

# Effects of Ti/Mg molar ratio on bi-supported SiO<sub>2</sub>/MgCl<sub>2</sub> (ethoxide type)/TiCl<sub>4</sub> catalysts in ethylene homopolymerization and ethylene/1-hexene copolymerization

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## ABSTRACT

SiO<sub>2</sub>/MgCl<sub>2</sub> (ethoxide type)/TiCl<sub>4</sub> Ziegler-Natta catalysts for use in ethylene polymerization and ethylene/1-hexene copolymerization have been prepared using silica with a supported layer of magnesium ethoxide (Mg(OEt)<sub>2</sub>) as a catalyst precursor, followed by treating with TiCl<sub>4</sub> at different Ti/Mg molar ratios, which showed significant effects on the active centers and pore structures of the catalysts. The formation amount of β-MgCl<sub>2</sub> carrier increased to a maximum with increasing the Ti/Mg molar ratio from 1.50 to 2.25, and then decreased with the further increasing of Ti/Mg molar to 2.50. When the Ti/Mg molar ratio reached 2.25, the catalyst showed the best performance of polymerization, which could be attributed to the most active centers, high surface area and loose surface structure, mainly owing to the high conversion of Mg(OEt)<sub>2</sub> to β-MgCl<sub>2</sub>. The polymers obtained showed medium and high molecular weight (Mw) with medium molecular weight distribution (MWD). In contrast to the conventional Mg(OEt)<sub>2</sub>-based ZN catalysts, the sphericity of particles was easy to control in this bi-supported catalyst. Furthermore, the prepared catalysts exhibited rather high activity, good copolymerization ability and hydrogen response. **Polyolefins J (2018) 5: 1-13**

**Keywords:** Polyethylene; magnesium ethoxide; Ti/Mg molar ratio; Ziegler-Natta catalyst; pore structure.

## INTRODUCTION

Polyethylene (PE) is one of the most indispensable materials in the world and widely applied to industrial and agricultural production, medical treatment and health, national defense and people's daily life due to its excellent chemical stability, low temperature resistance and electrical insulation, etc. The successful development of polyethylene is closely related to the development of Ziegler-Natta catalyst which was discovered by Karl

Ziegler and Giulio Natta in 1950s, respectively [1]. Since then, a large number of researches have been done, and therein supported Ziegler-Natta catalysts, namely third-generation Ziegler-Natta catalysts have greatly promoted the development of polyolefin industry, especially the discovery of MgCl<sub>2</sub>-supported catalysts in 1960s [2,3]. So far, Ti/Mg Ziegler-Natta catalysts have been the most widely used catalysts in the industrial production of olefin polymerization because of their high activity of polymerization and good morphology

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control of products.

Ti/Mg Ziegler-Natta catalysts could be classified into two types according to the methods of obtaining MgCl<sub>2</sub> carrier. The first type directly used the magnesium chloride-containing materials (anhydrous MgCl<sub>2</sub>, MgCl<sub>2</sub>·nEtOH, etc.) as Mg-source. Typically, Kashiwa [4] who first discovered MgCl<sub>2</sub>-supported TiCl<sub>4</sub> catalysts in 1968, destroyed magnesium chloride crystal by the addition of n-butanol or methyl acetate and confirmed recrystallization of MgCl<sub>2</sub> by removing the added compound using an excess amount of TiCl<sub>4</sub>. Then, the MgCl<sub>2</sub>-supported TiCl<sub>4</sub> catalyst was successfully prepared and many further researches were done after that [5,6,7]. The second type of Ti/Mg Ziegler-Natta catalysts was characterized by in situ forming MgCl<sub>2</sub> support using the materials (Mg(OEt)<sub>2</sub>, MgR<sub>2</sub>, MgRCl, etc.) as Mg-source during catalysts preparation. Ahmadjo et al. [8] employed C<sub>4</sub>H<sub>9</sub>MgCl as the starting chemical which was mixed with CH<sub>3</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and AlCl<sub>3</sub>, followed by the treatment with TiCl<sub>4</sub>, and the MgCl<sub>2</sub>-supported catalyst was obtained. A productivity of 14700 g PE/mmol Ti·h was obtained at monomer pressure of 8 bar. Taniike et al. [9,10] prepared a novel core-shell type MgO/MgCl<sub>2</sub>/TiCl<sub>4</sub> catalyst for the production of polypropylene using single-crystal MgO nanoparticles as core material which was treated with refluxing TiCl<sub>4</sub> to form the shell. However, the catalysts did not show a highly active polymerization. Fortunately, Liu and co-workers [11,12,13] invented a series of novel (SiO<sub>2</sub>/MgO/MgCl<sub>2</sub>)-TiCl<sub>x</sub> Ziegler-Natta catalysts in that the silica was taken into account, and this kind of catalysts exhibited high activity and low production cost for ethylene polymerization at the expense of sphericity of supported catalyst.

Mg(OEt)<sub>2</sub>-based Ziegler-Natta catalyst was initially discovered by Böhm [14,15], and high-dispersed MgCl<sub>2</sub> support was directly in situ synthesized with the reaction between Mg(OEt)<sub>2</sub> and TiCl<sub>4</sub>. Comparing with anhydrous MgCl<sub>2</sub>, Mg(OEt)<sub>2</sub>-based catalysts showed some advantages due to Mg(OEt)<sub>2</sub> which is chlorine-free and not liable to deliquesce. However, the morphology of the catalyst particle was difficult to control, and many literatures reported about this, recently. Terano et al. [16] dramatically altered the pore structures of Mg(OEt)<sub>2</sub>-based ZN catalysts by the addition of a small amount of i-propanol during

the synthesis of Mg(OEt)<sub>2</sub>. The incorporated i-propanol distorted the crystalline structure of Mg(OEt)<sub>2</sub>, and finally resulted in the phase transformation and densification of particles. The morphology of magnesium could also affect the particle size distribution and sphericity of the prepared Mg(OEt)<sub>2</sub>, and the layered magnesium metal was more likely to form spherical Mg(OEt)<sub>2</sub> particles, which further influenced the morphology of catalysts [17]. SiO<sub>2</sub> is known to be an ideal support with good morphology and thermostability for the preparation of catalysts for use in industrial olefin polymerization. Zohuri et al. [18-21] prepared bi-supported ZN catalysts of SiO<sub>2</sub>/MgCl<sub>2</sub> (ethoxide type)/TiCl<sub>4</sub> by treating calcined SiO<sub>2</sub> and Mg(OEt)<sub>2</sub> with excess TiCl<sub>4</sub> twice in toluene. Furthermore, this kind of catalyst was applied in the production of polyethylene, polypropylene and copolymers.

In this work, a kind of bi-supported SiO<sub>2</sub>/MgCl<sub>2</sub> (ethoxide type)/TiCl<sub>4</sub> type ZN catalysts was synthesized. The catalyst showed a high surface area with a high catalytic activity toward ethylene polymerization and ethylene/1-hexene copolymerization. A specific amount of Mg(OEt)<sub>2</sub> was dissolved in a solvent and impregnated with silica. After drying, a supported layer of magnesium ethoxide (Mg(OEt)<sub>2</sub>) was formed on the surface of silica, and with further reaction with titanium tetrachloride the magnesium dichloride carrier was in situ synthesized and the titanium species was supported simultaneously. A series of catalysts with excellent sphericity were obtained at different Ti/Mg molar ratios. In addition, the effects of Ti/Mg molar ratio on the catalysts in ethylene polymerization and ethylene/1-hexene copolymerization were systematically investigated.

