

Insights into the effect of vanadium on chromium-vanadium Phillips catalysts for the ethylene polymerization

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ABSTRACT

The chromium/vanadium bimetallic Phillips catalysts developed by our research group have been proved to be a promising process to produce bimodal polyethylene using a single-reactor process. The vanadium loading of CrV-1/1, CrV-1/2, and CrV-1/3 has a significant effect on the polymerization activity, product molecular weight (MW), as well as the molecular weight distribution (MWD). Due to the unstable and easy deactivation of vanadium active centers at atmospheric or low (0.4 MPa) reaction pressure [Macromol. React. Eng. 2015, 9, 462–472], the reaction is carried out at 1.0 MPa to strengthen the V active center on the activities of ethylene homopolymerization, ethylene/1-hexene copolymerization, and the H₂ responds properties. The reaction carried out at higher pressure promotes the polymerization activities. With the same amount of cocatalyst, the highest activity of the three Cr-V bimetallic catalysts CrV-1/1, CrV-1/2 and CrV-1/3 decreases with the increase of vanadium loading. The Cr-V bimetallic catalysts require more cocatalyst than the single metal Cr cat. It was found two obvious peaks in the GPC curves of homopolyethylene and ethylene/1-hexene copolymer. It means that the higher reaction pressure benefits the promotion of the active center of catalyst for higher MW. By increasing the loading from 0.48 wt.% (CrV-1/1) to 0.96 wt.% (CrV-1/2), the molecular weight increases by nearly 30%. Besides, according to the deconvolutions of the GPC curves of homopolymers, ethylene/1-hexene copolymers, and the homopolymers with H₂ modulation, the synergetic effect between Cr and V center is presented. As the vanadium loading increases, the active site accounted for the high molecular weight portion increases, and the Cr-V catalyst presents better hydrogen responds. When the partial pressure of hydrogen is 0.1 MPa, the molecular weight is reduced by nearly half. Specifically, the high molecular weight peak is weakened, while the low molecular weight peak is strengthened. The peak position does not change significantly. The higher vanadium content and the greater sensitivity of hydrogen modulation indicate that the vanadium active center has better hydrogen responds than the chromium active center does. The homopolymerization product of the Cr/V-1/1 catalysts exhibits higher tensile strength and elongation-at-break. The tensile properties of the copolymerized product of CrV-1/1 are further improved. **Polyolefins J (2020) 7: 61-78**

Keywords: Bimodal polyethylene; Cr-V Phillips catalyst; vanadium loading; GPC; deconvolution analysis.

INTRODUCTION

With the development of the polyolefin industry, high-grade polyethylene materials with controlled molecular architectures have been developed, and the quality and performance requirements for polyethylene products with mechanical properties and processing properties are still increasing [1]. The polymer behaviors are determined by the molecular weight (MW), the molecular weight distribution (MWD), the incorporation of comonomer and macromer, and the location of both short-chain and long-chain branches

within the MW distribution.

Nowadays, polyethylene with a broad/bimodal MWD and a balancing between processing and mechanical properties is common. Cascade-reactor technology is a relatively mature method for producing broad/bimodal polyethylene. The multi-branched, high molecular weight polyethylene product is produced by varying the polymerization conditions. This method requires that the catalyst be very sensitive to hydrogen as well as the copolymerization properties [2-5].

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However, its operation is complicated and the multi-tank connection leads to high equipment cost and high energy consumption.

In recent years, the single-reactor process for broad/bimodal polyethylene has proven to be attractive and promising. The single-reactor process means that a bimodal polyethylene is produced in a single-reactor by a dual center or multisite catalyst with different active centers on the same support. This technology means low equipment cost, low energy consumption, simple process, convenient operation, and uniform mixing of high molecular weight and low molecular weight parts. However, this process is achieved by catalyst technology, which requires a plurality of active centers to maintain a certain activity under the same reaction conditions, and can separately catalyze the synthesis of high and low molecular weight polyethylene. The key to the single-reactor process is, therefore, the development of high-performance catalysts.

At present, the catalysts used to produce bimodal polyethylene in industry are mainly some composite catalysts [6-8]. A typical solution is a combination of metallocene (MAO) and Ziegler-Natta (Z-N) catalyst. However, the poor compatibility of the polyethylene by two types of active centers led to two melting peaks of the bimodal polyethylene. Alternately, Liu et al. [9] used multi-catalysts reactor particle technology (MRGT) that the catalysts were gradually added during the polymerization, which was optimized by the corresponding alkylaluminum and methylalumoxane cocatalysts. However, the polyethylene produced by the two active centers still had poor compatibility and was difficult to industrialize.

A supported multiactivity site on the catalyst is another way to improve the performance [10]. Various combinations of homogeneous and heterogeneous catalysts are investigated. Ziegler-Natta hybrid $MgCl_2$ -supported dual-site catalysts and different single-site silica co-supported catalysts could produce bimodal polyethylene. Because of the rather tedious process of the covalent anchoring of catalysts on silica, an immobilization of the activator prior to addition of the transition metal complex was applied. However, the metallocene might be merely a physical absorption instead of a chemical bonding [9].

All the above hybrid Z-N catalysts and MAO metal catalysts have outstanding differences in active centers, and they often require different types of cocatalysts control to obtain the controlled molecular weight distribution (MWD) [6, 7, 11]. Moreover, the high

technical requirements for the two different catalysts, such as the high cost of preparation process and the balanced activity in polymerization conditions, as well as the kinetic and chemical compatibility have to be considered in industry application.

Recently, our group focused on an SiO_2 -supported chromium-based catalyst and developed a bimodal MWD polyethylene based on industrial Phillips and S-2 catalysts in order to get the merits from two important catalysts [12]. Using the residual surface hydroxyl groups in the silica gel, the active site of inorganic CrO_x and organic bis (triphenyl silyl) chromate (BC) hybrid catalyst produced the ethylene/1-hexene copolymer with higher MW, boarder MWD than that obtained from Phillips catalyst, as well as higher SCBs content in the highest temperature TREF fractions of copolymer.

Further, with the introduction of vanadium, a series of Cr-V bimetallic center catalysts have been developed by simply impregnation method [13-16]. Our group [17-19] reported the SiO_2 -supported silylchromate/ VO_x bimetallic catalyst based on S-2 catalyst. The activity was higher than that of the S-2 catalyst, and the product showed a broader molecular weight (MW) with a bimodal molecular weight distribution (MWD). Through the modification of VO_x by isocyanate, the silylchromate(Cr)/imido-vanadium(V) bimetallic catalyst was also developed [18]. By this strategy, a bimodal UHMWPE/HDPE in-reactor blends was explored [20].

For the inorganic CrO_x Phillips catalyst, we [21] prepared CrO_x-VO_x/SiO_2 by coimpregnation of $Cr_3(OOCCH_3)_7(OH)_2$ and NH_4VO_3 . The process was similar to that of the traditional Phillips catalyst without cumbersome procedures. Besides the higher polymerization activity than the sum of that of CrO_x/SiO_2 and VO_x/SiO_2 entities, a significant improved ethylene/1-hexene copolymerization performance than CrO_x/SiO_2 also was found at the reaction pressure of 0.4 MPa. Moreover, the activity of bimetallic catalysts also manifested itself as a process of rapid growth and rapid decline, as well as a process of slow growth and slow decay, suggesting that the two metal centers presented a synergistic effect. Later, a series of bimetallic center catalyst with the modification of the silica gel support by TiO_2 , F and acid were developed to meet the various requirements for the single-reactor process [22, 23]. During the polymerization at atmospheric or lower pressure (0.4 MPa), the unstable vanadium active centers and easy deactivation were obvious and the effect of V active site did not fully

display [21], while the industry processing would take place at high pressures.

In this work, the polymerization was carried out at an increased pressure of 1.0 MPa to strengthen the V active center on the activities of homopolymerization, ethylene/1-hexene copolymerization, and the H₂ responds properties. The synergetic effect of Cr and V centers on the molecular weight of the product and their distribution in terms of the vanadium loading and the amounts of cocatalyst were explored. The tensile properties of the product were also studied.

EXPERIMENTAL SECTION

Raw Materials

Basic chromium acetate (with 24 wt.% Cr) was purchased from Johnson Matthey Medical Company. Ammonium metavanadate (AR) was supplied by Sinopharm Chemical Reagent Co., Ltd. Triisobutyl aluminum was purchased from Shanghai Brilliant Chemical Technology Co., Ltd. Ethylene and hydrogen were purchased from Shanghai Wetry Criterion Gas Co., Ltd. Pure nitrogen and pure air (78%N₂/22%O₂) were supplied by Air Liquide (Shanghai) Compressed Gas Co., Ltd. Triisobutylaluminium (TIBA, 1.0 M in heptane) was purchased from Alfa Aesar.

The reaction materials such as nitrogen, ethylene, hydrogen, 1-hexene and 1-heptane were purified before used [24]. The 1-hexene was purified by a sodium block method. The 1-heptane was treated by a solvent purification apparatus of MIKROUNA, China.

