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Characteristics of zirconocene catalysts supported on Al-MCM-41 for ethylene polymerization

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Abstract

Ethylene polymerization was carried out by using the zirconocene catalysts supported on MCM-41 (or Al-MCM-41), which had a uniform hexagonal array of linear channels constructed with a honeycomb-like silica matrix, and about 40 Å d-spacing. The zirconocene catalysts supported directly on silicious MCM-41 (Cp_2ZrCl_2/MCM-41) did not show any activity in ethylene polymerization. On the other hand, the activities of the zirconocene catalysts supported directly on Al-MCM-41 (Cp_2ZrCl_2/Al-MCM-41) were comparable to those of homogeneous zirconocenes, and much higher than the activities of those supported on Al-MCM-41 modified by methylaluminoxane (Cp_2ZrCl_2/MAO/Al-MCM-41). The Lewis acidity in Al-MCM-41 seemed to play an important role for anchoring the zirconocenes, such that lower value of Si/Al ratio resulted in higher catalytic activity. Modification with MAO must have reduced the role of acidity. The difference in the catalytic activity among the supported zirconocenes was discussed through the surface species models on the interaction between zirconocene and Lewis acids in Al-MCM-41. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Zirconocene; MCM-41; Al-MCM-41; Ethylene polymerization; Methylaluminoxane

1. Introduction

Even if there are many advantages of homogeneous metallocene catalysts, such as high activity and stereoregularity, there are also some critical problems for the commercial applications [1,2], such as the difficulties in controlling the polymer morphology, instabilities for slurry or gas phase processes and the requirement of a large amount of expensive methylaluminoxane (MAO) [3]. In this regard, it is desirable to heterogenize the homogeneous catalysts for their possible industrial applications. Many studies were reported on the immobilization of metallocenes on metal oxide carriers (silica or alumina), $MgCl_2$, or polymer supports, most of which have broad pore size distributions [4–6]. Mesoporous MCM-41 molecular sieves, however, are well known for their crystalline structures with narrow pore size distribution and large surface area [7,8]. Recently, Braca et al. [9] and Michellotti et al. [10] reported that zeolites could be suitable supports due to the possi-

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bility of entrapping organometallic complexes in their pores.

In this work, three different zirconocene compounds were immobilized on Al-MCM-41s, and their catalytic characteristics in ethylene polymerization were investigated and compared with those of homogeneous zirconocene catalysts. The effect of Lewis acid site on the catalytic activity in ethylene polymerization was correlated with proper surface species models of metallocene on the Al-MCM-41.

2. Experimental

2.1. Materials

Ethylene and nitrogen were purified by removing traces of residual oxygen and moisture with columns packed with oxygen scavenger (Fisher RIDOX) and molecular sieve 5A, respectively. Toluene used in the polymerization and catalyst preparation was dried by refluxing through a distillation column over sodium metal under dry nitrogen. Other materials were used without further purification.

2.2. Synthesis of MCM-41 and Al-MCM-41

A clear solution of sodium silicate was prepared by combining aqueous NaOH solution with colloidal silica (Ludox HS40) and heating the resulting gel mixture with stirring for 2 h at 353 K (for Al-MCM-41, a mixture of sodium silicate and sodium aluminate solution was used instead). The solution of sodium silicate (or and sodium aluminate) was added dropwise to a polypropylene bottle containing a mixture of NH_3 solution and hexadecyltrimethylamonium chloride (HTACl) solution as surfactant under vigorous magnetic stirring at room temperature. After stirring for more than 1 h, the gel mixture was heated to 373 K for 1 day and was then cooled to room temperature. The precipitated product was filtered, washed with distilled water, and dried at 373 K in an oven. The product was calcined in air under static conditions. The calcination temperature was increased from room temperature to 773 K over 10 h and maintained at 773 K for 4 h.

