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Study on Kinetics of Ethylene Polymerization Catalyzed by Supported Binuclear Metallocene

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Abstract: The kinetics of ethylene polymerization catalyzed by supported binuclear metallocene catalyst $[(\eta^5\text{-}C_5H_5)ZrCl_2]_2[\mu, \mu\text{-}(SiMe_2)_2(\eta^5\text{-allyl } C_5H_2)_2]/MAO/SiO_2$ in slurry phase was investigated. The effects of polymerization factors, such as diffusion index, polymerization pressure and temperature on the kinetics were studied. The kinetics parameters such as reaction order (n), the apparent activation energy (E_a) and the chain propagation rate constant (K_p) were determined and the concentration of active site (C^*) was obtained by kinetic extrapolation method. The result indicates that the supported binuclear metallocene/MAO catalyst system exhibits a higher catalytic activity than that of mononuclear system, attributed to the higher C^* concentration and higher K_p of the former. The slurry phase polymerization reaction rates show 1.11 order dependency on monomer concentration, and $E_a = 72.47$ kJ/mol, $C^* = 0.33$ mol/mol and $K_p = 1.06\times10^6$ L·(mol·h)$^{-1}$ are found.

Key words: kinetics; ethylene polymerization; supported binuclear metallocene
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In the past decades, numerous metallocene complexes have been synthesized and used as efficient catalysts for the polymerization of olefin because of their high activity and excellent copolymerization capability. However, the molecular weight distribution (MWD) of the resulting mPE is very narrow ($M_w/M_n = 2\sim3$), which causes some trouble on the processibility due to the high shear viscosity and low melt extensional viscosity. To overcome this disadvantage, binuclear catalysts were developed, in which two reactive metal centers are locked in close proximity to offer the opportunity to produce cooperative chemical behavior, and broaden MWD and even bimodal polymers could be obtained with the binuclear catalyst systems[1-4].

The kinetic study is very important for the optimization of the reactor parameters, control of polymer properties (molecular weight, MWD, polymer density and component) and have attracted tremendous research interests[5-7]. In the kinetic study, Kp is a function of the C^* and offers many necessary information about catalyst structure and catalytic mechanism. Meanwhile, K_p and C^* are important indicators to evaluate new catalysts.

In general, supported catalysts are prepared by immobilization of metallocene on a porous material such as SiO_2, $MgCl_2$, zeolite, clay, Al_2O_3 and polystyrene by physical or chemical techniques. Compared with homogeneous catalyst, a supported catalyst shows some advantages like increasing molecular weight, enhancing the stability of catalyst, reducing the dosage of cocata-

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lyst MAO , decreasing the probability of β-H elimination and the inactivation of bimolecular metallocene. More importantantly, supported catalysts exhibit template function, improving the morphology and bulk density of polymer product . On the other hand, when the polymerization was carried out with supported catalyst, the polymerization process was stable and easy to control. At the same time, supported catalysts can be easily applied to gas-phase and slurry polymerization process with the existing industrial equipments.

Numerous research work on polymerization kinetics of mononuclear supported-metallocene catalyst have been published[8-9]. In 2003, Wanke group[7b] prepared supported (n-BuCp)$_2$ZrCl$_2$ catalysts on porous material with different pore sizes, and studied their application in ethylene polymerization. They found that these supported catalyst system contains many types of active centers. The type of catalyst active center is strongly dependent on the aperture size of the load material. In 2005, McAuley[7c] developed the first dynamic mathematical model and gave a parameter estimation for gas-phase ethylene polymerization catalyzed with supported metallocene, which fit well with the relationship between the polymerization rate and the concentration of hydrogen, but it failed to accurately predict the molecular weight and molecular weight distribution. Yao's group[7d] investigated a gas-phase ethylene/hexene copolymerization with metallocene catalyst in a laboratory-scale reactor and found that the deactivation rate increased when the polymerization rate is increased.

