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Supporting a Metallocene on Functional Polypropylene Granules for Slurry Ethylene Polymerization

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ABSTRACT: We report on the exploration of functional polypropylene as supporting material for homogeneous metallocene catalyst. The copolymerization of propylene and 5-hexenyl-9-BBN by a spherical $MgCl_2$-supported $TiCl_4$ catalyst containing diisobutyl phthalate internal electron donor combined with $AlEt_3$ activator and dimethoxydiphenylsilane external donor afforded isotactic polypropylene granules bearing reactive alkyl-9-BBN groups, which, upon being treated with H_2O_2/NaOH, resulted in polypropylene granules containing hydroxy functionality. Immobilization of Cp_2ZrCl_2/MAO was then conducted in toluene solution at an elevated temperature following the procedure of treating the hydroxyl-containing polymers sequentially with MAO and Cp_2ZrCl_2. Elemental analysis of the Zr contents of the supported catalysts reveals that they are proportional to the concentrations of hydroxy group on the support. In turn, the efficiency of the supported catalysts in slurry ethylene polymerization also exhibits a significant dependency on the hydroxy group concentration: the higher the concentration, the higher the polymerization efficiency. The polymers produced by the functional polypropylene-supported catalysts possess improved apparent morphology as compared with those by the homogeneous catalyst as well as by the hydroxyl-free, net polypropylene-supported one.

Introduction

One of the most exciting achievements in catalysis field in the past two decades should be the advent and the then fast development of metallocene complexes as catalysts for olefin polymerization. Because of their great combination of high activity and the possibility of tailoring polymer properties such as molecular weight and molecular weight distribution, comonomer incorporation and distribution, and stereoregularity by simply tuning the structure of the catalyst, metallocenes have proven themselves attractive and promising catalysts for olefin polymerization in the new century. As such, great efforts aiming for industrialization of these valuable catalysts are being taken in both academic and industrial laboratories.[1] Owing to their homogeneous nature in solution, one of the indispensable procedures that metallocene catalysts have to go through before they can be applied in industrial “drop-in” polyolefin production is the heterogenization process that immobilizes the soluble metallocene catalysts on a solid carrier to, on one hand, prevent reactor fouling associated generally with soluble catalyst systems and, on the other hand, control morphology of the resulting polymer to facilitate the subsequent polymer working up process.[2]

Traditional supports for metallocenes are high surface area inorganic materials, such as SiO_2, Al_2O_3, or $MgCl_2$, etc.[3] However, inorganic supports having rigid and polar surfaces are known to present incompatible environment for homogeneous catalysts that may to some extent restrict the performance of the catalyst. In contrast, organic supports based on some hydrocarbon polymers with sufficient chain flexibility provide analogous environment as that prevailing in homogeneous polymerization that greatly reduce the negative support effect on the properties of the catalyst and are now receiving more and more attention.[4] To date, polystyrene-based polymers are the mostly studied polymeric materials used as support of metallocene catatlyst.[5] This is mainly due to (i) their good solubility and flexibility in functionalization that favor a facile introduction and homogeneous distribution of the desired catalyst-anchoring sites across the support particle from exterior to interior and (ii) the excellent availability of several convenient methods for the controlled particle formation (via cross-linking reaction) to provide insoluble support with good swellability. These wonderful merits of polystyrene-based polymeric supports ensure the anchoring of the catalyst occurring effectively in the inner of the swellable support particle and therefore will greatly benefit the support fragmentation process during polymerization that has a major influence on the activity of the catalyst and the uniformity of the product.[6]

Polyolefins are crystallizable polymers that possess good chemical and physical stabilities. The semicrystalline nature determines that they are insoluble but swellable in hydrocarbon solvents like toluene at some elevated temperatures. With desired forms, they are potentially applicable as supporting materials for met-

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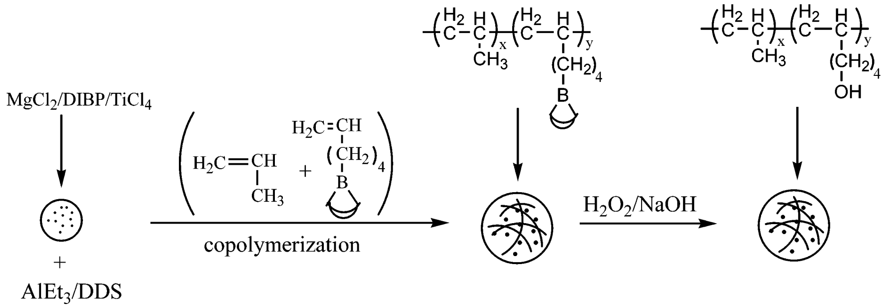


Figure 1. Schematic representation of the formation of the hydroxylated polypropylene support.

allocene catalyst. In fact, a number of technical patents[7] have been issued claiming the preparation of heterogeneous metallocene catalysts using polyolefins as support. One representative example[7a] is a gas-phase catalyst supported on granular polyethylene (PE) powder for ethylene copolymerization. Another one is the supporting of a metallocene on granulated polypropylene (PP) for gas-phase production of ethylene−propylene elastomer.[7b] However, because of the lack of functional groups on polyolefin chains, there are no evident catalyst anchoring sites existing on polyolefin support, and as the result, the loading mechanism of metallocene is merely physical absorption instead of chemical bonding. This often causes (i) very small amount of catalyst loading and (ii) ready detachment of catalyst components from the support when the polymerization is conducted in the presence of liquid medium or monomers as in slurry reaction, and so the application of polyolefin-supported metallocene catalysts is usually restricted to gas-phase polymerization.

