Preparation of Highly Active Heterogeneous Ziegler-Natta Catalyst for Polymerization of Ethylene

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A B S T R A C T

Highly active supported catalyst of Ziegler-Natta type was prepared by reaction of a Grignard reagent. The starting chemicals for preparing $MgCl_2$, the support, were butyl magnesium chloride which mixed with $AlCl_3$ and $CH_3Si(OC_2H_5)_3$, following to two steps treatment of the chemicals with $TiCl_4$ in toluene. Ti Concentration in the solid catalyst was 3.19%. Slurry polymerization of ethylene was carried out using the catalyst in dry heptane, while; triethylaluminium was used as cocatalyst. The cocatalyst effects, such as cocatalyst/catalyst molar ratio, polymerization time, temperature, H_2 concentration and the monomer pressure on activity of the catalyst were studied. There was an optimum [Al]/[Ti] molar ratio and temperature to obtain the highest activity of the catalyst. The maximum activity was obtained at 60ºC, and [Al]/[Ti]=714:1. Productivity of 14700 g PE/mmol Ti.h was obtained at monomer pressure of 8 bar. Addition of hydrogen decreased the activity of catalyst and the viscosity average molecular weight ($\overline{M}_v$) of the polymer obtained, while; increasing monomer pressure increased its activity. Density of the polymer obtained was 0.93-0.95 g/cm^3 which is in the range of high density polyethylene. Melting point of the polymer was in the range of 140-144ºC.

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INTRODUCTION

Since the discovery of $MgCl_2$ as the best support for $TiCl_4$ based Ziegler-Natta catalyst, many reports have been published about highly active supported catalysts for polymerization of α-olefins [1-5]. Different methods have been proposed for preparation of the active $MgCl_2$ as an effective support for the catalyst [6]. The process includes mechanical activation of $MgCl_2$ without $TiCl_4$, mechanical plus chemical routes [4,7], and purely chemical methods

[1,8-10]. Among the techniques, those based on purely mechanical or mechanical plus chemical treatment were used in the early stage of the $MgCl_2$-supported catalysts development. Although the methods are simple with low cost, but control of morphology of the catalyst particles and particles size distribution (PSD) are almost impossible [6].

The chemical routes have been preferred as they proved to be more suitable for the synthesis of the catalysts, and, thus, controling morphology with controlled shape, size and PSD via phenomenon known as replication [1,6,8,11].

Preparation of $MgCl_2$ using decomposition of an organomagnesium (RMgX) compound with various organic and inorganic halides have been less studied. The preparation mainly takes place in the presence of reaction mixture of $AlCl_3$ and $CH_3Si(OC_2H_5)_3$ or $Si(OC_2H_5)_4$ [12-14].

In the present work active $MgCl_2$ was prepared using C_4H_9MgCl with $CH_3Si(OC_2H_5)_3$ and $AlCl_3$. $MgCl_2$ was reacted with $TiCl_4$ to prepare the catalyst which was studied for polymerization of ethylene. New method was used for the catalyst preparation which led to a higher range of density in HDPE and almost stable rate/time profile comparing with $TiCl_4$ supported $MgCl_2$ catalyst, characteristics of the catalyst [15].

EXPERIMENTAL

Chemical

n-Heptane, *n*-hexane and toluene were supplied by Arak Petrochemical Co. (Arak, Iran) and distilled over calcium hydride and stored over 13X and 4A type activated molecular sieves and sodium wire. $AlCl_3$ and titanium tetrachloride were supplied by Merck (Darmstadt, Germany). Diethyl ether solution of C_4H_9MgCl, and $CH_3Si(OC_2H_5)_3$ were purchased from Sigma-Aldrich, Chemicals Co. (Steinheim, Germany). Triethyl aluminium (TEA) was acquired from Schering Co. Ltd (Bergkaman, Germany). Polymerization grade ethylene (purity 99.9%) was supplied by Iran Petrochemical Co. (Tehran, Iran) and was purified by passage through a column of activated 13X and 4A molecular sieves. Nitrogen gas (purity 99.99%) was supplied by Roham Co. (Tehran, Iran)

and dried by passage through P_2O_5, KOH, activated silica gel and 4A molecular sieve columns. Decaline (purity 97%) was supplied by Merck Schuchardt OHG (Hohenbrun, Germany) and was used with antioxidant (0.1%, 2,6-di-tertbutyl-*p*-cresol).

