

Study on ethylene polymerization catalyzed by Cp_2ZrCl_2 /carbon nanotube system

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Abstract

Pristine CNTs and open-ended CNTs were used as supports for Cp_2ZrCl_2 . The effects of the structure of the supports on the activity of the catalyst in ethylene polymerization and the resulting PE morphology were studied. It was found that the two supported catalysts had similar activity. The SEM studies proved that the resulting PE prepared with pristine CNT-supported catalyst exhibited fibrous morphology, while the other PE mainly exhibited fractional morphology. The possible formation mechanism of these two kinds of morphology was proposed.
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1. Introduction

The development of metallocene catalysts can be considered as an exciting achievement in the catalysts field in the last two decades, which made a tremendous impact on polyolefin industries [1,2]. Owing to the difficulties in controlling the polymer morphology and preventing reactor fouling in homogeneous polymerization [3], it is desirable to heterogenize the homogeneous catalysts for the possible industrial process. Such inorganic supports as silica, alumina and magnesium compounds are in common use [4,5]. Several reports on the use of polymer as supports in the olefin polymerization have appeared in the literature [6,7].

Carbon nanotubes (CNTs) are well known as long and slender fibers with superior mechanical, thermal and electrical properties [8–10]. Some hydroxyl and carboxylic groups contained on the surface of the purified CNTs [11–13] can make the metallocene catalyst stabilized on its surface. The structure is different from the CNTs and open-ended CNTs, which can affect the location of the active sites and the morphology of the resulting polymer consequently.

In the present study, the effects of structural features of the CNTs and open-ended CNTs supports on the Cp_2ZrCl_2 catalyst

activity in ethylene polymerization and the morphology of the resulting PE were investigated.

2. Experimental

2.1. Materials

All manipulations were carried out under argon atmosphere using the standard Schlenk techniques. Polymerization-grade ethylene was purified by passing through 4Å molecular sieves and K/Na alloy to remove residual traces of moisture; Cp_2ZrCl_2 (Cp: cyclopentadienyl) was synthesized according to the literature [14]; methylaluminoxane (MAO) was purchased from Aldrich as 10 wt.% aluminium in toluene; toluene was refluxed over sodium with benzophenone as an indicator and distilled under nitrogen atmosphere. Multiwalled carbon nanotubes (CNTs) were provided by Professor Xiaobin Zhang, which are synthesized by cobalt-catalyzed decomposition of acetylene. The open-ended CNTs were obtained by a refluxing CNTs in nitric acid at 120 °C for 4 h [15]. The CNTs were all heat-treated at 80 °C for 8 h under vacuum.

2.2. Catalyst preparation

A certain amount of the heat-treated CNTs was added to toluene solution of MAO. The slurry was stirred for 2 h at room

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temperature. The solid was filtered, washed three times with toluene. Subsequently, the MAO-treated CNTs were mixed with toluene solution of a desired amount of Cp_2ZrCl_2 . After stirring for 2 h at room temperature, the solid was filtered and washed three times with toluene, and then dried under vacuum at room temperature. As a control, carbon black (CB) supported Cp_2ZrCl_2 was also prepared in the same way.

2.3. Polymerization of ethylene

Ethylene polymerization was carried out in a 100 ml round bottom flask equipped with a mechanical stirrer. Fifty millilitres of toluene was added to the flask containing 1 atm of ethylene pressure at the polymerization temperature. Then a certain amount of MAO was added under stirring. The polymerization was started by the introduction of CNTs-supported catalyst and terminated with acidified ethanol. The polymerization product was washed with ethanol several times and dried in vacuum at 60°C for 24 h.

2.4. Characterization

The morphologies of the CNTs before and after supported catalysts were examined using a scanning electron microscope (SIRION, FEI, USA). The Raman spectrum at excitation laser wavelength of 514 nm was recorded on an Almega Dispersive Raman spectrometer. The morphologies of the resultant polyethylene were also observed with SEM. The pore volume, average pore diameter and specific surface area of the pristine CNTs were measured using an Omnisorp (TM) 100CX VER 1G adsorption apparatus.