Catalyst Preparation

A certain mass of silica gel (Davison 955) was heated to 300°C in a fluidized bed under N₂ for 2 h [24]. After cooling to 150°C, the silica gel was collected and stored. The catalysts were prepared by impregnation of the pre-treated silica gel with the solution of appropriate amount of chromium acetate and/or ammonium metavanadate. The sample dried at 120°C overnight was transferred to a calcining tube and placed in a vertical muffle furnace. At N₂ flow rate of 600~800 mL/min, the temperature was increased from room temperature to 150°C in 60 min and maintained for 90 min. After that, the fluidizing gas was switched from N₂ to air, and the temperature was raised to 300°C in 90 min, and kept for 90 min. The temperature was increased to 400°C in 30 min.

Further, the temperature was maintained at 500°C for 4 h, and then cooled to 400°C with switching the gas to N₂ at room temperature. Finally, the sample was collected in a horn bottle and stored in a glove box for use.

Characterization of Catalysts

Inductively Coupled Plasma (ICP)

The loading of metal component was characterized on Varian 710-AES ICP. The operating power, pump speed, atomization pressure, auxiliary gas flow rate and plasma gas flow rate were 1.1 kW, 13 rpm, 200 kPa, 1.5 L min⁻¹ and 15 L min⁻¹, respectively.

X-Ray Photoelectron Spectroscopy (XPS)

XPS analysis was performed using a Kratos Analytical Shimadzu. The monochromatic X-rays used (E = 1486.6 eV) were obtained from an Al Ka excitation source with an operating power of 300 W and a chamber operating pressure of 10⁻⁹ Torr. The binding energy was corrected using Si_{2p} = 103.3 eV as a standard.

Ethylene and Ethylene/1-Hexene Polymerization

Ethylene homopolymerization and ethylene/1-hexene copolymerization experiments were carried out in a 300 mL Parr stainless steel autoclave [17]. 60 mL of heptane, a certain amount of TIBA and another 60 mL of heptane were charged into the reactor, respectively. Then the catalyst suspension with 30 mg catalyst powder suspended in 10 mL heptane was transferred to the reactor with 0.55 MPa ethylene through a bypass on it. After the reactor pressure was increased to the set point, a valve connected to the catalyst bomb was opened to start the polymerization. The instantaneous consumption of ethylene was recorded by an online mass flow meter (Brooks SLA5860). The polymer suspension was filtered, washed with ethanol, and dried overnight at 60°C in an oven. To the ethylene/1-hexene copolymerization experiments and the hydrogen adjustment experiments were, respectively, added an appropriate amount of 1-hexene and hydrogen by bypass before the last addition of the solvent, and the other operations were the same.

Polymer Characterizations

High Temperature Gel Permeation Chromatography (HT-GPC)

The molecular weight and molecular weight distribution

of the polymer were measured using HT-GPC (Agilent PL220) [20]. The column was packed with a PL gel-Olexis packing column at 160°C and a feed rate of 1.0 mL min⁻¹. The standard for correction was a narrow molecular weight distribution of polystyrene (PS) in a solvent of 0.5 wt.% 1, 2, 4-trichlorobenzene (TCB) stabilized trichlorobenzene.

Differential Scanning Calorimetry (DSC)

The melting point (T_m) and melting enthalpy (ΔH_f) of the polymer were measured by a TA DSC Q200 [17]. The heating and cooling rates of the whole process were all 10°C min⁻¹. T_m , T_c , and ΔH_f were determined by the peak of the melting curve, the peak of crystallization curve and the peak area of the melting curve, respectively.

Successive Self-nucleation and Annealing (SSA)

SSA separates the components with different crystallization abilities in the polymer by continuously heating and cooling processes and reflects them on the final melting curve. The whole test process was still carried out on TA DSC Q200 with the specific cyclic heating and cooling procedure [21]. The melting curve of the heating process was recorded.

Universal Tensile Testing

Tensile performance was tested by GB/T1040 standard. An appropriate amount of dried sample was taken in a mold and pressed. Then the pressed sample was cut into a dumbbell-shaped tensile spline placed on a universal tensile tester to test the tensile properties of the sample at a tensile rate of 20 mm min⁻¹.

RESULTS AND DISCUSSION

Characterization of Catalysts

Table 1 shows the actual loadings of the catalysts **Cr cat**, **V cat**, **CrV-1/1**, **CrV-1/2** and **CrV-1/3** measured by ICP. The lower actual metal loading for each catalyst than the theoretical one is mainly attributed to the mass loss of processes such as impregnation, transfer, and calcination of the catalyst precursor. At the same time, it is seen that the component loss of the bimetallic catalyst is more serious than that of the single metal catalyst. The limitation of the specific surface area and active site of the surface of the silica gel, as well as the competitive adsorption of the metal ions, result in

Table 1. Cr and V loadings of various catalysts^(a).

Catalyst	Cr loading (wt.%)		V loading (wt.%)	
	Theoretical	Actual	Theoretical	Actual
Cr cat	0.50	0.47	/	/
V cat	/	/	0.48	0.42
CrV-1/1	0.50	0.42	0.48	0.43
CrV-1/2	0.50	0.40	0.96	0.92
CrV-1/3	0.50	0.36	1.44	1.30

^(a)measured by ICP.

a decrease in the loading of both components. With the increase of V content, the loss of Cr component is more obvious.

Ethylene Homopolymerization over Cr-V Catalysts

In the industrial production of polyethylene, a small amount of an alkyl metal compound is usually added as a cocatalyst to the reaction system to increase the polymerization activity or to modulate the product properties. In the reaction system, the cocatalyst can not only remove trace amounts of water, oxygen, aldehydes and the like in the reaction vessel, but also promote the polymerization reaction chain by reducing, alkylating and affecting the coordination environment of the active center. The active center either affects the polymerization activity or alters the structural properties of the product. Based on the 0.5-1.0 wt.% Cr in commercial Phillips catalysts, the amount of chromium here was used as 0.5 wt.%. Three catalysts with molar ratios of Cr:V of 1:1, 1:2 and 1:3, were prepared and recorded as **CrV-1/1**, **CrV-1/2** and **CrV-1/3**, respectively. Figure 1 shows the ethylene consumption rate curves for the homopolymerization conditions of the (a) **Cr cat**, (b) **CrV-1/1**, (c) **CrV-1/2**, (d) **CrV-1/3**, and (e) **V cat** catalysts in terms of dosages of TIBA. All curves show similar trends, namely the characteristics of rapid growth and slow decay. It may be that the active center of ethylene polymerization is produced by the reduction of the promoter and ethylene, respectively [25-27]. The rapid growth in the early stage may correspond to the surface-active site of the promoter activation. In the early stage of the reaction, the concentration of the promoter is high, and some metal centers can be rapidly activated by means of reduction, alkylation, etc., and the activity is rapidly increased. However, this active center also prefers its rapid decline. The simultaneous slow growth of the slowly decaying active center may correspond to the active center of ethylene reduction activation and

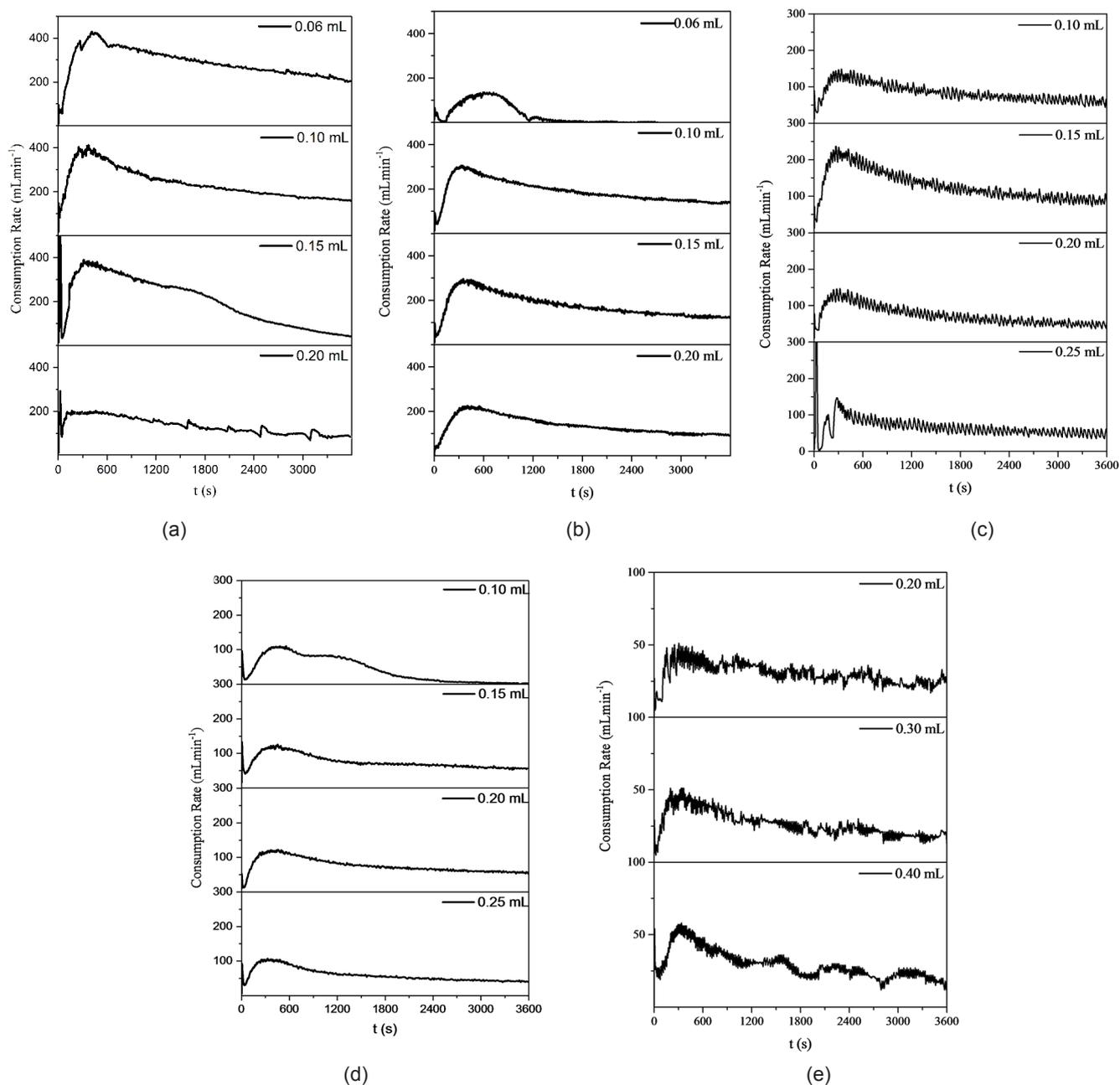


Figure 1. Kinetic curves of (a) **Cr cat**, (b) **CrV-1/1**, (c) **CrV-1/2**, (d) **CrV-1/3**, (e) **V cat** for ethylene homopolymerization under different dosages of TIBA.

