

Evidence of Nanoconfinement Effects of MCM-41 on Propylene Polymerization Catalyzed by MCM-41 Supported Metallocene Catalyst in the Presence and Absence of β -Cyclodextrin

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Propylene polymerization was carried out with MCM-41 supported $rac\text{-Et(Ind)}_2\text{ZrCl}_2$ catalysts, in the presence and absence of β -cyclodextrin. The resultant PP was studied by X-ray diffraction, scanning electron microscopy, thermogravimetric analysis, and differential scanning calorimetry. Through comparison of the results, it was found that the channels of MCM-41 could act as a nanoreactor of propylene polymerization and the polypropylene (PP) contained in the channels had noncrystal structure. However, the PP could grow out of the channels and form some crystals after the active sites on the surface of MCM-41 were destroyed. This showed that the channels of MCM-41 had great confinement effects on propylene polymerization.

Introduction

Metallocene catalysts for the polymerization of olefins have been developed tremendously in the past decades because of their high activity.^{1–3} To carry out polymerization in slurry, the metallocenes have to be supported on carriers, such as SiO_2 , Al_2O_3 , MgCl_2 , or organic supports.^{4–8} Studies of metallocene heterogeneous polymerization have indicated that the confined geometries of carriers could affect the properties of polymers on a nanoscale.⁹

Recently, the discovery of mesoporous zeolites (such as MCM-41 and SBA-15) provided a new kind of support for supporting metallocene catalysts.¹⁰ This kind of material contains mesopores uniformly arranged in a direction parallel to the pore axis.¹¹ Aida et al.¹² first prepared nanopolyethylene fibers with MSF (mesoporous silica fiber) supported titanocene catalyst under high ethylene pressure (10 atm). Subsequently, Ye et al.¹³ also prepared polyethylene (PE) nanofibers with MCM-41 supported titanocene dichloride under higher ethylene pressure (20 atm). We prepared nanopolyethylene fibers with MCM-41 and SBA-15 supported Cp_2ZrCl_2 catalysts, respectively, under atmosphere pressure.^{14,15} Using mesoporous silica as a nanoreactor, Sano et al.^{16,17} prepared a polypropylene (PP)/metal–MCM-41 composite and found that the crystallization of polypropylene confined in mesopores was strongly hindered.

In this paper, we carried out propylene polymerization using an MCM-41 supported $rac\text{-Et(Ind)}_2\text{ZrCl}_2$ catalyst in the presence and absence of β -cyclodextrin, respectively. Through the comparison of these two kinds of PP obtained in the presence and absence of β -cyclodextrin, the nanoconfinement effects of MCM-41 on the polymerization behavior were proved. The possible mechanisms of propylene polymerization and polypropylene crystallization were also proposed.

Experiments

Materials. All manipulations were carried out in argon atmosphere using standard Schlenk technique. rac -Ethylene-(bisindenyl)zirconium dichloride ($rac\text{-Et(Ind)}_2\text{ZrCl}_2$) was pur-

chased from Aldrich. Methylaluminoxane (MAO) was purchased from Aldrich as 10 wt % solution in toluene. Polymerization-grade propylene was purified through 4 Å molecular sieves. Toluene was refluxed over sodium with benzophenone as indicator and distilled in argon atmosphere before use. β -Cyclodextrin was dried at 80 °C in a vacuum for 16 h to remove the adsorbed water.

Preparation of $rac\text{-Et(Ind)}_2\text{ZrCl}_2/\text{MCM-41}$ Catalyst. MCM-41 was synthesized according to analogous procedures published in the literature.¹⁸ The internal pore structure was characterized by nitrogen adsorption–desorption and X-ray diffraction. The characterization results showed that MCM-41 had a pore diameter of 2.90 nm, a pore volume of 0.79 mL/g, and a specific surface area of 1082 m²/g.¹⁵

A 0.3342 g sample of MCM-41 was treated with 2 mL of MAO at 50 °C in 50 mL of toluene for 2 h and washed with toluene three times. Subsequently, 0.036 mmol of $rac\text{-Et(Ind)}_2\text{ZrCl}_2$ in 50 mL of toluene was added to the pretreated MCM-41 and kept stirring at 50 °C for 2 h; the resultant solid was collected and washed three times with toluene. After drying in a vacuum at room temperature, MCM-41 supported $rac\text{-Et(Ind)}_2\text{ZrCl}_2$ catalyst, named “Zr–MCM-41”, was obtained. Spectrophotometric analysis indicates that Zr content was 0.102 mmol of Zr/g of catalyst.