3. Results and discussion

3.1. Characterization of the CNTs

Fig. 1 shows the Raman spectra of the CNTs before and after treatment with nitric acid. Both CNTs have two adsorptions at about 1334 and 1567 cm^{-1} , respectively. The strong similarity between the two Raman spectra indicates that the principal structure of CNTs is not destroyed. The relative peak intensity of the band at 1580 cm^{-1} is weak and that at 1335 cm^{-1} strong in spectrum 'b' compared to spectrum 'a'. In the presence of nitric acid, the cap of the CNTs can be opened at the defect sites to shorten the length of CNTs and introduce hydroxylic functional groups to CNTs. The schematic drawing of the process is shown in Fig. 2 [16].

Fig. 3 shows the SEM image of the CNTs before and after the treatment with nitric acid. In Fig. 3(a), there are some bright caps on the end of the CNTs, and the CNTs have a smooth

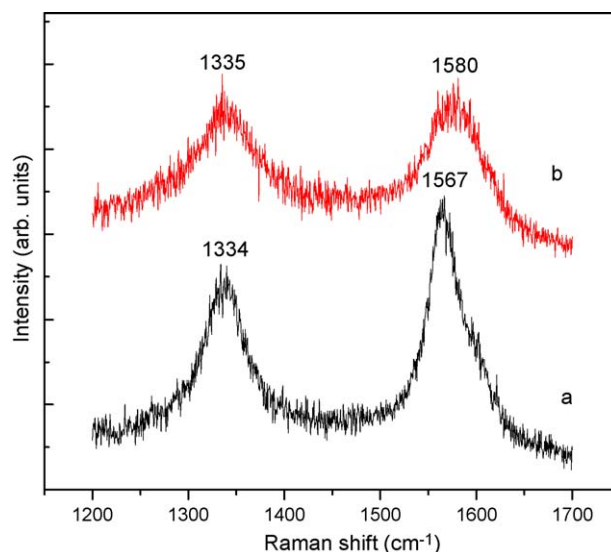


Fig. 1. Raman spectra of CNTs before (a) and after (b) the treatment with nitric acid.

surface. The diameters of the CNTs are 30–50 nm. After being treated with nitric acid, the caps decrease and the small particles increase on the surface of CNTs, as shown in Fig. 3(b). The results indicate that some caps of the CNTs have been opened under the reflux in nitric acid.

Similar fibre morphologies of the CNTs are also observed after loading of Cp_2ZrCl_2 , as shown in Fig. 3(c) and (d), which also indicates that the process of supporting does not destroy the structure of CNTs.

The pore size of the CNTs was determined by nitrogen adsorption/desorption measurement (Fig. 4). The S_{BET} surface area, pore volume and average pore diameter were $133.9\text{ m}^2/\text{g}$, $1.25\text{ cm}^3/\text{g}$ and 37.3 nm , respectively. It is important that there is enough space ($1.25\text{ cm}^3/\text{g}$) to contain the catalyst and ethylene polymerization inside.

3.2. Polymerization of ethylene

Ethylene polymerization was carried out with CNTs-supported Cp_2ZrCl_2 catalysts in different polymerization conditions. Fig. 5 shows the influence of the $[\text{Al}]/[\text{Zr}]$ molar ratio on ethylene polymerization activities. The results reveal that the supported catalysts have high catalytic activity ($10^6\text{ g PE/mol Zr h}$). With the increase in the $[\text{Al}]/[\text{Zr}]$ molar ratio, the activity of catalysts increases and two supported catalysts have similar activity.

Fig. 6 shows the influence of the $[\text{Al}]/[\text{Zr}]$ molar ratio on the ethylene polymerization rate of the two catalysts. The rate of

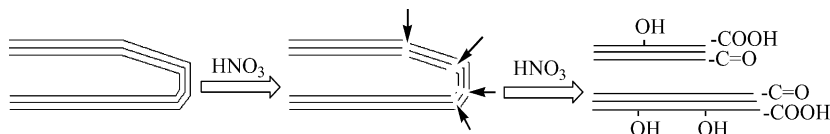


Fig. 2. The schematic process of opening the cap of the CNTs.

