

# How can pH value during catalyst preparation affect the performance of vanadium-modified (SiO<sub>2</sub>/MgO/MgCl<sub>2</sub>)•TiCl<sub>x</sub> Ziegler-Natta polyethylene catalysts

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## ABSTRACT

Vanadium-modified (SiO<sub>2</sub>/MgO/MgCl<sub>2</sub>)•TiCl<sub>x</sub> Ziegler-Natta catalysts were prepared through co-impregnation of water-soluble magnesium and vanadium salts under different pH values. Several key factors such as pH value of co-impregnation solution during catalyst preparation, catalyst performances including catalytic activity, ethylene/1-hexene copolymerization and hydrogen response were investigated. It is found that the components, structures and performance of the catalysts are obviously affected by changing the pH value (pH=5, 7 and 9) of co-impregnation solution. An appropriate pH value (pH=7) can maximize catalytic activity and hydrogen response, while lower pH value (pH=5) is beneficial to the 1-hexene incorporation. The GPC results show that the polymers obtained have high average molecular weight. **Polyolefins J (2018) 5: 31-45**

**Keywords:** Ziegler-Natta catalysts; polyethylene; polymerization kinetics.

## 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 and laboratory equipment, etc. Since the breakthrough discoveries during early 1950s by Karl Ziegler and Giulio Natta, Ziegler-Natta catalysts have achieved great

progress and become indispensable catalysts for industrial production of polyolefins. Ziegler-Natta catalysts still constitute the largest proportion of current industrial polyethylene production.

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

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Natta catalyst immobilized on anhydrous MgCl<sub>2</sub> and SiO<sub>2</sub> bi-support (M-1 catalyst) for UNIPOL gas-phase polyethylene process. BP Company [10] utilized alkyl magnesium (MgR<sub>2</sub>) as starting Mg-source, followed by reacting with SiO<sub>2</sub> and TiCl<sub>4</sub> to synthesize Si/Mg bi-support catalyst for industrial polyolefin production. In our previous work, Wang et al. successfully developed a novel (SiO<sub>2</sub>/MgO/MgCl<sub>2</sub>)•TiCl<sub>x</sub> Ziegler-Natta catalyst for ethylene and ethylene/1-hexene polymerization showing high activity, good hydrogen response and copolymerization ability [11]. The method was simple and cost-effective.

In the past decades, some efforts have been devoted to the improvement of the Ziegler-Natta catalyst performance by further introduction of transition metals, which has made great progress because these catalysts could get merits from each of the individual metals or show synergistic effect between two metal components, leading to a better catalyst performance. Hsieh et al. invented a mixed catalyst comprising a chromium ethylene polymerization catalyst and a MgO-supported Ti-based Ziegler ethylene polymerization catalyst which gave significantly broader molecular weight distribution polymers, and the usual poisoning of the chromium catalysts did not occur [12, 13]. Ciaccia et al. used a mixed catalyst system comprising one late transition metal polymerization catalyst (Fe and/or Co) and one Ziegler polymerization catalyst for broad molecular weight distribution polymers and long-chain branching [14]. Some literatures reported the modification of Ziegler-Natta catalysts by doping inorganic compounds in the supports such as FeCl<sub>3</sub> [15], MnCl<sub>2</sub> [16], ZnCl<sub>2</sub> [17, 18], ZnCl<sub>2</sub>-SiCl<sub>4</sub> mixtures [18] and AlCl<sub>3</sub> [19, 20]. On the basis of the novel (SiO<sub>2</sub>/MgO/MgCl<sub>2</sub>)•TiCl<sub>x</sub> Ziegler-Natta catalyst, Wang et al. modified the catalyst through the introduction of chromium and vanadium species, respectively [21, 22], and the Cr-modified catalyst showed better catalytic performance with 13% higher activity, 40% higher hydrogen response, and 20% higher 1-hexene incorporation ability with better short chain branch distribution. Moreover, proper addition amount of vanadium modification induced much better catalytic performance with 27% higher activity, 48% higher hydrogen response, and 60% higher 1-hexene incorporation ability with better short chain branch distribution.

Therefore, based on the efficiency of the introduction of vanadium interaction on catalyst surfaces [23], systematically investigation on the effects of preparation condition over the vanadium-modified (SiO<sub>2</sub>/MgO/MgCl<sub>2</sub>)•TiCl<sub>x</sub> Ziegler-Natta catalyst was of great importance to further optimize the experimental preparation conditions. In this work, experiments on the effects of pH value of co-impregnation solution during catalyst preparation were conducted and the vanadium-modified (SiO<sub>2</sub>/MgO/MgCl<sub>2</sub>)•TiCl<sub>x</sub> Ziegler-Natta catalysts were prepared by co-impregnation of water-soluble magnesium and vanadium salts on SiO<sub>2</sub> under different pH values, followed by calcination at high temperature in dry air and refluxing reaction with TiCl<sub>4</sub>. The obtained catalysts were used for ethylene polymerization without/with hydrogen and ethylene/1-hexene copolymerization. By characterization of the catalysts and their polymers, the polymerization behaviors and several key factors such as the pH value of the co-impregnation solution, cocatalyst amount, hydrogen and dosage of 1-hexene were systematically investigated.

## EXPERIMENTAL

### Materials

Silica gel (Grace Davison 955, specific surface area 282.3 m<sup>2</sup>.g<sup>-1</sup>, pore volume 1.64 cm<sup>3</sup>.g<sup>-1</sup> and average pore size 17.5 nm, donated by Qilu Branch Co., SIN-OPEC) was employed as supports.

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 silver 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<sub>2</sub>O < -80°C) were purchased from Shanghai Wetry Criterion Gas. Co., Ltd.

Magnesium acetate tetrahydrate (C<sub>4</sub>H<sub>6</sub>O<sub>4</sub>Mg.4H<sub>2</sub>O, AR) and ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Titanium (IV) chloride (TiCl<sub>4</sub>, 99 wt%), acetic acid (CH<sub>3</sub>COOH, AR grade), ammonium hy-

dioxide ( $\text{NH}_3$ , AR grade) and hydrochloric acid ( $\text{HCl}$ , AR grade) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. and used without further treatment.

