

# Preparation of Porous Spherical MgCl<sub>2</sub>/SiO<sub>2</sub> Complex Support as Precursor for Catalytic Propylene Polymerization

Tao Jiang,<sup>1,2,3</sup> Wei Chen,<sup>2</sup> Feng Zhao,<sup>2</sup> Yuexiang Liu,<sup>2</sup> Ruen Wang,<sup>2</sup> Hongbin Du,<sup>2</sup> Tianyi Zhang<sup>2</sup>

<sup>1</sup>Department of Material Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

<sup>2</sup>Sinopec Beijing Research Institute of Chemical Industry, Beijing 100013, China

<sup>3</sup>Department of Chemical Engineering, Daqing Petroleum Institute, Daqing 163318, China

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**ABSTRACT:** The MgCl<sub>2</sub>/SiO<sub>2</sub> complex support was prepared by spray drying using alcoholic suspension, which contained MgCl<sub>2</sub> and SiO<sub>2</sub>. The complex support reacted with TiCl<sub>4</sub> and di-*n*-butyl phthalate, giving a catalyst for propylene polymerization. The catalyst was spherical and porous with high specific surface area. TEA was used as a cocatalyst, and four kinds of alkoxysilane were used as external donors. The bulk polymerization of propylene was studied with the catalyst system. The effect of the reaction conditions and external donor on the polymerization were

investigated. The results showed that the catalyst had high activity, high stereospecificity, and sensitive hydrogen responsibility. Polypropylene has good grain morphology because of duplicating the morphology of the catalyst. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1296–1299, 2005

**Key words:** alkoxysilane; complex supports; poly(propylene) (PP); silica/magnesium chloride; Ziegler–Natta polymerization

## INTRODUCTION

It is well known that support and donor have very important impact on Ziegler–Natta catalyst systems for propylene polymerization. More and more novel donors have been found and used in an MgCl<sub>2</sub> based catalyst system in which the internal donors are ethyl benzoate, dialkyl phthalate, diether, and succinate ester, and the external donor is alkoxysilane.<sup>1</sup> A variety of metal halides and oxides have been reported as suitable supports for the catalysts.<sup>2</sup> Inorganic oxides, such as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, have also been used as catalyst supports because of their high specific surface areas and good morphology.<sup>3,4</sup> However, SiO<sub>2</sub>-supported titanium catalysts often show very low activity and yield polypropylene with low isotacticity.<sup>5</sup> Anhydrous MgCl<sub>2</sub> has been known as a preferred support of highly efficient Ziegler–Natta catalysts for olefin polymerization, because it can stabilize the active centers and increase the activity of the catalysts. But the preparation process of spherical MgCl<sub>2</sub> is rather complicated, and the catalyst is apt to be broken up and produces fine powder during polymerization.<sup>6</sup> SiO<sub>2</sub>/MgCl<sub>2</sub> supported TiCl<sub>4</sub> catalysts have been used for the polymerization of ethylene and propylene and for

their copolymerization. In general, the complex supports were often prepared by codeposition or dip-molding.<sup>7</sup> In this study, we assembled SiO<sub>2</sub>/MgCl<sub>2</sub> by a spray drying technology and obtained a complex support. The complex support reacted with TiCl<sub>4</sub>, and an internal donor gave the catalyst. The behavior of the catalyst for polymerization of propylene was investigated using propylene bulk polymerization and alkoxysilane as the external donor.

## EXPERIMENTAL

### Materials

Polymerization-grade propylene and high pure nitrogen were obtained from Beijing Yanshan Petrochemical Co., Ltd. (BYPC), and used after passage through a 4A molecular sieve. Cyclohexylmethyldimethoxysilane (CHMDMS), dicycloamyldimethoxysilane (DCPDMS), Di-*i*-butyldimethoxysilane (DIBDMS), di-*i*-propyldimethoxysilane (DIPDMS), and triethylaluminum (TEA) were received from Aldrich. TS610 SiO<sub>2</sub> (diameter is 0.02 ~ 0.1 μm and specific surface area is 200 ± 50 m<sup>2</sup>/g) was supplied by Cabot Corp. and was calcined at 400 °C under N<sub>2</sub> for approximately 4 h before use. Titanium tetrachloride, di-*n*-butyl phthalate, *n*-hexane, and anhydrous magnesium chloride were obtained from Beijing Chemical Reagents Co., Ltd. (Beijing, China).

