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Immobilization of a zirconium complex bearing bis(phenoxyketimine) ligand on MCM-41 for ethylene polymerization

Shangtao Chen[a,b], Cunyue Guo[a,*], Lei Liu[c], Hong Xu[c], Jinxiang Dong [c], Youliang Hu [a,*]

[a] *Joint Laboratory of Polymer Science and Materials, Key Laboratory of Engineering Plastics, Institute of Chemistry,*
Chinese Academy of Sciences, Beijing 100080, China
[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100039, China*
[c] *Research Institute of Special Chemicals, Taiyuan University of Technology, Taiyuan 030024, China*

Abstract

A novel zirconium complex bearing bis(phenoxyketimine) ligand (**1**) bis((3,5-di-tert-butyl-C_6H_2-2-O)PhC=N(2,4-di-fluoro-C_6H_3))$ZrCl_2$ (**2**) was prepared and successfully immobilized on a mesoporous molecular sieve MCM-41 in chemical method. Results of slurry polymerization of ethylene with MCM-41-supported catalyst (**MC**) indicated that the morphologies of polyethylene obtained differed greatly in heptane and toluene. Homogeneous catalyst **2** exhibited a very high initial activity in ethylene polymerization at room temperature resulting in great viscosity of the system. When immobilized on MCM-41, **MC** showed a smooth yet highly active kinetic behavior. With MAO as the cocatalyst, the effects of Al/Zr molar ratio and polymerization temperature on catalytic activity and properties of polyethylene obtained were investigated. The results showed that polyethylene obtained with **MC** possessed higher molecular weight (M_n) and broader molecular weight distribution (M_w/M_n) than those formed with its homogeneous counterpart.
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1. Introduction

Recently, considerable attention has been paid to the early and late transition metal non-metallocene complexes incorporating [N,O]-based multidentate ligands due to their special characteristics, which might open up the possibility for preparing novel polyolefin materials with well-defined microstructures and controllable polymer properties [1–11]. However, for this new generation of single-site catalysts to be successfully employed in olefin polymerization, an efficient way is to make them heterogeneous by supporting on certain inorganic or organic carriers, such as SiO_2, $MgCl_2$, Al_2O_3 and polymers to control the morphology [12]. One strategy of catalyst heterogenization involves impregnating the catalyst on MAO treated support. However, the catalysts precursor added to the immobilized MAO exhibits reduced polymerization activity [13–15]. The disadvantage is overcome by employing partially hydrolyzed trimethyl aluminum (PHT) in the presence

of an external carrier like silica, for the activation of new diimine pyridine complexes of iron (II) [16].

Molecular sieves open another route to the immobilization of olefin polymerization catalysts where the porous environment plays a double role of catalysts' carrier and confined geometry for the polymerization reaction to occur [17,18]. Cp_2ZrCl_2 and Cp_2TiCl_2 immobilized onto MAO-pretreated NaY, a kind of zeolite molecular sieves, can polymerize ethylene with a small amount of additional MAO. However, the limited pore size of this microporous NaY zeolite prevents large metallocene or non-metallocene complexes from being entrapped inside the supercage [19,20]. With the discovery of MCM-41 [21–23], a well-defined and designable mesoporous molecular sieve with narrow pore size distribution, large internal surface area, distinct adsorption properties and hexagonal arrangement of uniform cylindrical pores (ca. 1.5–10 nm in diameter), and the successful preparation of polyethylene nanofibrils over metallocene complex supported onto a mesoporous silica fiber [24], enormous academic interests sprout in olefin polymerization concerning the employment of molecular sieves due to their ordered mesopores [25–33]. Thus, mesoporous materials are drawing more and more attention not only in view of the control of

polymerization locus but also for fabrication of polymeric materials of novel properties.

In this paper, a novel non-metallocene zirconium complex was synthesized and supported on MCM-41 for the first time for ethylene polymerization in slurry phase with emphasis on the polymerization kinetics and polymer properties.

