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Effects of Temperature and Cocatalyst Concentration on the Number of Active Sites in a $TiCl_4/Mg(OEt)_2$ Catalyst for Ethylene Polymerization

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Abstract
The slurry polymerization of ethylene was studied by employing a ($TiCl_4/Mg(OEt)_2$/TEA) catalyst system in hexane. The effects of triethylaluminum concentration and temperature on polymer yield and polymer viscosity average molecular weight, M_v, were investigated. The maximum polymer yield was obtained at an *Al/Ti* molar ratio of 124. The highest yield and M_v were achieved at 60 °C. The concentration of active sites of the obtained catalyst system for ethylene polymerization was evaluated as a function of Al/Ti molar ratio and polymerization temperature. Increasing *Al/Ti* molar ratio from 62 to 124 raised the active site concentration of catalyst, *[C*]*, from 0.0003 to 0.0017, whereas a further increase in *Al/Ti* molar ratio from 124 to 231 reduced *[C*]* from 0.0017 to 0.0013. Similarly, increasing the temperature from 40 °C to 60 °C increased the *[C*]* from 0.0002 to 0.0017, but when temperature was increased above the optimum value, *[C*]* decreased.

Keywords: Active Site Concentration, Triethylaluminum, Ziegler-Natta Catalyst, Ethylene Polymerization, Molecular Weight

Introduction
More than 50 years have been passed since the Ziegler-Natta catalysts were discovered. A great deal of efforts has been made on the improvement of the catalyst performance, such as activity and stereospecifity [1]. The elucidation of fundamental matters concerning the active sites, however, has not been attained, even though the nature of active sites plays a crucial role in determining the catalyst performance [2]. The determination of the structure and concentration of active sites is indispensable in elucidating the kinetics and mechanism of Ziegler-Natta polymerization. There have been continuous efforts to determine the concentration of active sites by different techniques. However, up to the present, there is no universal method to evaluate active sites directly [3]. Nevertheless, because only indirect methods are available, this determination is particularly difficult and at the same time controversial [4].

Reviews of active site measurement have been given in different works [5-9]. In the present study, using a highly active supported titanium-magnesium catalyst, the number of active sites and the propagation rate constant in ethylene polymerization were determined. The objective of this work was to study the effects of temperature and cocatalyst concentration on the number of active sites.

Experimental
Materials
Polymerization grade ethylene (Messer Company) was passed through a 4Å molecular sieve before use. N-hexane, a highly pure industrial grade supplied by Arak petrochemical company, was dried over a 4Å molecular sieve and Na wires. Triethylaluminum was purchased from Fluka and used without further purification. Supported titanium catalyst ($Mg(OEt)_2/TiCl_4$), supplied by Arak petrochemical company, was used as received. To degas the reactor, ultra pure (99.999%) nitrogen was passed through molecular sieve (4Å) and then was flowed into the reactor. All solutions and catalyst components were kept and transformed under a dry N_2 blanket.

Polymerization Procedure
The experiments were carried out in a one-liter jacket- and stirrer-equipped vessel reactor (Buchi), at a constant

pressure of ethylene using n-hexane as the slurry medium. 400 ml of n-hexane was charged into the reactor under a purge of dry N_2 that was to remove impurities from the reaction system. After purging by ethylene, the co-catalyst and catalyst were added to the reactor by means of two separate syringes under a dry N_2 flow.

With the addition of catalyst and ethylene, the reaction immediately started and the ethylene consumption rate, at a constant pressure of ethylene (1 bar), was measured as a function of time using a flow rate meter. At the end of the polymerization, the reaction was quenched and stopped by adding 10% acidic methanol. The obtained slurry was washed and dried under vacuum at 60 °C.

Molecular Weight Measurement

Molecular weights of the produced polymers were determined by employing viscosity method in decalin at 135 °C using the Mark-Houwink equation. The measurement of thin solutions is a simple and common method in determination of polymer molecular weight. In fact, the Mark-Houwink equation is used to correlate the viscosity of the polymer solution to its molecular weight. For measuring viscosity, specific amount of polymer was dissolved in decalin at 135 °C and was added to an ubbelohde viscometer. The time needed for passing the solution through the capillary tube was measured for four times, and then the measurement was carried out again after the solution was diluted and reached the bath temperature. The same procedure was performed for four different concentrations and the required calculations, based on a and k Mark-Houwink constant values equal to 0.70 and 0.062 ($ml.g^{-1}$) for polyethylene [10], were carried out to measure the final M_v.

Results and Discussion

Active Site Determination

In this study, the effects of polymerization temperature and *Al/Ti* molar ratio on polymer yield and viscosity average molecular weight, Mv, were investigated (see Tables 1 and 2). The concentration of active sites was determined with the help of polymer yield and viscosity average molecular weight.

