

# Preparation of Novel Microspherical MgCl<sub>2</sub>-Based Titanium Catalyst for Propylene Polymerization

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**ABSTRACT:** Lowering the particle size of support is one of methods to reduce breakage of supported catalyst during polymerization, which may cause serious problems for fine polymer particles from those broken catalysts. Microspherical MgCl<sub>2</sub> support could be obtained by emulsion way, but we found that they easily aggregated after emulsification and they are difficult to keep good spherical morphology. Up until now, hardly paper on the morphology improvement of micro size supports has been published. With the addition of an amount of Poly(propylene glycol)(PPG), microspherical MgCl<sub>2</sub> supports with good morphology were obtained. 1, 3, 15, 35, 80% PPG were added, respectively, and the results of SEM study on obtained particles showed that appropriate addition of

PPG obviously improved the morphology of supports. The optimum dosage was 3% in our experiment and the activity of catalyst supported on obtained support was 32.3 kg PP/g cat h. The function of PPG was explored preliminarily. In spite of the improvement of morphology the activity of supported catalyst was decreased gradually compared to those without PPG. So the further XRD and IR analysis were carried out to find reasons. The results indicated that PPG might plug pores of support and interfere with the reaction between supports and TiCl<sub>4</sub>. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3448–3454, 2008

**Key words:** supports; morphology; catalysts; Ziegler-Natta polymerization; poly(propylene) (PP)

## INTRODUCTION

As one of important materials, from the starting production in 1957<sup>1,2</sup> to now, the polypropylene industry has been developing vigorously. The driving force behind this high-speed growth may attribute to the development of catalysis technology.<sup>3</sup> In the development process of Ziegler-Natta catalysis, the first important breakthrough obtained in the late 1960s is the discovery of MgCl<sub>2</sub>-supported catalyst with high activity and high selectivity,<sup>4</sup> which eliminated the need of the removing of atactic fraction and catalyst residues and simplify the production processes. The second revolution is the appliance of the "Reactor Granule Technology" (RGT).<sup>5</sup> The final produced polymer may replicate the morphology of the catalyst particle. With the proper control the morphology of the catalyst, desired polymer granules can be obtained and the porous particles may be used as a mini reactor, which is especially useful

in the preparation of polymer alloy. The recent development of catalytic system represented by the mixed catalyst (Multicatalyst Reactor Granule Technology).<sup>6</sup> The morphology and texture of support directly decided that of catalyst, and all these technology progresses must build on the support technology. So the control of architecture and morphology of support play an important role in the preparation of catalyst. However, it is rather complicated and difficult to control.<sup>7</sup> Although some articles have been published on the preparation of support,<sup>8–11</sup> there are no articles on the morphology improvement of micro size supports having been published.

The spherical form of the final polymer granules has huge advantages in the downstream handling and the industrial processing of polymer.<sup>12</sup> So great efforts have been made to achieve spherical MgCl<sub>2</sub> supports and some methods have been developed such as fast melt quenching,<sup>13,14</sup> spray drying,<sup>15</sup> and spray cooling.<sup>16,17</sup> But there still exist many problems that should be resolved. For example, catalysts supported on these supports have a tendency to generate fine polymer particles, etc. Lowering the particle size of support is one of methods to reduce particle breakage. Microspherical MgCl<sub>2</sub> support can be obtained by emulsion, but we found that they easily aggregated after emulsification.

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In this work, a new method for preparation of microspheric  $\text{MgCl}_2$  adducts with good morphology by adding PPG has been developed. After it was treated with  $\text{TiCl}_4$ , the formed catalysts possess good activity despite it was lower than that of catalysts based on no-PPG supports. The resulted polymer granules have good morphology, which are in particular important for industry. The mechanism of the action of PPG and the reason of the less activity of the supported catalyst with the addition of PPG were also preliminarily explored.

