Effective activation of metallocene catalyst with AlMCM-41 in propylene polymerization

Tsuneji Sano, Tsunehito Niimi, Toyoaki Miyazaki, Shingo Tsubaki, Yasunori Oumi and Toshiya Uozumi

School of Materials Science, Japan Advanced Institute of Science and Technology, Tatsunokuchi, Ishikawa 923–1292, Japan
E-mail: t-sano@jaist.ac.jp

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AlMCM-41 was prepared by a post-synthesis alumination of MCM-41 and applied to propylene polymerization with *rac*-ethylene(bisindenyl)zirconium dichloride and triisobutylaluminium. The resulting catalyst system gave selectively isotactic polypropylene and the polymer yield was strongly dependent upon the evacuation temperature in the pretreatment of the AlMCM-41 before use. From the linear relationship between the polymer yield and the number of Lewis acid sites on the AlMCM-41 evaluated by pyridine adsorption, it was found that Lewis acid sites on AlMCM-41 are able to activate effectively the metallocene compound, resulting in the formation of active species.

KEY WORDS: AlMCM-41; metallocene; cocatalyst; polymerization; propylene

1. Introduction

Since the synthesis of purely siliceous mesoporous materials with large pore diameter (2–10 nm) such as MCM-41, FSM-16 and SBA-15 is reported, much effort has been devoted to insertion of catalytically active components into the framework of mesoporous material. Typically, various metals are incorporated into the framework by isomorphous substitution of the metal for silicon atoms during hydrothermal synthesis [1]. This direct synthesis method often suffers from an undesirable decrease in the structure ordering. Recently, several researchers have shown the effectiveness of a post-synthesis method, which consists of reacting the surface silanol groups present in the inner wall surfaces with various metal alkoxides or chlorides in nonaqueous solution followed by calcination [2]. The post-synthesis method does not cause serious structural deformation of the resulting materials. We have also studied the post-synthesis alumination of MCM-41 using organoaluminium compounds, especially trimethylaluminium. It was found that the post-synthesis alumination with trimethylaluminium is effective for incorporation of aluminium into the framework of MCM-41 [3]. The catalytic reactions studied with the metal-substituted mesoporous materials were mainly oxidation and acid catalysis based on the Brønsted acidity. Only a few papers have dealt with the potential use of Lewis acid sites generated on aluminated MCM-41 (AlMCM-41), especially for Friedel–Crafts alkylation [4].

It is now generally accepted that the active species in the metallocene catalyst system for olefin polymerization is a coordinately unsaturated transition metal cation and is stabilized by bulky counter-anions such as the Lewis acidic methylalumoxane (MAO) and triphenylcarbenium tetrakis(pentafluorophenyl)borate [5]. Soga and we have already reported that some inorganic carriers exhibiting Lewis acidity such as Al_2O_3, $MgCl_2$ and heteropolyacids also function as counter-anions [6–8]. However, an influence of the Lewis acidity of such carriers on the polymerization behavior of metallocene catalyst was not investigated systematically.

In the present study, therefore, it was tried to apply the AlMCM-41 prepared by the post-synthesis method with TMA into the metallocene catalyst system in order to clarify the nature of Lewis acidity of the AlMCM-41. This communication reports the preliminary result of propylene polymerization with *rac*-ethylene(bisindenyl)zirconium dichloride, which shows isospecificity in α-olefin polymerization, and the triisobutylaluminium catalyst system combined with AlMCM-41.

2. Experimental

2.1. Synthesis of AlMCM-41 and characterization

Siliceous MCM-41 was prepared following the procedure described in the literature [9]. The MCM-41 prepared was calcined at 500 °C for 20 h to decompose the surfactant (hexadecyltrimethylammonium bromide) and obtain the white powder. This white powder was used as the parent MCM-41. Prior to alumination with trimethylaluminium (TMA), the MCM-41 sample was dried at 280 °C for 24 h under vacuum in order to remove adsorbed water because TMA is very sensitive to water. The number of silanol groups in the parent MCM-41 was estimated to be ca. 3 mmol/g if the weight loss from 400 to 1300 °C in the thermogravimetric curve was assumed to be attributed to the dehydroxylation process ($2SiOH \rightarrow SiOSi + H_2O$). Taking into account the number of silanol groups, for alumination,