counteract the tendency of the former to decay rapidly.

Table 2 shows the effect of the amount of TIBA cocatalyst on the polymerization activity and polymer properties of the catalysts **Cr cat**, **CrV-1/1**, **CrV-1/2**, **CrV-1/3**, and **V cat**. On the one hand, with the increase of vanadium loading, the highest activity decreases with the same amount of cocatalyst and the amount of cocatalyst increases when the reaction reaches the highest activity. The **V cat** shows very low activity compared to the **Cr cat** even at the relatively

higher amount of cocatalysts. With the increase of vanadium loading in Cr-V catalysts, more cocatalyst is needed at the highest activity due to the cumbrance of V sites. On the other hand, when the amount of cocatalyst is 0.06 mL, the polymerization activity of **Cr cat** reaches the maximum value of $765.7 \text{ g}_{\text{PE}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$, but the polymerization activity decreases with the increased amount of cocatalyst. This may be due to the excessive reduction of the cocatalyst to the active center [28]. In general, Phillips catalysts can catalyze the

Table 2. Influence of different dosages of TIBA on ethylene homopolymerization activities and polymer properties for **Cr cat**, **CrV-1/1**, **CrV-1/2**, **CrV-1/3** and **V cat**^(a).

Catalyst	Cocat (mL)	Activity ($\text{g}_{\text{PE}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$)	T_m ^(b) (°C)	T_c (°C)	ΔH_f ($\text{J} \cdot \text{g}^{-1}$)	X_c ^(c) (%)
Cr cat	0.06	765.7	136.7	117.5	188.1	64.2
	0.10	621.9	136.1	117.8	184.9	63.1
	0.15	494.9	136.7	117.3	180.1	61.4
	0.20	330.8	136.3	117.8	183.7	62.7
CrV-1/1	0.06	87.2	136.2	118.4	212.2	72.4
	0.10	500.6	135.3	118.4	204.5	69.8
	0.15	479.8	135.4	118.6	202.1	69.0
	0.20	387.1	135.8	118.4	199.2	68.0
CrV-1/2	0.10	233.3	135.9	118.9	195.2	66.6
	0.15	346.9	136.0	118.7	198.3	67.7
	0.20	283.3	136.0	118.8	181.0	61.9
	0.25	236.2	135.9	118.8	192.3	65.6
CrV-1/2	0.10	131.5	136.3	118.2	212.3	72.5
	0.15	241.2	135.4	119.3	191.2	65.3
	0.20	216.2	135.7	118.8	189.3	64.6
	0.25	174.1	135.6	119.0	182.3	62.2
V cat	0.20	23.1	135.0	119.1	165.6	56.5
	0.30	27.6	135.1	119.2	156.0	53.2
	0.40	24.6	135.0	119.3	160.7	54.8

^(a) Polymerization conditions: catalyst 30 mg, TIBA, ethylene pressure 1.0 MPa, temperature 80 °C, 1-heptane 130 mL;

^(b) T_m , T_c , ΔH_f by DSC;

^(c) $X_c = \Delta H_f / \Delta H_{f0}$, where ΔH_f is the enthalpy of fusion of the PE samples and ΔH_{f0} is enthalpy of fusion of 100 % crystalline PE ($\Delta H_{f0} = 293 \text{ J} \cdot \text{g}^{-1}$).

ethylene polymerization in a commercial application without the need of cocatalyst with a longer induction period (5-30 min) and lower activity [1]. However, for this experiment, when the amount of boosting is lower, the catalyst shows almost no activity. This may be due to traces of impurities such as water and oxygen in the reactor, resulting in catalyst poisoning inactivation. The **V cat** exhibits a poor activity compared to the **Cr cat**, while the amount of cocatalyst required is relatively high to achieve the highest activity. At the same time, the **CrV-1/1** catalyst activity is still low with the addition of 0.06 mL cocatalyst due to insufficient reduction of the active center. The highest activity of the catalyst is $500.6 \text{ g}_{\text{PE}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ in the presence of 0.10 mL cocatalyst. As the amount of cocatalyst increased, the activities of the three Cr-V bimetallic catalysts showed a tendency to increase first and then decrease. The former is mainly caused by the elimination, reduction and alkylation of the cocatalyst, while the latter may be due to excessive reduction of the cocatalyst.

The molecular weight distribution curves of the products obtained by **Cr cat**, **CrV-1/1** and **V cat** are shown in Figure 2. The polyethylene prepared by the **V cat** has a molecular weight of $2.17 \times 10^6 \text{ g} \cdot \text{mol}^{-1}$ and

belongs to the ultrahigh molecular weight polyethylene [29]. The product has the broadest molecular weight distribution of 99.1. It exhibits a distinct unimodal distribution in the high molecular weight fraction and a longer tailing in the low molecular weight fraction. The polyethylene prepared by the **Cr cat** has the molecular weight distribution with $\bar{M}_w = 46.8$ and a molecular weight of $7.96 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$. As the **CrV-1/1** catalyst, the molecular weight distribution obtained by adding 0.06 mL cocatalyst is similar to that of the **Cr cat** with a broad MWD. The molecular weight of the polymer increases slightly from 6.93×10^5 to $11.7 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$ with the addition TIBA amount in the range of 0.10-0.20 mL, indicating that the effect of TIBA on the promotion of MW is not obvious.

Compared to our previous report that obtained at lower reaction pressures [21], the pressure effect is noticeable. Under the corresponding optimal conditions, the reaction activities over **CrV-2/1** are 14.4, 162.2, and $184.6 \text{ g}_{\text{PE}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ at the reaction pressures of 0.15, 0.4, and 1.0 MPa, respectively. And the molecular weight increases from 2.76×10^5 to 3.18×10^5 and $10.2 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$, respectively, while the molecular weight distribution increases from 30.1 to 35.3 and 42.8. At the same time, the high pressure makes the

