



Investigating the Behaviour of a Bi-supported $\text{SiO}_2/\text{TiCl}_4/\text{THF}/\text{MgCl}_2$ Catalyst in Slurry Ethylene Polymerization: Activity and Molecular Weight

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ABSTRACT

Bi-supported catalyst $\text{SiO}_2/\text{TiCl}_4/\text{THF}/\text{MgCl}_2$ was prepared via four steps including, (i) heat activation of silica at 600°C , (ii) preparation of precursor composition, (iii) impregnation of catalyst components on silica, and (iv) catalyst pre-reduction with alkyl-aluminium. Homopolymerization was carried out at 3-15 bar pressure and $65\text{-}85^\circ\text{C}$ temperature. The GPC data was analyzed using the concept of multicentre catalysis and four types of active centres detected that differ in molecular weight. The constancy of molecular weight of each active centre with respect to monomer concentration showed that a bimolecular chain transfer mechanism exists. An increase in the ethylene concentration led to a gradual decrease of polymer fractions produced by centres I, II and III and a progressive increase in the fraction produced by centre IV. The dependency of molecular weight and activity on some other parameters such as temperature, Al/Ti ratio, polymerization time and hydrogen concentration were examined. Activity as a function of polymerization temperature showed a maximum at 70°C . The polymerization rate was first order with respect to monomer concentration. A correlation was obtained between the average molecular weight and hydrogen concentration. The molecular weight decreased with increasing polymerization temperature, H_2 concentration and Al/Ti ratio.

Key Words:

bi-support;
Ziegler-Natta;
molecular weight;
polymerization;
ethylene.

INTRODUCTION

Several catalysts based on a three-component system $\text{THF}/\text{MgCl}_2/\text{TiCl}_4$ have been produced by different research groups which had moderate catalytic activity, good hydrogen response, comonomer incorporation property, and low productive cost [1-2].

Anhydrous MgCl_2 has been

known as a preferred support for highly efficient Ziegler-Natta catalysts for the polymerization of olefins. However it is often inconvenient for use, because of the high decay rate of the polymerization activity and the difficulty in producing polymer with good morphology. Ahmadjo et al. [3] synthe-

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sized a heterogeneous MgCl_2 -supported Ziegler-Natta catalyst by Grignard method. They found it an active catalyst but less thermally stable than the conventional one with a more stable rate-time profile. Ochedzan-SiodLak et al. [4] synthesized three titanium catalyst systems supported on the $\text{MgCl}_2(\text{THF})(\text{AlEt}_2\text{Cl})_{0.34}$ complex which were proved to be single site. Inorganic oxides, such as SiO_2 and Al_2O_3 , have been used as catalyst supports because of their high specific surface areas and good morphology. However, SiO_2 -supported titanium catalysts show low activity. To overcome these problems bi-supported TiCl_4 catalysts have been used [5-7]. Kim et al. [6] studied the kinetics of ethylene polymerization over a silica-supported $\text{THF}/\text{MgCl}_2/\text{TiCl}_4$ catalyst. However the number of active sites and their behaviour in different reaction conditions were not studied by these researchers.

In this study a $\text{SiO}_2/\text{TiCl}_4/\text{THF}/\text{MgCl}_2$ catalyst was synthesized and used for the homopolymerization of ethylene. In this work it was tried to investigate not only the macroscale properties of the polymer synthesized by this bi-supported catalyst but also the types of catalyst active centres and their behaviour at different monomer pressures which are important from the microstructural point of view.

The activity and molecular weight of these polymers were evaluated in different conditions such as temperature, pressure and triethylaluminium concentration.

Analysis of molecular weight distribution data was performed under the assumption that each type of active centre produces a set of polymer molecules called "Flory component" with a narrow molecular weight distribution described by Flory theory [8]. The number of active sites was identified by deconvolution of GPC curves and the behaviour of active sites in two different ethylene pressures was investigated.