## EXPERIMENT

### Materials

Anhydrous  $\text{MgCl}_2$  and silicon oil were used without further purification. The viscosity of silicon oil was 500 cp at 25°C. Anhydrous ethanol, hexane, PPG were dried over 4A molecular sieves before use. Polymerization-grade propylene and high pure nitrogen were obtained from Beijing Yanshan Petrochemical Co., Ltd. (BYPC), and passed through a 4A molecular sieve before use. Triethylaluminum (TEA) was received from Aldrich. Titanium tetrachloride, di-*n*-butyl phthalate, *n*-hexane, and anhydrous magnesium chloride were obtained from Beijing Chemical Reagents Co., Ltd. (Beijing, China). All experimental manipulations were carried out under dry, a high-purity nitrogen atmosphere.

### Preparation of spherical adducts

About 250 mL of silicon oil, 15 g of  $\text{MgCl}_2$ , an amount of PPG and 26 mL of ethanol were charged into a 1L vessel containing stirrer and equipped with speed control and an exit port. The content of the reactor was heated to 130°C while stirring continually. After fully reacted, the mixture was forced out of the 1 L vessel by pressurizing it, passing through a steel tubing to a high shearing emulsor, where the mixture were emulsified, and the formed emulsion were transferred to cold hexane cooled to about -30°C beforehand. The white solid precipitated particles were washed with hexane five times and dried under vacuum.

### Catalyst preparation

The method of preparing catalyst was similar to that described by L.WU et al.<sup>16</sup> The mixture of  $\text{TiCl}_4$  (240 mL) and hexane (molar ratio:  $\text{TiCl}_4/\text{hexane} = 1$ ) was introduced into a four-necked glass reactor. When it was cooled to -20°C, 8 g of spherical adducts was added, and then the mixture was heated slowly from -20 to 50°C in about 6 h while stirring gently. When the temperature reached 50°C, 1.5 mL of dibu-

tyl phthalate, as an electron donor, was added to the reactor. The temperature of the reactor was increased slowly to 110°C in 3 h and kept at 110°C for 1 h. After filtration, they were washed by an additional 240 mL of  $\text{TiCl}_4$  two times. The reaction product in the reactor was then cooled to 50°C and washed with hexane three times. The particles so obtained were dried under vacuum at room temperature for 30 min.

### Polymerization procedure

A 5-L stainless steel autoclave was used as propylene bulk polymerization reactor. Stoichiometric TEA, an external donor, an *n*-hexane slurry of solid catalyst, quantitative hydrogen, and 2.5-L liquid propylene were introduced into the autoclave. Then the mixture was heated to 70°C within a few minutes to perform the main polymerization for the prescribed polymerization time. The polymerization was terminated when opening the vent valve and allowing the unreacted monomer to evaporate quickly. After flashing and flushing with nitrogen several times, the product was discharged from the valve at the bottom of the autoclave and dried 2 h in a vacuum oven at 60°C.

### Characterization

The morphology of samples was observed by using a Philips environmental scanning electron microscope XL-30 ESEM FEG (Philips, The Netherlands). X-ray diffraction (XRD) powder patterns were obtained with Rigaku D/max 2500 VB2+/PC instrument equipped with a source using Cu anode, operating at 40 kV and 40 mA for Cu  $k\alpha_1$  radiation. The samples were sealed under a polyethylene film in sample frames. The diffraction pattern was recorded in the range,  $5^\circ < 2\theta < 70^\circ$ , with a scanning speed of  $3^\circ/\text{min}$ . Specific surface area (SSA) and pore size distribution (PSD) of the samples were determined by nitrogen adsorption-desorption isotherm at 77 K on nitrogen absorption apparatus (Micrometrics ASAP 2020). Prior to the analysis the samples were degassed at 20°C for at least 8 h. SSA was calculated via the Brunauer, Emmet, and Teller (BET) model. The PSDs were obtained from the desorption branch of the isotherm through the Barret, Joyner, and Halenda (BJH) analysis.