2.3. Catalysts preparation

The MCM-41 (or Al-MCM-41) was dehydrated at 873 K for 10 h with nitrogen purging. 6 g of dehydrated MCM-41 (or Al-MCM-41) was reacted with 120 mmol of MAO at 323 K for 1 h. The solid part was washed with plenty of toluene and dried with nitrogen purging. 2 g of MCM-41 (or Al-MCM-41), treated with MAO (MAO/MCM-41 or MAO/Al-MCM-41), was reacted with 1.54×10^{-3} M of zirconocene compounds (Cp_2ZrCl_2, $Cp_2^*ZrCl_2$, rac-Et(Ind)$_2$ZrCl$_2$; Cp = cyclopentadienyl, Ind = indenyl, and Cp* = pentamethylcyclopentadienyl) in 100 cm^3 toluene at 323 K for 1 h and washed with plenty of toluene and dried with nitrogen purging to obtain zirconocene/ MAO/MCM-41 (or zirconocene/MAO/Al-MCM-41). On the other hand, 2 g of dehydrated MCM-41 (or Al-MCM-41) was directly reacted with 1.54×10^{-3} M of zirconocene (Cp_2ZrCl_2, $Cp_2^*ZrCl_2$, rac-Et(Ind)$_2$ZrCl$_2$) in toluene at 323 K for 1 h and washed with plenty of toluene and dried with nitrogen purging to obtain zirconocene/MCM-41 (or zirconocene/Al-MCM-41). The surface areas of supports and prepared catalysts were determined by nitrogen adsorption (with ASAP 2000, Micrometrics). The surface areas of MCM-41, Al-MCM-41(30), Cp_2-$ZrCl_2$/Al-MCM-41(30), Cp_2/ZrCl$_2$/MAO/Al-MCM-41(30) were 1340, 1270, 1080 and 460 m^2/g, respectively.

2.4. Polymerization and polymer characterization

Ethylene polymerization was carried out in a batch glass reactor. The reactor was filled with toluene and a desired amount of the MAO was added. Nitrogen was evacuated and the reaction mixture was saturated with ethylene. Polymer-

ization started with the addition of catalyst in the slurry phase. Ethylene pressure was kept constant during the polymerization by pressure regulator. The ethylene flow rate was measured by a mass flow meter. Polymerization reactions were stopped by venting off excess ethylene and by adding hydrochloric acid. The precipitated polymers were washed with plenty of ethanol and dried at 80°C for 6 h under vacuum.

The differential thermal analysis of polymers was carried out with a calorimeter (Du Pont Instruments, Thermal Analyst 2000) under a nitrogen atmosphere at a heating rate of 10°C/min. The results of the second scanning were recorded to eliminate the differences in the thermal history of sample. The intrinsic viscosity of the polymers was determined in decalin at 135°C with Ubbelohde viscometer and the values of M_v were calculated from the conventional method [11].

3. Results and discussion

Mesoporous molecular sieve Al-MCM-41 obtained by hydrothermal synthesis had a uniform hexagonal array of linear channels constructed with a honeycomb-like silica matrix. The pore diameter (based on the lattice spacing calculated from the X-ray diffraction pattern) and the surface area (measured by N_2 adsorption) of MCM-41 were about 40 Å and 1200 m^2/g, respectively. The SEM and TEM images of Al-MCM-41 (Si/Al = 30) are shown in Fig. 1.

In our previous work [12], the metallocene compounds supported on modified SiO_2 treated with small amounts of MAO, $AlEt_3$, or $(C_2H_5)MgCl$ were investigated for ethylene polymerization. Among the various supported catalysts examined, Cp_2ZrCl_2 supported on SiO_2 modified by MAO showed the highest activity, whereas Cp_2TiCl_2-based systems showed the lowest activity. In general, most of SiO_2 supported catalysts, required an additional treatment of MAO to modify the surface of metal oxide support in ethylene or propylene
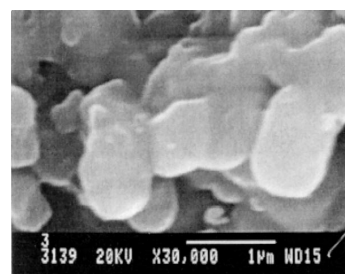
(a) SEM image
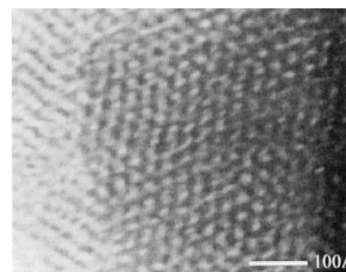
(b) TEM image

Fig. 1. SEM and TEM images of Al-MCM-41 supports: Si/Al = 30.

