIBP > Cat-DEB. Among the IDs used, BMMF turned out to be the best ID for the catalyst preparation. That may be attributed to the different structure of the IDs, such as the distance between the two oxygen atoms in the ID compounds.

Table 1 Polymerization results of different ID catalysts ^a

Run No.	Catalyst	Ti content (wt%)	Activity (gPP/(gTi·h))
1 ^b	Cat 4	4.46	275.1
2	Cat-DIBP	4.30	294.2
3	Cat-PE	3.89	729.3
4	Cat-BMMF	3.84	2166.8
5	Cat-DEB	3.67	228.5

^a Polymerization conditions: catalyst 100 mg, propylene 0.15 MPa, *n*-heptane 80 mL, TIBA, 50 °C, 1 h; ^b Catalyst without internal donor

Secondly, in order to find proper progress of catalyst preparation, the ID adding sequence during the catalyst preparation had also been studied. One way was that ID was added with TiCl₄ simultaneously, and the other way was that the ID was added after the addition of TiCl₄. We found that the different ID adding sequence had an effect on the catalyst performance. Catalysts prepared by adding ID after the addition of TiCl₄ showed a better activity. The reason might be that after the formation of MgCl₂, the ID was more likely to play a role in forming an active center. Considering the low activity of catalyst prepared with other IDs, catalysts synthesised with BMMF as ID had been systematically studied in the following experiment to understand the characteristics of this catalyst.

Characterization of Catalysts

Three supports with different initial magnesium contents and the corresponding Ziegler-Natta catalysts were prepared following the procedure described above using BMMF as the internal electron donor. The results of catalyst characterization are summarized in Table 2. A slight reduction in the magnesium loading of these novel catalysts could be seen compared with the amount added initially during catalyst preparation, which might be a limitation of the loading capacity on the surface of SiO₂ and some magnesium could be moved into solvents during the catalyst synthesis. Comparing the titanium contents of Cat 1, Cat 2 and Cat 3, it showed an increasing tendency with the increase of magnesium content. The reason was more MgO reacted with TiCl₄ to generate more MgCl₂ and thus leading to more Ti species coordinated on the magnesium atom to form an active center. Otherwise, Cat 4 prepared without an internal donor had a higher titanium content than Cat 1, Cat 2 and Cat 3. The reason might be that the added BMMF could occupy some coordination sites on which Ti could be coordinated, resulting in less coordination sites for Ti species. It is also worth noting that the Cl content of these catalysts was much lower compared with MgCl₂ supported catalyst (about 50 wt%), and with the increasing Mg content in catalysts, the Cl content increased because of the formation of the more MgCl₂ and the more Ti species.

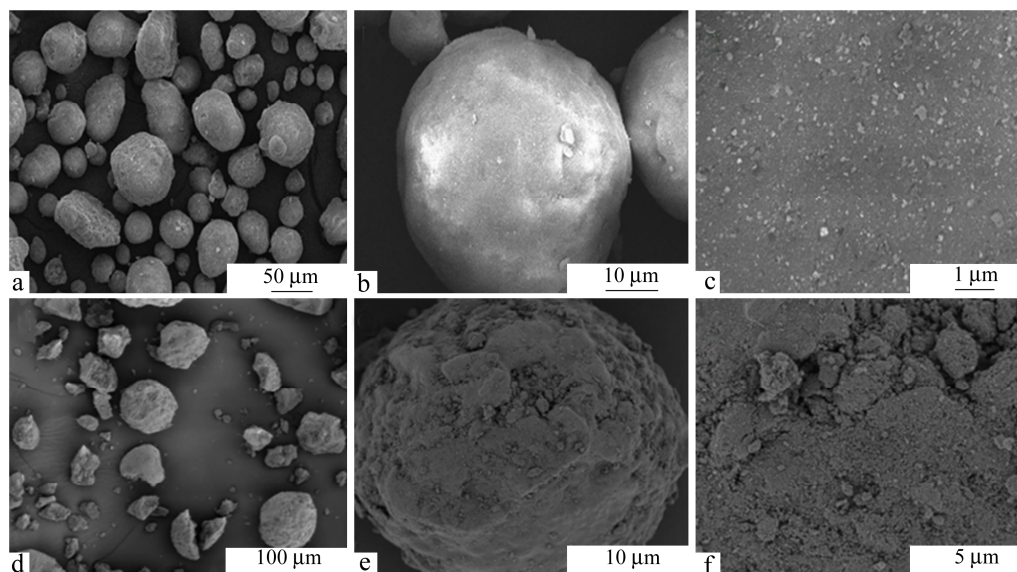
In general, propylene polymerization was performed on the surface and in the pore of the catalysts. Therefore, the surface area and the pore of the catalyst could affect the catalyst performance. The results in Table 2 show that the surface area (SA) and pore volume (PV) of these catalysts all decreased obviously compared with those of the SiO₂ raw material. This could be ascribed to the elements loading on the surface of SiO₂. However, the pore diameter (PD) of the catalyst prepared with BMMF increased while the catalyst prepared without an internal donor decreased. This might be due to the interaction of BMMF with magnesium atom leading to a change on the pore structure of the catalyst.