The solvents including n-hexane (AR grade) and n-heptane (AR grade) which were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. were firstly purified by 4A molecular sieves and subsequently purified 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 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 purified through distillation in the presence of sodium metal slices 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<sup>-1</sup> 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 glove box techniques.

Firstly, silica was calcined in a fluidized bed reactor in purified nitrogen at 300°C, and cooled to ambient temperature before use. The purpose of the dehydration step was to eliminate the influence of environment and ensure the same condition of silica for each catalyst preparation. When preparing the catalyst, typically about 10 g calcined silica was impregnated in an aqueous solution of water-soluble magnesium acetate tetrahydrate and ammonium metavanadate with a magnetic stirrer at 65°C. The Mg loading was constant at 5 wt%, while Mg/V molar ratio was set to 5 (V of 2.1 wt%, the best performance in our previous work). The pH value of the co-impregnation solution

was adjusted to 5, 7 and 9 by  $\text{NH}_3$ , respectively. 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<sup>-1</sup> in high-purified dry air for 4 h before it was sealed.

Secondly, under nitrogen protection, about 2 g of mixed support prepared above was transferred into a three-necked flask with a magnetic stirrer, then about 30 mL titanium (IV) chloride ( $\text{TiCl}_4$ , 99 wt%) was injected. The mixtures were refluxed and stirred for approximately 2 h at 145 °C before they were cooled to room temperature, and then 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 for 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, MgV/Ti/Si catalyst (Cat-1, Cat-2 and Cat-3 corresponding to pH value of co-impregnation solution of 5, 7 and 9, respectively) was cooled down, prepared and transferred into a glove box.

For comparison, Mg/Ti/Si catalyst (named Cat-0) was prepared without a third metal element under pH=7. The following procedures were the same as mentioned above.

### Ethylene, ethylene/1-hexene and ethylene/hydrogen 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 catalyst, 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 with nitrogen for at least three times for 0.5 h, then was purged with ethylene monomer for three times and finally was full of monomer until the ethylene pressure was about 0.12 MPa. Then, 80 mL n-heptane and a certain amount of TIBA were injected into the reactor, and a certain amount of purified 1-hexene (the relative addition amount of puri-

fied 1-hexene was defined as the volume ratio between 1-hexene and n-heptane such as 1, 3, and 5 vol%, which were 0.8, 2.4, and 4.0 mL, respectively) or a certain amount of hydrogen (e.g., 10 mL) if necessary were 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 was continued for 1 h. The instantaneous consumption rate 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.

### Catalysts characterization

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<sub>2</sub>O<sub>2</sub> to form a yellow peroxotitanium complex, then was diluted with deionized water to 25 mL. UV-visible spectra of the resultant solution were recorded by a MAPADA UV3200 type ultraviolet spectrophotometer. The peak intensity at 409 nm was used to quantify the titanium contents.

In order to determine the fully supporting of Mg and the third metal components on the surface of silica gel, inductively coupled plasma spectrometry (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<sup>-1</sup> and 1.50 L•min<sup>-1</sup>, respectively. The pressure of nebulizing gas was 200 kPa and pump speed was 13 rpm.

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<sup>-1</sup>. The injection volume was 25 μL and the mobile phase was KOH.

Nitrogen adsorption-desorption isotherms were

measured at 77 K using an automatic micropore physiosorption 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 BET method, and the pore volume (V<sub>p</sub>) and average pore size (d) were evaluated using Barrett-Joyner-Halenda (BJH) method.

Thermogravimetric analysis-differential thermal analysis (TG-DTA, SDTQ 600) was employed to analyze the decomposition temperature of catalysts under N<sub>2</sub> (100 mL/min) at 10°C•min<sup>-1</sup> from 25°C to 800°C. The surface properties of the samples were detected by NH<sub>3</sub> temperature-programmed desorption with an Autochem 2920 equipment (Micromeritics). In these TPD experiments, all the samples (100 mg) were firstly treated at 150°C for 60 min (10°C/min) in He and cooled down and saturated with ammonia at 150°C for 30 min. After the samples were purged with He (30 mL/min) for 30 min, the measurements of the desorbed NH<sub>3</sub> were performed from 150 to 800°C (10°C/min) under He (30 mL/min).

### Polymers characterization

The molecular weight (MW) and molecular weight distribution (MWD) of polymers were measured by high-temperature gel-permeation chromatography (HT-GPC, Agilent PL-220) with two PL gel-Olexis columns at 160°C, and the flow rate of 1.0 mL•min<sup>-1</sup>. 1,2,4-Trichlorobenzene (TCB) and polystyrene (PS) were used as solvent and standard sample, respectively.

About 5 mg PE sample was weighted and then heated to 165°C at the rate of 10°C•min<sup>-1</sup> for 5 min to remove thermal history, then cooled down to 40°C at 10°C•min<sup>-1</sup> and finally heated to 165°C at 10°C•min<sup>-1</sup> using a differential scanning calorimetry (DSC) analyzer (TA, DSC Q200) to record the second heating curve and melting temperature (T<sub>m</sub>). The enthalpy of fusion (ΔH<sub>f</sub>) of each sample was calculated from the DSC curve. Degree of crystallization (X<sub>c</sub> = ΔH<sub>f</sub> × 100/ΔH<sub>f</sub><sup>0</sup>) was calculated based on 100% defect-free polyethylene crystalline with ΔH<sub>f</sub><sup>0</sup> = 293 J/g enthalpy of fusion [24].

The 1-hexene incorporation was measured by high temperature <sup>13</sup>C NMR. Each sample (about 100 mg) was equipped into a 5 mm NMR tube with 1,4-di-

chlorobenzene-d4 (DCB-d4) as a solvent (sample concentration: ca. 15 mg·mL<sup>-1</sup>) and scanned by Varian Inova-400 MHz at 110°C and 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 <sup>13</sup>C NMR spectrum according to Seger's work for reference [25].

## RESULTS AND DISCUSSION

### Characterization results of catalysts

A series of catalysts were characterized by UV-Vis, ICP and IC to evaluate elements contents. The N<sub>2</sub> absorption/desorption measurements for supported catalysts were taken under the same conditions to determine pore structure parameters. The characterization results of different catalysts are listed in Table 1.

