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EFFECTS OF AMINO GROUPS AND MICROSTRUCTURE OF ORGANIC MESOPOROUS SILICA SUPPORTED METALLOCENE CATALYSTS ON ETHYLENE POLYMERIZATION[*]

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Abstract Mesoporous silica (MS), 3-aminopropyltriethoxysilane (APTES) modified mesoporous silica (AMS), bis(3-trimethoxysilylpropyl)amine modified mesoporous silica (BAMS) and APTES modified solid spherical silica (AS) were prepared and used to immobilize metallocene catalysts for ethylene polymerization. Gel permeation chromatography results showed that polyethylenes (PEs) catalyzed by AMS (or BAMS) supported metallocene catalysts at the molar ratios of Al/Zr = 100, 300 and 500 were of bimodal molecular weight distribution (BMWD); while PEs catalyzed by the above catalysts at the molar ratios of Al/Zr ≥ 800 were of monomodal molecular weight distribution (MMWD). However, MS (or AS) supported metallocene catalysts could only produce PEs with MMWD in spite of the molar ratio of Al/Zr. It was because that AMS (or BAMS) supported catalysts possessed two active sites for ethylene polymerization at low molar ratios of Al/Zr due to the combination effects of mesopore geometrical constraint and amino groups of the supports, which was confirmed by X-ray photoelectron spectroscopy. This brings forward a novel and easy method for the synthesis of polyolefin with BMWD.

Keywords: Organic mesoporous silicas; Supported metallocene catalysts; Polyethylene; Bimodal molecular weight distribution.

INTRODUCTION

Immobilizing metallocene catalysts over supports is a desirable way to overcome problems encountered in commercial applications of homogeneous metallocene catalysts, such as difficulty in controlling polymer morphology, instability of catalyst in slurry or gas-phase process and the use of large amount of expensive MAO[1−4]. The most commonly used supports are spherical amorphous silica, alumina and $MgCl_2$. Recently, a new type of silica-based mesoporous particles has been used for the synthesis of heterogeneous metallocene catalysts in olefin polymerization[5−10]. The geometrical constraint of the mesopores in these particles as polymerization microreactors affects the way of monomer insertion and chain growth processes, offering a new possible route to control chain structure and crystal morphology of polyolefin during polymerization[8−10]. For better processing and improving mechanical properties, polyethylene (PE) with bimodal molecular weight distribution (BMWD) was favorable. Several methods had been used to synthesize PE with BMWD, such as supporting two or more kinds of metallocene catalysts or one kind of metallocene catalyst with multiple catalytic active structures on supports for ethylene polymerization[11−15].

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In this work, amino groups modified mesoporous silicas were prepared *via* one-pot synthesis. After treated with MAO, they were used to immobilize bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2) for the synthesis of supported metallocene catalysts. As there were two kinds of functional groups (hydroxyl groups and amino groups) on the supports, two kinds of catalytic active sites might be formed in the supported catalysts, which would be profitable to the synthesis of PE with BMWD during ethylene polymerization. Mesoporous silica and amino groups modified solid spherical silica were also prepared to immobilize Cp_2ZrCl_2 for ethylene polymerization for comparison.

EXPERIMENTAL

Materials

Analytical grade tertraethyl orthosilicate (TEOS) was purchased from Beijing Huaxueshiji Factory. Non-ionic surfactant poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (PEO-*b*-PPO-*b*-PEO, average M_n = 5800), 3-aminopropyltriethoxysilane (APTES) and bis(3-trimethoxysilylpropyl)amine (BMSPA) were all from Aldrich. Solid spherical SiO_2 was purchased from Qingdao Chemical Factory. Bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2, Boulder Scientific Company), methylaluminoxane (MAO: 10 wt% in toluene, Ethyl Corporation) and ethylene (polymerization grade, Liaoyang Chemical Corporation) were used. All the above materials were used without further treatment. Toluene was dried over 0.4 nm molecular sieves for 10 days, and then was refluxed over Na/K alloy for at least 8 h.

