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ORIGINAL PAPER

Imido-modified SiO_2-supported Ti/Mg Ziegler-Natta catalysts for ethylene polymerization and ethylene/1-hexene copolymerization

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ABSTRACT

A novel imido-modified SiO_2-supported Ti/Mg Ziegler-Natta catalyst for ethylene and ethylene/1-hexene polymerization is investigated. The catalyst is prepared by modification of $(SiO_2/MgO/MgCl_2)TiCl_x$ Ziegler-Natta catalysts via supporting vanadium species followed by reaction with p-tolyl isocyanate as imido agents, to get the merits from both the SiO_2-supported imido vanadium catalyst and the $(SiO_2/MgO/MgCl_2)TiCl_x$ Ziegler-Natta catalyst. The effects of cocatalyst amount, hydrogen and dosage of 1-hexene on the polymerization behavior and the microstructures of their polymers are systematically investigated. Compared with $(SiO_2/MgO/MgCl_2)TiCl_x$ Ziegler-Natta catalysts and vanadium-modified $(SiO_2/MgO/MgCl_2)TiCl_x$ Ziegler-Natta catalysts, the imido-modified SiO_2-supported Ti/Mg catalysts show lower but more stable activity for homopolymerization, polymerization with hydrogen and copolymerization owing to imido ligands, indicating that p-tolyl isocyanate is unfavorable for improving catalytic activity but beneficial for the stability, and the products of all catalysts show lower 1-hexene incorporation but much higher molecular weight (MW) with medium molecular weight distribution (MWD). The most unique feature of the novel catalysts is the excellent hydrogen response without lowering the polymerization activity, showing great potential for industrial application. **Polyolefins J (2016) 3: 103-117**

Keywords: Ziegler-Natta catalyst; imido V compound; ethylene polymerization; polymerization kinetics; copolymerization

INTRODUCTION

Amongst polyolefins, polyethylene (PE) is the fastest growing and widely used bulk commodity plastic material in multiple aspects of our daily life including pipe materials, containers, packaging, automobile parts, laboratory equipments and etc. Although more recent researches focus on metallocene catalysts discovered by Kaminsky et al., Ziegler-Natta catalysts still constitute the largest proportion of current industrial polyethylene production. Since the breakthrough discoveries during early 1950s by Karl Ziegler and Giulio Natta, Ziegler-Natta catalysts have got great progress and become indispensable catalysts for industrial production.

Lots of works on Ziegler-Natta catalysts including several important literatures and patents published by Kashiwa[1-3], Galli[4, 5], Böhm[6], Stevens and George[7], Taniike and co-workers[8], which involved advances in ZN catalysts have been published. Besides, companies like UCC Company [9] used Ti/Mg ZN

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catalyst, based on anhydrous $MgCl_2$ and SiO_2 bi-support, represented by M-1 catalyst in UNIPOL gas-phase polyethylene process, and also BP Company[10] utilized alkyl magnesium (MgR_2) as starting Mg-source, followed by reacting with SiO_2 and $TiCl_4$ to synthesize Si/Mg bi-support catalyst for industrial polyolefin production. In our previous work, Wang et al.[11] developed a novel ($SiO_2/MgO/MgCl_2$)$TiCl_x$ Ziegler-Natta catalyst for ethylene and ethylene/1-hexene polymerization which exhibited high activity, good hydrogen response and copolymerization ability. The method was simple and cost-effective.

In the research area of Ziegler-Natta olefin polymerization, classic vanadium-magnesium catalysts ($VOCl_3/MgCl_2$, $VCl_4/MgCl_2$), named as VMC [12-17], showed lower activity in ethylene polymerization than titanium-magnesium catalysts (TMC), which might be attributed to very quick deactivation of active sites, resulting from the reduction of vanadium (III) to vanadium (II), the latter was not active in polymerization reaction. However classic Ziegler-type vanadium catalysts displayed unique characteristics regarding the regulation of molecular structure of PE and copolymers of ethylene with α-olefin. Unlike TMC, VMC produced PE with broad MWD had a very high hydrogen response and provided an effective control of PE molecule mass in ethylene polymerization with hydrogen. These were the reasons for the increasing interests in the use of vanadium-based catalysts for ethylene polymerization as well as ethylene/α-olefin copolymerization.

Several literatures have also been published regarding the vanadium-modified catalysts to improve catalytic activity and polymer branching. Matta et al. [8] synthesized various hetero-bimetallic Phillips catalysts. They found that vanadium and zirconium were considered as potential candidates for the best hetero-bimetallic Phillips catalyst. Cheng et al. [18] prepared a novel SiO_2-supported chromium oxide(Cr)/vanadium oxide(V) bimetallic catalyst for producing bimodal polyethylene. Zhao et al. [19] investigated the addition of vanadium composition to the traditional SiO_2-supported Cr-based UCC S-2 catalyst. They found that the activity and polymer branching were both improved. Additionally, Wang et al. [20] synthesized vanadium-modified ($SiO_2/MgO/MgCl_2$) $TiCl_x$ Ziegler-Natta catalysts. The results showed that the introduction of vanadium species could improve the catalyst performance including activity, hydrogen response and 1-hexene incorporation ability.

On the other hand, transition metal imido complexes having the general formula [(L)nM(NR)] (where M is the transition metal, and (L)n is a supporting ligand, and R typically is alkyl or aryl) have been known since the late 1950s[21, 22]. Because of the high π-donor strength, the imido group promoted high oxidation state coordination and organometallic chemistry as a spectator ligand, both the structural and reaction chemistry of metal imido compounds could be profoundly changed by modification of the N-substituent. The imido ligand was found to be a useful supporting ligand in group 4-6 metal catalysts. Much attention has been paid to the imido vanadium catalysts for olefin polymerization by many researchers. The first example of an imido-supported olefin polymerization catalyst was reported by Gibson et al. in 1994[23, 24], and Kress et al. [25] reported a series of imido vanadium complexes supported by tris(pyrazolyl)borate ligands for ethylene polymerization in 1995, which were immobilized onto various inorganic supports by Santos et al. [26]. Ghosh[27] found that the imido vanadium catalyst supported on the SiO_2 with MAO as the cocatalyst had higher activity than that supported on other supports. Nomura and Zhang[28] focused on high oxidation state imido vanadium complexes containing anionic ancillary donor ligands because olefin coordination onto the highest oxidation state vanadium-alkyl complexes would be suitable for the subsequent insertion. In our lab, Zhao et al. [29] investigated the modification of vanadium oxides on the silica with organic isocyanate to synthesize the supported imido-vanadium catalyst based on the SiO_2-suported Cr-V bimetallic catalysts which improved ethylene polymerization activity significantly. The search for new long-lasting catalytic system based on vanadium and maintaining the most desirable characteristics should, therefore, be oriented towards design of new ligand systems.

Here, it could be summarized that it was a matter of account to modify the vanadium-modified (SiO_2/$MgO/MgCl_2$)$TiCl_x$ Ziegler-Natta catalyst with organic isocyanate to obtain a novel imido-modified SiO_2-supported Ti/Mg Ziegler-Natta catalyst for ethylene and ethylene/1-hexene polymerization for higher catalytic activity with better polymer performance. In this work, the effects of cocatalyst amount, hydrogen and dosage of 1-hexene on polymerization behavior and the microstructures of their polymers have been systematically investigated. By characterization of the catalysts and polymers, investigation on the polymerization behavior, several key factors such as the vanadium component, the concentration of cocatalyst, the dosage of 1-hexene and hydrogen, which could influence the properties of novel catalysts and their polymers, have been also systematically investigated.