In recent years, the many disadvantages of polyolefin materials that are caused by their inert nature have become more and more prominent as efforts aiming to promote their overall properties in order to further broaden their application areas were made in all aspects. As such intensive researches dedicated to introduction of polar functionality to polyolefins have been conducted by employing versatile chemical approaches.[8] Among them, Chung's unique combination of Ziegler−Natta polymerization and borane chemistry has resulted in one of the most effective methods that can bring up functional polyolefins with a variety of functional groups in a controlled manner.[9] One of the expanded application areas of polyolefin materials after functionalization is deemed in the immobilization of soluble catalysts via chemical bonds and has been exemplified by using polypropylene containing hydroxy groups to support Lewis acids such as $EtAlCl_2$ and BF_3 for cationic polymerization.[10]

Results and Discussion

In this paper, we present the results of our recent research on the application of functional polyolefin to the immobilization of homogeneous metallocene catalyst for olefin polymerization. Hydroxylated polypropylene (PP-OH) granules with controlled amount of hydroxy functionality, resembling porous inorganic SiO_2 particles, were used as support to chemically bond Cp_2ZrCl_2 in toluene solution. The thus-prepared supported catalysts were then studied in slurry ethylene polymerization with emphasis on the effect of the presence of hydroxy groups on the support on catalyst activity and productivity and morphology of the obtained polyethylene.

Preparation and Characterization of the Support. Although polypropylene polymers having excellent processability are easy to be fabricated into many desired forms, in the current study the polymer fabrication process was exempted, and the granular polypropylene support was obtained directly in the process of propylene polymerization with a spherical Ziegler−Natta catalyst via a catalyst/polymer replication effect.[11] As schemed in Figure 1, a spherical $MgCl_2$-supported Ziegler−Natta catalyst was combined with $AlEt_3$ activator and dimethoxydiphenylsilane (DDS) external donor to copolymerize propylene and an alkylborane-containing α-olefin monomer (borane monomer) to obtain polypropylene granules containing bulky alkyl-9-BBN side groups. Upon being treated with H_2O_2/NaOH for the oxidation and hydroxylation of the incorporated borane groups, the borane-containing polypropylene granules were quantitatively transformed to hydroxyl-functionalized polypropylene without any alteration of their apparent morphology. As already mentioned above, the functionalization of polyolefins by using borane reagents has been extensively studied and described in numerous papers published by Chung and co-workers.[9] Borane monomers such as 5-hexenyl-9-BBN have been copolymerized with propylene by $TiCl_3$·AA/$AlEt_2Cl$ catalyst.[15c] However, it is reasonable to believe that the fourth-generation, spherical $MgCl_2$-supported Ziegler−Natta catalyst would perform much better than $TiCl_3$·AA/$AlEt_2Cl$ for this copolymerization.

The $MgCl_2$-supported Ziegler−Natta catalyst was prepared by treating $MgCl_2 \cdot C_2H_5OH$ complex spheres with excess $TiCl_4$ in the presence of diisobutyl phthalate (DIBP). This catalyst presents spherical form (illustrated by SEM in Figure 2) with an average diameter of 20 μm. The copolymerization runs of propylene and 5-hexenyl-9-BBN with this catalyst were carried out in toluene solution at 50 °C by slowly flowing propylene gas (pressure 1.013×10^5 Pa) into the glass flasks containing the catalyst, the cocatalyst, the external donor, and the borane monomer. After a certain period of time, the reaction flasks were cooled to 0 °C to allow the addition of H_2O_2/NaOH. The hydroxylated polypropylene (PP-OH) products were collected by filtration followed by a thorough purification as described in the Experimental Section.

As expected, all polymerization runs resulted in homogeneously distributed polymer granules. As is exemplified in Figure 2 which shows the comparison of SEM photographs between a representative PP-OH polymer granule (support PPOH-2 in Table 1) and the original $MgCl_2$/DIBP/$TiCl_4$ catalyst spheres, the obtained polypropylene polymers duplicate the morphology of the catalyst fairly well and present spherical granules with good size uniformity, providing the ap-

Table 1. Preparation Conditions[a] and Characterization Results of the Polypropylene Supports

run no.	obtained support no.	B-monomer[b] in feed (mmol)	yield (g)	B-monomer conv (%)	[OH−] (mol %)	M_w (g/mol)	PDI (M_w/M_n)	T_m (°C)	ΔH_f (J/g)	S_g[c] (m^2/g)
1	net PP	0	15.2		0	341 014	7.5	163.3	83.8	16.5
2	PPOH-1	5.0	14.5	38.1	0.57	392 378	6.7	161.1	72.1	17.4
3	PPOH-2	15.0	14.5	39.8	1.81	443 794	7.5	158.0	68.7	18.6
4	PPOH-3	25.0	16.1	40.8	2.70	318 615	5.2	153.6	62.7	18.9

[a] Propylene pressure = 1.013×10^5 Pa, [Ti] = 0.07 mmol, Al/Ti = 100, Si/Ti = 10, temperature = 40 °C, time = 1 h, solvent = 100 mL of heptane. [b] B-monomer = 5-hexenyl-9-BBN. [c] Specific surface area measured by the BET method.