## EXPERIMENTAL

### Raw materials

Magnesium ethoxide (purity 98%) and 1-hexene (total purity 97%) were purchased from J&K Chemical Co. and 1-hexene was used as comonomer after purification through distillation in the presence of sodium. Silica gel (Grace Davison 955) was donated from Qilu Branch Co., SINOPEC. Titanium tetrachloride (AR) was purchased from Ling Feng Chemical Reagent Co., Ltd. n-Hexane (AR), n-heptane (AR), n-octane

(AR), and toluene (AR) were supplied from Sinopharm Chemical Reagent Co., Ltd. and were purged through distillation in the presence of sodium. Methanol (AR) was also purchased from Sinopharm Chemical Reagent Co., Ltd. and was further purified by 4A molecular sieves (purchased from Sinopharm Chemical Reagent Co., Ltd.). High-purity nitrogen ( $N_2 \geq 99.999\%$ ) was further purified by passing through one column of 4A molecular sieves (purchased from Sinopharm Chemical Reagent Co., Ltd.) for dehydration and through one column of silver molecular sieves (28 wt% of silver (I) oxide on alumina, purchased from Sigma Aldrich) for deoxidation. High purity hydrogen ( $H_2 \geq 99.999\%$ ) was supplied from Shanghai Wetry Criterion Gas Co., Ltd. Ethylene monomer was purified by passing through three columns of 4A 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. Triisobutylaluminum (TIBA, 1.0 M in toluene) as cocatalyst was purchased from Alfa Aesar.

### Catalyst preparation

Firstly, about 10 g silica was weighted and put into a fluidized-bed quartz reactor. The reactor was heated to 600°C slowly under a certain temperature-controlling program and maintained for 4 h under a nitrogen flow for thermal activation. After cooling to room temperature, a bottle was used for storage of the activated silica in  $N_2$  atmosphere and transferred into a glove box before use. Secondly, about 5 g activated silica was impregnated with  $Mg(OEt)_2$  dissolved in 150 mL methanol/toluene solution (1/5 v/v) with 15 wt% magnesium content by stirring at 50°C under  $N_2$  for 4 h. The mixture was dried at 120°C under  $N_2$  and the  $SiO_2/Mg(OEt)_2$  sample was obtained and then transferred into a glove box for storage. Thirdly, about 5 g  $SiO_2/Mg(OEt)_2$  mixture was dispersed by stirring in  $N_2$  atmosphere in 100 mL n-octane in a 250 mL three-necked flask equipped with a dropping funnel. A specific amount of titanium tetrachloride (calculated from Ti/Mg molar ratio) was added dropwise to the dispersion at a certain rate at 85°C. Then the reaction system was heated to 120°C and kept for 5 h. After reaction, magnetic stirring was closed and this state was kept

for 10 h. The product was washed several times with n-hexane and then dried under  $N_2$ . The obtained catalyst was transferred into a glove box for storage before use. Hereto, five catalysts (Cat1-Cat5) with different Ti/Mg molar ratios (1.50, 1.75, 2.00, 2.25, 2.50) were prepared for polymerization.

### Ethylene and ethylene/1-hexene polymerization

Ethylene, ethylene/1-hexene and ethylene/hydrogen polymerizations were carried out in a 250 mL three-necked glass flask (i.e. reactor) with a magnetic stirrer at atmospheric pressure. A small ampoule tube with about 100 mg catalysts, which was previously weighed and sealed in the glove box, was connected to a 250 mL three-necked flask placed at a thermostatic bath keeping at 70°C. The reactor system was firstly heated in vacuum and purged by nitrogen for at least three times for 0.5 h, then purged by ethylene monomer for three times and finally filled with monomer until the ethylene pressure was about 0.12 MPa. Then, 70 mL n-heptane and a certain amount of TIBA (Al/Ti molar ratio at 2.5, 5, 10, 15 and 20) were injected into the reactor, and a certain amount of purified 1-hexene (the relative addition amount of purified 1-hexene was defined as the volume ratio between 1-hexene and n-heptane such as 1, 3, and 5 vol%, which were 0.7, 2.1, and 3.5 mL, respectively) or a certain amount of hydrogen (e.g., 10 mL), if necessary, was subsequently injected into the reactor with mechanical stirring. As the solution was saturated at the ethylene pressure of 0.15 MPa, the polymerization was started after opening the sealed catalyst tube and continued for 1 h. The instantaneous consumption of monomeric ethylene was recorded by an on-line mass flow meter (Brooks SAL5851). Finally, the polymerization was terminated by adding 200 mL ethanol/HCl solution and the polymers were collected. All the obtained polymers as mentioned above were washed again with ethanol, filtered out from the solution, and dried under vacuum at 60°C for at least 6 h before weighing.

### Characterization of catalysts

#### *Ion chromatography (IC)*

The chlorine contents of the obtained catalysts were determined by IC using a Dionex DX-600 spectrometer with an AS11-HC column and AERS-500 suppressor.

The suppressed current was 25 mA and the flow rate was 1.0 mL·min<sup>-1</sup>. The injection volume was 25 µL and the mobile phase was KOH.

#### *Inductively coupled plasma (ICP)*

ICP was used to measure the magnesium contents of the prepared catalysts. The power of the ICP spectrometer (Varian 710-ES) was 1.10 kW. The flow rates of plasma gas and auxiliary gas were 15.0 and 1.50 L·min<sup>-1</sup>, respectively. The pressure of nebulizing gas was 200 kPa and the pump speed was 13 rpm.

#### *Ultraviolet-visible spectrophotometer (UV-vis)*

The titanium contents of the obtained catalysts were determined by UV-vis through hydrogen peroxide colorimetric method. The catalyst was dissolved in an acidic media followed by dilution with deionized water to 25 mL. The diluted solution was reacted with H<sub>2</sub>O<sub>2</sub> to form peroxotitanium complex [TiO(H<sub>2</sub>O<sub>2</sub>)]<sup>2+</sup>. UV measurements were carried out in 10 mm quartz glass cells on a Mapada UV-3200 spectrophotometer. The intensity of a peak at 409 nm was used to quantify the titanium content.

#### *Nitrogen adsorption/desorption experiments*

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 (SA) which was calculated based on the Brunauer-Emmett-Teller (BET) method and the pore volume (PV) and average pore diameter (PD) which were evaluated using the Barrett-Joyner-Halenda (BJH) method.

#### *Scanning electron microscopy (SEM)*

Morphological characteristics of the obtained catalysts particles were analyzed by scanning electron microscopy (SEM, Nova Nano SEM 450). All samples were prepared under nitrogen atmosphere and subjected to Pt sputtering for 60s prior to the measurement.

#### *X-ray diffractometry (XRD)*

The crystal information of the obtained catalysts was measured by an X-ray diffractometer (D/MAX 2550 VB/PC). The range of wide angle diffraction 2θ was 5°~75°. The measurement accuracy was Δ2θ < 0.02°.