Table 2 Characterization results of silica and different catalysts

Catalyst ^a	Mg ^b (wt%)	Ti ^c (wt%)	Cl ^d (wt%)	ID ^e (wt%)	Pore structure parameters ^f		
					PV (mL/g)	SA (cm ³ /g)	PD (nm)
Silica	—	—	—	—	1.59	261.6	17.7
Cat 1	10.9	3.84	11.7	17.6	0.78	144.1	21.5
Cat 2	8.3	3.79	10.3	14.2	0.84	153.9	21.9
Cat 3	4.5	3.59	9.8	9.1	0.97	182.8	21.1
Cat 4	11.3	4.46	10.8	—	0.87	183.6	14.8

^a Cat 1, Cat 2 and Cat 3 were prepared with initial magnesium content of 15 wt%, 10 wt% and 5 wt%, respectively; Cat 4 was prepared with 15 wt% initial magnesium content and without internal donor; ^b Measured by ICP; ^c Measured by UV-Vis; ^d Measured by IC; ^e Measured by HPLC; ^f Measured by nitrogen adsorption/desorption experiments

The images of scanning electron microscopy (SEM) in Fig. 3 clearly show the surface changing of the catalysts. This could be ascribed to the elements loaded and active sites formed on the surface of the support. Furthermore, the dried silica support was almost spherical and the catalyst could conform the shape of the carrier very well. Some catalyst samples were partly broken up into small irregular fragments. This might be caused by the mechanical and thermal treatments on silica gel support during the fluidized-bed experimental condition. Scanning electron microscopy and energy dispersive spectrometer (SEM/EDS) method was used to analyze the element distribution on the surface of the catalyst. From the EDS spectrum of Cat 2 (Fig. S1, in supporting information, SI), it can be seen that the distribution of the elements on the catalyst surface was relatively uniform.

**Fig. 3** SEM images for (a–c) silica and (d–f) Cat 2 with different magnifications

In our previous work, Wang *et al.*^[18] proposed a possible mechanism of the generation of MgCl₂ during the catalyst preparation; that is, the trace amount of moisture in the reaction system played a significant role in producing MgCl₂. In view of the reaction between TiCl₄ and hydroxyl on the surface of silica and MgO, three kinds of possible surface titanium precursors in the catalyst for ethylene polymerization were put forward: titanium in the form of Si—O—Ti linkage, titanium in the form of Mg—O—Ti linkage, and TiCl₄ supported on the MgCl₂ clusters. As is well known, an internal donor is an important composition of polypropylene catalyst and is almost indispensable for obtaining polypropylene with satisfactory stereoregularity. The interaction between ID and Ti species and the support had been extensively studied^[22]. Researchers now agree that donor molecules adsorbing on MgCl₂ surfaces and interacting with nearby Ti species in a non-bonded manner improve

the stereospecificity of the active Ti species^[23–26]. Hence, three different kinds of active sites could be proposed for this novel catalyst as shown in Fig. 4. Since the interaction between TiCl_4 and internal donor could change the binding energies of the Ti species, an XPS survey scan was performed to investigate the states of the titanium species of these novel catalysts. The results showed that the values of the binding energies in the supported catalysts with and without an internal donor were almost the same (Table S1, in SI). This indicated that the BMMF might not directly interact with titanium species and instead of adsorbing on MgCl_2 surfaces it might interact with nearby Ti species in a non-bonded manner.

