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Novel Cr/Ti bimetallic polyethylene catalysts synthesized through introduction of chromium species into the $(SiO_2/MgR_2/MgCl_2)\cdot TiCl_x$ Ziegler-Natta catalyst

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ABSTRACT

A series of novel Cr/Ti bimetallic polyethylene catalysts were successfully synthesized for the first time through introduction of chromium species into the $(SiO_2/MgR_2/MgCl_2)\cdot TiCl_x$ Ziegler-Natta catalysts. The bimetallic catalysts, which showed high activity, were simply prepared by refluxing titanium choloride with chromium modified silica gel/alkyl Mg adducts. Moreover, the effects of chromium content and calcination temperature were investigated in detail. The results obtained in the study were used to systematically discuss a clear relationship between the catalyst preparation condition and the relative performance of different metal active centers. Factors including surface hydroxyl content, catalyst performance in homo-polymerization, ethylene/1-hexene copolymerization were systematic investigated. Comparably, the chromium modified catalyst shows catalytic performance with 89% higher activity, 41.5% higher hydrogen response and 46.3% higher 1-hexene incorporation than the original $(SiO_2/MgR_2/MgCl_2)\cdot TiCl_x$ Ziegler-Natta catalyst. A new schematic model was proposed to explain the accelerated activation process of the bimetallic catalysts with kinetic and SEM results: chromium active sites on the outer surface of support react 10 times quicker than Ti active sites initially and help to crack the catalyst particle in the first stage; then the released inner surface active sites start to accelerate the polymerization reaction in the second stage.

1. Introduction

Polyethylene (PE) is one of bulky industrial scale consumption mainly manufactured with supported Phillips catalyst, Ziegler-Natta catalyst, and metallocene catalyst. The material is used in various fields because of its advantages of low cost, excellent mechanical ability and benign processability. Among all the catalyst systems, Ziegler-Natta catalyst and Phillips catalyst hold the most of market shares [1,2].

After the originated discovery of $TiCl_4/AlEt_3$ and $TiCl_3/AlEt_2Cl$ systems by Ziegler and Natta in 1950s, the well-known supported Ziegler-Natta catalysts ($MgCl_2/TiCl_4$ system) was invented independently by Kashiwa [3] and Galli [4] in 1968. In Kashiwa's work [5,6], the anhydrous $MgCl_2$ which was used as the Mg source recrystallized after alcohol treatment, and then excess amount of $TiCl_4$ was introduced as the active species. This novel invention greatly promoted the development of industrial polyolefin process. Another important industrial Ziegler-Natta catalyst based $Mg(OEt)_2$ was invented by Böhm [7], this catalyst selected $Mg(OEt)_2$ as the Mg source and *in situ* reacted with $TiCl_4$ directly to form $MgCl_2$ as the support while loading Ti active center simultaneously. Industry also patented kinds of Ziegler-Natta catalysts: Union Carbide Corporation (UCC) company invented the UNIPOL gas-phase polyethylene process using the SiO_2 and $MgCl_2$ bi-support catalyst [8]; British Petroleum (BP) company started with alkyl magnesium, followed by adding SiO_2 and $TiCl_4$ to synthesis bi-support catalyst [9]. This alkyl magnesium type catalyst was generally neglected by industry owing to its requirement of relative expensive magnesium reagent. However, as the pre-reduction effect of alkyl aluminum reagent (TIBA and TEA) discovered in chromium based polyethylene catalysts [10,11], the alkyl magnesium reagent can similarly reduce the amount of cocatalyst consumption greatly in the successive

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polymerization process, which offsets the disadvantage mentioned above and made the catalyst industrially valuable.

Another type of polyethylene catalyst was Phillips catalyst invented by Hogan and Banks [12,13] in 1950s. The catalyst was prepared by impregnating aqueous chromium solution onto the silica gel, and followed by calcination with dry air in high temperature to disperse chromium oxide on the surface of SiO_2. Unlike the relatively narrow molecular weight distribution (MWD, usually lower than 10) of Ziegler-Natta catalyst, the Phillips catalyst exhibits board MWD (usually between 10 and 30) which own great merit in processability.

In recent years, great efforts were focused on developing bimetallic catalysts for ethylene polymerization. Bimetallic catalysts could possible inherit the merits of parental catalyst and improve polymer performance. Lowery [14] physically mixed $MgCl_2$ supported Ziegler-Natta vanadium catalyst with the SiO_2 supported chromium catalyst. Polymerization activity of obtained catalyst increased significantly, while the obtained polymer structure was controllable to some extent. Matta [15] synthesized bimetallic Phillips catalyst and the preparation conditions including pH value, vanadium content and vanadium sources were systemic studied. Heieh [16,17] combined MgO based Ziegler-Natta titanium catalysts and chromium catalysts, and the resulting catalysts could produce board MWD polymer. Ahmadi [18] hybridized a Ziegler-Natta/metallocene catalyst and the kinetic behavior was studied. The obtained polymers exhibited bimodal MWD patterns, suggesting that both components of the hybrid catalyst were active in the polymerization process.

Recently, our group developed various of bimodal catalysts by introducting the second metal content into basis polyethylene catalysts [10,11,19–24]. These series of catalysts including: (1)SiO_2-supported silyl-chromate (Cr)/vanadium-oxide(V) bimetallic catalyst; (2) SiO_2-supported silyl-chromate (Cr)/imido-vanadium(V) bimetallic catalyst; (3) SiO_2-supported chromium oxide (Cr)/vanadium oxide(V) bimetallic catalyst; (4) chromium/vanadium modified inorganic magnesium Ziegler-Natta catalyst; (5) $TiCl_4$/$VOCl_3$ hybrid Ziegler-Natta catalyst. These novel catalysts all showed several advantages of both metal active sites. In our previous work, a novel chromium SiO_2/MgO based Ziegler-Natta catalyst was synthesized using water soluble magnesium sources by Wang [19]. The Cr–Ti catalyst showed slightly higher activity and was capable to produce PE with good hydrogen response. However, in the work, the maximum reduction of polymer average MW produced by Cr–Ti catalyst was merely 24.2%, and the MWD even became narrower than the counterpart produced by unmodified Ziegler-Natta catalyst. This result indicated that the chromium modification effect by inorganic magnesium based Ziegler-Natta catalyst is unsatisfactory. Moreover, the high cocatalyst consumption was still a problem for potential industrial use. Triggered by the pre-reduction effect of alkyl aluminum on Phillips Cr-base catalyst in our recent work [10,11], the organic magnesium reagent were chose as a reducing reagent for chromium modification and simultaneously form $MgCl_2$ support. Based on that, an original bimetallic chromium SiO_2/MgR_2 based Ziegler-Natta catalyst were designated.

Fig. 1 compared the difference between typical preparation method of inorganic magnesium based Ziegler-Natta catalyst and organic magnesium based Ziegler-Natta catalyst. It was noticeable that the magnesium alkyl reagent is more than merely serve as support for titanium active species. The Mg alkyl reagent could reduce the chromium oxide into activation stage and scavenge the impurities on the silica gel. Besides, the pre-reduction could highly increase the modification metal active sites performance.

According to Nowlin et al. [25], hydroxyl groups (–OH) on the residual SiO_2 surface highly determined the magnesium loading in the catalyst preparation process. On the one hand, hydroxyl groups regulated original MgR_2 loading, then controlled the amount of $MgCl_2$ that *in situ* formed in the titanium reflux process, and would ultimately influence the titanium active species amount. On the other hand, hydroxyl groups were found to directly influence the

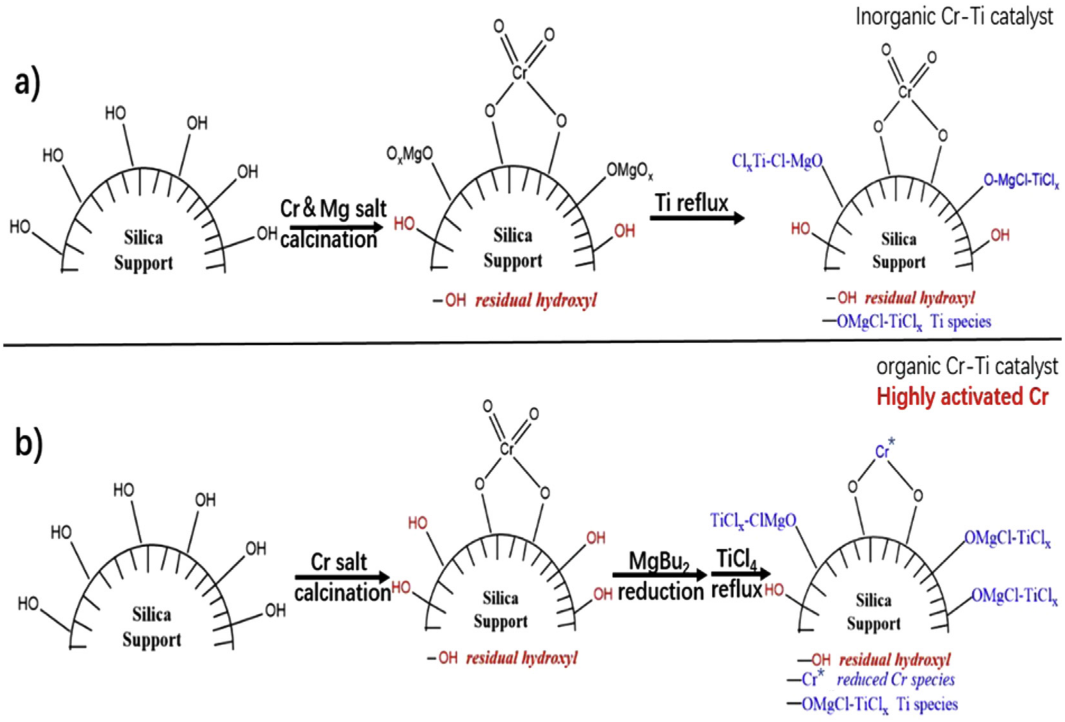

Fig. 1. Typical preparation procedure of the Cr–Ti bimetallic catalyst and the corresponding monometallic catalysts.

catalyst activity [2,26–28] and polymer property [2,27,29,30] in many silica supported polyolefin catalysts.

