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**MgCl<sub>2</sub> • 6H<sub>2</sub>O-BASED ZIRCONOCENE CATALYST  
FOR ETHYLENE POLYMERIZATION**

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**Abstract** Several supported zirconocene catalysts were prepared by using MgCl<sub>2</sub> • 6H<sub>2</sub>O as a precursor for producing an active support. Such catalysts combined with methylaluminoxane (MAO) obtained by reacting MgCl<sub>2</sub> • 6H<sub>2</sub>O with AlMe<sub>3</sub> show good activity for ethylene polymerization similar to that of anhydrous MgCl<sub>2</sub> supported zirconocene catalyst.

**Keyword** MgCl<sub>2</sub> • 6H<sub>2</sub>O, Supported zirconocene catalyst, Ethylene polymerization

**INTRODUCTION**

Much effort has recently been made to develop active heterogeneous metallocene catalysts to control the polymer morphology and to suit gas phase olefin polymerization technology without changing their special properties. One of the preparation methods of supported metallocene catalysts is usually to support the metallocene on inorganic compounds such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgCl<sub>2</sub> with or without MAO<sup>[1-3]</sup>.

In our earlier studies we reported that reacting MgCl<sub>2</sub> • 6H<sub>2</sub>O with AlMe<sub>3</sub> produces MAO and a byproduct-solid residue MgCl<sub>2</sub>\*<sup>[4]</sup>.

By elemental analysis, it was confirmed that MgCl<sub>2</sub>\* contains H<sub>2</sub>O and Al. We have recently found that the MgCl<sub>2</sub>\* supported zirconocene catalysts, which was pretreated with a small amount of MAO, can effectively catalyze ethylene polymerization.

**EXPERIMENTAL**

**Materials**

MgCl<sub>2</sub> • 6H<sub>2</sub>O was obtained from Beijing Hongxin Chemical Plant and anhydrous MgCl<sub>2</sub> from Fu Shun 301 Plant. SiO<sub>2</sub>(silica 955 from USA) was calcinated at 400°C for 4 h.

AlMe<sub>3</sub> (2 mol/L in toluene, from Aldrich Chem. Co.) and Cp<sub>2</sub>ZrCl<sub>2</sub> (from Fluka Co.) were used without further treatment. Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> was prepared according to the literature<sup>[5]</sup>. Toluene was purified by refluxing for 24 h over metallic sodium, followed by fractional distillation.

Ethylene (from Yanshan Petrochemical Corporation) was purified by passing through a column of Ni catalyst and 4A molecular sieve.

**Preparation of MAO and MgCl<sub>2</sub>\***

MgCl<sub>2</sub> • 6H<sub>2</sub>O was reacted with AlMe<sub>3</sub> to obtain MAO and MgCl<sub>2</sub>\* (solid residue) according to the

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method reported previously<sup>[4]</sup>. The Mg, Al and Cl contents of the  $\text{MgCl}_2^*$  were determined by EDTA and  $\text{Hg}(\text{NO}_3)_2$  titrations respectively.

### Preparation of Supported Catalysts

#### Catalyst A

The  $\text{MgCl}_2^*$  (4.5g) was slurried in 50 mL toluene, treated with 10mL  $\text{SiCl}_4$  under stirring at 50°C for 1 h. The solid was filtered and washed 3 times with 30 mL toluene. To the resulting solid was added 10 mL  $\text{Cp}_2\text{ZrCl}_2$  ( $2.77 \times 10^{-2}$  mol/L in toluene), followed by vigorous stirring at 50°C for 30 min. The solid part was then separated by filtration and washed 5 times with 30 mL of toluene and dried in vacuum at 40°C to obtain catalyst A.

#### Catalyst B

After treating with  $\text{SiCl}_4$  using the same procedure as catalyst A, the solid was reacted with 10 mL MAO (1 mol/L in toluene) at 50°C for 30 min. The subsequent reaction with  $\text{Cp}_2\text{ZrCl}_2$ , washing and drying procedures were the same as described above.

#### Catalyst C

4.5 g  $\text{MgCl}_2^*$  was treated directly with 10 mL MAO (1 mol/L in toluene). The following reaction with  $\text{Cp}_2\text{ZrCl}_2$ , and washing procedures were the same as described for catalyst A.

#### Catalyst D and E

They were also prepared by the same method as described for catalyst C, using anhydrous  $\text{MgCl}_2$  and  $\text{SiO}_2$  respectively.

The contents of zirconium and aluminum in the supported catalyst were determined by Inductively Coupled Plasma (ICP) spectroscopy.