From Table 1, it can be seen that the actual loadings of both Mg and V in these catalysts were largely less than the initial addition amounts, which might be due to the limitation of loading capacity on the surface of silica resulting partial Mg- and V-losing during the catalyst preparation, or some supported species might be lost during the reaction process with the high concentration TiCl<sub>4</sub> [11, 21, 22]. The pore structure parameters results showed that the specific surface area, pore volume and average pore size of the catalysts decreased compared with the original SiO<sub>2</sub> raw material (Grace Davison 955 with specific surface area 261.8 m<sup>2</sup>·g<sup>-1</sup>, pore volume 1.67 cm<sup>3</sup>·g<sup>-1</sup> and average pore size 17.4 nm), which could be attributed to the supporting of catalytic components on the catalyst surface and fragmentation of catalyst particles during catalyst preparation [26, 27].

Comparing Cat-0 with Cat-2, an increase in titanium and chlorine contents was found after adding the vanadium component into the catalyst system, the trend of which was similar to our previous work under Mg/V=5:1 [21]. As the pH value of co-impregnation increased (Cat-1, Cat-2 and Cat-3), both Ti and V contents increased. For Mg and Cl elements, there were maximum and minimum values at pH=7, respectively. Moreover, the pore volume and average pore size reached maximum values, while the specific surface area had a minimum value at pH=7.

Thus, to further investigate the differences of these three MgV/Ti/Si catalysts, firstly, TG-DTA (SDTQ 600) analysis was employed to analyze the decomposition temperature of Cat-2 catalyst in Figure 1 (Left). From the DTA curve, it was obvious that an exotherm peak at 350°C was observed. Combining the TG curve of weight loss at 150°C, the results indicated that the catalyst decomposed before 400°C. Therefore, the catalyst was treated at 150°C for 1 h for dehydration before NH<sub>3</sub>-TPD characterization.

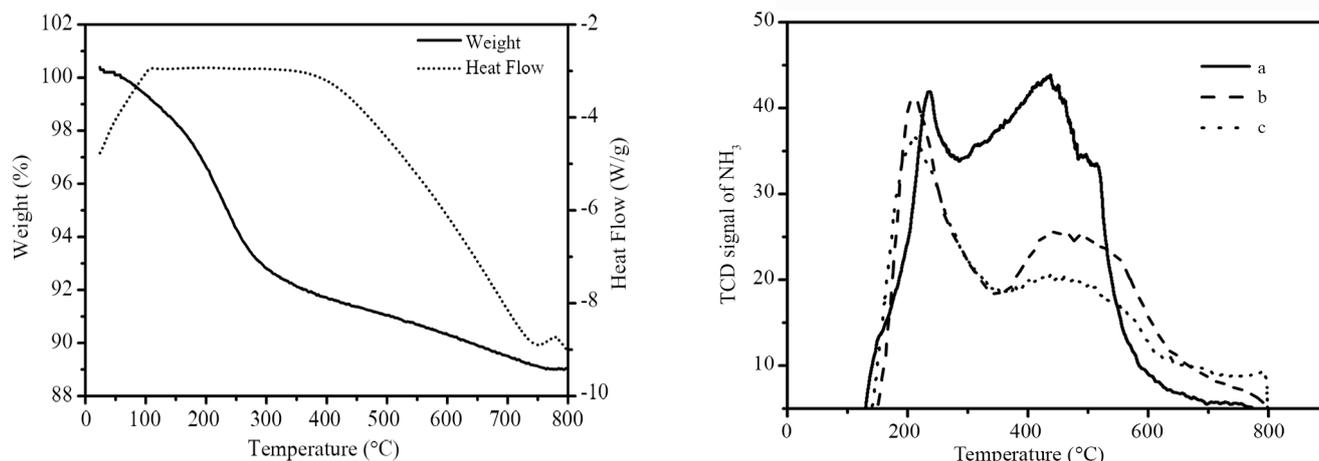
Then, the NH<sub>3</sub>-TPD experiments were conducted for the series of vanadium-modified (SiO<sub>2</sub>/MgO/MgCl<sub>2</sub>)·TiCl<sub>x</sub> Ziegler-Natta (MgV/Ti/Si) catalysts in Figure 1 (Right).

The NH<sub>3</sub>-TPD profiles of the MgV/Ti/Si catalysts at different pH values of co-impregnation solution (pH5, pH7 and pH9) showed that three NH<sub>3</sub> desorption peaks were detected in the tested temperature range (from 100 to 800°C). The results illuminated the presence of three different acid sites owing to different NH<sub>3</sub> absorption energies on the samples. The weak, medium and strong acid sites were estimated from the desorption peak in the temperature ranges 180-280°C, 280-450°C and 450-750°C, respectively [28]. It could be obviously found that the amount of desorbed NH<sub>3</sub> detected decreased with the increase of pH value, and

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

Sample	Catalyst	Elements contents				Pore structures <sup>(d)</sup>		
		Ti <sup>(a)</sup> [wt%]	Mg <sup>(b)</sup> [wt%]	V <sup>(b)</sup> [wt%]	Cl <sup>(c)</sup> [wt%]	SBET [m <sup>2</sup> g <sup>-1</sup> ]	Vp [cm <sup>3</sup> g <sup>-1</sup> ]	d [nm]
Mg/Ti/Si	Cat-0	3.33	.8	--	5.6	196.0	0.948	15.0
MgV/Ti/Si pH=5	Cat-1	3.08	.7	0.26	7.2	218.8	1.053	15.0
MgV/Ti/Si pH=7	Cat-2	3.45	3.6	0.39	6.0	182.0	1.229	19.7
MgV/Ti/Si pH=9	Cat-3	3.67	3.0	0.46	7.2	219.8	0.823	12.5

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



**Figure 1.** (Left) TG-DTA curves of Cat-2; (Right)  $\text{NH}_3$ -TPD profiles of MgV/Ti/Si catalysts at different pH values of co-impregnation solution (a: Cat-1, b: Cat-2, c: Cat-3).

the amount of acid sites decreased sharply and weakened gradually with lower acidity. Meanwhile, the acidic strength of the weak acid sites weakened. The results indicated that the strength of weak acid sites and the amount of medium and strong acid sites on the surface of catalysts could be improved with the lower pH value of the co-impregnation solution. The results also demonstrated that the nature of the catalysts was affected by the pH value of the co-impregnation solution.

