Organic–inorganic hybrid supported zirconocene catalysts for ethylene polymerization

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Abstract

Silica-poly[3-(trimethoxysilyl)propyl methacrylate-co-4-vinylpyridine] inorganic–organic hybrid (SMV) has been synthesized, and by loading zirconocene catalyst on the carrier, novel zirconocene supported catalyst has been made and tested for ethylene polymerization. The silica monomer (SM) is prepared by coupling reaction of hydroxyl group of silica surface with 3-(trimethoxysilyl)propyl methacrylate (MPS) and then, SMV is synthesized by copolymerization of SM with 4-vinylpyridine. The formation of SM and SMV has been confirmed by FTIR, solid-state ^{13}C NMR, XPS, and elemental analysis (EA). Loading Cp_2ZrCl_2 on SMV resulted in the zirconocene supported catalyst. Ethylene polymerization data demonstrate that the SMV supported catalyst has higher activity than the SM supported one and yields polyethylene with much higher molecular weight than that produced by the corresponding homogeneous zirconocene catalyst.
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1. Introduction

Heterogenization of metallocene catalyst aiming at practical applications using slurry and gas phase processes for polyolefin production is an important subject on which many efforts have been made [1–9] in the past two decades.

Silica is the most common carrier for metallocene immobilization. But silica supported metallocene catalysts usually suffer from low activity that might be caused by the silica surface itself, which acts as a steric hindrance ligand around the active site. From such a point of view, the modification of the support with organosilane compounds playing the role of spacers prior to catalyst grafting aiming at separating the active metallocene from the silica surface has led to an increase in activity [10]. In contrast to the rigid surfaces of inorganic supports, polymer supports which provide a much closer analogue to the environment prevailing in homogeneous polymerization possess many advantages: easy preparation, lower residues in the polymer products than inorganic supports, controllable morphology of the polymer, and adaptability to numerous functionalization procedures utilizing both nucleophiles and electrophiles. It is more interesting to adopt an inorganic–organic hybrid material as a support, which combined the advantages of polymer supports and inorganic supports.

Silica has already been modified with methoxysilane [11,12] to graft unsaturated double bonds capable of copolymerization with styrene or methyl methacrylate in order to improve the heat stability of polymers. In this paper, monomeric silica (SM) is prepared by coupling reaction of 3-(trimethoxysilyl)propyl methacrylate (MPS) with hydroxyl group of silica surface and silica-poly(MPS-co-4-vinylpyridine) (SMV) is prepared by copolymerization of SM with 4-vinylpyridine. SMV is used as a carrier for preparation of zirconocene supported catalyst, which was used for ethylene polymerization.

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2. Experimental

2.1. Chemicals

Silica was activated at 400 °C for 6 h. 4-Vinylpyridine (Aldrich) was distilled under reduced pressure. Benzoyl peroxide (BPO) (Beijing Reagents Factory) was recrystallized in ethanol and dried under vacuum at 30 °C for 8 h. Ethylene (polymerization grade, Liaoyang Chemical Corporation) was used without further treatment. Toluene (Beijing Reagents Factory) was purified according to the usual procedures. Cp_2ZrCl_2 (Aldrich) was of commercial origin. MAO in toluene (10 wt%) was purchased from the Albar Corporation. Trimethylaluminium (TMA) was purchased from Aldrich Chemical Company.

2.2. Preparation of organic–inorganic hybrid supports (SMV)

2.2.1. Preparation of SM

Vinyl group functionalized silica was prepared by treating silica with 3-(trimethoxysilyl)propyl methacrylate. To a suspension of silica (5.0 g) in toluene (40 mL), 5.0 mL of MPS was added. The mixture was stirred mechanically at 25 °C for 24 h under argon. After the reaction, unreacted MPS was extracted with toluene for 48 h using a Soxhlet apparatus. The purified SM was then placed in a vacuum oven at 40 °C for 24 h to remove the captured solvent.

2.2.2. Preparation of SMV

SM (5.0 g) and 4-vinylpyridine (5 mL) were mixed in toluene. After raising the temperature to 70 °C, BPO (0.05 g) was added in a slow stream of dry nitrogen. After reaction for 4 h, the suspension was filtered and then purified by extraction with absolute ethanol for 48 h using a Soxhlet apparatus, and then dried in a vacuum oven at 40 °C for 24 h.

