

STUDY ON HIGHLY ACTIVE ZIEGLER-NATTA CATALYSTS FOR POLYMERIZATION OF OLEFINS*

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ABSTRACT

In this paper, highly active Ziegler-Natta catalysts of MgCl_2 supported TiCl_4 for synthesis of polyolefins, using di-n-butyl phthalate (DNBP) as internal donor and diphenyl dimethoxyl silane (DPDMS) as external donor, have been prepared. The conditions controlling the treatment of support were studied. The interactions of various components present in the catalysts and their influences on catalytic performance were investigated. It is found that by using DNBP and DPDMS as internal and external donors together the polymer products with higher isotactic index can be obtained. Plausible structure model and mechanism were proposed.

INTRODUCTION

In recent years, many researchers have discovered and developed new, highly active titanium-based catalysts suitable for the production of polyolefins, particularly for polypropylene, polyethylene and copolymers of ethylene-propylene^[1-3]. Continued fundamental investigations have made the basic understanding and control of the polymerization active sites on the catalyst support, thus led to obtain the catalysts with high activity and high stereospecificity. It was claimed that the treatment of MgCl_2 was the key step on the preparing procedure in order to make the catalyst supports becoming loose and porous granules and the catalyst having high activity and stereospecificity^[4-6]. And the situations of Ti-coordinating with MgCl_2 , especially with the internal and external donors, also influence the activity and stereospecificity virtually. Since there have been few articles describing

* This work was supported by the National Natural Science Foundation of China

Received October 18, 1993

the influence of treatment conditions for properties of supports and the influence of external and internal donors for coordination situations of active sites, this paper will report the influence of BuOH and TiCl_4 treatment for MgCl_2 support and coordination situations of Ti with MgCl_2 , external and internal donors. By using ESR technique plausible structure models and mechanisms on the interaction of Ti with MgCl_2 , DNBP and DPDMS are proposed.

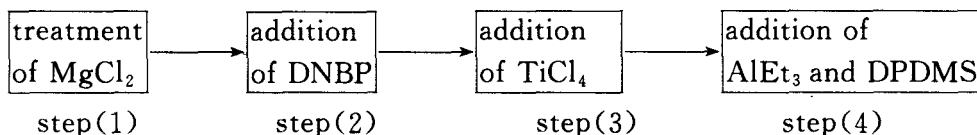
EXPERIMENTAL

1. Materials

MgCl_2 dried at 670K. Di-n-butyl phthalate (DNBP), diphenyl dimethoxyl silane (DPDMS) and butyl alcohol were used after distillation. n-Octane and n-hexane for suspending and washing the catalysts were refluxed with metal sodium before use.

2. Preparation of catalysts

All manipulations were carried in N_2 atmosphere. The procedure of preparing catalysts can be divided into the following four steps:



The Ti contents were determined by titration.

3. Polymerization procedure

Polymerization procedures have been described in reference [7-9]. Polymerization of olefins was carried out at atmospheric pressure. Olefins (such as ethylene or propylene) were rapidly bubbled through the stirred solvent in a reactor and then stoichiometric amounts of AlEt_3 and DPDMS, followed by the solid catalyst, were added. After the polymerization was completed, a solution of ethanol (containing hydrochloric acid) was injected into reactor and the polymerization was quenched. The resultant polymer was washed several times with ethanol and dried in a vacuum oven at 60°C .

4. IR and ESR measurement

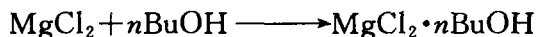
IR spectra were recorded using a Nicolet 5DX-FTIR spectrometer. ESR spectra were recorded on a JEOL JES-FEIXG spectrometer under N_2 . Mn^{2+} standard provided precise field calibration for the calculation of g value. The simulating of ESR spectra was carried out according to reference [10].

RESULTS AND DISCUSSION

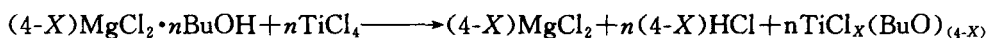
1. *Treatment of $MgCl_2$ support with BuOH and $TiCl_4$ (at step 1)*

To obtain high catalytic activity, it is important to make the supports as loose and porous granules. The proper mechanical strength of granule leads the polymer chains to grow not only outward from the surface but also inward. It may be obtained by treating $MgCl_2$ with BuOH and $TiCl_4$ at step 1 in the preparation procedure of catalyst mentioned above.