2. Experimental

2.1. Materials and measurements

All manipulations of air- and/or moisture-sensitive compounds were carried out using drybox procedures or standard Schlenk techniques. MCM-41 was prepared in accordance with literature-reported method [34]. Ethylene of polymerization grade was purchased from Yanshan Petro-Chemical Ltd Co. (China) and used without further purification. MAO solution in toluene (1.4 mol/L) was purchased from Albemarle Corp. (USA). N-(2,4-difluorophenyl)benzamide was prepared by treating equimolar amounts of benzoyl chloride, 2,4-difluor-obenzenamine, and triethylamine in methylene chloride at 0 °C. The amide was recrystallized from hot toluene and dried before use. Toluene, hexane and tetrahydrofuran (THF) were refluxed with sodium/benzophenone and freshly distilled prior to use. Methylene chloride was vigorously degassed to remove oxygen and then distilled from P_2O_5. All other chemicals were obtained commercially and used as received.

^{1}H NMR (300 MHz) spectra were performed on a Bruker DMX-300 spectrometer. Mass spectra were carried out with an electron impact (EI) instrument (Kratos AEI MS-50). Elemental analyses were obtained using Carlo Erba 1106 and ST02 apparatus. Molecular weights (M_w and M_n) and molecular weight distribution (M_w/M_n) were determined by high temperature gel-permeation chromatography (GPC) on a PL-GPC220 instrument at 140 °C in trichlorobenzene and the data were analyzed relative to polystyrene standards. The melting temperatures (T_m) of polyethylenes were determined by differential scanning calorimetry (DSC) with a Perkin–Elmer DSC-7 operating under nitrogen at a heating rate of 10 °C min^{-1} from 50 to 160 °C, and T_m was recorded for each scan. The loading of zirconium in **MC** was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES POEMS TJA Co.). SEM images of the morphology of polyethylene obtained with supported and homogeneous catalysts were recorded on a JEOL JSM-6700F field emission scanning electron microscope.

2.2. Synthesis of the ligand (3,5-di-tert-butyl-C_6H_2-2-OH) PhC=N(2,4-di-fluoro-C_6H_3) (1)

Ligand **1** was prepared in a way similar to the published procedure [35]. The synthetic route of **1** and the corresponding catalyst **2** is depicted in Scheme 1.

N-(2,4-di-fluoro-phenyl)benzamide (3.50 g, 15.16 mmol) and PCl_5 (3.16 g, 15.16 mmol) were combined in a Schlenk flask under argon, dry methylene chloride (20 mL) was slowly added at 0 °C. The cold bath was removed, the solution was stirred for 0.5 h at room temperature and then refluxed for 4 h under argon. After removing the solvent under vacuum, the solid residue was dissolved in methylene chloride and filtered through a Celite pad. The resulting clear solution was transferred via cannula to a Schlenk flask filled with a slurry of $AlCl_3$ (2.42 g, 18.19 mmol) in 10 mL methylene chloride at 0 °C. The solution was stirred for 10 min before 10 mL methylene chloride solution of 2,4-di-tert-butylphenol (2.97 g, 14.42 mmol) was added. The reaction mixture was stirred at room temperature for 24 h. Pouring the resulting solution to ice water, the organic layer was separated and then washed with water, 1.0 M Na_2CO_3 and brine, and dried over Na_2SO_4. After filtration and solvent removal, the residual yellow solid was chromatographed on silica (10% ethyl acetate/hexane). The solution obtained was concentrated and placed at −30 °C overnight. The ligand **1** was obtained as yellow solid in 61% yield (based on phenol employed). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.48 (1H, d, ^4J(H,H)=2.4 Hz), 7.32 (3H, m), 7.17 (2H, m), 6.90 (1H, d, ^4J(H,H)=2.4 Hz), 6.71–6.59 (3H, m), 1.53 (9H, s, C(CH$_3$)$_3$), 1.13 (9H, s, C(CH$_3$)$_3$); MS (EI): 421 (55, M$^+$), 406 (100, M$^+$−15).
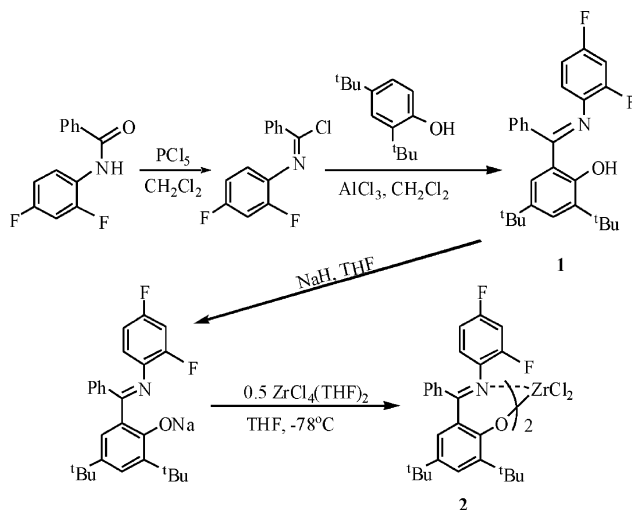
Scheme 1. Synthesis of ligand **1** and corresponding zirconium complex **2**.