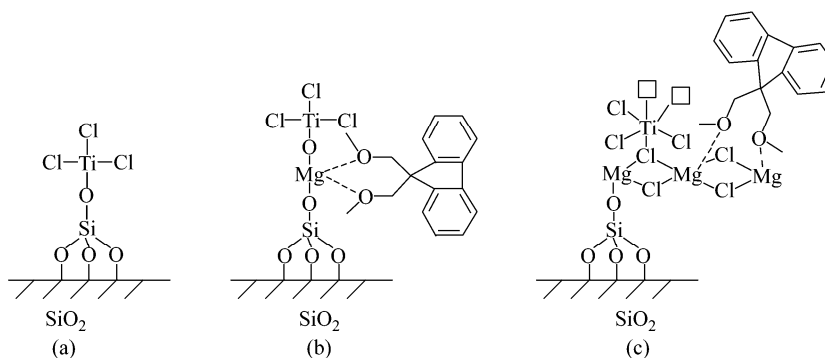


Fig. 4 Possible structures of different kinds of active sites

Effect of Temperature

These series of catalysts were first used in propylene homo-polymerization. The effect of temperature on the polymerization behavior was studied and the results are given in Table 3. According to Table 3, the activity of the catalyst yielded a plateau value at 50 °C and then decreased with increasing temperature. An explanation for the activity decrease was a destruction of the active site at the higher temperature in the polymerization condition and this process was irreversible in nature^[27].

Table 3 Effect of temperature on catalyst activity and polymer properties^a

Run No.	Catalyst	Al/Ti	<i>T</i> (°C)	Activity ^b	<i>T</i> _m ^c (°C)	<i>M</i> _w ^d × 10 ^{−5} (g/mol)	MWD ^e
1	Cat 1	10	40	1837.9	157.8	4.1	11.9
2	Cat 1	10	50	2067.9	157.9	3.8	14.5
3	Cat 1	10	60	1690.5	158.5	4.5	12.1
4	Cat 1	10	70	1418.2	158.3	3.9	13.2

^a Polymerization condition: catalyst 100 mg, propylene 0.15 MPa, *n*-heptane 80 mL, TIBA, no ED, 1 h; ^b The unit of catalyst activity is gPP/(gTi·h); ^c *T*_m was measured by DSC thermograms; ^d *M*_w was estimated by GPC; ^e MWD (*M*_w/*M*_n)

Effect of Co-catalyst

Propylene polymerization was studied in terms of the concentration and the nature of cocatalyst, and the parameters and the characterization results of the polymers are shown in Table 4.

It is worth noting that with the increase of the Al/Ti molar ratio the activity of the catalyst increased first and then decreased, and the maximum activity of the novel catalysts was observed at the TIBA/Ti molar ratio of 5, which was much lower than the Al/Ti molar ratio used in industrial propylene catalyst. It is well known that the cocatalyst plays an important role in initiating the active center by reducing and alkylating the transition metal and generating a transition metal-carbon bond^[28, 29]. However, an excess cocatalyst might lead to deactivation of the active sites through over-reduction of Ti^{4+} to Ti^{2+} and these species were not active for propylene polymerization^[30], which might decrease the activity. Moreover, by comparing the performance data of Cat 1, Cat 2 and Cat 3 with Cat 4 presented in Table 4, it was found that Cat 4 without internal donor showed much lower activity in propylene polymerization. This indicated that after the addition of BMMF, new active sites were formed with BMMF as shown in Figs. 4(b) and 4(c), resulting in a significant increase of propylene

polymerization activity. The MWD of polypropylene produced by this Si/Mg composited catalyst was broad when there was no external donor. The active site as described in Fig. 4(a) may lead to this result. This kind of active site has no magnesium nearby and can hardly be affected by internal donor, and it shows the character like TiCl_3 which produces polymer with broad MWD. From Cat 3 to Cat 1, the increase of the initial magnesium content led to an increasing polypropylene yield. This was because more MgO reacted with TiCl_4 to generate more MgCl_2 , which favored the formation of more active sites. Otherwise, the three different magnesium content catalysts (Cat 1, Cat 2 and Cat 3) showed the same influenced tendency with the cocatalyst concentration, indicating that the preparation process of the catalyst was quite stable, resulting in the same polymerization behaviors of catalysts. It is well known that the Ti-based Ziegler-Natta catalysts are frequently activated by cocatalysts of TIBA and TEA. By comparing the results of runs 2 and 3 in Table 4, it seemed that TIBA was a better cocatalyst for this novel catalyst compared with TEA since the catalyst showed higher activity. The higher catalytic activity produced by TIBA as cocatalyst than TEA was attributed to the bulky isobutyl groups with hinder dimerization which resulted in the higher concentration of aluminum alkyl in the monomeric form. As also demonstrated by our previous work^[18, 19], this made it more efficient in activating the catalyst system^[31].