Catalyst Preparation

Anhydrous $AlCl_3$ (15 mmol) was transferred in a glove box into a catalyst preparation reactor. Toluene (100 mL) was added to the reactor under a flow of dry N_2. $CH_3Si(OC_2H_5)_3$ (15 mmol) was added to the toluene slurry of $AlCl_3$ dropwise. The mixture was stirred at room temperature for 1 h. An exothermic reaction took place which was cooled using an oil bath system. The reaction mixture was cooled from 0ºC to -10ºC and diethylether solution of C_4H_9MgCl (30 mol) was added. The white powder precipitated was filtered and washed with toluene (100 mL) at room temperature. Toluene (100 mL) was added to the reactor under a flow of dry N_2. The content of the reactor was heated and $TiCl_4$ (150 mmol) was slowly added, while, the content of the reactor was stirred. The temperature was raised to 70-100ºC and stirred for 1-2 h. The solid product was filtered and washed using toluene (100 mL). Toluene (100 mL) and $TiCl_4$ (150 mmol) were added, respectively. The reaction was carried out for further 1-2 h, at 90-115ºC. The solid catalyst was washed with *n*-heptane and dried at 70ºC.

Elemental analysis of the catalyst was: Ti=3.19%, Mg=12.13%, Cl=81.92%, Al=0.3% and Si=1.36%.

Polymerization and Polymer Characterization

Ethylene polymerization reaction was carried out in accordance with procedure in ref. 16. The monomer was continually introduced to the reactor as polymerization proceeded. The catalyst productivity, R_p(average), expressed as g PE/mmol Ti.h, was determined after 1 h polymerization for each run.

The viscosity average molecular weight ($\overline{M}_v$) of some polymers was determined according to refs. 16 and 17. Density of the polymer was determined by using an Ohuas Voyager Pro VP64C balance with densitometer facility. Melting point of the polymer was measured using DSC PL model STA 780. Crystallinity of the polymer was determined according to ref. 18.
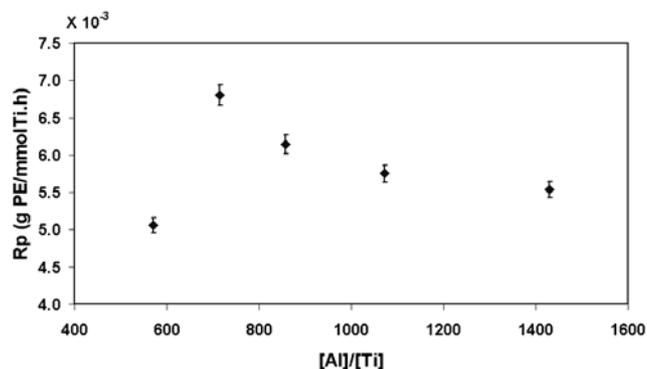
Figure 1. Effect of [Al]:[Ti] molar ratio on average rate of polymerization. Polymerization conditions: [Ti] = 0.007 mmol/L solvent; Temperature = 60ºC; monomer pressure = 2 bar; polymerization time = 1 h; stirrer speed = 800 rpm; heptane = 500 mL (for optimization of [Al]/[Ti] molar ratio all measurements were repeated three times).

RESULTS AND DISCUSSION

Effect of Triethylaluminium

Effect of triethylaluminium (TEA) concentration on polymerization behaviour was studied. A different amount of TEA was used, while, concentration of the catalyst, monomer pressure, stirrer speed and polymerization temperature were kept constant. Figure 1 shows the polymerization behaviour in the case of average rate of polymerization against [Al]:[Ti] molar ratio. Optimum activity occurred at [Al]:[Ti] ratio of 714:1 mol/mol. The optimum TEA/Ti ratio obtained is at higher level of the alkyl required (general 80-800) [19,20].

At lower concentration of TEA relative to the optimum value, the decrease in productivity obtained was sharper than the higher concentration. At low concentration of TEA it is probable that the small amount of impurity present in the system has affected the polymerization behaviour and decreased the activity of the catalyst. At higher concentration than the optimum value, over reduction of Ti^{IV} to Ti^{II} may have occurred which did not affect the productivity so much [21-23].