EXPERIMENTAL

Raw materials

In this work, silica gel (Grace Davison 955, surface 282.3 $m^2.g^{-1}$, pore volume 1.64 $cm^3.g^{-1}$ and average pore size 17.5 nm, donated by Qilu Branch Co., SINOPEC) was employed as support.

Prior to use, the high-purified nitrogen (≥99.999%) was further purified by passing through one column of 4A molecular sieves (purchased from Sinopharm Chemical Reagent Co., Ltd.) for dehydration and one column of sliver molecular sieves (28 wt% of silver(I) oxide on alumina, purchased from Sigma-Aldrich) for deoxidation. In addition, hydrogen (≥99.999%) and high-purified dry air (total impurity <1 ppm, dew point of H_2O <−80°C) were purchased from Shanghai Wetry Criterion Gas. Co., Ltd.

Magnesium acetate tetrahydrate ($C_4H_6O_4Mg•4H_2O$, AR) and ammonium metavanadate (NH_4VO_3, AR) as vanadium precursors were purchased from Sinopharm Chemical Reagent Co., Ltd., while p-tolyl isocyanate as imido agents was purchased from Alfa Aesar. Titanium(IV) chloride ($TiCl_4$, 99 wt%) and hydrochloric acid (HCl, AR grade) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd and used without any further treatment.

All the solvents including n-hexane (AR grade), n-heptane (AR grade) and toluene (AR grade), which were all purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd, were firstly purified by 4A molecular sieves and subsequently purged through distillation in the presence of sodium metal slices and diphenyl ketone as an indicator until the indicator showed pure blue before use or for storage in a stainless-steel storage tank under purified nitrogen.

Ethylene monomer used for ethylene and ethylene/1-hexene polymerization was purified by subsequently 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. 1-Hexene (total purity 97%) as comonomer was purchased from J&K Chemical Co. and also purged through distillation in the presence of sodium and diphenyl ketone as an indicator until the indicator showed pure blue and transferred into storage tank under purified nitrogen before use. Triisobutylaluminium (TIBA, 1.0 mol L^{-1} solution in n-hexane) as cocatalyst was purchased from J&K Chemical Co.

Catalyst preparation

All experiments were performed under nitrogen using standard Schlenk, vacuum-line, or inert-atmosphere box techniques.

Firstly, silica was calcined in a fluidized bed reactor in purified nitrogen at 300°C, and cooled to ambient temperature before use. Typically about 10 g calcined silica was impregnated in an aqueous solution of water-soluble magnesium acetate tretrahydrate and ammonium metavanadate with a magnetic stirrer at 65°C. The Mg loading content was constant at 5 wt%, while Mg/V molar ratio was 5:1 (2.1 wt% V) which showed the best performance in our previous work. The slurry was stirred for approximately 4 h, then heated to 120°C and dried in air for 12 h. After that, it was placed in a fluidized-bed quartz reactor with a temperature-programmed heating controller and electric furnace around it and heated to 600°C with a flow rate of 600 $mL.min^{-1}$ in high-purified dry air for 4 h before it was sealed.

Secondly, a Schlenk flask was charged with about 100 mL purified toluene as solvent, the catalyst prepared above and p-tolyl isocyanate (molar ratio of p-tolyl isocyanate and V was 1:1) as imido agents. The mixtures were refluxed and continuously stirred for 20 h at 120°C in the purified nitrogen till complete reaction. Then the solvent was removed at 120°C under dry nitrogen for 5 h and in vacuum for 30 min. The catalyst was cooled down and transferred into a glove box.

Thirdly, under nitrogen protection, about 2 g catalyst prepared above was transferred into a three-necked flask with a magnetic stirrer, then about 30 mL titanium(IV) chloride ($TiCl_4$, 99wt%) was injected. The mixtures were refluxed and stirred for approximately 2 h at 145°C before they were cooled to room temperature and stilled for 10~20 min without agitation. Then, the supernatant liquid was removed and the precipitates were washed with about 30~40 mL purified n-hexane 5 times. While the residual solvent was removed at 145°C under dry nitrogen for 1.5 h and in vacuum for 30 min. In the end, i-Mg/V/Ti/Si catalyst was cooled down, prepared and transferred into a glove box.

For comparison, another two catalysts namely, i-Mg/Ti/Si catalyst (5 wt% Mg, without vanadium component, the volume of p-tolyl isocyanate determined by theoretical vanadium content with respect to magnesium content) and i-V/Ti/Si catalyst (2.1 wt% V, without magnesium component) were prepared with the impregnation of silica with an aqueous solution of water-soluble magnesium acetate tretrahydrate or ammonium metavanadate, respectively. The following procedures were the same as mentioned above.

Ethylene, ethylene/1-hexene and ethylene/hydrogen polymerizations

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.

Catalyst characterization

Ultraviolet spectrophotometer

The titanium contents of the synthesized catalysts were determined by ultraviolet-visible spectrophotometer (UV-Vis) through hydrogen peroxide colorimetric method. The supported catalysts were dissolved in an acidic media followed by reaction with H_2O_2 to form a yellow peroxotitanium complex $[TiO(H_2O_2)]^{2+}$, then diluted with double distilled water to 25 mL. UV-visible spectra of the resultant solution of complexes were recorded on a MAPADA UV3200 type ultraviolet spectrophotometer. The peak intensity at 409 nm was used to quantify the titanium contents.

Inductively coupled plasma spectrometry (ICP)

In order to determine the fully supporting of Mg and V active species on the surface of silica gel, ICP characterizations of catalysts prepared were conducted. 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 $L.min^{-1}$ and 1.50 $L.min^{-1}$, respectively. The pressure of the nebulizing gas was 200 kPa and pump speed was 13 rpm.

Ion chromatography (IC)

The chlorine contents of the prepared catalysts were determined by ion chromatography using a Dionex DX-600 spectrometer with AS11-HC column and AERS-500 suppressor. The suppressed current was 25 mA and the flow rate was 1.0 $mL.min^{-1}$. The injection volume was 25 μL and the mobile phase was KOH.

Fourier transform infrared spectroscopy (FTIR)

About 10 mg of the catalyst sample was weighed out, mixed with KBr (sample: KBr=1:100,w/w), and pressed into a small sample disc for scanning by FTIR spectrometer (Bruker,Vertex70) with 4 cm^{-1} resolution and 32 accumulation cycles to record the IR spectroscopy.

Scanning electron microscopy (SEM)

The surface morphology observation of all the catalysts was performed by a high resolution scanning electron microscope (Nova Nano SEM 450). Samples were coated with a 1.5 nm Pt-layer before testing to improve the conductivity.

Brunner-Emmet-Teller (BET) measurements

Nitrogen adsorption-desorption isotherms were measured at 77 K using an automatic micropore physisorption analyzer (Micromeritics ASAP 2020, USA). Prior to measurements, all the samples were degassed under a vacuum at 573 K for 6 h. The specific surface area (SBET) was calculated based on the BET method, and the pore volume (Vp) and average pore size (d) were evaluated using the Barrett-Joyner-Halenda (BJH) method.

Polymer Characterization

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

The molecular weight (MW) and molecular weight distribution (MWD) of polymers were measured by HT-GPC (Agilent PL-220) with two PL Gel-Olexis columns at 160°C, and the flow rate was 1.0 mL.min^{-1}. 1, 2, 4-Trichlorobenzene (TCB) and polystyrene (PS) were used as solvent and standard sample, respectively.