### **Characterization of polymers**

#### *Differential scanning calorimetry (DSC)*

About 5 mg polyethylene sample was weighted and the DSC experiments were performed on TAQ200 under N<sub>2</sub> atmosphere. The temperature was firstly raised up to 160°C at the rate of 10°C·min<sup>-1</sup> from 40°C and kept for 3 min to eliminate the thermal history, then cooled down to 40°C at 10°C·min<sup>-1</sup>. Finally, the temperature was increased to 160°C again at the rate of 10°C·min<sup>-1</sup> and the DSC curves were collected. Melting temperature (T<sub>m</sub>) and enthalpy of fusion (ΔH<sub>f</sub>) of each sample were calculated by the DSC curve.

#### *High temperature gel permeation chromatography (HT-GPC)*

The molecular weight (MW) and molecular weight distribution (MWD) of the obtained polyethylene were measured by HT-GPC (PL220) with two PL gel-Mix-B columns at 160°C, and the flow rate was 1.0 mL·min<sup>-1</sup>. 1, 2, 4-Trichlorobenzene (TCB) and polystyrene (PS) were used as solvent and standard sample, respectively.

#### *High-temperature <sup>13</sup>C NMR*

The 1-hexene incorporation of the copolymers was measured by high-temperature <sup>13</sup>C-NMR, and each sample (about 100 mg) was transferred into a 5 mm NMR tube with 1,4-dichlorobenzene-d<sub>4</sub> (DCB-d<sub>4</sub>) as the solvent (sample concentration ~15 mg·mL<sup>-1</sup>) and scanned by Varian Inova-400 MHz at 110°C at 100.62 MHz with delay index of 3 s for 10 h. The backbone carbon of the copolymer chain was regarded as the internal reference at 30.00 ppm. The 1-hexene incorporation was calculated in accordance to Seger's work [22].

## **RESULTS AND DISCUSSION**

### **Characterization of catalysts**

Various supported SiO<sub>2</sub>/Mg(OEt)<sub>2</sub>/TiCl<sub>4</sub> catalysts were prepared according to the procedures described in the experimental section. The chemical compositions of these supported catalysts were measured by

**Table 1.** Characterization results of different catalysts.

| Catalyst | Ti/Mg<br>(molar ratio) | Mg <sup>(a)</sup> (wt%) | Ti <sup>(b)</sup> (wt%) | Cl <sup>(c)</sup> (wt%) | Pore Structures <sup>(d)</sup> |                       |        |
|----------|------------------------|-------------------------|-------------------------|-------------------------|--------------------------------|-----------------------|--------|
|          |                        |                         |                         |                         | PV(ml/g)                       | SA(m <sup>2</sup> /g) | PD(nm) |
| Silica   | -                      | -                       | -                       | -                       | 1.63                           | 251.9                 | 18.2   |
| Cat1     | 1.50                   | 4.0                     | 13.33                   | 20.78                   | 0.64                           | 252.3                 | 8.2    |
| Cat2     | 1.75                   | 4.6                     | 13.50                   | 20.97                   | 0.62                           | 237.8                 | 7.9    |
| Cat3     | 2.00                   | 5.4                     | 15.45                   | 21.07                   | 0.62                           | 282.8                 | 8.0    |
| Cat4     | 2.25                   | 5.4                     | 14.86                   | 24.96                   | 0.61                           | 281.4                 | 6.9    |
| Cat5     | 2.50                   | 5.4                     | 15.51                   | 22.15                   | 0.59                           | 287.4                 | 6.5    |

<sup>(a)</sup>Measured by ICP; <sup>(b)</sup>Measured by UV-vis; <sup>(c)</sup>Measured by IC; <sup>(d)</sup>Measured by nitrogen adsorption/desorption experiments.

PD: Average pore diameter; PV: Pore volume; SA: Surface area.

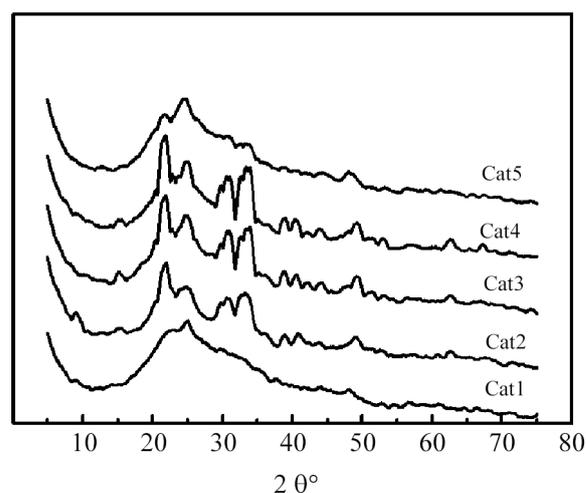
ICP, UV-vis and IC, respectively. The surface area and pore structure parameters of the catalysts were determined by nitrogen adsorption/desorption experiments. All the results are listed in [Table 1](#).

It can be seen that the magnesium contents of the catalysts increase and level off with increasing the Ti/Mg molar ratio. Mg-loading amounts could be related to two phenomena: a) the loading capacity on the surface of SiO<sub>2</sub> had a limitation, resulting in limited Mg-loading and partial Mg-lossing during the catalysts preparation steps including the impregnation and TiCl<sub>4</sub> treatment steps. b) The conversion of Mg(OEt)<sub>2</sub> to MgCl<sub>2</sub> obviously increased with increasing the Ti/Mg molar ratio, which was beneficial for reducing the Mg-lossing. Generally, the active centers of titanium are the key factors which could significantly influence the activity of catalyst. From [Table 1](#), it can be seen that the titanium contents of the SiO<sub>2</sub>/Mg(OEt)<sub>2</sub>-supported catalysts are much higher than those of conventional MgCl<sub>2</sub>-supported Ziegler-Natta Ti-based catalysts, owing to the (OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-bridged complex between the Ti and Mg in these catalysts. Moreover, for the same reason, the titanium contents increased overall with increasing the Ti/Mg molar ratio.

In this study, the conversion of Mg(OEt)<sub>2</sub> to MgCl<sub>2</sub> occurred on the surface of SiO<sub>2</sub>/Mg(OEt)<sub>2</sub> sample. Thus, the series of catalysts were characterized by X-ray diffractometry (XRD) and the results are shown in [Figure 1](#). The strongest diffraction peaks of β-MgCl<sub>2</sub> and TiO<sub>2</sub> were 32° and 25°, respectively. From [Figure 1](#), it can be seen clearly that the formation amount of β-MgCl<sub>2</sub> carrier increases to the maximum with the increasing the Ti/Mg molar ratio from 1.50 to 2.25, and then decreases with the further increasing the Ti/Mg molar to 2.50. It could be inferred that there was

a proper Ti/Mg molar ratio, which permitted to maximize the conversion of Mg(OEt)<sub>2</sub> to β-MgCl<sub>2</sub>. However, the formation amount of TiO<sub>2</sub> increased with increasing the Ti/Mg molar ratio, resulting in decline of the titanium active centers in the loaded titanium and decrease of the average pore diameter (PD), as seen in [Table 1](#).