Anal. Calcd for $C_{27}H_{29}NOF_2$: C, 76.93; H, 6.93; N, 3.32. Found: C, 76.89; H, 6.85; N, 3.37.

2.3. Synthesis of the catalyst (2)

Ligand **1** (210 mg, 0.50 mmol) and excess NaH were combined in a 50 mL three neck flask, 10 mL THF was slowly added at 0 °C. The solution was stirred at room temperature for 5 h. Another 10 mL THF was added, the mixture was centrifugated for 30 min. The above clear solution was transferred via cannula to a Schlenk flask filled with $ZrCl_4$ (THF)$_2$ (94 mg, 0.25 mmol) at −78 °C. The cold bath was removed and the reaction mixture was stirred at room temperature overnight. Evaporation of the solvent in vacuum yielded a crude product. Methylene chloride (6 mL) was added to the resulting solid, and the mixture was stirred for 10 min and centrifugated for 30 min. The above clear solution was transferred. The organic filtrates were concentrated in vacuum. The resulting product was washed with hexane (10 mL×3) and dried to afford complex **2** as light yellow solid in 46% yield. ^1H NMR (CDCl$_3$, 300 MHz): major C_2 isomer only, δ 7.50 (2H, d, ^4J(H,H)=2.4 Hz), 7.34 (6H, m), 7.19 (4H, m), 6.92 (2H, d, ^4J(H,H)=2.4 Hz), 6.71–6.59 (6H, m), 1.53 (18H, s, C(CH$_3$)$_3$), 1.13 (18H, s, C(CH$_3$)$_3$). Anal. Calcd for

$C_{54}H_{56}Cl_2F_4N_2O_2Zr$: C, 64.65; H, 5.63; N, 2.79. Found: C, 64.38; H, 5.66; N, 2.82.

2.4. Preparation of MCM-41-supported complex 2 (MC)

0.6 g of MCM-41 was dried at 120 °C in vacuum to constant weight and reacted with MAO at 50 °C for 15 h before washed with large amount of toluene to remove un-reacted MAO. Then, 24 μmol of complex **2** together with 6 mL of toluene were added and reacted at 40 °C for 7 h. The supported catalyst was washed several times with toluene until the upper liquid layer turned colorless and dried in vacuum at 50 °C to give 0.8 g of light yellow powder. Loading of zirconium in the resultant **MC** was 29 μmol g^{-1}.

