Structural Study of Mono- and Bi-supported Ziegler-Natta Catalysts of MgCl₂/SiO₂/TiCl₄/Donor Systems

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ABSTRACT

Due to various components present in the Ziegler-Natta catalyst system and different interactions, taking place between them during the preparation and polymerization, studying of the system is usually very difficult. In this study mono- and bi-supported catalyst systems of MgCl₂ (ethoxide type)/TiCl₄/ID and SiO₂/MgCl₂ (ethoxide type)/TiCl₄/DNBP were prepared for the polymerization of propylene, whilst for polymerization of ethylene, MgCl₂ (ethoxide type)/SiO₂/TiCl₄ was prepared. Di-n-butyl phthalate (DNBP) and diisobutyl phthalate (DIBP) were used as internal donors (ID), whilst triethyl-aluminium (TEA) was used as the cocatalyst. Structural study was carried out using FTIR, SEM, XRF and BET techniques. The observed shift in vibration of C=O, and C–O bands of the electron donors indicate some interactions between the donors, support and the catalyst itself. Surface area of the mono-supported catalyst having the electron donor and bi-supported catalyst without electron donor were about 230 m²/g. For the bi-supported having DNBP as the donor, however, a value of 177 m²/g was obtained. SEM study shows that the spherical morphologies of SiO₂ are replicated on catalyst and to a lesser extent on final polyethylene obtained. Dimethoxymethyl cyclohexyl silane (DMMCS) was used as an external donor for the polymerization of propylene.

Key Words: Ziegler-Natta catalyst, supported catalyst, polymerization, structural study

INTRODUCTION

The first generation of Ziegler-Natta (ZN) catalyst was a two-component system. However, the present-commercially used catalyst is a multi-component type of catalyst. As a result, the structural study of this system is highly complicated. A great number of investigations have been carried out so far on the polymerization of olefins using these catalysts.

However, the polymerization efficiency, mech-

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anism of polymerization, structure of active centers and stereoregularity are still open for discussion. A variety of compounds have been used to enhance the performance of $TiCl_4$-based ZN catalyst. The most effective support has resulted from the use of $MgCl_2$. Since the excellent properties of $MgCl_2$-supported ZN catalyst for production of PP was discovered, a large number of papers have been published [1-6]. $MgCl_2$ is a good support for preparation of highly efficient ZN catalysts. Inorganic oxides such as SiO_2, Al_2O_3, and etc., have been used as catalyst supports due to their high surface area and good morphology.

Simple silica-supported Ti catalyst shows low catalyst activity for ethylene as well as propylene polymerization and a large production of atactic PP [7, 8]. To improve catalyst activity, silica is reacted with a magnesium compounds such as $MgCl_2$ or alkylmagnesium (MgR_2) before supporting $TiCl_4$ to obtain the so called bimetallic supported catalysts used for ethylene polymerization. These kinds of SiO_2/$MgCl_2$/$TiCl_4$ bi-supported catalysts can be prepared by different methods [9-11].

SiO_2/$MgCl_2$ bi-supported Ti catalysts prepared by combining $MgCl_2$ with SiO_2 and then treated with $TiCl_4$, can be expected to exhibit features of $MgCl_2$ as well as SiO_2 [12]. These catalysts showed high activity for homopolymerization of ethylene [13], propylene and copolymerization [9, 10, 13].

Different methods used to fix $MgCl_2$ and $TiCl_4$ onto silica can be classified into two main types. Physical deposition methods are those in which the components $MgCl_2$ and $TiCl_4$ are more or less physically deposited on silica, whereas, chemical fixing involves the reaction of $MgCl_2$ and $TiCl_4$ with the surface hydroxyls of the silica support. Chemical fixing can be accomplished by using alkylmagnesium compounds R_2Mg or $RMgX$ (X=Cl, OR) [14-16]. The alkylmagnesium compound is fixed onto silica via a Si–O–Mg moiety [14, 17], and the amount fixed onto support depends on the hydroxyl population and the calcining temperature of the support [14]. The catalyst activity depends both on the amount of $MgCl_2$ fixed onto silica and Mg/Ti ratio [18]. Chemical bond layer with both Si–O–Mg and Si–O–Ti moieties on the silica surface has been observed [15].