Effect of Temperature

The effect of temperature of 30ºC to 70ºC on polymerization behaviour at [Al]:[Ti]=714:1 molar ratio was studied. Figure 2 shows the polymerization
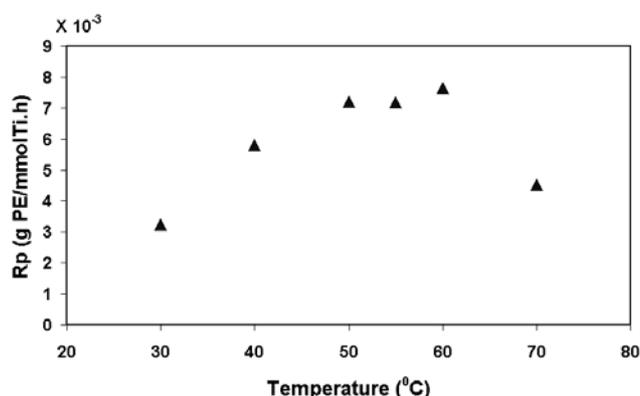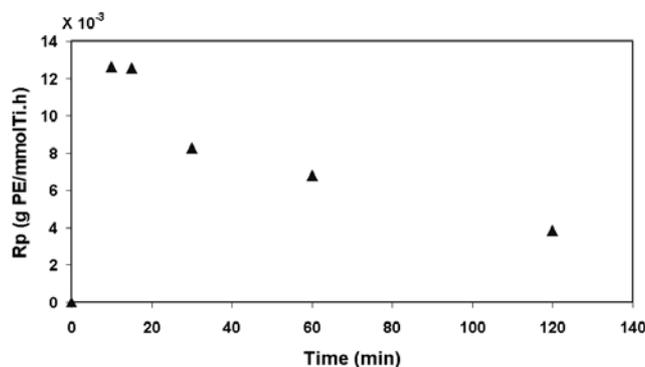

Figure 2. Effect of temperature on average rate of polymerization. Polymerization conditions: [Al]:[Ti] = 714:1 other conditions as Figure 1.

behaviour. The figure indicates that polymerization activity was increased with increasing temperature from 30ºC to 60ºC. An increase in the propagation rate coefficient with increasing temperature and irreversible deactivation of active sites at higher temperature was reported [6,24,25] so the decrease of polymerization activity at higher temperature could be due to low solubility of ethylene monomer in the media used. Optimum temperature for supported Ziegler-Natta catalyst was generally between 60ºC to 70ºC. The higher temperatures decrease the activity of these catalysts. The catalyst behaviour used in this project is an indication of high sensitivity to temperature higher than 60ºC (Figure 2).

Effect of Polymerization Time

The effect of polymerization time between 15 min and 90 min on the rate of polymerization was studied. The

Figure 3. Effect of polymerization time on average rate of polymerization. Polymerization conditions: [Al]:[Ti] = 714:1 other conditions as Figure 1.

results are shown in Figure 3. Polymerization was carried out at 60ºC, as previously determined to be the optimum temperature. The highest activity was obtained shortly after starting polymerization leading to a decay period. The behaviour is common for the $MgCl_2$ supported Ziegler-Natta catalysts. The behaviour could be because of decrease in activity of some active centres with time [6,26]. Although, the rate decreased further with time, but it was not very pronounced. The rate/time profile obtained was more stable than the one obtained for $TiCl_4$ supported $MgCl_2$ catalyst [4].

Effect of Hydrogen Concentration

Effect of hydrogen concentration of 20-100 mL/L solvent on polymerization behaviour was studied. The addition of hydrogen was batch-wise. Polymerization behaviour of the catalyst is shown in Table 1 and Figure 4. Addition of hydrogen decreased both the activity of the catalyst and the viscosity average molecular weight of the polymer obtained. The

Table 1. Effect of hydrogen concentration on the polymerization behaviour.

| Run	H_2 (mL/1000 mL solvent)	g PE	Rp (g PE/mmolTi. h)
1	0	51.96	7652.4
2	20	44.53	6558.2
3	40	39.78	5858.6
4	60	37.19	5477.2
5	80	38.83	5717.7
6	100	35.85	5279.8

behaviour could be due to competition of hydrogen with monomer to be adsorbed on active centres and chain transfer facility due to the presence of hydrogen, respectively [20,24,27].
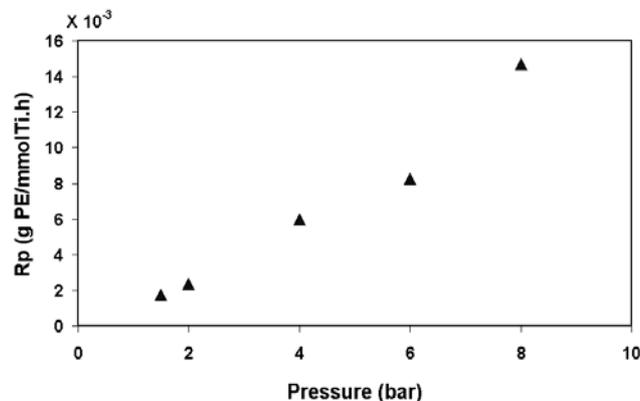
Effect of Monomer Pressure