EXPERIMENTAL

Materials and Methods

n-Hexane was obtained from Arak Petrochemical, distilled over calcium hydride and stored over 13X, 4 Å activated molecular sieves and sodium wire. Decahydronaphthalene of 97% purity was supplied by

Aldrich Chemical and was used with an antioxidant (0.1% 2,6-di-tert-butyl-*p*-cresol). Polymerization grade ethylene was supplied by Arak Petrochemical Co. and nitrogen (purity = 99.9%) was supplied by Niro Gas Co. These gases were purified by passing through columns of activated 13X and 4 Å type molecular sieves. Analytical grade of tetrahydrofuran (Merck) was purified by refluxing with Na and benzophenone (Merck) for several hours.

Anhydrous magnesium chloride, titanium tetrachloride, triethylaluminium and silica were supplied by Aldrich, Merck, Schering and Kerman Rubber Industry, respectively and used without further purification. Intrinsic viscosities were measured in tetrahydronaphthalene at 135°C by an Ubbelohde viscometer.

GPC analysis of the polymers was performed at 145°C with a PL GPC 220 with 1,2,4-trichlorobenzene as a solvent [8].

UV-Vis tests were recorded with a CECIL CE 1021 (1000 series) at 410 nm for titanium concentration (ambient condition) [15].

A CHEMBET 3000 Quantachrom was used for study of the catalyst surface area (inert condition). The sample was prepared in glove box under nitrogen atmosphere. The sample container was then sealed and attached to BET instrument.

Catalyst Preparation

The catalyst was prepared via four steps, including (i) heat activation of silica at 600°C (ii) preparation of precursor composition, (iii) impregnation of catalyst components on silica, and (iv) catalyst prereduction with alkyl-aluminium [7,9-14]. These are described in more detail as follows.

(i) Heat activation of silica: First, 11 g silica was weighed and put in a quartz boat, which was then laid into a tube furnace. Under a N_2 flow the tube was heated to 600°C within 3 h and was maintained at this temperature for 6 h. Finally the tube was cooled to room temperature, and silica was removed and preserved under N_2 for further use [2].

(ii) Preparation of precursor composition: In a 250 mL glass reactor equipped with a magnetic stirrer, 1 g (0.105 mol) of anhydrous MgCl_2 was mixed with 50 mL of pure tetrahydrofuran under nitrogen. The mixture was stirred vigorously at 60°C until MgCl_2 was completely dissolved. Then 0.471 mL

(0.0043 mol) of TiCl_4 was added dropwise at 60°C over 15 min under stirring. The highest activity comes from the formation of a bimetallic complex with $\text{Mg/Ti} = 2$ [6]. After complete addition, the content of the flask was heated to reflux for about 1 h to dissolve the solids. Then 190 mL of pure *n*-hexane was slowly added over a period of 15 min till a yellow solid was precipitated. The supernatant was decanted and the solids were washed with *n*-hexane three times. The solids were filtered and dried under nitrogen purge at 60°C for 6 h to assure free flowing powder [2,9].

(iii) & (iv) Impregnation of catalyst components on silica: Under ambient N_2 , to a 200 mL flask equipped with a mechanical stirrer 5 g heat activated silica, 1 g of precursor and 50 mL hexane were added. Under stirring the suspended solution was adjusted to 25°C and then the desired amount of AlEt_3 solution (1 mmol/mL) was added slowly. After completion of these steps, the mixture was heated to the boiling point, reacted for 30 min and dried by sweeping with N_2 , thereby obtaining a flowable powder catalyst, which was the final catalyst product [2,7].

Polymerization

Polymerization runs were carried out in a 1 L stainless steel autoclave with a mechanical stirrer (Buchi bmd 300). *n*-Hexane, cocatalyst, catalyst and ethylene were introduced in turn and temperature was raised to the desired value. When polymerizing in the presence of hydrogen, the reactor was pressurized with it, previous to the introduction of monomer [15].