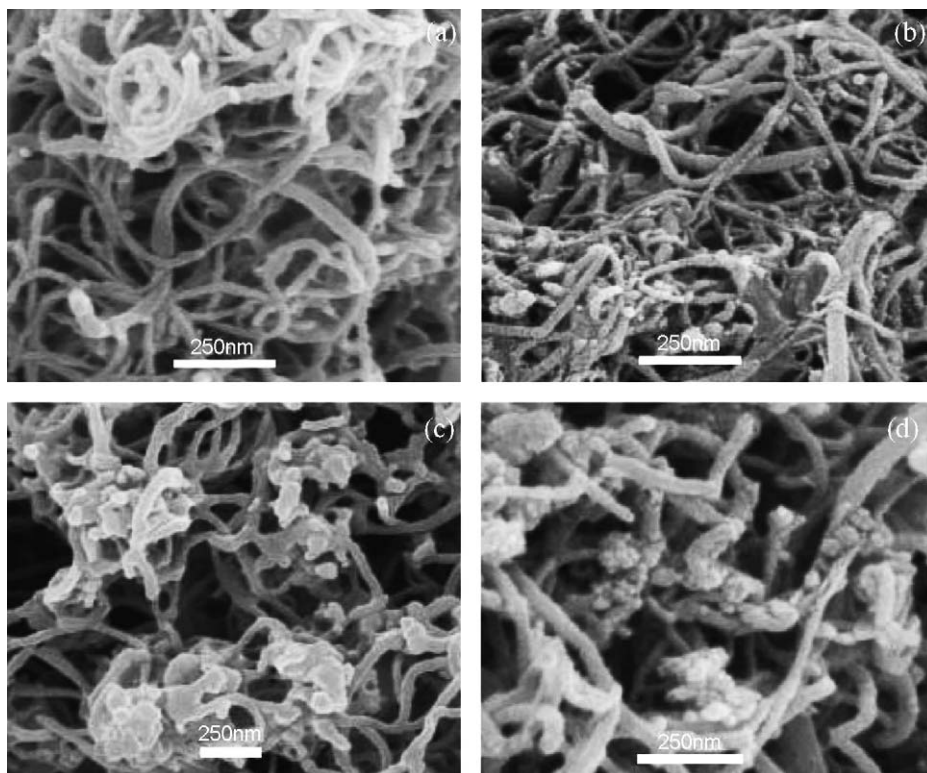


Fig. 3. SEM micrographs of CNTs: (a) pristine CNTs, (b) after treatment with nitric acid, (c) pristine CNTs supporting Cp_2ZrCl_2 catalyst and (d) open-ended CNTs supporting Cp_2ZrCl_2 catalyst.

polymerization increases in about 5 min and reached the maximum, then slowly decayed.

3.3. Morphology of the resultant polyethylene

The morphology of the resultant polyethylene was studied with SEM in detail. Fig. 7(a) and (b) shows the SEM images of the polyethylene prepared by pristine CNT-supported Cp_2ZrCl_2 catalyst at different polymerization temperature ($T_p = 50$ and

60°C , respectively). It is clear that, owing to the effect of the CNTs on the polyethylene, the resulting polyethylene is mostly nano-fibres. The diameters of the fibres are mostly 50–70 nm and larger than those of the pristine CNTs, indicating the presence of the polyethylene on the surface of the CNTs. That comes from the special structure of the CNTs: the pristine CNTs are long and slender fibres and capped at each end [17], so the Cp_2ZrCl_2 could not disperse into the pores and only adsorb on the surface of the CNTs. The resultant PE possibly encapsulates the sur-

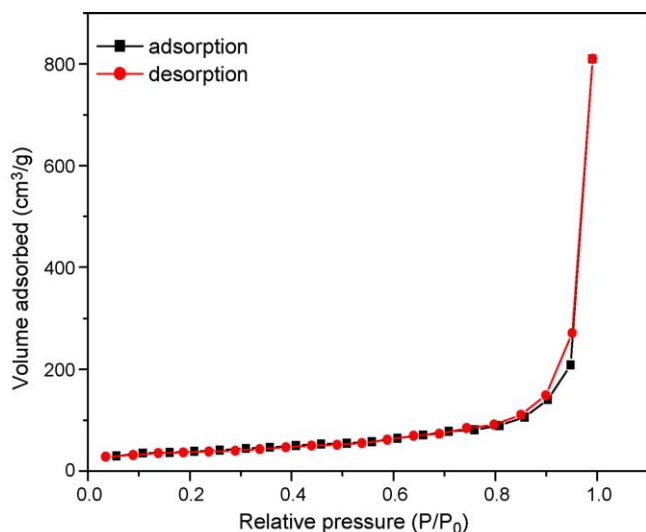


Fig. 4. Nitrogen adsorption/desorption isotherms of the pristine CNTs.