After $MgCl_2$ was mixed with BuOH at stirring for several hours, IR spectra of the resultant product showed different character. The former absorption bands due to O—H stretching and C—O stretching appearing at 3320 cm^{-1} and 1030 cm^{-1} respectively, shifted to 3250 cm^{-1} and 1020 cm^{-1} . In addition, a new absorption band which can be regarded as the characteristic absorption band of resultant product appears at 1410 cm^{-1} , which indicates the following reaction takes place:



When $MgCl_2 \cdot nBuOH$ was treated with $TiCl_4$, the interaction between them can be depicted as follows:



At the above reaction, treatment temperatures play an important role in reacting completely. The IR spectra of the support prepared from the $MgCl_2 \cdot BuOH$ alcohol adducts treated with $TiCl_4$ at lower temperature (about 30°C , LTC) and higher temperature (about 90°C , HTC) are shown in Fig. 1. The characteristic absorption band of $MgCl_2 \cdot nBuOH$ at 1410 cm^{-1} in the IR spectrum of LTC disappeared in that of HTC. This implies that, at lower temperature, the reaction of $TiCl_4$ with $MgCl_2 \cdot nBuOH$ alcohol adducts is carried out incompletely. At higher treating temperature, $MgCl_2 \cdot nBuOH$ alcohol adducts may react with $TiCl_4$ completely. This treatment results in $MgCl_2$ becoming porous and loose granules with large specific surface area (comparing with LTC as shown in Fig. 2a.).

From Tab. 1, it is observed that higher treated temperature increased the catalytic activity of catalyst prepared from the corresponding $MgCl_2 \cdot nBuOH$ treated with $TiCl_4$. Balancing catalytic activity with morphology of catalyst, proper treating conditions are selected as stirring for 5h at about 75°C (due to the similarities of the catalytic efficiency of catalysts prepared from supports treated at between 60°C and 90°C).

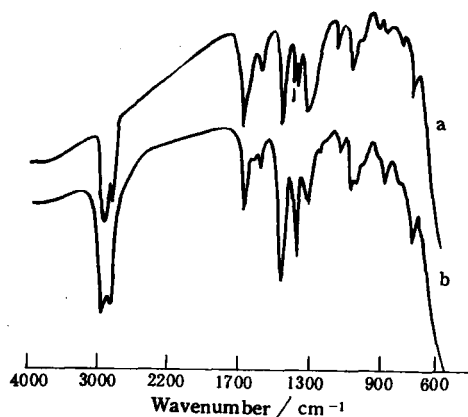
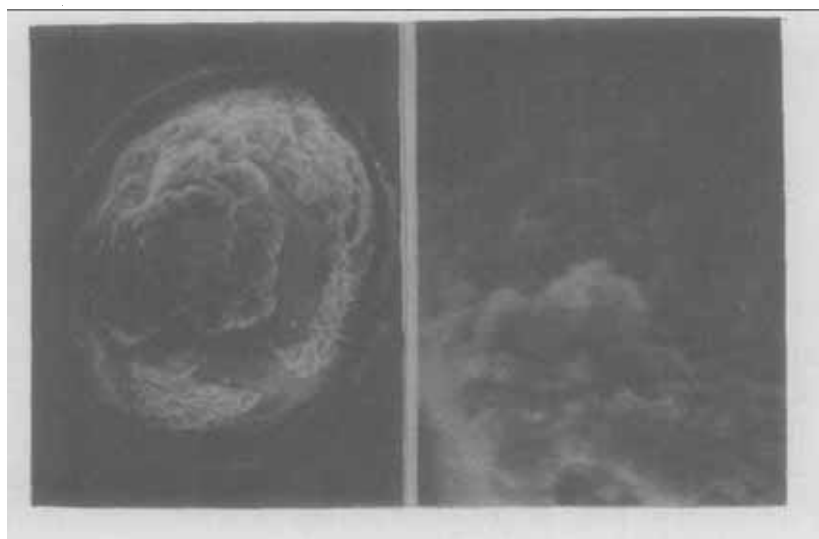


Fig. 1 IR spectra of $\text{MgCl}_2 \cdot n\text{BuOH}$ treated with TiCl_4
(a) LTC; (b) HTC



(a) (b)
Fig. 2 SEM photographs of $\text{MgCl}_2 \cdot n\text{BuOH}$ treated with TiCl_4
(a) LTC 500; (b) HTC 1000

Table 1 The catalytic efficiency of catalysts prepared from the supports treated at different temperatures

Treating Temperature (°C)	30	40	50	60	90
Efficiency (KgP/g _{Ti} ·h)	3.60	3.71	3.75	5.90	5.94