Differential scanning calorimetry (DSC)

About 5 mg PE sample was weighted and then heated to 165°C at the rate of 10°C.min^{-1} for 5 min to remove thermal history, then cooled down to 40°C at 10°C.min^{-1} and finally heated to 165°C at 10°C.min^{-1} using a DSC analyzer (TA, DSC Q200) to record the second heating curve and melting temperature (T_m). The enthalpy of fusion (ΔH_f) of each sample was calculated by the DSC curve.

High temperature ^{13}C NMR

The 1-hexene incorporation was measured by high temperature ^{13}C NMR. Each sample (about 100 mg) was equipped into a 5 mm NMR tube with 1,4-dichlorobenzene-d4 (DCB-d_4) as a solvent (sample concentration: ca. 15 mg.mL^{-1}) and scanned by a Varian Inova-400 MHz at 110°C at 100.62 MHz with delay index of 3 s for 10 h. The carbon backbone of the polymer chain was regarded as the internal reference at 30.00 ppm. The inserted 1-hexene content of each sample was calculated according to normalized integrating area in the ^{13}C NMR spectrum according to Seger's work for reference [30].

RESULTS AND DISCUSSION

Catalysts characterization

It has been widely accepted that catalytic performances of catalysts largely depend on their preparation processes and conditions. Before catalysts are used, it is important to first characterize them and investigate the influence of preparation conditions on the nature of catalysts. In this work, three catalysts prepared were investigated by the subsequent six characterization methods.

The catalysts were characterized by UV, ICP and IC to evaluate their element contents. The magnesium and vanadium contents of the catalysts were determined by inductively coupled plasma, titanium contents by ultraviolet-visible spectroscopy, and chlorine contents by ion chromatography. The initial and actual loadings of titanium, magnesium and vanadium in these catalysts are all listed in Table 1. It could be seen that both Mg and V actual loadings in those catalysts before reaction with $TiCl_4$ were largely less than the initial values. The loading loss might be due to the limitation of the silica gel loadings capacity during preparation procedures namely, impregnation, calcination and reaction with p-tolyl isocyanate. Compared with those catalysts before reaction with $TiCl_4$, catalysts after reaction with $TiCl_4$ showed part of Mg- and V- loss, which could attribute to the interaction with high concentration $TiCl_4$. On the other hand, as a significant factor which could greatly affect the activities of the catalysts, the Ti contents of these three SiO_2-supported catalysts varied a lot, 4.02 wt%, 4.52 wt%, and 5.56 wt%. From comparison of i-V/Ti/Si and i-Mg/V/Ti/Si, adding Mg component increased both actual Ti content and Cl content, while from i-Mg/Ti/Si and i-Mg/V/Ti/Si, the Ti content and Cl content were also increased with the addition of V component. One

Table 1. The initial and actual loadings of Ti, V and Mg in different catalysts.

Catalyst	Initial loading[wt%]		Actual loading[wt%]			
	Mg	V	Ti$^{(a)}$	Mg$^{(b)}$	V$^{(b)}$	Cl$^{(c)}$
i-Mg/Si	5	--	--	3.5	--	--
i-Mg/Ti/Si	5	--	4.02	3.2	--	4.43
i-V/Si	--	2.1	--	--	1.8	--
i-V/Ti/Si	--	2.1	4.52	--	1.0	3.07
i-Mg/V/Si	5	2.1	--	3.5	1.8	--
i-Mg/V/Ti/Si	5	2.1	5.56	3.5	1.4	5.93

$^{(a)}$ Measured by UV-VIS; $^{(b)}$ Measured by ICP; $^{(c)}$ Measured by IC reasonable explanation might be the refluxing reaction of catalyst precursors containing magnesium oxide and vanadium oxide with p-tolyl isocyanate and $TiCl_4$ consecutively. While the reactions between catalyst precursors with p-tolyl isocyanate were verified by the releases of carbon dioxide making the clear limewater turbid during the preparation processes. Then further reaction with $TiCl_4$ could generate insoluble complexes during the experimental procedures. The molar ratio of V element and p-tolyl isocyanate was 1:1, so adding Mg component resulted in more conversion of MgO to $MgCl_2$ (Mg/V molar ratio was 5) occurred for the catalyst precursors that containing magnesium oxide during the refluxing reaction with excess $TiCl_4$, thus enhanced the adsorption of active species of titanium and upgraded Cl content. Under the condition of adding V element, more undesired p-tolyl isocyanate/$TiCl_4$ insoluble complexes or titanium imido complexes [31] could be generated, improving the titanium supporting, which was reflected by the increase of Cl content and would be explained later.

The FTIR method was used to further confirm the reaction between the imido agents and catalyst precursors. The IR spectra are shown in Figure 1. According to the results, the strong absorbance at 1091 cm^{-1} was attributed to the Si-O-Si stretch of silica, and the absorbances at 1630 and 3417 cm^{-1} were assigned to the surface hydroxyl groups of silica. Additionally, the intensity of the band at 3600-3200 cm^{-1}, was referred to the stretching vibrations of -OH groups. As expected, the isocyanate stretch at ~2270 cm^{-1} was absent in the catalysts indicating that the isocyanate groups were completely reacted. Meanwhile, the bands of 3050 and 1460 cm^{-1} belonged to the stretching and asymmetric bending bands of the CH_3 in the p-tolyl ligand. It indicated that the imido groups were successfully introduced on our catalysts. In the case of i-Mg/Ti/Si without V components, p-tolyl isocyanate possibly reacted with magnesium oxide or the silica. However, for the later the signals corresponding to the C=O and C-N stretches of the formed carbamate linkages between the silica and the isocyanate at 1635cm^{-1} and 1150cm^{-1} might be likely merged with the band of surface hydroxyl groups of silica and Si-O-Si band, respectively. On the other hand, the reaction between catalyst precursors with $TiCl_4$ generated insoluble complexes during the catalyst preparation procedure, manifesting that imido ligands actually affected titanium active centers.

Particle morphological characteristics of catalyst particles were observed by scanning electron microscopy as shown in Figure 2. Only a small number of prepared catalysts particles had spherical shapes, indicating replication of the spherical SiO_2 particles. But it was notable that most of the particles showed cracked structures, which might happen due to the severe stirring process with a magnetic stirrer during the complicated preparation process including impregnation and reaction with p-tolyl isocyanate and $TiCl_4$. In addition, agglomerates of catalyst particles or irregular shapes were present, which possibly resulted from the contact of catalyst particles with moisture and oxygen during the testing process or particle agglomeration during the preparation process[32]. The loss in the spherical morphologies of raw SiO_2 particles for catalyst particles was disadvantageous to the catalyst system.