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1 g of MCM-41 was dispersed in 10 ml of dry toluene containing 4 mmol of TMA. The resulting mixture was maintained at room temperature for 48 h without stirring. The powder (designated as AlMCM-41) was filtered, washed with dry toluene three times, dried at room temperature under vacuum and calcined at 500 °C for 6 h. As a reference, amorphous silica gel (grade P3; Fuji Silysia Co. Japan) was similarly aluminated by TMA. Identification of the products was carried out by X-ray diffraction (Rigaku, RINT2000). Elemental composition was determined by X-ray fluorescence (Philips, PW2400). Textural properties (BET surface area, pore diameter, pore volume) were evaluated by nitrogen adsorption at −196 °C (Bel Japan, Belsorp 28SA).

2.2. Acidity measurement

The nature of acid sites of the AlMCM-41 and the aluminated silica gel was investigated using pyridine as the probe molecule. The sample (ca. 20 mg) was pressed into self-supporting wafers and placed into the FTIR cell allowing heating under vacuum up to 900 °C. Pyridine was dried over an activated Linde 5A molecular sieve and further degassed by the conventional freeze–pump–thaw technique. Prior to adsorption the sample was evacuated to ca. 10^{-3} Pa at the desired temperature (500–800 °C) for 2 h. The sample was then cooled to 150 °C where nearly 1.3×10^2 Pa of pyridine was introduced into the FTIR cell. After 1 h of adsorption, the excess and weakly adsorbed pyridine was removed by evacuation at the same temperature for 30 min. FTIR spectra of chemisorbed pyridine on AlMCM-41 or aluminated silica gel were measured at room temperature using a Jeol JIR-7000 spectrometer.

2.3. Propylene polymerization and analytical procedures

Polymerization of propylene was conducted in a 100 cm^3 stainless-steel autoclave equipped with a magnetic stirrer. After the reactor was filled with nitrogen, measured amounts of toluene, triisobutylaluminium (TIBA) as an alkylating agent, AlMCM-41 or aluminated silica gel evacuated at the desired temperature (500–800 °C) and *rac*-ethylene(bisindenyl)zirconium dichloride (*rac*-Et(Ind)$_2$ $ZrCl_2$) were added to the reactor in this order at room temperature. The reactor was then evacuated at liquid-nitrogen temperature, and 7 dm^3 of propylene were introduced. Polymerization was started by quickly heating the reactor up to the polymerization temperature (40 °C), and quenched with acidified methanol (5 wt% HCl). The resulting polymers were extracted with boiling *o*-dichlorobenzene for 8 h. The weight-average molecular weight ($\overline{M}_w$) and molar mass distribution ($\overline{M}_w/\overline{M}_n$, $\overline{M}_n$: number-average molecular weight) of the polymers were measured at 145 °C by gel-permeation chromatography (GPC, Senshu Scientific SSC7100) using *o*-dichlorobenzene as a solvent. The melting points (T_m) of the polymers were measured on a Seiko DSC-220C calorimeter with a heating rate of 10 °C/min. ^{13}C NMR spectra of the polymers were measured in 1,2,4-trichlorobenzene/benzene-d_6 (9/1 v/v) at 140 °C using a Varian GEM-300 spectrometer operating at 75.4 MHz.

3. Results and discussion

3.1. Characterization of AlMCM-41

Figure 1 shows X-ray diffraction patterns of the parent MCM-41 and a series of AlMCM-41 samples evacuated at various temperatures. The bulk Si/Al ratio of the AlMCM-41 was 4.0. The parent MCM-41 exhibited a typical X-ray diffraction pattern with four-peaks as described by Beck et al. [10]. The AlMCM-41 samples gave slightly lower quality X-ray diffraction patterns than the MCM-41 sample. The (210) diffraction peak disappeared by the alumination with TMA. The intensities of the other three diffraction peaks ((100), (110) and (200)) slightly decreased by alumination followed by thermal treatment at 500–800 °C. To get more reliable information about the mesoporous structure of AlMCM-41, nitrogen adsorption isotherms were measured. All isotherms exhibited sharp inflection characteristic of capillary condensation at the relative pressure of ca. 0.3. As listed in table 1, a large reduction in the BET surface, the pore diameter and the pore volume of the AlMCM-41 by thermal treatment was not observed. These results indicate that serious degradation of the AlMCM-41 framework hardly takes place during the thermal treatment.