polymerization [13–16]. Table 1 shows the results of ethylene polymerization using various zirconocene-based catalysts with MAO at the Al/Zr ratio of 3000. It can be seen that the activities of supported metallocene catalysts were smaller than those of homogeneous metallocene catalysts. However, the molecular weights of polyethylene prepared over supported catalysts are much higher than those over homogeneous counterparts as reported elsewhere [17–19]. The activities of zirconocene catalysts supported directly on Al-MCM-41 (Cp_2ZrCl_2/Al-MCM-41, Si/Al = 30) were higher than those over the zirconocene catalysts supported on MAO-treated Al-MCM-41 (Cp_2ZrCl_2/MAO/Al-MCM-41). It was found that the surface area of the Cp_2ZrCl_2/Al-MCM-41 catalyst was higher than those of Cp_2ZrCl_2/MAO/Al-MCM-41 catalyst. The zirconocene catalyst supported directly on pure silicate MCM-41 (Cp_2ZrCl_2/MCM-41) hardly showed any activity in ethylene polymerization, while the zirconocene catalyst supported directly on Al-MCM-41 (Cp_2ZrCl_2/Al-MCM-41) did. The difference in catalytic activities be-

Table 1
The results of ethylene polymerization over different types of homogeneous and supported zirconocene catalysts

Catalysts	Al/Zr[a]	Yields	Activity[b]	T_m (°C)	M_v^c
Cp_2ZrCl_2	3000	9.7	5400	132.4	9800
Rac-Et(Ind)$_2$ZrCl$_2$	3000	13.5	7500	129.9	22,400
$Cp_2^*ZrCl_2$	3000	9.3	5200	129.9	8400
$Cp_2ZrCl_2/MAO/SiO_2^d$	3400	3.4	515	–	–
$Cp_2ZrCl_2/(C_2H_5)MgCl/SiO_2^d$	3400	0.2	33	–	–
Cp_2ZrCl_2/MCM-41	3000	n. d.	–	–	–
Cp_2ZrCl_2/Al-MCM-41(30)^e	3000	n. d.	–	–	–
$Cp_2ZrCl_2/MAO/MCM$-41	3000	0.6	350	138.9	59,000
$Cp_2ZrCl_2/MAO/Al$-MCM-41(30)	3000	0.5	280	138.8	52,600
Cp_2ZrCl_2/Al-MCM-41(15)	3000	5.0	2800	134.3	25,400
Cp_2ZrCl_2/Al-MCM-41(30)	3000	4.5	2530	133.6	33,100
Cp_2ZrCl_2/Al-MCM-41(60)	3000	3.0	1680	135.4	22,200
Rac-Et(Ind)$_2$ZrCl$_2$/Al-MCM-41(30)	3000	1.2	680	138.3	71,000
$Cp_2^*ZrCl_2/Al$-MCM-41 (30)	3000	1.5	830	138.5	36,600

Co-catalyst: MAO.
Polymerization conditions: [Zr] = 2.68 μmol, 0.1 l toluene, ethylene pressure = 10 psig, temperature = 60°C and time = 1 h.
The numbers in parenthesis are Si/Al mole ratio in Al-MCM-41 supports.
[a] Total aluminoxane to Zr ratio.
[b] Activity unit: kg PE/[mol Zr atm h].
[c] Viscosity average molecular weight.
[d] In Ref. [12].
[e] Trialkylaluminum (TME, TEA and TIBA) was used as co-catalysts.

tween MCM-41 and Al-MCM-41 must be due to the presence of Lewis acid sites in Al-MCM-41. Cp_2ZrCl_2/Al-MCM-41(30) was not active with common trialkylaluminums such as TMA, TEA or TiBA, but it was active with MAO. The active site of Cp_2ZrCl_2 catalyst might be formed through the alkylation of Cp_2Zr^+Cl on the surface of support. However, the deactivation of cationic active site $[Cp_2ZrR]^+$ also took place by α-hydrogen transfer during the interaction with co-catalyst [20,21]. It is believed that this deactivation by α-hydrogen transfer must be suppressed by MAO in comparison with trialkylaluminum, mainly due to its coordinating effect or bulkiness.

Fig. 2 shows the activities of ethylene polymerization over the homogeneous zirconocene catalysts and those supported directly on Al-MCM-41 as a function of Al/Zr mole ratio. As the Al/Zr ratio increases, the activity also increases. Even if the homogeneous catalysts showed mostly higher activities, the catalytic activity of Cp_2ZrCl_2/Al-MCM-41 was higher than that of homogeneous catalyst in the range

of low Al/Zr mole ratio (< 1000). This suggests a possible advantage of supported metallocene catalysts for commercialization since the need of expensive MAO can be reduced.