It is well known that the polymerization reaction rate can be expressed by:

$$R_p=k_p[C^*][M] \quad (1)$$

where, R_p and k_p are polymerization reaction rate and propagation rate constant respectively, while *[C*] (mol/molTi)* and *[M]* are the concentrations of active sites and monomer accordingly.

The rate of macromolecule creation equals transfer reaction rates, such as transfer to monomer and hydrogen, which can be given by [11-12]:

$$dN_t/dt=R_{tr}=K_{tr}[C^*]_t[M] \quad (2)$$

By integrating Equation (2), one may obtain:

$$[N]_t-[N]_0=k_{tr}[C^*]_t[M]t \quad (3)$$

where, $[N]_o$, $[N]_t$ are the concentrations of macromolecules at time 0 and t respectively and k_{tr} is transfer reaction rate constant.

As the concentration of macromolecules at time 0 is equal to the concentration of active sites, i.e.:

$[N]_0=[C^*]_0=[C^*]$

Table 1: Effect of time on polymer yield and molecular weight using different cocatalyst concentrations; Polymerization conditions are: *[Ti]*=3.24×10^{-2} *mmol.l*$^{-1}$, *t*=1 *hr*., T=60 °C, *P*=1 bar, and Hexane=400 *ml*

	Al/Ti=62		*Al/Ti=124*		*Al/Ti=231*	
t (min)	*Yield (gr)*	M_v	*Yield (gr)*	M_v	*Yield (gr)*	M_v
60	77	885584	100.3	663036	89	522727
30	53.4	840364	58	494245	54.3	435340
15	32.9	799275	40	480184	37	---
10	16.9	641295	28	430817	10	187998
5	3.8	-----	18	396241	8	149966

Table 2: Effect of time on polymer yield and molecular weight at different reaction temperatures; Polymerization conditions are: *[Ti]*=3.24×10^{-2} *mmol.l*$^{-1}$, *t*=1 *hr*., *Al/Ti*=124, *P*=1 *bar*, and Hexane=400 *ml*

	T=40 °C		*T*=60 °C		*T*=80 °C	
t (min)	Yield (gr)	M_v	Yield (gr)	M_v	Yield (gr)	M_v
60	70.7	1431301	100.3	663036	54.8	242031
30	49.6	1365708	58	494245	33.1	212217
15	23.7	1346275	40	480184	18.5	160467
10	18.6	1244162	28	430817	12.6	148021
5	9.7	1199391	18	396241	8.3	-----

the concentration of macromolecule at time t, $[N]_t$, can then be calculated from the experimental results, polymer yield and viscosity average molecular weight as follows:

$$[N_t]=W_t/M_{v,t} \quad (4)$$

where, W_t and $M_{v,t}$ are polyethylene yield and viscosity average molecular weight of polyethylene at time t accordingly. Therefore:

$$W_t/M_{v,t}= [C^*]+ktr[C^*][M]t\ [M]t \quad (5)$$

$$[N]_t=[C^*]+ktr[C^*][M]t=A+Bt \quad (6)$$

Taking advantage of the presented equation and experimental changes in polymer yield and viscosity average molecular weight versus time, the concentration of active sites, $[C^*]$, can be calculated.

Effect of Cocatalyst

Invariably triethylaluminum is the most common and effective alkyl metal compound used as cocatalyst in ethylene polymerization. In general, polymerization kinetics in these catalytic systems is strongly dependent upon the type of the alkylation and aluminum molar ratio to the transition metal. Changes in the concentration of triethylaluminum might result in profound variations in the olefin polymerization kinetics as studied by Tait [13-14] and Keii [15].

For this catalyst system, the effect of molar ratio of triethylaluminum to titanium (*Al/Ti*) on the ethylene polymerization and on the viscosity average molecular weight (M_v) of the polyethylene synthesized was studied. The results are shown in Figures 1 and 2. It can be seen that polymerization rate increases sharply by increasing *Al/Ti* molar ratio from 60 to 124. A further increase in this ratio, however, causes the activity of catalyst to decrease. One possible explanation for the maximum rate at a certain cocatalyst concentration is competitive adsorption between monomer and cocatalyst on the same site, which can be attributed to the change of catalyst active site [3,16,17]. Howevere, since the reaction rate of chain transfer to cocatalyst compounds increases as the concentration of cocatalyst rises, a reduction in the molecular weight [3,17] is expectable.