The N_2 absorption/desorption measurements for supported catalysts were taken under the same condition. The results in terms of surface area, pore volume, and average pore size are listed in Table 2. The pore structures results showed that the surface area, pore volume and pore size of all the catalysts including before and after reaction with $TiCl_4$ decreased obviously compared with the original SiO_2 raw material (Grace Davison 955, surface 282.3 m^2/g, pore volume 1.64 cm^3/g and average pore size 17.5 nm). Huang et al. [33] discussed the reasons for the decrease of pore structure parameters of catalysts. The results showed that MgO depositing on the surface of silica might block some micro-pores thus lower the measured surface area and the fragmentation of

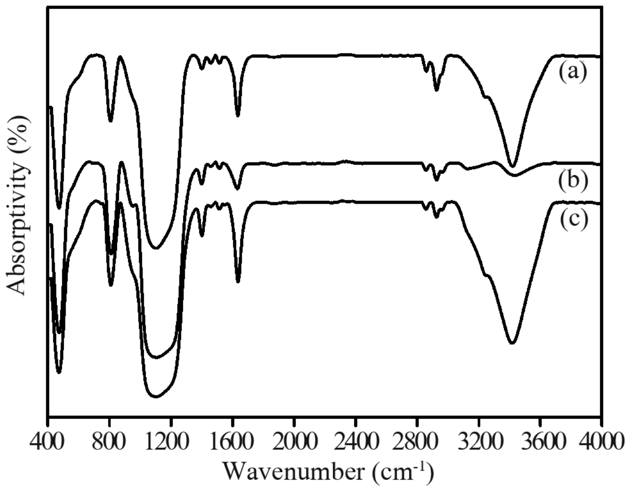
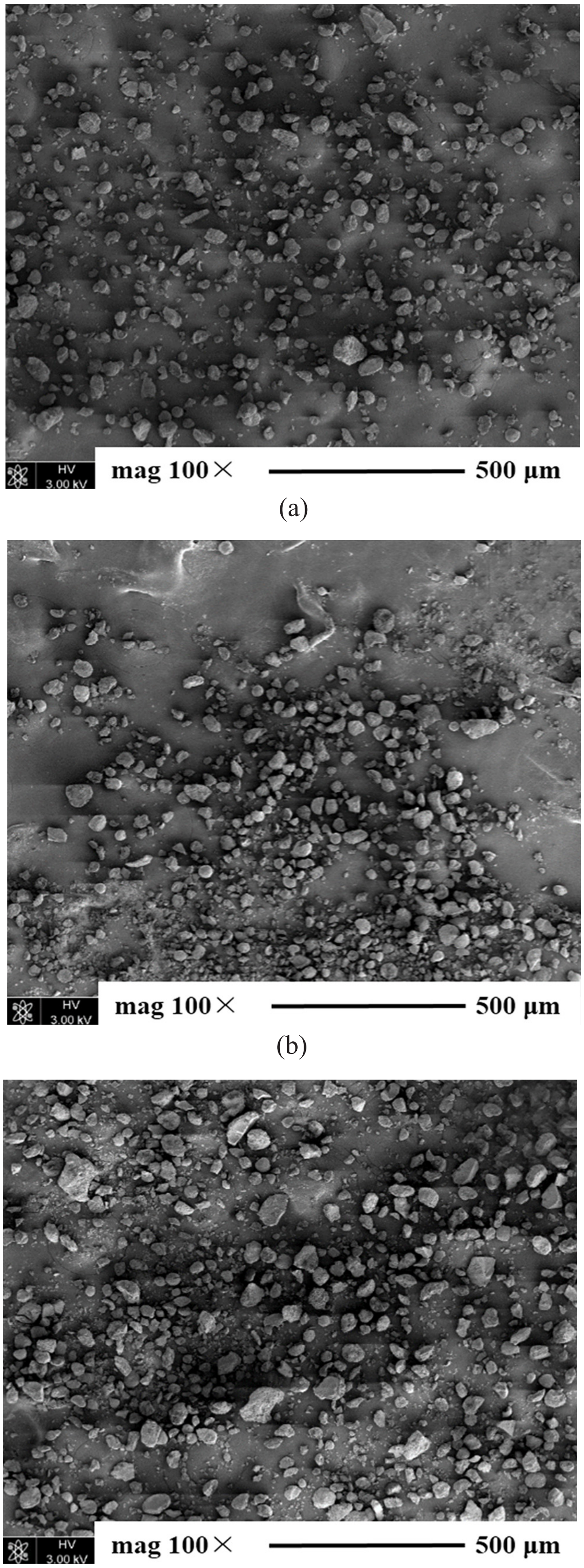


Figure 1. IR spectra of different catalysts. (a) i-Mg/Ti/Si, (b) i-V/Ti/Si, (c) Mg/V/Ti/Si catalyst.



(a)

(b)

(c)

Figure 2. SEM micrographs of the (a) i-Mg/Ti/Si; (b) i-V/Ti/Si; (c) i-Mg/V/Ti/Si catalyst.

catalyst particles resulted in obvious decrease of pore volume and average pore size. Thus, the decrease in pore structure parameters was more likely attributed to the supporting of catalytic components on catalyst surface and fragmentation of catalyst particles during catalyst preparation. The pore volume and surface area of the catalysts were largely decreased after reaction with high concentration of $TiCl_4$, although the average pore size basically kept unchanged, indicating that the catalysts were actually influenced by the interaction with $TiCl_4$. Otherwise, with the introduction of magnesium and vanadium in the catalysts, the average pore size, pore volume and surface area were all reduced on the whole due to the particle agglomeration or the pore blocking by loadings. These results corresponded to element contents analysis results, which might be not beneficial for the catalyst performances.

The homopolymerization and copolymerization of catalysts

These different SiO_2-supported Ti-based catalysts were used in ethylene homopolymerization. The alkyl aluminum concentration largely affected the polymerization kinetics through activation and deactivation of titanium species, so the dosage of cocatalyst became an important factor in this course. And the addition of vanadium was also considered to be a vital factor.

The activities of three SiO_2-supported Ti-based catalysts with different dosages of TIBA and polymers characterization are shown in Table 3. Ethylene homopolymerization activities of different catalysts with different Al/Ti molar ratio are shown in Figure 3. The Al/Ti molar ratio was set from 2.5 to 20. It was found that with the increase of Al/Ti molar ratio, the activity of i-Mg/Ti/Si and i-Mg/V/Ti/Si increased to a maximum value and then decreased in the range of Al/

Table 2. Comparison of surface area, pore size and pore volume of different catalysts by BET.

Sample	Average Pore Size (nm)	Pore Volume (cm^3/g)	Surface Area (m^2/g)
i-Mg/Si	17.7	1.14	199.7
i-Mg/Ti/Si	17.1	0.78	119.0
i-V/Si	15.1	1.11	216.1
i-V/Ti/Si	16.0	0.87	165.3
i-Mg/V/Si	15.2	1.02	195.3
i-Mg/V/Ti/Si	16.0	0.64	118.8

Ti molar ratio. For i-V/Ti/Si, the homopolymerization activity decreased with the increase of cocatalyst from Al/Ti molar ratio of 2.5 to 20. To further confirm the effect of cocatalyst, the ethylene polymerization was conducted at Al/Ti molar ratio of 1 with i-V/Ti/Si, the ethylene consumption rate was much lower than that at Al/Ti=2.5 (Figure S1 in Supporting Information). Tiny amounts of samples were obtained. The proper dosage of cocatalyst was very likely at Al/Ti molar ratio between 1 and 2.5. The results indicated that the proper amount of cocatalyst could enhance the activity of the catalyst. Because the roles of cocatalyst were well known to reduce and alkylate the transition metal-carbon to initiate the first polymer chain[34] and scavenge impurities[32]. But too large amount of cocatalyst could lead to deactivation of the active site through over-reduction and the chain transfer reaction to cocatalyst was also enhanced, which was not beneficial for catalytic activities[2].