## RESULTS AND DISCUSSION

Ethanol was reacted with anhydrous magnesium dichloride (with or without the addition of PPG) in the silicon oil. The resultant  $\text{MgCl}_2$  adducts after complete reaction was molten in the medium of silicon oil at 130°C, and with the subsequent process of

**TABLE I**  
Preparation Conditions for the Supports and the Activity of Resulted Catalysts

Sample	PPG (Molar percent based on MgCl <sub>2</sub> )	Resultant catalyst	Activity <sup>a</sup> (kg PP/g cat · h)
SP-0	0	SPC-0	35.7
SP-1	1%	—	—
SP-2	3%	SPC-2	32.3
SP-3	15%	SPC-3	29.2
SP-4	35%	SPC-4	20.7
SP-5	80%	—	—

<sup>a</sup> Polymerization conditions: catalyst loading: 10 mg; time: 1 h; Al/Si = 20.

emulsification and quenching, microspheric granules were obtained. To eliminate silicon oil, the granules were rinsed with *n*-hexane five times. The preparation condition was presented in Table I and the corresponding resultant catalysts were named SPC-2, SPC-3, and SPC-4.

### Surface morphology of supports

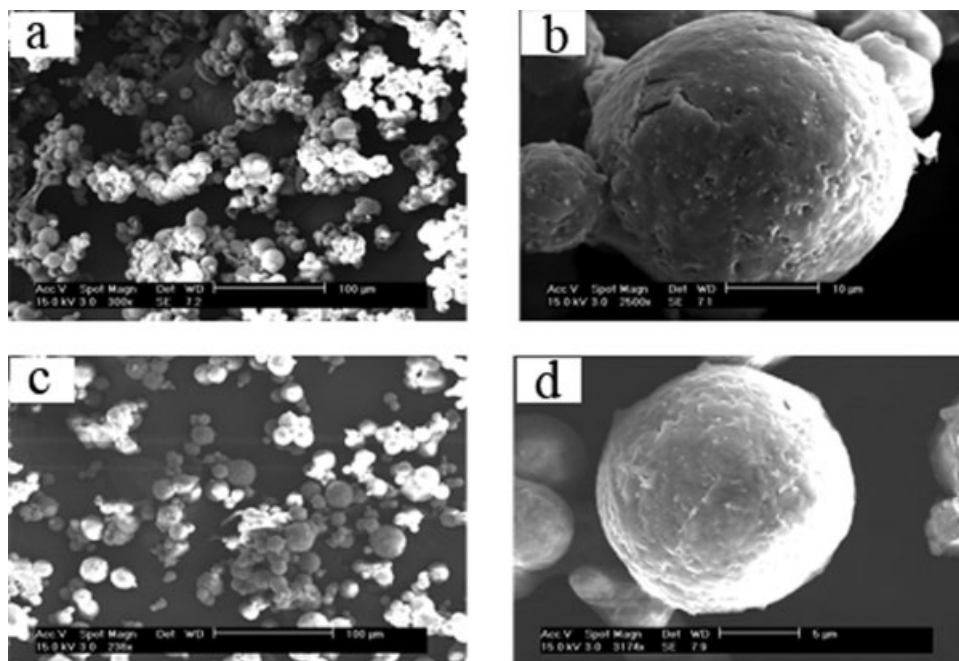
The surface morphology of the obtained supports was studied by SEM and the results were shown in Figure 2. It can be clearly found that here good spherical MgCl<sub>2</sub> adducts can be obtained by using this special emulsion technique. The diameter of the particles is mainly in the range of 10–30 μm.

Compared with Figures 1 and 2, it is found that with the addition of PPG the dispersion and morphology of obtained support particles are improved

obviously. As mentioned above, for the existence of shape replication of the catalyst to polymer, the catalyst based on agglomeration support will result in polymer caking that is undesired in olefin industry. With the appropriate amount addition of PPG, the obtained supports have good spherical morphology and the phenomena of caking are decreased obviously. However, excessive addition of PPG will result in agglomeration of MgCl<sub>2</sub> particles, which can be seen from e and f in Figure 2. Although more beautiful spherical morphology can be obtained, the supports obtained by the addition of PPG have smoother surface. From the picture b in Figure 1 some pores of the supports can be seen clearly; however, these kinds of pores cannot be seen in picture d in Figure 2. Generally speaking, higher porous supports immobilizing more active Ti species and the obtained catalyst showed higher activity. The addition of PPG which decreased the surface area of supports may do harm to the activity of the supported catalysts. This has been proved by the activity data of supported catalyst.