Table 4 Propylene homopolymerization activities and the characterization results of the homopolymers^a

Run No.	Catalyst	Al/Ti	Activity ^b	T_m ^c (°C)	ΔH_f ^c (J/g)	$M_w^d \times 10^{-5}$ (g/mol)	MWD ^e
1	Cat 1	2.5	1837.9	157.8	69.32	4.1	11.9
2	Cat 1	5	2166.8	157.9	75.31	3.8	14.5
3 ^f	Cat 1	5	1612.1	158.1	58.20	3.1	13.1
4	Cat 1	10	2067.9	158.5	70.01	4.5	12.1
5	Cat 1	20	1892.4	158.6	68.9	4.3	11.2
6	Cat 2	2.5	1747.4	156.6	58.06	4.6	9.8
7	Cat 2	5	2057.6	156.6	65.87	3.8	15.6
8	Cat 2	10	1866.3	157.7	62.74	3.9	14.5
9	Cat 2	20	1812.1	158.7	65.48	4.7	11.1
10	Cat 3	2.5	1731.7	158.3	51.39	2.6	10.5
11	Cat 3	5	1792.3	158.3	60.11	3.3	14.9
12	Cat 3	10	1769.7	159.0	59.27	3.9	12.3
13	Cat 3	20	1304.3	159.3	60.65	3.7	13.8
14	Cat 4	5	216.9	156.1	61.23	—	—
15	Cat 4	10	295.6	156.5	58.12	—	—
16	Cat 4	20	286.7	157.7	58.34	—	—

^a Polymerization conditions: catalyst 100 mg, propylene 0.15 MPa, *n*-heptane 80 mL, TIBA, 50 °C, no ED, 1 h;

^b The unit of catalyst activity is gPP/(gTi·h); ^c T_m and ΔH_f were measured by DSC thermograms; ^d M_w was estimated by GPC; ^e MWD (M_w/M_n); ^f TEA as cocatalyst

The kinetic curves of propylene homopolymerization with these catalysts under the Al/Ti molar ratio of 5 and Cat 1 with different cocatalyst dosages are shown in Fig. 5 and the other homopolymerization curves are shown in Fig. S3 (in SI). It is interesting to see that the kinetic curves showed a smooth increase in the first few minutes and then reached a max value and remained relatively stable, which was totally different from the industrial polypropylene catalyst DQ whose kinetic curves increased rapidly in the first one or two minutes and then decreased quickly as shown in Fig. 6. This indicated that these catalysts had a more stable dynamics during the propylene polymerization compared with MgCl_2 supported catalyst DQ. The reason might be that the three different kinds of active sites formed in this Ziegler-Natta catalyst, as shown in Fig. 4, were different from the MgCl_2 supported catalyst, resulting in different dynamics curves. From the kinetic curves, it seemed that more AlR_3 was needed to initiate the active site of the MgCl_2 supported catalyst at the beginning, while only a small amount of cocatalyst was needed for the Si/Mg composited catalyst. The effects of cocatalyst concentration on the kinetic curves are shown in Fig. 5(b). For Cat 1, it is clearly shown that the kinetic curves were basically of the same stability under different dosages of TIBA.