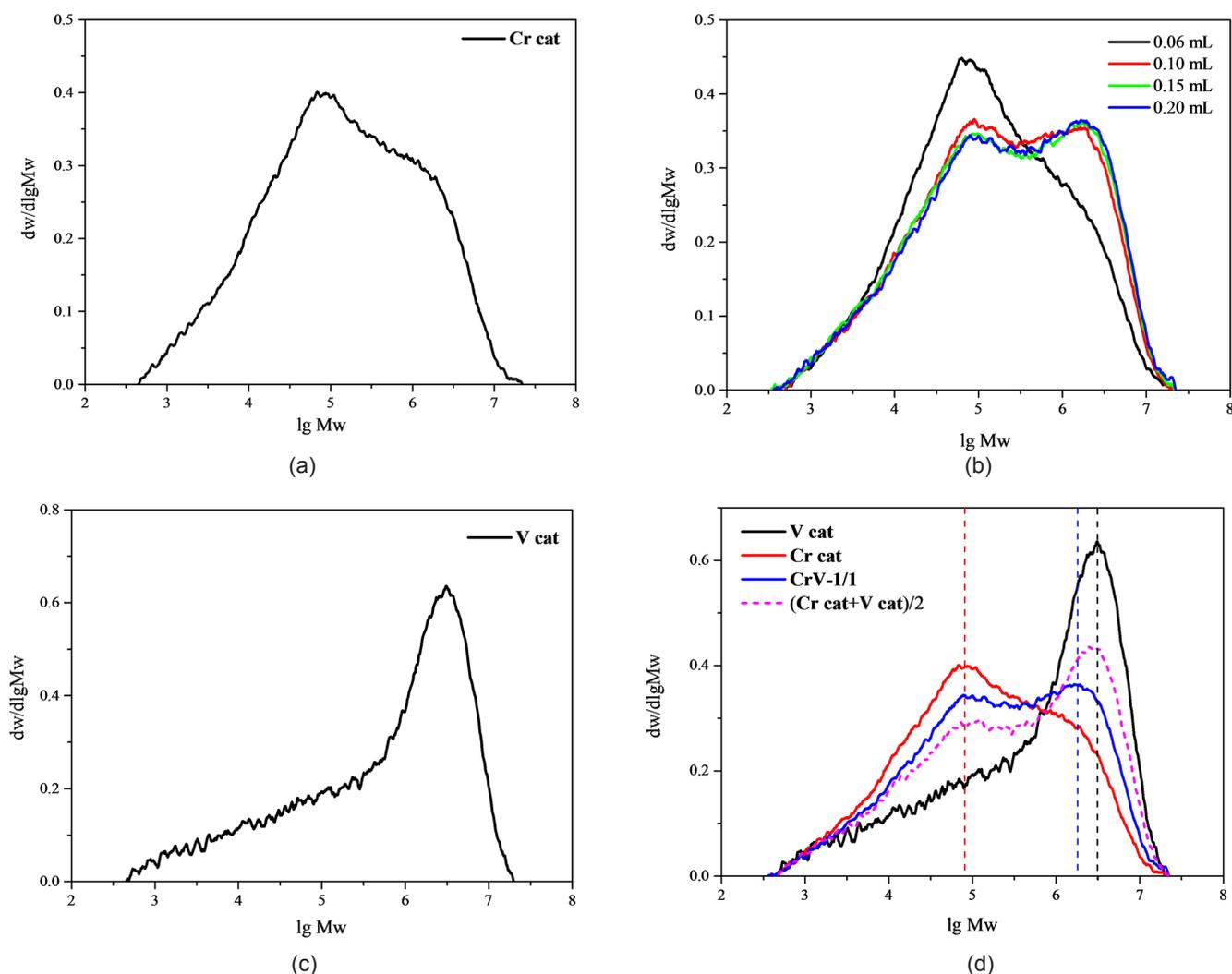


Figure 2. GPC curves of homopolymer synthesized by (a) **Cr cat**, (b) **CrV-1/1** with various amount of TIBA, (c) **V cat**, and (d) their combination.

product with two more obvious peaks in GPC profile. A distinct bimodal distribution (Figure 2(b)) presents a low molecular weight fraction with the molecular weight of less than 10^5 g.mol⁻¹ and a higher one than 3×10^6 g.mol⁻¹. The molecular weight distribution increases from 50.1 to 60.4, which is between that of the **Cr cat** and **V cat** products. It means that the higher reaction pressure benefits the promotion of the active for higher MW. With the increased TIBA amount, the low molecular weight fraction slightly decreases, and the high molecular weight fraction slightly increases.

Figure 2(d) provides a more intuitive response to the relationship between the three samples. The strongest peak position of the **V cat** product is significantly higher than that of the **Cr cat** and **CrV-1/1** samples. Compared with the **Cr cat** sample, the introduction of the vanadium center slightly changes the peak position of the high molecular weight portion of the

CrV-1/1 product, but the peak intensity is significantly increased. The content of the high molecular weight portion is remarkably increased. Combining the values of **Cr cat** and **V cat**, the curve of $(\text{Cr cat} + \text{V cat})/2$ shows weaker and stronger peaks than that of the **CrV-1/1**, suggesting that the vanadium active center which produces a synergistic effect with the Cr active center causes the much lower activity of the **V cat**, which is advantageous for the formation of the high molecular weight polyethylene product and the broader MWD.

Figure 3 shows the molecular weight distribution of the different catalysts at the highest activity. As the vanadium content increases, the molecular weight of the product increases significantly from 6.93×10^5 to 21.7×10^5 g.mol⁻¹. As the low molecular weight peaks gradually weaken, the high molecular weight peaks continue to increase. The chromium center is mainly

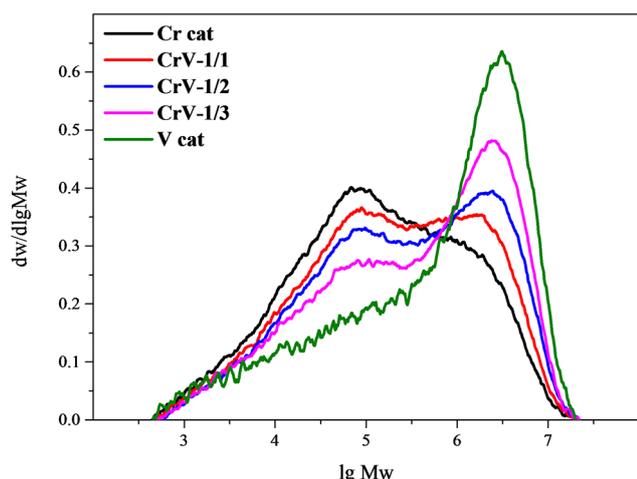


Figure 3. GPC curves of homopolymer synthesized by **Cr cat**, **CrV-1/1**, **CrV-1/2**, **CrV-1/3** and **V cat**.

attributed to the part of lower molecular weight, while the vanadium centers reflect the high one. On the one hand, vanadium acts as an active center, and the increased loading increases the high molecular weight fraction. On the other hand, an increase in the vanadium content also affects the action of chromium, leading to decrease its loading and relatively reduce the corresponding low molecular weight fraction. Overall, as the vanadium loading increases, the high molecular weight fraction and molecular weight increase. The increase of vanadium successfully constructs the bimodal structure of polyethylene.

In order to further explore the interaction between the active centers of bimetal catalysts in the ethylene homopolymerization, a deconvolution analysis method was used to analyze the molecular weight distribution curve of the polymerization product of the Cr-V catalysts by overlaying multiple molecular weight distribution curves that conform to Flory's most probable distribution to describe the broad molecular weight distribution of polymer products [30, 31].

This method can explain the special microstructure properties of the polymerization products caused by the nature of the multiple active centers of the catalyst [32, 33]. The minimum number of active Cr-V catalysts is seven after analysis. **Figure 4 (a)** compares the results of deconvolution analysis of the molecular weight distribution curves of the three polymerization products. It can be seen that each of the Flory components obtained by deconvolution analysis of **CrV-1/1**, **CrV-1/2**, and **CrV-1/3** is corresponded. It is shown that the molecular weight of the polymer and its distribution change significantly with the increasing load

of vanadium. In **Figure 4 (b)**, as the vanadium loading increases the active site 7 of the high molecular weight portion increases. Due to the narrow high molecular weight peaks and less active site distribution, active site 7 increases significantly, indicating that the activity of vanadium is significantly enhanced. At the same time, sites of 2, 3, 4 and 5 of the low molecular weight portions are relatively weakened.

Table 2 shows that the melting temperature (T_m) is around 136°C , and the order from high to low is **Cr cat** > **CrV1/1** \approx **CrV-1/2** \approx **CrV-1/3** > **V cat**. The polyethylene produced by **V cat** presents a melting temperature of only 135°C . In the presence of vanadium component in the catalyst, the crystallinity (X_c) of the polymer increases. The polyethylene formed by the **V cat** presents a long molecular chain, which is difficult to fold. The resulting platelets are thin and

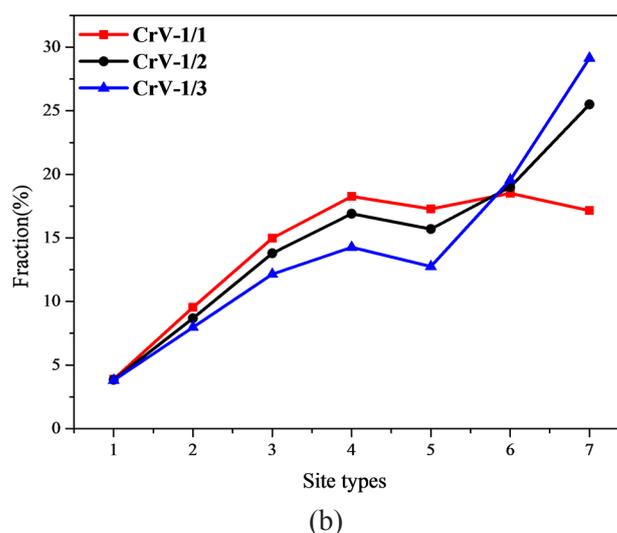
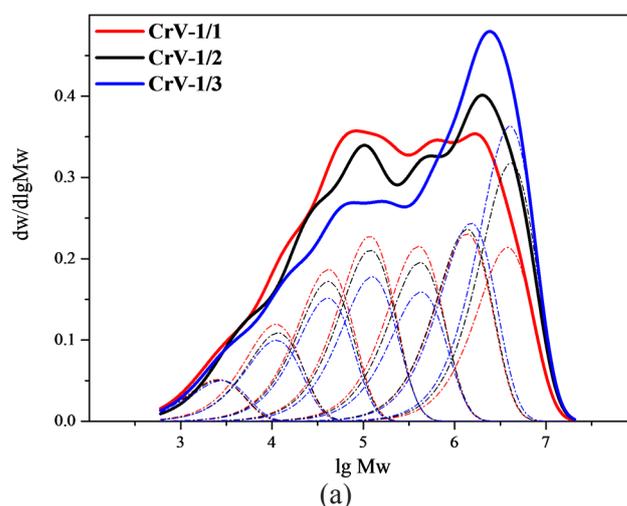


Figure 4. MWD deconvolutions (a) and mass fractions in different site types (b) of polymers by **CrV-1/1**, **CrV-1/2**, **CrV-1/3**.

low crystallinity with a lower melting point of 56.5%. The **Cr cat** is formed into a polyethylene, which has a short chain length and a mostly linear structure, and it is easy to carry out chain movement and chain folding, and thus it has a high melting temperature and crystallinity. For the Cr-V bimetallic catalyst, the product crystallinity is higher due to the high molecular weight portion inducing crystallization and the lubrication of the low molecular weight portion [34]. And the low molecular weight fraction acts as a lubricant to promote chain mobility and chain folding of the ultrahigh molecular weight fraction [35]. However, for each catalyst, the amount of cocatalyst has no significant effect on the molecular chain structure, so the thermodynamic properties of the product do not show significant changes. The thermodynamic properties of the polymer are mainly related to the content and distribution of short-chain branches. The molecular chains of ethylene homopolymerization products are mainly linear structures with very few short chain branches. On the other hand, although the increase in the amount of the cocatalyst causes an increase in the high molecular weight portion of the polymer, the influence is small.