In this work, a novel Cr modified $(SiO_2/MgR_2/MgCl_2)\cdot TiCl_x$ Ziegler-Natta catalyst was designated and a systemic study which was focused on better modification effect and how the preparation condition affects the balance of Cr/Ti active species were carried out. The effect of chromium content and the calcination temperature effect on the catalyst activity and polymer properties were investigated in detail. The catalysts exhibited greatly improved activities and the resulting polymers showed a clear tendency in the shift of two metal species balance with the preparation condition changes. A scheme model was originally proposed to explain the synergistic effect of bimetallic catalyst based on kinetic and SEM results. This work were expected to give a deep insight into the Cr–Ti bimetallic catalyst and to provide a simplified model as a theoretical basis for synergistic effect of heterogeneous multimetallic catalysts.

2. Experimental section

2.1. Materials

In this work, silica gel (Grace Davison 955, surface area 261.8 m^2/g, pore volume 1.67 cm^3/g and average pore size 17.4 nm) and chromium (III) acetate (24 wt% Cr) was donated by Qilu Branch Co., SINOPEC. Dibutyl Magnesium ($MgBu_2$, 1.0 M in heptane) as Mg source and Triisobutylaluminum (TIBA, 1.0 M in toluene) as cocatalyst were purchased from Aladdin Co. Ltd. Titanium chloride ($TiCl_4$, 99 wt%) and hydrochloric acid (HCl, AR grade) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., and used without further treatment. The solvents including ***n***-hexane (AR grade, Sinopharm Chemical Reagent) and ***n***-heptane (AR grade, Sinopharm Chemical Reagent) were purified by distillation in the presence of sodium metal slices and diphenyl ketone as an indicator until the indicator showed pure blue and purified solvent were stored in a stainless-steel storage tank under purified nitrogen. The ultrahigh purity nitrogen ($\geq$99.999%) was further purified by passing through one column of 4A molecular sieves (purchased from Sinopharm Chemical Reagent Co., Ltd.) for dehydration and one column of sliver molecular sieves (28 wt% of silver (I) oxide on alumina, purchased from Sigma-Aldrich) for deoxidation. Hydrogen ($\geq$99.999%) and high-purified dry air (99.99%) were purchased from Shanghai Wetry Criterion Gas Co., Ltd. Ethylene monomer (polymer-grade, Wetry) 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 commoner 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 before use.

2.2. Catalyst preparation

All the experiments were performed under nitrogen using standard Schlenk, vacuum-line, or inert-atmosphere box techniques. First, about 6 g silica was calcined in a fluidized bed reactor with purified nitrogen at 300 °C for at least 1 h, and cooled to ambient temperature before use. Second, about 5 g of calcined silica impregnated with calculated amount of chromium acetate in aqueous solution with a magnetic stirrer at 50 °C for 4 h before drying in 120 °C overnight. After impregnation, the supported silica were calcined under dry highly purified air with the flow rate of 600 ml/min in fluidized-bed quartz reactor for 4 h at various temperature (300 °C, 400 °C, 500 °C and 600 °C) before it sealed. Third, under nitrogen, about 3 g of catalyst prepared above were transferred into a three-necked flask with a magnetic stirrer, then about 2 wt% dibutyl magnesium solution were injected with 50 ml purified n-heptane. The mixtures were stirred at 55 °C for 2 h, and washed with fresh purified heptane for 5 times. After swept with nitrogen for 1.5 h, the precursor was vacuum dried at 110 °C for 30 min. The dry silica powder was mixed with 30 ml of titanium chloride ($TiCl_4$, 99 wt%) and refluxed at 140 °C for 2 h before cooling to room temperature for 10–20 min. Then, the supernatant liquid was removed and the precipitates were washed with about 40 ml purified n-hexane for 5 times. The residual solvent was removed at 145 °C with nitrogen flow for 1 h and was dried in vacuum for 0.5 h. Finally, the catalysts were cooling to room temperature and stored in glove box before use. Herein, bimetallic Ziegler-Natta catalyst $((CrO_x/SiO_2/MgR_2/MgCl_2)\cdot TiCl_x)$ with 0.5 wt% of Cr content which calcined at different temperature including 300 °C, 400 °C, 500 °C and 600 °C were prepared and denoted as 3CMT, 4CMT, 5CMT, 6CMT, respectively. To investigate how the chromium content affects catalyst performance, 1 wt% and 2 wt% chromium content $(CrO_x/SiO_2/MgR_2/MgCl_2)\cdot TiCl_x$ catalysts at optimum temperature (500 °C) were prepared and denoted as 5C1MT, 5C2MT. For comparison, unmodified $(SiO_2/MgR_2/MgCl_2)\cdot TiCl_x$ and SiO_2/CrO_x Phillips catalyst, both calcined at 500 °C were prepared in the same way and donoted as 5 MT and 5Cr.

2.3. Ethylene and ethylene/1-hexene polymerization

The slurry polymerization was carried out at atmospheric pressure for polymerization. First, one small tube with about 100 mg catalyst was weighed and sealed in the glove box beforehand. The tube was transferred to a 250 ml three-necked flask with a thermostatic oil bath keeping at 70 °C. Before use, the reactor system was heated in vacuum and purged by nitrogen for at least three times, then purged by ethylene monomer for three times to ensure the monomer fill in the flask about 0.12 MPa. Secondly, 80 ml n-heptane, a certain amount of cocatalyst TIBA (at certain Al/Ti molar ratio), and 10 ml hydrogen or certain amount of 1-hexene (if necessary, 1 vol%, 3 vol% and 5 vol% of n-heptane) were subsequently injected into the flask with magnetically stirring. After the injection, the system was saturated at the ethylene pressure of 0.15 MPa and stay until the ethylene consumption stopped, and the polymerization started after opening the sealed catalyst tube to let the catalyst contact the slurry. The entire polymerization was carried out at 70 °C for 1 h. An on-line mass flow meter (Brooks SAL5800E) recorded the real-time ethylene consumption profile. Last, the polymerization was terminated by the addition of 200 ml ethanol/HCl solution and the polymers were collected. All the obtained polymers were washed with ethanol, filtered out from the solution and dried under vacuum at 60 °C for at least 6 h before weighing.

2.4. Characterization of catalyst and polymer

The magnesium and chromium loading of the prepared catalysts was determined by inductively coupled plasma spectrometry (ICP) (Varian 710-ES, Varian Company, USA). The power of the ICP spectrometer was 1.10 kW. The flow rates of plasma gas and auxiliary gas were 15.0 L/min and 1.50 L/min, respectively. The pressure of nebulizing gas was 200 kPa and the pump speed was 13 rpm.

In order to ensure the titanium content of the prepared catalyst, ultraviolet–visible spectrophotometer (UV–vis) through hydrogen peroxide colorimetric method [31] were used. The catalyst was dissolved in 2 M sulfuric acid followed by dilution with deionized water to 25 ml. The diluted solution was reacted with H_2O_2 to form peroxotitanium complex [$TiO(H_2O_2)$]. UV–vis measurements were carried out in 10 mm quartz glass cells on a Mapada UV-3200 spectrophotometer (Mapada UV-3200, Mapada company, UK). The intensity of a peak at 409 nm was used to quantify the titanium content.

Nitrogen adsorption/desorption experiments were conducted on the automatic physisorption analyzer (Micromeritics ASAP 2020, Micromeritics company, USA) at 77 K to obtain the value of the catalyst specific surface area (S_{BET}) which was calculated based on the Brunauer-Emmett-Teller (BET) method, and the catalyst pore volume (Vp) and average pore size (d) were evaluated using the Barrett-Joyner-Halenda (BJH) method.

To investigate the polymer feature, Differential Scanning Calorimetry (DSC), High Temperature Gel Permeation Chromatography (HT-GPC) and ^{13}C NMR were used in the characterization. For DSC test, about 5 mg polyethylene sample was sealed in an aluminum sample cell as a test carrier. The aluminum cell was heated to 160 °C at the rate of 10 °C/min and stay for 5 min to remove thermal history, then cooled down to 40 °C at 10 °C/min and finally heated to 160 °C at 10 °C/min in a DSC analyzer (DSC Q200, TA Company, USA) to record the second heating curve and melting temperature (T_m). The enthalpy of fusion ($\varDelta H_f$) of each sample was also calculated by the DSC curve.

The MW and MWD of produced polyethylene were measured by HT-GPC (Agilent PL-220, Agilent company, UK) with two PL gel-mixed B columns at 160 °C, and the flow rate was 1.0 ml/min 1,2,4-trichlorobenzene (TCB) and polystyrene (PS) were used as solvent and standard sample, respectively. Polymers were dissolved at 160 °C in TCB at a concentration of 1.0 mg/ml before injection to the chromatography.

The 1-hexene incorporation of the copolymer was measured by high temperature ^{13}C NMR. Each sample (about 10 mg) was equipped into a 5 mm of NMR tube with 1,4-dichlorobenzene-d_4 (DCB-d_4) as the solvent (sample concentration: ca. 15 mg/ml) and scanned by high temperature ^{13}C NMR (Varian Inova-400 MHz, Varian company, USA) at 110 °C at 600 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.

3. Result and discussion

3.1. Characterization of the catalyst

The prepared catalysts were characterized by UV–Vis and ICP to evaluate elements contents. The N_2 absorption/desorption measurements for supported catalysts were taken to determine specific surface area and pore structure parameters.

From Table 1, catalysts showed a clear trend that actually loading of magnesium content and titanium content that were negative correlated with the calcination temperature. The result was consistence with the finding of Nowlin [25] and McDaniel [2] in that the reduced calcination temperature remained more hydroxyl groups for metal loading. Further the BET results exhibited an slightly drop in specific surface area and pore parameters with the rising addition of metal element, which is accordance with plenty of earlier work [2,27,31–33]. For different calcination temperature, the structure parameter was similar due to the relative low calcination temperature would not effect in a limited way on catalyst particle structure.