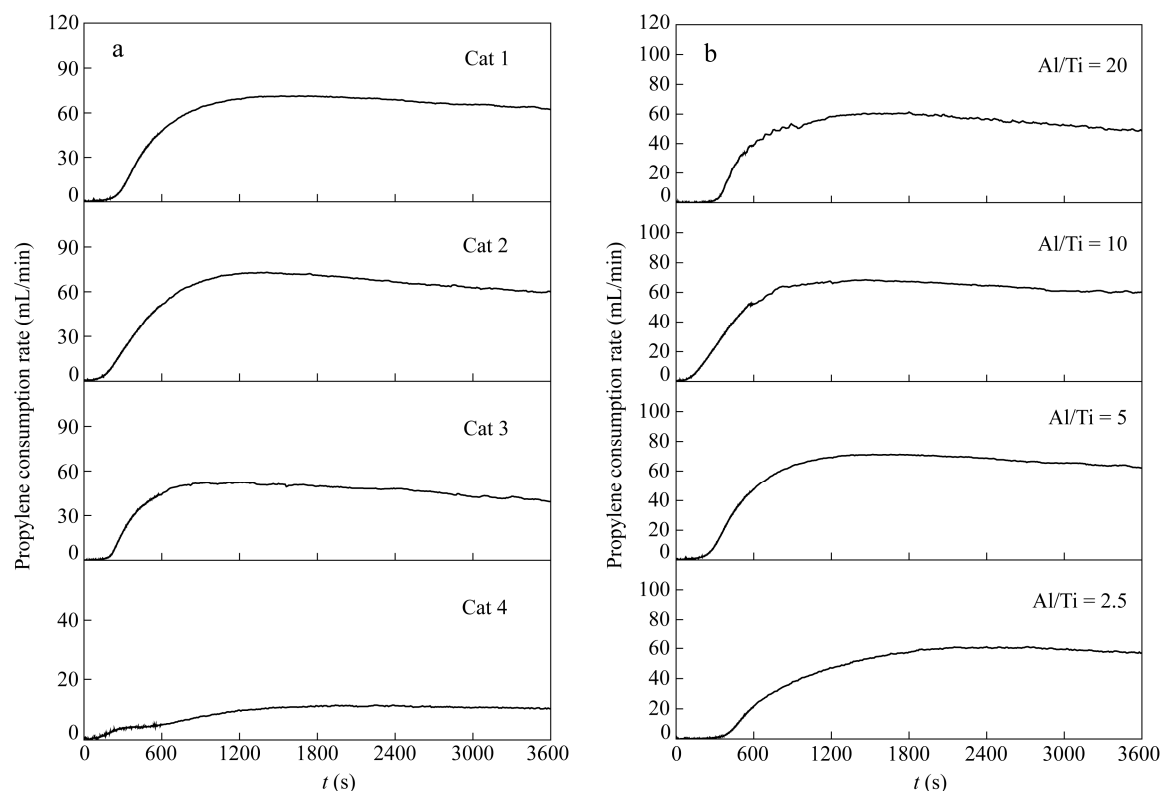


Fig. 5 Kinetic curves of propylene homopolymerization: (a) with different catalysts at the same Al/Ti molar ratio of 5 (corresponding to runs 2, 7, 11, 14 in Table 4), (b) with Cat 1 at different cocatalyst concentrations (corresponding to runs 1, 2, 4, 5 in Table 4)

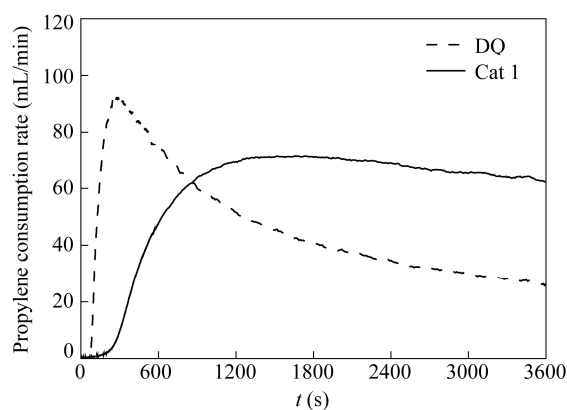


Fig. 6 Kinetic curves of propylene homopolymerization (Polymerization conditions: catalyst $m_{DQ} = 20$ mg and Al/Ti = 100, $m_{Cat1} = 100$ mg and Al/Ti = 5, propylene 0.15 MPa, *n*-heptane 80 mL, TIBA, 50 °C, no ED or H₂.)

Effect of External Donor

The external donor played an important role in the promotion of isotactic degree of PP product^[32]. As is well known, alkoxysilane is usually used as an external donor, and the performance of alkoxysilane is thought to be affected by the number, size and nature of the alkoxy groups on the silicon atom^[33]. In this study, dicyclopentyl dimethoxy silane (D-donor) was used as an external donor. The effect of the amount of D-donor on the performances of these series catalysts was investigated. The results are listed in Table 5. From the results, it can be seen that the external donor showed the effect to improve polymer isotacticity. Moreover, the molecular weight of the polymer increased drastically and the molecular weight distribution was narrowed compared with

the materials produced without an external donor. This was because the change of Si/Ti molar ratio altered the amount of external donor available at the active sites, resulting in slight changes in the stereospecificity and k_p of the activity sites, which might affect molecular weight and molecular weight distribution of the polymer^[34, 35].

The kinetic curves of propylene homopolymerization with Cat 2 under different ED concentrations are shown in Fig. 7 (the kinetic curves of Cat 1 and Cat 3 can be seen in Fig. S5 in SI). It can be clearly seen that the dynamic curves were also stable after adding the external donor, but the propylene consumption rate decreased with increasing concentration of the ED.