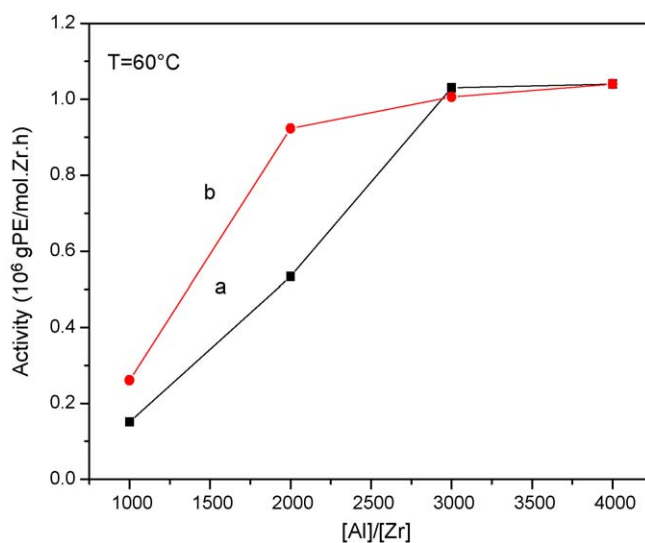


Fig. 5. Influence of $[\text{Al}]/[\text{Zr}]$ molar ratio on polymerization activity: (a) pristine CNTs-supported Cp_2ZrCl_2 and (b) open-ended CNTs supported Cp_2ZrCl_2 .

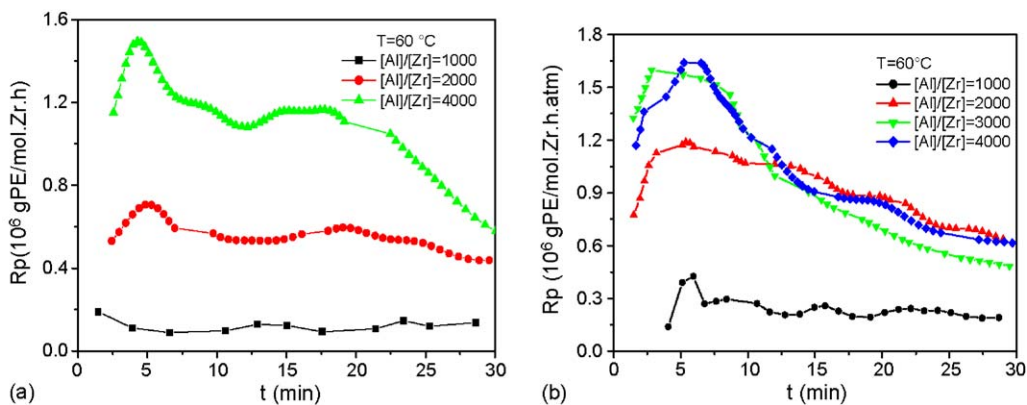


Fig. 6. The influence of $[\text{Al}]/[\text{Zr}]$ molar ratio on ethylene polymerization rate: (a) pristine CNTs-supported Cp_2ZrCl_2 and (b) open-ended CNTs supported Cp_2ZrCl_2 .

