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Preparation of nanosize Pt clusters using ion exchange of $Pt(NH_3)_4^{2+}$ inside mesoporous channel of MCM-41

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Mesoporous molecular sieve MCM-41 with a Si/Al ratio of 35 was obtained by hydrothermal synthesis using a gel mixture with a molar composition of 6 SiO_2 : 0.1 Al_2O_3 : 1 hexadecyltrimethylammonium chloride : 0.25 dodecyltrimethylammonium bromide : 0.25 tetrapropylammonium bromide : 0.15 $(NH_4)_2O$: 1.5 Na_2O : 300 H_2O. The MCM-41 sample was calcined in O_2 flow at 813 K and subsequently ion exchanged with Ca^{2+}. A small Pt cluster has been supported on the MCM-41 sample following a procedure using ion exchange of $Pt(NH_3)_4^{2+}$. The $Pt(NH_3)_4^{2+}$ ion supported on MCM-41 has been activated in O_2 flow at 593 K and subsequently reduced with H_2 flow at 573 K, in the same way used for the preparation of a Pt cluster entrapped inside the supercage of zeolite NaY. The resulting Pt cluster supported on the MCM-41 shows hydrogen chemisorption of *total* two H atoms per Pt at 296 K (based on the total amount of Pt) and high catalytic activity for hydrogenolysis of ethane. The chemical shift in ^{129}Xe NMR spectroscopy of adsorbed xenon indicates that the Pt cluster is located inside the mesoporous molecular sieve.

Keywords: MCM-41; zeolite; ion exchange; Pt cluster; ^{129}Xe NMR

1. Introduction

MCM-41 is a mesoporous silica molecular sieve with linear channels of a uniform diameter in the range of 2–10 nm which are arranged in a hexagonal way [1]. The novelty of the MCM-41 is large pore sizes achieved by the use of a surfactant micelle as template. Furthermore, the channel diameter can be tailored by the surfactant size [2]. The molecular sieve structure of the MCM-41 with large pore sizes has great possibilities of application for catalytic conversion of molecules too large to enter conventional zeolite pores. Corma et al. [3] and more recently Tanev et al. [4] incorporated Ti in MCM-41 and showed that the resulting TiMCM-41 was active for partial oxidation of bulky organic compounds using H_2O_2 [3,4]. Inui et al. supported Pt by impregnating H_2PtCl_6 on FSM-16 synthesized from kanemite, which seemed to be identical to MCM-41. The supported platinum was useful for hydrogenation of olefins [5]. Armengol et al. demonstrated that MCM-41 was useful for Friedel–Crafts alkylation of a bulky aromatic compound [6].

Aluminum incorporation within MCM-41 promotes acidity on the material [7] and also provides an ion exchange capacity [8,9], which is of great importance for catalytic applications. Recently, Kim et al. have shown that MCM-41 with framework aluminum (AlMCM-41), if properly synthesized and treated, can have a considerable ion exchange capacity [9]. They have also reported that ion exchange of AlMCM-41 with calcium and yttrium led to a significant increase in thermal stability, up to 1170 K under heating for 2 h in O_2 flow containing 2.3 kPa H_2O vapor.

The present work was undertaken to investigate if the ion exchange property of AlMCM-41 was useful for supporting catalytically active transition metal ions and clusters inside the AlMCM-41 channel, similar to metal clusters supported on zeolites. We have investigated the preparation of a supported Pt cluster using ion exchange of $Pt(NH_3)_4^{2+}$ into AlMCM-41, followed by calcination and reduction, similar to the preparation of Pt clusters within the supercages of NaY [10] and EMT [11] zeolites. We have characterized the Pt cluster using hydrogen chemisorption, ^{129}Xe NMR spectroscopy and catalytic hydrogenolysis of ethane. In the present paper, Pt clusters prepared by ion exchange in AlMCM-41 are compared with those prepared by impregnation with H_2PtCl_6.

2. Experimental

2.1. Synthesis of AlMCM-41

A pure-silica MCM-41 sample was synthesized following the procedure reported in ref. [12]. The procedure was modified to synthesize an AlMCM-41 sample using a gel mixture with a molar composition of 6 SiO_2 : 0.1 Al_2O_3 : 1 hexadecyltrimethylammonium chloride : 0.25 dodecyltrimethylammonium bromide :

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0.25 tetrapropylammonium bromide : 0.15 $(NH_4)_2O$: 1.5 Na_2O : 300 H_2O. Details of the AlMCM-41 synthesis procedure are described elsewhere [9]. The synthesized product was washed using an ethanol–hydrochloric acid mixture and subsequently calcined in O_2 flow at 813 K, which is similar to the procedure reported in ref. [13]. Elemental analysis for the Si/Al ratio was performed with inductively coupled plasma emission spectroscopy (Shimadzu, ICPS-1000III). The Si/Al ratio was 35. The calcined AlMCM-41 sample was ion exchanged with Ca^{2+} as reported elsewhere [9]. The Ca/Al ratio for the ion exchanged sample was determined to be 0.12 using ICP.