Table 5 Effect of external donor concentration and hydrogen on catalyst activities and the characterization results of the homopolymers^a

Run No.	Catalyst	ED (Al/Si)	H ₂ (mL)	Activity ^b	T_m ^c (°C)	X_c ^c (%)	M_w ^d × 10 ⁻⁵ (g/mol)	MWD ^e	II ^f (%)
1	Cat 1	20	—	1203.9	157.9	46.2	9.1	8.0	92.6
2	Cat 1	10	—	638.4	160.5	52.6	9.3	8.3	97.3
3	Cat 1	5	—	431.3	161.7	53.1	9.8	8.1	98.2
4	Cat 1	20	10	1563.2	158.1	49.4	2.5	6.7	93.0
5	Cat 1	10	10	954.7	161.1	53.4	3.6	6.5	98.1
6	Cat 1	5	10	613.4	163.0	57.4	3.2	4.8	98.6
7	Cat 2	20	—	841.6	159.5	40.8	8.6	8.2	92.0
8	Cat 2	10	—	489.2	160.8	42.1	9.3	9.1	97.7
9	Cat 2	5	—	407.9	162.3	45.0	12.2	8.5	98.6
10	Cat 2	20	10	1139.5	161.1	52.5	4.5	6.7	93.9
11	Cat 2	10	10	878.9	162.0	49.5	4.3	8.9	98.2
12	Cat 2	5	10	647.9	164.0	49.4	4.3	6.1	98.9
13	Cat 3	20	—	604.0	161.0	40.7	9.1	9.6	90.9
14	Cat 3	10	—	430.3	161.4	40.8	9.3	8.5	96.8
15	Cat 3	5	—	306.6	162.8	41.7	10.0	7.6	98.5
16	Cat 3	20	10	1178.3	161.5	43.8	3.1	6.2	93.5
17	Cat 3	10	10	560.3	163.0	48.3	4.5	6.6	98.7
18	Cat 3	5	10	538.3	163.1	47.1	4.7	6.1	98.8

^a Polymerization conditions: catalyst 100 mg, propylene 0.15 MPa, *n*-heptane 80 mL, TIBA, 50 °C, 1 h; ^b The unit of catalyst activity is gPP/(gTi·h); ^c T_m and X_c were measured by DSC thermograms; ^d M_w was estimated by GPC; ^e MWD (M_w/M_n); ^f Refluxing in boiling *n*-heptane for 6 h

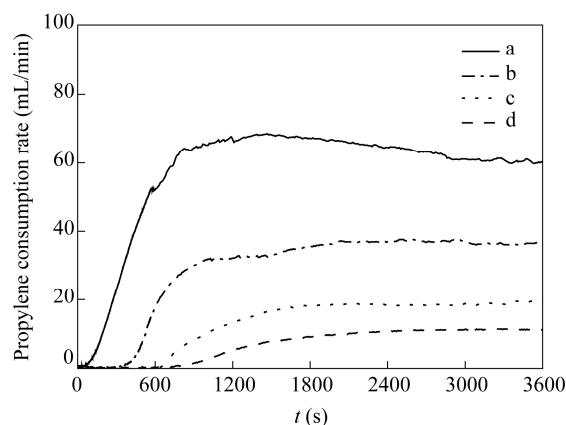


Fig. 7 Kinetic curves of propylene homopolymerization with Cat 2 under different ED concentrations: (a) without ED, (b) Al/Si = 20, (c) Al/Si = 10, (d) Al/Si = 5 (corresponding to runs 7, 8 and 9 in Table 5)

Effect of Hydrogen

Hydrogen was widely used for controlling molecular weight as a chain-transfer agent^[36–38]. The effects of H₂ on these catalysts were studied, and the results are shown in Table 5 (GPC curves are shown in Fig. S4, in SI). It is

observed that the catalyst activity enhanced significantly after adding hydrogen as shown by comparing the results in Table 5. The explanation for such enhancement of the catalyst activity had been proposed in the literature; that is, after a regioirregular (2,1-) insertion of propylene into the growing chain, a species that had a very low reactivity produced with respect to further propagation, which remained dormant until chain transfer when hydrogen was added^[38, 39]. Moreover, the M_w of the products obtained in the condition of H_2 for Cat 2 decreased 47.9% (comparing run 7 and run 10 in Table 5), 53.7% (comparing run 8 and run 11 in Table 5), 64.7% (comparing run 9 and run 12 in Table 5), respectively. Similar effects were also observed for Cat 1 and Cat 3. Therefore, these catalysts exhibited good hydrogen response. According to the isotactic degree results listed in Table 5, the II_v value of the obtained PP was insignificantly affected by H_2 , which was similar to Forte and Coutinho's work^[40]. However, the T_m and X_c values of the PP products increased with the introduction of H_2 , which might be due to the addition of H_2 producing shorter chain of PP, leading to a decrease in the nature and frequency of the steric errors and facilitating more regular PP particles to form.