Correspondence to: W. Chen (chenwei@brici.ac.cn).

### Synthesis and characterization of catalyst

All operations were carried out under dry nitrogen using standard Schlenk techniques. The  $\text{SiO}_2/\text{MgCl}_2$  complex support was prepared by spray drying, using a B-290 dryer (Buchi, Switzerland); then, the complex support reacted with  $\text{TiCl}_4$  and an internal donor according to the method in literature,<sup>8</sup> giving the catalyst. The content of the titanium in the catalyst was 2.34%, determined by a 722 spectrophotometer. Particle size analysis results showed that the  $D_{50}$  of the catalyst was  $28.3\mu\text{m}$ . The total specific surface area of the catalyst was  $306.5\text{ m}^2/\text{g}$  and total pore volume was  $0.39\text{ mL/g}$ , obtained from nitrogen adsorption measurements (Carlo Erba Strumentazione, Sorptomatic 1800).

### Propylene polymerization

Propylene bulk polymerizations were carried out as follows: Stoichiometric TEA, an external donor, an *n*-hexane slurry of solid catalyst, quantitative hydrogen, and 1L liquid propylene were added to a 2L clean stainless steel autoclave. The autoclave was heated to the desired polymerization temperature within a few minutes to perform the main polymerization for the prescribed polymerization time. The polymerization was terminated by opening the vent valve, 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  $80^\circ\text{C}$ .

### Polymer characterization

The isotacticity index (II) of polypropylene was obtained by boiling heptane extraction for 6 h through conventional methods. The molecular weight and molecular weight distribution (MWD) of the polypropylene were determined by a Waters Alliance GPCV2000 gel permeation chromatograph (GPC) equipped with a refractive index detector, using three

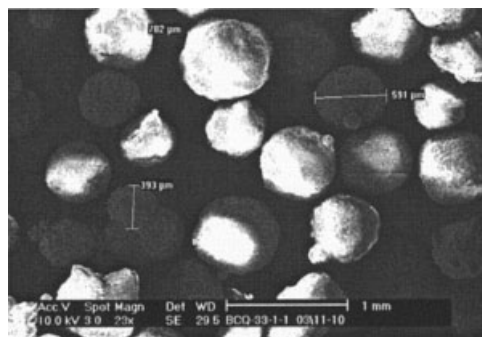


Figure 2 SEM picture of the polypropylene grain.

Polymer Laboratory MIXED-B columns and 1,2,4-trichlorobenzene as solvent at  $150^\circ\text{C}$ . The number-average and weight average molecular weight ( $M_n$  and  $M_w$ , respectively) were determined with reference to a polystyrene standard calibration. The pore characterization of the propylene was determined by Mercury intrusion (Micromeritics, Autopore 9410).

## RESULTS AND DISCUSSION

### The morphology of the catalyst and polypropylene

The SEM picture of the catalyst and polypropylene are shown in Figures 1 and 2, respectively. From Figure 1 we can see that the catalyst is spherical and well distributed. The polypropylene grains in Figure 2 were also spherical and well distributed because of duplicating the morphology of the catalyst. Figures 3 and 4 give the surface SEM picture of the complex support and polypropylene. From Figure 3 we can see that the complex support was built from many spherical  $\text{SiO}_2$  and  $\text{MgCl}_2$  particles. We can see from Figure 4 that the polypropylene grains were porous and spherical. Mercury intrusion determined the total specific surface area is  $224.6\text{ m}^2/\text{g}$  and total pore volume is  $0.46\text{ g/L}$ .

### Effect of TEA concentration on polymerization

Table I shows the effect of TEA concentration on the polymerization reaction. The increase of the Al/Ti

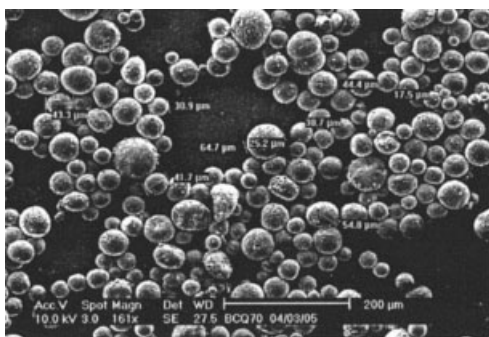


Figure 1 SEM picture of the catalyst grain.



Figure 3 SEM picture of the complex support surface.