Ethylene/1-Hexene Copolymerization over Cr-V Catalysts

After the comparison of ethylene homopolymerization behavior of CrV-1/1, CrV-1/2, and CrV-1/3

catalysts, the ethylene/1-hexene copolymerization behavior was further investigated. Figure 5 shows the copolymerization kinetics curves for the three catalysts. It can be seen that the addition of comonomers causes a significant decrease in the initial activity of the polymerization, but the rate of deactivation does not change significantly. As the amount of 1-hexene increased, the polymerization activities of the three catalysts decreased significantly. The activities of the three catalysts are in the order of CrV-1/1 > CrV-1/2 > CrV-1/3, which is consistent with the case of homopolymerization.

Regarding the influence of comonomers on the polymerization activity of ethylene, for the Z-N catalyst, a small amount of comonomer can significantly improve the polymerization activity, while higher comonomer was not conducive to the increase of polymerization activity; the copolymerization activity over the metallocene catalyst varied with the amount of comonomer [36, 37]. The significant increase in polymerization activity by adding a small amount of comonomer is called a "comonomer effect" [38]. The newly formed polyethylene chain might be entangled near the active center, hindering the diffusion and adsorption of fresh ethylene molecules. The more the amorphous region contents in the polyethylene, the weaker this hindrance. The insertion of the comonomer reduces the crystallinity of the polymer, and obtains more amorphous regions, which facilitates the diffusion of

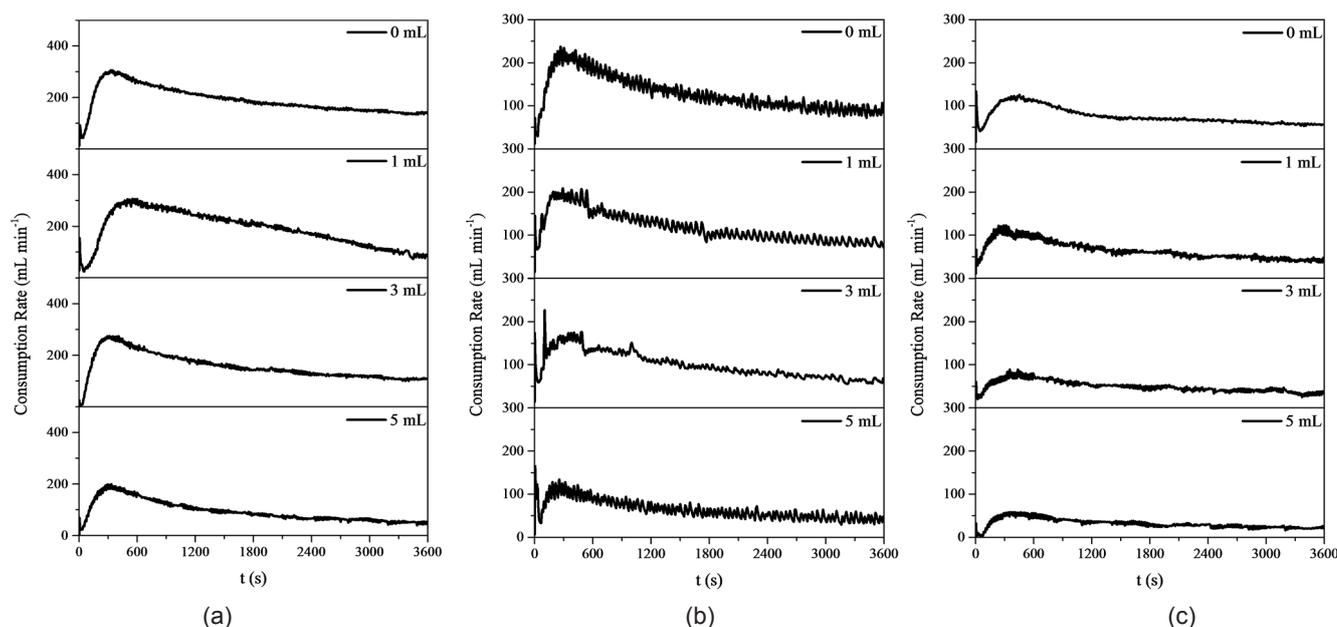


Figure 5. Kinetic curves of (a) CrV-1/1, (b) CrV-1/2, (c) CrV-1/3 with different dosages of 1-hexene for ethylene/1-hexene copolymerization.

ethylene molecules to the vicinity of the active center and further promotes the reaction. However, for various chromium-based Phillips [39], S-2 catalysts [12], and the Cr-V bimetallic catalyst reacted at lower pressure [21], the activity of copolymerization was decreased. The insertion of the comonomer causes the short chain and increases the steric hindrance around the active center, which is disadvantageous for further insertion of ethylene [40].

Compared to our previous report that obtained at lower reaction pressures [19, 21], the reaction activities over **CrV-2/1** are 87.4 and 138.1 $\text{g}_{\text{PE}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ at the reaction pressures of 0.4 and 1.0 MPa, respectively, and the molecular weight increases three times to $7.21 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$, while the molecular weight distribution increases from 35.0 to 58.0. **Figure 6** compares the molecular weight distribution of ethylene homopolymerization and copolymerization products. With 3.0 mL 1-hexene, the molecular weights of the products by **CrV-1/1**, **CrV-1/2** and **CrV-1/3** are 11.6×10^5 , 11.6×10^5 , and $14.4 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$, and \bar{M} is 64.4, 58.5, and 69.2, respectively. Similarly, the two peaks are more obvious than the case obtained at 0.4 MPa [21]. On the one hand, the copolymerized product has a reduced molecular weight compared to the homopolymerized product, which may be due to the fact that 1-hexene acts not only as a comonomer but also as a chain transfer agent in the reaction. Due to the insertion of the comonomer, the β -H bonded carbon atoms in the polymer chain are changed from a secondary carbon atom to a tertiary carbon atom, resulting in the β -H being more easily removed. The β -agostic effect is a key step in the chain transfer reaction, and the insertion of the comonomers decreases the molecular weight of the product. On the other hand, the specific decrease in molecular weight is manifested by a decrease in high molecular weight peaks and an increase in low molecular weight peaks. And as the V content increases, the effect of this comonomer on the molecular weight is weakened, indicating that the Cr center of the low molecular weight fraction is more sensitive to the 1-hexene as a chain transfer agent than the V center of the high molecular weight.

Similarly, the same deconvolution analysis method is used to analyze the molecular weight distribution curves of the copolymers of **CrV-1/1**, **CrV-1/2**, and **CrV-1/3**. In **Figure 7 (a)**, the number of active sites of the Cr-V catalysts is still seven and each of the Flory components can be corresponded. In **Figure 7 (b)**, as

the vanadium loading increases, the active sites 6 and 7 presenting the high molecular weight portion are en-