Preparation of Supports

Amino groups modified mesoporous silicas were synthesized by one-pot synthesis method[16]. The preparation procedure required a molar ratio of 1.00 Si:0.2 PEO-*b*-PPO-*b*-PEO:80 H_2O:0.5 H_2SO_4, in which APTES (or BMSPA) and TEOS were used as the silica resources and the molar ratio of APTES (or BMSPA)/TEOS was 1:9. After PEO-*b*-PPO-*b*-PEO was added to deionized water, the solution was stirred for 30 min in a closed polyethylene bottle, then H_2SO_4 was added to adjust pH = 2. TEOS and APTES (or BMSPA) were slowly added to the surfactant solution under stirring in turn. After stirring for 4 h, white precipitate was formed. The mixture was then aged at 80°C for 24 h. White powder was collected by filtration, washed thoroughly with deionized water and then air-dried. The template was removed off *via* solution extraction for 72 h. Inorganic mesoporous silica (MS) was also synthesized according to the above procedure except for the use of TEOS as the silica resource instead of the mixture of APTES (or BMSPA) and TEOS.

APTES modified solid spherical SiO_2 (AS) was synthesized by the post synthesis method[17]. 10.0 g of solid spherical SiO_2 was dried for 24 h at 150°C in vacuum to remove the physical adsorbed water and then cooled to room temperature under nitrogen protection. Later on, the SiO_2 was added to a flask in which there were 5.2 g of APTES and 115 mL of dried toluene. The suspension was kept stirring for 4 h at 40°C. The white powder was collected by filtration, washed thoroughly with toluene and then heated at 150°C for 4 h.

Immobilization of Cp_2ZrCl_2 over Supports

1.0 g of support was dried in vacuum at 100°C for 2 h to remove the physical adsorbed water and then cooled to room temperature under nitrogen protection. 20 mL of dried toluene and 2.0 mL of MAO (10 wt% in toluene) were added, the mixture was then kept stirring at 60°C for 8 h. After the slurry was washed with 20 mL × 3 of dried toluene, 15 mL of dried toluene and 14.6 mg of Cp_2ZrCl_2 were added, and the mixture was kept stirring at 60°C for 24 h. Pale yellow powder was obtained by filtration and washed with 20 mL × 3 of dried toluene, and then dried in vacuum at room temperature. All the above operations were carried out under nitrogen pretection.

Ethylene Polymerization

Ethylene polymerization was carried out in a 0.4 L glass reactor. Toluene, MAO and heterogeneous catalyst were added to the reactor in turn, in which the concentration of Zr was 50 μmol/L. The total volume of polymerization medium was 150 mL. The above operations were carried out under nitrogen protection. The polymerization reaction was initiated by introducing ethylene into the reactor under stirring. Temperature and partial pressure of ethylene were kept constant during reaction (60°C and 1.22×10^5 Pa). Polymerization was terminated by the addition of acidified ethanol. The product was isolated by filtering and washed with ethanol.

The polymer was then air-dried under ambient conditions. At last, the products were dried at 60°C in a vacuum oven.

Characterization

Nitrogen sorption ($T = -196$°C) data were obtained with a Micromeritics Tristar 3000 automated gas adsorption analyzer. Before sorption measurements, the samples were degassed in a Micromeritics Vac Prep061 degasser overnight at 150°C under 13.3 kPa pressures. Isotherms were evaluated with the Barrett-Joyner-Halenda (BJH) theory to give the pore parameters, including surface areas, pore size and its distribution. Elemental analyses were conducted with an Elemental Analysensysteme GmbH VarioEL. Aluminum and zirconium contents fixed on the catalyst surface were determined by inductively coupled plasma (ICP) emission spectroscopy. The sample was treated with chloridic, nitric, fluoridic and perchloric acids and heated by using a microwave oven. A solution was prepared in a volumetric flask, and the contents were determined in a Perkin-Elmer 2000, calibrated with standard solutions containing known amounts of the same concentration magnitude of the analyzed solutions. Molecular weight and molecular weight distribution of the products were measured with gel permeation chromatography (GPC) operated at 135°C and equipped with four Waters Styragel columns (HMW2, 2 × HMW6W, HMW7) and an RI detector. 1,2,4-Trichlorobnezene was applied as solvent at a flow rate of 1.0 cm^3/min. The columns were calibrated with narrow molar mass distribution polystyrene standards using a universal calibration method. X-ray photoelectron spectroscopy (XPS) results were recorded on a VG Escalab MK II spectrometer using an Al-K$_\alpha$ exciting radiation from an X-ray source operated at 10.0 kV and 10 mA.