2.3. Preparation of supported catalysts

The supported catalyst was prepared in a completely dried and degassed Schlenck apparatus equipped with a magnetic stirrer. One gram of SMV and 30 mL toluene were added into the reactor and the mixture was stirred for 20 min. A prescribed amount of MAO or TMA (10 mmol) was added and then the mixture was stirred for 2 h. The MAO-treated support was collected by filtration and washed several times with toluene. Cp_2ZrCl_2 (0.1 mmol) in 20 mL toluene was then injected into the reactor by syringe. After reaction for 2 h, the catalyst was collected by filtration, washed with toluene and dried in vacuum.

2.4. Polymerization of ethylene

Ethylene polymerization was carried out in a 200 mL Schlenck-type glass reactor with stirring equipment. After heating and evacuating the reactor alternatively for about 30 min, the reactor was placed into a water bath of given temperature. Ethylene, toluene, and MAO were sequentially led into the reactor and polymerization started when catalyst as a suspension in toluene was introduced. After reaction for 30 min, an acidic ethanol solution was injected to terminate the polymerization. The precipitated polymer was collected and washed with ethanol for several times, and then dried under vacuum at 40 °C for 24 h.

2.5. Characterizations

The elemental contents of aluminum and zirconium in the supported catalysts were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using Plasma-Spec (I) of the America Leeman Laboratory. Infrared spectra of the silica, SM, and SMV were recorded on a Bio-Rad FTS 135 Spectrophotometer. The solid-state ^{13}C NMR spectra of SM and SMV were obtained with a Varian Unity-400 MHz spectrometer. The elemental analysis of SM and SMV were obtained using an Elementar Vario EL element analyzer. The surface composition of silica, SM, and SMV were examined using a VG ECSALAB MK II instrument. DSC was measured on a Perkin-Elmer DSC-7 instrument at a heating rate of 10 °C/min. The heating cycle was performed twice, but only the results of the second scan were recorded.

3. Results and discussion

Scheme 1 shows the formation reactions of SM and SMV. Fig. 1a and b shows the FTIR spectra of silica and SM, respectively. The peak at 1100 cm^{-1} is the characteristic absorption of the Si–O–Si bond. Fig. 1b shows a peak at 1703 cm^{-1} corresponding to the absorption of the C=O stretching band of SM. The C=C bond of SM is hard to be identified by FTIR, since the absorption at 1637 cm^{-1} assigned to C=C of SM (Fig. 1b) is close to that observed in silica (1635 cm^{-1} in Fig. 1a). Therefore, solid-state ^{13}C NMR is used to confirm if MPS is chemically bonded on the surface of silica. In Fig. 2, the peaks at 126 and 136 ppm corresponding to C=C and the peak at 169 ppm corresponding to C=O demonstrate the existence of C=C and C=O, confirming the formation of monomeric silica by chemical reaction between MPS and the hydroxyl group of silica surface as shown in Scheme 1.