2.5. Ethylene polymerization under atmospheric pressure

To an ethylene purged 250 mL thermostated flask with a magnetic stirrer (unless otherwise noted) were added 100 mL of solvent and MAO to predetermined amount. The mixture was stirred until the solution was saturated with ethylene. Then desired amount of catalyst was injected to initiate the polymerization at atmospheric pressure. The reaction was quenched with 10 wt% acidified ethanol after 0.5 h.
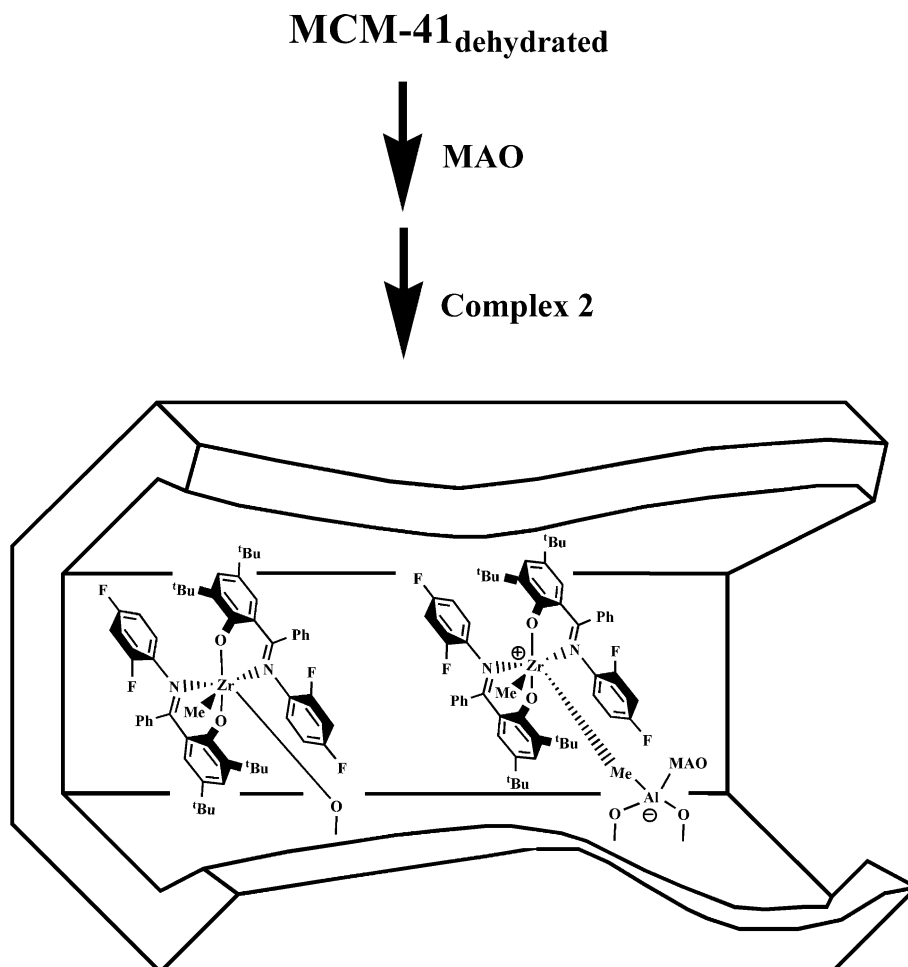

Fig. 1. Schematic representation of the preparation of Zr-MCM-41 (**MC**).