RESULTS AND DISCUSSION

Catalyst Synthesis Results

(i) Before using silica, most of the hydroxyl groups (on the surface) must be removed. The content of surface hydroxyls of SiO_2 decreases as the heating temperature is increased.

(ii) By dissolving MgCl_2 and TiCl_4 together in THF, a complexation system is formed in situ (reaction 1):

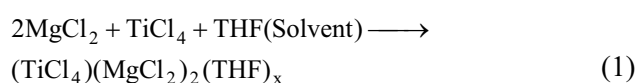
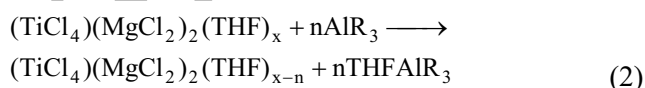


Table 1. Titanium content and surface area of the catalyst.

Test	Catalyst	Silica
Titanium content (%) [g(Ti)/g(cat)]	4.01	0
Specific surface area (m^2/g)	140.6221	129

(iii) It has been shown that prereduction of catalyst increases the activity that can be explained by at least two reasons: First, oxidation number of Ti is gradually reduced from (IV) to (III) and (II). Ti (III) and Ti (II) are more active than Ti(IV) in ethylene polymerization. Second, THF occupies the vacant sites of active centres and reduces its activity. By adding AlEt_3 , due to a competition between Ti and AlEt_3 for coordination with THF (reaction 2), more active sites would be free resulting in more catalyst activity [2].



Catalyst Characterization

Table 1 gives analytical details for the catalyst. The increase of surface area is due to breaking during the catalyst preparation.

Polymer Synthesis Results

Effect of Monomer Concentration on Molecular Weight and Activity

A series of polymerization experiments was carried out under the same sets of conditions (temperature, time, AlEt_3 and H_2) but with different ethylene partial pressures. The concentration of ethylene in the reactor was calculated by using Henry's equation [16,17]. Two polymer samples produced at different ethylene pressures were analyzed by GPC and the content of each Flory component was determined.

The deconvolution of the molecular weight distributions resulted in four active centres for this catalyst. It is seen from Figure 1 and Table 2 that the molecular weight of each Flory component remains constant during the change of ethylene concentration.

The molecular weight (for each active centre) depends on the ratio between the overall propagation rate and total chain transfer rates, $\bar{P}_n = \Sigma R_p / \Sigma R_t$, and in general independent of number of active centres, that is independent of the observed catalyst productivity as shown in eqns (3) and (4) [18,19]:

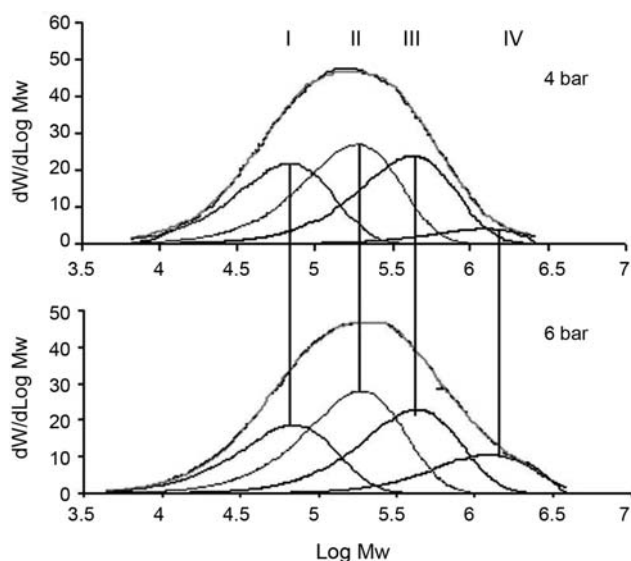


Figure 1. Effect of monomer pressure on molecular weight distribution, $T = 70^{\circ}\text{C}$, $\text{Al/Ti} = 300:1$ molar ratio, polymerization time = 2 h, $[\text{Ti}] = 3.37 \times 10^{-5}$ mol/L, $P_{\text{H}_2} = 0.5$ bar.