3.2. Ethylene homopolymerization

3.2.1. Effect of calcination temperature

It was noticed that the calcination temperature of many support material correlated negatively with hydroxyl groups on the supported precursor and catalyst, silica gel included [2,27,31–33]. Meanwhile, the hydroxyl groups on the precursor would affect metal sites loading significantly, which would further influence the catalyst activity and polymer feature. However, too much hydroxyl groups would in turn serve as impurities in the reaction system that industry made all efforts to avoid. To investigate the effect of calcination temperature on polymerization, four 0.5 wt% Cr modified Cr–Ti bimetallic catalysts were synthesized at varying calcination temperature (300 °C, 400 °C, 500 °C, and 600 °C, respectively), labeled as 3CMT, 4CMT, 5CMT, 6CMT, respectively and further used in ethylene homopolymerization. The model catalyst without chromium active sites were synthesized at 500 °C for comparison, labeled as 5 MT. Still, monometallic Cr catalyst prepared under 500 °C for comparison, labeled as 5Cr. Previous works showed that TIBA as the cocatalyst leads to higher activity for Zigler-Natta Ti catalyst [21,22]. Thus, in this work, TIBA was employed as cocatalyst for polymerization. The ethylene homopolymerization activity of various catalysts and product properties were listed in Table 2. The activity results and the kinetic curves showed a good reproducibility.

Run 1–20 in Table 2 showed that, ethylene polymerization activities increase firstly to a maximum value until 500 °C with the rise of calcination temperature and then decrease. Combined with Fig. 2, it's even clear that the first activity enhancement stage in relative low temperature was accordance to the traditional 1 wt% CrO_x Phillips catalyst's trend that increasing polymerization activity vesus increasing calcination temperature in catalyst preparation process [28]. This trend was explained by the phenomenon that too much hydroxyl groups impurities under low calcination temperature decreased the polymerization activity, which was remedied under higher calcination temperature. Then in the higher calcination temperature zone (above 500 °C), activity reduction can be

Table 1
Basic features of different catalysts.

No.	Catalyst	Elements Contents			Pore Structures[c]		
		Ti[a] [wt%]	Mg[b] [wt%]	Cr[b] [wt%]	S_{BET} [$m^2\ g^{-1}$]	V_p [$cm^3\ g^{-1}$]	d [nm]
1	3CMT	4.0	1.9	0.29	221.8	0.95	18.8
2	4CMT	3.4	1.7	0.31	223.2	0.98	18.4
3	5CMT	3.1	1.6	0.30	218.5	0.96	19.2
4	6CMT	2.6	1.5	0.31	219.5	0.97	18.5
5	5C1MT	2.9	1.5	0.67	209.1	0.88	17.4
6	5C2MT	2.9	1.3	1.30	204	0.81	18.2
7	5Cr	/	/	0.42	219.1	1.19	23.7
8	5 MT	3.2	1.6	/	250	1.25	20.6

[d] Measured by UV–Vis; [b] Measured by ICP; the initial addition amounts of magnesium of the catalysts were 5 wt %; [c] Measured by nitrogen adsorption/desorption experiments.

Table 2
Ethylene homopolymerization activities of different catalysts and polymer properties.

No.	Catalysts	Al/Ti	Activity [gPE/g Cat.·h^{-1}]	Activity [kg PE/mol Ti.·h^{-1}]	T_m[a] [°C]	△H_f[a] [J/g]	M_w[b] [$\times 10^5$ g/mol]	MWD[c]
1	3CMT	1.25	74	88.56	135	128.9	14.64	6.14
2	3CMT	2.5	81	96.94	135	137	14.31	7.16
3[d]	3CMT	2.5	70	83.77	135	152.9	9.59	9.08
4	3CMT	5	73	87.36	135	139.3	14.03	7.80
5	3CMT	10	64	76.59	135	138.6	13.61	8.12
6	4CMT	0.3125	88	123.90	135	139.9	12.18	11.25
7	4CMT	0.625	90	126.71	135	136.6	13.11	8.09
8[d]	4CMT	0.625	64	90.11	135	154.7	9.26	10.53
9	4CMT	1.25	85	119.68	135	134.6	12.76	8.62
10	4CMT	2.5	80	112.64	135	132.1	12.50	10.36
11	5CMT	0.625	95	146.70	135	133.2	12.04	9.21
12	5CMT	1.25	121	186.85	135	137	11.54	11.51
13[d]	5CMT	1.25	92	142.07	135	142.7	7.81	10.69
14	5CMT	2.5	105	162.14	135	142.7	11.64	14.71
15	5CMT	5	88	135.89	136	143.4	11.18	21.79
16	6CMT	1.25	88	162.02	135	139.9	10.62	12.86
17	6CMT	2.5	95	174.91	136	134.2	10.41	13.93
18[d]	6CMT	2.5	82	150.97	135	145	7.08	5.28
19	6CMT	5	90	165.70	136	140.8	10.29	15.24
20	6CMT	10	85	156.50	135	139.9	10.27	18.01
21	5 MT	0.625	62	92.75	135	139.2	17.40	5.34
22	5 MT	1.25	64	95.74	135	143.8	17.11	4.24
23[d]	5 MT	1.25	50	74.80	135	141.6	12.00	4.93
24	5 MT	2.5	64	95.74	135	130.4	17.38	4.75
25	5 MT	5	53	79.28	135	126.4	17.05	5.92
26	5C1MT	1.25	95	156.82	135	133.2	10.92	6.82
27	5C1MT	2.5	98	161.77	135	137	10.36	13.54
28[d]	5C1MT	2.5	90	148.56	135	162.2	6.69	3.54
29	5C1MT	5	86	141.96	135	142.7	10.94	9.08
30	5C1MT	10	82	135.36	135	143.4	10.02	10.60
31	5C2MT	1.25	72	118.85	135	134.5	12.66	6.39
32	5C2MT	2.5	75	123.80	135	139.2	12.67	6.49
33	5C2MT	5	99	163.42	135	137.3	12.36	6.70
34[d]	5C2MT	5	78	128.75	136	153.1	7.14	5.23
35	5C2MT	10	80	132.06	136	141.9	12.26	5.89
36[e]	5Cr	/	19	/	135	140.2	9.41	38.54

Other polymerization conditions: catalyst 100 mg, ethylene 0.15 MPa, n-heptane 80 ml, TIBA, 70 °C, 1 h.

[a] T_m and ΔH_f by DSC thermograms.

[b] M_W estimated by HT-GPC in TCB, average molecular weight.

[c] MWD (M_W/M_n) measured by HT-GPC.

[d] Polymerization with 10 ml H_2.

[e] same cocatalyst amount as run 12.

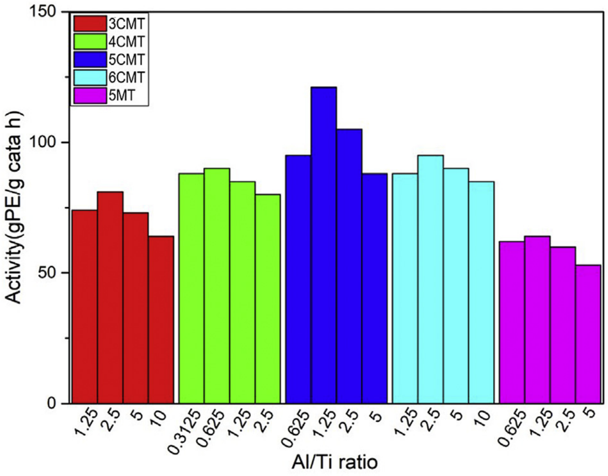

Fig. 2. Ethylene homopolymerization activities of catalysts with different dose of TIBA. Other polymerization conditions: catalysts 100 mg, ethylene pressure 0.15 MPa, heptane 80 ml, 70 °C, 1 h.

explained that high calcination temperature leads to prominent decrease of surface —OH group which is essential for the magnesium loading. Further, the titanium active species on $MgCl_2$ crystal reduces sharply along with the polymerization activity, as shown in Table 1.

For each catalyst, the optimum cocatalyst amount was reached at extremely low Al/Ti ratio value. This unique advantage for industrial use results from our organic magnesium alkyl source, which is similar to the reaction pattern of pre-reduction catalyst, as our lab reported before [11]. For run 12, the highest polymerization activity was reached at 121 gPE/g cata h. Contrasting with unmodified 5 MT catalyst (run 22) under similar cocatalyst concentration, 89% increase in polymerization activity with merely 0.5 wt% chromium modification indicated chromium species were highly activated in the catalyst. As compared with the chromium modification of inorganic magnesium $(SiO_2/MgO/MgCl_2)\cdot TiCl_x$ catalyst's increasing 13% overall polymerization activity, the chromium modification on organic magnesium $(SiO_2/MgR_2/MgCl_2)\cdot TiCl_x$ Ziegler-Natta catalyst showed significant advantage in reaction rate and great effect in polymer feature, we will discuss that below [19]. The activity of all Cr—Ti bimetallic $CrO_x\cdot(SiO_2/MgR_2/MgCl_2)\cdot TiCl_x$ Ziegler-Natta catalysts showed remarkably higher activity than $(SiO_2/MgR_2/MgCl_2)\cdot TiCl_x$ Ziegler-Natta model catalyst 5 MT. This allowed us to identify that chromium modification was an effective way to enhance the activity in the organic magnesium Ziegler-Natta catalyst system.

Fig. 3 showed the kinetic curve of ethylene homopolymerization with bimetallic catalysts at different calcination temperature and the monometallic model catalysts. It can be observed that the ethylene homopolymerization behavior over bimetallic catalysts showed similar kinetic profiles, the polymerization rate first increased rapidly to an initial point during first 30 s after the induction time, then raised steadily until reached a peak platform in about a quarter and kept it until the reaction ends. From the kinetic curves, the catalyst activities were arranged in the order of 5CMT>6CMT>4CMT>3CMT>5 MT > 5Cr. Further analyzing the kinetic curves, a conclusion can be drawn that these catalysts performed similarly in the relative low Al/Ti ratio. While the ratio increasing to 5 or 10, the activity declined remarkably. This was because the pre-reduction effect of organic magnesium reagent has already reduced the active site into proper valence and a slightly high dosage cocatalyst would cause deactivation from over-reduction.

Moreover, as the calcination temperature increased, the proportion of Ti species in bimetallic catalyst would decline. First, for catalysts with low calcination temperature, like 3CMT and 4CMT, the initial reaction rate in the first 1 min was slow with low Cr/Ti ratio value, and the platform zone showed a gradually enhancement, which makes the kinetic curve share the shape of Ti monometallic catalyst (Fig. 3(e)). Similarly, the kinetic curve of higher calcination temperature catalyst 5CMT and 6CMT exhibited the feature of Cr monometallic catalyst (Fig. 3(f)), which reach the platform in a short time and gradually drops. This was an exciting evidence that the balance of two active sites change with the relative metal species proportion altering.