Polymerization conditions; wt. of cat. = 30mg; propylene pressure = 1 atm; temp. = 50°C;
vol. of hexane = 100ml

2. The mechanism of influence of internal and external donors (at step 2, step 3 and step 4)

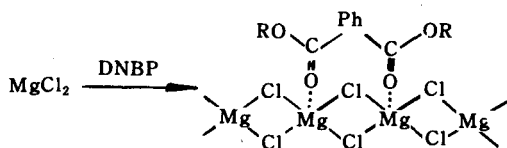
It is known that Ti^{3+} on Mg-Ti support Ziegler-Natta catalyst is the polymerization active site. Therefore ESR spectra could be a logical research tool to aid in elucidating the structure changes of the active sites with the addition of internal and external donors due to the signals of Ti^{3+} being observable fundamentally by ESR technique^[10-14].

The compositions of typical sample (having finished preparation of step 3) used in this work are shown in Table 2.

Table 2 The compositions of typical sample (having finished preparation of step3)

Sample No.	1	2	3	4
DNBP/Mg	0	0.05	0.10	0.20
Ti%(w/w)	2.68	2.41	1.61	1.56

As shown in Tab. 2, when DNBP/Mg ratio was increased, a decrease in contents of Ti was observed, which might be caused by covering of aromatic esters on MgCl_2 . The result indicates that the variation of DNBP contents used in the preparation procedure of catalysts at step 2 and step 3 could control Ti contents fixed on the support effectually. Some authors also have claimed that aromatic esters used as internal donors chemically interact with MgCl_2 ^[15]. The model of the reaction between MgCl_2 and aromatic esters might be shown as the following scheme:



ESR spectrum of sample 1 showed no ESR signals of Ti^{3+} (as seen in Fig. 3a) and only appeared a signal $g_0 = 2.0018$ corresponding to the free electron resonance similar to signals reported at reference[11], [16].

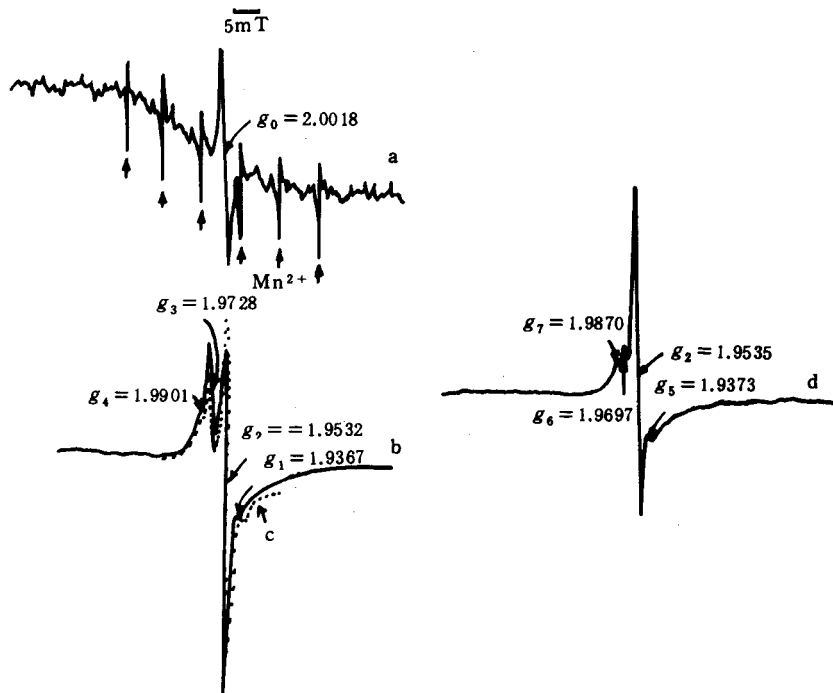
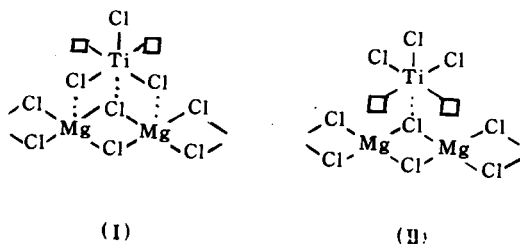