RESULTS AND DISCUSSION

The nitrogen adsorption-desorption results and nitrogen contents of 3-aminopropyltriethoxysilane (APTES) modified mesoporous silica (AMS), bis(3-trimethoxysilylpropyl)amine (BMSPA) modified mesoporous silica (BAMS), mesoporous silica (MS) and APTES modified solid spherical silica (AS) are shown in Table 1. From Table 1, it could be found that AMS, BAMS and MS were mesoporous materials, and the extents of the incorporated amino silane in AMS, BAMS and AS were 1.4, 1.1 and 0.4 mmol/g, respectively. AMS, BAMS, MS and AS were then used to immobilize metallocene catalyst for the preparation of supported catalysts, namely, Zr/AMS, Zr/BAMS, Zr/MS and Zr/AS. Their zirconium and aluminum contents are shown in Table 2.

Table 1. Structural parameters and nitrogen content of different supports

Support	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	Nitrogen content (mmol/g)
AMS	432	0.45	5.5	1.4
BAMS	403	0.35	6.1	1.1
MS	451	0.56	5.2	–
AS	31	0.0	0.0	0.4

Table 2. Zirconium and aluminium contents

Supported catalyst	Support	Al (mg/g)	Zr (mg/g)
Zr/AMS	AMS	89.7	7.8
Zr/BAMS	BAMS	76.3	7.2
Zr/MS	MS	101.3	10.2
Zr/AS	AS	47.2	3.6

The results of ethylene polymerizations *via* catalyst Zr/AMS are showed in Table 3. Figure 1 shows GPC curves of the polyethylene (PEs). As Zr/AMS was activated by MAO at the molar ratio of Al/Zr = 100 (including the aluminium amount of the supported metallocene catalyst), the activity of the catalyst was only 11 kg PE/(molZr·h), the molecular weight (M_w) of the PE was 33.0 kg/mol, and the value of M_w/M_n was as high as 9.2, GPC curve shows that the PE was of bimodal molecular weight distribution (BMWD) (Al/Zr = 100 in Fig. 1). At the molar ratio of Al/Zr = 300, the activity of the catalyst and the M_w of the PE increased to 288 kg PE/(molZr·h) and 56.2 kg/mol, respectively, the value of M_w/M_n decreased to 9.0, and GPC curve

(Al/Zr = 300 in Fig. 1) showed that the PE was also of BMWD. As the molar ratio of Al/Zr increased to 500, both the activity of the catalyst and the M_w of the PE increased, and the value of M_w/M_n decreased to 5.4. GPC curve (Al/Zr = 500 in Fig. 1) showed that the PE was of wide monomodal molecular weight distribution. As the molar ratio of Al/Zr increased to 800 and 1200, although the activity of the catalyst and the M_w of the PE kept increasing, the value of M_w/M_n decreased to 2.7 and 2.5, respectively, and GPC curves (Al/Zr = 800 and 1200 in Fig. 1) showed that the products were of monomodal molecular weight distribution (MMWD). As the molar ratio of Al/Zr further increased to 2000 and 3000, the activity of the catalyst also increased, but the M_w of the PE decreased, GPC curves (Al/Zr = 2000 and 3000 in Fig. 1) showed that the products were of MMWD. These meant that there might be two catalyst activity sites in Zr/AMS as it was activated by MAO at low molar ratios of Al/Zr.