The initial reaction rate of Cr species was sharply higher than Ti active species for per metal element atom (Fig. 3(e) and (f) and Table 1). Further, the far higher Cr species activation rate would collapse the catalyst particle and the polymerization accelerated. As one of the evidence, the time high Cr/Ti ratio catalysts (5CMT and 6CMT) with high calcination temperature takes to reach the platform zone also seen an extremely reduction in the kinetic curve, compared with lower Cr/Ti ratio catalysts (3CMT and 4CMT) with low calcination temperature.

To further investigated the reason why the modified catalyst shows high activity after modified with Cr active species, SEM was took to analyst the reaction process. Fig. 4 clearly showed that the catalyst particles all remains in good shape. In the second row, catalyst 5 MT remained intact with minor polymer dotted on the catalyst surface while the catalyst 5CMT had already to crack into fragment. In 120 s row, the fragment degree of modified catalyst 5CMT was sharply higher than the left part. Thus, the internal active center may release in a short time, that is why the platform of chromium modified catalyst is much higher than unmodified one [34]. Combined with kinetic result and SEM result, a simplified model was presented in Fig. 5 to depict the accelerate activation process. This was why the bimetallic catalyst showed 89% higher activity than unmodified Ti catalyst with merely 0.5 wt% Cr modification. In addition, the kinetic and SEM evidence showed how the bimetallic catalysts showed synergies that greatly enhance the reaction rate was first to discovered in this area.

Based on the kinetic curve feature in Fig. 3 and SEM result in Fig. 4, a simplified model was proposed to explain the highly increased activity of our Cr modified catalysts. The accelerate activation process scheme was shown in Fig. 5, combing two

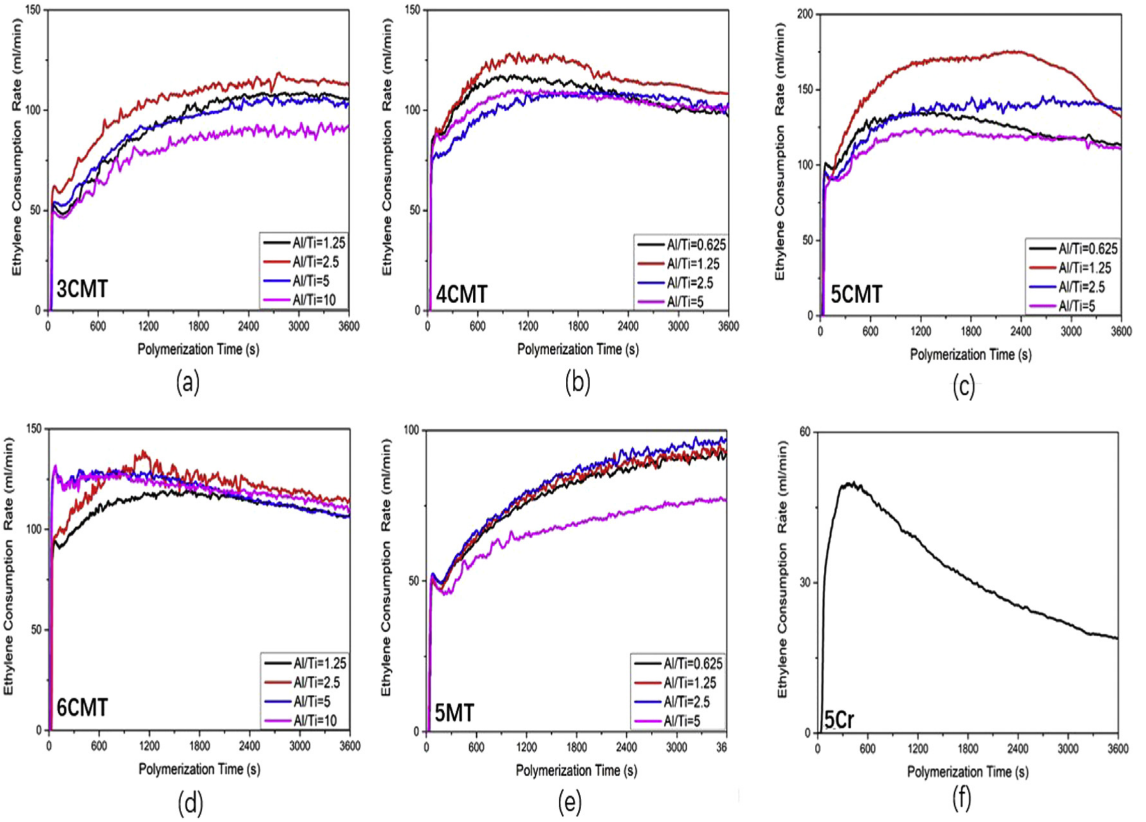

Fig. 3. Kinetic curve of ethylene homopolymerization using catalysts: (a) 3CMT; (b) 4CMT; (c) 5CMT; (d) 6CMT; (e) 5 MT; (f) 5Cr, at different dose of TIBA. Other polymerization conditions: catalysts 100 mg, ethylene pressure 0.15 MPa, heptane 80 ml, 70 °C, 1 h.

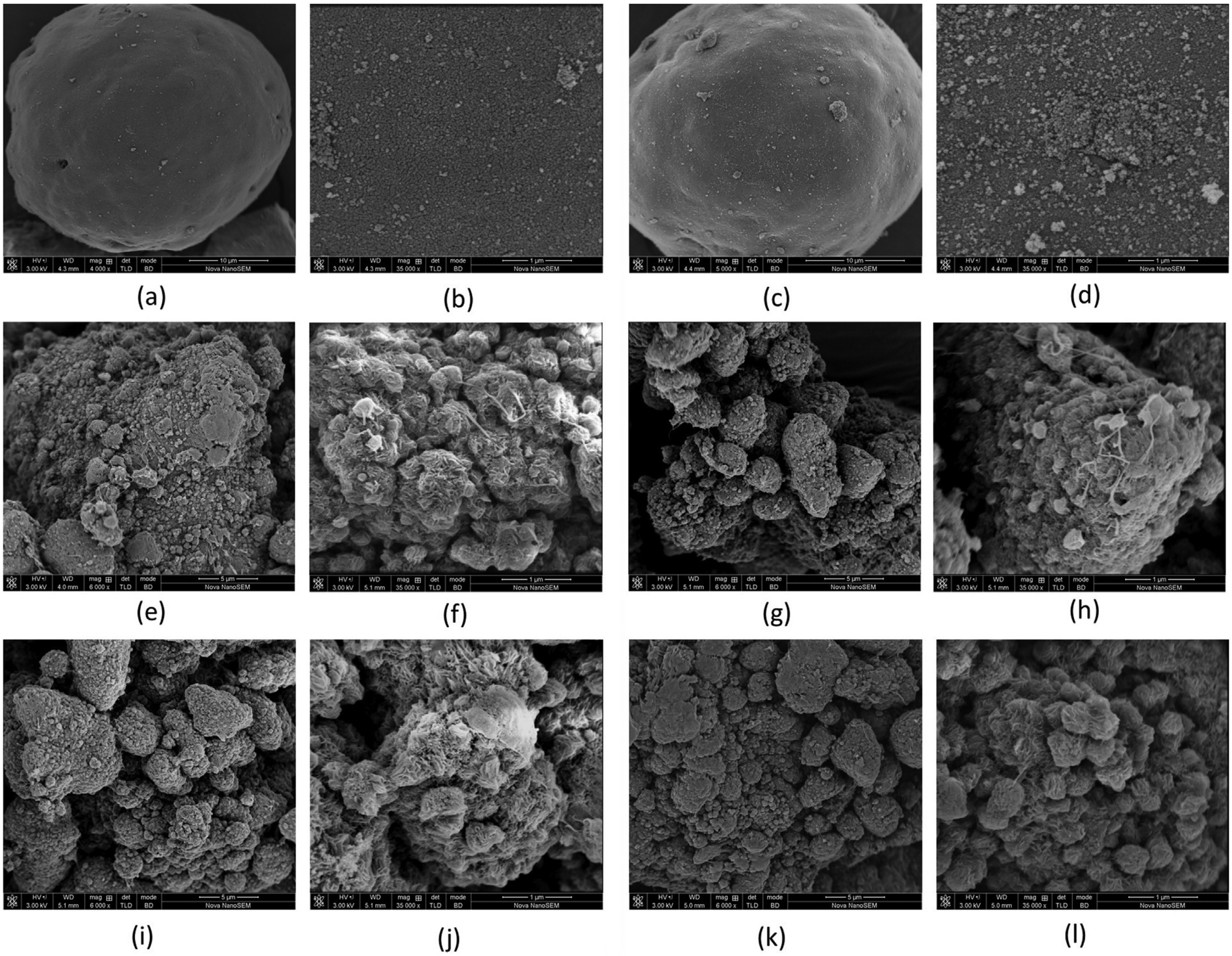

Fig. 4. SEM picture of polymer and catalyst particle in different times. (a–d) 0 s; (e–h) 60 s; (i–l) 120 s. Catalyst in polymerization: (a, b, e, f, i, j) 5 MT; (c, d, g, h, k, l) 5CMT.

separate stages. In the first accelerating stage, Cr and Ti active species on the outer silica surface start to react with ethylene. Because of the far higher activity of Cr species vast polyethylene generated in the short seconds forced the silica support to collapse into fragments. Thus, in the second stage, the much greater amount inner surface active sites start to expose in the reaction environment, and the reaction rate went up rapidly.

HT-GPC method was applied to characterize the resulting homopolymers in order to get further details of these catalysts on ethylene polymerization. Fig. 6 showed the GPC curve of each given catalyst with increasing cocatalyst dosage. It could be observed that the increasing alkyl aluminum concentration would induce a slightly decreasing molecular weight and boarder MWD. This may due to strong chain transfer effect of alkyl metal salts that would transfer the nascent polymer chain out of active sites, lower the molecular weight and widen MWD [35].