Figure 4 Surface SEM picture of the polypropylene.

molar ratio from 100 : 1.0 to 200 : 1.0 increased the productivity of the catalyst, whereas with a further increase in the ratio the productivity declined. This is because TEA was used as cocatalyst in the propylene polymerization, and it can alkylate the active centers of the catalyst and reduce  $Ti^{4+}$  to  $Ti^{3+}$  and  $Ti^{2+}$ .  $Ti^{3+}$  is the active center for propylene polymerization. When the concentration of TEA was increased beyond the optimum value,  $Ti^{4+}$  was reduced to  $Ti^{2+}$ , resulting in the decrease of activity. The isotactic index (II) value of the polypropylene slightly decreased with an increasing ratio Al/Ti. This is because with the increase of TEA concentration, the internal donor displaced from the surface of the solid component by TEA increased, which resulted in the decrease of the II value of polypropylene. Molecular weight ( $M_w$ ) decreased with the increase of the Al/Ti molar ratio because of chain transfer to Al. Similar results were reported by Zohuri and coworkers.<sup>9</sup>

### Effect of $H_2$ loading on polymerization

The effects of  $H_2$  concentration on polymerization behavior of the complex support catalyst are listed in Table II. Different amounts of  $H_2$  were used as a chain-transfer agent during propylene polymerization. The optimum productivity of the catalyst was obtained with 4.0NL of  $H_2$  loading. The catalyst productivity, compared with the polymerization in the absence of hydrogen, increased by four times with the

TABLE I  
Effect of TEA Concentration on Polymerization

[Al]/[Ti] molar ratio	Activity kg PP/g cat	II (%)	MI <sub>2.16</sub>	Mw 10 <sup>4</sup>	MWD
1000	15.1	96.64	53.58	16.68	7.23
600	15.0	97.21	42.34	19.66	5.92
400	24.9	97.75	33.40	21.40	5.56
200	26.3	98.09	25.53	24.41	8.10
100	10.3	98.46	9.81	31.96	11.95

Temperature = 70°C; catalyst loading = 10mg; polymerization time = 60min;  $H_2$  = 4.0NL; [Al]/[CHMDMS] = 10.

TABLE II  
Effect of  $H_2$  Loading on Polymerization

$H_2$ loading (NL)	Activity kg PP/g cat	II (%)	MI <sub>2.16</sub>	Mw 10 <sup>4</sup>	MWD
6.0	19.5	95.29	84.75	15.91	7.39
4.0	24.9	97.75	33.40	21.40	5.56
2.0	24.4	97.97	11.43	30.42	4.29
1.0	16.5	98.26	2.68	43.16	4.85
0	5.7	98.52	0.11	150.45	6.09

Temperature = 70°C; catalyst loading = 10mg; [Al]/[Ti] = 400; polymerization time = 60min; [Al]/[CHMDMS] = 10.

addition of hydrogen (Table II). Molecular weight and II value of the polymer decreased with the increase of  $H_2$ . Several hypotheses have been proposed to account for the enhancement of the polymerization rate caused by hydrogen. Okura and colleagues<sup>10</sup> suggested that hydrogen and the cocatalyst interact to further reduce the catalytic surface, forming new active sites not available when the cocatalyst is the single reducing agent. The formation of additional active sites has also been proposed by Buls and Higgins.<sup>11</sup> There is another explanation for this behavior, that  $H_2$  activates some dormant centers in the catalyst. Hydrogen is the most widely used chain-transfer agent for molecular weight control in industrial practice with Ziegler–Natta systems. The rate of chain-transfer reaction increases with the increasing of hydrogen, resulting in  $M_w$  decreasing. A considerable activity enhancement effect of hydrogen has been observed in the polymerization of propylene with an  $MgCl_2$ -supported Ziegler–Natta catalyst and metallocene/MAO catalyst systems.<sup>12,13</sup>

### Effect of temperature on polymerization

The propylene bulk polymerizations were carried out from 50 to 80°C with the optimum  $H_2$  concentration and Al/Ti molar ratio. Table III shows the effect of temperature on the polymerization of propylene. The highest yield occurred at 70°C (see Table III). Molecular weight and II decreased with the increase of the temperature. An increase in the values of the propagating rate constant with increasing temperature and

TABLE III  
Effect of Temperature on Polymerization

Temperature (°C)	Activity kg PP/g cat	II (%)	MI <sub>2.16</sub>	Mw 10 <sup>4</sup>	MWD
50	12.1	98.25	29.64	22.61	5.56
60	16.4	98.21	30.01	22.23	5.96
70	24.9	97.75	33.40	21.40	5.56
80	21.7	96.87	35.87	17.81	6.63

Catalyst loading = 10mg; polymerization time = 60min; [Al]/[Ti] = 400; [Al]/[CHMDMS] = 10;  $H_2$  = 4.0 NL.