To evaluate the amount and type of acid sites on the AlMCM-41 prepared by the post-synthesis alumination of MCM-41 with TMA, FTIR spectra of pyridine adsorbed on various AlMCM-41 samples evacuated at 500–800 °C were

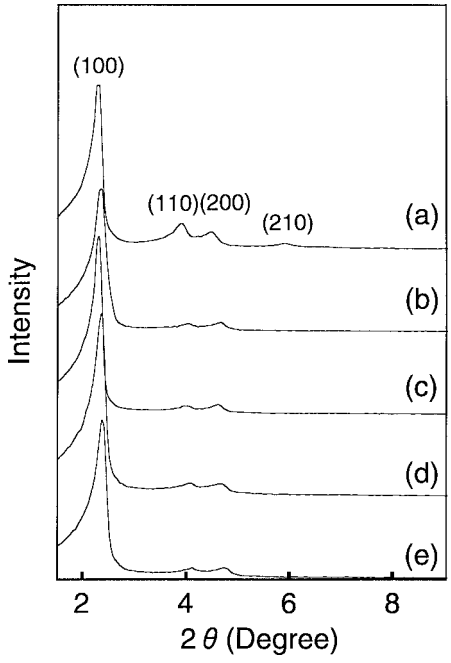

Figure 1. Powder X-ray diffraction patterns of the parent MCM-41 and AlMCM-41 evacuated at various temperatures. (a) MCM-41, (b) 500 °C, (c) 600 °C, (d) 700 °C and (e) 800 °C.

Table 1
Characteristics of AlMCM-41 and aluminated silicas evacuated at various temperatures.

Sample No.	Porous material	Bulk Si/Al	Evacuation temp. (°C)	BET surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
1	Parent MCM-41	–	–	973	2.74	0.90
2	AlMCM-41	4.0	500	703	2.32	0.52
3	AlMCM-41	4.0	600	702	2.32	0.52
4	AlMCM-41	4.0	700	689	2.32	0.52
5	AlMCM-41	4.0	750	684	2.12	0.52
6	AlMCM-41	4.0	800	653	2.12	0.50
7	Parent silica gel	–	–	636	8.94	1.34
8	Aluminated silica	5.0	600	495	7.06	1.05
9	Aluminated silica	5.0	700	415	7.06	0.93
10	Aluminated silica	5.0	800	402	6.58	0.88

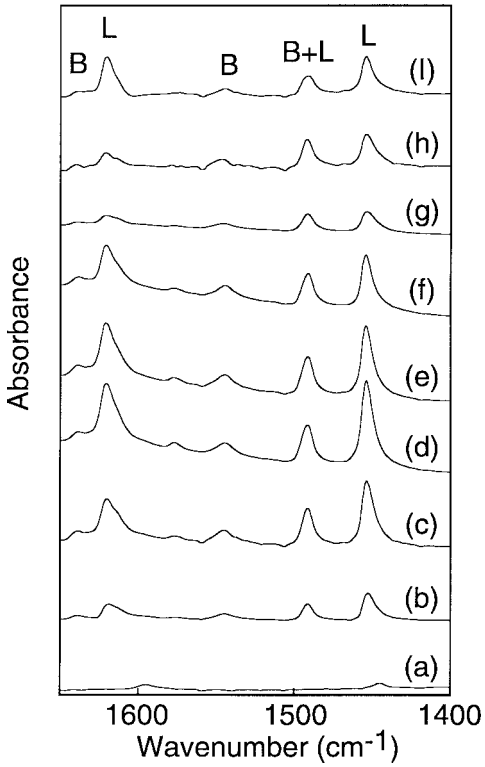

Figure 2. FTIR spectra of pyridine adsorbed on AlMCM-41 and aluminated silicas evacuated at various temperatures. MCM-41: (a) 600 °C; AlMCM-41: (b) 500, (c) 600, (d) 700, (e) 750 and (f) 800 °C; aluminated silica gel: (g) 600, (h) 700 and (i) 800 °C. B and L denote Brønsted- and Lewis-bound pyridines, respectively.