Propylene Polymerization. Propylene polymerization was carried out in a 100 mL flask equipped with a propylene inlet and outlet, under atmosphere pressure. Two methods were used in this work for the addition of the supported catalyst, cocatalyst, and β -cyclodextrin. Method a: At the selected temperature, toluene was introduced into the flask and saturated with propylene; then the required MAO and supported catalyst were added. Method b: At the selected temperature, toluene, β -cyclodextrin, and supported catalyst were added to the flask and stirred for several minutes, followed by saturation with propylene, and the required MAO was added. After 30 min, the polymerization was terminated by the addition of acidified ethanol. The polymer was separated by filtration and then dried at 50 °C.

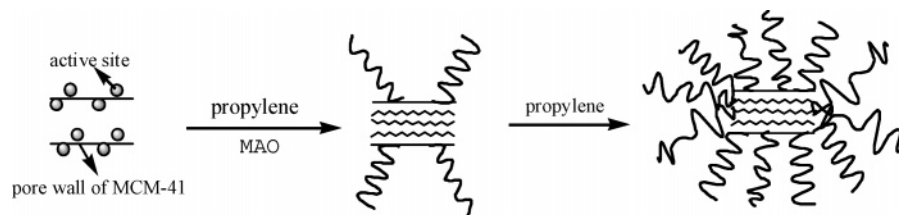
Characterization of the Polypropylene. X-ray powder diffraction (XRD) analyses were performed using a D/max-3BX

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TABLE 1: Results of Propylene Polymerization Catalyzed by Zr–MCM-41 and *rac*-Et(Ind)₂ZrCl₂ Catalysts^a

run	catalyst	T_p (°C)	activity ^b	T_m (°C)	ΔH (J/g)	X_c (%)
1	Zr–MCM-41	30	0.33	134.8	43.6	20.9
2	Zr–MCM-41	50	0.37	121.9	27.4	13.1
3	Zr–MCM-41	60	0.45	108.7	11.5	5.5
4	<i>rac</i> -Et(Ind) ₂ ZrCl ₂	30	6.25	135.0	72.0	34.4
5	<i>rac</i> -Et(Ind) ₂ ZrCl ₂	50	23.6	113.6	51.5	24.6
6	<i>rac</i> -Et(Ind) ₂ ZrCl ₂	60	25.5	93.1	24.4	11.7

^a Polymerization conditions: toluene = 50 mL, propylene pressure = 1 atm, t = 30 min, $[Al]/[Zr]=3000$. ^b $\times 10^5$ g of PE/mol of Zr·h·atm.

SCHEME 1: Propylene Polymerization with Zr–MCM-41

diffractometer with Cu radiation (40 kv, 80 mA). The melting points (T_m 's) of polypropylene were recorded on a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) at a heating rate of 10 °C/min, and the second run was recorded. Thermogravimetric analysis (TGA) was measured with a Perkin-Elmer Pyris 1 thermogravimetric instrument, at a heating rate of 20 °C/min in N₂ atmosphere. The morphology of the polypropylene was observed with scanning electron microscopy (SEM; SIRION, FEI, USA).

Results and Discussion

Table 1 shows the results of propylene polymerization catalyzed by Zr–MCM-41 and *rac*-Et(Ind)₂ZrCl₂, respectively. The results indicate that the activity of Zr–MCM-41 catalyst was much lower than that of *rac*-Et(Ind)₂ZrCl₂. A possible reason is that, due to the confinement effect of MCM-41, the diffusion of propylene monomer into the channels was greatly affected and decreased the activity in the case of Zr–MCM-41.