There was much difference of pore structure parameters except pore volume (PV) among these catalysts. As [Table 1](#) shows, the surface areas increased overall with increasing the Ti/Mg molar ratio and leveled off when the Ti/Mg molar ratio reached to 2.00, which was basically agreed with the trend of Mg-loading amount. The most possible explanation of this phenomenon was that more conversion of Mg(OEt)<sub>2</sub> to MgCl<sub>2</sub> occurred for the SiO<sub>2</sub>/Mg(OEt)<sub>2</sub> sample with increasing the Ti/Mg molar ratio as mentioned above, resulting in higher surface area and less Mg-lossing amount. The surface areas of the obtained catalysts

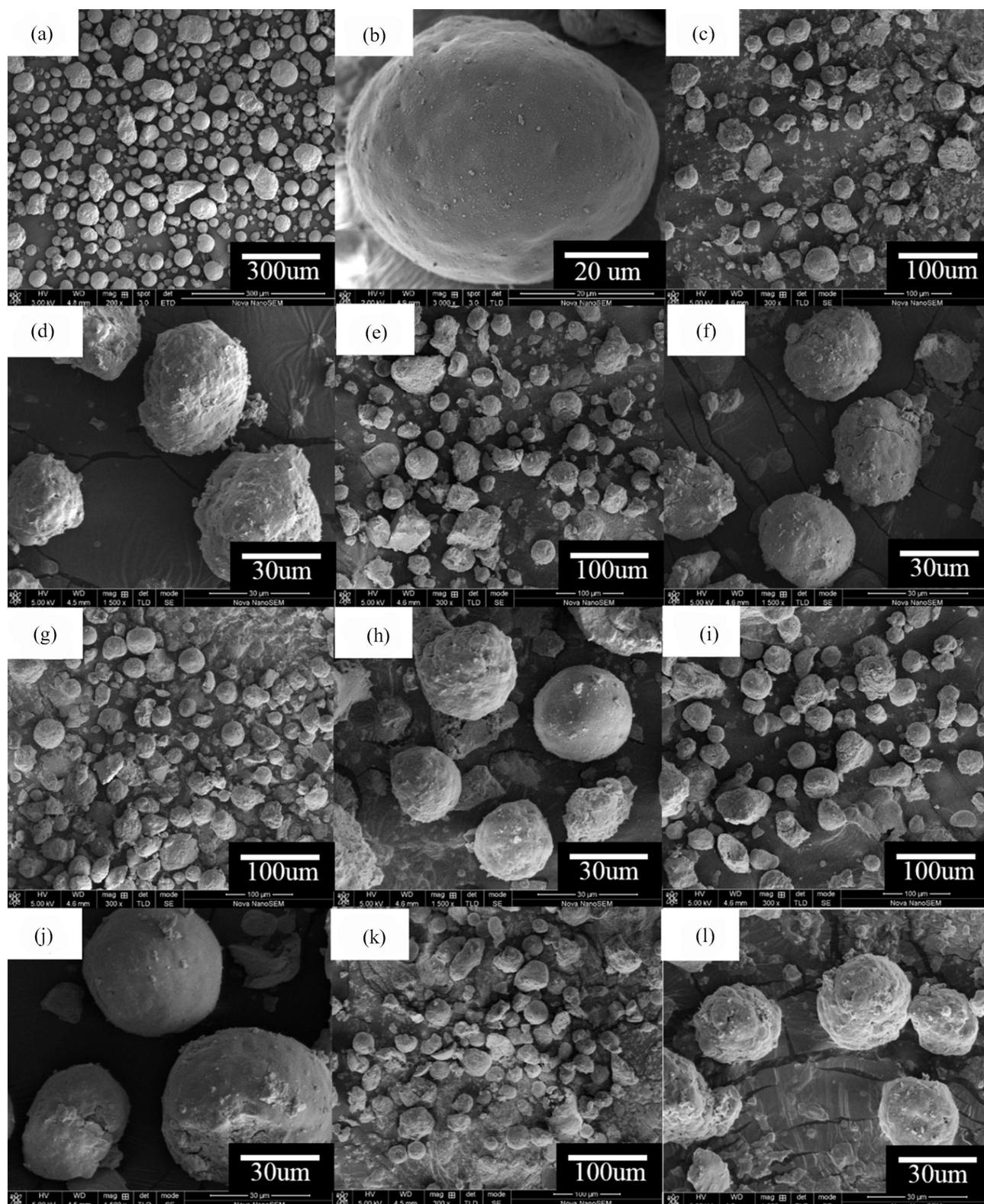


**Figure 1.** XRD of catalysts particles Cat1-Cat5 prepared at Ti/Mg molar ratios of 1.50, 1.75, 2.00, 2.25 and 2.50, respectively.

increased comparing with those of the silica raw material. This could be ascribed to the elevated surface area provided by a large number of active magnesium

chloride carriers during the preparation of catalyst.

The morphology of the obtained catalysts particles were analyzed by SEM and the results are shown in



**Figure 2.** SEM images of catalysts particles: (a,b) Silica gel ( $\times 200$ ,  $\times 3000$ ), (c,d) Cat1 ( $\times 300$ ,  $\times 1500$ ), (e,f) Cat2 ( $\times 300$ ,  $\times 1500$ ), (g,h) Cat3 ( $\times 300$ ,  $\times 1500$ ), (i,j) Cat4 ( $\times 300$ ,  $\times 1500$ ), (k,l) Cat5 ( $\times 300$ ,  $\times 1500$ ).

Figure 2 and Figure 3. From Figure 2, it can be seen that there are many spherical particles which also provide high surface areas in the samples, although some particles are destroyed during the preparation of catalyst.  $\text{SiO}_2$  was taken into account in this catalyst to provide good sphericity and mechanical strength and make the morphology of the  $\text{Mg}(\text{OEt})_2$ -based catalysts easy to control. As Figure 3 shows, the surface structures of these catalysts are loose because of the massive formation of  $\beta\text{-MgCl}_2$ .

### Ethylene homopolymerization and characterization of the homopolymers

The obtained catalysts were first used in ethylene homopolymerization. The homopolymerization activities of the catalysts and the characterization results of the homopolymers are listed in Table 2. From these results, it was found that the activities of the catalysts increased to a maximum and then decreased with increasing the Al/Ti molar ratio. This phenomenon indicated that the proper amount of cocatalyst could improve the activity of the catalyst. The function of

the cocatalyst is well known to reduce and alkylate the transition metal, which can generate a transition metal-carbon bond to initiate the first polymer chain. However, too large amount of cocatalyst may lead to deactivation of the active sites through over-reduction and enhancement of the chain transfer reaction to cocatalyst, which could decrease the activity.