Experimental data on ethylene polymerization over Al-MCM-41-supported Cp_2ZrCl_2 cat-
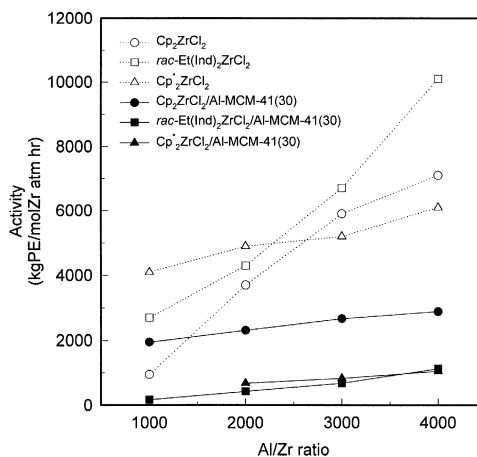

Fig. 2. Activities of homogeneous zirconocene and Al-MCM-41-supported zirconocene catalysts as a function of Al/Zr mole ratio in the ethylene polymerization; [Zr] = 2.68 μmol, P_E = 10 psig, T_p = 60°C, and t_p = 1 h.

alysts were given in Table 2. The Cp_2ZrCl_2 catalysts supported directly on Al-MCM-41 (with Lewis acid sites) showed significantly high catalytic activities (almost the same order of magnitude with its homogeneous counterpart). The activities of Cp_2ZrCl_2/Al-MCM-41 were higher than those of Cp_2ZrCl_2/MAO/Al-MCM-41. It is noted that the activities of Cp_2ZrCl_2/MAO/MCM-41 and Cp_2ZrCl_2/MAO/Al-MCM-41 are comparable even if Cp_2ZrCl_2/MCM-41 showed no activity. MAO pretreatment may be covering up the difference due to the presence of Lewis acidity between MCM-41 and Al-MCM-41. For Al-MCM-41-supported catalysts, the catalyst with lower Si/Al ratio (accordingly, with higher acidity) of Al-MCM-41 support showed higher activity.

Plausible models on the surface species could be proposed as in Fig. 3. Being supported on MCM-41 which is silicate, Cp_2ZrCl_2 is believed to be anchored through the formation of μ-oxo-like bond with hydroxyl group of support

[14] as represented by Scheme I. For Al-MCM-41 with Lewis acid site, however, a transfer of ancillary ligand from the Cp_2ZrCl_2 to an acceptor site on the surface might occur as in Scheme II [14]. Schemes I and II could explain why the Cp_2ZrCl_2 catalysts supported directly on MCM-41 were not active in ethylene polymerization but those supported directly on Al-MCM-41 were active. For MAO-modified support, however, metallocene ionic species are trapped and stabilized by multi-coordinating oligomeric MAO complexes (see Scheme III) as proposed by Chien and He [22].

Three zirconocene precursors with different ligands directly supported on Al-MCM-41(30) were compared in their catalytic activities in ethylene polymerization as given in Table 3. The catalytic activity decreased in order of bulkiness of ligand in metallocene precursors Cp_2ZrCl_2/Al-MCM-41(30) > rac-Et(Ind)$_2$ZrCl$_2$/Al-MCM-41(30) > $Cp_2^*ZrCl_2$/Al-MCM-41(30). This must be due to the steric hindrance

Table 2
The results of ethylene polymerization over homogeneous and supported Cp_2ZrCl_2 catalysts

Catalysts	Al/Zr[a]	Yields	Activity[b]	T_m (°C)	M_v^c
Cp_2ZrCl_2	4000	11.1	6200	132.0	12,900
Cp_2ZrCl_2/MAO/MCM-41	4000	1.1	600	139.2	49,900
Cp_2ZrCl_2/MAO/Al-MCM-41(30)	4000	1.0	540	138.7	40,300
Cp_2ZrCl_2/Al-MCM-41(15)	1000	2.3	1300	139.4	40,200
	2000	3.7	2100	135.2	26,800
	3000	5.0	2800	134.3	25,400
	4000	6.0	3400	134.3	23,500
Cp_2ZrCl_2/Al-MCM-41(30)	1000	3.1	1740	134.0	26,900
	2000	3.9	2190	135.6	32,900
	3000	4.5	2530	133.6	33,100
	4000	5.0	2780	133.9	35,300
Cp_2ZrCl_2/Al-MCM-41(60)	1000	0.2	90	131.1	28,100
	2000	1.9	1070	133.3	21,100
	3000	3.0	1680	135.4	22,200
	4000	3.4	1900	134.0	18,700

Co-catalyst: MAO.
Polymerization conditions: [Zr] = 2.68 μmol, 0.1 l toluene, ethylene pressure = 10 psig, temperature = 60°C and time = 1 h.
The numbers in parenthesis are Si/Al mole ratio in Al-MCM-41 supports.
[a] Total aluminoxane to Zr ratio.
[b] Activity unit: kg PE/[mol Zr atm h].
[c] Viscosity average molecular weight.