It was also found that the polypropylene prepared with Zr–MCM-41 had a higher melting point and lower crystallinity than that obtained with *rac*-Et(Ind)₂ZrCl₂. These differences are possibly attributed to the effect of MCM-41 on the crystalline structure of the resultant PP. On one hand, the channels of MCM-41 could hinder the PP chains in crystallizing to produce some uncrystalline PP in the channels, which reduced the crystallinity of the resultant PP. On the other hand, the PP molecular chains grown out of the channels of MCM-41 could align regularly and formed a perfect crystal, which increased the melting point of the resultant PP.

Figure 1 shows the kinetic curves of propylene polymerization catalyzed by Zr–MCM-41 and *rac*-Et(Ind)₂ZrCl₂, respectively. In Figure 1a, at the beginning of the polymerization, the polymerization rate (R_p) is slow; after 10 min R_p reaches the maximum and then has mild polymerization behavior. However, in Figure 1b, the maximum R_p is reached in less than 5 min and then has a fast decay after the maximum R_p . The difference in the polymerization kinetic curves suggests that the MCM-41 support had a great influence on the polymerization behavior. A similar conclusion was obtained by our group for MCM-41 supported Cp₂ZrCl₂ catalyzing ethylene polymerization.¹⁹ It is possible that the large pore diameter of the MCM-41 support may allow the anchoring of active sites at the surface as well as inside the MCM-41 channels. The channels had a confinement effect on the propylene monomer and blocked it from

reaching the active sites in the channels. At the same time, the PP first formed on the surface of MCM-41 also blocked the monomer from reaching the active sites in the channels. These effects led to a slow increase in the polymerization rate and resulted in mild polymerization behavior.

In addition to the influence on the polymerization activity and kinetics, the confinement effect also influenced the morphology of the resultant PP. The SEM images of the PP prepared with *rac*-Et(Ind)₂ZrCl₂ and Zr–MCM-41 at different conditions are shown in Figure 2. It was found that the PP prepared with Zr–MCM-41 mainly had amorphous morphology compared to the PP obtained by *rac*-Et(Ind)₂ZrCl₂. There is a plausible explanation for this result: owing to the confinement effects, the propagation of PP chains in the channels of MCM-41 was affected. Then, the PP formed on the surface of MCM-41 made the resultant PP have amorphous morphology, as shown in Scheme 1.

To investigate the properties of the PP outside and inside the channels of MCM-41, the resultant PP prepared with Zr–MCM-41 (T = 50 °C, $[Al]/[Zr]$ = 3000, t = 30 min) was extracted with boiling *o*-dichlorobenzene (ODCB) for 12 h. The polypropylene could be divided into two parts. The part dissolved in boiling ODCB was named “PP^{out}”, and the other was named “MCM-41-PP”.

Figure 3 shows the XRD patterns of MCM-41 and MCM-41-PP. In Figure 3b, the presence of Bragg peaks indicates that the structure of MCM-41 was not destroyed in the process of polymerization. However, the diffraction peak intensities of

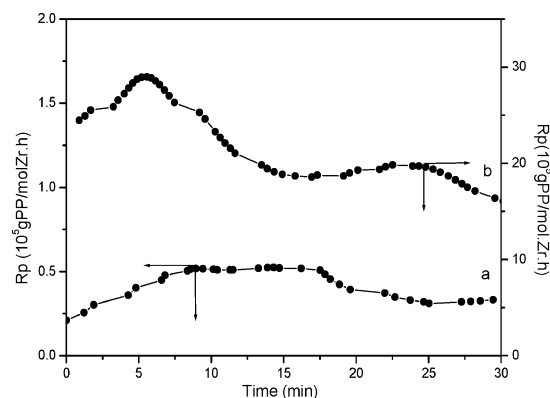


Figure 1. Propylene polymerization kinetic profile of (a) Zr–MCM-41 catalyst and (b) *rac*-Et(Ind)₂ZrCl₂ catalyst (toluene = 50 mL, $[Al]/[Zr]$ = 3000, T = 50 °C).