It could be seen that, the highest polymerization activities of these catalysts showed an increasing tendency and then decreased with increasing the Ti/Mg molar ratio and reached to the maximum when the Ti/Mg molar ratio was 2.25. As Table 1 shows, the surface areas of the catalysts increase significantly when the Ti/Mg molar ratio increases from 1.50 to 2.00, resulting in improving availability of titanium and thus increasing activities. The reason of reaching the highest activities to the maximum might be that the more conversion of  $\text{Mg}(\text{OEt})_2$  to  $\text{MgCl}_2$  occurred for the  $\text{SiO}_2/\text{Mg}(\text{OEt})_2$  sample with the further increasing of Ti/Mg molar ratio to 2.25. It was agreed with the related results from the proportion of  $\beta\text{-MgCl}_2$  (Figure 1) and the surface images (Figure 3) as mentioned

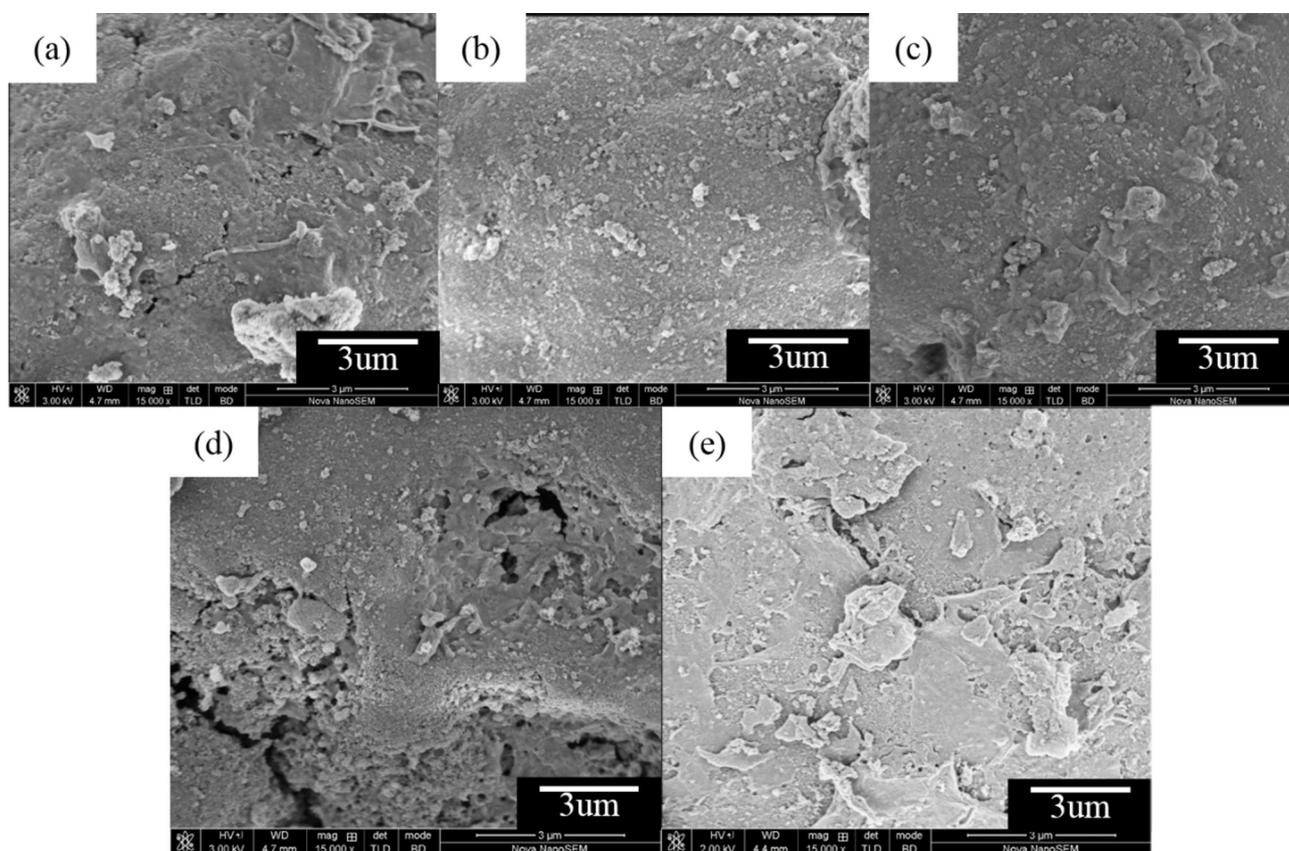


Figure 3. Surface morphology of catalysts: (a) Cat1 ( $\times 15000$ ), (b) Cat2 ( $\times 15000$ ), (c) Cat3 ( $\times 15000$ ), (d) Cat4 ( $\times 15000$ ), (e) Cat5 ( $\times 15000$ ).

**Table 2.** Ethylene homopolymerization activities and characterization results of homopolymers.

| No. | Catalyst | Al/Ti | H <sub>2</sub> (mL) | Activity <sup>(a)</sup> | T <sub>m</sub> <sup>(b)</sup> (°C) | ΔH <sub>f</sub> <sup>(b)</sup> (J·g <sup>-1</sup> ) | M <sub>w</sub> <sup>(c)</sup><br>(×10 <sup>5</sup> g mol <sup>-1</sup> ) | MWD <sup>(d)</sup> |
|-----|----------|-------|---------------------|-------------------------|------------------------------------|---|--|--------------------|
| 1   | Cat1     | 10    | 0                   | 44.50                   | 137.5                              | 164.6   | 5.1  | 3.8                |
| 2   | Cat1     | 20    | 0                   | 54.00                   | 137.7                              | 160.9   | 4.8  | 5.2                |
| 3   | Cat1     | 30    | 0                   | 56.65                   | 137.4                              | 158.0   | 5.1  | 4.1                |
| 4   | Cat1     | 40    | 0                   | 63.62                   | 137.1                              | 163.2   | 4.9  | 4.8                |
| 5   | Cat1     | 40    | 10                  | 45.51                   | 137.4                              | 170.8   | 3.2  | 5.6                |
| 6   | Cat1     | 50    | 0                   | 57.33                   | 137.5                              | 154.2   | 4.8  | 4.4                |
| 7   | Cat2     | 10    | 0                   | 43.54                   | 137.3                              | 162.7   | 5.5  | 3.3                |
| 8   | Cat2     | 20    | 0                   | 54.50                   | 137.1                              | 150.1   | 5.1  | 5.6                |
| 9   | Cat2     | 30    | 0                   | 56.62                   | 137.9                              | 151.8   | 5.2  | 5.7                |
| 10  | Cat2     | 40    | 0                   | 64.14                   | 137.6                              | 148.8   | 5.2  | 5.1                |
| 11  | Cat2     | 40    | 10                  | 54.07                   | 137.1                              | 139.3   | 3.2  | 3.6                |
| 12  | Cat2     | 50    | 0                   | 57.83                   | 137.5                              | 146.3   | 6.2  | 4.9                |
| 13  | Cat3     | 10    | 0                   | 55.74                   | 136.8                              | 169.7   | 5.6  | 3.8                |
| 14  | Cat3     | 20    | 0                   | 56.33                   | 136.8                              | 163.5   | 6.5  | 4.1                |
| 15  | Cat3     | 30    | 0                   | 58.31                   | 137.5                              | 145.9   | 6.2  | 4.7                |
| 16  | Cat3     | 40    | 0                   | 65.58                   | 136.7                              | 151.2   | 5.0  | 4.2                |
| 17  | Cat3     | 40    | 10                  | 47.91                   | 136.7                              | 186.1   | 3.2  | 3.7                |
| 18  | Cat3     | 50    | 0                   | 58.53                   | 136.6                              | 149.5   | 6.5  | 6.3                |
| 19  | Cat4     | 10    | 0                   | 47.81                   | 137.5                              | 140.4   | 4.4  | 3.0                |
| 20  | Cat4     | 20    | 0                   | 52.20                   | 137.3                              | 149.3   | 4.6  | 5.2                |
| 21  | Cat4     | 30    | 0                   | 70.83                   | 137.4                              | 154.3   | 5.0  | 7.6                |
| 22  | Cat4     | 30    | 10                  | 60.91                   | 136.7                              | 146.1   | 3.5  | 5.5                |
| 23  | Cat4     | 40    | 0                   | 65.64                   | 136.8                              | 149.5   | 6.2  | 5.0                |
| 24  | Cat4     | 50    | 0                   | 67.13                   | 137.0                              | 144.3   | 5.1  | 5.0                |
| 25  | Cat5     | 10    | 0                   | 51.80                   | 137.2                              | 159.9   | 4.7  | 4.4                |
| 26  | Cat5     | 20    | 0                   | 53.52                   | 137.2                              | 168.6   | 3.7  | 4.1                |
| 27  | Cat5     | 30    | 0                   | 57.27                   | 137.4                              | 167.0   | 3.2  | 3.4                |
| 28  | Cat5     | 40    | 0                   | 64.02                   | 137.0                              | 157.6   | 3.1  | 3.4                |
| 29  | Cat5     | 40    | 10                  | 51.94                   | 136.7                              | 168.7   | 2.5  | 3.8                |
| 30  | Cat5     | 50    | 0                   | 60.47                   | 136.9                              | 152.4   | 3.1  | 3.1                |