### Ethylene homo-polymerization and characterization of the homopolymers

The ethylene homo-polymerization experiments of the pH effects were further conducted. The effects of pH on ethylene homo-polymerization experiments were examined. It is well known that cocatalyst can influence the catalytic activity significantly, thus, the dosages and types of cocatalyst must be taken into consideration. Wang et al. studied the influence of cocatalyst on  $\text{SiO}_2/\text{MgO}/\text{MgCl}_2$  catalyst system [11], and the results proved that higher activity was produced by triisobutylaluminum (TIBA) as cocatalyst than triethylaluminum (TEA), which was attributed to the bulky isobutyl groups hindering dimerization resulting in higher concentration of alkyl aluminum in the monomeric form and making it more efficient to activate the catalytic system. In this work, TIBA was employed as cocatalyst for ethylene polymerization. The ethylene polymerization activity and product properties of various vanadium-modified  $(\text{SiO}_2/\text{MgO}/$

$\text{MgCl}_2)\cdot\text{TiCl}_x$  Ziegler-Natta catalysts were compared with those of  $(\text{SiO}_2/\text{MgO}/\text{MgCl}_2)\cdot\text{TiCl}_x$  Ziegler-Natta catalyst listed in Table 2.

Table 2 shows that with the increase of Al/Ti molar ratio, ethylene homo-polymerization activities increase to a maximum value and then decrease. Optimal Al/Ti molar ratios were varied for different catalysts. This result indicated that the proper amount of cocatalyst could enhance the activity of the catalyst. It is well known that the cocatalyst can reduce and alkylate the transition metal-carbon to initiate the first polymer chain [29] and scavenge impurities [30]. 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]. On the other hand, after adding vanadium elements, the optimal Al/Ti ratio was upgraded due to that more cocatalyst was needed to reduce the vanadium precursors after adding vanadium active species. Meanwhile, ethylene homo-polymerization activity was improved after adding vanadium element (Run 2 and Run 10), corresponding to our previous work [21]. Wang et al. considered that the vanadium species might influence the polymerization through creating electronic effect to the active titanium species to improve their catalyst performance for ethylene polymerization [21].

Comparing the highest activity of Cat-1, Cat-2 and Cat-3, namely Runs 6, 10 and 15, as the pH value of co-impregnation solution increased, ethylene homo-polymerization activity of Cat-2 had a maximum

**Table 2.** Ethylene polymerization activities of different catalysts and characterization of their polymers.

	Catalyst	Al/Ti	Activity (g PE/g Cat·h <sup>-1</sup> )	T <sub>m</sub> <sup>(a)</sup> [°C]	X <sub>c</sub> <sup>(a)</sup>	M <sub>w</sub> <sup>(b)</sup> [×10 <sup>5</sup> g/mol]	MWD <sup>(c)</sup>
1	Cat-0	0.75	44.7	135	55.4	14.9	4.2
2	Cat-0	1	52.9	134	55.1	17.0	4.1
3	Cat-0	2.5	44.5	135	55.6	16.1	4.0
4	Cat-0	5	38.8	135	57.0	13.7	4.4
5	Cat-1	5	41.1	134	55.0	14.8	3.8
6	Cat-1	10	50.3	134	55.6	15.0	4.6
7	Cat-1	15	45.1	135	57.1	14.7	5.3
8	Cat-1	20	39.0	135	55.6	13.9	4.6
9	Cat-2	1	43.0	134	56.2	16.9	4.2
10	Cat-2	2.5	59.7	134	56.5	15.2	3.8
11	Cat-2	5	55.3	135	58.6	15.7	3.9
12	Cat-2	10	53.2	135	56.9	15.3	4.7
13	Cat-3	2.5	45.2	134	54.5	14.4	3.6
14	Cat-3	5	51.6	134	54.9	13.3	3.7
15	Cat-3	10	52.3	135	56.5	12.7	3.6
16	Cat-3	15	46.6	135	56.3	12.5	3.5

Conditions: catalyst 100 mg, ethylene 0.15 MPa, *n*-heptane 80 mL, TIBA, 70°C, 1 h; <sup>(a)</sup> T<sub>m</sub> and ΔH<sub>f</sub> by DSC thermograms, X<sub>c</sub> evaluated by ΔH<sub>f</sub><sup>100</sup>/ΔH<sub>f</sub><sup>0</sup>, ΔH<sub>f</sub><sup>0</sup> (enthalpy of fusion of 100 % crystalline PE) = 293 J/g; <sup>(b)</sup> M<sub>w</sub> estimated by HT-GPC in TCB, average molecular weight; <sup>(c)</sup> Polydispersity index (M<sub>w</sub>/M<sub>n</sub>).