Fig. 7 showed the GPC curves of the polymer produced by each catalyst under optimum cocatalyst condition (run 2, 7, 12, 17, 23, 36). As reported [2,21], the chromium oxide Phillips catalyst produced PE with board MWD (with both considerable high and low molecular weight ends), while silica supported Ziegler Natta catalyst produced narrow MWD with higher molecular weight than Phillips. For Cr–Ti catalysts, the GPC curve of 4 chromium modified catalysts showed intensive trend of left shifting, with a significant long tail in low molecular weight part, compared with the unmodified Ti catalyst. The result indicated that both Cr and Ti are activated active centers in the polymerization process; the Ti center produced high molecular weight part peak as the Cr molecular center preferred produced low molecular weight shoulder and ultrahigh molecular weight tails. Meanwhile, the increased calcination temperature lead catalysts a prominent molecular weight drop with broader MWD. The finding could be explained that the increasing calcination temperature would reduce the surface hydroxyl groups which will subsequently decreasing the organic magnesium loading [25]. As reported in series of literature [36,37], the titanium chloride would supported on the imperfect surface of magnesium chloride crystal. The titanium content in the final catalyst would be determined by the magnesium loading and further effect the titanium active center amount. The explanation reinforced by the ICP result of various catalyst in Table 1. Due to the decreasing titanium loading, the balance of two metal active sites affected the proportion of low and high molecular weight part. Less titanium loading resulted from higher calcination temperature which will make the obtained polymer a lower molecular weight and wider MWD, and the balance of polymerization dominated by the chromium part gradually, vise versa.

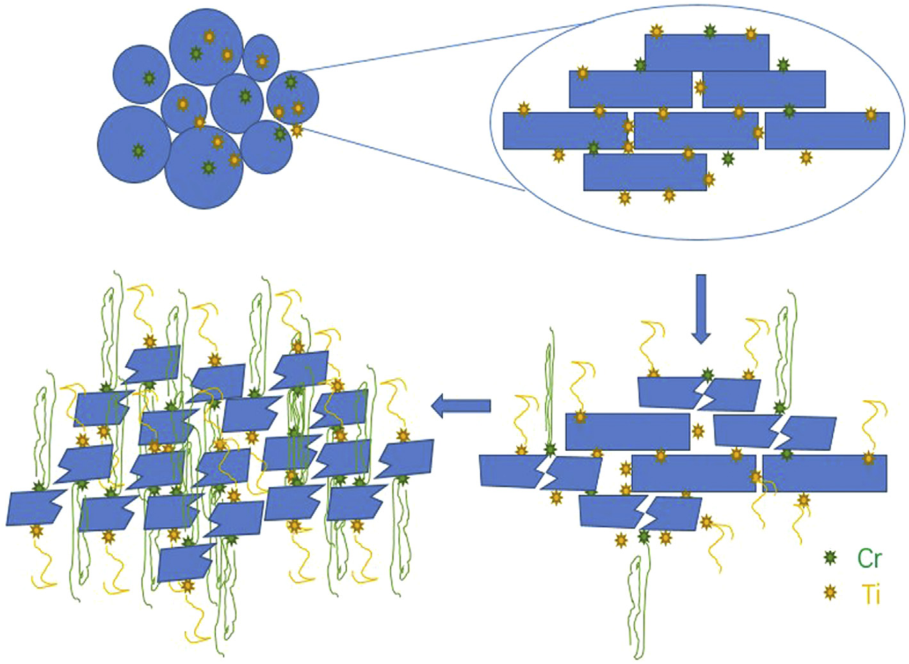

Fig. 5. Schematic model of the two-stage accelerate activation process. The blue platelets represent catalyst particle with adsorbed CrOx (green dots) and $TiCl_4$ (yellow dots) as the precursor of active sites, and the zigzag lines represent polyethylene chains produced with different active sites. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

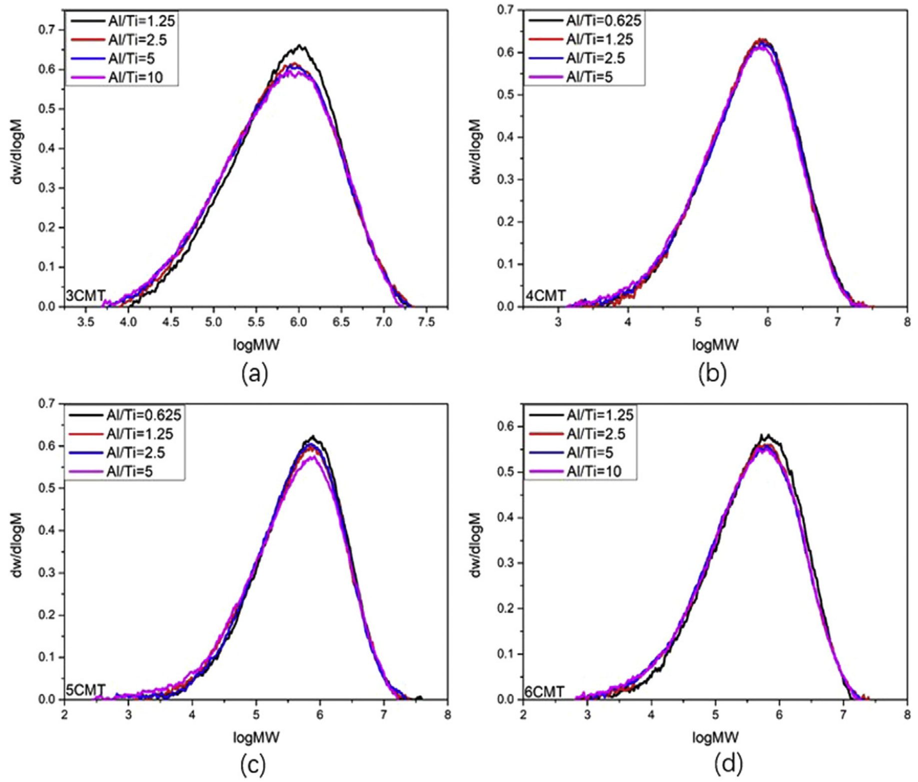

Fig. 6. GPC curves of polyethylene produced by catalysts: (a) 3CMT; (b) 4CMT; (c) 5CMT; (d) 6CMT, at different TIBA dose. Other polymerization conditions: catalysts 100 mg, ethylene pressure 0.15 MPa, heptane 80 ml, 70 °C, 1 h.

Fig. 8 clearly demonstrated that the molecular weight as a function of catalyst type and cocatalyst concentration. From the diagram, the monometallic Ti catalyst labeled 5 MT produced ultra-high molecular weight PE (UHWMPE, with MW much higher than 10^6 g/mol), while the Phillips catalyst produced much lower polymer molecular weight (in our case, run 36 in Table 1). Strengthened

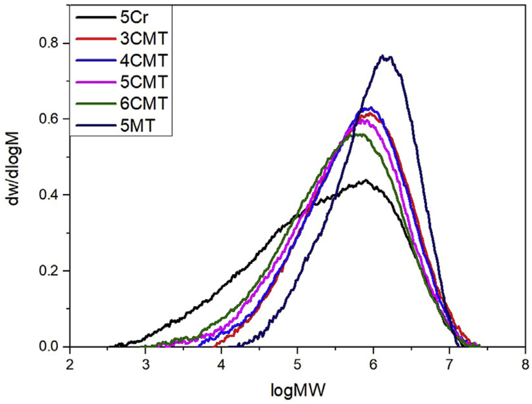

Fig. 7. GPC curves of polyethylene produced by catalysts at optimum TIBA dose. Other polymerization conditions: catalysts 100 mg, ethylene pressure 0.15 MPa, heptane 80 ml, 70 °C, 1 h.

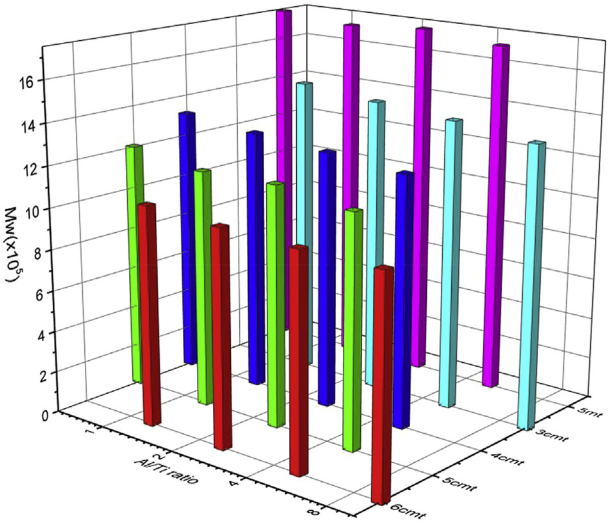

Fig. 8. Molecular weight of the resulting polyethylene as a function of catalyst type (calcination temperature effect) and cocatalyst dosage. Other Polymerization conditions are: catalyst 100 mg; temperature 70 °C; ethylene pressure 0.15 MPa; n-hexane 80 ml; 1 h.

by the ICP result, the higher calcination temperature would introduce less titanium center, and the proportion of UHMWPE by Ti active center would decline. Simultaneously, the decreasing Ti content makes the chromium center more prominent in the catalyst system, that's why the low molecular weight shoulder taken place gradually in the lower molecular weight part (about 10^5 g/mol, see Fig. 7). Based on balance shift between the two metal active centers, continually decreasing of molecular weight and widen MWD was identified versus the increasing calcination temperature.

3.2.2. Effect of chromium content

After investigating the effect of calcination temperature in the above, the activity of the Cr—Ti catalyst indicated a noticeable enhancement (89% than unmodified Ti catalyst 5 MT) at 500 °C. Meanwhile, the polymer molecular weight of catalyst 5CMT decreased 32.55% than 5 MT, under same optimum condition (run 12 and run 22). The phenomenon was proposed to be caused by the relative low titanium content in turn makes relatively high performance of chromium active center. For better understanding the Cr—Ti organic magnesium bimetallic catalyst, we would look into the relationship between chromium loading and catalyst performance directly. In this part, four different chromium loading content catalysts were used in the polymerization to discuss the effect on polymerization. The compared catalysts all calcined at 500 °C named 5 MT, 5CMT, 5C1MT, 5C2MT. The initial chromium loading of the catalysts is 0 wt%, 0.5 wt%, 1 wt%, 2 wt%, respectively.