Table 3. Results of ethylene polymerizations *via* Zr/AMS

Code	Al/Zr	Yield (g)	M_w (kg/mol)	M_w/M_n	Specific activity[a]	Catalytic activity[b]
1	100	0.08	33.0	9.2	0.9	11
2	300	2.16	56.2	9.0	24.6	288
3	500	3.02	62.0	5.4	34.5	403
4	800	4.66	191.6	2.7	53.1	621
5	1200	10.58	399.5	2.5	120.6	1410
6	2000	17.32	379.4	2.8	197.5	2310
7	3000	22.20	321.3	2.6	253.1	2960

Polymerization condition: 150 mL of toluene, 87.7 mg of catalyst or 7.5 μmol of Zr, 60°C; 1.22×10^5 Pa of ethylene; 1 h; [a] In g PE/(gcat·h); [b] In kg PE/(molZr·h)

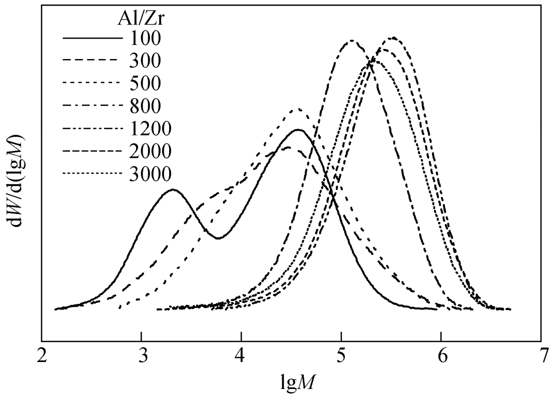

Fig. 1 GPC curves of polyethylenes catalyzed by Zr/AMS at various molar ratios of Al/Zr

The results of ethylene polymerizations *via* Zr-BAMS are showed in Table 4. From Table 4, it can be found that the M_w/M_n of PEs from ethylene polymerization carried out at the molar ratio of Al/Zr = 100 and 500 were 7.4 and 5.2. GPC curves (Al/Zr = 100 and 500 in Fig. 2) showed that they were of bimodal or wide molecular weight distribution. As the molar ratio of Al/Zr increased to 800 and 3000, the M_w/M_n decreased to 2.7 and 2.6. GPC curves (Al/Zr = 800 and 3000 in Fig. 2) showed that these PEs were of MMWD. These results indicated that there might be two catalyst activity sites in amino mesoporous silica supported metallocene catalysts (Zr/AMS and Zr/BAMS) as they were activated by MAO at low molar ratios of Al/Zr.

The results of ethylene polymerizations *via* Zr/AS and Zr/MS are showed in Table 5. Zr/AS (or Zr/MS) could only produce PEs with MMWD whether the molar ratio of Al/Zr was low or high, suggesting that the production of PEs with BMWD was due to the combination effect of mesopore geometrical constraint and amino groups of the supports. It could also be found that at the same molar ratio of Al/Zr, the catalytic activity of Zr/MS was higher than that of Zr/AMS (or Zr/BAMS), suggesting that the incorporation of amino groups into the support decreased the activity of the catalyst.

Table 4. Results of ethylene polymerizations *via* Zr/BAMS

Code	Al/Zr	Yield (g)	M_w (kg/mol)	M_w/M_n	Specific activity[a]	Catalytic activity[b]
1	100	0.21	10.8	7.4	2.2	28
2	500	1.48	63.1	5.2	15.6	197
3	800	4.29	79.7	2.7	45.2	572
4	3000	22.58	191.6	2.6	237.7	3011

Polymerization condition: 150 mL of toluene, 95.0 mg of catalyst or 7.5 μmol of Zr, 60°C; 1.22×10^5 Pa of ethylene; 1 h; [a] In g PE/(gcat·h); [b] In kg PE/(molZr·h)