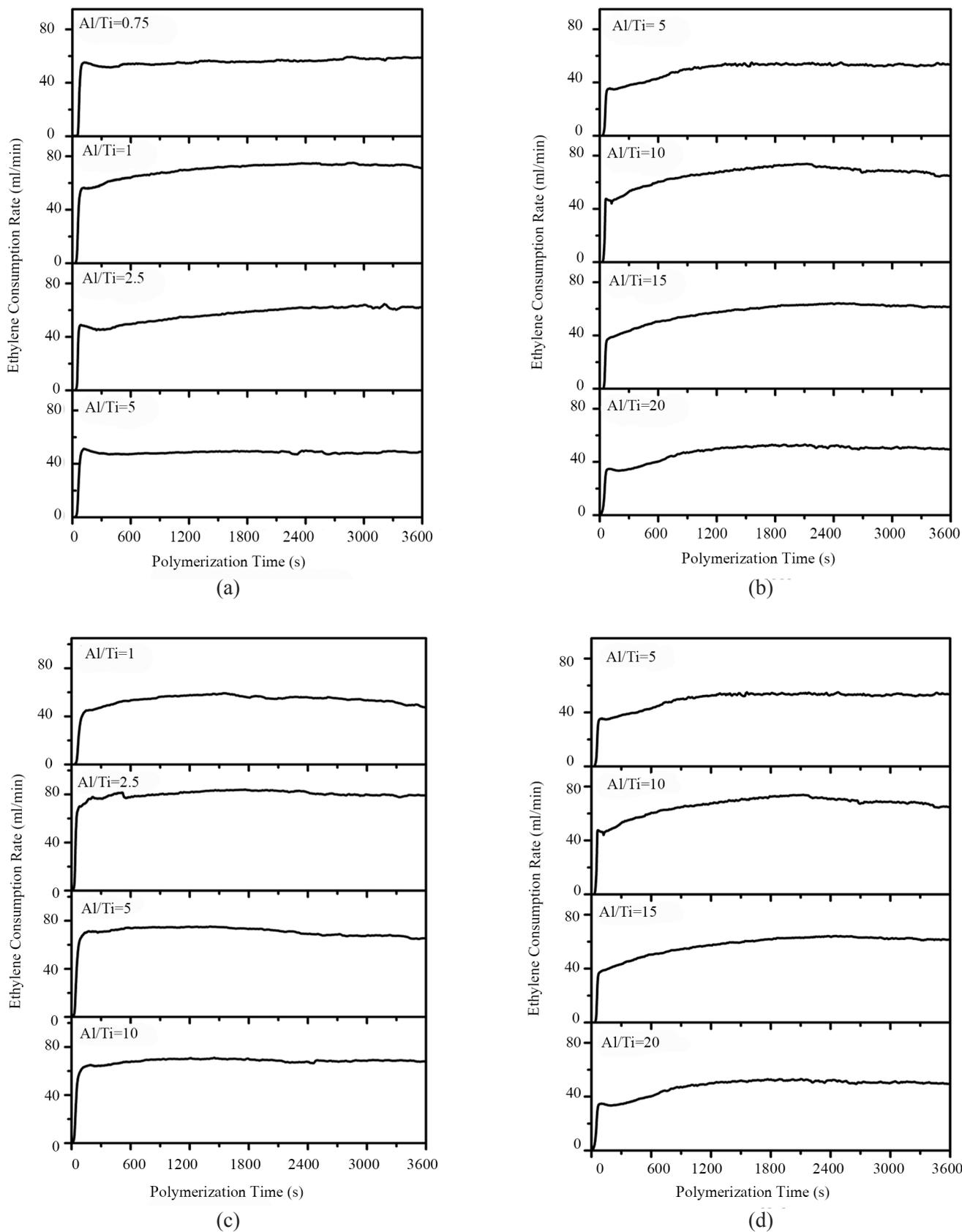
value of 59.7 g PE/g Cat·h<sup>-1</sup> at pH=7 with only 2.5 of optimal Al/Ti molar ratio, which was lower than those for other two catalysts (Cat-1 and Cat-3) and much lower than industrial value, resulting in much lower production cost. This might be attributed to different metals (titanium and vanadium) contents and different kinds of possible titanium and vanadium precursors with different structures on the surfaces of the catalysts [26]. It meant that the pH value of the co-impregnation solution could largely influence the catalytic performance and both lower and higher pH values were not favorable for the catalytic activity, which has been mentioned in Matta's work on the Phillips catalyst system [8].

DSC and HT-GPC methods were used to characterize the obtained homopolymers in order to further investigate the influence of these different catalysts on the homo-polymerization, and the results are also listed in Table 2 (GPC curves are shown in the Supporting Information as Figure S1). It can be seen that T<sub>m</sub> and X<sub>c</sub> of the homopolymers are nearly the same with rather high crystallinity. The possible explanation was that there were very few short-chain branches in the homopolymers obtained from these different catalysts.

The GPC results showed that the homopolymers were all high molecular weight polyethylenes with medium molecular weight distributions, which indicated that pH value of the co-impregnation solution had little influence on MW and MWD of products with good mechanical properties.

The kinetic curves of ethylene homo-polymerization with these four catalysts at different cocatalyst concentrations are shown in Figure 2. It is observed that the shapes of these curves are almost the same, increasing rapidly to a maximum within 1 to 2 minutes of the polymerization and then maintaining a steady state or keeping an increase tendency.

However, there was a relatively smaller maximum value and a slow rising process after rapidly increasing in the polymerization for Cat 1 and Cat 3 in comparison to Cat 2. However, the kinetic profile of the polymerization reaction depended on many factors, including the nature of monomer, pre-catalyst, co-catalyst, temperature, and the presence of modifying agents. There is no clear explanation for the phenomenon yet, and it needs further investigation. Overall, all the kinetic curves were rather stable with no decay of polymerization rates, which would be beneficial for



**Figure 2.** Kinetic curves of ethylene homo-polymerization with different catalysts at different cocatalyst concentrations: (a) Cat-0; (b) Cat-1; (c) Cat-2; (d) Cat-3. Other polymerization conditions: catalyst 100 mg, ethylene 0.15 MPa, n-heptane 80 mL, TIBA, 70°C, 1 h.

the future industrialization.

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

The copolymers of ethylene with  $\alpha$ -olefins often have good mechanical properties, thus, it is necessary to investigate the copolymerization performance of these catalysts. As mentioned above, the proper dosages of TIBA cocatalyst in homo-polymerization of each catalyst were used in ethylene/1-hexene copolymerization. The addition amount of  $\alpha$ -olefin as an important factor in the ethylene/ $\alpha$ -olefin copolymerization could greatly influence the polymerization behaviors of catalyst and the microstructures of its polymer. In this work, to investigate its effect, different amounts of 1-hexene were added in the subsequent polymerization for all the catalysts. The influences of 1-hexene on catalytic properties are shown in Table 3.