Table 1
Results of ethylene polymerization with **2**/MAO and **MC**/MAO

Run	Cat.	Al/Zr	Temp. (°C)	Activity[a]	T_m (°C)	M_n[b] (10^4 g/mol)	M_w/M_n[b]
1	**2**	2000	25	16.72	33.2	6.6	1.87
2	**2**	2000	40	10.25	132.8	–	–
3	**2**	2000	60	5.56	131.1	1.5	2.03
4	**MC**	500	25	0.04	–	–	–
5	**MC**	1000	25	0.09	–	15.2	3.28
6	**MC**	1500	25	1.64	135.0	17.4	3.83
7	**MC**	2000	25	4.51	134.2	13.6	4.51
8	**MC**	2500	25	5.16	–	9.6	5.22
9	**MC**	2000	40	3.62	133.8	5.7	6.67
10	**MC**	2000	60	2.83	132.5	4.8	7.18
11[c]	**MC**	2000	60	1.24	132.6	–	–

Polymerization conditions: Zr = 1.0 μmol, solvent = 100 mL toluene, ethylene pressure = 0.1 MPa. Polymerization time = 30 min, Run 1–3 with mechanical stirrer.
[a] 10^6 g (molZr)$^{-1}$ h^{-1}.
[b] Determined by GPC.
[c] Heptane instead of toluene was used.

The polymer was kept in excess of acidified ethanol overnight, filtered and washed with ethanol and water, separated and dried at 70 °C in vacuum to constant weight.

3. Results and discussion

For bis((3,5-di-tert-butyl-C_6H_2−2-O)PhC=N(2,4-di-fluoro-C_6H_3))ZrCl$_2$ to be supported on MCM-41, MAO was firstly employed to modify the mesoporous MCM-41 by reacting with the silanol groups lined along its internal walls of pores. Then the homogeneous catalyst could be anchored onto MCM-41 by means of the 'bridge' of MAO or μ-oxo-like bonding (Fig. 1).

Table 1 lists the results of ethylene polymerization by **2** and **MC**. Seen from it is that the MCM-41-supported catalyst prepared by the way described herein catalyzed ethylene polymerization in a moderate mode and no sudden exothermal phenomenon from implosion occurred during the polymerization process. In fact, ethylene polymerization employing **2**/MAO at room temperature can hardly last more than 10 min under similar conditions to that of using **MC**/MAO as catalyst because the reaction system becomes too viscous due to so high an initial polymerization activity and the poor morphology of the produced polymers. When the polymerization was carried out for **2** at 20 °C, very fast ethylene absorption was observed. The reactor was filled with large amount of polymers. The significant decrease of catalytic activity might result from the difficulty of ethylene diffusion (Fig. 2(a)). The polymerization of homogeneous catalyst **2** at 40 °C (Fig. 2(b)) and 60 °C followed the same trend.

The immobilization of complex **2** on MCM-41 reduces the initial polymerization activity. Fig. 2(c) and (d) shows that **MC**/MAO exhibited a different catalytic behavior from **2**/MAO. **MC** is a long lasting and highly effective catalyst and its catalytically active centers do not decay significantly over the time frame of the experiments. The homogeneous catalyst shows very high initial activity but it sharply falls down in the course of polymerization. However, the catalytic activity of **MC** decreases slowly after the peak value and maintain steady

yet high values compared to its unsupported counterpart **2**. This phenomenon can be attributed to the steric hindrance of MCM-41's inner walls around the active sites, preventing the aggregation of active species of the system which may led to sudden release of great quantity of heat during polymerization. The steric effect of the surface of molecular sieves may also hinder the activation reaction of catalyst **MC**, therefore, prolongs the induction period of the catalyst. In addition, the bimolecular interactions, which would result in the deactivation of catalyst, are suppressed by immobilizing **2** on MCM-41, so **MC** can maintain high and steady activity over prolonged periods [25,26,36,37]. Also reflected in Table 1 is that the catalytic activities of **MC**/MAO decrease with increasing polymerization temperatures. Like common silica-supported catalysts, increasing amount of cocatalyst to **MC** also give polymerization activities from 0.04×10^6 g mol^{-1}Zr h^{-1} (Run 4 in Table 1) to 5.16×10^6 g mol^{-1}Zr h^{-1} (Run 8 in Table 1) [14].