However, there has been no generally accepted kinetics equation because different supported processes were studied by different groups. Herein, we report the polymerization dynamics of supported binuclear metallocene catalyst. SiO$_2$ supported binuclear catalyst system-[(η^5-C$_5$H$_5$)ZrCl$_2$]$_2$[μ, μ-(SiMe$_2$)$_2$(η^5-allyl C$_5$H$_2$)$_2$]/MAO/SiO$_2$ was prepared and used for ethylene polymerization in slurry phase. The relationships between polymerization rate with ethylene pressure and temperature were investigated and the kinetic equation was given. The kinetics parameters such as reaction order(n), E$_a$ and K$_p$ were also determined.

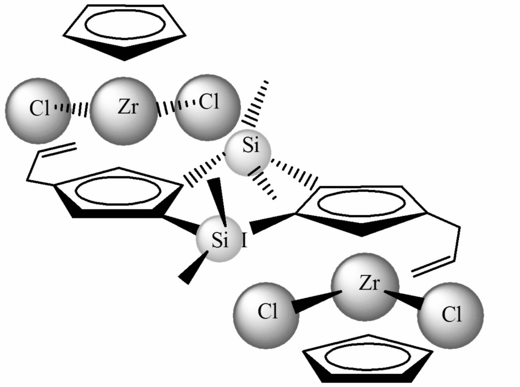
1 Experimental

1.1 Materials

Ethylene was purified by passing through 0.4 nm molecular sieves. n-Hexane was freshly distilled from sodium-benzophenone ketyl. AlEt$_3$ (0.95 mol/L, in n-hexane) was purchased from Ethyl Co.. SiO$_2$ (average diameter = 55 μm, specific surface = 322 m^2/g, bulk density = 0.28 g/cm^3) was kindly donated by Lanzhou Petrochemical Research Center, Petro China.

1.2 Supported catalyst

All manipulations were carried out under an argon atmosphere using standard Schlenk technique. Binuclear catalyst [(η^5-C$_5$H$_5$)ZrCl$_2$]$_2$[μ, μ-(SiMe$_2$)$_2$(η^5-allylC$_5$H$_2$)$_2$] was synthesized according to literature precedure [3].



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Supported catalyst [(η^5-C$_5$H$_5$)ZrCl$_2$]$_2$[μ, μ-(SiMe$_2$)$_2$(η^5- allylC$_5$H$_2$)$_2$] /MAO/ SiO$_2$ was prepared according to the literature precedure[10] (aluminous mass content = 16.50% ~18.65%, zirconium mass content = 0.55% ~0.80%). Supported catalyst: Specific surface = 307 m^2/g, pore volume = 1.40 m^3/g, average pore diameter =18.84 nm.

1.3 Ethylene polymerization

1.3.1 Ethylene polymerization under 0.1 MPa

Polymerization was carried out in a 250 mL autoclave equipped with a magnetic stirrer. The reactor was heated at 100 ℃ under vacuum for 30 min and then cooled to the desired temperature by immersed into a thermostatically heating bath. Proper amount of AlEt$_3$ solution, supported binuclear catalyst and n-hexane were successively added to the autoclave with a final volume to 150 mL and the reactor was filled with pre-dried ethylene. The ethylene pressure was kept at 0.1 MPa during the polymerization by replenishing the flow. The reaction mixture was stirred vigorously for 1.0 ~ 2.0 h. 10% HCl in ethanol was then added to quench the polymerization. The mixture in the reactor were transferred to a beaker and then separated from the solution by filtration. The collected polymer was washed to neutral with ethanol and then dried overnight in a vacuum oven at 60 ℃ to a constant weight.

1.3.2 Pressurized polymerization Pressurized polymerization was performed in 500 mL stainless steel autoclave. Before use, the autoclave was treated as described in 2.3.1. Proper amount of $AlEt_3$ solution, n-hexane and supported binuclear catalyst were added in that sequence. The autoclave was heated to certain temperature and stirred, and the reactor was pressurized with pre-dried ethylene. The temperature fluctuation was control into ±1℃ range, and the ethylene pressure was kept constant during the polymerization by replenishing controlled with electronic valve. The moment consume of ethylene was recorded automatically. The reaction mixture was stirred vigorously for 2.0 h and then vented. The workup of product was the same as described in 1.3.1.