measured. As shown in figure 2 (b)–(f), the strong peak at 1454 cm^{-1}due to pyridine bound on Lewis acid sites as well as the weak one at 1546 cm^{-1} due to pyridinium ions on Brønsted acid sites were observed for all samples [2]. No peak was observed in the FTIR spectrum of the pure siliceous MCM-41 (figure 2(a)). This indicates that a majority of acid sites on the AlMCM-41 are Lewis acid sites. Moreover, it was also found that the peak intensity at 1454 cm^{-1} increased with an increase in the evacuation temperature and reached a maximum at ca. 700 °C, and then decreased again with the evacuation temperature, while the peak intensity at 1546 cm^{-1} hardly changed.

As it is well known that the pore wall of MCM-41 is amorphous, the amorphous silica gel was similarly aluminated with TMA as a reference. The bulk Si/Al ratio was 5.0. The BET surface area, the average pore diameter and the pore volume of the aluminated silicas evacuated at various temperatures were also listed in table 1. A slight reduction in the BET surface area and the pore volume was observed. Although the characteristic peaks due to pyridine species adsorbed on Lewis and Brønsted acid sites were observed in the FTIR spectrum of the aluminated silica gel evacuated at 600 °C, the peak intensities were considerably lower than those on the AlMCM-41 evacuated at 600 °C and only a slight increase in the peak intensities was observed after the higher thermal treatment, as shown in figure 2 (g)–(i). Taking into account that the bulk Si/Al ratio of the aluminated silica gel was almost the same as that of the AlMCM-41, the above results strongly indicate that Lewis acid sites are effectively generated on MCM-41 as compared with the amorphous silica gel.

3.2. Propylene polymerization

Polymerization of propylene was conducted at 40 °C with *rac*-Et$(Ind)_2ZrCl_2$ and AlMCM-41 evacuated at 500–800 °C using TIBA as the alkylating agent. The catalyst system gave only isotactic polypropylene. Figure 3 shows the correlation between the evacuation temperature in the pretreatment of the AlMCM-41 before use and the yield of polypropylene. The polymer yield increased, passed through a maximum value at ca. 700 °C and decreased again. The tendency of the polymer yield in dependence of the evacuation temperature was very similar to that of Lewis acid sites as shown in figure 2 (b)–(f). The use of siliceous MCM-41 in place of the AlMCM-41 gave no polymer. A trace amount of polymer was obtained using the liquid fraction of the *rac*-Et$(Ind)_2ZrCl_2$/AlMCM-41/TIBA catalyst system after aging. These results strongly indicate that existence of Al in the MCM-41 framework is a critical factor for formation of active species in the polymerization of propylene. Taking into account the high surface area of the AlMCM-41, most of the active species seems to exist in the pores of the AlMCM-41.

Figure 4 shows the relationship between the normalized amount of Lewis acid sites and the polymer yield. The amount of Lewis acid sites is normalized based on the peak intensity at 1454 cm^{-1} in the FTIR spectrum of the pyridine

Table 2
Analytical data of polypropylenes obtained.

Run No.	Porous material	Evacuation temp. (°C)	T_m (°C)	$\overline{M}_w$ $\times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	[mmmm] (%)
1	AlMCM-41	500	131.7(140.5)	20	3.3	80.5
2	AlMCM-41	600	131.7(143.0)	16	3.2	80.4
3	AlMCM-41	700	131.7(140.5)	20	3.5	79.1
4	AlMCM-41	750	129.2(139.3)	17	3.6	–
5	AlMCM-41	800	129.8(140.5)	16	3.3	81.6
6	Aluminated silica	600	135.5(144.3)	15	3.9	81.9
7	Aluminated silica	700	138.0(147.4)	17	3.4	80.1
8	Aluminated silica	800	136.7(146.1)	16	3.2	81.0
9[a]	(MAO)	–	121.7	41	2.4	80.6

[a] Polymerization conditions: *rac*-Et(Ind)$_2$ZrCl$_2$ = 0.001 mmol, Al(from MAO)/Zr = 1000, propylene = 7 dm^3 (STP), temperature = 40 °C, time = 30 min, polymer yield = 11.4 g.