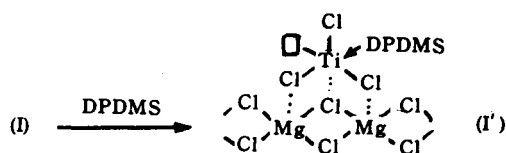
Fig. 3 (a) ESR spectrum of sample 1; (b) ESR spectrum of sample B (obtained through sample 1 mixing with AlEt_3 solution at $\text{Al/Ti}=37$); (c) Simulated spectrum of "b"; (d) ESR spectrum of sample C (obtained through sample B mixing with DPDMS at $\text{Si/Ti}=3.72$)

Sample 1 was mixed with AlEt_3 solution at $\text{Al/Ti}=37$ and its ESR spectrum was recorded immediately to give Fig. 3b. The spectrum in Fig. 3b is characterized by four resonances in decreasing order of magnetic field $g_1=1.9367$, $g_2=1.9532$, $g_3=1.9728$ and $g_4=1.9901$. One of plausible interpretation for the observed signals is the following: there are two Ti^{3+} species, one of which (I) has rhombic ligand fields with principal g values g_1 , g_3 and g_4 similar to signals reported in ref. [11]. And another species (II) is free to rotate owing to being seen as narrow ESR lines at room temperature. The structures of two Ti^{3+} species corresponding to g_1, g_3, g_4 and g_2 respectively could be described as follows:



Species (I) is free to rotate around Ti-Cl bond present in the support. According to above analyses, the simulation spectrum is obtained as seen from Fig. 3c. The simulated spectrum coincides with experimental spectrum very well, which denotes that the analyses above may be reasonable. However, it is also possible there are bi- or multi-nuclear Ti species. Unfortunately, there is more than one reason for failure to observe the ESR signals of these species.

DPDMS as external donor was added to sample B at Si/Ti=3.72 and its ESR spectrum changed obviously (Fig. 3d). Signal g_2 is similar to that at Fig. 3b. Signals g_1 , g_3 and g_4 disappear and new signals ($g_5 = 1.9373$, $g_6 = 1.9697$, $g_7 = 1.9870$) appear. However, it is plausible to assume the DPDMS can coordinate with Ti atom, which sterically hinder the migration of chlorine ligands. As a consequence, (I) changes to the potential highly isospecific species (I') according to g_5, g_6 and g_7 signals. Possible reaction may be denoted as follows:



Some small peaks can be detected closing to g_5 , g_6 and g_7 respectively at Fig. 3d which are possibly caused by isomerides of (I'). On the other hand, the relative intensities of signals corresponding to two Ti^{3+} were unchanged obviously. It illustrates that DPDMS fails to make rotating species fix on support fundamentally.

Sample 3 showed a signal with $g_0 = 2.0018$, owing to free electron resonance (Fig. 4a). When sample D was mixed with AlEt_3 solution at $\text{Al/Ti} = 37$, comparing with Fig. 3b, relative signal intensity of (I) species decreased. And it is found that signals g_1 , g_3 and g_4 changed to g_8 , g_9 and g_{10} respectively. The difference between sample 1 and sample 3 is only that DNBP was added to the sample as internal donor. The changes of signals above may be attributed to that Ti species at (I) and (I) were coordinated with internal donor forming new surface complex (II) on MgCl_2 support. This procedure can be described simply as follows:^[15]