### Polymerization of Ethylene

For the polymerization of ethylene, a 500 mL glass reactor equipped with a mechanical stirrer was filled with 100 mL toluene, followed by the addition on MAO and supported catalyst. The polymerization was carried out at  $1.01 \times 10^5$  Pa of  $\text{C}_2\text{H}_4$  and at 60°C for 1 h, and terminated by adding acidic ethanol. The polymer product was filtered, washed with ethanol and dried in vacuum.

### Analysis

The melting point ( $T_m$ ) of PE was determined with a Perking-Elmer Model DSC-7 instrument at a heating rate of 10°C/min. The crystallinity was calculated from the heat of fusion ( $H_f$ )<sup>[6]</sup>. Molecular weight and molecular weight distribution of the polyethylene were measured in decahydronaphthalene solution at 135°C by an AVS300 Viscometer.

## RESULTS AND DISCUSSION

The solid residue  $\text{MgCl}_2^*$  was a by-product obtained from the reaction of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with  $\text{AlMe}_3$  to prepare MAO. It was therefore expected that the  $\text{MgCl}_2^*$  would contain  $\text{MgCl}_2$ ,  $\text{H}_2\text{O}$  and Al compound. Table 1 shows the chemical composition of the  $\text{MgCl}_2^*$  and the Al content

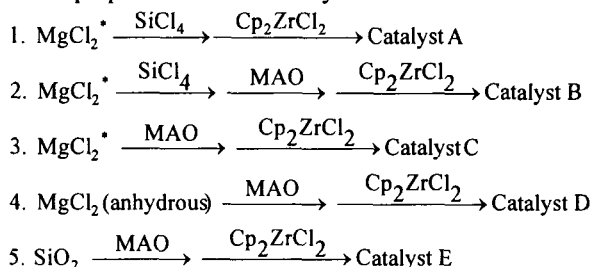
Table 1. The chemical composition of  $\text{MgCl}_2^*$

| $\text{AlMe}_3$<br>hydrolyzing<br>temperature (°C) | Chemical composition of $\text{MgCl}_2^*$ |          |          |                 |
|----------------------------------------------------|-------------------------------------------|----------|----------|-----------------|
|                                                    | Mg (wt%)                                  | Cl (wt%) | Al (wt%) | Cl/Mg (mol/mol) |
| 40                                                 | 9.1                                       | 20.4     | 20.4     | 1.97            |
| 50                                                 | 9.6                                       | 27.7     | 23.0     | 1.97            |
| 60                                                 | 11.3                                      | 32.9     | 24.1     | 1.98            |
| 70                                                 | 10.8                                      | 31.5     | 25.3     | 1.98            |

Hydrolyzing conditions:  $\text{H}_2\text{O}/\text{AlMe}_3=1.1$ , time=24h

increase with the increase in hydrolyzing temperature of AlMe<sub>3</sub> from 40 °C to 70 °C and Cl/Mg molar ratio was found to be 1.97–1.98, indicating the presence of MgCl<sub>2</sub>. That the crystal H<sub>2</sub>O was not completely removed and that Al component existed in MgCl<sub>2</sub> · 6H<sub>2</sub>O were confirmed by IR spectra of MgCl<sub>2</sub> · 6H<sub>2</sub>O and MAO<sup>[7]</sup>.

The procedures of the preparation of five catalysts are shown in Scheme 1.



Scheme 1

Chemical composition of supported zirconocene catalyst was analyzed and the results are given in Table 2. Polymerization of ethylene was then conducted at 60 °C for 1 h with these catalysts using MAO (obtained from reaction between MgCl<sub>2</sub> · 6H<sub>2</sub>O and AlMe<sub>3</sub>) as cocatalyst. The results of polymerization are given in Table 3.

Table 2. Content of Zr and Al in supported Zirconocene catalysts

| Run No. | Supported catalyst | Zr content (wt%) | Al content (wt%) |
|---------|--------------------|------------------|------------------|
| 1       | A                  | 0.013            | 24.4             |
| 2       | B                  | 0.35             | 24.3             |
| 3       | C                  | 0.35             | 26.9             |
| 4       | D                  | 0.28             | 2.79             |
| 5       | E                  | 0.77             | 6.02             |