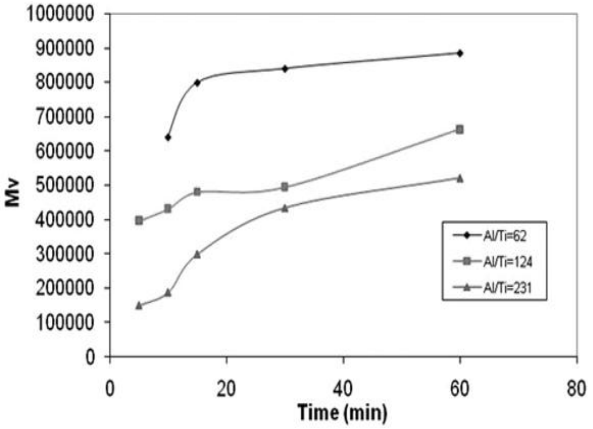

Figure 2: Variation of molecular weight as a function of time in different cocatalyst concentrations. For polymerization conditions, see Table 1.

Effect of Temperature

In Ziegler-Natta polymerization systems, chain transfer reactions tend to increase by increasing polymerization temperature. It is normally observed that higher initial polymerization rate and much catalyst deactivation are obtained at higher reaction temperatures [18]. The apparent effect of an increase in the polymerization temperature is a dramatic increment in the catalyst activity up to a certain optimal temperature, beyond which a further increase in the reactor temperature leads to a reduction in the activity. Thus, all site activation, chain propagation, and site deactivation steps vary significantly with temperature.

The dependence of the catalyst activity and molecular weight of polyethylene on polymerization temperature is shown in Figures 3 and 4. The molecular weight of the polyethylene, because of an increment in chain transfer reaction rate, decreased by increasing polymerization temperature [19-21].

Calculation of Active Site Concentration

The coefficients of the linear equation $[N]_t=A+Bt$ and the concentration of active sites are listed in Tables 3 and 4, and the corresponding experimental results are depicted in Figures 5 and 6.

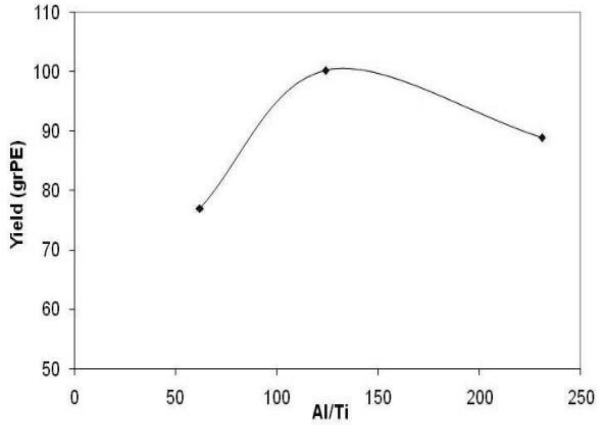

Figure 1: Effect of cocatalyst concentration on polymer yield. For polymerization conditions, see Table 1.

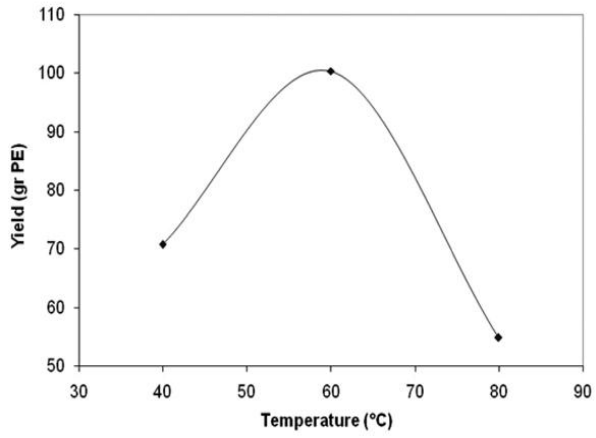

Figure 3: Effect of reaction temperature on polymer yield. For polymerization conditions, see Table 2.

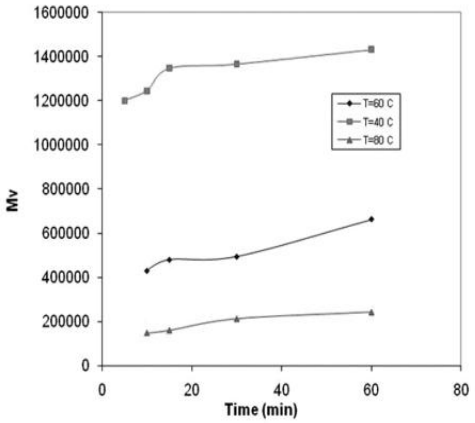

Figure 4: Variation of molecular weight as a function of time at different reaction temperatures. For polymerization conditions, see Table 2.