The kinetic curves for each catalyst with and without hydrogen are shown in Fig. 8. It is significant to see that the kinetic curves for each catalyst presented very similar tendency. In addition, it is interesting to see that the activation period disappeared for all the catalysts, which might be due to a great enhancement of the activity of the catalyst after the addition of H_2 .

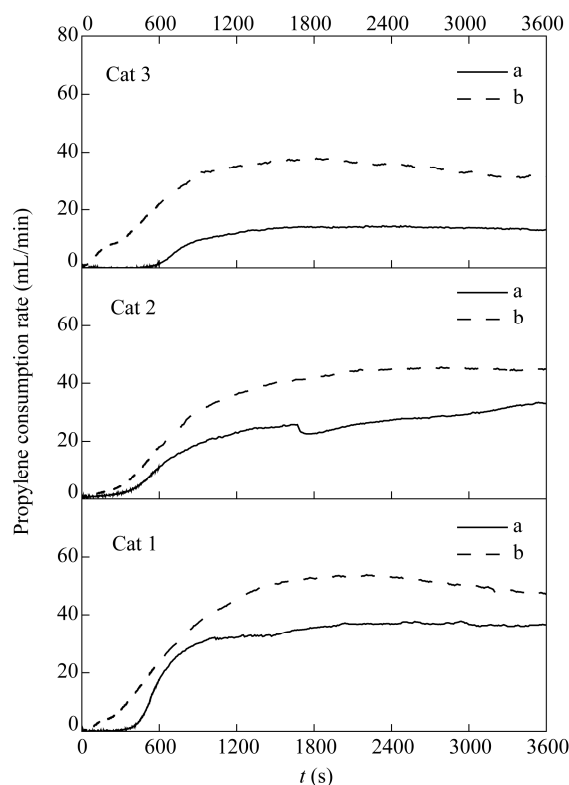


Fig. 8 Kinetic curves of propylene homopolymerization (a) without and (b) with hydrogen (Other polymerization conditions: catalyst 100 mg, Al/Ti = 10, propylene 0.15 MPa, *n*-heptane 80 mL, TIBA, 50 °C, 1 h.)

The influences of an ED and hydrogen were indicated by a closer examination of the molar mass distributions of the materials as illustrated in Fig. 9. The addition of a small amount of the D-donor shifted the entire distribution to higher molar masses and the more D-donor addition also resulted in a further shift in distribution (results of a, b, c, d in Fig. 9). It is also noted that the largest shift observed occurs at the lower molar mass end of the distribution since these kinds of active sites are the prime candidates for modification *via*

external donor addition. On the other hand, the addition of 10 mL of H_2 made the entire distribution shift to low molar masses through the results of c and e. From the GPC curve (Fig. 9), the influence on the molecular weight distribution by the ED and hydrogen could also be clearly identified. Comparing GPC curve a with b, c, and d, the curve narrows after introducing ED, and it becomes even more narrowed after the addition of H_2 .

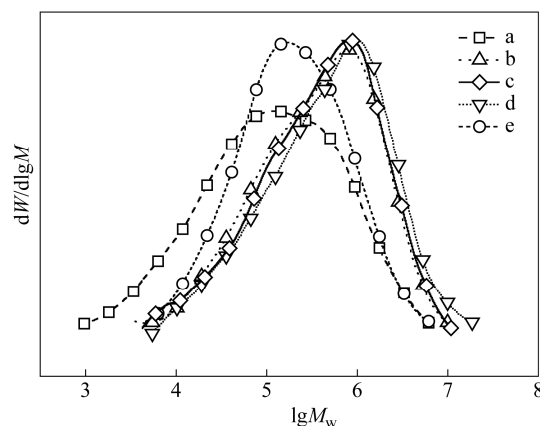


Fig. 9 HT-GPC curves of propylene with different polymerization conditions: (a) Al/Ti = 10, no ED, no H_2 ; (b) Al/Ti = 10, Al/Si = 20, no H_2 ; (c) Al/Ti = 10, Al/Si = 10, no H_2 ; (d) Al/Ti = 10, Al/Si = 5, no H_2 ; (e) Al/Ti = 10, Al/Si = 10, H_2 = 10 mL