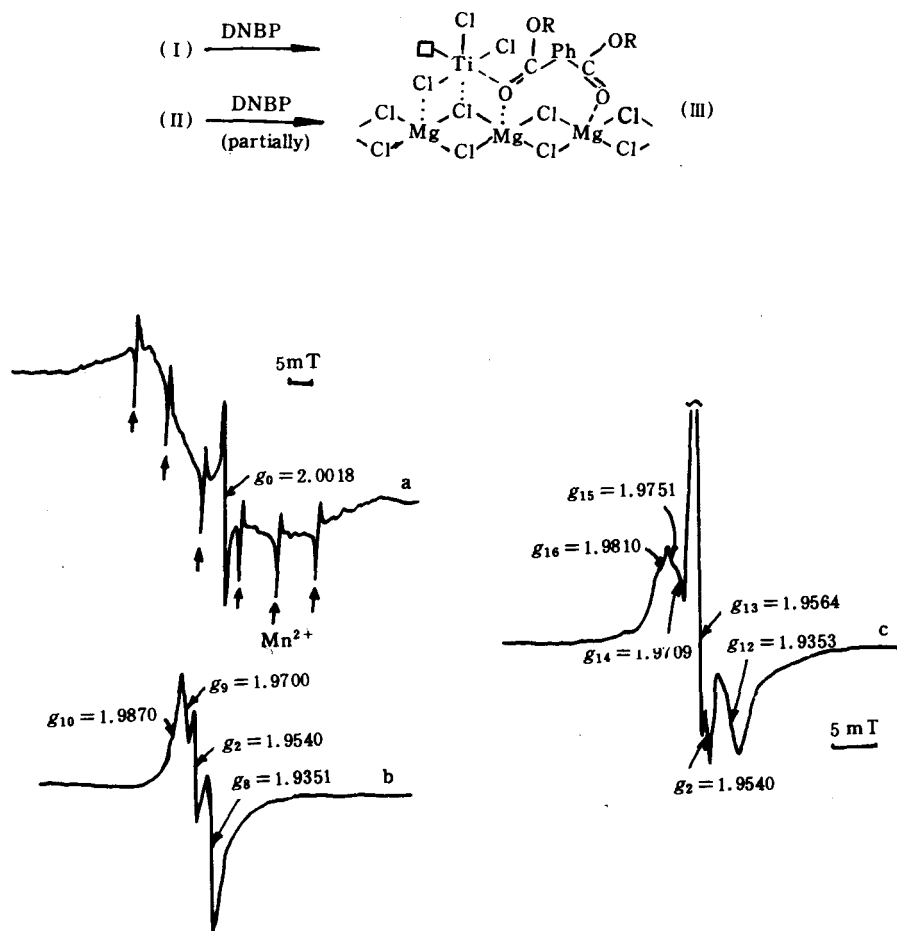
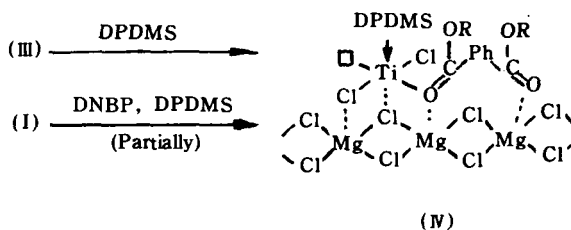


Fig. 4(a) ESR spectrum of sample 3 (sample D); (b) ESR spectrum sample E (obtained through sample 3 mixing with AlEt_3 solution at $\text{Al/Ti} = 37$); (c) ESR spectrum of sample F (obtained through sample E mixing with DPDMS at $\text{Si/Ti} = 11.72$)

Isotactic indexes of polymers obtained by using sample 3 is higher than that sample 1. This may indicate that species (III) is potential highly isotactic species. After DPDMS was added to sample E at $\text{Si/Ti} = 11.72$, ESR spectrum was recorded immediately as seen in Fig. 4c. Some new signals $g_{12} = 1.9353$, $g_{13} = 1.9564$, $g_{14} = 1.9709$, $g_{15} = 1.9751$ and $g_{16} = 1.9810$ appear. This phenomenon demonstrates that the DPDMS has coordinated with (III), forming new surface complex (IV). It is favourable by using external and internal donors together to fix rotating species on support. A more plausible mechanism on the additive effect of DPDMS for the coordination environment around Ti may be depicted schematically as

follows:



Polymerization results show that using sample 3 as starting material of catalyst, followed by DPDMS, higher isotactic index of products could be obtained (as shown in Tab. 3), which indicates that the presence of (IV) species seems not only to be the polymerization active center but also to be the highly isotactic active center.

Table 3 Isotactic index of products

Treating temp. (°C)	30	40	50	60	90
Sample 3' (I. I.)	90.0	89.1	88.2	89.1	89.1
Sample 3 (I. I.)	83.1	84.0	84.0	84.0	84.0

Sample 3': using DPDMS as external donor

Sample 3: not using DPDMS as external donor

Polymerization conditions: wt. of cat. = 30 mg; propylene pressure = 1 atm;
temp. = 50°C; hexane = 100ml

In summary, the present results demonstrate that the effects of internal and external donors on the catalysts have been satisfactorily explained from a phenomenological point of view.

CONCLUSION

The system of MgCl_2 -supported TiCl_4 catalysts (DNBP as internal donor; DPDMS as external donor) were prepared by chemical reaction method. The treatment conditions of MgCl_2 were discussed. It is found that higher treating temperature is favourable for the formation of porous and loose MgCl_2 . At the similar situation of catalyst preparation, ESR spectra were recorded at each preparation step. The results indicate that it is necessary using DNBP and DPDMS together as internal donor and external donor respectively to increase the isotactic indexes of polymers.

Keywords :

Ziegler-Natta catalyst; Polymerization of olefins; ESR; Internal and external donors

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