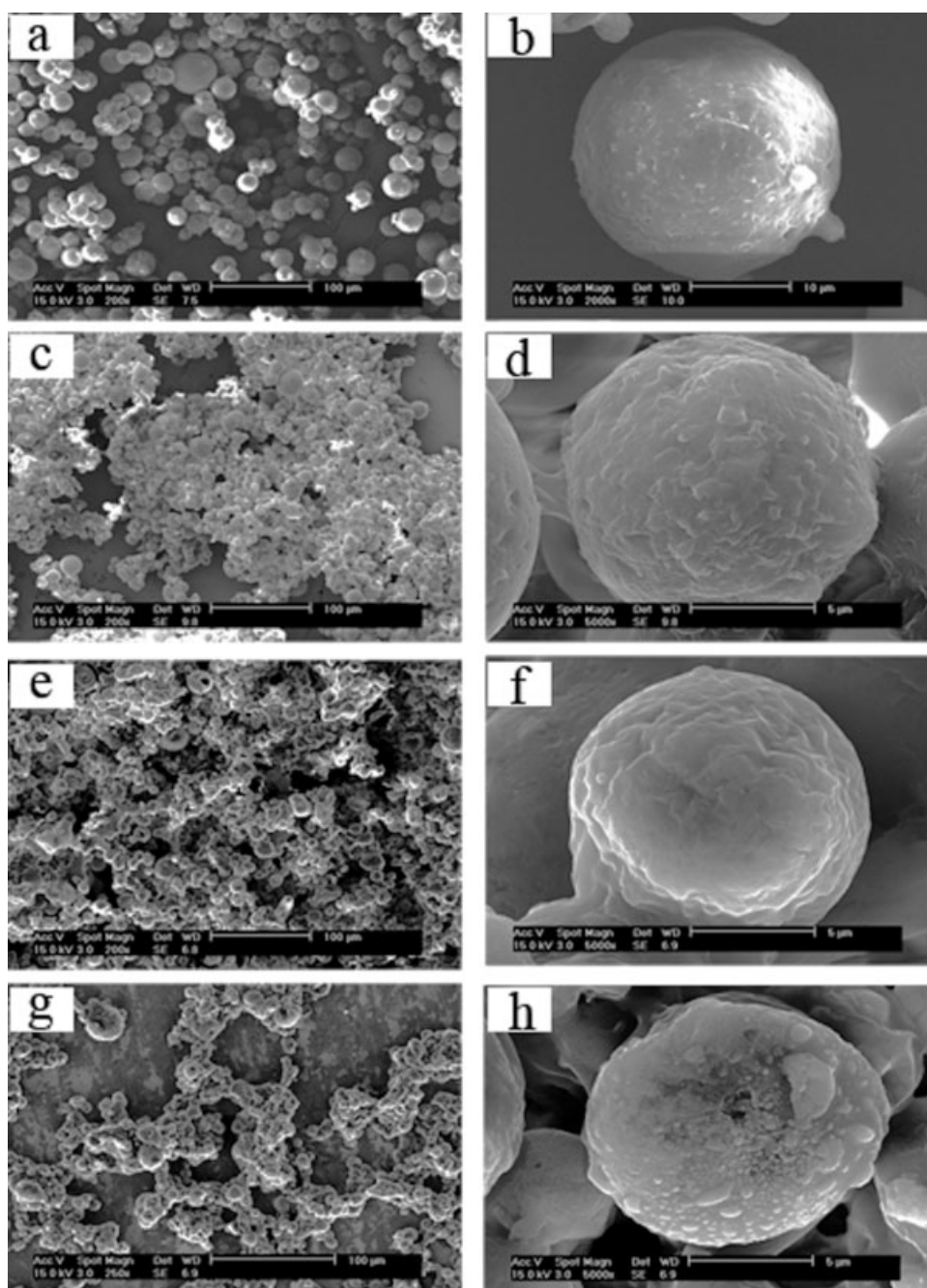
### Function of PPG

The action mechanism of PPG in the process of improving morphology of support was illustrated in Figure 3. After a small count of PPG was added, with the changes in surface tension between the granules of magnesium dichloride-alcohol adducts and silicate oil, the surface energy of particles decreased. In addition, under the force of steric