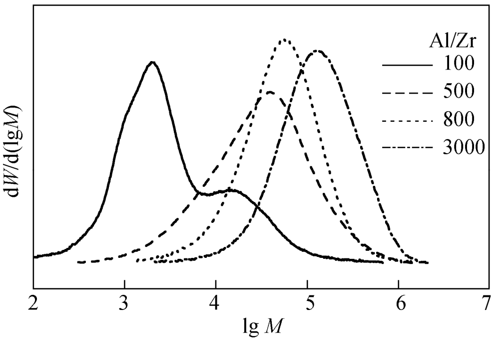

Fig. 2 GPC curves of polyethylenes catalyzed by Zr/BAMS at various molar ratio of Al/Zr

Table 5. Results of ethylene polymerizations *via* Zr/MS and Zr/AS

Code	Support	Al/Zr	Yield (g)	M_w (kg/mol)	M_w/M_n	Specific activity[a]	Catalytic activity[b]
1	MS	100	0.90	99.5	2.3	4.7	120
2	MS	800	6.40	146.9	3.2	33.7	853
3	AS	100	0.41	69.4	2.9	6.1	55
4	AS	800	6.92	76.7	2.6	103.3	923

Polymerization condition: 150 mL of toluene, 7.5 μmol of Zr, 60°C; 1.22×10^5 Pa of ethylene; 1 h;
[a] In g PE/(gcat·h); [b] In kg PE/(molZr·h)

Figure 3 presents possible catalytic active structures in Zr/AMS. For the supported metallocene catalyst over MAO modified silica, such as Zr/MS, the metallocene catalyst is connected to the support *via* the formation of Al-Cl bond (structure “d” in Fig. 3A). After activated by MAO, structure “e” is formed (Fig. 3B)[18]. But for Zr/AMS, there were amino groups on the AMS surface except for silica hydroxyl groups, therefore metallocene molecule was also connected to the support in the form of structure “f” (Fig. 3A) besides structure “d”. After Zr/AMS was activated by MAO, structure “f” was turned to structure “g” (Fig. 3B), and the M_w of PE produced from structure “g” was different from that from structure “e”[19]. Structure “g” was unstable to MAO and could react with MAO to form structure “h” (Fig. 3C), which was similar to structure “e” in the behavior of ethylene polymerization from their structures. However, when Zr/AMS was activated by MAO with low molar ratio of Al/Zr, such as Al/Zr =100, owing to the space limitation of the mesopore in the support, the concentration of MAO in the mesopores further decreased, and the amount of MAO around the supported metallocene molecules was enough to react with structure “f” to form structure “g”, but not enough to further react with structure “f” to form structure “h”, hence, there were two kinds of active sites (structures “e” and “g”) in Zr/AMS under this condition, which produced PE with BMWD. When Zr/AMS was activated by MAO with high molar ratio of Al/Zr, such as Al/Zr = 800, the amount of MAO in each mesopore increased, which was enough to react with structure “f” to form structure “h”, thus there was only one kind of active site (the molecular weight of PE polymerized from structure “e” was obviously the same to that from structure “h”) in Zr/AMS, which produced PE with MMWD under the condition. The situation of Zr/BAMS was similar to that of Zr/AMS. However, There was not the space limitation in the case of Zr/AS, the co-catalyst MAO could easily touch the immobilized metallocene molecule on the surface of AS, thus even though at low molar ratio of Al/Zr, such as Al/Zr = 100, the added MAO could easily diffuse to the metallocene catalyst site and react with structure “f” to form structure “h”, therefore Zr/AS could only produce PE with MMWD.

