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A Facile One-Step Method for Spherical Support Preparation of Ziegler-Natta Catalyst

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ABSTRACT: This study reports a novel one-step method to synthesize a new spherical support for Ziegler-Natta catalyst under moderate condition. The support is obtained from a dispersion system where the particle stabilizer polyvinylpyrrolidone plays a main role to stabilize the spherical particles. The new chemical of the support is $CH_3CH_2OMgOCH(CH_2Cl)_2$, which is first reported here, has been approved by newly filed patents and also confirmed by solution NMR, solid state NMR, pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), and ICP-MS. The support and catalyst particles have uniform distributions. The catalyst prepared from this support has been evaluated with high activity. The polypropylene obtained has high isotacticity. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41014.

KEYWORDS: catalysts; polypropylene (PP); supports; Ziegler-Natta polymerization

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INTRODUCTION

Ziegler-Natta catalysts supported on spherical $MgCl_2{\cdot}nCH_3CH_2OH$ adducts has made great progress in controlling polypropylene (PP) morphology as spherical particles. Catalysts supported on spherical $MgCl_2{\cdot}nCH_3CH_2OH$ adducts not only simplify the polyolefin production processes but also can yield many tailor-made polymers.[1–5] The method of preparing the $MgCl_2{\cdot}nCH_3CH_2OH$ support, especially the nature of the support, immensely influences the catalytic activity through porosity.[6] Generally, spherical $MgCl_2{\cdot}nCH_3CH_2OH$ support is recrystallized from a mixture of ethanol, methyl siloxane oil, and paraffin oil in a system at low temperature. In this typical system, $MgCl_2$ is dissolved in the mixture of ethanol and paraffin oil at a temperature of 125°C and then dispersed in the methyl siloxane oil at the same temperature. Under high stir rate, $MgCl_2{\cdot}nCH_3CH_2OH$ solution is dispersed as small drops with wide size distribution in the oil system, then the resultant mixture is introduced into *n*-hexane at −30°C and $MgCl_2{\cdot}nCH_3CH_2OH$ adducts are recrystallized as spherical particles.[7,8] This procedure is a classical system to produce spherical $MgCl_2{\cdot}nCH_3CH_2OH$ support but seems more or less complicated. The researchers have spent much time to develop simple methods to prepare spherical $MgCl_2$ support in the past decades; however, there is no exciting news.

Our group has been searching new supported catalyst for propylene polymerization for several decades. Here we report recent progress of the project in which we applied a novel dispersion system and synthesized a new spherical support from a one-step method under a moderate temperature of 80°C. The chemical composition of the support is new and unique, which has been confirmed by solution NMR, solid state NMR, Py-GC-MS, and ICP-MS.

EXPERIMENTAL

Materials

All chemicals except deuterated solvents were purchased from Sinopharm Chemical Reagent, Beijing, and were used as received, unless mentioned otherwise. *n*-hexane, *n*-heptane, and *n*-decane were dried and stored over molecular sieve 4 Å. Deuterated solvents for NMR measurements were obtained from Cambridge Isotope Laboratories. All manipulations with air and moisture-sensitive compounds were carried out under nitrogen atmosphere in a glove box.

Synthesis of Support

In a 0.5-L glass autoclave with a mechanical stirrer, 22 g anhydrous $MgCl_2$, 162 mL anhydrous ethanol, and 2.25 g polyvinylpyrrolidone (PVP, Mw = 10,000) were added and heated at 80°C for 1 hour until the $MgCl_2$ and PVP were dissolved in ethanol, and then 72.5 mL epichlorohydrin was added to this