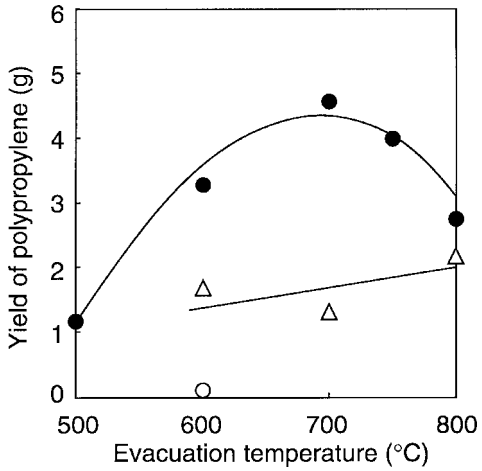

Figure 3. Effect of evacuation temperature of AlMCM-41 on yield of polypropylene. Polymerization conditions: AlMCM-41 = 0.5 g, *rac*-Et(Ind)$_2$ZrCl$_2$ = 0.02 mmol, TIBA/Zr = 50, propylene = 7 dm^3 (STP), temperature = 40 °C, time = 2 h. (●) AlMCM-41, (○) MCM-41 and (△) aluminated silica gel.

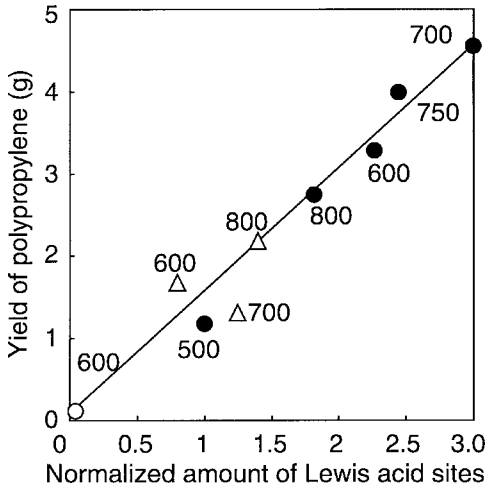

Figure 4. Relationship between normalized amount of Lewis acid sites and yield of polypropylene. (●) AlMCM-41, (○) MCM-41 and (△) aluminated silica gel. Arabic numbers denote evacuation temperature of porous materials (°C).