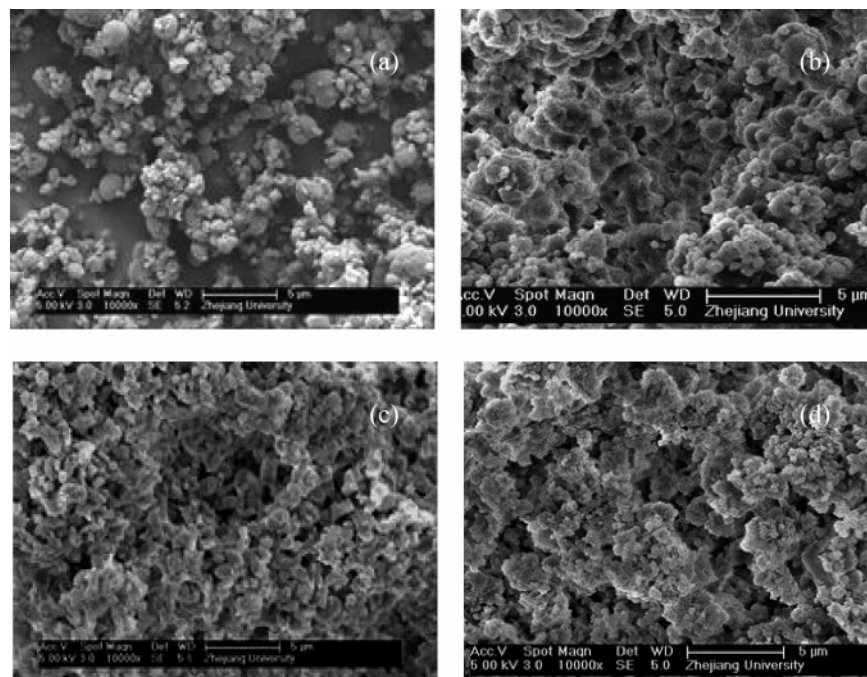


Figure 2. SEM images of polypropylene prepared with $rac\text{-Et(Ind)}_2\text{ZrCl}_2$ at (a) $T = 30\text{ }^\circ\text{C}$ and (b) $T = 50\text{ }^\circ\text{C}$ and Zr-MCM-41 at (c) $T = 30\text{ }^\circ\text{C}$ and (d) $T = 50\text{ }^\circ\text{C}$ ($[\text{Al}]/[\text{Zr}] = 3000$, $t = 30\text{ min}$).

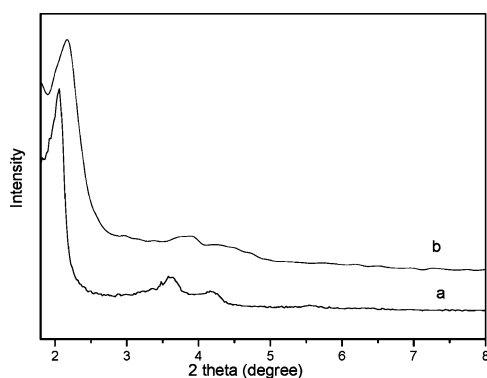


Figure 3. XRD patterns of (a) MCM-41 and (b) MCM-41-PP.

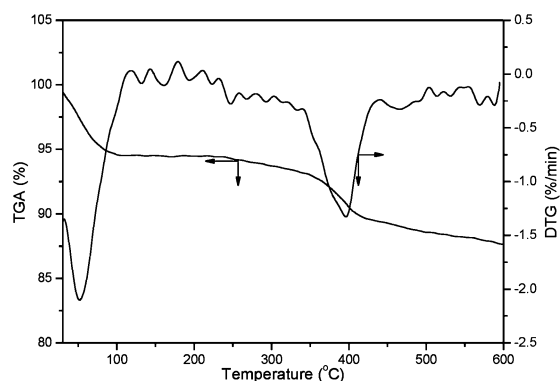


Figure 4. TGA and DTG curves of MCM-41-PP.

MCM-41-PP were reduced compared to those of MCM-41. The reduction of peak intensities might be attributed to the existence of PP in the channels of MCM-41.¹⁶ The result also testifies that the amorphous morphology of PP was not due to the fragmentation of channels.