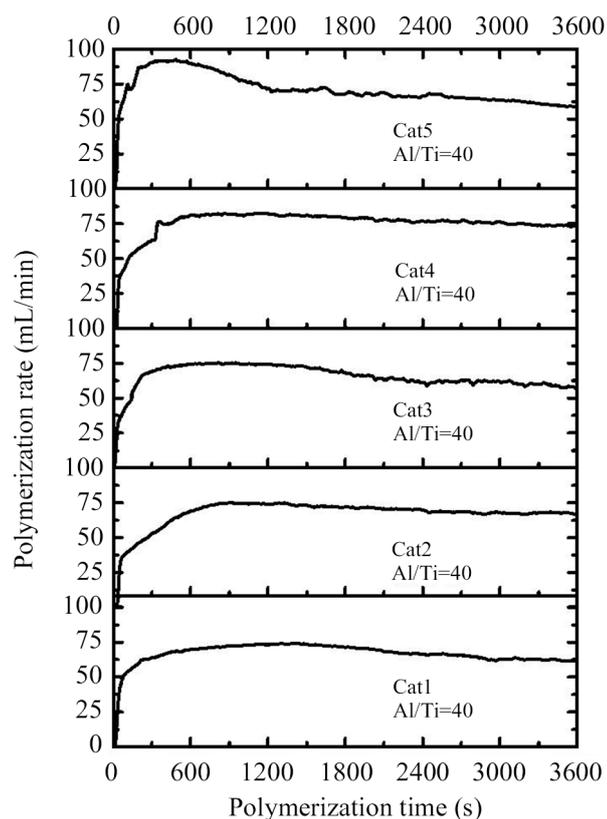
Cat1-Cat5 were prepared at Ti/Mg molar ratios of 1.50, 1.75, 2.00, 2.25 and 2.50, respectively. Polymerization conditions: catalyst 100 mg, ethylene pressure 0.15 MPa, *n*-heptane 80 mL, TIBA, 70 °C, 1 h. <sup>(a)</sup>The unit of catalyst activity is gPE (gcatalyst)<sup>-1</sup> h<sup>-1</sup>; <sup>(b)</sup>T<sub>m</sub> and ΔH<sub>f</sub> were measured by DSC; <sup>(c)</sup>M<sub>w</sub> was estimated by HT-GPC; <sup>(d)</sup>MWD (M<sub>w</sub>/M<sub>n</sub>).

before. The highest activity of the catalyst (Cat5) decreased when the Ti/Mg molar ratio continued to rise to 2.50. The possible explanation is that the average pore size (PD) further decreased, which was not beneficial for the insertion of monomer and growth of polymer in the polymerization.

The influences of these catalysts on the homopolymerization were further investigated by the characterization of the polymers using DSC and HT-GPC. From Table 2 (GPC curves are presented in the Supporting Information as Figure S1), it can be found that T<sub>m</sub> and ΔH<sub>f</sub> of the polymers are almost the same and the crystallinity of the polymers is relatively high. The GPC results showed that the homopolymers were all medium and high MW PE with medium MWD except the polymers obtained from Cat5, which showed lower MW. One possible explanation was that

the relative narrow PD of Cat5 blocked the growth of polymers in the polymerization as mentioned before.

All of the kinetic curves of homopolymerization with different catalyst at different Al/Ti mole ratio were shown in Figure S2 in Support Information. Figure 4 showed the kinetic curves of ethylene homopolymerization with this series of catalysts at their optimal Al/Ti molar ratio. It can be seen that the tendency of these curves is almost the same. The ethylene consumption rate increased relatively slowly in the initial period of polymerization and showed high level on the whole, since the catalysts had a large number of active sites like Mg(OEt)<sub>2</sub>-based catalysts [23]. By comparing with the other catalysts, it could be seen that the maximum polymerization rate of Cat5 was higher than that of the other catalysts, but the activity decreased significantly along with proceeding of the polymer-



**Figure 4.** Kinetic curves of ethylene homopolymerization with different catalysts at their optimal Al/Ti molar ratios: Cat1-Cat5 were prepared at Ti/Mg molar ratios of 1.50, 1.75, 2.00, 2.25 and 2.50, respectively. Polymerization conditions: catalyst 100 mg, ethylene pressure 0.15 MPa, *n*-heptane 80 mL, TIBA, 70 °C, 1 h.

ization. One possible explanation of this phenomenon might be that many active centers were initiated to polymerize at the beginning of the polymerization, owing to its high surface area and titanium contents. However, the chemical stability of partial active centers was low, which might result in the decrease of polymerization rate.