EXPERIMENTAL

Materials

Polymerization grade propylene and ethylene were supplied by Arak Petrochemical Co. and was purified by passage through columns of activated 13X and 4A type molecular sieves. Methylcyclohexyldimethoxy silane was also obtained from Arak Petrochemical Co. and dried over activated 13X/4A type molecular sieves.

Nitrogen (purity≅99.9%) was supplied by Niro Gas Co. and was purified by passage through columns of P_2O_5, KOH and activated 13X/4A type molecular sieves. n-Heptane and n-hexane was supplied by Iran Petroleum Co. and were distilled over calcium hydride and stored over activated 13X/4A types molecular sieves and sodium wire for further drying.

Di-n-butyl phthalate, diisobutyl phthalate, decalin, titanium tetrachloride, 13X and 4A type molecular sieves, toluene and $Mg(OEt)_2$ were supplied by Merck. SiO_2 was supplied by Kerman Tire Manufacturing Co. and triethylaluminium (TEA) was supplied by Schering Co. was diluted using n-heptane prior to use.

Preparation of Catalysts

$MgCl_2$ (ethoxide type)/DNBP/$TiCl_4$ catalyst was prepared in accordance to reference (19). SiO_2/$MgCl_2$ (ethoxide type)/ID/$TiCl_4$ catalyst was prepared using a modified method developed at Polymer Research Institute of Iran. SiO_2 was calcined for 5 h at 600 °C.

The calcined SiO_2 (5 g) and $Mg(OEt)_2$ (10 g) were transferred into a degassed, evacuated and filled with purified N_2 catalyst preparation reactor using a glove box.

Toluene (120 mL) was added and the temperature of the reactor was increased to 80 °C while stirred. $TiCl_4$ (30 mL) and electron donor (ID) (4.1 mL) was added, to the slurry. The temperature was raised to 115 °C and the content of the reactor was stirred for 2 h at the temperature. Then the content of the reactor was filtered out. The product was washed three times with toluene (3×100 mL); toluene (120 mL) was added and treated with $TiCl_4$ (30 mL) for 4 h at 115 °C. The final product was

washed using n-hexane (14×100 mL) at 40 °C and dried under vacuum. The composition of the catalyst is: Mg, 9.19 %; Si, 23.73%; Cl, 63.36%; Ti, 3.72 %.

No donor was used in the catalyst for polymerization of ethylene.

Polymerization Procedures

Slurry polymerization procedures were adapted for propylene and ethylene at pressures from +0.5 to 7 atm in n-heptane (400 mL). The reactor used was Buchi (bds 488) type. When reactor temperature reached to a predetermined value, the initiator reagents were added in the following order: TEA, external donor (for propylene monomer), catalyst, and hydrogen. At the end of the polymerization period (2 h) isopropanol (20 mL) was added. The obtained polymer was filtered and dried at 70 °C.

Characterization of Catalysts and Polymer Synthesized

The shift of hydroxyl group vibration due to calcination procedure, the shift of C=O and C–O bonds of donors during catalyst preparation were studied using FTIR instrument of Bruker IF 548 model.

Morphological study of supports, catalysts and polymer was carried out using Stero Scan 360 SEM. Elemental analysis of the catalysts were also carried out with the SEM equipment. Surface area of the catalysts was determined using the BET method.

Viscosity average molecular weight ($\overline{M}_v$) was determined in accordance to reference [20].

RESULTS AND DISCUSSION

Structural Studies of Catalyst

FTIR Studies

FTIR spectrum of $MgCl_2$ and $Mg(OEt)_2$ shows absorptions at about 1600 cm^{-1} and 1435 cm^{-1}, respectively (Figure 1). The same result was found by Jeonge [21], the band belonging to $MgCl_2$ was observed at 1590–1612 cm^{-1} in all the prepared catalyst but the absorptions at 1435 cm^{-1} of ethoxide group, almost disappeared in the spectrum of the catalyst (Figure 1).