TREF Analysis of the Polymer

To achieve a better understanding of the influence of external donor and hydrogen on the catalyst, three PP samples synthesized with different conditions were fractionated by TREF into 9 fractions. The data are presented in Figs. 10 and 11. Figure 10 showed that PP samples produced with an external donor had a significant reduction amount of material eluting at lower temperature ($\leq 40^\circ C$) and an increase at the high temperature ($\geq 115^\circ C$). This presented a clear indication that those active sites producing material which elutes at lower temperatures are affected by introducing the external donor and some atactic active center turned into isotactic activity center. It is also worth noting that the percent of each component eluted below $115^\circ C$ showed a decrease tendency with the increase of ED, and the content of each component eluted above $115^\circ C$ existed with an increasing tendency. If we classify these elution contents into three categories: low isotacticity ($\leq 80^\circ C$), middle isotacticity ($\leq 110^\circ C$) and high isotacticity ($\geq 115^\circ C$), the results discussed above indicate that the ED converted both low and middle isotacticity sites into high isotacticity sites.

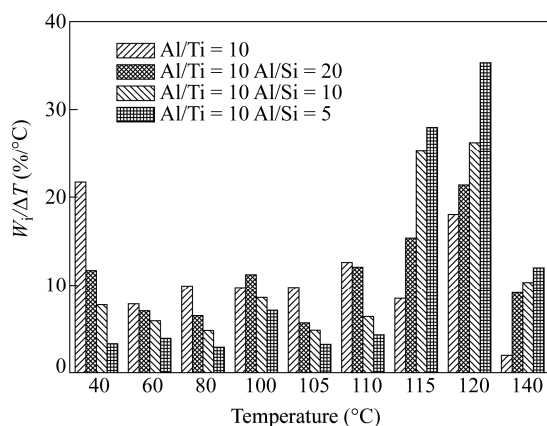


Fig. 10 The distribution of TREF fractions for the samples produced with different dosages of DCPMS

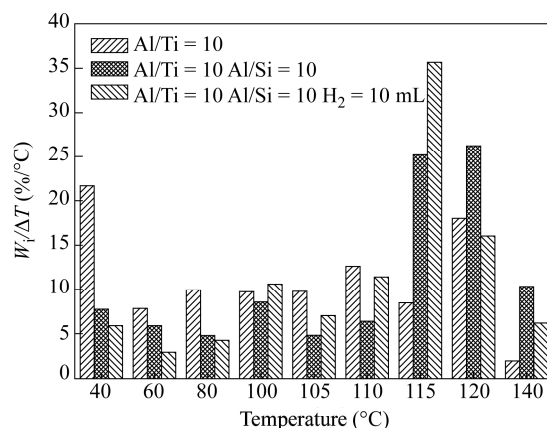


Fig. 11 The distribution of TREF fractions for the samples produced with and without hydrogen

From the results of Fig. 11, we can clearly see the influence of H₂ on the polymers. The materials eluted at high temperature (≥ 120 °C) had a shift to lower eluting temperature. The main eluting content was at 115 °C. This was because the H₂ had a function of chain transfer, which decreased the molecular weight of the polymer chains.

CONCLUSIONS

In this work, we provided a new method for preparing a series of Si/Mg composite supported Ziegler-Natta catalysts for propylene polymerization. Four kinds of internal electron donors were used for the catalyst preparation. The catalysts showed good spherical shape. The polymerization results indicated that the catalyst prepared with BMMF showed much better activity with the best Al/Ti molar ratio of 5, which resulted in great cost saving. Additionally, the polymerization kinetic curves of the catalyst exhibited a very stable increase in the first few minutes and remained stable when the propylene consumption reached a relatively high value. With the increase of the Mg content (from 5 wt% to 15 wt%) in catalyst preparation, the activity showed an increasing tendency. The isotactic index of the PP products could be higher than 98% in the presence of both internal and external electron donors. After adding H₂, the catalyst activity increased distinctly and the catalyst exhibited good hydrogen response. Compared with TEA, TIBA was a better cocatalyst for these novel polypropylene catalysts.

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