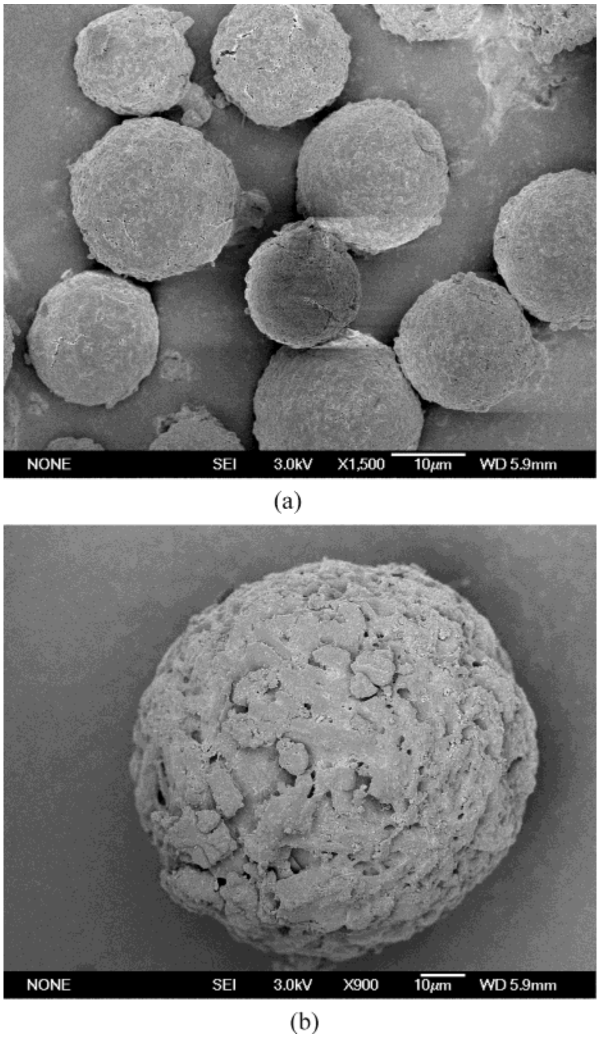


Figure 2. SEM photographs of (a) the $MgCl_2$/DIBP/$TiCl_4$ catalyst spheres (1500×) and (b) a PP-OH support granule (support PPOH-2 in Table 1) (900×).

propriate support prototype for metallocene. Following the above-described procedure, we prepared three granular PP-OH polymers with different OH contents by varying the molar ratio of propylene/5-hexenyl-9-BBN in the copolymerization reaction, along with a net, unfunctionalized polymer (net PP) that was polymerized in the absence of the borane monomer. It is worthy to note that all four polymers, originating from one and the same catalyst, exhibit quite similar average particle size (around 70 μm) and surface roughness, therefore ensuring a good comparability between them when being used as support.

The granular polymers were then subjected to analyses with NMR, viscometer, and DSC for a thorough characterization. Table 1 summarizes the detailed analytical results. Figure 3 compares ^{1}H NMR spectra between two PP-OH polymers (supports PPOH-1 and PPOH-2 in Table 1) and the net PP. As is observed, in addition to the three major peaks at 0.95, 1.35, and 1.65 ppm corresponding to the $C\mathbf{H}_3$, $C\mathbf{H}_2$, and $C\mathbf{H}$ protons in the PP backbone, there is, for the PP-*g*-OH polymers, a minor peak at 3.54 ppm that corresponds to $-C\mathbf{H}_2-$OH protons in the hydroxylated borane side groups, indicating clearly the existence of OH groups in the polymers. The OH content of each polymer was then calculated by comparing the integrated intensity of the peak at 3.54 ppm with that of the sum of the peaks at 0.95, 1.35, and 1.65 ppm with the number of protons each chemical shift embodies being taken into account.

In summary, by systematically increasing the comonomer feed ratio between 5-hexenyl-9-BBN/propylene, we obtained three PP-OH polymers in granular form having 0.57, 1.81, and 2.70 mol % of OH groups. These three polymers along with the net PP that was obtained under similar conditions show very close productivity, molecular weight, and molecular weight distribution. However, because the OH group is bored at the end of the short side chain of polypropylene molecule, the crystallization properties of PP-OH polymers are affected. As shown in Table 1 and illustrated in Figure 4, both the melting point (T_m) and thermal enthalpy (ΔH_f) of the PP-OH polymers are reduced as compared with those of the net PP. The higher the OH content, the lower the T_m and ΔH_f. The reduced T_m and ΔH_f suggesting enhanced solvent swellability are advantageous to the subsequent catalyst supporting process by allowing a more ready diffusion of the components of a metallocene catalyst (metallocene and MAO) into the inner of the polymeric support granule that is essential for the achievement of homogeneous distribution of the metallocene catalyst on the support and will benefit the catalyst-fragmentation process during polymerization.