FTIR spectrum of DNBP and DIBP show strong band at 1729 cm^{-1} and 1728 cm^{-1} belonging to $v_{C=O}$, respectively (Figure 2). The band in the corresponding catalysts $MgCl_2$ (ethoxide type)/$TiCl_4$/DNBP and $MgCl_2$ (ethoxide type) $TiCl_4$/DIBP were shifted to 1643 cm^{-1}, respectively (Figure 2). Shine [22] has reported a similar result for the catalyst $MgCl_2$/$TiCl_4$/DNBP. Arzoumanid [23] has predicted that electron donor can be bonded with $MgCl_2$ from carbonyl group. Thus, it can be said that:

$Mg(OEt)_2$ is mainly converted to $MgCl_2$ during treatment with $TiCl_4$, and the electron donor band to catalyst component via C=O group.

SiO_2 was calcined for 5 h at 600 °C. FTIR spectra of silica before and after calcination are shown in (Figure 3). There is a broad absorption band at about 3400 cm^{-1}. According to McDaniel [24, 25]
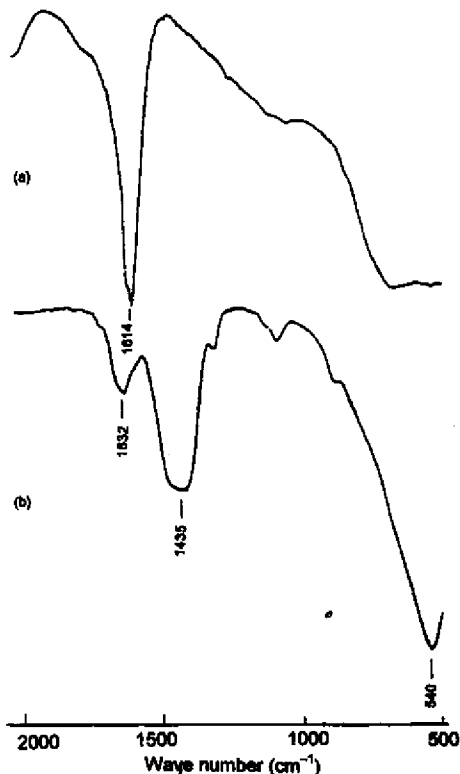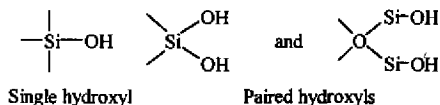

(a)

1614

1852

(b)

1435

540

2000   1500   1000   500

Wave number (cm^{-1})

Figure 1. FTIR Spectra of (a) $MgCl_2$, (b) $Mg(OEt)_2$.

studies there are three types of hydroxyl groups on the surface of silica.

Single hydroxyl   Paired hydroxyls

Scheme I

The bond at the 3400 cm⁻¹ corresponds to the paired hydroxyl group [12]. The formation of epoxy groups is evident from the Scheme I. The band is so broad, which may cover some bands at higher wavelength. After the calcination the intensity of the band so weakened that the bond at about 3740 cm⁻¹ was observed. The bond corresponds to single group of hydroxyl [12]. This suggests that the paired hydroxyls groups have condensed. It is clear that the content of Ti and Mg in the catalyst is dependent on the content of surface hydroxyl groups [12]. The bond at 1097 cm⁻¹ characteristic of calcined SiO₂ was observed in FTIR spectra of prepared catalysts at about 1088–1097 cm⁻¹ (Figure 2). Blitz [26], suggests that bond at 1090–1100 cm⁻¹ is resulted from the interaction between SiO₂ and MgCl₂. The bond was not observed in mono-supported catalyst spectrum. Other bonds of MgCl₂ and SiO₂ were observed in the bi-supported catalyst as well. Vibrations at 1728 and 1729 cm⁻¹ of free donors were shifted to about 1670–1693 cm⁻¹ (Figures 2 and 4).