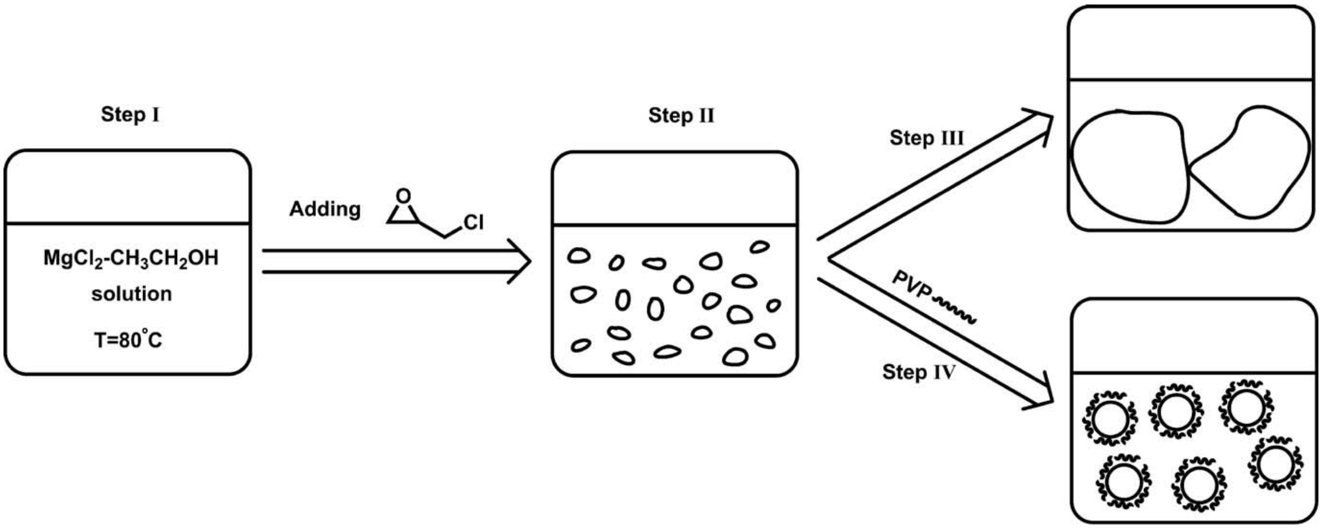


Figure 1. The sketch of the support preparation.

system. The dispersion formed right after the addition of epichlorohydrin. After 30 minutes, the liquid was removed and the obtained support particles were washed with *n*-hexane three times. The particles obtained were dried in vacuo at room temperature.

Preparation of Catalyst

Before the catalyst preparation, the support (16 g) obtained above was pretreated with titanium ethoxide (4 mL) in *n*-hexane at the temperature from −10°C to 60°C. Then, $TiCl_4$ (100 mL) was added into a 300 mL glass reactor with a reflux condenser, and it was cooled at −20°C. After 8 g pretreatment support was added, the mixture was heated to 110°C. In the heating process, 1.5 mL of dibutyl phthalate was added to the reactor. After the liquid was removed, the obtained catalyst particles were washed with $TiCl_4$ two times and *n*-hexane three times. The obtained particles were dried in vacuo at room temperature.

Polymerization of Propylene

Under ultra high pure N_2 atmosphere, 2.3 L propylene, 2.5 mmol aluminum triethyl (solution in 5 mL *n*-hexane), 0.1 mmol cyclohexyl methyl dimethoxy silane (solution in 1 mL *n*-hexane), 10 mg catalyst, and 1.5 L H_2 were added into a 5 L stainless steel autoclave in turn. The polymerization was carried out at 70°C for 1 hour, and PP particles were obtained.

Characterization

The ^{1}H NMR spectrum of the new compound was recorded on a Bruker AVANCE 300 spectrometer and the compound was dissolved in the mixture of deuterated toluene and triisobutyl phosphate. Solid state ^{13}C NMR spectrum of the compound was recorded on a Bruker AVANCEIII 400 spectrometer. The high temperature ^{13}C NMR spectrum was recorded on a 400 MHz Bruker AVANCEIII spectrometer to measure the tacticity of PP obtained. The sample was dissolved in deuterated 1,2-dichlorobenzene at 125°C. Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) test of the compound was carried out using Trace GC Ultra/DSQ II from Thermo Fisher. Mg content in the compound was determined using Agilent ICP-MS 7500CX spectrometry. Optical microscope images were taken using Nikon ECLIPSE E200. Particle size and particle size distribution (PSD) were determined by Masters Sizer 2000 from Malvern Instruments. The porosities of catalyst were determined using AutoChem 2920 from MICROMERITICS. The porosities of PP particles were determined using PoreMasterGT 60. The molecular weight of PP obtained was measured using Waters Alliance GPCV2000 Gel Permeation Chromatography. The PP sample was dissolved in 1,2,4-trichlorobenzene at 150°C. Melt mass-flow rate test was carried out using the standard of ASTMD1238-99.