$$\bar{P}_n = \frac{k_p [\text{C}^*] [\text{M}]}{k_{\text{tr}}^{\beta} [\text{C}^*] + k_{\text{tr}}^{\text{M}} [\text{C}^*] [\text{M}] + k_{\text{tr}}^{\text{A}} [\text{A}]^m [\text{C}^*] + k_{\text{tr}}^{\text{H}_2} [\text{H}_2]^n [\text{C}^*]} \quad (3)$$

$$\frac{1}{\bar{P}_n} = \frac{k_{\text{tr}}^{\text{M}}}{k_p} + \frac{1}{k_p [\text{M}]} (k_{\text{tr}}^{\beta} + k_{\text{tr}}^{\text{A}} [\text{A}]^m + k_{\text{tr}}^{\text{H}_2} [\text{H}_2]^n) \quad (4)$$

where \bar{P}_n is average number of monomers in each chain, k_p is propagation kinetic constant, M is monomer concentration, C^* is concentration of active centres, A is cocatalyst concentration, H_2 is hydrogen concentration, k_{tr}^{β} is beta transfer termination kinetic constant, k_{tr}^{M} is transfer termination kinetic constant to monomer, k_{tr}^{A} is transfer termination kinetic

Table 2. Effect of monomer concentration on molecular weight and content of Flory components in the polymerization of ethylene. $T = 70^{\circ}\text{C}$, $\text{Al/Ti} = 300:1$ molar ratio, polymerization time = 2 h, $[\text{Ti}] = 3.37 \times 10^{-5}$ mol/L, $P_{\text{H}_2} = 0.5$ bar.

Active centres	Fraction (%) (4 bar)	Fraction (%) (6 bar)	M_w (4 bar)	M_w (6 bar)
I	28.28	22.98	7.05×10^4	6.99×10^4
II	35.65	35.03	1.88×10^5	1.88×10^5
III	31.33	28.77	4.26×10^5	4.37×10^5
IV	4.72	13.20	1.66×10^6	1.74×10^6

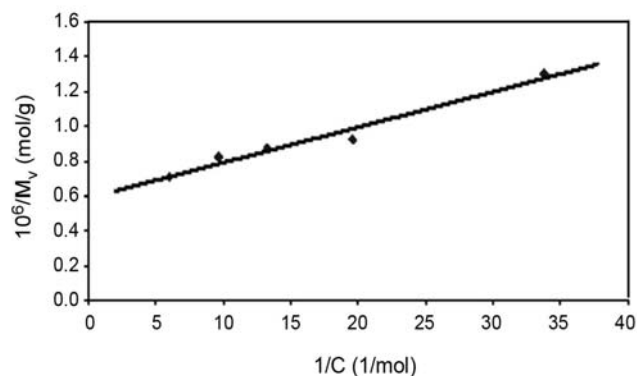


Figure 2. Effect of monomer concentration on average molecular weight, $T = 70^{\circ}\text{C}$, $\text{Al/Ti} = 300:1$, $t = 2$ h, $[\text{Ti}] = 3.37 \times 10^{-5}$ mol/L, $P_{\text{H}_2} = 0$, $R^2 = 0.97$ bar.

constant to cocatalyst, and $k_{\text{tr}}^{\text{H}_2}$ is transfer termination kinetic constant to hydrogen.

Our results show that the dominant chain transfer reaction for each active centre has the same reaction order as the chain growth reaction. The most probable chemistry of such a reaction is bimolecular chain transfer to ethylene [8,19-21] as shown in eqns (3) and (4).

Kissin [8] also showed for some of the catalysts that the molecular weight is constant for each of the Flory components at different ethylene concentrations.