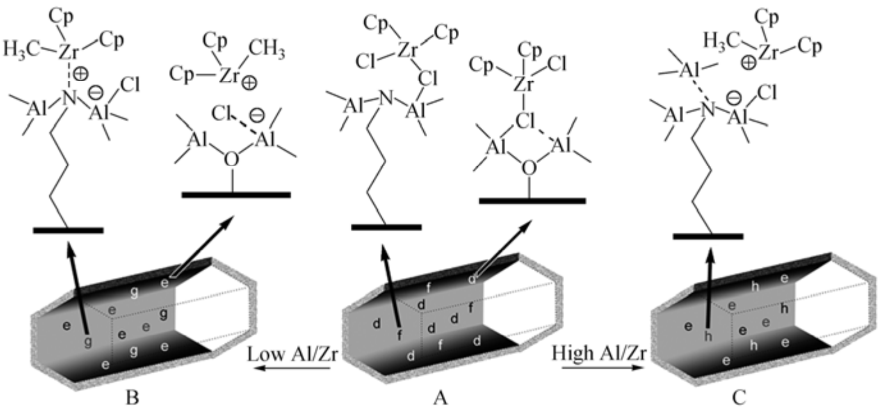

Fig. 3 The possible catalytic active structures in the mesopores of (A) Zr/AMS, (B) Zr/AMS activated by MAO at low ratio of Al/Zr, (C) Zr/AMS activated by MAO at high ratio of Al/Zr

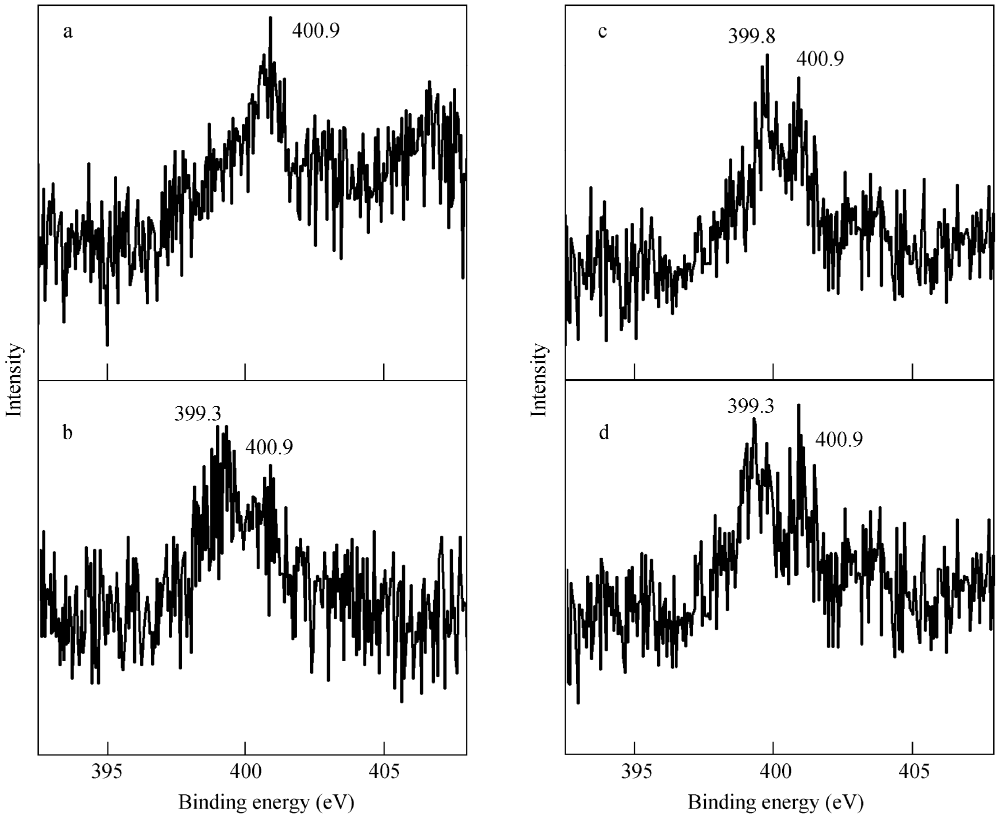

Fig. 4 XPS patterns of N_{2p} electron binding energy of (a) AMS, (b) Zr/AMS, (c) Zr/AMS activated by MAO with Al/Zr = 100, (d) Zr/AMS activated by MAO with Al/Zr = 800