RESULTS AND DISCUSSION

Design of the New Support Preparation Method

We are stimulated by the traditional dispersion polymerization process during the preparation of the novel support. In the traditional dispersion polymerization process, an initially homogeneous system composes of monomer, organic solvent, initiator, and particle stabilizer (usually uncharged polymers such as PVP). The system becomes heterogeneous on polymerization because the polymer is insoluble in the solvent. Polymer particles are stabilized by adsorption of the particle stabilizer.[9] Dispersion polymerization usually yields polymer particles with sizes about 1–10 μm in diameter. In our system, an initially homogeneous system composes of $MgCl_2$, organic solvent ethanol, and particle stabilizer PVP under the temperature of 80°C (as indicated in the step I of the Figure 1). The system becomes heterogeneous on adding epichlorohydrin because the new chemical formed is insoluble in the solvent (as indicated in the step II of the Figure 1). The newly formed particles are stabilized by adsorption of the particle stabilizer, PVP. PVP protected the particles from further contacting and precipitating. Therefore perfect spherical particles were fall down from the dispersion system (as indicated in the step IV of Figure 1). The particle size yield from our new method with sizes about 20–80 μm in diameter.

In our new system, three common compounds are selected which were widely used in Ziegler-Natta catalyst system–$MgCl_2$,

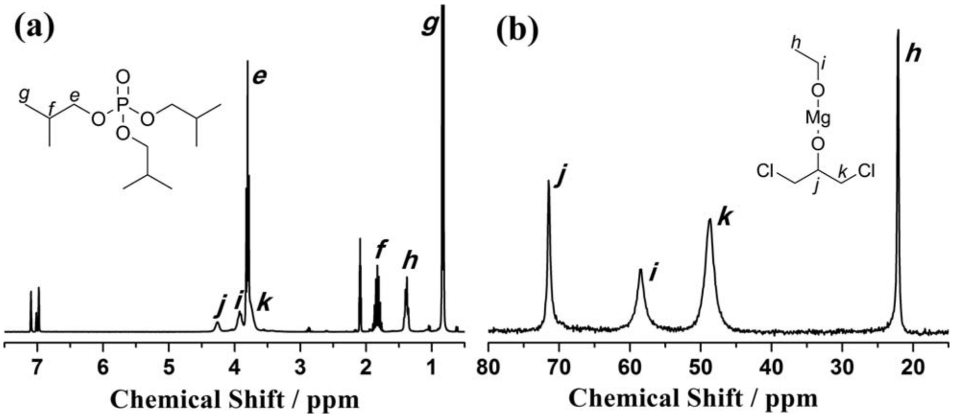


Figure 2. (a) ^{1}H NMR and (b) solid ^{13}C NMR spectrum of support.

ethanol, and epichlorohydrin. The PVP was also the common particle stabilizer in dispersion polymerization. The use of PVP in our system is crucial to obtain perfect spherical particles with relatively narrow particle size distribution. A parallel experiment has been carried out with no PVP. Many particles are conglutinated with each other and the precipitates are formed with much bigger size and irregular shape (as indicated in the step III of the Figure 1).

The procedure of traditional system to prepare spherical $MgCl_2 \cdot nCH_3CH_2OH$ support can be divided into the following four steps. First, in reactor 1, a certain amount of $MgCl_2$ is completely dissolved in the mixture of ethanol and paraffin oil at a temperature of about 125°C. Second, the mixture in the first reactor is transferred into reactor 2 to form dispersion within which a certain volume of methyl siloxane oil is heated at about 125°C. Third, the resultant mixture is introduced into *n*-hexane at −30°C in reactor 3, and $MgCl_2 \cdot nCH_3CH_2OH$ is recrystallized. Fourth, the solid particles are transferred into reactor 4 and rinsed with *n*-hexane and dried in vacuo.[7,8]

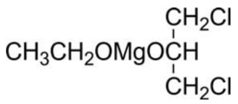
While in the new dispersion system to prepare spherical $CH_3CH_2OMgOCH(CH_2Cl)_2$ support, the whole process can be accomplished with only one reactor. Besides, in the new dispersion system, the whole process can be achieved at a moderate temperature of 80°C. The new procedure is simple, efficient and energy saving.