**Figure 1** SEM images of: (a) and (b) MgCl<sub>2</sub> adducts particles (SP-0, 0% PPG addition); (c) and (d) MgCl<sub>2</sub> adducts particles (SP-1, 1% PPG addition).

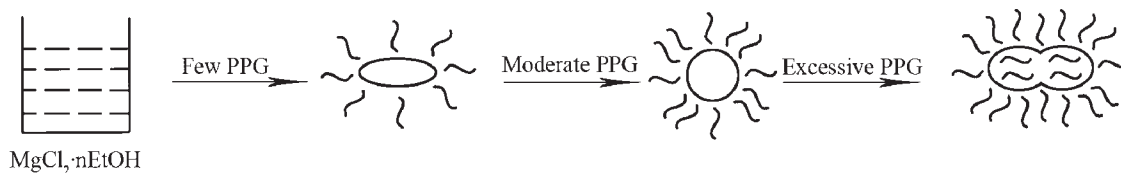




**Figure 2** SEM images of: (a) and (b)  $\text{MgCl}_2$  adducts particles (SP-2, 3% PPG addition); (c) and (d)  $\text{MgCl}_2$  adducts particles (SP-3, 15% PPG addition); (e) and (f)  $\text{MgCl}_2$  adducts particles (SP-4, 35% PPG addition); (g) and (h)  $\text{MgCl}_2$  adducts particles (SP-5, 80% PPG addition).

hindrance and electrostatic interaction caused by PPG attached on the surface of granules, the granules tend to have longer stabilization time. However, because of the shortage amount of PPG, they cannot form steady buffer layers circle around the granules. Accordingly, their weak isolation cannot prevent the adhesion of granules completely and the granules are not easy to keep spherical shape after emulsion. So the desired spherical morphology of supports is difficult to be obtained. As the continued increasing

of PPG concentration until up to appropriate amount, on the surface of granules a relatively steady buffer layers would come into being. For these layers the granules are difficult to come close to others. This dispersive action effectively kept the granules from agglomeration and the support with good morphology can be obtained. With further addition of PPG and supersaturated adsorption of PPG on the surface of the granules, PPG come into the interior of the granules and this destroy the



**Figure 3** Action Mechanism of PPG.

steady state of spherical granule and the conglutination formed again.

### Supported catalysts and polymer particles

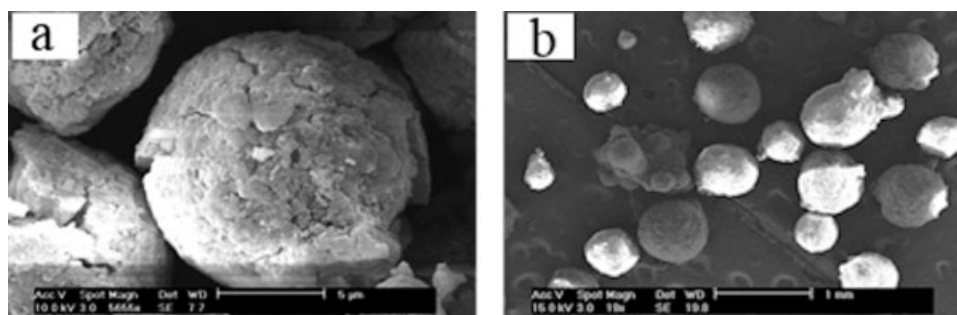
SEM images of the catalyst and the obtained polypropylene particles are shown in Figure 4. After treating with  $\text{TiCl}_4$  on the surface of the smooth spherical supports few pores start to appear, which can be seen from the photographs, and their surface become a bit coarse and porous. In the meantime, the nitrogen adsorption–desorption isotherms for samples and their corresponding pore size distributions are reported in Figure 5. The SSA of supports and catalysts, calculated from the BET equation using the adsorption data in the relative pressure ( $P/P_0$ ) range of 0.05–0.25, were 4.70 and 187.73  $\text{m}^2/\text{g}$ , respectively. The SSA value of catalysts was two orders of magnitude higher than that of supports. The pore size distributions (inset) indicated that pores with their width in the range of 25–50 Å, possess more volume in the catalysts than that in the supports. The higher SSA of catalysts can be attributed to the formation of a bit coarse and porous surface as can be seen from SEM graphs, and that was due to the removal of the ethanol from the supports during the procedure of the treatment of  $\text{TiCl}_4$ , which is coincident with the result reported earlier.<sup>11</sup> The photographs of the supports, catalysts, and the polymer particles indicate that the morphology replication phenomena have taken place elementarily well. The activity of the catalysts named SPC-2, SPC-3, and SPC-4 is 32.3, 29.2, and 20.7 kg PP/g cat·h,