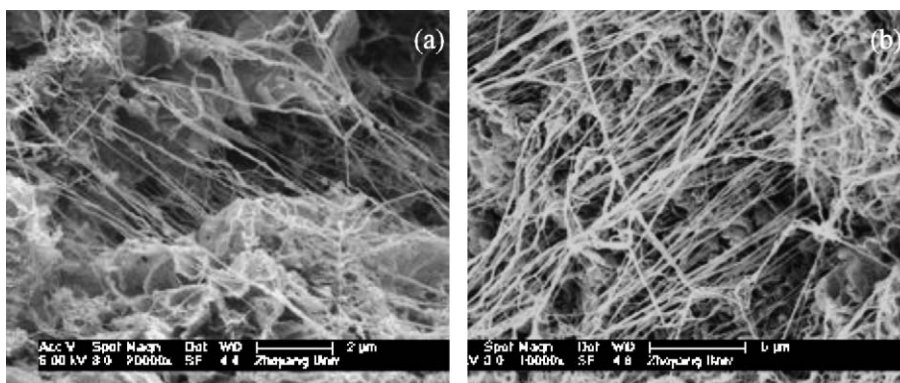


Fig. 7. SEM micrographs of polyethylene prepared by pristine CNTs supported Cp_2ZrCl_2 catalyst ($[\text{Al}]/[\text{Zr}] = 3000$): (a) $T = 50^\circ\text{C}$ and (b) $T = 60^\circ\text{C}$.

face of the CNTs and presents fibre morphology. The possible process is shown in Fig. 8.

Fig. 9(a) and (b) shows the SEM image of the polyethylene prepared by open-ended CNTs supported Cp_2ZrCl_2 catalyst. The polyethylene has mainly fractional morphology. This result comes from the change of the structure of CNTs. After treated with nitric acid, the capped ends of the CNTs were opened. The catalyst not only can adsorb on the surface of the CNTs but can also disperse into the pores. At 60°C , the polymerization proceeds rapidly, the hydraulic pressure of ethylene polymerization making the CNTs all break up into fragments. Therefore, the

polyethylene morphology resembles the broken particles. Since at 50°C , the polymerization rate decreases, the hydraulic pressure of ethylene polymerization cannot make the CNTs break up completely and some PE pieces have fibre morphology. The plausible process is shown in Fig. 10.

The intensity of the Raman peak at 1345 cm^{-1} is high, which indicates the present CNTs have a low degree of graphitization. As a comparison, carbon black (CB) was also used as supports of Cp_2ZrCl_2 catalyst for ethylene polymerization. Fig. 11 shows the SEM image of the CB and polyethylene prepared with CB-supported Cp_2ZrCl_2 , respectively. The CB has

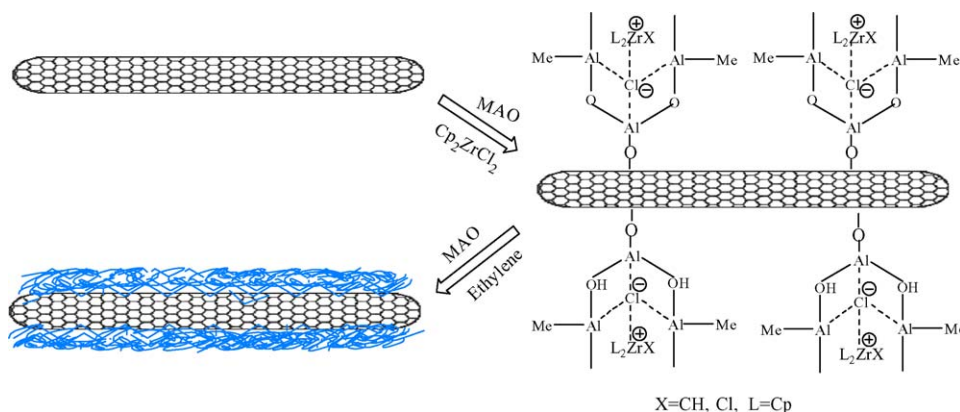


Fig. 8. The possible formation process of nano-polyethylene fibre with CNT-supported Cp_2ZrCl_2 catalyst.