Supporting the Metallocene. The supporting of the metallocene Cp_2ZrCl_2 on the functional PP-OH supports as well as the net PP was carried out directly with the as-polymerized polymer particles after they were fully deoxygenized and completely removed with moisture. Since the functional groups are acidic hydroxyls, the supports were treated with MAO first before they were brought into contact with the metallocene. For comparison's sake, the same operation was also performed on the net PP although it does not contain any functionality. The supporting process was set adequately long for a maximum loading of the metallocene. During this process, toluene was used as the suspension medium and the temperature was raised to 80 °C for a better swelling of the polymeric supports while still keeping their preformed solid shape. After the supported catalysts were obtained, ICP (inductively coupled plasma atomic emission spectroscopy) was used to determine their Zr loadings. The results were included in Table 2. Because ICP requires solution sample, the Zr needs to be removed from the support into solution to conduct the measurement. To ensure the high accuracy of the measuring results, we adopted an ultimate method for

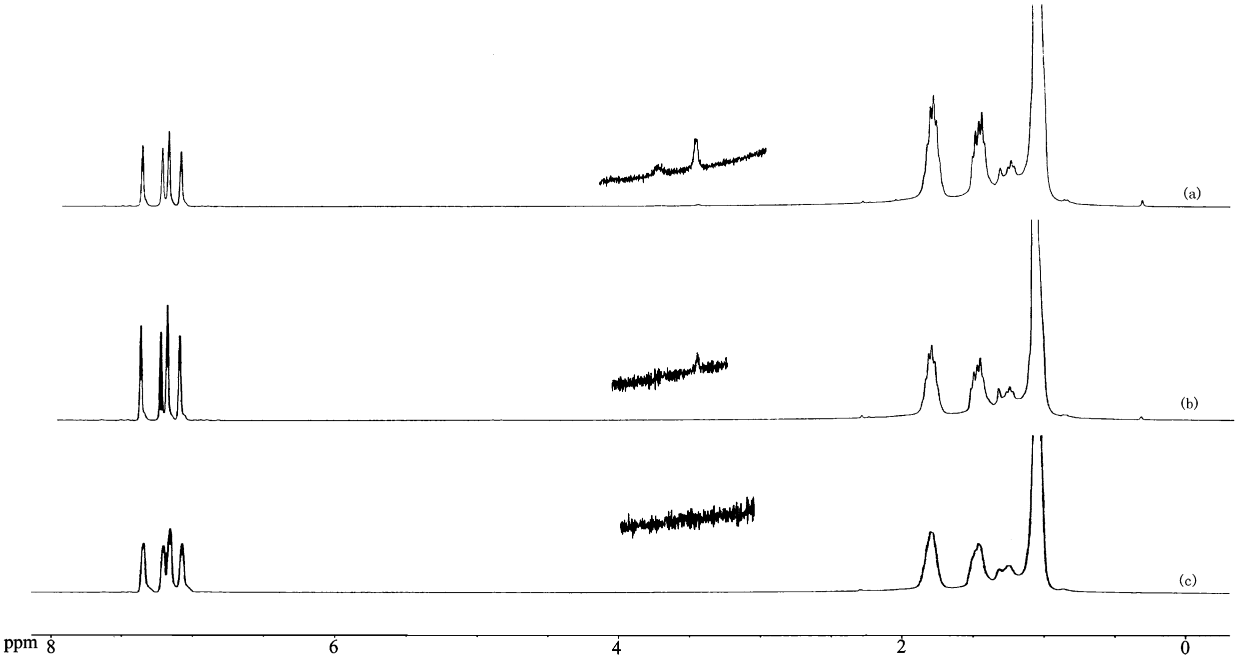


Figure 3. Comparison of ^{1}H NMR spectra between two PP-OH polymers containing (a) 1.81 mol % and (b) 0.57 mol % of OH groups and (c) net PP (solvent: $C_6D_4Cl_2$; temperature: 110 °C).

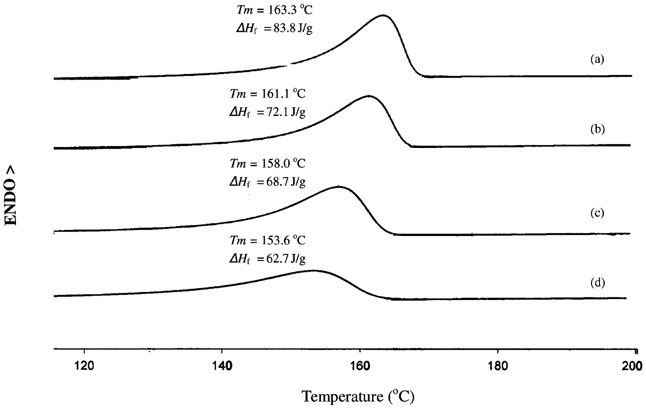


Figure 4. DSC curves of (a) net PP and PP-OH polymers, containing (b) 0.57, (c) 1.81, and (d) 2.70 mol % of OH groups.

the preparation of the solution samples, in which the supported catalysts with precisely measured amounts underwent extremely careful, stepwise treatment with hydrogen fluoride acid, high-temperature ablation, and nitric acid again to transform the solid sample to a clear solution one.

As shown in Table 2, the Zr loadings on the three functional PP supports are proportionally related to their corresponding OH− contents. The higher the OH− content, the higher the Zr loading, suggesting that the functional groups did play the role of catalyst-anchoring site. Only a very small amount of Zr was detected with the net PP support, which is much less than that supported on the functional PP containing the least amount of OH− group and is ascribed to physical absorption.

As a further evidence of the successful immobilization of metallocene with the PP-OH supports, XPS spectra were compared between the three PP-OH-supported catalysts containing 2.38, 3.54, and 4.40 μmol/g of Zr and the net PP-supported one. In fact, although Zr was detected by ICP method in the net PP-supported catalyst, it is hardly seen in the XPS spectrum of the same sample, due mainly to the very low Zr loading on the net PP support. To the contrary, Zr is clearly discerned in the spectra of the PP-OH-supported catalysts as a sharp peak at 182.3 eV corresponding to Zr 3d^5, of which the intensity increases with increasing the OH content of the support.

