HIGH ACTIVITY AND GOOD HYDROGEN RESPONSE SILICA-SUPPORTED ZIEGLER-NATTA CATALYST FOR ETHYLENE POLYMERIZATION

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Abstract  A silica-supported Ziegler-Natta catalyst with dimethyldichlorosilane (DMDS) as modifier and small silica as support was successfully prepared and characterized. Results from pilot screen showed that the new catalyst exhibited higher catalytic activity, better hydrogen response ability and better copolymerization ability than the commercial M catalyst. Pilot screen in ethylene gas phase fluidized bed polymerization, the catalytic activity of the new catalyst was up to 8000 g PE/g cat, which was twice of that of the commercial M catalyst. The bulk density of polyethylene obtained with the new catalyst was 0.38 g/cm³. The new catalyst is suitable for condensed and super-condensed process in fluidized bed ethylene polymerization.

Keywords: Ziegler-Natta catalyst; Ethylene polymerization; Silica; Dimethyldichlorosilane.

INTRODUCTION

Gas phase fluidized bed technology has been one of the principal processes for catalytic ethylene polymerization to produce polyethylene (PE) since the 1980s. Ziegler-Natta catalyst systems are utilized extensively in commercial processes that produce high density and low density polyethylene with various molecular weights. Considerable interest in these catalysts persists since their discovery in 1950s [1-4] in industrial and academic institutions which is reflected by the amount of patents [5-9] and publications [10-16] covering this subject. Silica supported Ziegler-Natta catalysts are commonly used in gas phase fluidized bed reactors, they have been proved to be good in fluidizability, stability and product morphology.

With the development of condensed [17-19] and super-condensed technology [20-22], the productivity of gas phase fluidized bed polymerization reactors is enhanced by removing the heat generated in reaction from the vaporization of associated liquid in gaseous steam. Furthermore, the actual productivity is limited by bulk density and particle distribution of produced polymer as well as the catalytic activity of catalyst. High bulk density and low percentage of fine polymer powder are favorable for high activity catalyst in condensed and super-condensed operated process [22].

It was reported by McKenna et al. [23, 24] and Fink et al. [25] that the particle diameter of the silica had an influence on the catalytic performance of metallocene catalyst for ethylene polymerization. In this work, with
dimethyldichlorosilane (DMDS) modified small silica as support, a new Ziegler-Natta catalyst was successfully prepared. The effects of DMDS and silica size on the catalytic performance and product properties were investigated.

**EXPERIMENTAL**

All experiments were carried out under moisture free and pure nitrogen atmosphere. A glove box was used for transferring chemical compounds.

**Materials**

Iso-pentane, tetrahydrofuran, hexane and DMDS were used after dehydration over molecular sieve. Polymer grade ethylene was used for polymerization process. Triethyl aluminum (AlEt3), diethyl aluminum chloride (AlEt2Cl) and tri-\(n\)-hexyl aluminium (Al(\(n\)-C6H13)3) purchased from Aldrich were diluted with hexane to 2 mol/L, 2 mol/L and 1 mol/L, respectively. TiCl4 and anhydrous MgCl2 from Aldrich were used as received. The small silica was purchased from Ineos. Commercial M catalyst with Davison 955 silica as support was obtained from Daqing Petrochemical Co. of China.

**Preparation of Catalyst**

The small silica was dehydrated under 200°C for 2 h and 600°C for 4 h under nitrogen atmosphere. About 5 g of dehydrated silica was shifted to a five-neck flask equipped with a mechanical stirrer. 50 mL of iso-pentane was added to the flask to suspend the silica. Under stirring, AlEt3 (hexane solution, 0.56 mmol per gram of silica) was added slowly to react with silica. After 30 min, certain amount of DMDS was added slowly to react with the AlEt3 treated silica for 30 min. Then iso-pentane was vaporized under nitrogen flow accompanying with stirring to obtain DMDS modified silica. The new catalyst was prepared according to the methods described by Luo. In a scale up test, 20 kg of silica was used in catalyst preparation.