Compared with homogeneous catalyst **2**/MAO, the molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polyethylene obtained with **MC** using MAO as cocatalyst
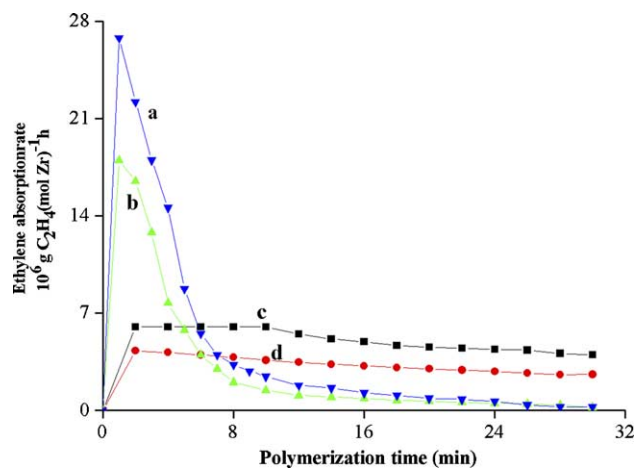

Fig. 2. Correlation of catalytic activity and polymerization reaction time: (a) **2**/MAO at 25 °C, Run 1 in Table 1; (b) **2**/MAO at 40 °C, Run 2 in Table 1; (c) **MC**/MAO at 25 °C, Run 7 in Table 1; (d) **MC**/MAO at 40 °C, Run 9 in Table 1.
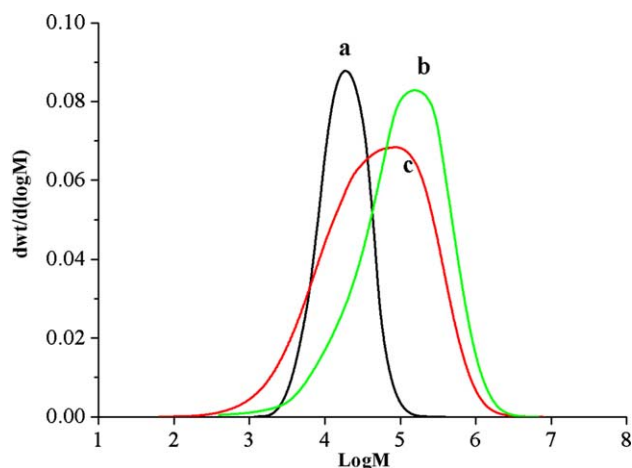
Fig. 3. GPC traces of polyethylenes: (a) **2**/MAO at 60 °C, Run 3 in Table 1; (b) **MC**/MAO at 25 °C, Run 7 in Table 1; (c) **MC**/MAO at 60 °C, Run 10 in Table 1.

are much higher (Table 1 and Fig. 3). The high M_n might be contributed to the suppression of β-hydrogen transfer. Moreover, the molecular weights depend significantly on MAO concentration and decrease with increasing Al/Zr molar ratio. The results can be attributed to the frequently occurred chain-transfer reaction to MAO especially at high concentrations [38].

As to the greatly increased value of M_w/M_n like depicted in Fig. 3 reasonable explanation for this is that some catalytically active sites dissociate from being anchored to pores of MCM-41 because quite a lot of MCM-41 framework collapse and more catalytically active sites are exposed to ethylene molecules due to both the formation of polyethylene chains

and release of large quantity of polymerization heat [27]. In a word, higher molecular weight and broader molecular weight distribution originates mainly from the low rate of termination and chain transfer reaction with the molecular sieve supported catalyst in addition to the formation of different active sites species during the polymerization process [39]. Additionally, it's a great advantage for the polymers to have relatively high molecular weight, and more important, broad molecular weight distribution in order to improve their mechanical properties and processability.