1.4 Characterization

The relative molecular weight(M_n) of PE was determined at 135 ℃ with decalin as the solvent. Intrinsic viscosity $[\eta]$ comes from Equation (1) and M_n is obtained with Equation (2).

$$[\eta] = (\eta_{sp} + 5\mathrm{Ln}\eta_r)/6\rho \tag{1}$$

$$[\eta] = 2.3\times10^{-4} M_n^{0.82} \tag{2}$$

η_{sp}: specific viscosity, η_r: relative viscosity, ρ: PE g/100 mL decalin.

2 Results and Discussion

2.1 The effect of diffusion index on kinetics

Under our applied condition, both the supported binuclear catalyst and resultant polymer are insoluble in n-haxane, so our polymerization system was a heterogeneous one. It is well known that diffusion index plays important role by possible internal diffusion and/or external diffusion[11], and so, the polymerization should be carried out in kinetics field without diffusion effect[12]. The effect of external diffusion on kinetics was tested and the results of agitation speed and catalyst mass concentration on the activities are shown in Fig. 1 and Fig. 2.

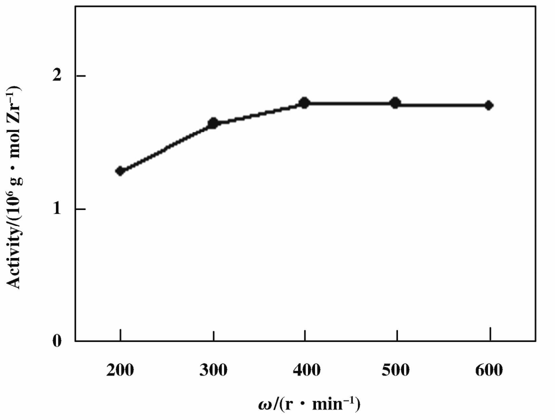

Fig. 1 Effect of agitation speed on polymerization activity

Polymerization conditions: m(catalyst concentration) = 70 mg/L; hexane 0.1L; T = 50 ℃; p = 0.1 MPa; t = 2 h; n(Al)/n(Zr) = 92; n(TEA)/n(Zr) = 1 000

It is clearly seen that the polymerization activity increases as the agitation speed increases when the stirring speed is lower than 400 r/min, which means that the monomer diffusion affects the polymerization significantly However, when the agitation speed is higher than 400 r/min, the activity keeps constant, indicating the polymerization was performed in kinetics field and the external diffusion has no effect on it.

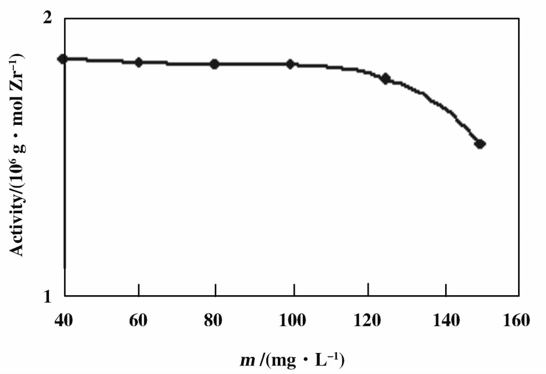

Fig. 2 Effect of catalyst concentration on polymerization activity

Polymerization conditions: ω(stirring speed) = 500 r/min; hexane 0.1L; T = 50 ℃; p = 0.1 MPa; t=2 h; n(Al)/n(Zr) = 92; n(TEA)/n(Zr) = 1 000

Fig. 2 shows that the activity slowly drop down when the supported binuclear catalyst mass content is more than 125 mg/L and the activity keep constant when the catalyst mass content are between 40 to 125 mg/L.

Thiele modulus φ-the ratio of specific diffusion time to specific reaction time, is often used as indicator to estimate the intra-diffusion effect, and the modulus φ is one of criterion to evaluate the effect of polymer on monomer diffusion as shown in equation 3[13]:

$$\varphi = (R_{p,\max} / D_m[M])^{1/2} S_0 \tag{3}$$

($R_{p,\max}$ is maximum polymerization rate, D_m is index of monomer diffusion, [M] is content of monomer, and S_0 is initialized diameter of catalyst grain)

Zhang et al[14] found that the polymerization reaction was controlled by diffusion when $\varphi > 10$. On the contrary, when $\varphi << 1$, the reaction was controlled by kinetics. Under our applied condition, we found that $\varphi = 0.025$ ($S_0 = 55\times10^{-4}$cm, $R_{pmax} = 7.36\times10^{-5}$ mol/(L. s), $D_m = 35\times10^{-6}$cm^2/s, [M] = 0.096 mol/L), which means the key step in polymerization reaction was controlled by kinetics. Our result is similar to that of Michiel et al [15-16].