### Ethylene/1-hexene copolymerization and characterization of the copolymers

It is known that the copolymers of ethylene with  $\alpha$ -olefins often show good mechanical properties. Thus, the ethylene/1-hexene copolymerization was investigated to research the copolymerization properties of the catalysts and the results are listed in Table 3. The activities of the catalysts increased first by the addition of 1-hexene and then decreased with the further increasing of co-monomer concentration as many literature reported. The explanations of the phenomenon can mainly be summarized into two parts: a) the addition of comonomer into the polymerization could enhance the stability of the active sites, leading to the increase of polymerization activity, and b) the incorporation of comonomer might reduce the crystallinity of the surrounding polymer layer, resulting in

**Table 3.** Ethylene copolymerization activities and characterization results of copolymers.

| No. | Catalyst | Al/Ti | 1-Hexene (vol%) | Activity <sup>(a)</sup> | $T_m^{(b)}$ (°C) | $\Delta H_f^{(b)}$ (J·g <sup>-1</sup> ) | $M_w^{(c)}$ ( $\times 10^5$ g mol <sup>-1</sup> ) | MWD <sup>(d)</sup> |
|-----|----------|-------|-----------------|-------------------------|------------------|---|---|--------------------|
| 1   | Cat1     | 40    | 0               | 63.62                   | 137.1            | 163.2                                   | 4.9   | 4.8                |
| 2   | Cat1     | 40    | 1               | 58.78                   | 128.0            | 126.7                                   | 3.2   | 7.3                |
| 3   | Cat1     | 40    | 3               | 77.74                   | 125.8            | 84.8                                    | 2.9   | 11.4               |
| 4   | Cat1     | 40    | 5               | 70.68                   | 125.3            | 71.7                                    | 2.3   | 11.8               |
| 5   | Cat2     | 40    | 0               | 64.14                   | 137.6            | 148.8                                   | 5.2   | 5.1                |
| 6   | Cat2     | 40    | 1               | 73.21                   | 128.0            | 117.0                                   | 3.2   | 6.6                |
| 7   | Cat2     | 40    | 3               | 82.14                   | 125.8            | 72.4                                    | 2.8   | 9.2                |
| 8   | Cat2     | 40    | 5               | 78.17                   | 124.7            | 32.4                                    | 2.5   | 9.8                |
| 9   | Cat3     | 40    | 0               | 65.58                   | 136.7            | 151.2                                   | 5.0   | 4.2                |
| 10  | Cat3     | 40    | 1               | 69.77                   | 127.7            | 128.8                                   | 3.6   | 5.4                |
| 11  | Cat3     | 40    | 3               | 85.83                   | 125.4            | 82.9                                    | 2.5   | 5.7                |
| 12  | Cat3     | 40    | 5               | 81.43                   | 124.6            | 54.3                                    | 2.8   | 7.7                |
| 13  | Cat4     | 30    | 0               | 70.83                   | 137.4            | 154.3                                   | 5.0   | 7.6                |
| 14  | Cat4     | 30    | 1               | 78.36                   | 128.8            | 110.5                                   | 3.2   | 5.1                |
| 15  | Cat4     | 30    | 3               | 85.25                   | 125.5            | 79.4                                    | 2.4   | 11.0               |
| 16  | Cat4     | 30    | 5               | 83.48                   | 125.4            | 47.4                                    | 2.6   | 8.3                |
| 17  | Cat5     | 40    | 0               | 64.02                   | 137.0            | 157.6                                   | 3.1   | 3.4                |
| 18  | Cat5     | 40    | 1               | 64.87                   | 127.8            | 127.4                                   | 2.1   | 6.1                |
| 19  | Cat5     | 40    | 3               | 72.55                   | 126.0            | 88.9                                    | 2.3   | 6.4                |
| 20  | Cat5     | 40    | 5               | 68.10                   | 125.2            | 67.7                                    | 1.7   | 7.1                |

Cat1-Cat5 were prepared at Ti/Mg molar ratios of 1.50, 1.75, 2.00, 2.25 and 2.50, respectively. Polymerization conditions: catalyst 100 mg, ethylene pressure 0.15 MPa, *n*-heptane 80 mL, TIBA, 70 °C, 1 h. <sup>(a)</sup>The unit of catalyst activity is gPE (gcatal)<sup>-1</sup> h<sup>-1</sup>; <sup>(b)</sup> $T_m$  and  $\Delta H_f$  were measured by DSC; <sup>(c)</sup> $M_w$  was estimated by HT-GPC; <sup>(d)</sup>MWD ( $M_w/M_n$ ).

accelerating the diffusion of monomers [24, 25].

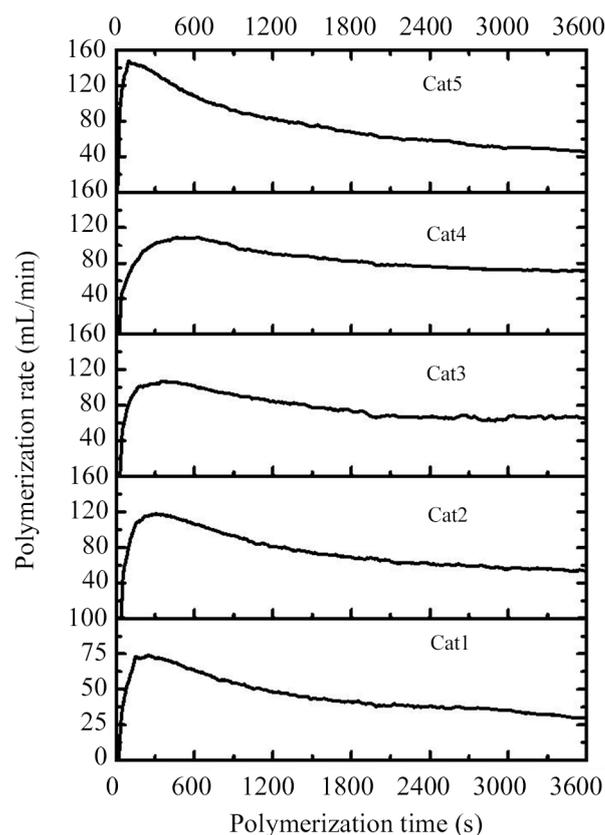
By comparing the copolymerization activities of different catalysts, Cat4 showed the best copolymerization ability overall. From the DSC characterization results listed in Table 3, the  $T_m$  and  $\Delta H_f$  of the copolymers decreased significantly with the increasing addition concentration of 1-hexene. The GPC characterization results in Table 3 (GPC curves are given in Figure S3 in the Supporting Information) showed that the molecular weight decreased obviously with the increasing addition concentration of 1-hexene from 0 to 5 vol%. The reason of the phenomenon was more incorporation of 1-hexene with increasing the 1-hexene concentration. Furthermore, the MW of the copolymers obtained from Cat5 was lower than that of the others at the same concentration of 1-hexene.

All of the kinetic curves of copolymerization with different catalysts at different Al/Ti mole ratios are shown in Figure S4 in the Support Information. Figure 5 shows the kinetic curves of ethylene/1-hexene copolymerization with 3 vol% of 1-hexene at the optimal Al/Ti molar ratios. All these curves show the similar tendency that the ethylene consumption rate increases obviously first and then decreases. In addition, the kinetic curve of Cat4 is relatively stable with less decrease of polymerization rate.

The results of 1-hexene incorporation of the copolymers synthesized with 3 vol% of 1-hexene measured by high-temperature <sup>13</sup>C NMR are listed in Table 4 (<sup>13</sup>C NMR spectra are given in Figure S5 in the Supporting Information). It can be seen that, Ti/Mg molar ratio has an influence on the incorporation of 1-hexene of the copolymers obtained from these catalysts, and the copolymer of Cat4 has the highest incorporation of 1-hexene.