Ethylene Polymerization. Both the PP-OH-supported catalysts and the net PP-supported one were tested in ethylene polymerization under slurry reaction conditions. For a better understanding of the activity of the catalyst supported on the PP supports, the homogeneous polymerization of ethylene with Cp_2ZrCl_2/MAO was also performed under similar conditions for comparison. To carry out the polymerization reaction, a prefixed amount of catalyst was added into a 250 mL glass flask containing 100 mL of anhydrous toluene that was saturated by atmospheric pressure of ethylene at 50 °C. When no MAO was added, ethylene was hardly consumed, suggesting that the amount of MAO on the support was not high enough to activate the metallocene. External MAO was then added necessarily to initiate the polymerization. For each catalyst, the MAO/Zr ratio was varied in order to investigate its influence on the activities and productivities of the catalysts. The results are summarized in Table 2.

As expected, because only a very tiny amount of Zr was loaded on net PP, the obtained net PP-supported catalyst generally showed very low polymerization productivities, despite its relatively normal activity values. In contrast, owing to the much higher Zr loadings, some functional PP-supported catalysts exhibited satisfactory productivities when high MAO/Zr ratios (>3000) were adopted in the polymerization reaction. For example, at MAO/Zr = 7000, the PP-OH-supported catalyst loaded with 4.4 μmol/g of Zr polymerized ethylene at a productivity as high as 32.8 g PE/(g cat. h bar) (run no. 12 in Table 2), which is in sharp contrast to the poor productivity (only 1.1 g PE/(g cat. h bar)) obtained with the net PP-supported catalyst under the same reaction conditions (run 3 in Table 2).

It is very interesting to investigate the activities of the PP-OH-supported catalysts. As shown in Table 2,

Table 2. Summary of Conditions[a] and Results of Ethylene Polymerization with PP-OH-Supported and Net PP-Supported Cp_2ZrCl_2/MAO Catalysts

run no.	supported catalyst	Zr loading of the catalyst (μmol/g)	[Zr]/[OH] (mol/mol)	[MAO]/[Zr] (mol/mol)	productivity (g of PE/ (g of cat. h bar))	activity ($\times 10^6$ g of PE/ (g of Zr h bar))	M_w ($\times 10^4$ g/mol)	PDI (M_w/M_n)	T_m (°C)
1	net PP-Cp_2ZrCl_2	0.30		1000	n.g.				
2	net PP-Cp_2ZrCl_2	0.30		3000	0.5	0.775			
3	net PP-Cp_2ZrCl_2	0.30		7000	1.1	1.76			
4	PPOH-1-Cp_2ZrCl_2	2.38	0.018	1000	n.g.				
5	PPOH-1-Cp_2ZrCl_2	2.38	0.018	3000	0.9	0.378			
6	PPOH-1-Cp_2ZrCl_2	2.38	0.018	7000	8.7	3.66	10.9	2.56	133.9
7	PPOH-2-Cp_2ZrCl_2	3.54	0.008	1000	1.7	0.466			
8	PPOH-2-Cp_2ZrCl_2	3.54	0.008	3000	12.2	3.43	9.3	2.27	134.2
9	PPOH-2-Cp_2ZrCl_2	3.54	0.008	7000	19.8	5.59	11.7	2.73	134.5
10	PPOH-3-Cp_2ZrCl_2	4.40	0.007	1000	2.1	0.477			
11	PPOH-3-Cp_2ZrCl_2	4.40	0.007	3000	16.8	3.82	10.0	2.24	134.1
12	PPOH-3-Cp_2ZrCl_2	4.40	0.007	7000	32.4	7.36	12.0	2.86	134.6
control_1[b]	Cp_2ZrCl_2			1000		3.24	4.0	2.42	131.2
control_2[b]	Cp_2ZrCl_2			3000		5.16	3.9	2.28	132.1
control_3[b]	Cp_2ZrCl_2			7000		5.54	2.3	2.32	132.4

[a] Other conditions: ethylene pressure = 1.013×10^5 Pa (1 bar), supported catalyst = 0.2 g, temperature = 50 °C, time = 20 min, solvent = 100 mL of toluene. [b] Ethylene polymerization with homogeneous Cp_2ZrCl_2/MAO catalyst: [Zr] = 1.0×10^{-6} mol. Other conditions same as supported catalyst cases.