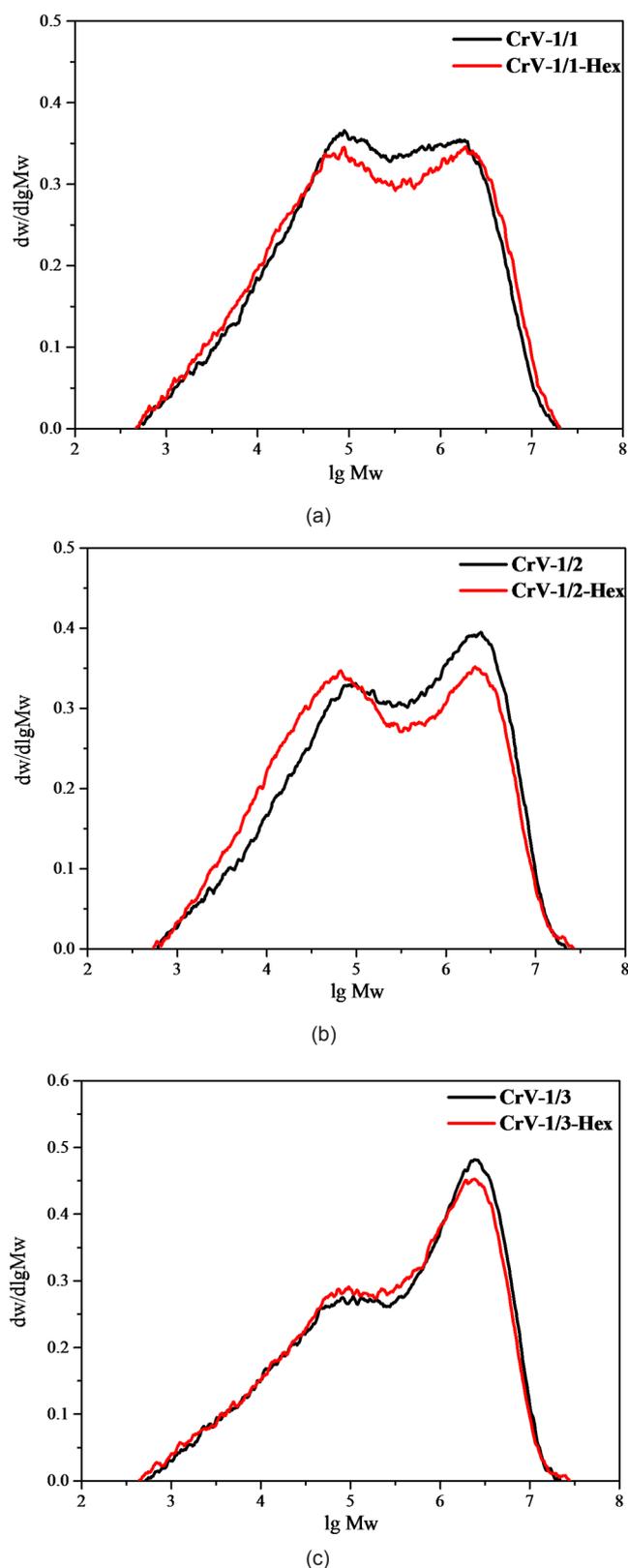


Figure 6. GPC curves of ethylene homopolymer and copolymer by (a) **CrV-1/1**, (b) **CrV-1/2**, (c) **CrV-1/3**.

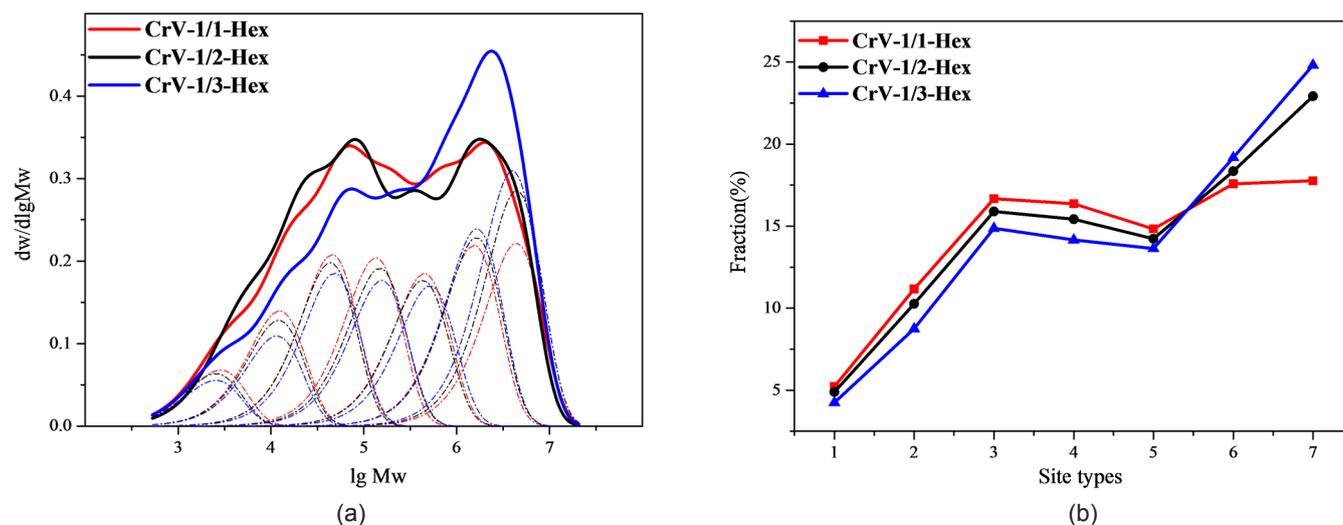


Figure 7. MWD deconvolutions (a) and mass fractions in different site types (b) of copolymers by **CrV-1/1**, **CrV-1/2**, **CrV-1/3**.

hanced. Meanwhile, the active sites 1, 2, 3, 4 and 5 of the low molecular weight portion decreases. It is shown that in the ethylene/1-hexene copolymerization reaction, the interaction between the two active centers was benefited to the vanadium center.

The thermodynamic properties of the ethylene/1-hexene copolymer product by **CrV-1/1**, **CrV-1/2**, and **CrV-1/3** are shown in Table 3. The melting temperature and crystallinity of all products decrease with varying degrees as the increased amount of comonomer. When 3.0 mL 1-hexene is added, the copolymerization activity of the catalyst decreases by

22.5%, 22.4%, and 33.3%, respectively. The addition of comonomers results in the formation of short chain branches on the polymer chain, which hinders the movement of molecular chains and the folding of chains. Thus, the crystallization process of polyethylene is hindered, resulting in thinner platelets and lowering the melting temperature and crystallinity of the polymerization product.

The copolymerization products of **CrV-1/1**, **CrV-1/2** and **CrV-1/3** were characterized by DSC to characterize the comonomer insertion rate. It can be seen from Figure 10(a) that the SSA melting curve of the

Table 3. Property of polymerization products by **CrV-1/1**, **CrV-1/2**, and **CrV-1/3** with different dosages of 1-hexene^(a).

Catalyst	1-Hexene (mL)	Activity ($\text{g}_{\text{PE}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$)	$T_m^{(b)}$ ($^{\circ}\text{C}$)	T_c ($^{\circ}\text{C}$)	ΔH_f ($\text{J} \cdot \text{g}^{-1}$)	$X_c^{(c)}$ (%)
CrV-1/1	0	500.6	135.3	118.4	204.5	69.8
	1.0	476.96	134.3	117.8	206.1	70.3
	3.0	329.74	133.9	117.7	184.9	63.1
	5.0	249.47	134.0	117.6	181.9	62.1
CrV-1/2	0	346.93	136.0	118.7	198.3	67.7
	1.0	328.18	134.8	118.1	188.9	64.5
	3.0	269.03	134.1	117.4	187.3	3.9
	5.0	174.98	133.7	118.1	177.9	60.7
CrV-1/3	0	224.47	135.4	119.3	191.2	65.3
	1.0	179.15	134.9	118.5	193.4	66.0
	3.0	149.67	134.7	118.5	188.7	64.4
	5.0	105.83	134.2	118.0	177.8	60.7

^(a) Polymerization conditions: catalyst 30 mg, optimum dosage of TIBA for different catalysts, ethylene pressure 1.0 MPa, temperature 80 $^{\circ}\text{C}$, 1-heptane 130 mL, 1-hexene;

^(b) T_m , T_c , ΔH_f measured by DSC;

^(c) $X_c = \Delta H / \Delta H_{f0} = \Delta H / 293 \text{ J} \cdot \text{g}^{-1}$.

CrV-1/3 copolymerized product exhibits only a high temperature melting peak around 136°C, and the low temperature melting peak is not obvious. **CrV-1/1** and **CrV-1/2** also show a shoulder peak before the high temperature melting peak. This indicates that the copolymer of the three catalysts is mainly composed of thick platelets, and the copolymerization abilities of **CrV-1/1** and **CrV-1/2** may be superior to that of **CrV-1/3**. In order to further distinguish the comonomer insertion rate of the three copolymerization products, the SSA curve was subjected to peak fitting, and the adjusted Thomas Gibbs equation (Eqn. 1) was used to correlate the relationship between the thickness of the platelet and each melting peak. The relative content of the platelet thickness is obtained from the peak area of each peak.

$$L = \frac{2\sigma T_{mp}^{\circ} \Delta z}{\Delta h (T_{mp}^{\circ} - T_{mp})} \quad (1)$$

In the equation, L - platelet thickness (nm); T_{mp}° - the melting temperature of linear polyethylene, 418

K; T_{mp} -melting temperature (K) corresponding to the SSA fitting peak; σ -surface free energy of polyethylene platelets, 5.0 kJ.mol⁻¹; Δh - the melting enthalpy of the ethylene unit, 8.2 kJ.mol⁻¹; Δz - the length of the ethylene unit on the polymer chain, 0.254 nm.