Fig. 9 showed the polymerization activities of the four catalysts with varying chromium content. Generally, for all four catalysts, the optimum activity occurs in the relative low alkyl aluminum concentration. This was also because the pre-reduction effect of organic magnesium reagent in the catalyst preparation process had already reduced some active sites, as discussed above.

For each catalyst, the polymerization activity increased steadily in the low cocatalyst concentration to the maximum activity showed that cocatalyst dosage can enhance the reaction markedly. As the cocatalyst concentration gradually increased, the further addition of cocatalyst gradually caused the deactivation of the active sites. Moreover, optimum activity of varying catalysts followed the sequence: 5CMT>5C1MT > 5C2MT > 5 MT. Each Cr—Ti bimetallic catalysts showed a considerable enhancement in activity than model 5 MT monometallic catalyst. To be precise, 89%, 53%, 40% enhancement versus 0.5 wt%, 1 wt%, 2 wt% loading, respectively. The result indicated that the chromium modification has remarkable merits in the polymerization performance, much higher than the sum activity of two parental catalysts. From the ICP results, we can observe that the chromium loading is lower than initial adding amount comparatively. This was caused by the organic magnesium reaction process and further titanium chloride reflux process, which makes some of the chromium sites lose in the silica surface in the competition with other metal species. Moreover, a clearly trend can be observed from the titanium content in the ICP result, that is, a prominent decline of titanium loading with high chromium feeding catalyst. Meanwhile, the chromium loading in the support surface OH groups would change the amount of residual hydroxyl groups. Early work had been done with the term of the effect of OH groups on the organic magnesium loading and titanium loading sequently [25]. It is highly likely that the decreasing of titanium loading is the main reason why activity decline sharply in the high chromium loading catalysts.

Thus, catalyst activity reduction, combined with the loss of titanium loading, confirmed the inadequacy of OH groups in high chromium loading. For low chromium loading catalyst 5CMT, the chromium active centers and titanium sites made an extraordinary high activity (almost 2 folds than Ti monometallic catalyst 5 MT and over 6 folds than Cr catalyst 5Cr). For high chromium loading catalyst (near or higher than industrial 1.0 wt% loading Phillips catalyst [28]), the hydroxyl populations may not be sufficient to anchor enough high effective magnesium support precursor. Further increasing the chromium to 2 wt%, not only the activity decreases, but also the chromium modified effect shrinking in the MW trend. This mean chromium itself may hardly preserve a benign disperse condition for polymerization.

Fig. 10 showed the kinetic curve of Cr—Ti catalyst with varying chromium content at different alkyl aluminum dose. The kinetic curve trend was similar among all Cr—Ti catalysts in our work. From the kinetic curves, it can also be confirmed the catalyst activities were arranged in the order of 5CMT>5C1MT > 5C2MT > 5 MT. In addition, these catalysts performed similarly in the relative low Al/Ti ratio and declines markedly when Al/Ti ratio over 5. This was because a slightly high dosage cocatalyst would cause deactivation from over-reduction, a unique feature of pre-reduction catalysts.

Fig. 11 showed the HT-GPC result of the products by four catalysts with various chromium content. For each catalyst, the optimum cocatalyst concentration was in low level due to the pre-

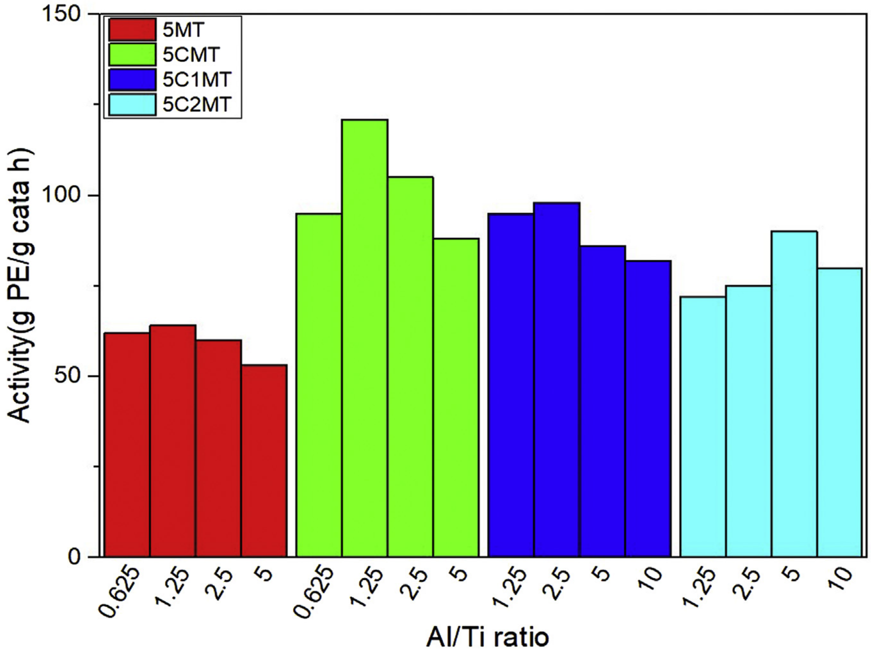

Fig. 9. Ethylene homopolymerization activities of catalysts with different dose of TIBA. Other polymerization conditions: catalysts 100 mg, ethylene pressure 0.15 MPa, heptane 80 ml, 70 °C, 1 h.

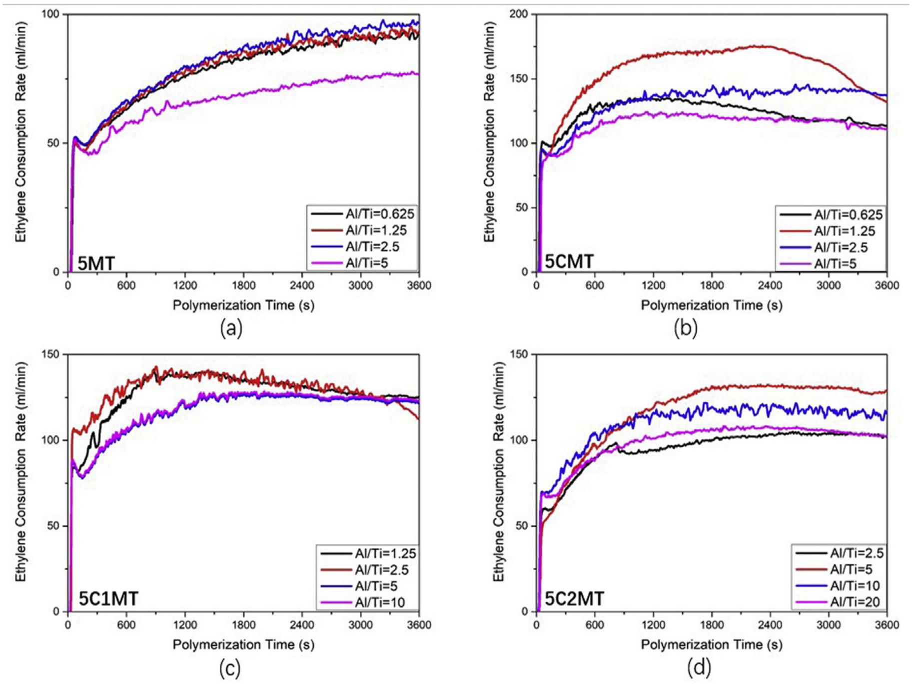

Fig. 10. Kinetic curve of ethylene homopolymerization using catalysts: (a) 5 MT; (b) 5CMT; (c) 5C1MT; (d) 5C2MT, at different dose of TIBA. Other polymerization conditions: catalysts 100 mg, ethylene pressure 0.15 MPa, heptane 80 ml, 70 °C, 1 h.

reduction effect. Also, the molecular weight was similar in the each Al/Ti ratio for each catalyst, while MWD becoming boarder with increasing cocatalyst feeding owing to the strong chain transfer effect of cocatalyst, as we read from literature [38,39]. Meanwhile, the phenomenon indicated that the catalyst is insensitive to the cocatalyst, which makes a potential advantage of less alkyl aluminum consumption for industrialization.

Fig. 12 showed the HT-GPC result of the optimum runs for catalysts 5Cr, 5CMT, 5C1MT, 5C2MT, 5 MT. The unmodified titanium monometallic catalyst showed a narrow high molecular weight distribution while chromium one shows wide low molecular weight distribution, as we mentioned above. For three bimetallic Cr—Ti catalysts, the molecular weight was apparently between the Cr and Ti model catalyst which means the activeness of both active sites. To be precise, the 0.5 wt% loading 5CMT catalyst showed the highest activity while the 1 wt% catalyst made the lowest molecular

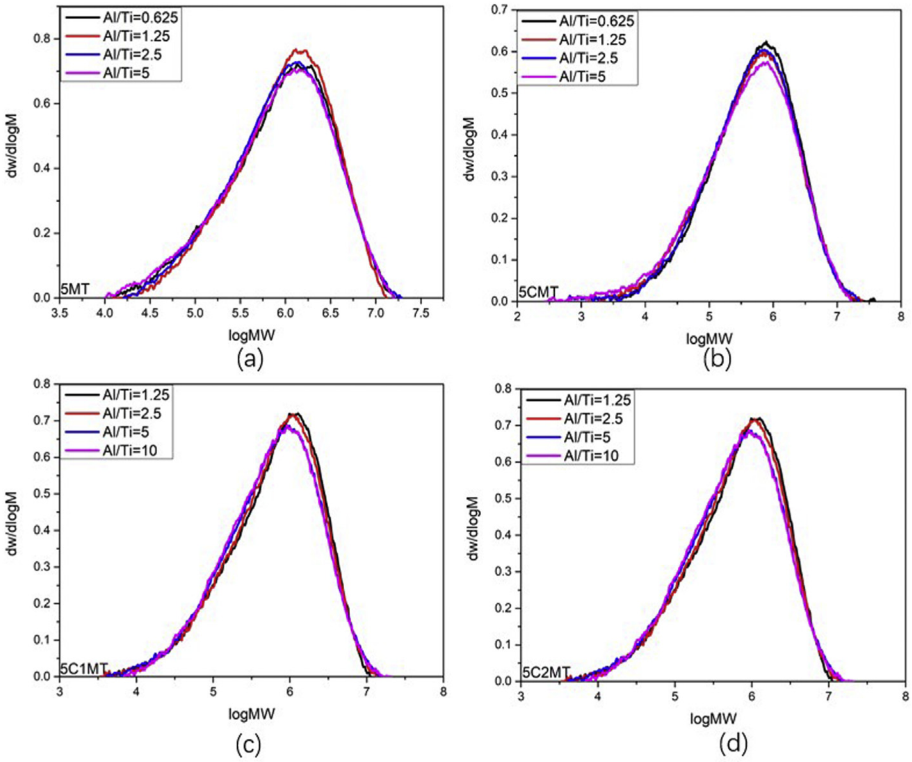

Fig. 11. GPC curves of polyethylene produced by catalysts: (a) 3CMT; (b) 4CMT; (c) 5CMT; (d) 6CMT, at different TIBA dose. Other polymerization conditions: catalysts 100 mg, ethylene pressure 0.15 MPa, heptane 80 ml, 70 °C, 1 h.