It is concluded from Table 2 that an increase in ethylene concentration produces a gradual decrease of polymer fractions produced by centres I, II and III and a progressive increase in the fraction produced by centre IV.

An inverse plot of viscometric average molecular

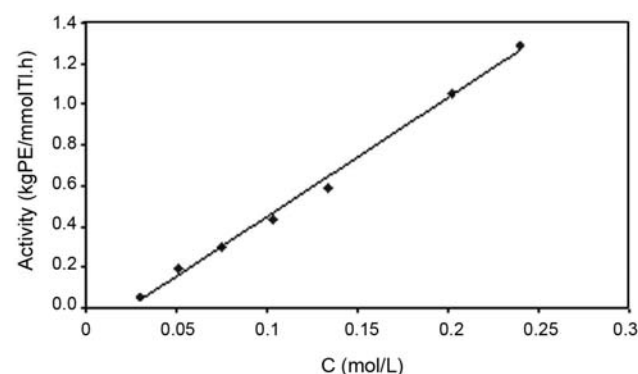


Figure 3. Effect of monomer concentration on activity, $T = 70^{\circ}\text{C}$, $\text{Al/Ti} = 300:1$, $t = 2$ h, $[\text{Ti}] = 3.37 \times 10^{-5}$ mol/L, $P_{\text{H}_2} = 0$, $R^2 = 0.995$.

weight versus monomer concentration is shown in Figure 2.

This shows an increase of molecular weight with ethylene concentration. Therefore the centres with higher molecular weight have higher kinetic constants and increase in ethylene concentration causes more increase in the fraction of the Flory components [8,20].

Figure 3 shows that a linear dependency of activity on monomer concentration exists.

As shown by Bergstra et al. [19] the rate of polymerization has a complex relationship with monomer concentration (eqn (5)):

$$R_p = k_p \cdot C^* \cdot \frac{K_A [M]^2}{1 + K_A [M]} \quad (5)$$

where R_p and K_A are the rate of polymerization and equilibrium constant in the reaction between active and inactive centres, respectively.

But it can be seen that for high monomer concentrations, the reaction rate dependency becomes first order on monomer concentration and the commonly used polymerization rate model is obtained.

Effect of Temperature on Molecular Weight and Activity

The viscometric average molecular weight decreases with increasing polymerization temperature as shown in Figure 4. This result indicates that temperature accelerates the rate of chain transfer reactions with respect to propagation as concluded from eqns (3) and

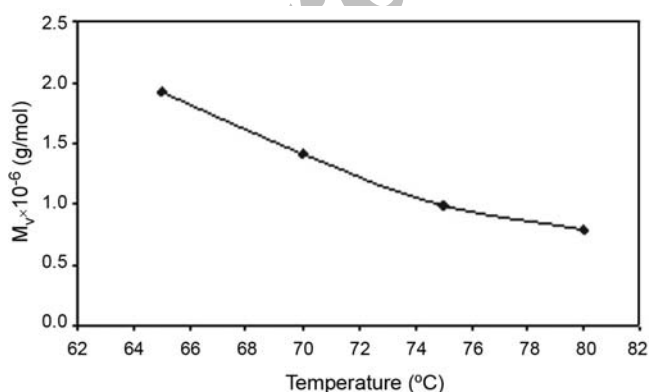


Figure 4. Effect of temperature on average molecular weight: P=8 bar, Al/Ti=300:1, t=2 h, [Ti] = 3.37×10^{-5} mol/L, $P_{H_2}=0$.

Table 3. Effect of [Ti] on average molecular weight: P=8 bar, Al/Ti=300:1, t=2 h, T=70°C, $P_{H_2}=0$.

[Ti] (mol/L)	M_v (g/mol)
5.33×10^{-5}	1326678
5.99×10^{-5}	1170713
8.33×10^{-5}	1264686
9.99×10^{-5}	937450

(4). In other words, the activation energy of the chain transfer reaction is higher than the activation energy of the propagation steps [19,22].