XPS patterns (Fig. 4 and Fig. 5) confirmed the above suggestion. The binding energy of N_{2p} electrons of AMS was 400.9 eV (Fig. 4a). There were two peaks of the binding energy of N_{2p} electrons in the XPS profiles of Zr/AMS, which located at 400.9 eV and 399.3 eV (Fig. 4b), suggesting that only part of amino groups reacted with MAO. The lower binding energy of N_{2p} electrons resulted from the formation of N—Al bonds. The N—Al bond is weaker than the N—H bond, and the N_{2p} electrons are easier to be excited. As Zr/AMS was activated by MAO with Al/Zr = 100, the peak at 399.3 eV disappeared and a new peak at 399.8 eV appeared (Fig. 4c), which was in accordance with the formation of N—Zr^+ bonds, because the N—Zr^+ bond was stronger than the N—Al bonds and the N_{2p} electrons were more difficult to be excited. When Zr/AMS was activated by more MAO with Al/Zr = 800, there was no peak at 399.8 eV in the XPS profiles (Fig. 4d), suggesting the absence of N—Zr^+ bonds, which was in accordance with the absence of structure "h" in Fig. 3(C). While for Zr/AS, there were two peaks of the binding energy of N_{2p} electrons at 400.9 and 399.3 eV in the XPS profiles (Fig. 5a). When Zr/AS was activated by MAO with Al/Zr = 100, there were the same two peaks at 400.9 and 399.3 eV, but there was no peak of the binding energy of N_{2p} electrons at 399.8 eV in the XPS profiles (Fig. 5b), suggesting the absence of N—Zr^+ bonds, which was in accordance with the absence of structure "g" in Zr/AS under the above condition.

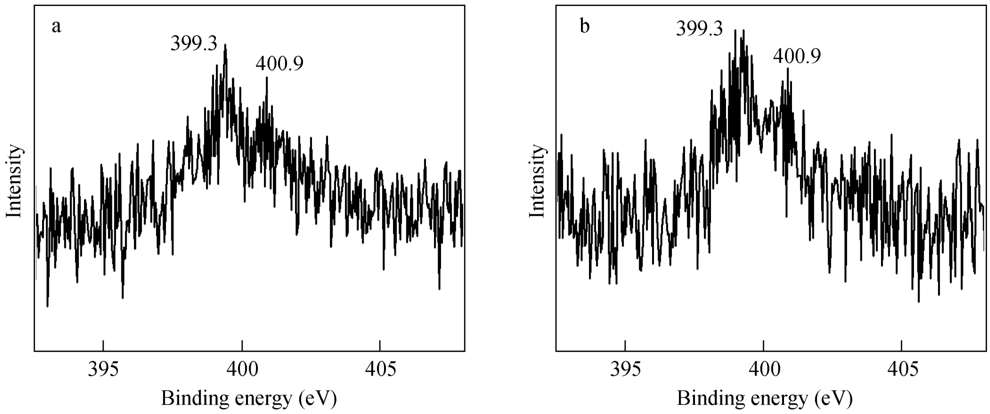

Fig. 5 XPS patterns of N_{2p} electron binding energy of (a) Zr/AS, (b) Zr/AS activated by MAO with Al/Zr = 100

CONCLUSIONS

PEs from ethylene polymerization catalyzed by Zr/AMS (or Zr/BAMS) at low molar ratio of Al/Zr were of bimodal molecular weight distribution due to the combination effect of mesoporous geometrical constraint and amino groups of the support, and PEs obtained from Zr/MS (or Zr/AS) were of monomodal molecular weight distribution in spite of various molar ratios of Al/Zr due to the lack of the combination effect. The incorporation of amino groups to the heterogeneous metallocene catalyst decreased the activity of the catalyst. More investigation on the catalytic behavior of the above supported catalysts for copolymerization of ethylene is being carried out by the authors.

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