for the PP-OH-supported Cp_2ZrCl_2/MAO catalyst, their activities are greatly influenced by the MAO/Zr ratios. At MAO/Zr = 1000, all three supported catalysts showed poor activities as compared with the homogeneous catalyst, which resulted in poor productivities. By increasing MAO/Zr ratio from 1000 to 7000, all catalysts realized a nearly 1 order of magnitude increase of activity, which is much greater than in the case of the homogeneous catalyst. We assume that the presence of the acidic OH groups on the PP-OH supports may cause the deactivation of the catalyst while MAO may function as an electronic protecting group[8] that is able to prevent the catalyst from being deactivated. In that sense, more MAO will provide better protection of the functional group and thus helps to maintain the high activity of the catalyst. It is also very interesting to one by one compare the activities of the three PP-OH-supported catalysts at the same MAO/Zr ratios. As shown in the comparative reaction sets (runs 4, 7, and 10, runs 5, 8, and 11, and runs 6, 9, and 12), increasing the Zr loadings of the catalysts resulted in the increases of not only the polymerization productivities (g PE/(g cat. h bar)) but also the catalyst activities (in g PE/(g Zr h bar)). Considering the facts that the amounts of Zr loaded on the PP-OH supports increase with the increase of their OH contents and so does the supports' solvent swellability, we believe that the increased activities of the catalysts having higher Zr loadings are the results of better catalyst fragmentation during polymerization that favors the transformation of more Zr from potential sites to active sites. In fact, we had been concerned about the fragmentation during polymerization of the PP-OH supported catalysts because of their semicrystalline property that might handicap the catalyst fragmentation process and prevent the Zr (especially those in the interior) from being extensively exposed to transform to active sites, which consequently would cause not only low catalyst activity but also poor polymer morphology.[6] With in hand the information on catalyst activity increasing with the increase of the Zr loadings of the supported catalysts, we were aware that the PP-OH supported catalysts possessed good fragmentability, and so good polymer morphology produced by them was expectable. It is worthy to note that the catalyst with 4.40 μmol/g of Zr loading reached an activity of 7.36×10^6 g PE/(g Zr h bar) at MAO/Zr = 7000 (run 12 in Table 2), which is at the same level as that of the homogeneous catalyst under similar reaction conditions (5.54×10^6 g PE/(g Zr h bar), run 15 in Table 2), adequately embodying the concept of heterogeneous polymerization in a microscopically homogeneous environment by using polymeric support.[4a]

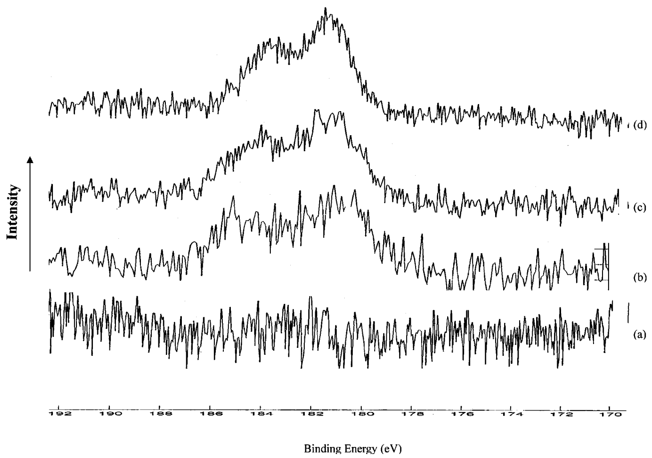
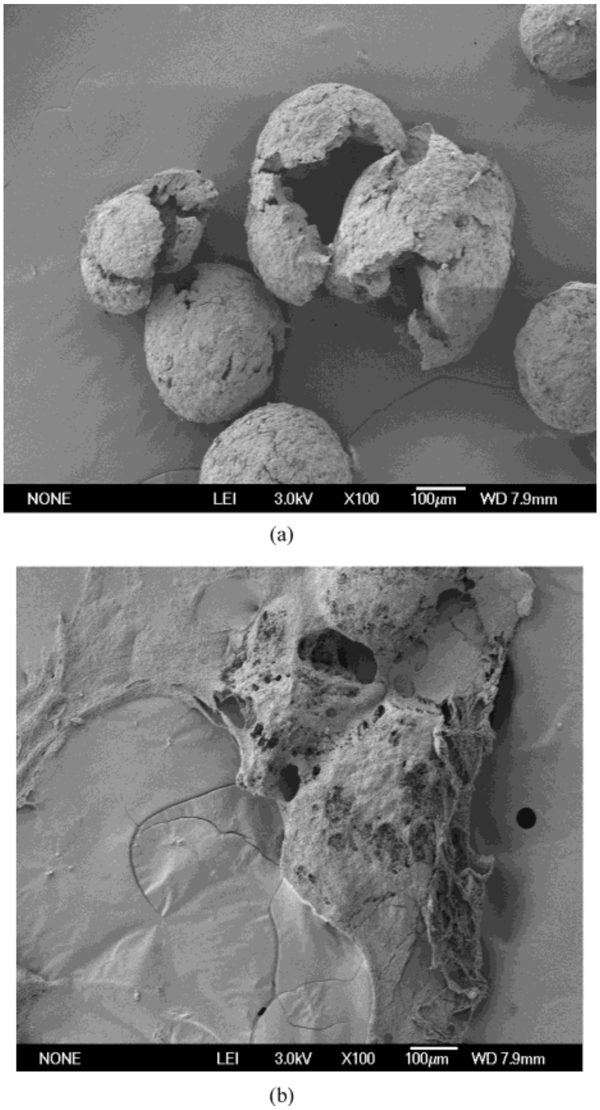


Figure 5. XPS spectra of (a) net PP-supported Cp_2ZrCl_2 catalyst and three PP-OH-supported Cp_2ZrCl_2 catalysts loaded with (b) 2.38, (c) 3.54, and (d) 4.40 μmol/(g of Zr).

Polymer Morphology. The morphology of the ethylene polymerization products by the PP-OH-supported catalysts as well as the net PP-supported one was examined by SEM. Figure 6 shows the SEM comparison between a typical polymer prepared by the PP-OH-supported catalysts (Figure 6a) (run 12 in Table 2) and a polymer by the net PP-supported catalyst (Figure 6b) (run 3 in Table 2).