**Ethylene Polymerization**

Ethylene slurry polymerization was carried out in a 2 L stainless steel reactor equipped with a mechanical stirrer, temperature control and pressure control. The reactor was dried and cleaned via evacuating and flushing (three times) with ethylene at 100°C before the temperature was cooled down to 60°C. Accompanying with stirring, 1 L of hexane was added as solvent, 1 mmol of AlEt3 (hexane solution) was added as cocatalyst, 40 mg of catalyst was added into the reactor one minute later. The desire amount of hydrogen and ethylene were introduced into the reactor, the temperature of the reactor was raised to 80°C and the desired pressure was maintained via adapting the pressure regulator. Reaction was stopped 2 h later by injecting ethanol. Polymer was separated from the slurry and dried in vacuum at 60°C for 2 h.

The gas fluidized bed ethylene polymerization was carried out in a pilot plant reactor with a production capacity of 50 kg PE/h.

**Characterization of Catalyst and Polymer**

The titanium contents of the catalyst were determined using inductively coupled plasma (ICP Swiss 3410 ARL). SEM and EDX analysis were carried out with high-resolution Hitachi field emission scanning electron microscopes. For preparation of the cross-sections, the samples were mixed with epoxy resin under a nitrogen atmosphere. GPC analysis was determined by a Waters Alliance GPCV2000 equipped with a refractive index detector, using three Polymer Laboratory MIXED-B columns and 1,2,4-trichlorobenzene as solvent at 150°C. The 13C-NMR spectrum of the polymer was recorded on a Bruker DMX-400. Bulk density of polymers was measured according to ASTM-D1895-69. Particle size distribution of polymers was measured by standard sieves.

**RESULTS AND DISCUSSION**

**Characterization of the Catalyst**

The analysis data of the new catalyst and the commercial M catalyst in terms of composition, porosity, pore volume and specific surface area are presented in Table 1. The BET investigation results show that the new
catalyst exhibits higher specific surface area, higher pore volume and average pore diameter than M catalyst. From the results of elemental analysis we can draw a conclusion that the new catalyst has the similar element content as M catalyst.

| Table 1. Characterization of new catalyst and commercial M catalyst |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
|                                | Particle size $D_{50}$ ($\mu$m) | BET area ($m^2/g$) | Pore volume ($mL/g$) | Average pore size (nm) | Ti (wt%) | Mg (wt%) | Al (wt%) |
| New catalyst                  | 27.32            | 125             | 0.66             | 21.0            | 1.14      | 2.09     | 3.34     |
| M catalyst                    | 45.51            | 100             | 0.60             | 20.1            | 1.18      | 2.13     | 3.21     |

The particle size distributions of the two catalysts are illustrated in Fig. 1. Obviously, the new catalyst has a narrower particle size distribution and less content of powder than the commercial M catalyst. The average diameter of the new catalyst is approximately 27.32 $\mu$m while the commercial M catalyst is 45.51 $\mu$m. The SEM pictures of the catalyst surface and cross-section of the new catalyst are shown in Fig. 2 and Fig. 3. It was found from Fig. 2 that the new catalyst particles have good morphology, well distribution and less content of fine powder. Furthermore, the spatial repartition of titanium, magnesium, chlorine and silica was also investigated on the cross-section by using EDX. The aim was to verify that the different compounds were uniformly anchored in the particle, so as to ensure a uniform distribution of the active sites during the catalytic polymerization. It can be seen from Fig. 3 that the spatial distribution of titanium and magnesium is homogeneous in the cross-section of the particle.
**Effects of DMDS**

The effects of DMDS on catalytic activity and polymer morphology were shown in Table 2. Results showed that with the addition of DMDS, the catalytic activity increased first, and then decreased. There is no significant change in the percentage of polymer powder. The bulk density of polymers keeps increasing with the addition of DMDS. It's supposed that the chlorine of DMDS participated in the coordination of MgCl₂/TiCl₄/THF and played an orientation role which was favorable to the deposition and dispersion of MgCl₂/TiCl₄/THF. Meanwhile, the well deposition and dispersion of MgCl₂/TiCl₄/THF are favorable for the increase of active site number and the uniform distribution of activation sites. During ethylene polymerization, the increase in activation site amount brings high catalytic activity. The uniform distribution of activation sites is benefit to the homogeneous fragmentation of catalyst grains and forms stacked polymer fragments which brings high bulk density. Also, with high catalytic activity, the catalyst grain can grow larger, which decreases the percentage of polymer particles smaller than 150 μm. A low DMDS/SiO₂ ratio can not provide adequate orientation role, while a high DMDS/SiO₂ ratio may act as poison to activation site. High activity catalyst with high polymer bulk density and low percentage of polymer powder can be obtained at the DMDS/SiO₂ ratio of 0.10 mL/g.