From Table 3, the introduction of 1-hexene firstly increased the catalytic reactivity and then decreased it obviously with more comonomer for all the catalysts. The maximum activities were achieved with adding 1-hexene of 1 vol%. A large amount of efforts have been devoted to investigate the mechanistic explanations of the comonomer effect [31-34]. Both chemical and physical factors have been proposed to explain the positive “comonomer effect” toward Ziegler-Natta catalysts. The chemical factors included that the insertion of ethylene into Ti-H bond became a dormant site through  $\beta$ -agostic interaction and inactive for ethylene polymerization, while the Ti-C6H13 formed by

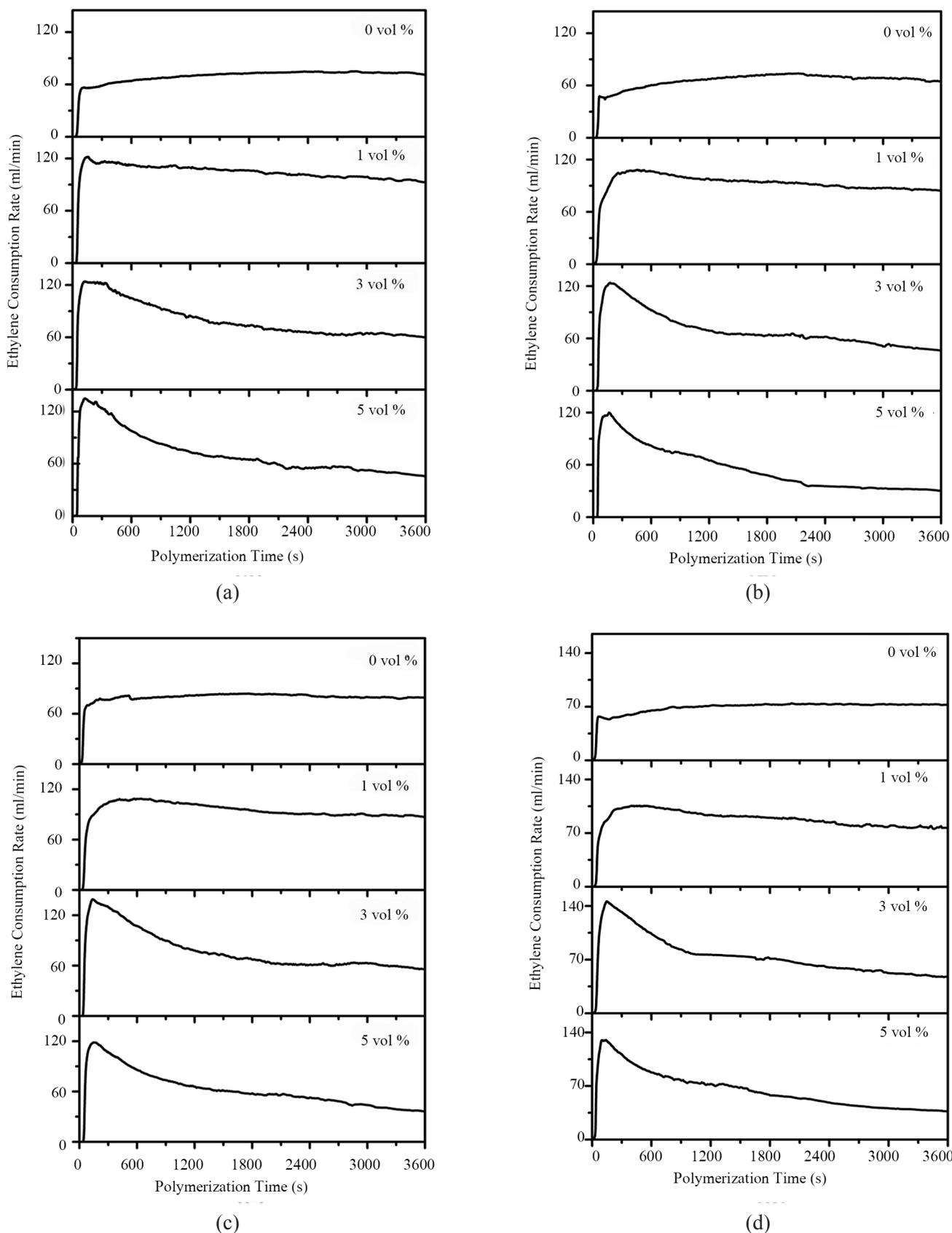
the insertion of a 1-hexene into the Ti-H bond led to the formation of an active site rather than a dormant site and the comonomer unit in the propagation chain might result in a positive influence through the donor effect. The physical factors included the introduction of comonomer into the polymerization system might improve the stability of the active species leading to the increase of activity in ethylene/ $\alpha$ -olefin copolymerization and/or accelerate the diffusion of monomer due to the reduced crystallinity of the surrounding polymer layer, or diffusivity plus mechanical phenomena involving the fragmentation of the growing catalyst-polymer particle. Which factor is the main reason for the “comonomer effect” in ethylene/ $\alpha$ -olefin copolymerization over Ziegler-Natta catalysts is still not clear. Further investigation is needed to provide clearer explanation.

The DSC characterization showed that with the increase of 1-hexene, the  $T_m$  and  $X_c$  of the copolymers were reduced obviously. This could be due to that more and more 1-hexene was inserted in the backbone of polymer chain with increasing 1-hexene concentration. Then the GPC characterization showed that with increase 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 and broadening of MWD with increasing 1-hexene could be clearly seen in Support Information as Figure S2. As mentioned by Yang et al. [35], in copolymerization with ethylene as the main monomer, the strength of comonomer effects

**Table 3.** Effects of 1-hexene on ethylene polymerization activities with different catalysts and characterization of their polymers.

	Catalyst	1-Hexene [vol%]	Activity [g PE/g Cat·h <sup>-1</sup> ]	$T_m$ <sup>(a)</sup> [°C]	$X_c$ <sup>(a)</sup>	$M_w$ <sup>(b)</sup> [ $\times 10^5$ g/mol]	MWD <sup>(c)</sup>	1-Hexene <sup>(d)</sup> [mol%]
1	Cat-0	1	82.1	125	45.0	10.3	4.3	--
2	Cat-0	3	67.5	122	29.1	9.0	5.3	3.66
3	Cat-0	5	65.5	121	21.6	7.7	5.1	--
4	Cat-1	1	74.7	125	41.0	9.0	6.2	--
5	Cat-1	3	65.5	122	37.4	6.6	6.7	8.43
6	Cat-1	5	60.5	122	17.7	5.5	8.2	--
7	Cat-2	1	75.7	125	42.7	9.7	4.2	--
8	Cat-2	3	67.3	121	31.7	8.0	4.5	5.53
9	Cat-2	5	58.8	120	25.9	7.8	5.9	--
10	Cat-3	1	68.6	125	43.1	8.1	5.2	--
11	Cat-3	3	68.0	122	29.9	6.5	6.1	4.48
12	Cat-3	5	65.1	122	20.7	5.3	6.6	--