respectively, which is all lower than that of SPC-0, 35.7 kg PP/g cat h. The addition of PPG decreased the activity of the supported catalyst. The more PPG was added, the lower activity of resulted catalyst was obtained. To find the reasons of the decrease of the activity of the supported catalyst further, IR and XRD of the supports were carried out.

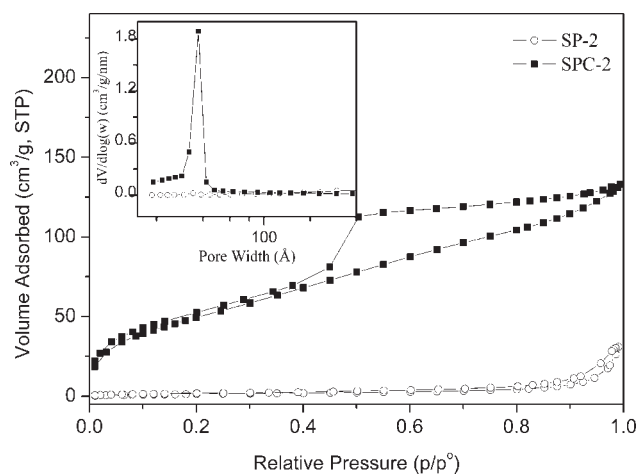
### XRD analyze

The crystal structure of  $\text{MgCl}_2$  is an important critical factor when used as support in catalyst preparation. So anhydrous  $\text{MgCl}_2$ , original support, PPG additional supports and supported catalysts were tested by XRD, and the patterns were shown in Figure 6.

The crystal structure deeply affects the activity of supported catalyst. Only activated  $\text{MgCl}_2$  supported catalyst can have high activity, one of which is  $\delta\text{-MgCl}_2$ .<sup>18</sup> They have a high-disordered crystalline structure, whose form reflected on the XRD pattern shows broad bands (SP-0, in Fig. 6), while the inactivated species exhibit sharp peaks ( $\text{MgCl}_2$ , in Fig. 6). The broaden peaks indicate that the former has a higher rotational disorder between the triple layers and a smaller crystalline size as against inactivated species. Compared with the XRD pattern of SP-0 and SP-2 to SP-4, very similar diffraction peaks reveal that the latter also has a highly disordered structure. Therefore, the addition of PPG does not interface the action between magnesium dichloride and ethanol, which is pivotal for the activity of subsequent catalyst. So the decrease of the activity of