As shown in **Figure 8** (b), the three copolymers have substantially the same platelet thickness distribution, and each contains a large number of thick platelets and less flake crystals. In comparison, the platelet thickness order of the three copolymers is: **CrV-1/2** (13.8 nm) < **CrV-1/1** (14.1 nm) < **CrV-1/3** (14.8 nm). The V center has a better copolymerization capacity than the Cr center. The increase in vanadium content facilitates the insertion of comonomer that the **CrV-1/2** copolymer has a platelet thickness of less than **CrV-1/1**. At the same time, the higher metal loading leads to the increasing steric hindrance of the active center, or sintering the carrier, and hindering the diffusion of 1-hexene molecules to the active center. The **CrV-1/3** copolymer with the highest vanadium content has the worst copolymerization ability. Zhao et al. [41] found

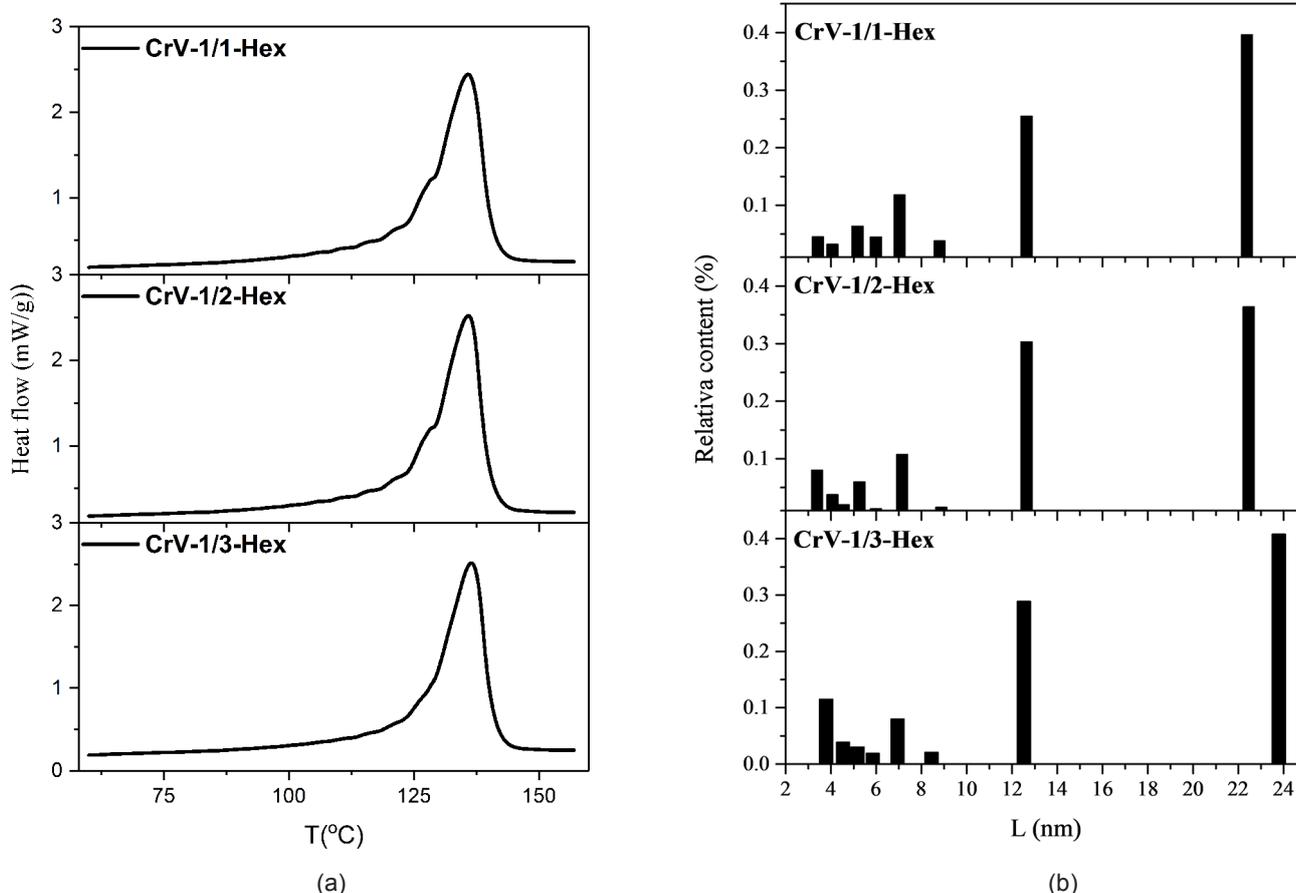


Figure 8. SSA analysis (a) and lamella thickness distribution (b) for the ethylene/1-hexene copolymers by **CrV-1/1**, **CrV-1/2**, **CrV-1/3**.

that the activity of vanadium catalyst showed a number of favorable performances like the better copolymerization performance than Cr catalyst for the S-2 catalyst. Therefore, the increasing vanadium loading benefits the copolymerization performance of the Cr-V catalysts.

Hydrogen Sensitivity of Cr-V Catalysts

Hydrogen is commonly used in the industry as a chain transfer agent for the polymerization of ethylene to adjust the molecular weight of the product. Therefore, in this experiment, 0.1 MPa hydrogen was introduced into the polymerization system to investigate the hydrogen responds of the Cr-V bimetallic catalysts. The experiments were carried out under the optimum amount of each catalyst, and the results are shown in Figure 9 and Table 4.

Table 4 shows that the addition of hydrogen significantly reduced the polymerization activity. The activities of CrV1/1, CrV-1/2 and CrV-1/3 decreased by 34.5%, 46.6%, and 53.9%, respectively. As the V loading increases, the effect of hydrogen on the polymerization activity becomes significant, showing that the V active center is more sensitive to hydrogen. The kinetic curve in Figure 9 indicates that the initial activity is reduced, as well as the total activity. Regarding the mechanism of hydrogen on ethylene polymerization, McDaniel believed the reaction of hydrogen with the active center of chromium generated a trace amount of water to poison the active center of Phillips catalyst [1]. Kissin et al. [42, 43] studied the Z-N catalyst and concluded that the introduction of hydrogen increased the content of Ti-C₂H₅ at the active center, which was not conducive to further reaction of the active center with ethylene.

At the same time, the molecular weights of the products obtained by CrV-1/1 and CrV-1/2 reduce by 23.3% and 17.8%, respectively. As is clear in Figure 10, the addition of hydrogen causes a decrease in the high molecular weight portion and an increase in the low molecular weight portion. However, there is no significant migration of the peak positions corresponding to the two molecular weight fractions, indicating that the hydrogen addition does not generate a new active center, and more likely to reflect the role of the chain transfer agent. High molecular weight active centers and low molecular weight active centers have different responses to hydrogen. Perhaps the former is more sensitive that fewer polymers are produced in

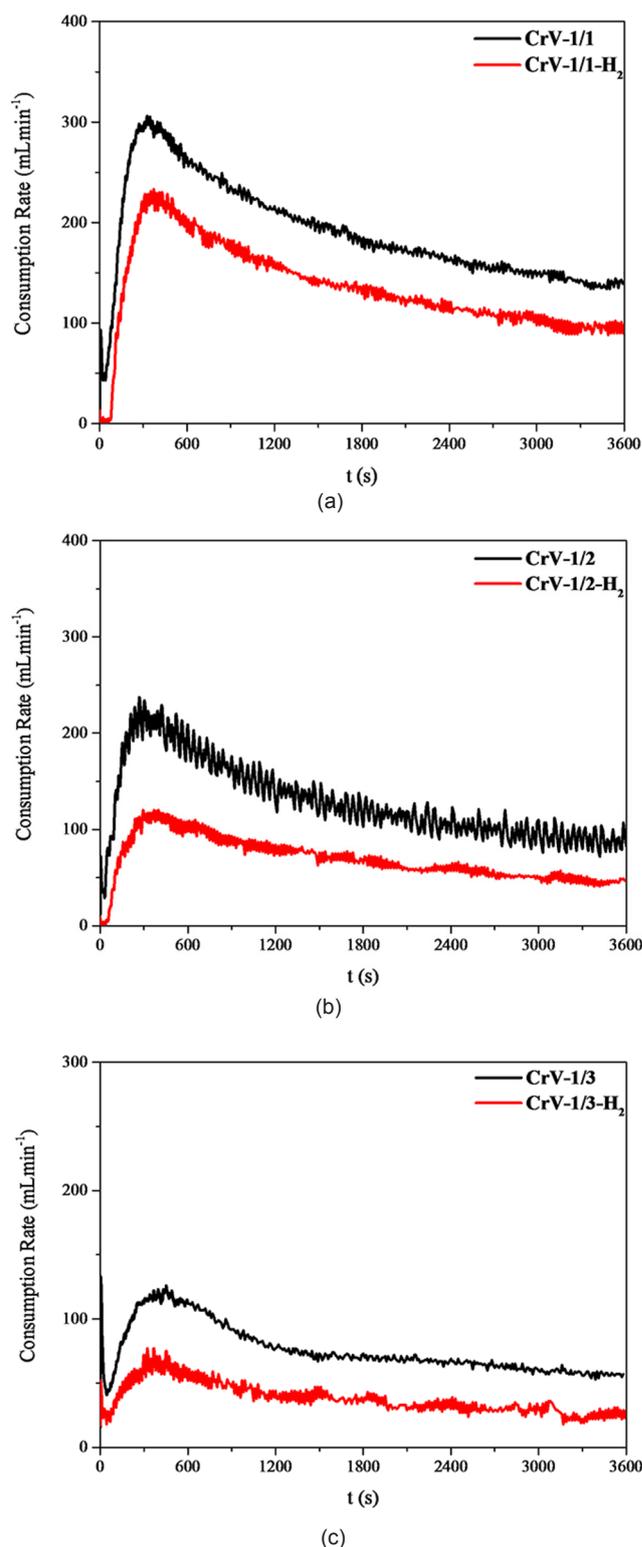


Figure 9. Kinetic curves of (a) CrV-1/1, (b) CrV-1/2, (c) CrV-1/3 for ethylene polymerization with or without 0.1 MPa H₂.

the corresponding active center, which ultimately results in changes in the molecular weight of the product and its distribution. At the same time, it also shows that hydrogen adjustment can be used as an effective

Table 4. Properties of PE by CrV-1/1, CrV-1/2, and CrV-1/3 with or without H₂^(a).