Similar to other Ti-based polymerization catalysts the activity of the catalyst increases with temperature up to a maximum value. After that a decrease is observed with increasing temperature (Figure 5). This may be due to the decay of active centres or decrease of monomer solubility at higher temperatures [23].

Effect of Catalyst Concentration on Molecular Weight and Activity

A slight decrease on molecular weight is observed with increasing the titanium concentration as shown in Table 3. It seems that monomer diffusion problem causes a decrease in molecular weight. No significant change in activity was observed with the increase of titanium concentration as previously observed [18].

Effect of AlEt₃ Concentration on Activity and Molecular Weight

Polymerizations were conducted at various Al/Ti molar ratios. A maximum of activity was obtained at molar ratio 310, as shown in Figure 6.

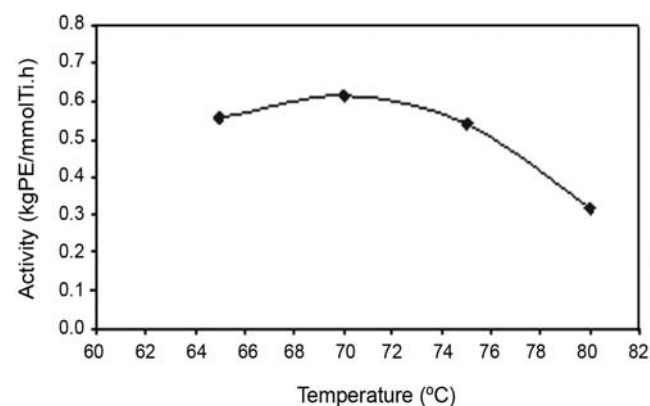


Figure 5. Effect of temperature on activity: P=8 bar, Al/Ti=300:1, t=2 h, [Ti]= 3.37×10^{-5} mol/L, $P_{H_2}=0$.

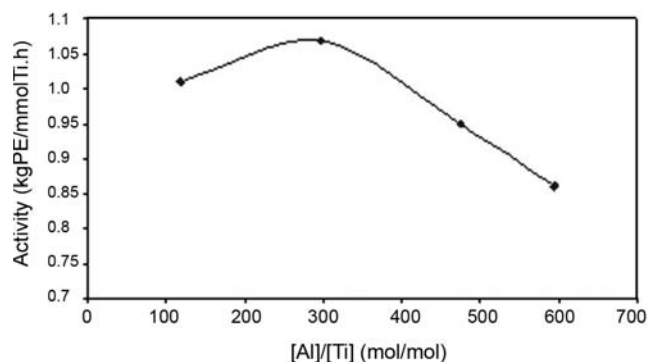


Figure 6. Effect of AlEt_3 concentration on activity: $P=8$ bar, $t=2$ h, $T=70^\circ\text{C}$, $[\text{Ti}]=3.37\times 10^{-5}$ mol/L, $P_{\text{H}_2}=0$.

This result shows that a dynamic equilibrium exists in which Al and Ti compete for coordination with THF and monomer. Therefore some THF would be removed from the Ti centre by AlEt_3 and the centres will exhibit higher catalytic activity [7]. Above the optimum value, further increase in the molar ratio reduces the productivity as reported earlier by Zohuri et al. [23]. Here an over reduction of Ti^{+4} to Ti^{+2} occurs.

Figure 7 shows that molecular weight decreases as AlEt_3 concentration increases thus indicating that transfer process with aluminium alkyl takes place in a significant way. A linear relationship between $1/M_v$ and Al/Ti exists.