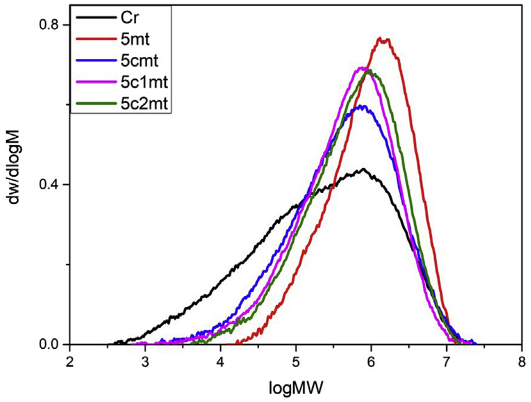

Fig. 12. GPC curves of polyethylene produced by catalysts at optimum TIBA dose. Other polymerization conditions: catalysts 100 mg, ethylene pressure 0.15 MPa, heptane 80 ml, 70 °C, 1 h.

weight which affected by highly activated chromium active sites. In low molecular weight part (MW about 10^5 g/mol), we can see clearly that the highest low molecular weight shoulder occurs in 0.5 wt% catalyst. That allowed us to identity that the low MW shoulder is not strictly related to Cr loading, meaning that chromium content has an optimum loading for chromium modification effect. In the high molecular part (MW about 10^6 g/mol), the increased parts of the high molecular weight can be seen with higher chromium content. This showed the high Cr loading (>1 wt %) makes the chromium modification effect worse. The reason may be that too much chromium impregnation induced agglomeration leading to the reducing effective chromium sites or even deactivated. Compared with unmodified 5 MT catalyst, the molecular weight decreased 33.8%, 39.8%, 28.9% versus 0.5 wt %, 1 wt%, 2 wt% Cr loading respectively. Overall, the most prominent MW modification effect by chromium loading for our organic magnesium catalyst is 1 wt%, as the industrial Phillips catalysts did. In addition, by comparing the highest activity evaluated by gPE/gCat h of each catalyst, Run 12 shows the highest activity at 0.5 wt% loading.

3.3. *Hydrogen response*

As a convenient chain transfer reagent, hydrogen is widely used in olefin polymerization process over the Ziegler-Natta catalyst. Supported Ziegler-Natta catalyst reacted in present of hydrogen for balancing the mechanical property and process property of obtained polymers. As literature reported [40,41], the hydrogen effect leads to slow polymerization reaction and low molecular weight with board MWD. In many literature, the existence of hydrogen was blamed for decreasing polymerization activity by the formation of Ti—H complex. However, in supported zirconium and titanium organometallic catalyst system, the significantly enhanced ethylene polymerization activity of surface titanium hydride or zirconium hydride were found when treated with hydrogen.

For Ziegler-Natta catalysts system, other works carried out a hypothesis to attribute the decreased reaction rate to hydrogen-accelerated formation of stable and poorly active Ti—C_2H_5 complex which shows disadvantageous in further ethylene insertion due to β-H agostic effect [42,43]. However, the hypothesis lacks evidences in chemical structures of titanium organic complex. Until now, the hydrogen effect is still waiting to be fully understood. In this work, the activities of all the catalysts exhibit a noticeable decline in present of hydrogen. GPC characterization indicates the molecular weight of polymers decreased significantly with the PDI almost doubled. In general, chromium modified catalyst shows much better hydrogen response than unmodified Ti catalyst.

From the kinetic curve Fig. 13, we can clearly found that the both

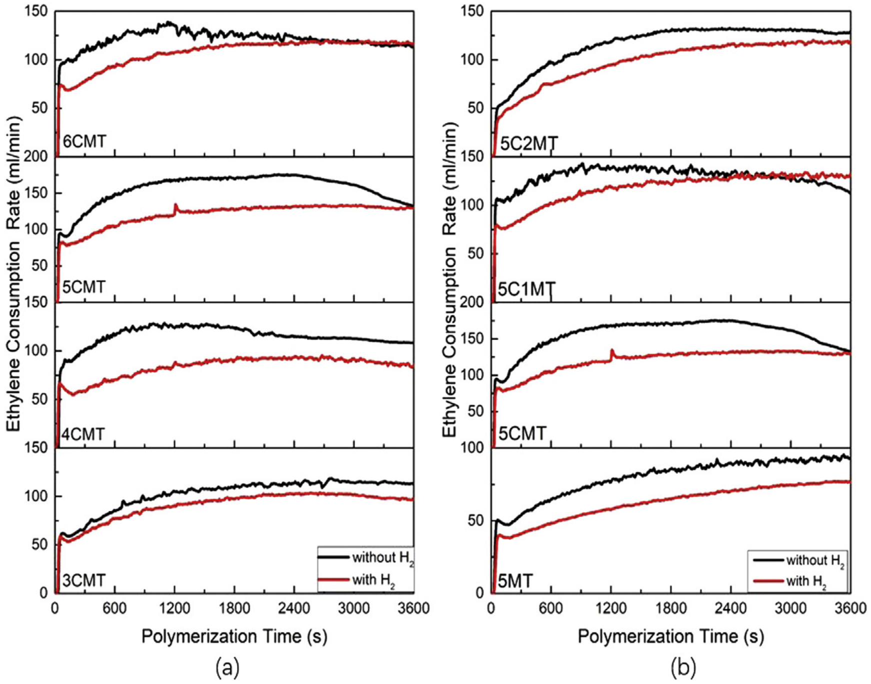

Fig. 13. Kinetic curve of catalysts groups: (a) calcination temperature; (b) chromium content, at optimum TIBA dose. Other polymerization conditions: catalysts 100 mg, ethylene pressure 0.15 MPa, heptane 80 ml, 70 °C, 1 h.

the initial reaction rate and plateau rate declines in present of hydrogen. In the present of hydrogen, the average MW of polymers produced by various calcination temperature groups catalysts drops over 30%. With regard to different magnesium content under 500 °C, the 5CMT, 5C1MT, 5C2MT showed a decline of 32.32%, 36.04%, 42.23%, respectively, while the unmodified 5 MT only decrease 29.86%. Fig. 14 obviously showed that the introduction of chromium species could better regulate the polymer MW with sacrificing the activity.

3.4. Ethylene/1-hexene copolymerization

Copolymers shows multiple advantages in flexibility, lower viscosity, great process ability in comparison with homopolymers. The introduction of commoner into polymer carbon backbone is the reason to these merits. C4—C8 α-olefins were commonly used in the polyolefin industry for manufacturing diversity commercial PE products. Among them, 1-hexene is one of the most important commoners in industry. Thus, for further investigating the copolymerization behavior, ethylene/1-hexene copolymerization was carried out to using our novel chromium modified organic magnesium Ziegler-Natta catalyst.

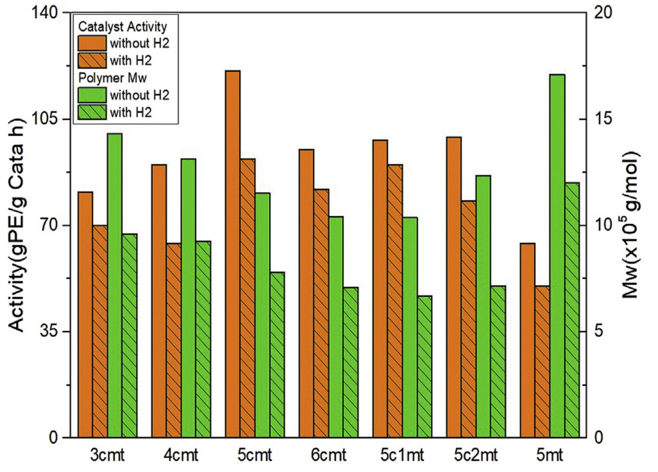

Fig. 14. Hydrogen effect on the catalyst activities and average molecular weight (MW) of the polymers. Other polymerization conditions: catalyst 100 mg, ethylene 0.15 MPa, n-heptane 80 ml, TIBA, 70 °C, 1 h.

From Table 3, noticeable enhancement on the activities were found with majority Cr—Ti bimetallic catalysts and model Ti catalyst. This finding implied that the commoner strongly activated the copolymerization of ethylene and 1-hexene. The significant initial improvement in the activity by the α-olefin has been studied for long time but not fully verified, named “commoner effect” [42,44–49]. The explanations can be classified by chemical effect and physical effect. Similar as the hydrogen effect, the insertion of ethylene into Ti—H bond would makes Ti—C_2H_5 complex which becomes a dormant site through β-agostic effect. This complex site is inactive for polymerization. However, with the insertion of 1-hexene in turn, the Ti—C_6H_{13} was formed as active sites. Besides, the commoner unit would cause donor effect to enhance the activity. On the other hand, the physical effect included that the reduction of crystallinity of polymers with the insertion of commoner further accelerate the monomer diffusion.

Fig. 15 showed the kinetic curve of catalysts with different commoner concentration. According to the kinetic curves, it can be clearly observed that the initial reaction rate raised rapidly as the commoner doses increase, which means the activation would accelerate sharply in present of 1-hexene. In 1 vol% 1-hexene copolymerization process, the ethylene consumption rate first increased steadily in minutes and then declined gradually. In higher 1-hexene case (3 vol% and 5 vol%), the reaction rate perpendicularly rose in few seconds and dropped sharply. This indicated that high 1-hexene dose activates the catalyst better but makes the plateau lower.