Figs. 1c and 3 show the FTIR and the solid-state ^{13}C NMR spectra of SMV, respectively. The absorption at 1723 cm^{-1} (Fig. 1c) indicates the existence of carbonyl groups. The absorption of C=O shifts from 1703 cm^{-1} (for SM) to higher wave number region (1723 cm^{-1}, for SMV) owing to the loss of the conjugate structure, indicating that the unsaturated double bond in SM has been polymerized. The absorption of Si–O–Si at 1100 cm^{-1} observed for SM also appears in SMV, but it is rather broader. Comparison of the solid-state ^{13}C NMR spectrum of SMV (Fig. 3) with that of SM (Fig. 2) indicates that the peak at 40–49 ppm corresponding to –CH–CH$_2$– supports the existence of the polymer
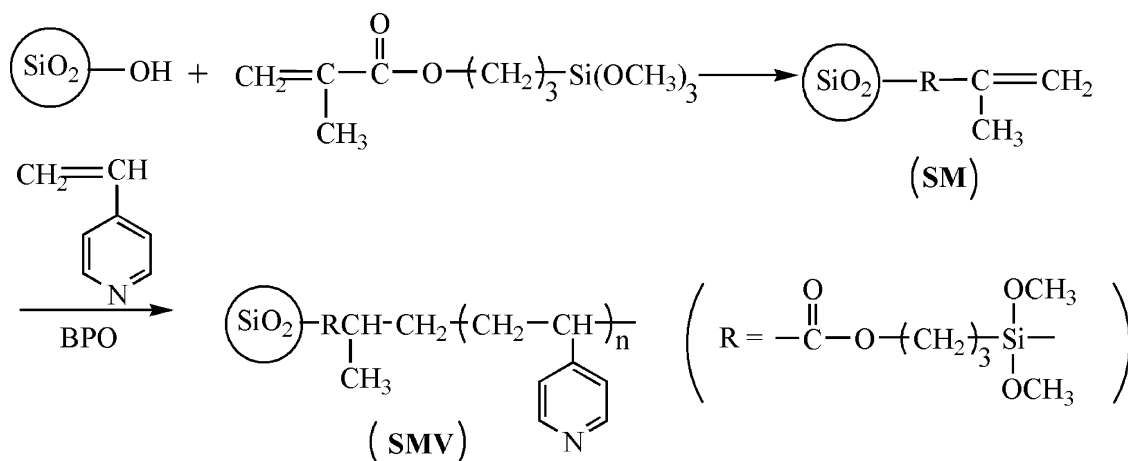
Scheme 1.
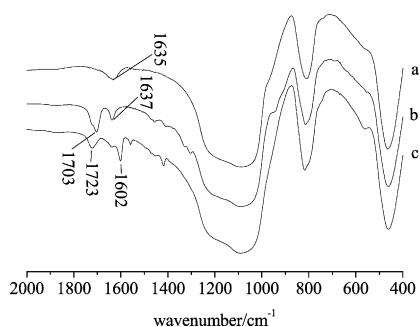
Fig. 1. FTIR spectra of SiO₂ (a), SM (b), and SMV (c).
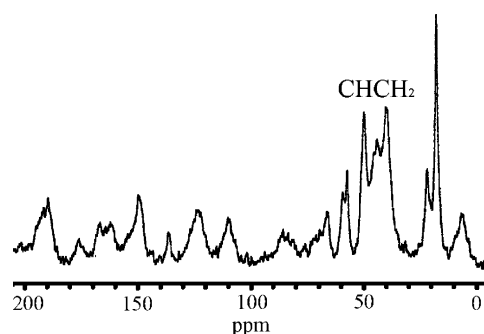
Fig. 3. Solid-state ^{13}C NMR spectrum of SMV.
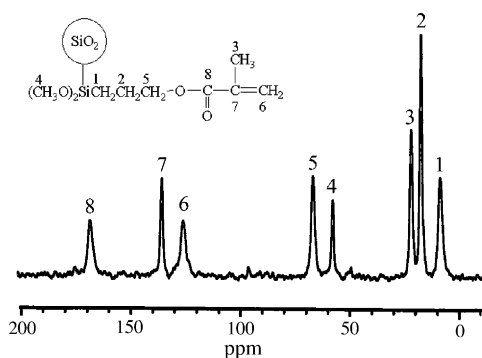
Fig. 2. Solid-state ^{13}C NMR spectrum of SM.

chain in SMV. This again furnishes evidence that SM and 4-vinylpyridine have been copolymerized. Thus, the formation of SMV by the polymerization of SM and 4-vinylpyridine can be concluded.

The compositions of the surface and the bulk of SM and SMV particles were analyzed by using XPS and elemental analysis (EA), respectively, and the results are shown in Table 1. The carbon contents both in the surface and in the bulk in SMV (15.1%, Table 1) were much higher than those in SM (8.76%, Table 1) due to incorporation of 4-vinylpyridine. The remarkably higher carbon contents on the surface than that in the bulk of SMV indicate that the carbon-containing components have been anchored on the silica particle surface. It is concluded that SMV support has a core/shell structure, in which silica is a core and poly4-vinylpyridine is the shell.

As shown in Table 1, even though the vinyl monomer has been chemically bonded to the silica surface, SM still showed a certain amount of Si (27.24%) on the surface, implying that SM had a certain amount of bare area on the surface. Consequently, the Si–OH groups of bare area of SM surface allowed loading more MAO and zirconocene easily than the case of SMV (Table 2) where the surface was almost organ-

Table 1
The compositions of the surface and bulk of SM and SMV particles

	XPS analysis				Elemental analysis	
	C (wt%)	Si (wt%)	O (wt%)	N (wt%)	C (wt%)	N (wt%)
SM	21.51	27.24	51.25	0	8.76	0
SMV	75.54	4.13	9.27	11.06	15.1	1.35

Table 2
Comparison of different supported zirconocene catalysts[a]

Support	Al (wt%)	Zr (wt%)	Activity (kg PE/mol Zr h)	T_m (°C)	ΔH_m (J/g)	M_w ($\times 10^5$)	M_w/M_n
Homogeneous	–	–	3.22×10^3	133.6	180.5	1.91	2.3
SiO$_2$/MAO/Cp$_2$ZrCl$_2$	3.14	0.17	0.24×10^3	135.1	79.6	2.39	2.87
SM/MAO/Cp$_2$ZrCl$_2$	1.80	0.14	1.64×10^3	136.9	164.0	2.86	2.09
SMV/MAO/Cp$_2$ZrCl$_2$	1.01	0.14	2.25×10^3	135.5	154.9	2.68	2.32
SiO$_2$/TMA/Cp$_2$ZrCl$_2$	2.88	0.09	0.11×10^3	135.0	89.6	2.60	2.34
SMV/TMA/Cp$_2$ZrCl$_2$	1.01	0.08	1.25×10^3	135.2	159.9	2.51	2.25

[a] *Reaction conditions*: 100 mL toluene; Zr = 5 μmol; Al/Zr (mol/mol) = 600 (the mole ratio is based on MAO added during polymerization only); ethylene pressure, 1 atm; 50 °C; polymerization time, 30 min.