Found in the SEM images of Fig. 4 is that the morphology of **MC** (Fig. 4(b)) copies the particle form of MCM-41, indicating with great possibility the modification of MAO on the inner walls of MCM-41 pores without significant change of the appearance of MCM-41 (Fig. 4(a)). However, **MC**/MAO-catalyzed polymerization of ethylene in heptane showed low activity and the polymers obtained have particle morphology of large size (Fig. 4(c)). The concrete reasons for this observation are unclear now. When the polymerization of ethylene is carried out in toluene, in addition to fine powders, extended-chain polyethylene nanofibrils [24,29–31] with diameters of about 10–100 nm (Fig. 4(d)) are observable indicating that polyethylene nanofibers are formed in ethylene extrusion polymerization, during which polyethylene chains grow out of the honeycomb nanotubes of MCM-41.

4. Conclusion

Bis((3,5-di-tert-butyl-C_6H_2-2-O)PhC=N(2,4-di-fluoro-C_6H_3))ZrCl$_2$ can be supported on MCM-41 and catalyze
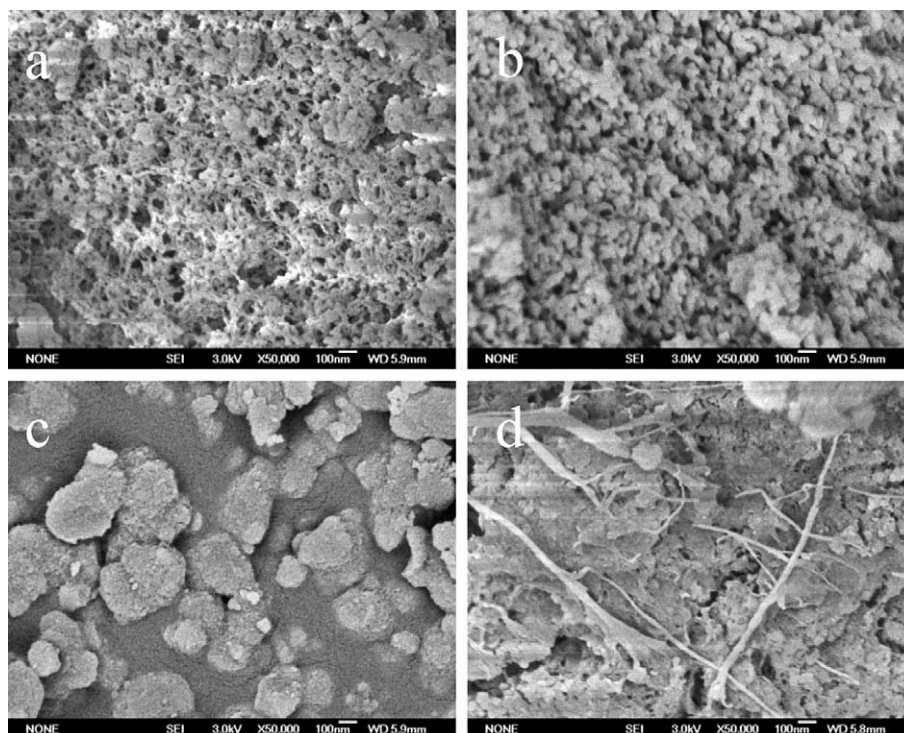

Fig. 4. SEM images: (a) MCM-41; (b) **MC**; (c) polyethylene formed with **MC**/MAO in heptane, Run 11 in Table 1; (d) polyethylene formed with **MC**/MAO in toluene, Run 3 in Table 1.

ethylene polymerization in a smooth yet highly active mode. Polyethylene obtained with supported catalyst has higher molecular weights, broader molecular weight distribution and higher melting temperatures compared to that of polyethylene formed with its homogeneous counterpart. In addition, polyethylenes of different morphologies are obtained when **MC**/MAO-catalyzed polymerization of ethylene proceeds in heptane and toluene. Extended-chain polyethylene nanofibrils with diameters of about 10–100 nm are observable when the polymerization of ethylene is carried out in toluene.

Acknowledgements

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