Effects of monomer pressure of 1.5 to 8 bar on catalyst behaviour and polymer obtained were studied. The polymerization was carried out using optimum

**Table 2.** Specification of some polymers. [Al]/[Ti]=714:1, pressure=1 bar, [Ti]= 0.007 mmol/L.

Temperature (ºC)	Time (min)	H_2 (mL)	Melting point (ºC)	Density (g/cm^3)	Crystallinity (%)
60	60	0	142.4	0.945	43.5
70	60	0	141.6	0.949	41.5
60	60	40	140.4	0.946	43.5
60	60	60	141.6	0.942	43.2
60	60	100	141.3	0.931	43
35	60	0	143.7	0.931	44
60	15	0	141.3	-	45
60	90	0	143.1	-	48.8
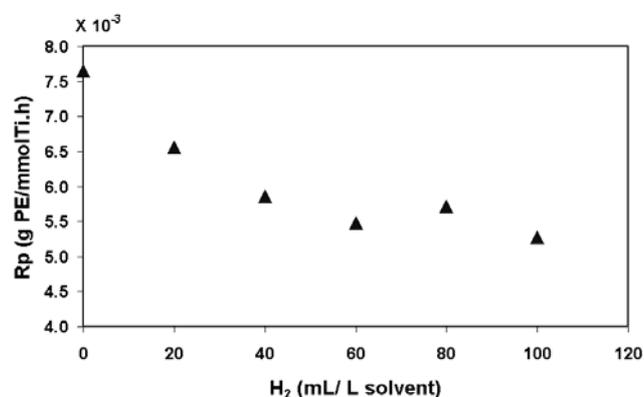
Figure 4. Effect of hydrogen on R_p.

Figure 5. Effect of monomer pressure on R_p.
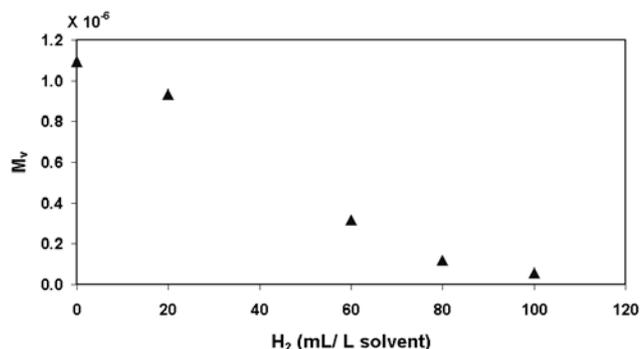
Figure 6. Effect of hydrogen concentration on $\overline{M}_v$.

condition obtained before. The polymerization activity was almost exponentially increased with increasing monomer pressure (Figure 5). The higher the monomer pressure, the higher concentration of ethylene close to the catalytic active centres and probably fragmentation of catalyst particularly at the early stage of polymerization. An increase in the activity with monomer pressure has been reported [5,28].

Characterization of Polymer

Density, crystallinity, melting point and $\overline{M}_v$ of some polymers obtained were determined. The result was in the range between 0.93 to 0.95 g/cm³ which indicates a high density polyethylene even, higher than the limit of HDPE. The melting point of the polyethylene obtained was in the range between 140°C to 144°C. Crystallinity of the polymer was between 41 to about 49 percent, indication of semi-crystalline polymer. Table 2 shows the results obtained.

$\overline{M}_v$ of the polymer was decreased with increasing H_2 concentration (Figure 6). The behaviour could be due to high chain transfer rate in the presence of H_2 [27,29].

CONCLUSION

The following results were obtained using the heterogeneous supported Ziegler-Natta catalyst prepared by Grignard method in slurry polymerization of ethylene:

- The prepared catalyst, based on $TiCl_4$ supported $MgCl_2$, produced was quite an active catalyst.

- There is an optimum ratio of [Al]/[Ti]=714:1 to obtain the highest activity which was quite high for

these type of catalysts.

- The highest activity of the catalyst obtained at 60°C under the condition used. The behaviour indicates a less thermally stable catalyst supported $MgCl_2$ prepared by Grignard method.

- Addition of hydrogen to the polymerization system decreased its activity and $\overline{M}_v$.

- Rate of polymerization curve against time was a decay type. The decay was not so sharp as expected for $MgCl_2$ supported catalysts.

- Increasing monomer pressure from 1.5 to 8 bar exponentially increases the activity of the catalyst.

- Density of the polyethylene obtained was in the range of 0.93-0.95 g/cm³ in the range of high density polyethylene produced.

- Melting point of the polymer was in the range of 140-144°C. The crystallinity of the polymer was between 41 to 49%.

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