Figure 4 shows the TGA and differential thermogravimetric (DTG) curves of MCM-41-PP. Except for the water losses due to desorption below $100\text{ }^\circ\text{C}$ and condensation of silanol groups to form siloxane bonds above $450\text{ }^\circ\text{C}$,²⁰ there is also a large

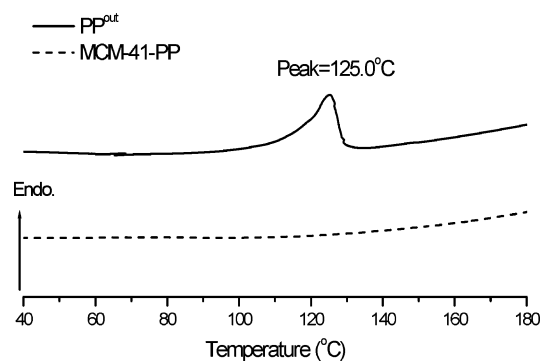


Figure 5. Differential scanning calorimetry (DSC) endotherms from the heating run at $20\text{ }^\circ\text{C/min}$. The top curve is from PP^{out} , and the other is from MCM-41-PP.

weight loss at $395\text{ }^\circ\text{C}$. This weight loss at $395\text{ }^\circ\text{C}$ corresponds to the decomposition of PP^{21} and proves the existence of PP in the channels of MCM-41. From the TGA curves, we could also know that the content of PP in the channels was about 5.0 wt %.

The melting behavior of PP^{out} and MCM-41-PP were investigated by DSC. Figure 5 compares the DSC thermograms of PP^{out} and MCM-41-PP. It was found that the PP^{out} has a narrow melting transition about $125.0\text{ }^\circ\text{C}$. On the other hand, the MCM-41-PP has no melting transition between 40 and $180\text{ }^\circ\text{C}$, which implies that the resultant PP inside the channels is uncrystalline.^{16,17} The result also directly proves that the crystallization of PP in the channels of MCM-41 was strongly hindered and only formed uncrystalline PP.

To further investigate the confinement effect of MCM-41 on the polymerization behavior, we prepared PP in the presence of β -cyclodextrin. β -Cyclodextrin has many hydroxy groups which could destroy the active sites of metallocene catalyst. However, the diameter of β -cyclodextrin is large. It was difficult to diffuse into the channels of MCM-41, and β -cyclodextrin destroyed only the active sites on the surface of MCM-41. Therefore, the effects of active sites on the surface of MCM-

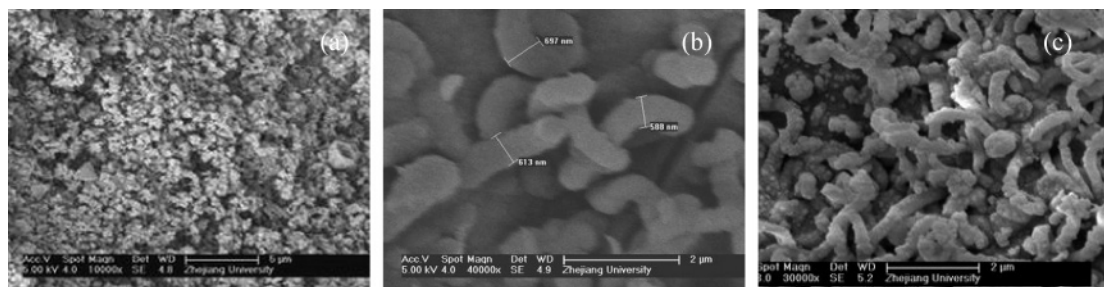
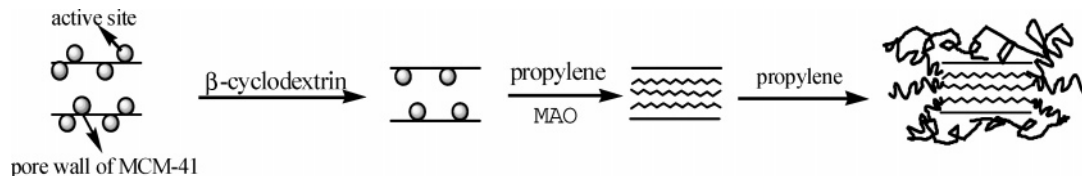


