

# 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 <sup>13</sup>C NMR, XPS, and elemental analysis (EA). Loading Cp<sub>2</sub>ZrCl<sub>2</sub> 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.  $\text{Cp}_2\text{ZrCl}_2$  (Aldrich) was of commercial origin. MAO in toluene (10 wt%) was purchased from the Albar Corporation. Trimethylaluminum (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.  $\text{Cp}_2\text{ZrCl}_2$  (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  $^{13}\text{C}$  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  $\text{cm}^{-1}$  is the characteristic absorption of the Si–O–Si bond. Fig. 1b shows a peak at 1703  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  assigned to C=C of SM (Fig. 1b) is close to that observed in silica (1635  $\text{cm}^{-1}$  in Fig. 1a). Therefore, solid-state  $^{13}\text{C}$  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  $^{13}\text{C}$  NMR spectra of SMV, respectively. The absorption at 1723  $\text{cm}^{-1}$  (Fig. 1c) indicates the existence of carbonyl groups. The absorption of C=O shifts from 1703  $\text{cm}^{-1}$  (for SM) to higher wave number region (1723  $\text{cm}^{-1}$ , 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  $\text{cm}^{-1}$  observed for SM also appears in SMV, but it is rather broader. Comparison of the solid-state  $^{13}\text{C}$  NMR spectrum of SMV (Fig. 3) with that of SM (Fig. 2) indicates that the peak at 40–49 ppm corresponding to  $-\text{CH}-\text{CH}_2-$  supports the existence of the polymer

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