Al/Ti molar ratio of 5 was used as the optimal amount of cocatalyst in the homopolymerization with i-Mg/Ti/Si. However, for i-Mg/V/Ti/Si, the optimal amount of cocatalyst was upgraded to 10. It was due to that with the adding of vanadium active species, more cocatalyst was needed to reduce the vanadium precursors. For our novel catalysts, Ti contents were affected by Mg loadings reflected by ICP and UV results. Therefore, the introduction of Mg in the catalyst was considered to be another important factor in the polymerization. Compared with i-V/Ti/Si, i-Mg/V/Ti/Si required more cocatalyst than i-V/Ti/Si by the reason of higher Ti loading for magnesium chloride carrier. Moreover, the activity of i-Mg/V/Ti/Si was higher than that of i-Mg/Ti/Si and i-V/Ti/Si, and i-V/Ti/Si showed the lowest. These results might suggest that adding vanadium component could improve the homopolymerization activity and Ti species supported through the Si-O-Ti linkage in i-V/Ti/Si might be a kind of low active Ti species. On the other hand, the activities of these novel catalysts were reduced after the modification of imido agents in comparison with the original systems [11, 20] (referring to $(SiO_2/MgO/MgCl_2)TiCl_x$ Ziegler-Natta catalysts and vanadium-modified $(SiO_2/MgO/MgCl_2)$ $TiCl_x$ Ziegler-Natta catalysts). The only difference during the preparation between those two catalyst systems was the introduction of p-tolyl isocyanate. The most possible reason was the insoluble complexes of low activity formed by the reaction of $TiCl_4$ and catalyst precursors in the catalyst preparation process owing to the imido ligands.

The kinetic curves of ethylene polymerization with i-Mg/Ti/Si, i-V/Ti/Si and i-Mg/V/Ti/Si with the same Al/Ti molar ratio of 10 are shown in Figure

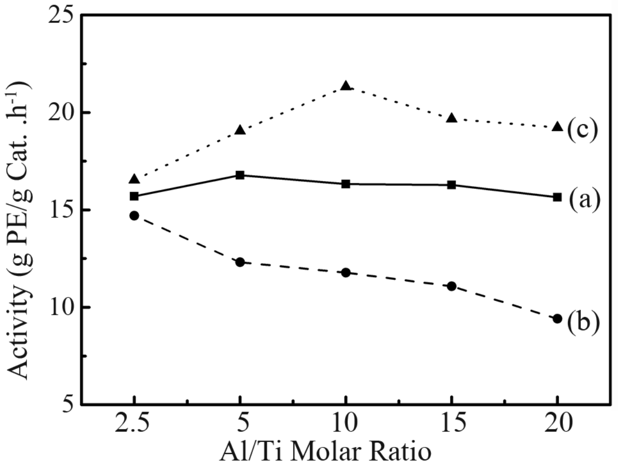


Figure 3. Ethylene homopolymerization activities of different catalysts with different Al/Ti molar ratio. (a) i-Mg/Ti/Si; (b) i-V/Ti/Si; (c) i-Mg/V/Ti/Si. Conditions: catalyst 100 mg, ethylene 0.15 MPa, n-heptane 70 mL, TIBA, 1 h.

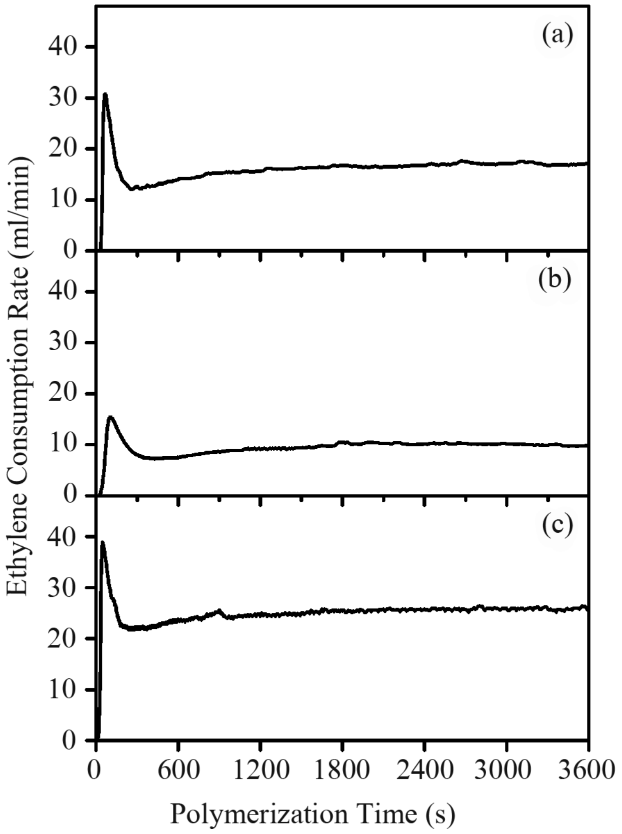


Figure 4. Kinetic curves of ethylene homopolymerization activities of different catalysts with the same Al/Ti molar ratio of 10 (corresponding to Run 3, 12, 21; (a) i-Mg/Ti/Si; (b) i-V/Ti/Si; (c) i-Mg/V/Ti/Si). Conditions: catalyst 100 mg, ethylene 0.15 MPa, n-heptane 70 mL, TIBA, 1 h.

4. It was found that the kinetic curves of ethylene homopolymerization with these catalysts were similar (Supporting Information Figure S2, S3, and S4) but different from the original systems, showing a rapid increase to the maximum within 1 to 2 minutes followed by a rapid deactivation, then kept an increasing tendency. The kinetic profile of the polymerization reaction depended on many factors, including the nature of monomer, pre-catalyst, cocatalyst, temperature, and the presence of modifying agents. However, the rate of catalyst decay depended on the catalyst type and increased with temperature. One of the possible reasons for catalyst deactivation was the reduction of active Ti^{3+} to Ti^{2+} or/and V^{3+} to V^{2+}[35].

Table 3. Ethylene polymerization activities of different catalysts and characterization of their polymers. Conditions: catalyst 100 mg, ethylene 0.15 MPa, n-heptane 70 mL, TIBA, 70°C, 1 h; (a) T_m and ΔH_f by DSC thermograms; (b) M_w estimated by HT-GPC in TCB; (c) Polydispersity index (M_w/ M_n).

Run	Sample	Al/Ti	H_2 [ml]	1-hexene [vol%]	Activity [g PE/g Cat.·h^{-1}]	T_m $^{(a)}$ [°C]	ΔH_f $^{(a)}$ [J/g]	M_w $^{(b)}$ [×10^5g/mol]	MWD $^{(c)}$
1	i-Mg/Ti/Si	2.5	0	0	15.7	133	157	18.8	5.0
2	i-Mg/Ti/Si	5	0	0	16.8	133	153.5	18.0	5.1
3	i-Mg/Ti/Si	10	0	0	16.3	133	161.1	17.3	5.8
4	i-Mg/Ti/Si	15	0	0	16.2	134	153.8	17.2	5.2
5	i-Mg/Ti/Si	20	0	0	15.7	134	147.8	18.4	5.0
6	i-Mg/Ti/Si	5	10	0	16.4	134	169.8	13.3	4.7
7	i-Mg/Ti/Si	5	0	1	17	128	139.3	16.0	5.2
8	i-Mg/Ti/Si	5	0	3	25.1	125	113.3	14.4	5.9
9	i-Mg/Ti/Si	5	0	5	26.1	125	103.3	14.0	6.5
10	i-V/Ti/Si	2.5	0	0	14.7	133	149.6	17.6	4.6
11	i-V/Ti/Si	5	0	0	12.3	133	143.6	18.0	4.5
12	i-V/Ti/Si	10	0	0	11.8	133	143.6	18.7	4.8
13	i-V/Ti/Si	15	0	0	11.1	134	142.6	17.3	5.3
14	i-V/Ti/Si	20	0	0	9.4	133	146.3	18.0	5.5
15	i-V/Ti/Si	2.5	10	0	12.3	134	173.9	9.9	5.2
16	i-V/Ti/Si	2.5	0	1	6.7	129	124.4	15.5	4.9
17	i-V/Ti/Si	2.5	0	3	7.4	129	122.6	14.2	5.2
18	i-V/Ti/Si	2.5	0	5	12.0	127	115.4	13.3	5.6
19	i-Mg/V/Ti/Si	2.5	0	0	16.5	133	143.4	21.7	4.8
20	i-Mg/V/Ti/Si	5	0	0	19.1	133	158.3	18.4	4.7
21	i-Mg/V/Ti/Si	10	0	0	21.3	133	155.9	18.1	4.7
22	i-Mg/V/Ti/Si	15	0	0	20.0	133	153.5	18.4	4.4
23	i-Mg/V/Ti/Si	20	0	0	19.2	133	147	19.2	5.4
24	i-Mg/V/Ti/Si	10	10	0	20.2	134	170.7	10.6	4.4
25	i-Mg/V/Ti/Si	10	0	1	27.3	127	130.2	14.1	6.4
26	i-Mg/V/Ti/Si	10	0	3	32.5	125	114.6	14.9	6.8
27	i-Mg/V/Ti/Si	10	0	5	34.4	125	67.5	14.1	7.8