Figure 6. SEM images of the polymer prepared with Zr-MCM-41 catalyst in the presence of β -cyclodextrin and MCM-41: (a) surface morphology of the resulting PP ($\times 10000$); (b) magnified image of the surface morphology ($\times 40000$). Polymerization conditions: $[Al]/[Zr] = 3000$, $T = 50^\circ\text{C}$, $t = 30$ min, β -cyclodextrin/Zr-MCM-41 = 31.7 wt %. (c) Morphology of MCM-41.

SCHEME 2: Propylene Polymerization with Zr-MCM-41 in the Presence of β -Cyclodextrin



41 on the morphology and properties of the resultant PP might be prevented after Zr-MCM-41 was treated with β -cyclodextrin.

Figure 6 shows SEM images of the polypropylene prepared with Zr-MCM-41 in the presence of β -cyclodextrin. As shown in Figure 6a, the resulting PP mainly has amorphous morphology. With increased magnification, the polymer presents rodlike morphology (Figure 6b). This rodlike morphology is similar to the morphology of MCM-41 particles, as shown in Figure 6c.²² However, the diameter of the PP particles (600–700 nm) is larger than that of MCM-41 (200–300 nm), which implies that there was some PP enwrapped on the surface of MCM-41. The possible mechanism of the polymerization process in the presence of β -cyclodextrin is shown in Scheme 2.

The melting behavior of the PP produced with Zr-MCM-41 in the presence and absence of β -cyclodextrin was investigated by DSC, as shown in Figure 7. Interestingly, a melting transition is observed in the thermogram ($T = 121.8^\circ\text{C}$) for the PP produced with Zr-MCM-41 in the presence of β -cyclodextrin. This melting behavior of PP is different from the PP inside the channels of MCM-41. The possible reason for such a difference is that the PP chains could grow out of the channels of MCM-41 and form some crystallization in the case of the presence of β -cyclodextrin. It also indicates that the channels of MCM-41 could serve as a nanoreactor of propylene polymerization. Moreover, owing to the confinement of MCM-

41, the PP prepared with the system of Zr-MCM-41 and β -cyclodextrin had lower crystallinity ($X_c = 6.4\%$) compared with PP prepared without β -cyclodextrin ($X_c = 13.1\%$).

Conclusions

Propylene polymerization was carried out with MCM-41 supported *rac*-Et(Ind)₂ZrCl₂ catalyst in the presence and absence of β -cyclodextrin, respectively. The resulting PP was studied with SEM, XRD, TGA, and DSC. It was found that the channels of MCM-41 could serve as a nanoreactor and had great confinement effects on the propylene polymerization behavior. The channels of MCM-41 could strongly hinder the crystallization of PP, and the resultant PP inside the channels was uncrystalline. After removal of the active sites on the surface of MCM-41 in the presence of β -cyclodextrin, the PP molecular chains could grow out of the channels and lead the PP to have some crystallization, but the crystallinity decreased.

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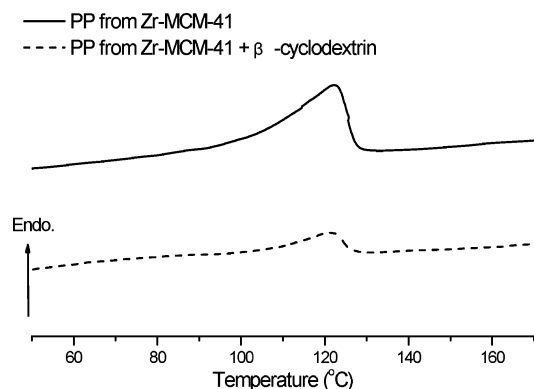


Figure 7. DSC curves of the resultant PP prepared with Zr-MCM-41 and Zr-MCM-41 + β -cyclodextrin. Polymerization conditions: $[Al]/[Zr] = 3000$, $T = 50^\circ\text{C}$, $t = 30$ min.

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