In this regard, the following polymerization reactions were carried out with stirring speed = 400 ~ 600 r/min and catalyst content = 40 ~ 100 mg/L, and the kinetics parameter under such condition reflect characteristic of the catalytic system.

2.2 The effect of ethylene pressure on kinetics

Ethylene polymerization kinetics test under different pressure are conducted and the curve of polymerization kinetics is shown in Fig. 3.

From Fig. 3 it is found that the curves of polymerization kinetics fit with standard slurry polymerization kinetics curves. It is also found that the R_p increased rapidly and reached a maximum at 30 ~ 40 min and then kept constant. It is obvious that the activity increased as the monomer ethylene pressure increased, attributed to the monomer content in slurry polymerization system increasing as the pressure increased.

Equation(4) shows the relationship between the R_p and [M].

the polymerization rate is:

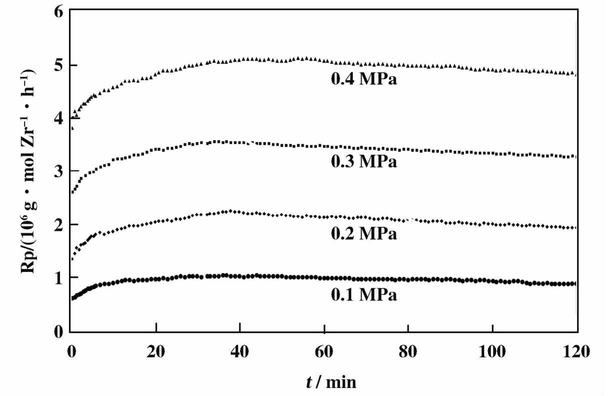

Fig. 3 Kinetic curves of different ethylene partial pressure

Polymerization conditions: *m*(catalyst concentration) = 70 mg/L; *ω*(stirring speed) = 500 r/min; hexane 0.2 L; T = 50 ℃; t = 2 h; *n*(Al)/*n*(Zr) = 98; *n*(TEA)/*n*(Zr) = 1050

$$R_p = K_p[C^*][M]^n \tag{4}$$

R_p is first order dependent on the monomer concentration[M][17-18], that is, n = 1 in equation (4). However, Dornik et al[19] found a two order ethylene polymerization reaction when using metallocene catalyst, which implied the R_p was two order dependent on the monomer concentration [M]. Chakravarti [18] and Kissin[20] found similar phenomena and the order is 1.24 and 1.8, respectively. Chien[21] ascribed it to the coordination between the monomer and the activated center. Although there are many differences in literature, the basic rule of ethylene polymerization kinetics is same.

Equation (5) was obtained by logarithm equation (4):

$$\mathrm{Ln}R_p = \mathrm{In}\ K_p[C^*] + n\ \mathrm{Ln}[M] \tag{5}$$

Equation(5) is linear equation and the slope is the reaction order *n*. Bergstra[15] simulated the relationships between the ethylene solubility in n-hexane and ethylene pressure. the ethylene solubility can be described by:

$$f_{\text{ethylene}} = k\ p \tag{6}$$

(f_{ethylene} is ethylene mole fraction in n-hexane, *p* is ethylene pressure)

They found a linear relationship between k and T^{-1} (shown in Fig. 4) and gave Equation (7):

$$k = 165.68\ T^{-1} - 0.3839 \tag{7}$$

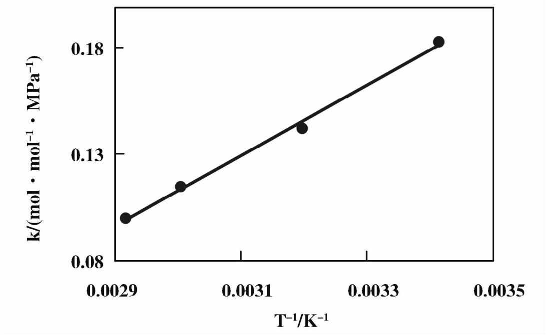

Fig. 4 The relationship between k and T^{-1}

With this equation, the curve of ethylene solubility in n-hexane at different temperature was obtained. Ethylene solubility in *n*-hexane at 50 ℃ (see Equation 8) was gained from Equation (7)

$$f_{ethylene} = 0.129\ p \qquad (8)$$

The result of ethylene solubility in *n*-hexane at 50 ℃ is shown in Table 1.