Conditions: catalyst 100 mg, ethylene 0.15 MPa, *n*-heptane 70 mL, TIBA, 70°C, 1 h; (a) T_m and ΔH_f by DSC thermograms; (b) M_w estimated by HT-GPC in TCB; (c) Polydispersity index (M_w/ M_n).

Under polymerization conditions, reducing V^{3+} to V^{2+} was much easier than Ti^{3+} to Ti^{2+}[13]. Although the activities were not so high, the increasing tendency and stability were beneficial for industrial application to some extent, which were likely brought by the presence of imido agents.

After the comparison of ethylene homopolymerization behaviors, the ethylene/1-hexene copolymerization behaviors of the three catalysts were further investigated. As mentioned above, the proper dosages of TIBA cocatalyst in homopolymerization of each catalyst were used in ethylene/1-hexene copolymerization. The addition amount of α-olefin was an important factor in the ethylene/α-olefin copolymerization, which could greatly influence the polymerization behaviors of catalysts and microstructures of their polymers. In this work, different amounts of 1-hexene were added in the subsequent polymerization using all the catalysts. The influences of 1-hexene on catalytic properties are listed in Table 3 and Figure 5.

Both i-Mg/Ti/Si and i-Mg/V/Ti/Si showed obvious comonomer activation effect, as the introduction of 1-hexene significantly increased catalytic reactivity. The possible explanations were the introduction of comonomer into the polymerization system which might stabilize the cationic active species to increase catalytic activity or the comonomer unit in the propagation chain which might result in a positive influence through the donor effect[36]. The polymerization activities were significantly enhanced by introducing comonomer. While for i-V/Ti/Si, the increase of initial 1-hexene concentration led to a rapid decrease in catalytic activity, then an obvious increase with more 1-hexene. But in comparison with homopolymerization activity, the addition of 1-hexene played a totally negative comonomer effect. The comonomer, however, might affect the reaction in different ways-depending on the polymerization conditions and on the types of the catalyst[37]. The most possible reason was that the vanadium components might play a more vital role as active centers than titanium in this catalyst system. Zhang et al. [38] have investigated the vanadium catalysts bearing thiophenol-phosphine ligands which showed a negative "comonomer effect". Białek et al. [37] used supported-vanadium and supported-titanium catalysts bearing salen-type ligand in ethylene/1-olefin copolymerization. For both catalysts, negative "comonomer effect" was observed. However, further investigations were still needed to elucidate the comonomer effects.

The kinetic curves of ethylene/1-hexene copolymerization are shown in Figure 6. It was found that the ethylene consumption rates were drastically increased with the addition of 1-hexene, especially for i-Mg/V/Ti/Si. The copolymerization rate was quite stable for all the catalysts like the homopolymerization rate.

Meanwhile, from Table 3, DSC characterization results show that with the increase of 1-hexene, the T_m and ΔH_f of the copolymers decrease obviously. This can be due to that more and more 1-hexene was inserted into the backbone of polymer chain with the increasing 1-hexene concentration. The GPC characterization results showed that with the increasing of 1-hexene concentration from 0 vol% to 5 vol%, the MW basically decreased. In the MWD curves of the polymer samples, shifting toward low-molecular-weight with increasing 1-hexene can be clearly seen (see Figure 7). As mentioned by Yang et al. [39], in copolymerization with ethylene as the main monomer, the strength of comonomer effects was much stronger in active centers producing low-molecular-weight polymer than those producing high-molecular-weight polymer, leading to a significant decrease in average molecular weight of the whole polymer and broadening of its MWD. MWD was clearly broadened with the increase of 1-hexene especially for using i-Mg/V/Ti/Si catalyst.

High temperature ^{13}C NMR was applied to

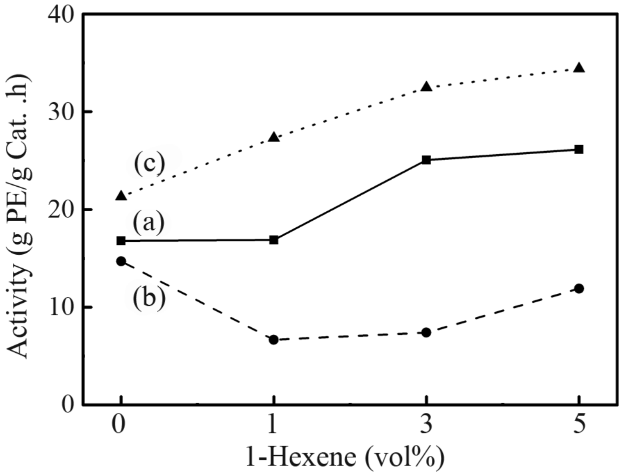


Figure 5. Ethylene/1-hexene copolymerization activities of different catalysts with different dosages of 1-hexene. (a) i-Mg/Ti/Si; (b) i-V/Ti/Si; (c) i-Mg/V/Ti/Si. Conditions: catalyst 100 mg, ethylene 0.15 MPa, n-heptane 70 mL, TIBA, 1 h.