Table 3: Calculated results *([C*], Rp, and k_p/k_{tr})* of ethylene polymerization using different cocatalyst concentrations

	Results according to Eq. (6)		*[C*]*	R_p(*gr*PE/(*mmol* Ti. *hr*))	k_p/k_{tr}
	A	*B*			
Al/Ti=62	0.0003	5×10^{-5}	0.0003	2374	4748×10^{4}
Al/Ti=124	0.0017	5×10^{-5}	0.0017	3093	6186×10^{4}
Al/Ti=231	0.0013	7×10^{-5}	0.0013	2744	3920×10^{4}

Table 4: Calculated results *([C*], R_p, and k_p/k_{tr})* of ethylene polymerization at different reaction temperatures

	Results according to Eq. (6)		*[C*]*	R_p(*gr*PE/(*mmol* Ti. *hr*))	k_p/k_{tr}
	A	*B*			
T=40 °C	0.0002	2×10^{-5}	0.0002	2180	109×10^{6}
T=60 °C	0.0017	5×10^{-5}	0.0017	3093	6186×10^{4}
T=80 °C	0.0014	1×10^{-4}	0.0014	1844	1844×10^{4}

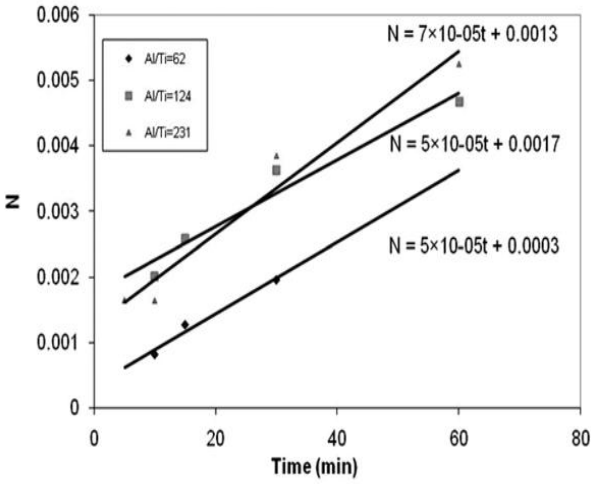

Figure 5: Variation of macromolecule concentration as a function of time in different cocatalyst concentrations

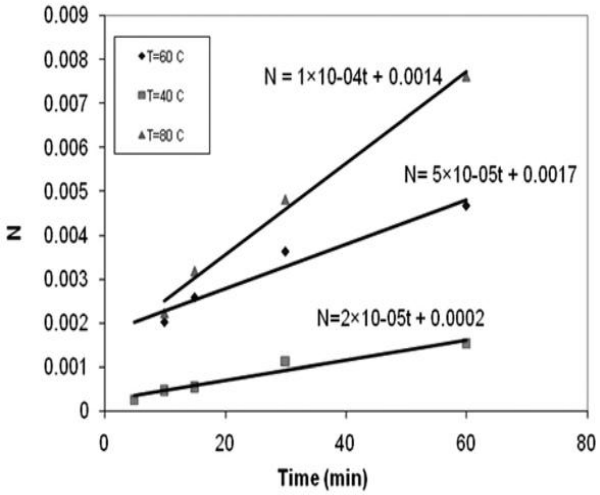

Figure 6: Variation of macromolecule concentration as a function of time in different reaction temperatures

As it can be seen in Figure 5 and Table 3, increasing *Al/Ti* molar ratio from 62 to 124 increased the concentration of active sites from 0.0003 to 0.0017, whereas a further increase in this parameter from 124 to 231 caused the concentration of active sites to fall from 0.0017 to 0.0013.

Figure 6 and Table 4 show the effect of temperature on the concentration of polyethylene macromolecules and the concentration of active sites. Increasing the temperature from 40 °C to 60 °C raised the concentration of active sites from 0.0002 to 0.0017. However, when temperature was increased above the optimum value, the concentration of active sites decreased [21].

Conclusion

In the present study, by employing a fourth generation Ziegler-Natta catalyst, the effects of cocatalyst concen

tration and temperature on the polymer yield and viscosity average molecular weight were investigated. The results showed that an *Al/Ti* molar ratio of 124 leads to maximum polymer yield. In addition, reactions carried out at 60 °C resulted in highest polymer yield and molecular weight. Another interesting feature of the current work was relevant to the measurement of variation of active site concentration versus *Al/Ti* molar ratio and temperature. Increasing *Al/Ti* molar ratio caused the concentration of active sites to pass a maximum. In other words, raising *Al/Ti* molar ratio from 62 to 124 increased the concentration of active sites from 0.0003 to 0.0017, while a further increase in *Al/Ti* molar ration from 124 to 231 reduced the concentration of active sites from 0.0017 to 0.0013. The same trend was also observed for the variation of the concentration of active sites versus temperature. The maximum concentration of active sites was reached at 60 °C.

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