![Fig. 3 Energy dispersive X-ray analysis (EDX) of new catalyst section](image)

| Run | DMDS/SiO₂ (mL/g) | Activity (g PE/g Cat) | Bulk density (g/cm³) | Powder smaller than 150 μm (wt%) |
|-----|------------------|-----------------------|---------------------|-------------------------------|
| 1   | 0                | 3536                  | 0.308               | 3.52                          |
| 2   | 0.05             | 4087                  | 0.332               | 2.84                          |
| 3   | 0.1              | 5818                  | 0.351               | 2.34                          |
| 4   | 0.2              | 3883                  | 0.362               | 3.29                          |
| 5   | 0.3              | 3004                  | 0.368               | 3.31                          |

**Comparison of Hydrogen Response Ability**

Hydrogen was used as chain-transfer agent in the low-pressure olefin polymerization process over the Ziegler-Natta catalyst. The presence of hydrogen affects both product’s molecular weight and catalytic activity. The comparison of hydrogen effects on the new catalyst and the commercial M catalyst is listed in Table 3. The melt index (MI) is a parameter commonly used for indicating molecular weight distribution. The polymer produced with the new catalyst seems to have higher melt index than that produced with the commercial M catalyst, which may indicate that the new catalyst has better hydrogen response ability than the commercial M catalyst. The polymer bulk density for the new catalyst is higher than that for the commercial M catalyst, and the catalytic activity of the new catalyst is almost twice as that of the commercial M catalyst. The polymer powder obtained with the new catalyst at the given reaction conditions is due to the low catalytic activity of ethylene slurry polymerization. With higher catalytic activity in fluidized bed of ethylene polymerization, the percentage of polymer powder is anticipated to reduce with the growth of small catalyst grains to larger ones.
Table 3. Effects of hydrogen/ethylene molar ratio on catalytic properties

| Catalyst | H₂/乙烯 (MPa/MPa) | Activity (g PE/g Cat) | MI (g/10min) | Bulk density (g/cm³) | > 850 μm | 150–850 μm | < 150 μm |
|----------|------------------|-----------------------|--------------|---------------------|---------|------------|---------|
| M catalyst | 0/1.03          | 5692                  | –            | 0.308               | 8.74    | 90.03      | 1.23    |
|           | 0.28/0.75       | 3266                  | 1.13         | 0.316               | 5.27    | 92.76      | 1.97    |
|           | 0.38/0.65       | 2190                  | 2.87         | 0.318               | 1.97    | 94.16      | 3.87    |
| New catalyst | 0/1.03          | 11636                 | –            | 0.351               | 4.67    | 92.99      | 2.34    |
|           | 0.28/0.75       | 6250                  | 1.30         | 0.345               | 3.26    | 93.18      | 3.56    |
|           | 0.38/0.65       | 3706                  | 3.19         | 0.355               | 1.22    | 94.01      | 4.77    |

Copolymerization of Ethylene with 1-Hexene

The copolymers of ethylene with α-olefins have low density and good mechanical properties. The comonomer effect also affects catalytic activity and polymer performance. The effects of 1-hexene on catalytic properties are listed in Tables 4. The addition of 1-hexene plays a positive comonomer effect at relatively low concentrations but a negative comonomer effect at high concentrations on catalytic activity. With the addition of 1-hexene, the bulk density decreased a little. The superiority of the new catalyst in catalytic activity at high 1-hexene concentrations seems to be not so obvious as that at low 1-hexene concentrations, but it is still higher than that of the commercial M catalyst.