Conditions: catalyst 100 mg, ethylene 0.15 MPa, *n*-heptane 80 mL, TIBA, 70 °C, 1 h; <sup>(a)</sup>  $T_m$  and  $\Delta H_f$  by DSC thermograms,  $X_c$  evaluated by  $\Delta H_f/100/\Delta H_f^0$ ,  $\Delta H_f^0$  (enthalpy of fusion of 100 % crystalline PE) = 293 J/g; <sup>(b)</sup>  $M_w$  estimated by HT-GPC in TCB, average molecular weight; <sup>(c)</sup> Polydispersity index ( $M_w/M_n$ ); <sup>(d)</sup> 3 vol%, 1-hexene incorporated in copolymers estimated by <sup>13</sup>C NMR.



**Figure 3.** Kinetic curves of ethylene/1-hexene polymerization with different catalysts at different 1-hexene concentrations: (a) Cat-0; (b) Cat-1; (c) Cat-2; (d) Cat-3. Other polymerization conditions: catalyst 100 mg, ethylene 0.15 MPa, n-heptane 80 mL, TIBA, 70°C, 1 h.

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.

On the other side, the kinetic curves of ethylene/1-hexene copolymerization are shown in Figure 3. It was found that the ethylene consumption rates were drastically increased with the addition of 1-hexene, then decreased promptly, which is according with the improvement of activity. All the kinetic curves had a similar shape, which showed that pH value of co-impregnation solution had little effect on the kinetic performance.

High temperature  $^{13}\text{C}$  NMR was utilized to investigate the contents of 1-hexene incorporation of the copolymers obtained from these catalysts. In this work, the copolymers synthesized with 3 vol% of 1-hexene were chosen to analyze the 1-hexene incorporation, and the results are listed in Table 3 ( $^{13}\text{C}$  NMR spectra are shown in the Supporting Information as Figure S3).

From these results, it was found that the 1-hexene incorporation showed a decreasing tendency from 8.43 (mol%) to 4.48 (mol%) in Table 3. These results indicated that the pH value of the co-impregnation solution had great effects on the incorporated short chain branches. Lower pH value was favorable to the 1-hexene incorporation, which was dissimilar to Matta's work on the Phillips catalyst system [8]. However, in this situation, the enhanced acidity obviously benefited the 1-hexene incorporation at least at the range of pH=5 to pH=9, which might be the strength of weak acid sites and the amount of the medium and strong acid sites discussed in the characterization results of the catalysts. However, for a clearer explanation, there is need for further investigation.

### Effect of hydrogen

Hydrogen is widely used as a chain-transfer agent in the low-pressure olefin polymerization process over the Ziegler-Natta catalyst. The presence of hydrogen has decreased both product's molecular weight and catalytic activity for ethylene polymerization, which is generally accepted for Ziegler-Natta catalysts [36-39]. Hydrogen effects on catalyst activities and average molecular weight ( $M_w$ ) of polymers are shown in Table 4 and Figure 4 (GPC curves are shown in the Supporting Information as Figure S4).

The decrease of catalyst activities with the introduction of hydrogen was similar, and the addition of 10 mL hydrogen resulted in that the Mw of polymers obtained from the Cat-0, Cat-1, Cat-2 and Cat-3 catalysts decreased 42.3%, 48.0%, 48.7% and 44.9%, respectively. The V-modified Ziegler-Natta catalyst (namely Cat-1, Cat-2 and Cat-3 catalysts) showed higher hydrogen response in comparison with that of the Mg/Ti/Si catalyst, which meant the V-modified Ziegler-Natta catalysts exhibited much better hydrogen response than the V-free Mg/Ti catalyst which is in agreement with Wang's work [21].

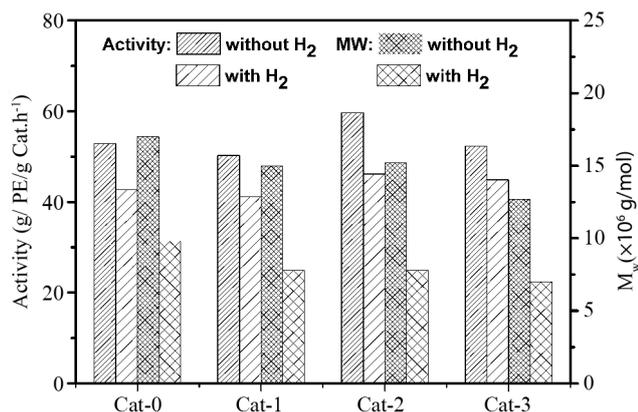
Besides, the V-modified Ziegler-Natta catalysts obtained the best hydrogen response at pH=7. Actually, similar to activity result, higher and lower pH values were not beneficial to the hydrogen response.

The kinetic curves for each catalyst kept the similar tendency with or without hydrogen, except for the decrease of ethylene consumption rate in the polymerization with hydrogen as shown in Figure 5. This meant that hydrogen did not affect the activation and deactivation rates of the polymerization centers. However, until now, the hydrogen effect is still very difficult to be fully understood and explained well, because it behaves in various aspects depending on the

**Table 4.** Effects of hydrogen on ethylene polymerization activities with different catalysts and characterization of their polymers.

Catalyst	Al/Ti	Activity [g PE/g Cat·h <sup>-1</sup> ]	T <sub>m</sub> <sup>(a)</sup> [°C]	X <sub>c</sub> <sup>(a)</sup>	M <sub>w</sub> <sup>(b)</sup> [×10 <sup>5</sup> g/mol]	MWD <sup>(c)</sup>
Cat-0	1	42.7	134	60.7	9.8	4.1
Cat-1	10	41.2	135	60.1	7.8	4.6
Cat-2	2.5	46.2	135	61.0	7.8	4.7
Cat-3	10	44.9	135	61.3	7.0	4.4

Conditions: catalyst 100 mg, ethylene 0.15 MPa, *n*-heptane 80 mL, TIBA, 70 °C, 1 h, 10 mL H<sub>2</sub>; <sup>(a)</sup> T<sub>m</sub> and ΔH<sub>f</sub> by DSC thermograms, X<sub>c</sub> evaluated by ΔH<sub>f</sub><sup>\*</sup>100/ΔH<sub>f</sub><sup>0</sup>, ΔH<sub>f</sub><sup>0</sup> (enthalpy of fusion of 100 % crystalline PE) = 293 J/g; <sup>(b)</sup> M<sub>w</sub> estimated by HT-GPC in TCB, average molecular weight; <sup>(c)</sup> Polydispersity index (M<sub>w</sub>/M<sub>n</sub>).