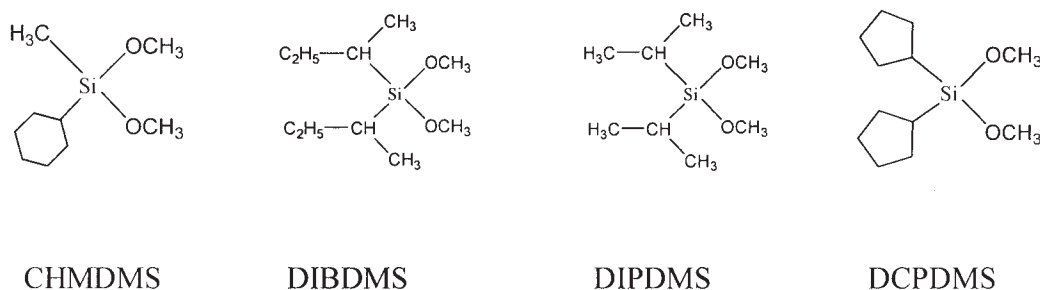


Figure 5 Four kinds of external donor used in propylene bulk polymerization.

an irreversible deactivation of active sites at high temperatures were reported early.<sup>14</sup> The solubility of  $H_2$  decreased at high temperatures, and this could affect the polymerization rate as well.

### Effect of external donor on polymerization

Four kinds of alkoxy silane were used as external donor in the  $Mg/Si$  support  $TiCl_4$  based catalysts during propylene polymerization. The structures of the external donors are given in Figure 5. The results of propylene polymerization are listed in Table IV. From it we can draw a conclusion that the propylene polymerization productivity with CHMDMS as external donor is the highest, and with DIPDMS as external donor is the lowest. The  $M_w$  and  $II$  were the highest using DCPDMS as external donor. This is because the alkyl of DCPDMS is a five member ring structure and has the highest bulk hindrance, which results in higher  $M_w$  and  $II$  than the others. The alkyl of CHMDMS has little bulk hindrance and gives the polypropylene with lower  $II$  and  $M_w$ . Toward DIBDMS and DIPDMS, the research result is consistent with literature.<sup>15</sup> Though  $i-C_4H_9$  has bigger bulk than  $i-C_3H_7$ , the polypropylene using DIPDMS as external donor has high  $II$  and  $M_w$ . This is because the chain of  $i-C_4H_9$  is more flexible than that of  $i-C_3H_7$ .

### CONCLUSIONS

We have developed a novel spherical  $MgCl_2/SiO_2$  complex support using spray drying technology. The

$MgCl_2/SiO_2$  complex support has better particle shape, with high specific surface area and porosity. Porous spherical polypropylene can be produced using the catalyst. It was found that the optimum  $Al/Ti$  molar ratio with respect to the catalyst activity is 200. With the increase of  $H_2$  concentration within 4.0NL, the productivity of the catalyst increased, but a higher concentration of  $H_2$  reduced the productivity. The highest productivity was obtained at 70°C. With the increase of TEA,  $H_2$  concentrations, and temperature, the  $II$  and  $M_w$  declined. In pair with di-*n*-butyl phthalate in  $MgCl_2/SiO_2/TiCl_4/TEA$  systems for propylene polymerization, the order of productivity is: CHMDMS > DIBDMS > DCPDMS > DIPDMS. The order of  $II$  and  $M_w$  are: DCPDMS > DIPDMS > DIBDMS > CHMDMS.

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TABLE IV  
Effect of External Donor on Polymerization

External donor	Activity kg PP/g cat	II (%)	$M_w$ 10 <sup>4</sup>	MWD
CHMDMS	24.9	97.15	21.40	5.56
DCPDMS	16.15	98.85	24.69	7.12
DIPDMS	13.85	98.01	23.62	5.99
DIBDMS	17.05	97.65	22.50	9.43

Catalyst loading = 10mg; polymerization time = 60min;  $[A1]/[Ti] = 400$ ;  $[A1]/[external\ donor] = 10$ ;  $H_2 = 4.0NL$ ; Temperature = 70°C.