Table 4. Effects of 1-hexene loading on catalytic properties

| Catalyst | 1-Hexene (mL/L) | Activity (g PE/g Cat) | MI (g/10min) | Bulk density (g/cm³) | > 850 μm | 150–850 μm | < 150 μm |
|----------|----------------|-----------------------|--------------|---------------------|---------|------------|---------|
| M catalyst | 0              | 3266                  | 1.13         | 0.316               | 5.27    | 92.76      | 1.97    |
|           | 1              | 3856                  | 0.28         | 0.315               | 6.35    | 91.97      | 1.68    |
|           | 4              | 4074                  | 1.20         | 0.307               | 7.13    | 91.11      | 1.76    |
|           | 10             | 2310                  | 1.78         | 0.312               | 1.57    | 93.85      | 4.58    |
| New catalyst | 0              | 6250                  | 1.30         | 0.345               | 3.26    | 93.18      | 3.56    |
|           | 1              | 7650                  | 0.87         | 0.361               | 3.78    | 93.33      | 2.89    |
|           | 4              | 5308                  | 0.37         | 0.355               | 3.47    | 93.18      | 3.35    |
|           | 10             | 3326                  | 1.17         | 0.352               | 1.35    | 93.52      | 5.13    |

Kinetic Profiles of the New Catalyst and the Commercial M Catalyst

The rate profiles obtained during slurry copolymerization of ethylene and 1-hexene with new catalyst and commercial M catalyst are shown in Fig. 4. It can be seen that the new catalyst has higher catalytic activity. In addition, the kinetic profile are different, the activation of the small particles is faster than that of the large ones. It is probably because of the higher resistance to mass transfer in the larger particles.

Fig. 4 Kinetic profiles obtained during slurry ethylene/1-hexene copolymerization
Pilot Polymerization in Fluidized Bed

The pilot polymerization was carried out in gas fluidized bed ethylene polymerization reactor in Daqing Chemical Research Center with the process conditions: temperature 88.0°C, total pressure 2.0 MPa, ethylene pressure 0.6–0.7 MPa, mole ratio of 1-butene to ethylene 0.44, mole ratio of hydrocarbon to ethylene 0.20 and residence time 1.5–2 h. Processing parameters were adjusted to produce linear low density polyethylene with density 0.918 g/cm³ and MI (melt index) 2.0 g/10min. Properties of the polymers are listed in Tables 5 and 6.

| Table 5. Properties of polymers obtained from pilot gas fluidized bed polymerization |
|----------------------------------|------|-------------------|-------------------|-------------------------|
| Catalyst                        | Activity (g PE/g Cat) | Bulk density (g/cm³) | Density (g/cm³) | Particle distribution (wt%) |
| M catalyst                      | 4056 | 0.340             | 0.9208           | > 850 µm: 11.76, 150–850 µm: 87.17, < 150 µm: 0.95 |
| New catalyst                    | 8083 | 0.381             | 0.9195           | > 850 µm: 13.27, 150–850 µm: 85.78, < 150 µm: 0.95 |

| Table 6. GPC and 13C-NMR analyses of polymers from pilot polymerization |
|----------------------------------|------------------|------------------|------------------|
| Catalyst                        | GPC              | 13C-NMR          |
|                                  | $M_w$ (g/mol) | $M_n$ (g/mol) | $M_w/M_n$ | Butyl (wt%) | Ethyl (wt%) |
| M catalyst                      | 113201          | 28610           | 3.96         | 7.88        | 92.12       |
| New catalyst                    | 113640          | 29784           | 3.82         | 7.94        | 92.06       |

The pilot polymerization results showed that the polymer prepared with the new catalyst is similar to that with the commercial M catalyst in performance, such as melt index, density and molecular weight distribution. More importantly, the catalytic activity of the new catalyst is twice as that of the commercial M catalyst, the polymer bulk density of new catalyst is 0.38 g/cm³ while that of the commercial M catalyst is 0.32 g/cm³. The percentage of polymer particles smaller than 150 µm in the cast of the new catalyst is lower than that in the case of commercial M catalyst.

CONCLUSIONS

With dimethyl dichlorosilane modified silica, a high activity Ziegler-Natta polyethylene catalyst with good hydrogen response and copolymerization performance was prepared. In fluidized bed polymerization process, the new catalyst gave catalytic activity up to 8000 g of polyethylene per gram of catalyst, the polymer bulk density of the product was 0.38 g/cm³ and the percentage of polymer particles smaller than 150 µm was 0.95%. The new catalyst is suitable for condensed and super-condensed process in fluidized bed ethylene polymerization because of its high activity, high polymer bulk density and low small particle percentage. The silica support plays an important function in determining the properties of the catalyst.

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