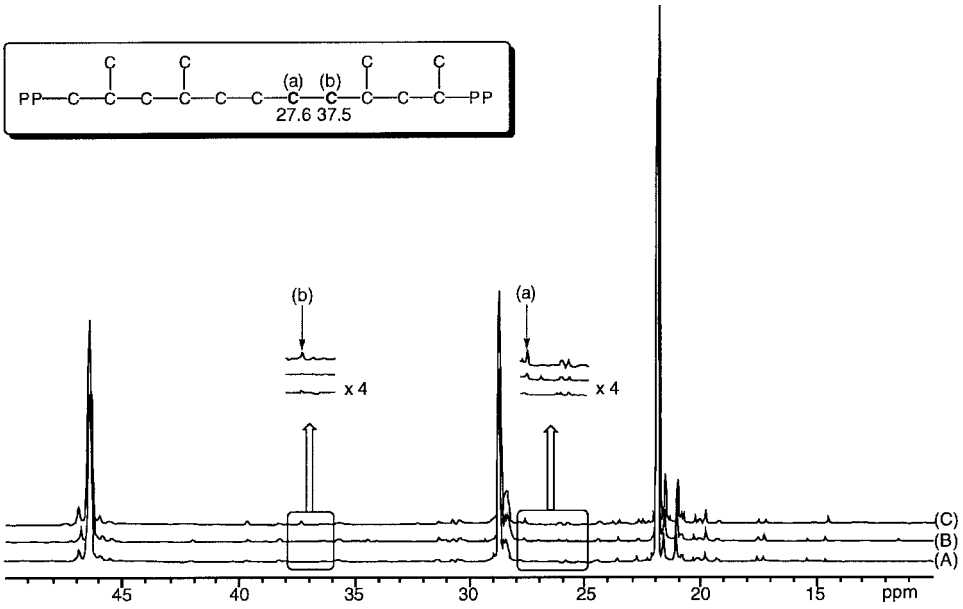

Figure 5. ^{13}C NMR spectra of polypropylenes obtained with *rac*-Et(Ind)$_2$ZrCl$_2$ using (A) aluminated silica, (B) AlMCM-41 and (C) MAO.

Table 3
Effect of *rac*-Et(Ind)$_2$ZrCl$_2$ content on propylene polymerization.[a]

Run No.	*rac*-Et(Ind)$_2$ZrCl$_2$ (mmol)	Yield of polypropylene (g)	T_m (°C)	$\overline{M}_w$ $\times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
10	0.02	4.55	131.7(140.5)	24	3.0
11	0.01	3.68	133.0(141.1)	15	3.5
12	0.002	3.24	132.9(142.4)	17	3.2
13	0.00002	1.58	136.1(143.0)	23	3.4
14	0.000002	0.0701	–	–	–

[a] Polymerization conditions: AlMCM-41 = 0.5 g, TIBA = 1 mmol, propylene = 7 dm^3 (STP), temperature = 40 °C, time = 2 h; evacuation temperature of AlMCM-41 = 700 °C.

adsorbed on the AlMCM-41 evacuated at 500 °C. The linear relationship between the polymer yield and the normalized amount of Lewis acid sites was observed, indicating the effective activation of metallocene catalyst by Lewis acid sites of the AlMCM-41. Table 2 summarizes analytical data of resulting polymers, e.g., the melting point (T_m), the isotacticity [mmmm] pentad, the weight-average molecular weight ($\overline{M}_w$) and molar mass distribution ($\overline{M}_w/\overline{M}_n$). As the DSC curves of polymers for T_m displayed shoulders at the high-temperature region, the temperatures of shoulders are also designated in parentheses. These values of T_m, [mmmm], $\overline{M}_w$ and $\overline{M}_w/\overline{M}_n$ were not dependent upon the evacuation temperature of the AlMCM-41. There was no difference in the isotacticity [mmmm] pentad between polypropylenes obtained using the AlMCM-41 and MAO. Commercial MAO (from Tosoh Akzo Co., Japan) was treated under vacuum in order to remove free TMA [3]. This indicates that the stereospecificity of *rac*-Et(Ind)$_2$ZrCl$_2$ hardly changed by activation of Lewis acid sites on the AlMCM-41. A large difference in T_m may be explained by a difference in the microstructure, i.e., the amount of –(CH$_2$)$_4$– units (1,3-insertion of propylene monomer) in a polymer chain as shown in figure 5 (B) and (C) [11–13].

Next, the aluminated silica gel was applied to propylene polymerization instead of the AlMCM-41. As shown in figure 3, the polymer yield was lower than that with the AlMCM-41 and slightly increased with the evacuation temperature in the pretreatment of the aluminated silica gel before use. This was consistent with the slight increase in the amount of Lewis acid sites after the higher thermal treatment in figure 2 (g)–(i). No deviation from the linear relationship between the polymer yield and the amount of Lewis acid sites was observed, as shown in figure 4. The isotacticity [mmmm] pentad, $\overline{M}_w$ and $\overline{M}_w/\overline{M}_n$ of the polymer produced were similar to those on the AlMCM-41 (table 2). These results indicate that the same active species as those on the AlMCM-41 are formed on the aluminated silica gel, although the active species on both systems differ somewhat in concentration. The higher T_m may be attributable to the absence of –(CH$_2$)$_4$– units in a polymer chain (figure 5(A)).

Therefore, it is clear from these above results that Lewis acid sites are effectively generated on MCM-41 by alumination with TMA and the amount of Lewis acid sites is strongly dependent upon the thermal treatment temperature as compared with the aluminated silica gel.