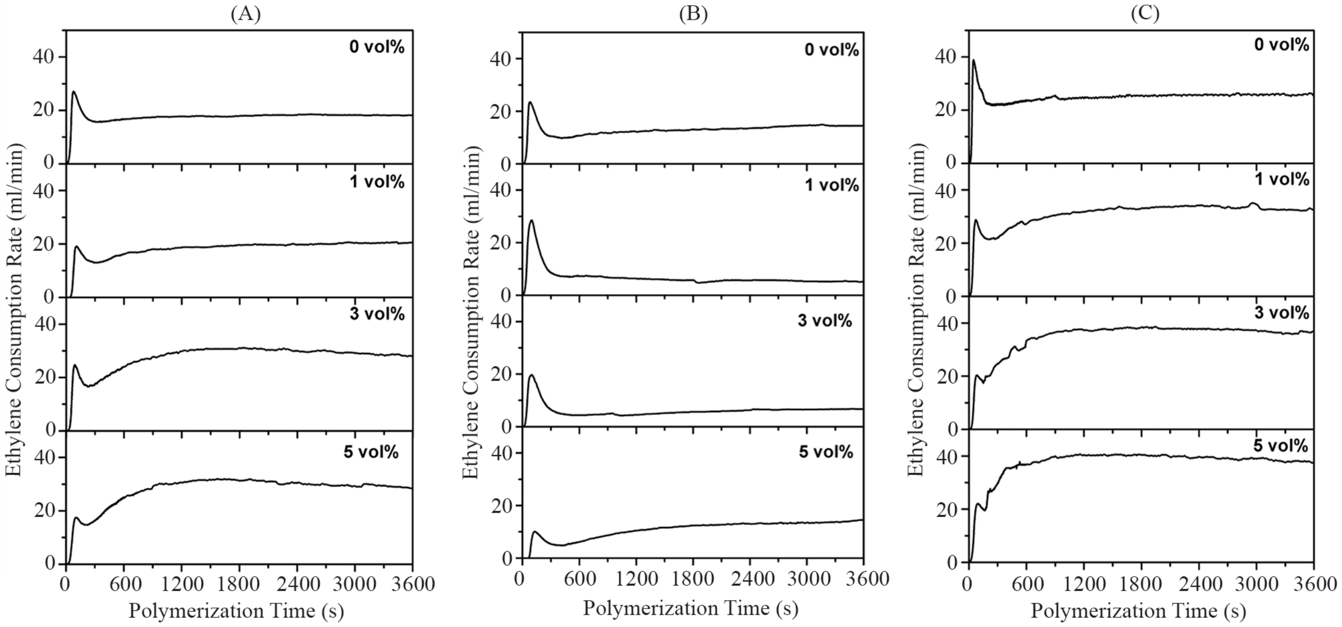


Figure 6. Kinetic curves of ethylene/1-hexene copolymerization (A) i-Mg/Ti/Si; corresponding to Run 2, 7, 8, 9; (B) i-V/Ti/Si; corresponding to Run 10, 16, 17, 18; (C) i-Mg/V/Ti/Si; corresponding to Run 21, 25, 26, 27). Conditions: catalyst 100 mg, ethylene 0.15 MPa, n-heptane 70 mL, TIBA, 1 h.

analyze the content of 1-hexene incorporation of the copolymers obtained from these catalysts. Considering that too small amount of 1-hexene could not affect the copolymerization behaviors of the catalysts and the influences of 1-hexene on the catalytic activities, the polymers obtained under the condition of 5 vol. % 1-hexene were selected for ^{13}C NMR characterization. The 1-hexene incorporation results are shown in Table 4 (^{13}C NMR spectra are shown in the Supporting Information as Figure S5).

Nomura and Wang[40] used (arylimino)(aryloxo) vanadium(V) complexes in ethylene/1-hexene copolymerization. However, poor 1-hexene incorporation was observed (0.8 mol%). In contrast, vanadium(III) complexes bearing salicylaldiminato ligands produced copolymers with high comonomer incorporation, at certain conditions even at 26.7 mol% of 1-hexene. Different modification ligands had totally contrary results. Compared with the original systems[11, 20], these catalyst systems showed much lower 1-hexene incorporation. The only difference was the modification agents, embodying that p-tolyl isocyanate was unfavorable to 1-hexene incorporation in this catalyst system. The imido agents actually had an influence on the titanium active sites, in accordance with the p-tolyl isocyanate/$TiCl_4$ insoluble complexes or titanium imido complexes in catalysts characterization.

Furthermore, from Table 4, it was found that i-Mg/V/Ti/Si showed the highest 1-hexene incorporation, while i-V/Ti/Si showed the lowest, implying the magnesium chloride carrier was crucial for ZN catalysts. On the other hand, 1-hexene incorporation was improved for i-Mg/V/Ti/Si comparing with that for i-Mg/Ti/Si, implied that adding vanadium could not only improve the catalytic activity but also enhanced the 1-hexene incorporation, indicating vanadium species could increase the incorporated short chain branches from 3.41 to 4.08 mol%.

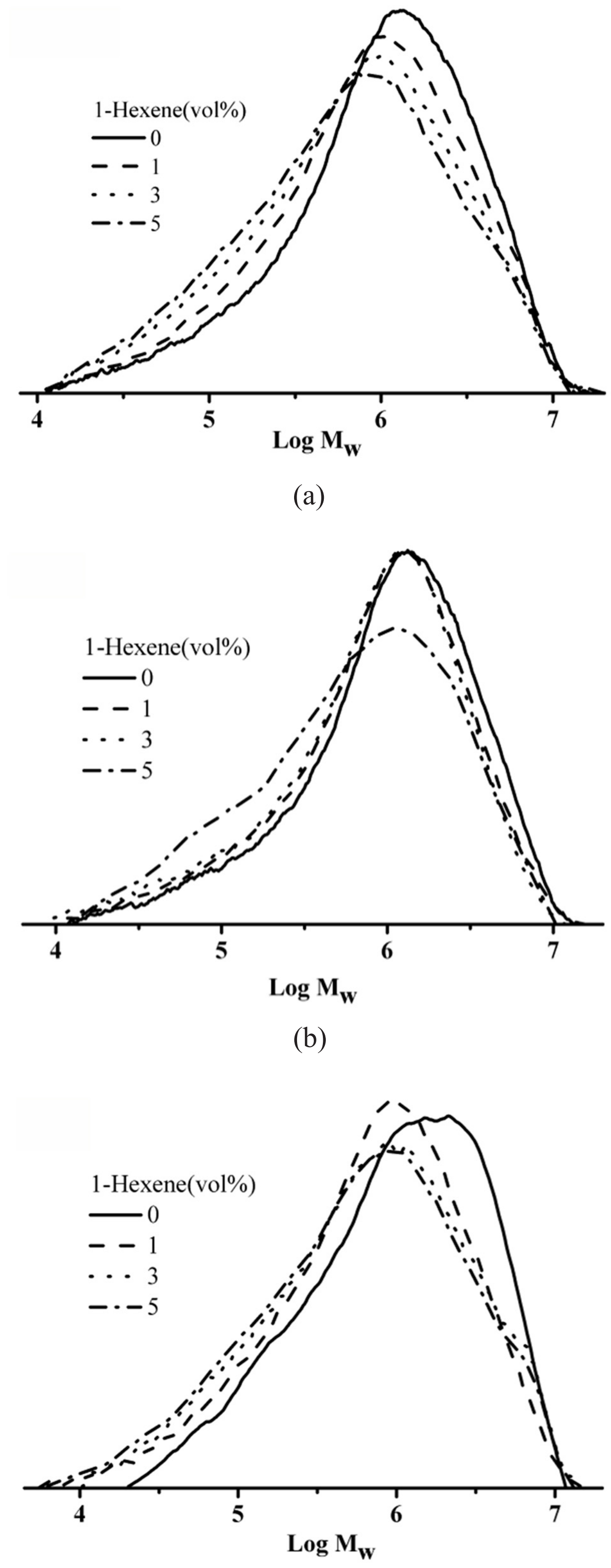
Effect of hydrogen

Hydrogen was used as chain-transfer agent in the low-pressure olefin polymerization process over the Ziegler-Natta catalyst. The presence of hydrogen affected both product's molecular weight and catalytic activity. The comparison of hydrogen effects of our

Table 4. The content of 1-hexene incorporated in the copolymers obtained from different catalysts by ^{13}C NMR.