Morphological Studies

Overall morphology of supports, catalysts and poly-ethylene obtained were studied. Scanning electron microscopy (SEM) of Mg(OEt)₂, mono-supported catalyst prepared using Mg(OEt)₂ and the polymer obtained using this catalyst shows no such similarity between support, catalyst and polymer obtained. This may be due to the vigorous reaction taking place between TiCl₄ and Mg(OEt)₂ during the catalyst preparation. SEM photograph of bi-supported catalyst using SiO₂/Mg(OEt)₂, however, indicates replication. SEM micrograph of SiO₂, SiO₂/MgCl₂ (ethoxide type)/TiCl₄ and polyethylene obtained using this
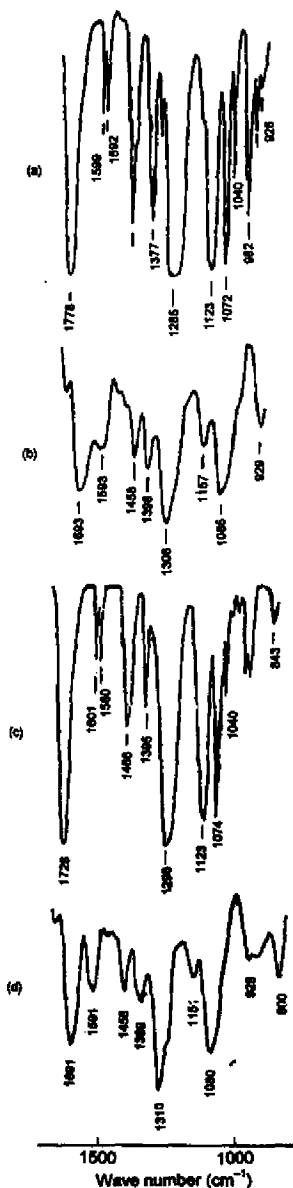
Figure 2. FTIR Spectra of (a) DNBP (b) DNBP/ MgCl₂/TiCl₄ (c) DIBP (d) DIBP/MgCl₂/ TiCl₄.

catalyst are shown in Figures 5, 6, and 7, respectively.

As it is observed from the pictures there are some spherical particles of SiO_2 and the catalyst. SEM of polyethylene obtained using the bi-supported catalyst at 1.5 atm pressure of monomer shows a number of spherical particles (Figure 7). The polymer obtained at 6 atm pressure of ethylene, however, indicates of much less spherical and uniform particles. This shows a cleavage and breaking down of polymer particles and may be catalyst particles at vigorous condition of polymerization condition (Figure 8).

Determination of Surface Area

Surface area of four different catalysts was studied. Table 1 gives the details. As it is evident the surface area of the bi-supported catalyst containing internal donor (catalyst 4) is smaller than the others. Surface area of 160–190 m^2/g for similar catalyst has been reported [27]. The value of 210–250 m^2/g is reported for mono- and bi-supported catalyst without electron donor [28, 12].

Polymerization Activity

Polymerization of ethylene was carried out using catalyst systems namely, $MgCl_2$ (ethoxide type)/$TiCl_4$/SiO_2, $MgCl_2$ (ethoxide type)/$TiCl_4$, whilst

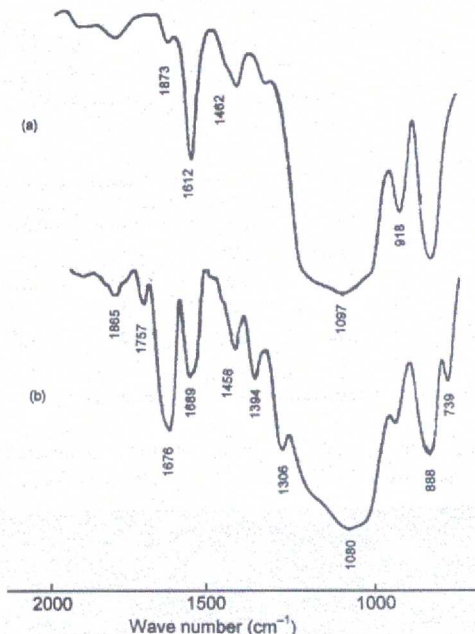**Figure 4.** FTIR Spectra of (a) TMS catalyst, (b) TMSD catalyst.