Effect of Polymerization Time on Molecular Weight and Activity

A series of slurry ethylene polymerization reactions

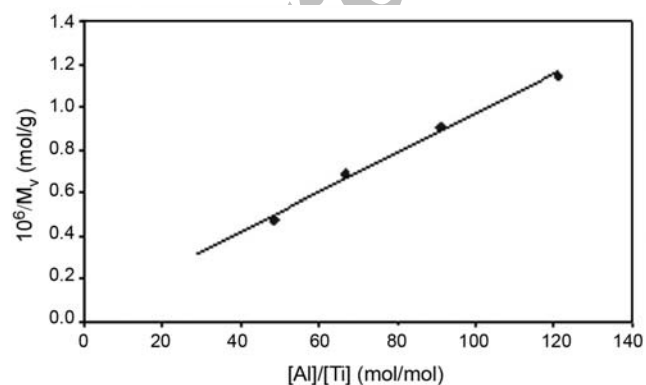


Figure 7. Effect of AlEt_3 concentration on average molecular weight: $P=8$ bar, $t=2$ h, $T=70^\circ\text{C}$, $[\text{Ti}]=3.37\times 10^{-5}$ mol/L, $P_{\text{H}_2}=0$, $R^2=0.992$.

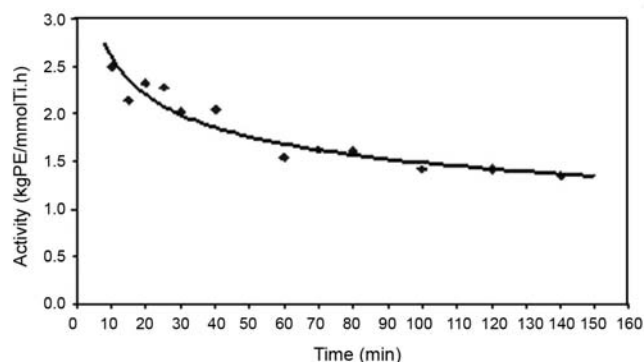


Figure 8. Polymerization kinetic at: $P=8$ bar, $T=70^\circ\text{C}$, $[\text{Ti}]=3.37\times 10^{-5}$ mol/L, $\text{Al/Ti}=300:1$, $P_{\text{H}_2}=0$.

was carried out at different periods of time.

This catalyst gives stable rate time profiles as shown in Figure 8, which indicates the superiority of bi-supported catalysts to mono-supported catalysts [14,24].

Figure 9 shows that molecular weight increases steadily with time. As Kissin showed [8], it seems that active centres are formed and decay at different rates. Those centres with lower molecular weight are formed and decay quickly but those with higher molecular weight are formed gently and have longer life time.

Effect of Partial Pressure of Hydrogen on Molecular Weight and Activity

Different amounts of hydrogen were used as chain transfer agent. The results are shown in Figures 10 and 11.

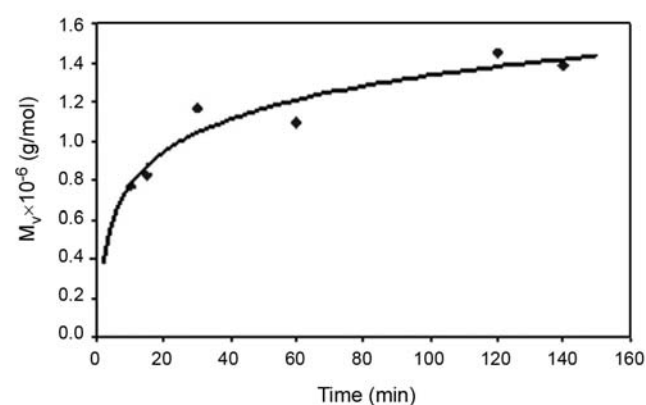


Figure 9. Effect of time on average molecular weight: $P=8$ bar, $T=70^\circ\text{C}$, $[\text{Ti}]=3.37\times 10^{-5}$ mol/L, $\text{Al/Ti}=300:1$, $P_{\text{H}_2}=0$.