**Figure 4** SEM images of: (a) Supported Catalyst (SPC-2); (b) obtained polymer particles from SPC-2.

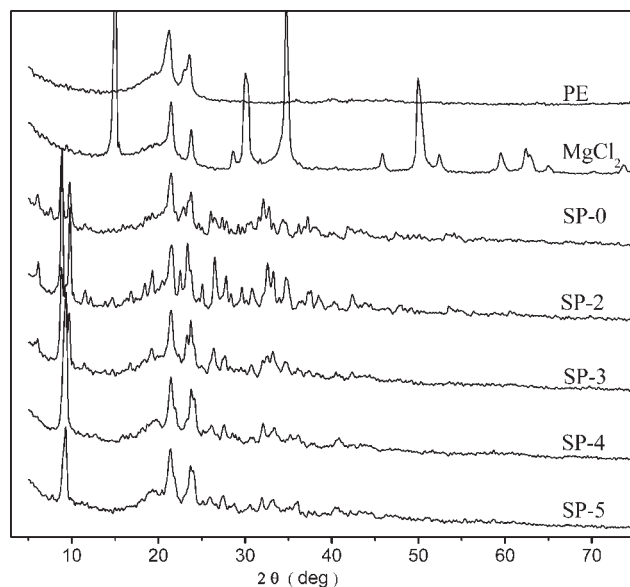


**Figure 5** The nitrogen adsorption-desorption isotherms and their corresponding PSDs (inset) of SP-2 and SPC-2.

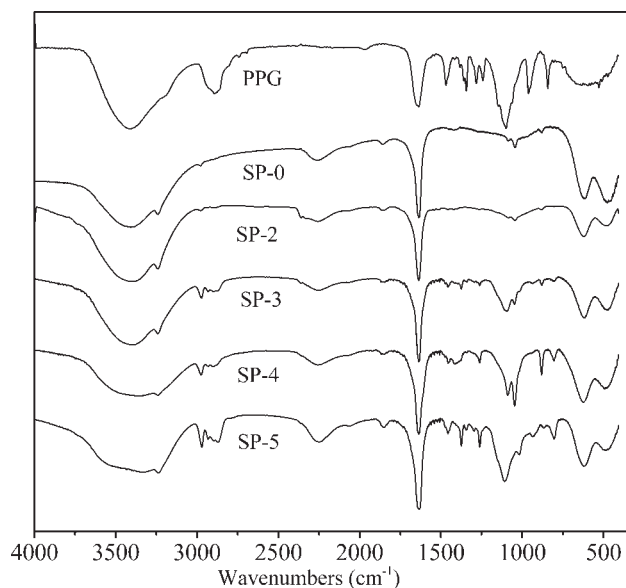
the supported catalysts may not occur in the procedure of the activation of  $\text{MgCl}_2$ .

### IR analyze

From the IR result (Fig. 7) we can see that at wave number of  $1099\text{ cm}^{-1}$  there is characteristic peak of PPG which is the peak of ether bonds  $\text{C}-\text{O}-\text{C}$  absorption. This shows that some PPG have come into the interior of support. The appearance of PPG in the supports exists for two reasons: one may be that the long chain of PPG restricts the molecules from moving freely, and the other may be that PPG is difficult to dissolve in hexane, so when the supports were washed with hexane PPG was difficult to be eluted, some PPG still being in the support. The remnant PPG may plug the pores in the granular



**Figure 6** XRD patterns of  $\text{MgCl}_2$ , and  $\text{MgCl}_2$  adducts.



**Figure 7** IR Spectrum of PPG  $\text{MgCl}_2$  adducts.

support and this may have an impact on the reaction between  $\text{TiCl}_4$  and support. The immobilization of active species was impaired and the amount of active species decreased accordingly. So the activity of the supported catalyst decreased. However, this phenomenon also gives us a hint that by this method hybrid support can be obtained through the addition of some appropriate materials. As far as this is concerned, we have explored to some extent and the correlative results will be reported later.

### CONCLUSIONS

With the absence of PPG, emulsification method for the preparation of spherical  $\text{MgCl}_2$  adducts gave particles with desired morphology. In our experiment spectrum, 3% addition showed the best effect. With this dosage, the morphology of supports was improved obviously and the activity of the supported catalyst was decreased just little. XRD data indicated that the addition of PPG affected little on the activation procedure of  $\text{MgCl}_2$ . The reasons for less activity might be caused by lower porosity of supports and the rudimental PPG in the supports, which might do harm to the reaction between  $\text{TiCl}_4$  and  $\text{MgCl}_2$  adduct.

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