Catalyst	H ₂ (MPa)	Activity (g _{PE} ·g _{cat} ⁻¹ ·h ⁻¹)	T _m (°C)	T _c (°C)	M _w (×10 ⁻⁵ g·mol ⁻¹)	Đ
CrV-1/1	0	554.6	136.2	118.4	10.2	50.1
	0.1	363.3	137.1	117.3	7.83	37.4
CrV-1/2	0	346.9	136.0	118.7	13.1	54.5
	0.1	185.3	137.3	116.8	10.8	51.8
CrV-1/3	0	241.2	135.4	119.3	/	/
	0.1	111.1	137.2	117.7 //	/	/

^(a) Polymerization conditions: catalyst 30 mg, optimum dosage of TIBA for different catalysts, ethylene pressure 1.0 MPa, temperature 80°C, 1-heptane 130 mL.

chain transfer method to adjust the molecular weight and distribution of the Cr-V bimetallic catalysts.

The molecular weight distribution curves of the po-

lymerization product with hydrogen were analyzed by the same deconvolution analysis method. In Figure 11 (a), the minimum number of active sites of Cr-V cata-

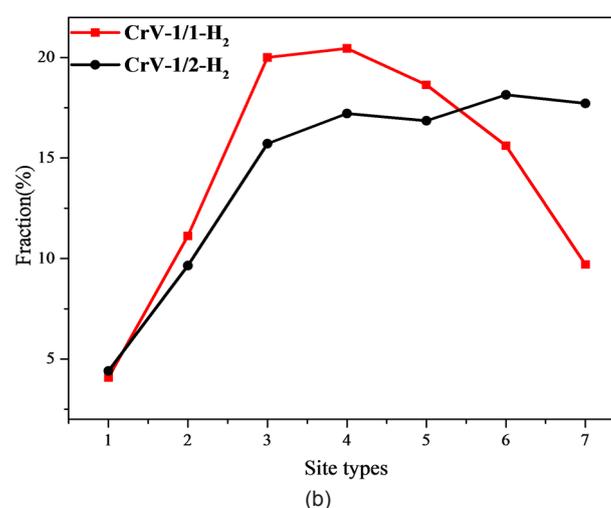
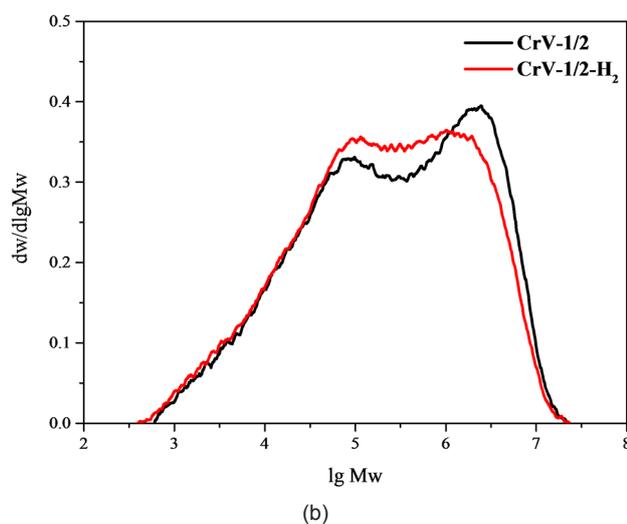
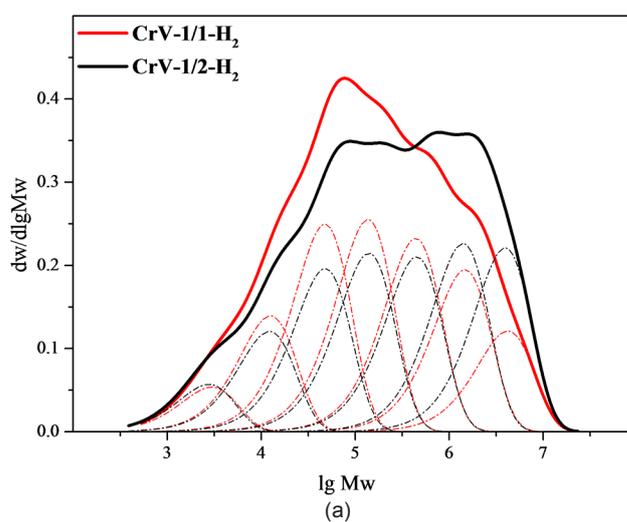
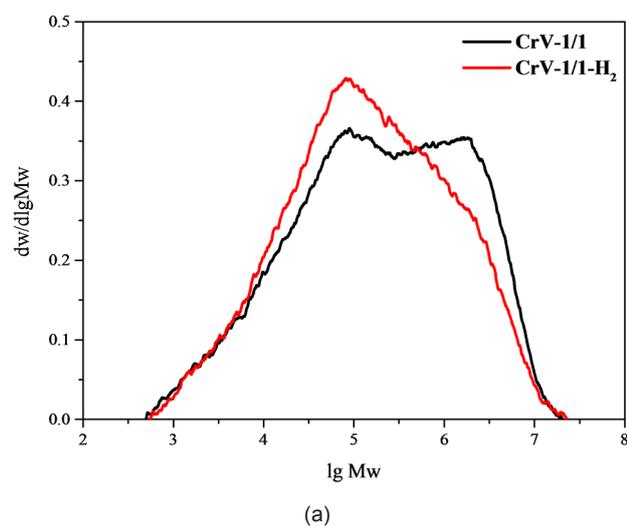

Figure 10. GPC curves of polymers by (a) CrV-1/1 and (b) CrV-1/2 with or without 0.1 MPa H₂.

Figure 11. MWD deconvolutions (a) and mass fractions in different site types (b) of PE by CrV-1/1, CrV-1/2, CrV-1/3 with 0.1 MPa H₂.

lysts is still seven without significant change. Figure 11 (b) shows as the vanadium loading increases, the active sites 6 and 7 of the high molecular weight portion obviously increases, indicating that the activity of vanadium is significantly enhanced, while sites of 2, 3, 4 and 5 of the low molecular weight portions are relatively weakened.

Tensile Properties

Table 5 shows that the tensile strength and elongation-at-break of the homopolymerized product of **CrV-1/1** are higher than those of the **Cr cat**. This may be the increased crystallinity, which is confirmed by the T_m values. The V active center mainly produces ultra-high molecular weight polyethylene, which increases the molecular weight and lengthens the molecular chain. The higher molecular weight with longer molecular chains also benefits to the promotion of the interaction among the polyethylene platelets to increase tensile strength. The increase of vanadium loading is beneficial to the optimization of the tensile properties of the homopolymer. For the copolymer by **CrV-1/1** with addition of 1.0 mL 1-hexene, the tensile strength and elongation-at-break of the product are the highest, which are 29.7 MPa and 903.3%, respectively. As the amount of 1-hexene increased, the tensile properties decreased, which may be due to the increase in the comonomer content and the increase in chain transfer, leading to a decrease in molecular weight and a decrease in molecular interactions.

In summary, due to the high migration of ethylene, 1-hexene and hydrogen in the reaction system, the more active sites might be accessible, thus the reaction on the V active sites is strengthening at higher pressure. Zhao et al. [41] and Jin et al. [29] found that the vanadium catalysts allowed the preparation of high molecular weight polymers, as well as the high α -olefin incorporation with satisfactory short-chain branch distribution (SCBD). Similarly, the H_2 respond of the catalyst, and the tensile property of the corre-

sponding products are also modified.

CONCLUSION

In this paper, the effects of the vanadium content on the polymerization behavior and product properties of the catalysts were investigated systematically for the Cr-V bimetallic catalysts developed by our research group. The Cr-V bimetallic catalysts can synthesize polyethylene with a bimodal MWD. The vanadium loading has a significant effect on the polymerization activity, MW, as well as the MWD. Carried out the reaction at higher pressure, the two peaks in the GPC curves of homopolyethylene and copolymerization are more obvious. It means that higher reaction pressure benefits the promotion of the active center for higher MW. According to the deconvolution of the GPC curves of homopolyethylene, ethylene/1-hexene copolymer and the products with H_2 responds presents the synergetic effect between of Cr and V center. However, the increase in vanadium content is unfavorable to the homopolymerization and copolymerization activities of the Cr-V catalysts. The Cr-V bimetallic catalysts required more cocatalyst than the **Cr cat**. The amount of cocatalyst is increased, and the molecular weight of the product is slightly increased. The Cr-V bimetallic catalysts have better hydrogen sensitivity. When the partial pressure of hydrogen is 0.1 MPa, the molecular weight is reduced by nearly half. Specifically, the high molecular weight peak is weakened, the low molecular weight peak is strengthened, and the peak position does not change significantly. The higher vanadium content and the greater the sensitivity of hydrogen modulation indicate that the vanadium active center has better hydrogen responds than the chromium active center does. The homopolymerization product of the **Cr/V1** catalysts has better tensile properties than that of the **Cr cat**. It exhibits higher tensile strength and elongation-at-break. The tensile properties of the copolymerized product of **CrV-1/1** further improved the properties.

Table 5. Tensile property of homopolymer by **Cr cat**, and **CrV-1/1** and copolymer by **CrV-1/1**

Catalyst	1-hexene (mL)	Tensile strength (MPa)	Elongation-at-break (%)
Cr cat	0	26.4	769.7
	1.0	29.7	903.3
CrV-1/1	0	30.7	785.5
	1.0	29.7	903.3

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