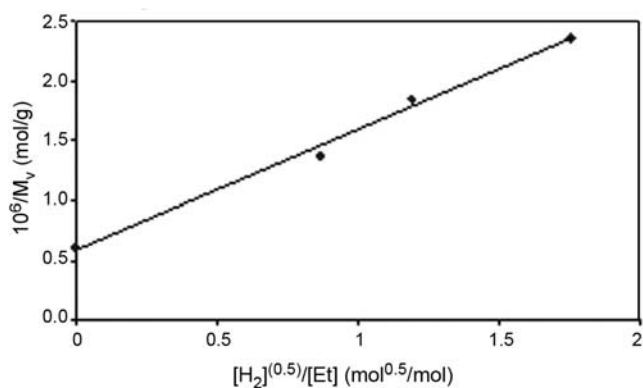


Figure 10. Effect of $[H_2]$ on average molecular weight: $P=8$ bar, $T=70^\circ\text{C}$, $[Ti]=3.37\times 10^{-5}$ mol/L, $Al/Ti=300:1$, $t=2$ h, $R^2=0.993$.

For this catalyst the following relationship (6) for the variation of M_v with hydrogen concentration was obtained.

$$\frac{10^6}{M_v} = 1.0095 \frac{\sqrt{[H_2]}}{[Et]} + 0.585 \quad (6)$$

Figure 11 shows a strong depression of activity with hydrogen concentration.

The effect of hydrogen on rate depression in ethylene polymerization reactions is explained by the preferred formation of the β -agostically coordinated species [8]. The population of $Ti-C_2H_5$ increases sharply with hydrogen and due to the high equilibrium constant of reaction (7), it is strongly shifted to the right. In other words $Ti-C_2H_5$ species with a non-coordinated hydrogen group is capable to insert ethylene into $Ti-C$ bond (the chain growth reaction).

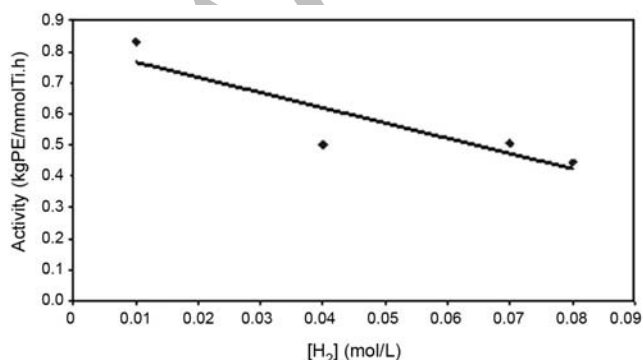
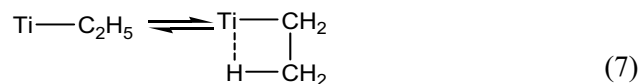


Figure 11. Effect of hydrogen concentration on activity: $P=8$ bar, $T=70^\circ\text{C}$, $[Ti]=3.37\times 10^{-5}$ mol/L, $Al/Ti=300:1$, $t=2$ h.

Resulted β -agostically stabilized group is inert (dormant) because the coordination vacancy for ethylene is occupied by the hydrogen atom of the methyl group.



CONCLUSION

1. A bi-supported catalyst $SiO_2/TiCl_4/THF/MgCl_2$ was synthesized.
2. Activity as a function of polymerization temperature showed a maximum at 70°C . The polymerization rate was first order with respect to monomer concentration. A correlation was obtained between average molecular weight and hydrogen concentration. The molecular weight decreased with increasing polymerization temperature, H_2 concentration and Al/Ti molar ratio.
3. Deconvolution of GPC curves of samples polymerized at two different ethylene pressures showed 4 active centres for this catalyst. It is seen that the molecular weight is constant for each of the Flory components and a bimolecular chain transfer to monomer exists. It is concluded that the centres with higher molecular weight have higher kinetic constants and increase in ethylene concentration results in further increase in the fraction of their Flory components.
4. An increase in the ethylene concentration led to a gradual decrease of polymer fractions produced by centres I, II and III and a progressive increase in the fraction produced by centre IV.

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