for polymerization of propylene, $MgCl_2$ (ethoxide type)/$TiCl_4$/ID and SiO_2/$MgCl_2$ (ethoxide type)/ID (ID were DNBP and DIBP) were used. Table 2 shows that polymerizations were studied using optimum Al:Ti molar ratio of each catalyst itself which
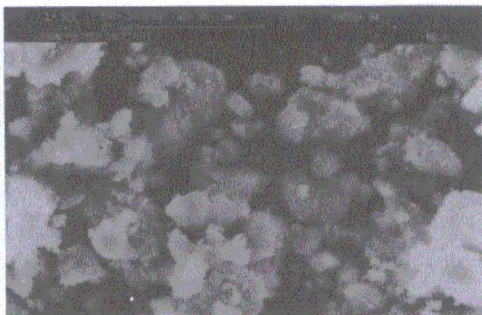

Figure 3. FTIR Spectra (a) SiO_2 (b) calcinated SiO_2.

Figure 5. SEM Photograph of SiO_2.

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Table 1. Surface area of the catalysts.

Catalyst	Catalyst₁	Catalyst₂	Catalyst₃	Catalyst₄
Surface area (m²/g)	233	231	232	177

P: 0.5 bar, T: 60 °C, V_reactor: 1 Liter, Time: 2 h, V_heptane: 400 mL, Cat₁: TMD (DNBP), Cat₂: TMD (DIBP), Cat₃: TMS, Cat₄: TMSD (DNBP).

Table 2. PP Polymerization behaviour of catalysts.

Type catalyst	Temp ($^\circ$C)	Pressure (atm)	Ratio Al/Ti	Volume H₂ (mL/dm³)	Isotacticity index (%)	$\overline{M}_V$	Product (g)
Cat₁	60	0.5	209	10	96.89	1.2×10^5	24.70
Cat₂	60	0.5	209	10	97.12	–	29.41
Cat₃	60	0.5	60	10	–	9.2×10^5	21.41
Cat₄	60	1.0	62	20	97.15	–	19.47

P: 0.5 bar, T: 60 °C, V_reactor: 1 Liter, Time: 2 h, V_heptane: 400 mL, Cat₁: TMD(DNBP), Cat₂: TMD(DIBP), Cat₃: TMS, Cat₄: TMSD (DNBP).

faciliated a number of polymerizations at different conditions [29]. Table 2 shows the behaviour of various catalysts towards polymerization of ethylene and propylene (Cat₃ for ethylene polymerization).
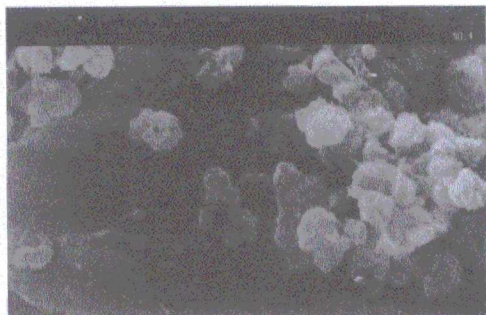
Figure 6. SEM Photograph of TMS catalyst.

CONCLUSION

Mg(OEt)₂ which was used as starting chemical for support of TiCl₄ catalyst was mainly converted to MgCl₂ during the catalyst preparation. Calcination of SiO₂ at about 600 °C causes elimination of –OH paired surface groups. Electron donor (bi-ester) used bonded to catalyst support via C=O group. The bi-supported catalyst shows higher activity than mono-supported catalyst for both ethylene and propylene polymerization. The bi-supported catalyst replicates morphology of the support to the catalyst and to the

Figure 7. SEM Photograph of polyethylene.
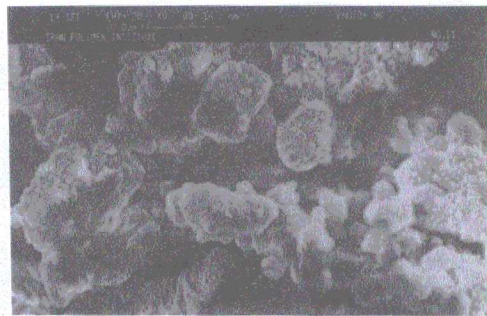
Figure 8. SEM Photograph of high-pressure polyethylene.

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polymer obtained. There is no reasonable relationship between activity of catalyst and its surface area.

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