To further study the copolymer feature, HT-GPC and DSC were

Table 3
Ethylene/1-Hexene copolymerization activities of different catalysts and polymers properties.

No.	Catalysts	1-Hexene [vol%]	Activity [gPE/g Cat.·h^{-1}]	T_m[a] [°C]	$\triangle H_f$[a] [J/g]	M_w[b] [$\times 10^5$ g/mol]	MWD[c]
1	3CMT	1	105	128	110	8.71	21.87
2	3CMT	3	80	124	79	7.74	22.91
3	3CMT	5	73	122	64.8	4.05	23.02
4	4CMT	1	103	130	126.7	8.29	14.49
5	4CMT	3	92	127	95.5	7.63	30.29
6	4CMT	5	86	125	49	4.48	13.87
7	5CMT	1	107	131	122.5	7.54	7.60
8	5CMT	3	87	129	90.4	6.32	14.43
9	5CMT	5	70	125	55.2	4.71	11.88
10	6CMT	1	102	131	124.2	6.83	12.44
11	6CMT	3	84	129	97.4	5.64	13.71
12	6CMT	5	73	122	40.9	4.16	12.48
13	5C1MT	1	104	129	123	6.72	11.37
14	5C1MT	3	72	122	54.9	6.44	10.00
15	5C1MT	5	73	122	40.2	4.98	11.70
16	5C2MT	1	103	125	102.4	8.62	6.55
17	5C2MT	3	82	123	55.3	6.64	10.18
18	5C2MT	5	83	123	50.5	5.18	12.25
19	5 MT	5	90	125	62.7	7.76	12.93

Other polymerization conditions: catalyst 100 mg, ethylene 0.15 MPa, n-heptane 80 ml, TIBA, 70 °C, 1 h.

[a] T_m and ΔH_f by DSC thermograms.

[b] M_W estimated by HT-GPC in TCB, average molecular weight.

[c] MWD (M_W/M_n) measured by HT-GPC.

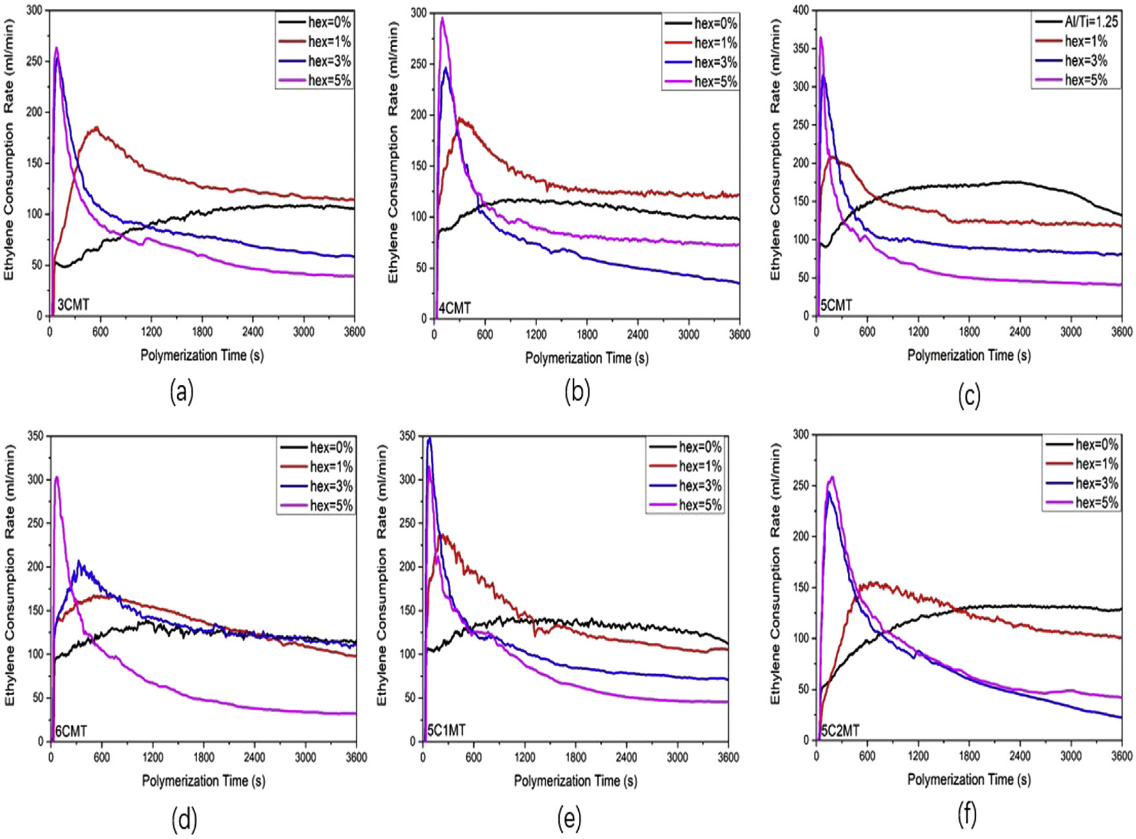

Fig. 15. kinetic curve of ethylene copolymerization using catalysts: (a) 3CMT; (b) 4CMT; (c) 5CMT; (d) 6CMT; (e) 5C1MT; (f) 5C2MT, at different amount of 1-hexene with optimum dose of TIBA. Other polymerization conditions: catalysts 100 mg, ethylene pressure 0.15 MPa, heptane 80 ml, 70 °C, 1 h.

used to characterize the resulting copolymers. The characterization result was shown in Table 2, the T_m and ΔH_f of the copolymer was affected strongly by the introduction of commoner. The copolymer melting point and ΔH_f of the polymer decreased gradually with the increasing introduction of commoner. The insertion of 1-hexene into the carbon backbone of polymer made the physical features change.

A sharply decline at the MW of polymers were observed in

Table 4
The content of 1-hexene incorporated in the copolymers obtained from different catalysts.

No.	sample	1-Hexene [vol%]	Activity [gPE $(gCat)^{-1}h^{-1}$]	Activity [KgPE $(molTi)^{-1}h^{-1}$]	Cr/Ti ratio	1-Hexene incorporation[a] [mol%]
1	3CMT	5	73	122	7.25	13.70
2	4CMT	5	86	125	9.12	14.00
3	5CMT	5	70	125	9.68	11.28
4	6CMT	5	73	122	11.92	11.04
5	5 MT	5	90	135	0.00	9.57
6	5C1MT	5	73	120	23.10	5.48
7	5C2MT	5	83	137	44.83	4.74

[b]1-Hexene incorporated in copolymers estimated by high temperature^{13}C NMR and calculated according to the literature methods [52].

[a] The sample 3CMT, 4CMT, 5CMT, 6CMT, 5 MT, 5C1MT, 5C2MT are corresponding Run 3, Run 6, Run 9, Run 12, Run 19, Run 15 and Run 18 in Table 3, respectively.

Table 3. The remarkable drop in MW and broaden in PDI was caused by the strong chain transfer ability of commoners as reported in literature [50,51]. Besides, the fast insertion of 1-hexene in the low molecular polymer produced more low-MW polymer, which made the MW even lower [42].

The commoner incorporation in the copolymer would greatly affect the polymer performance in ways. Small amount of α-Olefin incorporation as the polymer contain, major copolymer properties, such as melting point, crystallinity, mechanical properties and processability, would exhibit a pronounced difference. Thus, to control of the comonomer content in copolymer chains is of importance. 1-hexene incorporation of the copolymer was determined by high temperature ^{13}C NMR and the results were summarized in Table 4.

The chromium modification extent exhibited a prominent effect on comonomer incorporation ability of hybrid Zigler-Natta catalyst. It's clear that in the initial stage, the relative low Cr/Ti ratio (lower than 10%) could promote the 1-hexene incorporation from 9.57% to 14.00%, for the catalyst 5 MT and 4CMT, with 46.30% higher incorporation. The 1-hexene incorporation would increase significantly with minor Cr content while reduce to the extent even lower than the Ti catalyst when Cr ratio higher than 20%. This trend was also observed in our previous work on Cr modified Zigler-Natta catalyst [19].

4. Conclusion

A series of novel Cr/Ti bimetallic polyethylene catalysts were successfully developed through Cr-modification to the $(SiO_2/MgR_2/MgCl_2)\cdot TiCl_x$ Ziegler-Natta catalysts. The bimetallic catalysts could be simply prepared by refluxing titanium choloride with chromium modified silica gel/alkyl Mg adducts, and it showed high activity for ethylene homopolymerizations and copolymerizations with 1-hexene. Two main factors in preparation process including calcination temperature and chromium feeding dose were studied for better understanding the balance of two active species in the bimetallic catalysts. The calcination temperature would influence the polymerization indirectly though surface hydroxyl groups which controls magnesium and titanium contents successively. Lower calcination temperature will make the titanium active sites dominate in the reaction. In general, the polymerization shows significant improvement after the introduction of the chromium species into the traditional Ziegler-Natta catalyst. The Cr/Ti bimetallic catalysts produced polyethylene with a molecular weight distribution in-between the Phillips Cr catalyst and the Ziegler-Natta Ti catalyst. Additionally, the increased Cr content (lower than 1 wt%) exhibited great modification effect on the promotion effects of polymerization activity with relatively broad MWD polymer, while the further higher Cr dosage (over 1 wt%) may lead to agglomeration which would weaken the Cr effects for the bimetallic catalysts.

The Cr–Ti bimetallic catalysts exhibited much higher activity in ethylene polymerization and the obtained polymer showed greatly higher MW than the unmodified Ti catalyst. The catalyst 5CMT showed 89% higher activity and 32.5% lower MW than the original Ti catalyst, under their extremely low cocatalyst dose. Meanwhile, the Cr/Ti bimetallic catalyst showed 41.5% higher hydrogen response and 46.3% higher 1-hexene incorporation in the copolymer than the original Ziegler-Natta Ti catalyst.

In this work, a simplified model was originally proposal to explain high activity and good modification effect of our bimetallic catalyst, and can be further used to explain synergistic effect of our supported bi-metallic catalyst. These chromium modified $(SiO_2/MgR_2/MgCl_2)\cdot TiCl_x$ Ziegler-Natta catalysts showed great promotion effects with very small cocatalyst consumption, which exhibited great potential for industrial application.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.02.024.

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