During the polymerization of ethylene with the net PP-supported catalyst, because the catalyst detached from the PP support, reactor fouling occurred, which was within our expectations. The polymers produced showed morphology (shown in Figure 6b) as poor as those by homogeneous catalyst system. As for the PP-OH-supported catalysts, however, due to the stable interaction between the support and the catalyst components that effectively prevented the catalyst from detaching from the support, no reactor fouling occurred during the polymerization, and the obtained polymers



(a)

(b)

Figure 6. SEM photographs of (a) a typical PE polymer prepared by a PP-OH-supported catalyst (run 12 in Table 2) (100×) and (b) a PE polymer prepared by net PP-supported catalyst (run 3 in Table 2) (100×).

all exhibited granular morphology (shown in Figure 6a) that was replicated from the PP supports.

Polymer Properties. The PP-OH-supported catalysts produced polyethylenes with higher molecular weights than their homogeneous counterpart, as listed in Table 2. The presence of the macromolecular PP chains adjacent to the catalyst that boost the steric hindrance of the active sites and impede the β-agostic interaction during the β-H elimination reaction[12] is attributed as the main reason for the enhanced polymer molecular weight, which, on another hand, indirectly proves the stable immobilization of the metallocene catalyst on the functional PP support even in slurry environment. In fact, the increase in polymer molecular weight caused by the heterogenization of homogeneous metallocene catalysts via chemical linkage has been widely observed in the cases of using silica as the support.[2e] Our own experiments of ethylene polymerization using Cp_2ZrCl_2/MAO supported on silica also resulted in increased polymer molecular weights as compared with their homogeneous counterpart, only with reduced catalyst activities. As such, it is reasonable to predict that the polymers produced by the net PP-supported catalyst possess molecular weights similar to those by the homogeneous catalyst system.[13] The metallocene that was only physically absorbed on the support easily detached from the support into the solution and actually catalyzed ethylene polymerization homogeneously. Despite the relatively high molecular weights, the polyethylenes produced by the PP-OH-supported catalysts still keep narrow molecular weight distribution that is indicative of metallocene polymerization. Interestingly, as the molecular weights of the homogeneously produced polymers show a decreasing trend with increasing the MAO/Zr ratios, which is understandable due to the potential role of MAO as a chain transfer agent, the polymers catalyzed by the PP-OH-supported catalysts however possess slightly higher molecular weights at higher MAO/Zr ratios (comparing run 9 with run 8 and run 12 with run 11). The more the MAO, the better the protection of the electron-rich O atom in the PP-OH supports and the weaker the complexation between the O atom and the active site, which favors the monomer coordination and accounts for this seemingly abnormal effect of MAO/Zr ratio on polymer molecular weight.

Conclusion

Taking hydroxylated polypropylene as example, we have demonstrated in this paper that functional polypropylenes are applicable as supporting materials for homogeneous metallocene catalysts. With a spherical, porous $MgCl_2$-supported fourth-generation Ziegler–Natta catalyst, the copolymerization of propylene with 5-hexenyl-9-BBN followed by a hydroxylated transformation reaction resulted in OH-containing functional polypropylene granules with reduced crystallinity and thus enhanced solvent swellability. Upon being treated successively with MAO and Cp_2ZrCl_2 in toluene solution at an elevated temperature, the functional polypropylenes performed very effectively in anchoring the metallocene catalyst, which was evidenced by the much higher Zr loadings of the functional polypropylene-supported catalysts as compared with that of the net PP-supported one. The high Zr loadings ensured the functional PP-supported catalysts with relatively high productivities in slurry ethylene polymerization. More importantly, as the morphology of the polyethylenes produced by the net PP-supported catalyst was not improved as compared with those produced by the homogeneous catalyst system, the functional PP-supported catalysts, however, exhibited much better control over the obtained polymer morphology, which is indicative of the stable immobilization of the homogeneous catalyst on the functional PP supports.

The significance of this work is not restricted only to providing a novel support for metallocene catalyst. As a matter of fact, the aforementioned work by Sugano et al.[7b] was actually targeted at reactor-made toughened PP alloys containing ethylene–propylene elastomers. Galli et al.[14] also used Ziegler–Natta-polymerized PP granules to support metallocene catalysts by vapor spraying for the gas-phase preparation of heterophasic PP alloys. By showing that functional PP having OH functionality are more efficient than its unfunctionalized counterpart in anchoring metallocene catalysts and the prepared supported catalysts are very active for olefin polymerization and stable against solvent, we may apply the functional PP to supporting metallocene catalysts to copolymerize ethylene and propylene or other high α-olefins even in slurry environment, which provides an alternative process for the in-reactor preparation of PP alloys. In fact, we are currently investigating the preparation of PP/ethylene-*co*-1-octene copolymer alloys using Et(Ind)$_2$ZrCl$_2$/MAO catalyst supported on PP-OH supports in slurry reaction conditions, and the results will be reported elsewhere.