Fig. 5 shows the liner relationship between Ln[M] and $LnR_{p\ max}$ under different ethylene pressure.

Table 1 [M] and $R_{p\ max}$ at different ethylene partial pressure

P/MPa	$f_{ethylene}/(10^{-2}mol \cdot mol^{-1})$	$[M]/(g \cdot L^{-1})$	$R_{p\ max}/(10^6 g \cdot molZr^{-1} \cdot h^{-1})$
0.1	1.29	2.69	1.04
0.2	2.58	5.45	2.26
0.3	3.87	8.28	3.55
0.4	5.16	11.19	5.12

Polymerization conditions the same as Figure 3.

[M], ethylene bulk concentration, $g \cdot L^{-1}$, calculated from $f_{ethylene}$ and hexane density at different pressures and 50 ℃, hexane density was 0.6313 ~ 0.6316 kg · L^{-1} under 0.1 ~ 0.4 MPa at 50 ℃

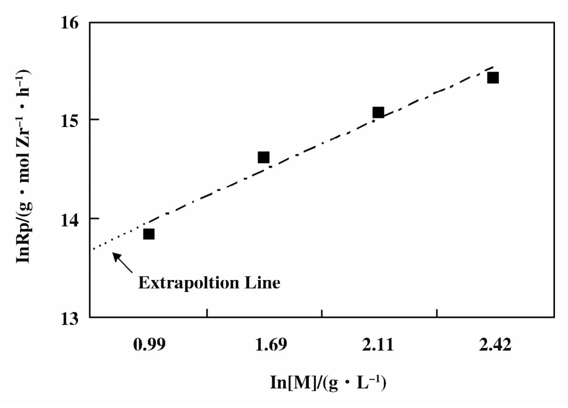

Fig. 5 The relationship between LnR_p and [M]

From Fig. 5, kenetic parameters are obtained: $Ln K_p[C^*] = 12.76$, $n = 1.11$, to give Equation (9):

$$R_p = K_p[C^*][M]^{1.11} \qquad (9)$$

2.3 The effect of temperature on kinetics

It is well known that reaction temperature plays important role in polymerization reaction such as the rate of chain initiation, chain propagation and chain termination[22], and the temperature affect catalytic behavior and polymer properties at the same time. The result of reaction temperature on polymerization rate is shown in Table 2.

Table 2 [M] and R_p at different polymerization temperature

T/K	$f_{ethylene}/(10^{-2}mol \cdot mol^{-1})$	$[M]/(g \cdot L^{-1})$	$R_p/(10^5 g \cdot molZr^{-1} \cdot h^{-1})$
293	1.83	4.01	1.14
303	1.63	3.51	2.53
313	1.42	3.01	5.71
323	1.29	2.69	9.47
333	1.14	2.34	24.40

Polymerization conditions: m(catalyst concentration) = 70 mg/L; ω(stirring speed) = 500 r/min; hexane 0.1L; p = 0.1 MPa; t = 0.5 h; $n(Al)/n(Zr)$ = 92; $n(TEA)/n(Zr)$ = 1 000

From the result, it is found that the polymerization rate increases as the reaction temperature increases. The propagation rate constant is assumed to be temperature dependent according to the Arrhenius equation:

$$K_p = K_{p0} e^{(-Ea/RT)} \qquad (10)$$

Equation (11) was obtained from Equation (9):

$$R_p/[M]^{1.11} = K_p[C^*] \qquad (11)$$

Then Equation (12 and 13) was obtained by combining Equation (10) and (11):

$$R_p/[M]^{1.11} = K_{p0}[C^*]\ e^{(-Ea/RT)} \qquad (12)$$

$$\mathrm{Ln}(R_p/[M^{1.11}]) = \mathrm{Ln}\ K_{p0}[C^*] - E_a/RT \qquad (13)$$

Fig. 6 is the relationship between Ln ($R_p/[M]^{1.11}$) and T^{-1}.