Table 3
Results of ethylene polymerization with SMV supported zirconocene catalyst[a]

Run	Al/Zr[b] molar ratio	Temperature (°C)	Activity (kg PE/mol Zr h)	T_m (°C)	ΔH_m (J/g)	M_w ($\times 10^{-5}$)	M_w/M_n
1	1000	50	2.43×10^3	135.9	155.2	2.63	2.66
2	800	50	2.63×10^3	135.9	173.0	2.81	2.60
3	600	50	2.25×10^3	135.5	154.9	2.68	2.32
4	400	50	0.493×10^3	136.3	136.6	n.d.[c]	n.d.
5	600	40	1.03×10^3	135.9	142.5	3.46	2.12
6	600	60	2.42×10^3	134.8	172.4	1.79	2.29
7	600	70	1.81×10^3	134.9	176.2	n.d.	n.d..
8[d]	600	50	1.89×10^3	135.7	155.9	2.65	2.22

[a] *Reaction conditions*: 100 mL toluene; Zr = 5 μmol; ethylene pressure, 1 atm; polymerization time, 30 min.
[b] The mole ratio is based on MAO added during polymerization only.
[c] Not detected.
[d] Polymerization was conducted using the solid after washed by MAO in the form of solution in toluene.

ically covered (C: 75.54%, Si: 4.13, Table 1), and MAO and zirconocene would be only loaded by the interaction with N of pyridine group.

The activity of SMV supported zirconocene was expectantly higher than that of SM supported zirconocene, though it was still a little lower than that of the corresponding homogenous system. Comprehensively, according to Table 2, the PEs produced with supported catalysts present a higher molecular weight than the one obtained with the homogeneous system. In the case of the supported catalysts, the bimolecular reaction between two zirconocene centers, which makes the β-hydrogen transfer possible, is hindered, resulting in a greater growth of the polymer chain (higher molecular weight).

As shown in Table 2, a little higher amount of Al was supported on the MAO-treated supports compared with the TMA-treated supports. The activities of the MAO-treated supports are much higher than those of the TMA-treated supports. But the polymers obtained with the different supported systems are nearly identical as to molecular weights and melting points.

It is important for supported catalysts that the immobilized zirconocene complex should not be able to be removed by washing or leached from the support in polymerization. Thus, the following experiments were conducted. In a Schlenk-type apparatus, the SMV supported catalyst was mixed with MAO under argon. After vigorous stirring at 50 °C for 0.5 h, the mixture was filtered. The solid and liquid were used to catalyze the ethylene polymerization in the usual procedure, respectively. After 0.5 h, the activity

of the solid (run 8 in Table 3) was similar to the activity of the SMV supported catalyst (run 3 in Table 3), whereas only a trace of PE was produced with the liquid. Therefore, the zirconocene complex was better anchored on the support.

The results of ethylene polymerization with SMV supported zirconocene catalyst are summarized in Table 3. No special trend could be observed for heat of fusion among PEs produced by the different ratios of Al/Zr. As polymerization temperature increased, the heat of fusion of the produced PEs increased and the molecular weights decreased. High temperatures should cause early deactivation of the active species, leading to PE of lower molecular weight.

4. Conclusions

Monomeric silica and silica-poly[3-(trimethoxysilyl)propyl methacrylate-co-4-vinylpyridine] inorganic–organic hybrid have been synthesized, and by loading zirconocene catalyst on the carrier, novel zirconocene supported catalyst has been made and tested for ethylene polymerization. The formation of SM and SMV has been confirmed by FTIR, solid-state ^{13}C NMR, XPS, and elemental analysis. The higher carbon content on the surface of the SMV (XPS analysis) compared to the entire silica particles (elemental analysis) gives evidence that the support has a core/shell structure. Ethylene polymerization data demonstrate that SMV supported catalyst has higher activity than the SM supported one and yields polyethylene with much higher

molecular weight than that produced by the corresponding homogeneous zirconocene catalyst.

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