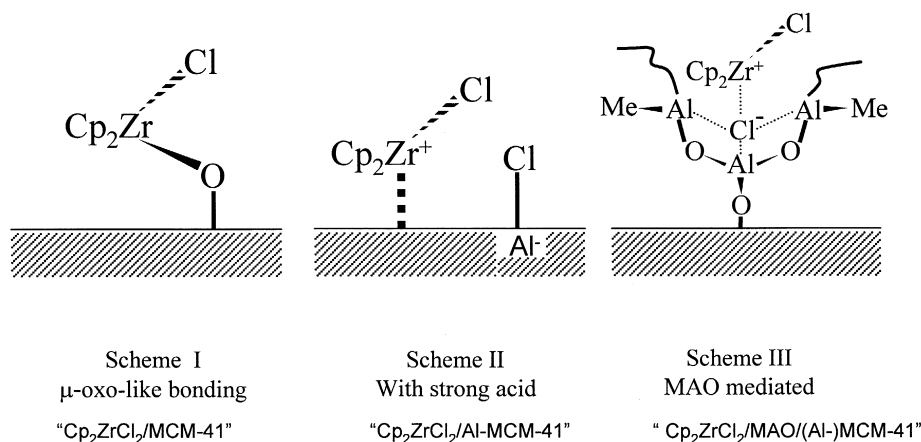| Scheme I	Scheme II	Scheme III
μ-oxo-like bonding	With strong acid	MAO mediated
"Cp$_2$ZrCl$_2$/MCM-41"	"Cp$_2$ZrCl$_2$/Al-MCM-41"	" Cp$_2$ZrCl$_2$/MAO/(Al-)MCM-41"

Fig. 3. Surface species models of various Cp$_2$ZrCl$_2$ supported on zeolites.

of metallocene precursors, which should provide some constraints to the accessibility of ethylene monomers. Fig. 4 shows the morphology of polyethylene obtained with our catalysts. The polymer morphology from homogeneous catalyst was sponge-like due to the removal of solvent. It is believed that the difference in morphology from Cp$_2$ZrCl$_2$/MAO/Al-MCM-41 and Cp$_2$ZrCl$_2$/Al-MCM-41 was due to the

difference in the polymerization rate. The polymer morphology from Cp$_2$ZrCl$_2$/MAO/Al-MCM-41 with lower activity would be determined inside the pore space of Al-MCM-41, the grown polymers would be emerging out of the pore channels and they looked like spheres. On the other hand, the morphology from Cp$_2$ZrCl$_2$/Al-MCM-41 with higher activity may follow the so-called replica phenomenon,

Table 3

Ethylene polymerization over various zirconocene catalysts directly supported on Al-MCM-41

Catalysts	Al/Zr[a]	Yields	Activity[b]	T_m (°C)	M_v^c
Cp$_2$ZrCl$_2$/Al-MCM-41(30)	1000	3.1	1740	134.0	26,900
	2000	3.9	2190	135.6	32,900
	3000	4.5	2530	133.6	33,100
	4000	5.0	2780	133.9	35,300
Rac-Et(Ind)$_2$ZrCl$_2$/Al-MCM-41(30)[d]	1000	0.3	170	136.6	120,900
	2000	0.8	430	138.6	73,200
	3000	1.2	680	138.3	71,000
	4000	2.0	1130	137.2	71,700
Cp$_2^*$ZrCl$_2$/Al-MCM-41(30)	1000	–	–	–	–
	2000	1.2	680	136.1	34,600
	3000	1.5	830	138.5	36,600
	4000	1.9	1050	134.2	26,700

Co-catalyst: MAO.

Polymerization conditions: [Zr] = 2.68 μmol, 0.1 l toluene, ethylene pressure = 10 psig, temperature = 60°C and time = 1 h.

The numbers in parenthesis are Si/Al mole ratio in Al-MCM-41 supports.

  [a] Total aluminoxane to Zr ratio.