To get further information concerning activation of *rac*-Et(Ind)$_2$ZrCl$_2$ by Lewis acid sites on the AlMCM-41, polymerizations of propylene were conducted varying the amount of *rac*-Et(Ind)$_2$ZrCl$_2$. The results obtained are summarized in table 3. Although a linear relationship between the amount of *rac*-Et(Ind)$_2$ZrCl$_2$ used and the polymer yield was not observed, the polymer yield increased with an increase in the amount of *rac*-Et(Ind)$_2$ZrCl$_2$. This suggests that the AlMCM-41 is useful as a heterogenized cocatalyst.

From the above results, it was concluded that the Lewis acid sites on the AlMCM-41 are able to activate effectively the metallocene catalyst and do function as counter-anions.

References

[1] A. Corma, V. Fornes, M.T. Navarro and J. Perez-Pariente, J. Catal. 148 (1994) 569;
Z. Luan, C. Cheng, W. Zhou and J. Klinowski, J. Phys. Chem. 99 (1995) 1018;
A. Sayari, I. Moudrakovski, C. Danumah, C.I. Ratclitte, J.A. Ripmeester and K.F. Preston, J. Phys. Chem. 99 (1995) 16373;
D.Y. Zhao and D. Goldfarb, J. Chem. Soc. Chem. Commun. (1995) 875;
Z.Y. Yuan, S.Q. Liu, T.H. Chen, J.Z. Wang and H.X. Li, J. Chem. Soc. Chem. Commun. (1995) 973;
D.M. Antonelli and J.Y. Ying, Chem. Mater. 8 (1996) 874;
H.H.P. Yiu and D.R. Brown, Catal. Lett. 56 (1998) 57;
Z. Zhu, Z. Chang and L. Kevan, J. Phys. Chem. B 103 (1999) 2680.

[2] R. Mokaya, W. Jones, Z. Luan, M.D. Alba and J. Klinowski, Catal. Lett. 37 (1996) 113;
R. Mokoya and W. Jones, J. Chem. Soc. Chem. Commun. (1997) 2185;
R. Ryoo, S. Jun, J.M. Kim and M.J. Kim, J. Chem. Soc. Chem. Commun. (1997) 2225;
M. Cheng, Z. Wang, K. Sakurai, F. Kumata, T. Saito, T. Komatsu and T. Yashima, Chem. Lett. (1999) 131;
Z. Luan, M. Hartmann, D. Zgao, W. Zhou and L. Kevan, Chem. Mater. 11 (1999) 1621;
M.S. Morey, G.D. Stucky, S. Schwarz and M. Fröba, J. Phys. Chem. B 103 (1999) 2037.

[3] Y. Oumi, H. Takagi, S. Sumiya, R. Mizuno, T. Uozumi and T. Sano, Micropor. Mesopor. Mater., in press.

[4] E. Armengol, M.L. Cano, A. Corma, H. Garcia and M.T. Navarro, J. Chem. Soc. Chem. Commun. (1995) 519.

[5] C. Sishta, R.M. Hathorn and T.J. Marks, J. Am. Chem. Soc. 114 (1992) 1112.
[6] M. Kaminaka and K. Soga, Makromol. Chem. Rapid Commun. 12 (1991) 367.
[7] K. Soga and M. Kaminaka, Makromol. Chem. 194 (1993) 1745.
[8] N. Kishi, C.-H. Ahn, J. Jin, T. Uozumi, T. Sano and K. Soga, Macromol. Rapid Commun. 21 (2000) 775.
[9] M. Kim, L.H. Kwak, S. Jun and R. Ryoo, J. Phys. Chem. 99 (1995) 16742.
[10] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins and J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[11] K. Soga, T. Shiono, S. Takemura and W. Kaminsky, Makromol. Chem. Rapid Commun. 8 (1987) 305.
[12] A. Grassi, A. Zambelli, L. Resconi, E. Albizzati and R. Mazzocchi, Macromolecules 21 (1988) 617.
[13] T. Tsutsui, N. Ishimaru, A. Mizuno, A. Toyota and N. Kashiwa, Polymer 30 (1989) 1350.