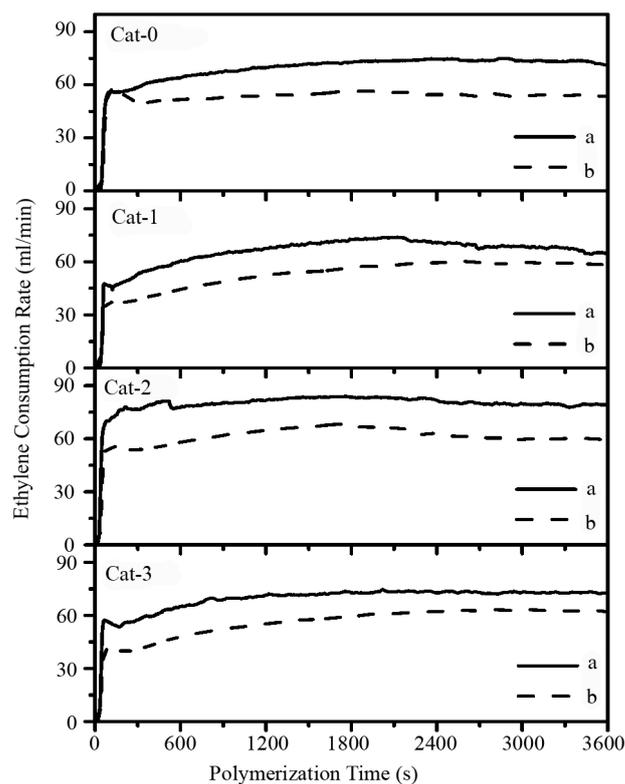
**Figure 4.** Hydrogen effects on catalyst activities and average molecular weight ( $M_w$ ) of polymers. Polymerization conditions: catalyst 100 mg, ethylene 0.15 MPa, n -heptane 80 mL, TIBA, 70°C, 1 h.

catalyst type and the polymerization conditions.

## CONCLUSION

In this work, in order to further optimize the experimental preparation conditions for the vanadium-modified  $(\text{SiO}_2/\text{MgO}/\text{MgCl}_2)\cdot\text{TiCl}_x$  Ziegler-Natta catalyst, experiments on the effects of pH value of co-impregnation solution during catalyst preparation were conducted and the vanadium-modified  $(\text{SiO}_2/\text{MgO}/\text{MgCl}_2)\cdot\text{TiCl}_x$  Ziegler-Natta catalysts were prepared by co-impregnation of water-soluble magnesium and vanadium salts on  $\text{SiO}_2$  under different pH values (pH= 5, 7 and 9), then several key factors such as the pH value of the co-impregnation solution during catalyst preparation, the catalyst performances including catalytic activity, ethylene/1-hexene copolymerization and hydrogen response for these catalysts were fully investigated.

By characterization of the catalysts and the polymers, and investigation of the polymerization behaviors, it was demonstrated that the pH value of co-impregnation solution as a critical factor actually had significant effects on the nature and the catalytic performance of vanadium-modified  $(\text{SiO}_2/\text{MgO}/\text{MgCl}_2)\cdot\text{TiCl}_x$  Ziegler-Natta catalysts. It was found that the components, structures and performance of the catalysts were obviously affected by changing the pH value (pH=5, 7 and 9) of co-impregnation solution during catalyst preparation. Ethylene homo-polymerization activity had a



**Figure 5.** Kinetic curves of ethylene polymerization with/without hydrogen using different catalysts with their optimal Al/Ti molar ratios: a without  $\text{H}_2$ ; b with  $\text{H}_2$  (10 mL). Other polymerization conditions: catalyst 100 mg, ethylene 0.15 MPa, n -heptane 80 mL, TIBA, 70°C, 1 h.

maximum value of 59.7 g PE/g Cat $\cdot$ h<sup>-1</sup> at pH=7 with only 2.5 of optimal Al/Ti molar ratio, which was lower than those for other two catalysts (at pH=5 and 9) and much lower than the industrial value, resulting in much lower production cost. This might be attributed to the different components (titanium and vanadium) contents and different kinds of possible titanium and vanadium precursors with different structures on the surfaces of the catalysts. The 1-hexene incorporation showed a decreasing tendency from 8.43 (mol %) to 4.48 (mol %), indicating that the enhanced acidity obviously benefited the 1-hexene incorporation (at least when pH=5, 7 and 9), which might be the strength of weak acid sites and the amount of the medium and strong acid sites discussed in catalysts characterization. From the hydrogen response experiments, the best hydrogen response was achieved for the vanadium-modified  $(\text{SiO}_2/\text{MgO}/\text{MgCl}_2)\cdot\text{TiCl}_x$  Ziegler-Natta catalyst prepared at pH=7. The GPC results showed that the polymers obtained from these catalysts had high average molecular weight with medium molecu-

lar weight distribution.

As a whole, the results showed that the pH value of the co-impregnation solution during catalyst preparation could largely influence the catalytic performance via affecting the catalysts, and an appropriate pH value (pH=7) could maximize catalytic activity and hydrogen response, while lower pH value (pH=5) was beneficial to the 1-hexene incorporation, therefore, it could be concluded that a better result could be obtained under the condition of pH value of 7 in this situation for the vanadium-modified  $(\text{SiO}_2/\text{MgO}/\text{MgCl}_2)\cdot\text{TiCl}_x$  Ziegler-Natta catalysts as a compromise.

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## SUPPORTED INFORMATION

Support Information is available for this article and is accessible for authorized users.

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