### Effect of hydrogen

In this work, the influences of hydrogen on the series



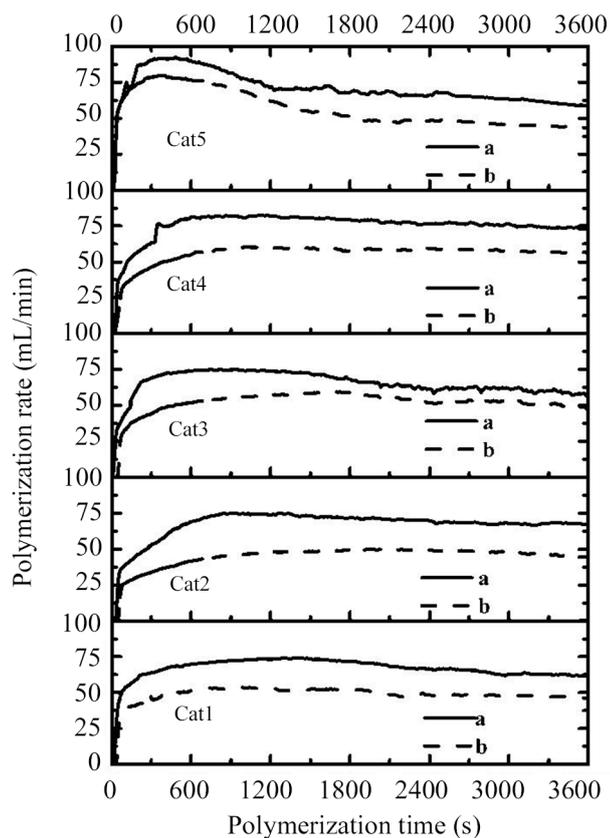
**Figure 5.** Kinetic curves of ethylene/1-hexene copolymerization with the catalysts at their optimal Al/Ti molar ratio with 3 vol% of 1-hexene: Cat1-Cat5 were prepared at Ti/Mg molar ratios of 1.50, 1.75, 2.00, 2.25 and 2.50, respectively. Polymerization conditions: catalyst 100 mg, ethylene pressure 0.15 MPa, n-heptane 80 mL, TIBA, 70°C, 1 h.

of obtained catalysts were investigated at their optimal Al/Ti molar ratio. The polymerization activities and characterization results are listed in Table 2 (GPC curves are given in Figure S6 in the Supporting Information). From the results, it can be seen that the activities and  $M_w$  both are decreased significantly by the addition of 10 mL H<sub>2</sub>, which is agreed with literature data [26]. The MW of the polymers obtained from Cat1-Cat5 decreased 34.7%, 38.5%, 36.0%, 30.0% and 19.4%, respectively, and it indicated that this series of catalysts all showed good hydrogen

**Table 4.** 1-Hexene incorporation content of the copolymers obtained from different catalysts.

| No. | Catalyst | Ti/Mg molar ratio | 1-Hexene (vol%) | Activity <sup>(a)</sup> | 1-Hexene incorporation <sup>(b)</sup> (mol%) |
|-----|----------|-------------------|-----------------|-------------------------|--|
| 1   | Cat1     | 1.50              | 3               | 77.74                   | 4.92   |
| 2   | Cat2     | 1.75              | 3               | 82.14                   | 4.14   |
| 3   | Cat3     | 2.00              | 3               | 85.83                   | 4.22   |
| 4   | Cat4     | 2.25              | 3               | 85.25                   | 5.16   |
| 5   | Cat5     | 2.50              | 3               | 72.55                   | 4.78   |

<sup>(a)</sup>The unit of catalyst activity is gPE (gcat)<sup>-1</sup> h<sup>-1</sup>; <sup>(b)</sup>1-Hexene incorporated in the copolymers measured by <sup>13</sup>C NMR.



**Figure 6.** Hydrogen effect on kinetics of ethylene polymerization with catalysts at their optimal Al/Ti molar ratios: -a without H<sub>2</sub>; -b with H<sub>2</sub>; Cat1-Cat5 were prepared at Ti/Mg molar ratios of 1.50, 1.75, 2.00, 2.25 and 2.50, respectively. Polymerization conditions: catalyst 100 mg, ethylene pressure 0.15 MPa, n-heptane 80 mL, TIBA, 70 °C, 1 h.

response except Cat5. In addition, the  $T_m$  and  $\Delta H_f$  of the polymers with hydrogen changed slightly. Figure 6 shows the kinetic curves for these different catalysts with and without H<sub>2</sub>. It can be seen that, the kinetic curves with and without H<sub>2</sub> for each catalyst shows a similar tendency and the extent of polymerization rate decrease with hydrogen is quite close. So far, it still needs further research to understand and explain the complicated hydrogen effect completely.

## CONCLUSION

In this study, a series of SiO<sub>2</sub>/MgCl<sub>2</sub> (ethoxide type)/TiCl<sub>4</sub> type Ziegler-Natta catalysts were prepared using silica with a supported layer of magnesium ethoxide (Mg(OEt)<sub>2</sub>) as a catalyst precursor, followed by treating with TiCl<sub>4</sub> at different Ti/Mg molar ratios. Then

the effects of Ti/Mg molar ratio on these catalysts were systematically investigated by ethylene homopolymerization, ethylene/1-hexene copolymerization and hydrogen effect. The titanium contents of the catalysts were all much higher than those of conventional Ziegler-Natta Ti-based catalysts, owing to the (OC<sub>2</sub>H<sub>5</sub>)-bridged complexation between the Ti and Mg in these catalysts. The formation amount of  $\beta$ -MgCl<sub>2</sub> carrier increased to a maximum with increasing the Ti/Mg molar ratio from 1.50 to 2.25, and then decreased with the further increasing of Ti/Mg molar to 2.50. With the increasing of Ti/Mg molar ratio, the surface areas (SA) of the catalysts increased first and then leveled off, and the average pore diameters (PD) showed a decreasing tendency owing to the formation of TiO<sub>2</sub>. Furthermore, the surface areas of Cat3, Cat4 and Cat5 were higher than those of silica. With the increasing of Ti/Mg molar ratio, the highest homopolymerization activities of these catalysts increased first and then decreased, and the maximum at 2.25 of Ti/Mg molar ratio was achieved with high activity of atmospheric ethylene polymerization. The highest copolymerization activities were all achieved with 3 vol% of 1-hexene, besides Cat4 showed the best copolymerization ability with high incorporation of 1-hexene. The GPC results showed that the homopolymers obtained from these catalysts had medium and high average MW with medium MWD. As mentioned above, the Ti/Mg molar ratio had a significant influence on the pore structures of the catalysts, and Cat4 showed the best performance of ethylene homopolymerization and ethylene/1-hexene copolymerization with relatively high incorporation of 1-hexene due to its high surface area and suitable average pore diameter with the most conversion of Mg(OEt)<sub>2</sub> to MgCl<sub>2</sub>. Furthermore, from the XRD results, the contents of TiO<sub>2</sub> and MgCl<sub>2</sub> were the most important influencing factors of the catalyst performance. In this initial study, the catalysts have not been investigated systematically from many aspects, such as reaction temperature and reaction time, which affect the contents of TiO<sub>2</sub> and MgCl<sub>2</sub> so much, so the catalyst still has greater potential to further research, and the details on the optimization of the catalyst and high pressure polymerization will be reported in the next paper.

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