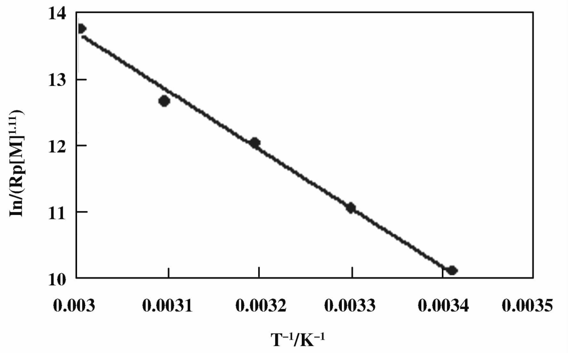

Fig. 6 The relationship between Ln($R_p/[M[^{1.11}$) and T^{-1}

From Fig. 6, some parameters were obtained: Ln $K_{p0}[C^*]$ = 39.83, E_a/R = 8716, E_a = 72.47 kJ/mol. It is similar to that of Bergstra[15] (ethylene pressure = 15 bar, T = 50 ~ 90 ℃, E_a = 74.90 kJ/mol) and Kaminsky[23] (ethylene pressure = 8 bar, E_a = 75 kJ/mol), but higher than Roos[24] (supported rac-$Me_2Si[Ind]_2ZrCl_2$/MAO, ethylene pressure = 5 bar, T = 40 ~ 80 ℃, gas phase polymerization, E_a = 39.2 kJ/mol).

2.4 Determination of [C*] and Kp

It is well known [C*] reveals the structure and property of active site, and plays an important roles to understand the reaction mechanism and evaluate the catalytic system. There are many methods for determination [C*] using kinetics and polymer molecular weight. The dynamic extrapolation method was chosen to measure [C*] of supported binuclear system in this study. Equation (14) was used to calculate [C*][25]:

$$Y/M_n = [C^*] + K_{tr}[X][C^*]t \qquad (14)$$

When t = 0, Y/M_n = [C*]. Y is the polymer yield at time t, and k_{tr} is chain transfer constant when chain transfer agent is X.

$$\text{with } Y = R_p \cdot t = K_p[C^*][M]^{1.11} \cdot t \qquad (15)$$

Equation (16) was obtained

$$Y/M_n = [C^*] + Y \cdot K_{tr}[X])/(K_p[M]^{1.11}) \qquad (16)$$

The plot of Y/M_n as a function of Y was made (see Fig. 7) and the intercept was obtained when t was extrapolated to zero, and the intercept is [C*].

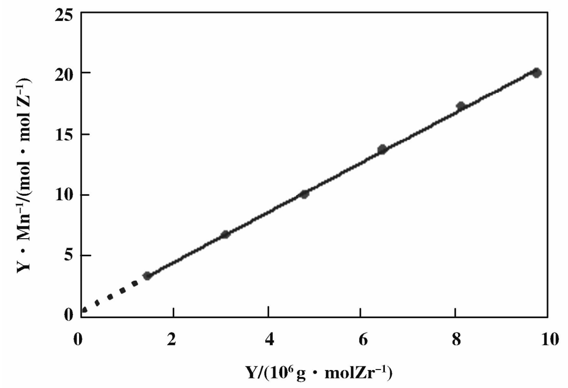

Fig. 7 The relationship between Y and Y/M_n

The result of $Y \cdot M_n^{-1}$ and M_n is shown in Table 3. From Fig. 7, it is found [C*] = 0.33 mol/mol, that is the concentration of [C*] is 33%, which is higher than that of Z-N catalyst[26-27]. Chien[28] have once determinate the [C*] of homogeneous polymerization system and found that [C*] = [Zr] and [C*] = 0.8 [Zr] when $n(Al)/n(Zr) = 10^3$ and 10^4, respectively, which means, most of the Zirconium cations exhibit activity in homogeneous system. In this regard, we suppose that the reduction of the activity of the supported catalyst was caused by the decrease of [C*].