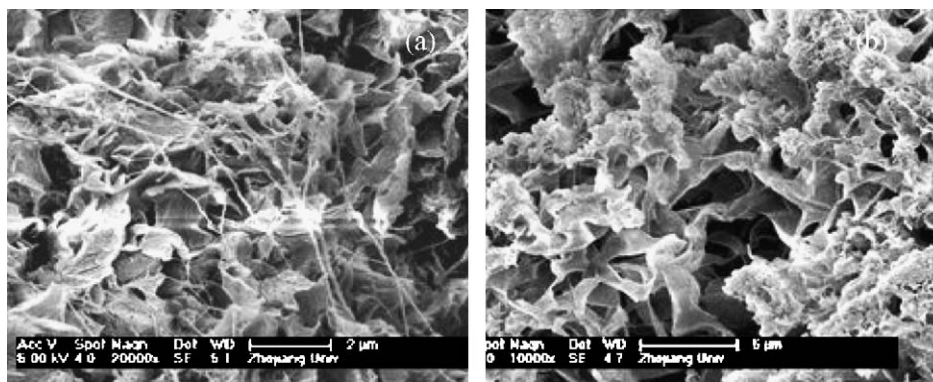


Fig. 9. SEM micrographs of polyethylene prepared with open-ended CNTs supported Cp_2ZrCl_2 catalyst ($[\text{Al}]/[\text{Zr}] = 3000$): (a) $T = 50^\circ\text{C}$ and (b) $T = 60^\circ\text{C}$.

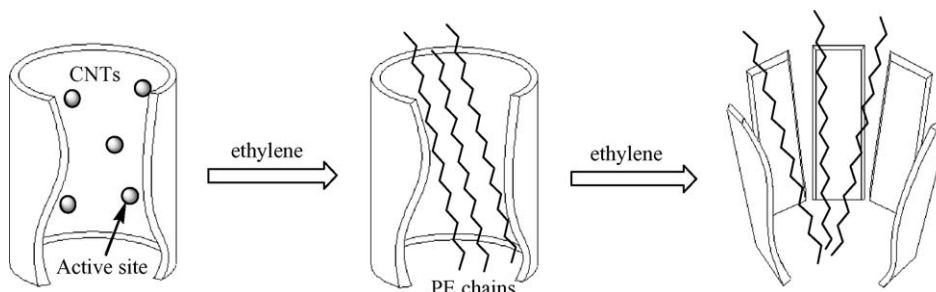


Fig. 10. The possible formation process of polyethylene fractional morphology.

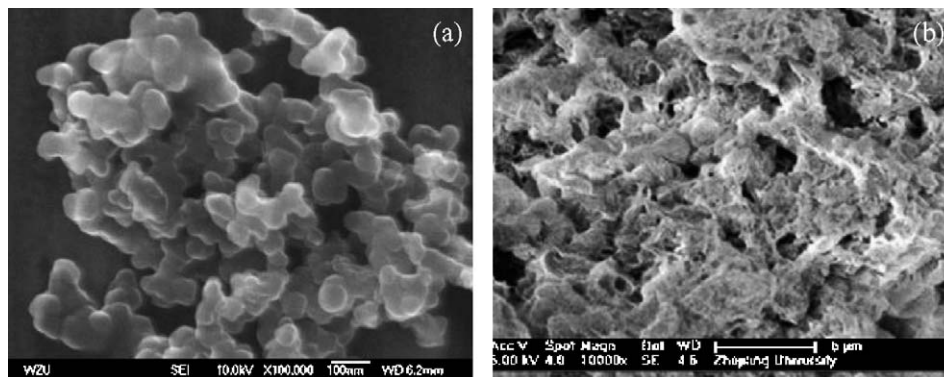


Fig. 11. SEM micrographs of (a) CB and (b) polyethylene prepared with CB-supported Cp_2ZrCl_2 catalyst ($[\text{Al}]/[\text{Zr}] = 3000$ and $T = 50^\circ\text{C}$).

spherical morphology with the diameter of 30–50 nm. The PE prepared with CB-supported Cp_2ZrCl_2 has amorphous morphology, which is different from the PE prepared with open-ended CNTs-supported Cp_2ZrCl_2 catalyst.

It is evident from these results that the structure of the CNTs has great effect on the morphology of the resulting polyethylene.

4. Conclusion

Both the pristine CNTs and open-ended CNTs supported Cp_2ZrCl_2 catalysts have high polymerization activities (10^6 g PE/mol Zr h). The SEM observation shows that the structure of the CNTs has a profound effect on the resulting PE morphology. For the pristine CNTs, the catalyst is mainly adsorbed on the surface of CNTs. Thus, polyethylene encapsulates the surface of CNTs and form fibrous morphology. After treatment

with nitric acid, the capped ends are opened partly. The catalyst can disperse into the pore of the CNTs, so the hydraulic pressure of ethylene polymerization make the CNTs break up into fragments and the resultant PE has fractional morphology.

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