Characterization of the New Chemical

Figure 2(a) shows the ^{1}H NMR spectrum of the new chemical which dissolved in the mixture of triisobutyl phosphate and deuterated toluene. The peak at 2.07 ppm is because of the residual proton signal from the deuterated toluene. The three resonances with chemical shift values of 0.83, 1.81, 3.79 ppm are because of the proton atom of the solvent of triisobutyl phosphate. The integral values are: $H(g) = 15.92$, $H(f) = 2.64$, $H(e) = 2 \times H(f) = 5.28$, respectively. Four resonances with chemical shift values of 1.36, 3.91, 4.24, 3.79 ppm come from the proton atoms of h, i, j, k of the new chemical, $CH_3CH_2OMgOCH(CH_2Cl)_2$. This new chemical is first reported here which has been approved by newly filed patents.[10] The structure of the new chemical is depictured in scheme 1. The integral value ($H(h) = 3.01$, $H(i) = 2.04$, $H(j) = 1.00$, $H(k) = 4.00$) further confirmed the structure of the new chemical. Figure 2(b) shows the solid ^{13}C NMR spectrum of the new chemical. The four resonances with ^{13}C chemical shift values of 22.2, 48.7, 58.4, and 71.5 ppm can be assigned as four types of carbon atom signals of h, k, i, j, respectively. These peaks assignment of the solid state NMR confirm again the structure of the new chemical. The MS peaks in Py-GC-MS also indicates the existence of groups $[CH_3CH_2O]$ and $[(CH_2Cl)_2CHO]$ in the compound. Py-GC-MS (EI-MS) *m/z* (%): 31 $[CH_2OH]^+$ (100%), 45 $[CH_3CH_2O]^+$ (92), 79 $[CH_2ClCHOH]^+$ (100%), 81 $[CH_2ClCHOH+2]^+$ (32). ICP-MS test shows the Mg content in the compound was 12.2 wt %, which is close to the theoretical value (12.1 wt %) of $CH_3CH_2OMgOCH(CH_2Cl)_2$. It should be mentioned here that another possible product of the ring opening reaction of epichlorohydrin with CH_3CH_2OMgCl, i.e., $CH_3CH_2OMgOCH_2CH(Cl)CH_2Cl$, is not observed. Therefore the ring opening reaction is very selective.

Morphologies

The new support has been made to catalyst, and the catalyst is used for propylene polymerization to get PP particles. Optical microscope images of the support, catalyst, and PP formed are shown in Figure 3. The particles are in perfectly spherical shape and none of the particles are agglomerated. The shape of the PP formed is related to the shape of the catalyst and also the shape of the support. This is a typical duplication phenomenon in Ziegler-Natta catalyst and polymerization which is very important for many kinds of manufacturing techniques.[1–3,11–14] Another characteristic of the new support is that the PSD is very narrow, about 0.70. The benefit of the narrow PSD is that the screening step is not needed and the uniform support can be made to catalyst directly. As for spherical support made by the traditional method mentioned above, because the PSD of the support is wide, so a screening step is needed to obtain uniform particles before the catalyst preparation. Particles with too small or too large diameters must be abandoned before preparing the catalyst. Catalysts made from small support particles



$$CH_3CH_2OMgO\overset{\overset{\displaystyle CH_2Cl}{|}}{\underset{\underset{\displaystyle CH_2Cl}{|}}{C}}H$$

Scheme 1. The chemical composition of the new support.