From Fig. 5, we figured out $\mathrm{Ln}K_p[C^*]$ = 12.76 at 50 ℃, and so, $K_p = 1.06 \times 10^6$ L · (mol · h)$^{-1}$, which is less than 1/10 of homogeneous polymerization system at 70 ℃ ($K_P = 3.64 \times 10^6$ L/(mol · h)[28]. We speculate that it is one of main reason for activity drop of the supported catalyst.

From Fig. 6, we figured out $\mathrm{Ln}K_{p0}[C^*]$ = 39.83, and $K_{p0}[C^*] = 1.99 \times 10^{17}$L · (mol · h)$^{-1}$, which is similar to literature [15] [$K_{p0}C^*$] = 6.03 ×

Table 3 M_n and $Y\cdot M_n^{-1}$ at different polymerization time

t/min	$Y/(10^6 g\cdot molZr^{-1})$	$M_n/(10^5 g\cdot mol^{-1})$	$Y\cdot M_n^{-1}/(mol\cdot molZr^{-1})$
20	1.45	4.46	3.25
40	3.12	4.62	6.75
60	4.81	4.81	10.00
80	6.48	4.75	13.64
100	8.14	4.71	17.28
120	9.76	4.88	20.00

Polymerization conditions: m(catalyst concentration) = 70 mg/L; ω(stirring speed) = 500 r/min; hexane 0.2 L; T = 50 ℃; p = 0.4 MPa; t = 2 h; $n(Al)/n(Zr)$ = 98; $n(TEA)/n(Zr)$ = 1 000

10^{17} L·(mol·h)$^{-1}$.

From Fig. 7, we figured out $(K_{tr}[X])/(K_p[M]^{1.11}) = 2.04\times10^{-6}$ mol·g^{-1}, and $K_{tr}[X] = 31.56$ h^{-1}. Actually, when $[X]_0 = 6.47\times10^{-3}$ mol·L^{-1}, T = 50 ℃, P = 0.4 MPa, our result $K_{tr} \geqslant 4.88\times10^3$ L·(mol·h)$^{-1}$, which is higher than that of Ziegle-Natta “CT” catalyst system[28] [$K_{tr} = 2.96\times10^2$ L·(mol·h)$^{-1}$], it is also response for the phenomenon that the M_n in Table 3 is lower than that of literature[28] ($M_n = 7.5\times10^5$ g·mol^{-1}).

The further investigation is carrying out in our group to gain more information about the kinetics of ethylene polymerization under slurry phase.

3 Conclusion

In conclusion, the ethylene polymerization kinetics using supported binuclear metallocene catalyst was studied and the dynamic equation was obtained. The polymerization rate was 1.11 order dependent on the monomer concentration. The polymerization rate increases as the temperature increases; the apparent activation energy of polymerization reaction Ea = 72.47 kJ/mol, $C^* = 0.33$ mol/mol, and $Kp = 1.06\times10^6$ L·(mol·h)$^{-1}$. Compared with homogeneous catalyst system, supported binuclear metallocene catalyst showed lower K_P and $[C^*]$ which lead to the reducing activity .

Acknowledgements

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负载双核茂金属催化剂催化乙烯聚合反应动力学研究

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摘　要：以 SiO_2 为载体，制备了负载的双核茂金属$[(\eta^5\text{-}C_5H_5)ZrCl_2]_2[\mu,\mu\text{-}(SiMe_2)_2(\eta^5\text{-}\mathrm{allyl}\ C_5H_2)_2]$/MAO/$SiO_2$ 催化剂，以己烷为溶剂进行了淤浆条件下乙烯聚合反应，研究了扩散因素、乙烯聚合压力和聚合温度对乙烯淤浆聚合动力学参数的影响，测定了聚合反应级数和表观活化能，采用动力学和相对分子质量法计算了负载催化剂的活性中心浓度，并对链增长速率常数等动力学参数进行了计算. 结果表明，以负载双核茂金属催化剂催化乙烯淤浆聚合反应速率对单体浓度呈 1.11 级依赖，反应活化能 E_a 为 72.47 kJ/mol，活性中心浓度 C^* 为 0.33 mol/mol，链增长速率常数 K_p 为 1.06×10^6 L·(mol·h)$^{-1}$.

关键词：乙烯聚合；动力学；负载双中心茂金属