Run.	Sample	Al/Ti	1-hexene[(a)] [vol%]	Activity [g PE/g Cat. h^{-1}]	1-Hexene[(b)] [mol%]
1	i-Mg/Ti/Si	5	5%	26.1	3.41
2	i-V/Ti/Si	2.5	5%	12.0	2.17
3	i-Mg/V/Ti/Si	10	5%	34.4	4.08

(a) Relative addition amount of 1-hexene in copolymerization;
(b) 1-hexene incorporated in copolymers estimated by ^{13}C NMR



(a)

(b)

(c)

Figure 7. MWD curves of ethylene/1-hexene copolymers. (a) i-Mg/Ti/Si; (b) i-V/Ti/Si; (c) i-Mg/V/Ti/Si. Conditions: catalyst 100 mg, ethylene 0.15 MPa, n-heptane 70 mL, TIBA, 1 h.

catalysts is listed in Table 3 and shown in Figure 8(GPC curves are shown in the Supporting Information as Figure S6). The kinetic curves for each catalyst kept the similar tendency with/without hydrogen in Figure 8 showing stable ethylene consumption rate. The activities of our catalysts and the molecular weights of the polymers decreased in the presence of hydrogen, which was in agreement with the literatures [41, 42]. Nevertheless, the decrease of catalytic activities with the presence of H_2 was limited, varying 2.4%, 16.3%, and 5.2% for i-Mg/Ti/Si, i-V/Ti/Si, and i-Mg/V/Ti/Si catalysts, respectively. The activity of i-Mg/Ti/Si catalyst was hardly influenced, following i-Mg/V/Ti/Si catalyst closely. Besides, the addition of hydrogen resulted in that the molecular weights of polymers obtained from i-Mg/Ti/Si, i-V/Ti/Si, and i-Mg/V/Ti/Si catalysts decreased 20.0%, 43.8%, and 41.4%, respectively. The V-modified ZN catalyst (namely, i-Mg/V/Ti/Si catalyst) showed 107.2% higher hydrogen response in comparison with that of i-Mg/Ti/Si catalyst, which means the V-modified ZN

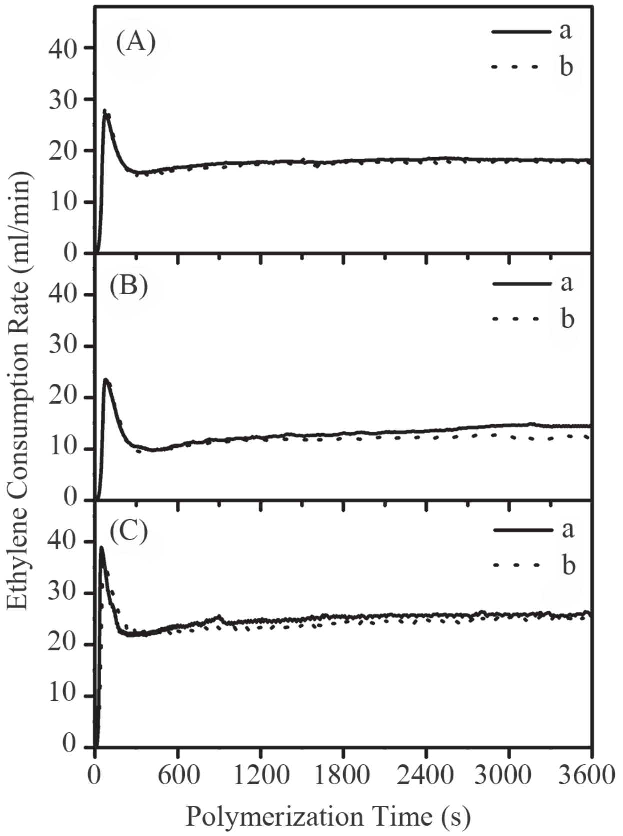


Figure 8. Kinetic curves of ethylene homopolymerization with/without hydrogen. (A): i-Mg/Ti/Si, Al/Ti=5, (a) without H_2, (b) with H_2, corresponding to Run 2, 6; (B): i-V/Ti/Si, Al/Ti=2.5, (a) without H_2, (b) with H_2, corresponding to Run 10, 15; (C): i-Mg/V/Ti/Si, Al/Ti=10, (a) without H_2, (b) with H_2, corresponding to Run 21, 24. Conditions: catalyst 100 mg, ethylene 0.15 MPa, n-heptane 70 mL, TIBA, 1 h, H_2 10mL.

catalysts exhibited much better hydrogen response than the V-free Mg/Ti catalyst which corresponded to Wang's work [20]. Therefore, the molecular weight could be controlled effectively in the presence of hydrogen nearly without affecting the activity with i-Mg/V/Ti/Si catalyst. In other words, the presence of imido agents could stabilize the catalytic centers in ethylene polymerization with hydrogen. But the explanations needed further investigations. Until now, the hydrogen effect has still been very difficult to be fully understood and explained well because it behaves in various aspects depending on the catalyst types and the polymerization conditions. The mechanism of reduction of Ziegler-Natta catalyst activity in ethylene polymerization in the presence of hydrogen is still not completely clear.

CONCLUSION

In this work, ethylene homopolymerization and ethylene/1-hexene copolymerization with series of the imido-modified SiO_2-supported catalysts were systematically investigated. These novel catalysts were successfully synthesized by first impregnation of aqueous solution of water-soluble magnesium salt and vanadium salt on silica, and then high temperature calcination in dry air were used to form a supported layer of magnesium oxide and vanadium oxide on the surface of silica, followed by further reaction with p-tolyl isocyanate as imido agents in toluene. The reaction occurred eventually in the presence of titanium tetrachloride to synthesize the magnesium dichloride carrier in-situ and to simultaneously support the active titanium species.

The polymerization behaviors and the microstructures of the polymers among the catalysts, such as activity, MW, MWD, 1-hexene incorporation were compared using HT-GPC, DSC, and ^{13}C NMR etc. methods . In homopolymerization, i-Mg/V/Ti/Si showed higher activity than i-Mg/Ti/Si and i-V/Ti/Si, and i-V/Ti/Si showed the lowest. This result might suggest that the addition of vanadium components could improve the homopolymerization activity and magnesium element form magnesium chloride carrier which was essential for Ziegler-Natta catalysts. In copolymerization, i-Mg/Ti/Si and i-Mg/V/Ti/Si showed obvious comonomer activation effect, as the introduction of 1-hexene significantly increased their catalytic reactivity. While for i-V/Ti/Si, the increase of initial 1-hexene concentration led to a rapid decrease in catalytic activity, then an obvious increase with more 1-hexene. Similar to the ethylene homopolymerization activity results, i-Mg/V/Ti/Si showed the highest 1-hexene incorporation, while i-V/Ti/Si showed the lowest, implying the magnesium chloride carrier was crucial for ZN catalysts and adding vanadium could not only improve the catalytic activity but also enhanced the 1-hexene incorporation. The GPC results showed that the polymers were very high molecular weight polyethylene with medium molecular weight distribution. On the other hand, the activity of our catalysts and the molecular weight of the polymers decreased in the presence of hydrogen, but the decrease of catalytic activities was quite limited.

Compared with $(SiO_2/MgO/MgCl_2)TiCl_x$ Ziegler-Natta catalysts and vanadium-modified $(SiO_2/MgO/MgCl_2)TiCl_x$ Ziegler-Natta catalysts, the imido-modified SiO_2-supported Ti/Mg Ziegler-Natta showed lower but more stable activity for homopolymerization, polymerization with hydrogen and copolymerization owing to the imido ligands, indicating that p-tolyl isocyanate was unfavorable for improving catalytic activity but beneficial for the stability. The kinetic curves were quietly similar for all the catalysts. On the other hand, the products of all catalysts showed lower 1-hexene incorporation but much higher molecular weight (MW) with medium molecular weight distribution (MWD). The modification of imido ligands influenced both catalyst polymerization behaviors and the microstructures of the polymers. However, the most unique features of theses novel catalysts were their excellent hydrogen responses without lowering the polymerization activities, showing great potential for application.

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