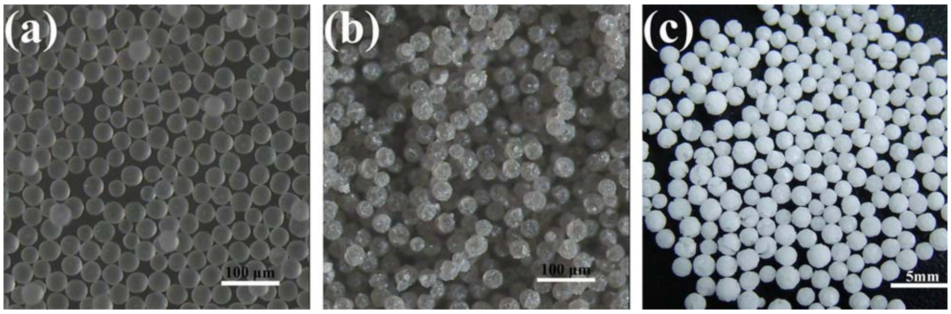


Figure 3. Optical microscope images of (a) support, (b) catalyst, and (c) PP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

will bring about much fines during polymerization while catalysts made from large support particles break easily during the polymerization because of nonuniform stress. The existence of the screening step will certainly lead to reducing of the catalyst production, and another serious problem is the post-treatment of the abandoned support. These above problems are going along with the traditional system for decades but there are no good methods to solve them. In our new support preparation system, these troublesome problems would be solved because the support obtained from our new system distribute uniformly.

It is noted that because there does not exist the screening step, the supports do not need to be dried after preparation and can be prepared to catalysts directly, so both the preparation of supports and catalysts can be connected and conducted in one set of system. This is also very important, efficient, and economical for industrial production because drying process is tough and time-consuming.

Catalyst Performance

The activity of the obtained catalyst is about 46.4 kg PP (g cat h)$^{-1}$ in propylene bulk polymerization. BET surface area analysis of catalyst shows a surface area of 444 m^2 g^{-1}, which is extremely high for a polymerization catalyst. The catalyst exhibits an average pore diameter of 32.7 Å and average pore volume of 0.37 cm^3 g^{-1}, while the surface area of most conventional $MgCl_2$-supported PP catalyst was lower than 300 m^2 g^{-1} and exhibits an average pore diameter of 37.3 Å and average pore volume of 0.28 cm^3 g^{-1}.[16] As for our catalyst, Pore size distribution analysis of active catalyst indicates that a major contribution from mesopores in a close pore diameter range of 30−50 Å occurs. The size and size distribution of pore in catalyst is suitable for the diffusion of propylene and stable occurrence of polymerization. High surface area could be the main reason for the high polymerization activity.

The Properties of the PP Obtained via New Catalyst

Mercury porosimetry analysis of PP particles shows a surface area of 11.28 m^2 g^{-1}, an average pore diameter of 0.09 μm and average pore volume of 0.26 cm^3 g^{-1}. Pore size distribution analysis of PP particles indicates that a major contribution from macropores occurs. The formation of macropores in PP particles could be attributed to the fragmentation of $MgCl_2$ supported catalyst and growth of primary PP particles on the primary small $MgCl_2$ crystallites from fragmentation of $MgCl_2$ supported catalyst. The melt mass-flow rate (230°C /2.16 kg) was 7.53 g/10 min and solubility in boiling n-heptane was 2.01 wt %. The percentage of mm triads and mmmm pentads determined by high temperature NMR are 96.0 and 92.2 mol %, which means the obtained PP owns high isotacticity.[16] The Mn and Mw of PP are 77,250 and 494,000 g/mol, respectively, and the molecular weight distribution is 6.39.

CONCLUSION

In conclusion, a novel and facile one-step method for preparing spherical Mg-contained support used for Ziegler-Natta catalyst was developed. The characteristics of the novel support as well as the catalyst obtained are:

1. A new spherical support has been synthesized using a dispersion system where the particle stabilizer PVP plays a main role to stabilize the spherical particles.
2. The spherical support is synthesized from a one-step method under a moderate temperature of 80°C which greatly simplifies the support preparation process.
3. The chemical of the support is new and unique, deduced as $CH_3CH_2OMgOCH(CH_2Cl)_2$, which was confirmed by solution NMR, solid state NMR, Py-GC-MS, and ICP-MS.
4. The support and catalyst particles are in perfectly spherical shape with narrow PSD, therefore, the support can be made to catalyst directly without screening, which will increase the catalyst production and reduce post-treatment problems.
5. The catalyst prepared from the new support owns high surface area than the most PP catalyst reported before and exhibits high activity in propylene polymerization.
6. The PP obtained has high isotacticity.

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