Content of MgCl<sub>2</sub> · 6H<sub>2</sub>O = 23.0 wt%

Table 3. Results of ethylene polymerization<sup>a</sup>

| Catalyst (g)       | [Zr] (μM) | Al/Zr (mol/mol) | PE (g) | Activity (Kg/molZr · h) | $M_w \times 10^{-5}$ | $M_w/M_n$ | $T_m$ (°C) | $X^c$ (%) |
|--------------------|-----------|-----------------|--------|-------------------------|----------------------|-----------|------------|-----------|
| A 0.146            | 0.21      | 24300           | trace  |                         |                      |           |            |           |
| B 0.109            | 4.8       | 1710            | 5.7    | 1190                    | 2.54                 | 2.6       | 135.7      | 77.6      |
| C 0.115            | 4.4       | 2090            | 4.3    | 970                     | 2.63                 | 2.6       | 136.5      | 68.1      |
| 0.142 <sup>b</sup> | 5.5       | 1550            | 7.5    | 1370                    |                      |           |            |           |
| D 0.114            | 3.5       | 2080            | 4.9    | 1400                    | 2.66                 | 2.4       | 135.7      | 70.3      |
| 0.098              | 3.0       | 1730            | 3.5    | 1170                    |                      |           |            |           |
| E 0.095            | 8.0       | 1120            | 5.1    | 640                     | 2.81                 | 2.7       | 134.5      | 63.0      |

a. Polymerization conditions: temperature=60 °C, time=1h; b. polymerization temperature=70 °C;

c. X=crystallinity

It is found that catalyst A prepared with MAO-untreated MgCl<sub>2</sub> · 6H<sub>2</sub>O showed an exceptionally low Zr content and was almost inactive for ethylene polymerization. When the MgCl<sub>2</sub> · 6H<sub>2</sub>O (modified or unmodified by SiCl<sub>4</sub>) was pretreated with a small amount of MAO, the resulting supported zirconocene catalysts B and C were found to have much higher Zr immobilization than that obtained with unmodified by MAO, and also showed good catalytic activity for ethylene polymerization. From this result, it can be postulated that MAO is necessarily required for catalyst activation.

Figure 1 shows the dependence of polymerization temperature on the activity of catalyst C. It was observed that the optimum polymerization temperature range for maximum activity appears at 60 °C.

Compared with anhydrous  $\text{MgCl}_2$  supported catalyst D,  $\text{MgCl}_2^*$  supported catalysts B and C give similar results (including activity, molecular weight, melting point and crystallinity) in spite of different support.

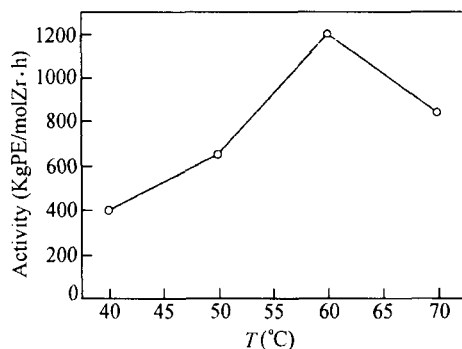


Fig. 1 Influence of polymerization temperature on activity

Polymerization of ethylene was further conducted with  $\text{Et(Ind)}_2\text{ZrCl}_2/\text{MgCl}_2^*$  catalyst by changing the Al/Zr ratio. The results are summarized in Table 4. The polymerization activity has a tendency to increase with an increase in the mole ratio of Al/Zr.

Table 4. Results of ethylene polymerization with  $\text{Et(Ind)}_2\text{ZrCl}_2/\text{MgCl}_2^*$  catalyst

| Al/Zr<br>(mol/mol) | Activity<br>(Kg/molZr · h) | $M_w \times 10^{-5}$ | $M_w/M_n$ | $T_m$<br>(°C) | Crystallinity |
|--------------------|----------------------------|----------------------|-----------|---------------|---------------|
| 350                | 49.8                       | 1.57                 | 2.4       | 140.7         | 51.3          |
| 640                | 50.7                       | 1.58                 | 2.4       | 136.8         | 63.5          |
| 860                | 52.8                       | 1.59                 | 2.4       | 136.0         | 66.5          |
| 1050               | 72.2                       | 1.97                 | 2.7       | 135.5         | 70.9          |

Polymerization conditions:  $[\text{Zr}] = 8.30 \mu\text{m}$ ,  $T = 60^\circ\text{C}$ ,  $t = 1 \text{ h}$  and the  $\text{Et(Ind)}_2\text{ZrCl}_2/\text{MgCl}_2^*$  catalyst was prepared by using the same method as catalyst C.

$\text{MgCl}_2^*$  by-product obtained from synthesis of MAO by reaction of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{AlMe}_3$  can be used as support material. The supported zirconocene catalysts from such  $\text{MgCl}_2^*$  show good activity for ethylene polymerization.

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