  [b] Activity unit: kg PE/[mol Zr atm h].

  [c] Viscosity average molecular weight.

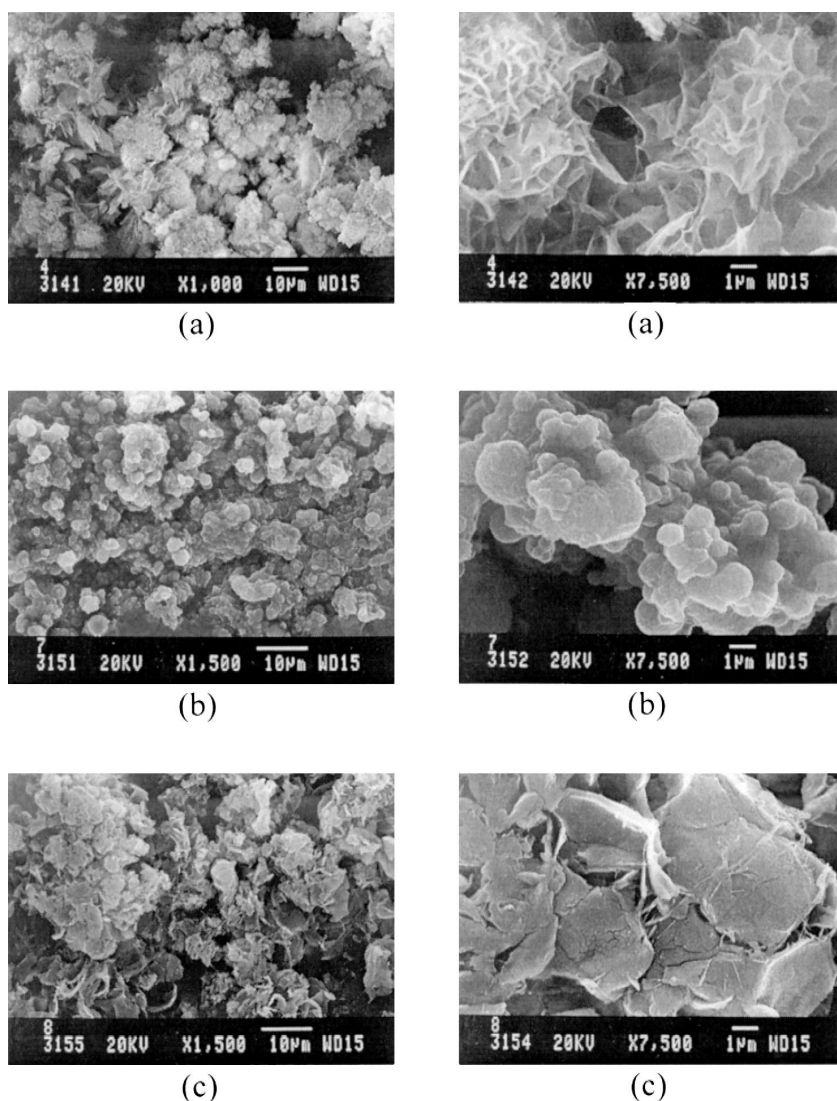 [d] Si/Al mole ratio in Al-MCM-41 support.

Fig. 4. SEM images of polyethylene prepared by (a) Cp_2ZrCl_2, (b) $Cp_2ZrCl_2/MAO/Al$-MCM-41(30), and (c) Cp_2ZrCl_2/Al-MCM-41(30) catalyst systems.

where the catalysts are broken into small pieces, and the polymer resembles the broken catalyst particles.

4. Conclusion

The activities of zirconocene catalysts directly supported on Al-MCM-41 $(Cp_2ZrCl_2/$ Al-MCM-41) were higher than those over the zirconocene catalysts supported on MAO-treated Al-MCM-41 $(Cp_2ZrCl_2/MAO/Al$-MCM-41). On the other hand, the zirconocene catalyst supported directly on pure silicate MCM-41 $(Cp_2ZrCl_2/MCM$-41) did not show any activity in ethylene polymerization. The difference in catalytic activities between MCM-41 and Al-MCM-41 must be due to the presence of Lewis acid sites in Al-MCM-41. The activities of zirconocene catalysts supported on Al-MCM-41 increased with the amount of Lewis acid sites (accordingly, with Si/Al ratio decreasing). The

difference in activities was explained with surface species models on the interaction between the metallocene and supports.

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