Experimental Details

Instrumentation and Materials. All room and high temperature ^{1}H NMR spectra were recorded on a Bruker AM-300 instrument in *o*-dichlorobenzene-d_4 at 115 °C. Apparent morphology of the polymers was examined by scanning electron microscopy (SEM) using a Topcon International Scientific Instruments ISI-SX-40 with secondary electron imaging. Samples were mounted on an aluminum stub and carbon coated to form a conductive coating. The melting temperatures of the polymers were measured by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 instrument controller. For the PP samples (PP-OH and net PP polymers), the DSC curves were recorded during the first heating cycle from 20 to 200 °C with a heating rate of 20 °C/min, whereas the DSC heating curves of the second cycle was recorded for the PE samples. The specific surface areas (S_g) of the PP-OH and net PP polymers were determined by BET method using N$_2$ as the absorption gas on a Thermo Finnigan Sorptomatic 1990 instrument. The bulk concentrations of Zr (in Cp$_2$ZrCl$_2$) on the PP supports were determined by inductively coupled plasma atomic emission spectroscopy using a ICP-AES Leeman Labs Plasma-Spec ICP model 2.5. The samples were prepared by stepwise treating the supported catalysts with hydrogen fluoride acid, high-temperature ablation, and nitric acid again to transform the solid samples to clear solution ones. X-ray photoelectron spectroscopy (XPS) was used to identify the surface Zr species in the supported catalysts using a Perkin-Elmer PHI 5400 model XPS instrument. The molecular weights and molecular weight distributions of the polymers were determined by high-temperature gel permeation chromatography (GPC) using a Waters Alliance GPC 2000V instrument operated at 150 °C with 1,2,4-trichlorobenzene as the eluent.

All O$_2$- and moisture-sensitive manipulations were carried out inside an argon-filled Vacuum Atmosphere drybox equipped with a dry train. CP grade toluene, heptane, hexane, and tetrahydrofuran (THF) were deoxygenated by argon purge before refluxing for 48 h and then distilled over sodium. Cp$_2$ZrCl$_2$ was purchased from Strem, MAO (10 wt % in toluene) from Albermarle, AlEt$_3$ (1.8 M in toluene), dimethoxydiphenylsilane (DDS) 1,5-hexadiene, and 9-BBN (0.5 M in THF) from Aldrich and used without further purification. Polymerization grade propylene was supplied by Yanshan Petrochemical Co. of China. The spherical MgCl$_2$/DIBP/TiCl$_4$ catalyst was kindly donated by Xiangyang Chemical Co. of China with a Ti content of 2.5 wt %. 5-Hexenyl-9-BBN was synthesized by the following literature procedure[9d] via the mono-hydroboration of 1,5-hexadiene with 9-BBN.

Synthesis of the Supports. The supports PP-OH polymers were synthesized by propylene copolymerization with 5-hexenyl-9-BBN catalyzed by the spherical MgCl$_2$/DIBP/TiCl$_4$ catalyst followed by a hydroxylated working-up treatment. In a typical reaction (support PP-OH-3 in Table 1), 100 mL of heptane was added into a 250 mL three-neck glass reactor equipped with a magnetic stirrer. The reactor was then saturated with atmospheric pressure of propylene at 40 °C. 4 mL of AlEt$_3$ (1.8 M in toluene) and 8 mL of DDS were subsequently injected with syringe at an Al/Si molar ratio of 10/1. 5.0 g of 5-hexenyl-9-BBN was added into the reactor in a heptane-diluted solution. The polymerization was started by adding 0.1 g of MgCl$_2$/DIBP/TiCl$_4$ catalyst. After 1 h of reaction, the reactor was cooled to 0 °C to allow the addition of 10 mL of degassed aqueous NaOH solution (20%) and 30 mL of H$_2$O$_2$ in THF (50%) for the oxidation and hydroxylation of the borane moieties. After the addition was completed, the reactor was warmed to 40 °C in 1 h, and at this temperature the reaction was allowed to proceed for 3 h with stirring. 10 mL of methanol was added to terminate the reaction. The product was collected by filtration and repeated washing with methanol, water, and acetone and dried at 60 °C under vacuum for 8 h to give 13.6 g of white polymer particles.

Net PP was synthesized by a similar procedure only without the hydroxylated transformation step. Instead, after the propylene homopolymerization with the spherical MgCl$_2$/DIBP/TiCl$_4$ catalyst, acidic ethanol was added into the reaction flask to terminate the polymerization. The product also underwent filtration, washing, and drying processes before the white particle form polymer could be obtained.

Supporting the Metallocene. The supporting of the metallocene on the PP supports was conducted by treating the supports with MAO followed by contacting with Cp$_2$ZrCl$_2$ in toluene solution. In a typical reaction (supporting Cp$_2$ZrCl$_2$ on PP-OH-3), in a flask equipped with a mechanical stirrer and a glass frit funnel was added 2 g of the PP-OH support, 100 mL of toluene, and 16 mL of MAO (10 wt % in toluene solution). The temperature was brought up to 60 °C, and the reaction proceeded at this temperature for 4 h with stirring. After filtration to remove the excess MAO, the flask was recharged with 100 mL of toluene, and the polymer was suspended upon stirring. Then 1 mmol of Cp$_2$ZrCl$_2$ in toluene solution was added, and the supporting reaction was allowed to proceed at room temperature for 3 h with stirring. The final supported catalyst was obtained by filtration, repeated washing with toluene, and drying under vacuum.

Ethylene Polymerization. In a typical reaction (run 12 in Table 2), in a 250 mL three-neck flask equipped with a magnetic stirrer was added 50 mL of toluene and 3 mL of MAO (10 wt % in toluene). The flask was then saturated with an atmospheric pressure of ethylene at 50 °C. 0.2 g of the supported catalyst was then added to initiate the polymerization reaction. After 20 min reaction, acidic ethanol was added to terminate the polymerization. The precipitated polymer was isolated and washed with ethanol several times and dried under vacuum.

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