2.2. Preparation of supported Pt cluster on AlMCM-41

The calcium ion exchanged AlMCM-41 sample was slurried in 1.05×10^{-3} M aqueous solution of $Pt(NH_3)_4(NO_3)_2$ (Aldrich) (100 ml g^{-1}) for 1 h at room temperature. Then, the sample was filtered, washed with doubly distilled water and dried in a vacuum oven at room temperature. The ion exchanged platinum species on the AlMCM-41 was activated by heating in O_2 flow. The sample temperature for the activation was linearly increased from room temperature to 593 K over 12 h and then maintained for 2 h. The O_2 gas was dried through a molecular sieve trap. The gas flow rate was 1 ℓ min^{-1} g^{-1}. After the activation treatment was over, the O_2 gas was evacuated from the reactor at 573 K. Subsequently, the Pt species was reduced with heating in H_2 flow (99.999%, passed through a MnO/SiO_2 trap). The H_2 flow rate was 200 ml min^{-1} g^{-1}. The reduction temperature was linearly increased from room temperature to 573 K over 4 h and maintained at 573 K for 2 h.

2.3. Characterization and catalytic reactions

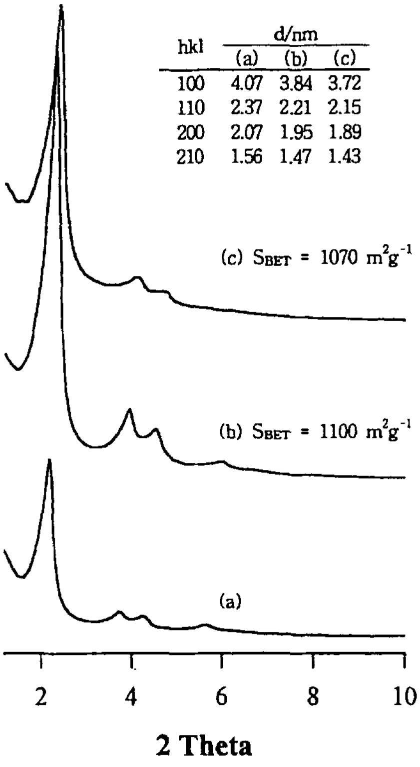
The platinum reduction was followed by evacuation under a nominal pressure of 1×10^{-3} kPa, while the temperature was linearly increased from 573 K to 673 K over 2 h and maintained there for 2 h, in order to remove chemisorbed hydrogen. A small portion of the evacuated Pt/AlMCM-41 sample was then flame-sealed in a special NMR tube equipped with vacuum stopcock for in situ ^{129}Xe NMR spectroscopy. The remaining sample was open to air at room temperature and stored in a sample vial. The air-exposed sample was reduced again with H_2 flow for 1 h at 573 K and subsequently evacuated for 1 h at 673 K. This sample was also sealed in a NMR tube and characterized with ^{129}Xe NMR. The platinum content of the dehydrated Pt/Ca-AlMCM-41 sample was 2.0 wt%, as determined using ICP.

The ^{129}Xe NMR spectra were obtained at 296 K with natural xenon gas (Matheson, 99.995%) at 53.3 kPa using a Bruker AM 300 instrument operating at 83.0 MHz with a 0.5 s relaxation delay. The two ^{129}Xe NMR measurements, in situ and reduced again after air exposure, showed no significant difference in the chemical shifts. Therefore, the air-exposed sample was used for the catalytic activity measurement. Hydrogen chemisorption was measured volumetrically at 300 K. The X-ray powder diffraction (XRD) pattern was obtained ex situ at room temperature using a Rigaku D/MAX-III (3 kW) instrument with a Cu K_α X-ray source.

The rate of catalytic hydrogenolysis of ethane was measured with a Pyrex batch recirculation rig. The reaction mixture consisted of H_2, C_2H_6 and He with partial pressures of 15.1, 1.6 and 87.8 kPa, respectively. The total volume of the rig was 620 ml. The gas recirculation rate was 3.6 ℓ min^{-1}. The reaction temperature was controlled to within 573 ± 1 K. Further details of the measurement are the same as described recently for the ethane hydrogenolysis over Ru/NaY [14].

3. Results and discussion

Fig. 1 shows XRD patterns and BET areas for the pure-silica MCM-41 sample and the AlMCM-41(Si/Al = 35) sample used in the present work. The XRD patterns display well resolved (100), (110), (200) and (210) diffraction lines, characteristic of a hexagonal structure of MCM-41 of very high textural uniformity. The BET areas are within 1100 ± 100 m^2 g^{-1}, in good agreement with typical MCM-41. No significant changes in the XRD intensities and BET areas were



hkl	d/nm		
	(a)	(b)	(c)
100	4.07	3.84	3.72
110	2.37	2.21	2.15
200	2.07	1.95	1.89
210	1.56	1.47	1.43

Fig. 1. X-ray diffraction patterns of various MCM-41 samples: (a) as-synthesized AlMCM-41; (b) calcined AlMCM-41; and (c) 2.1 wt% Pt/AlMCM-41 prepared by ion exchange with $Pt(NH_3)_4^{2+}$ on calcined AlMCM-41.

observed when Pt clusters were supported on the samples using either H_2PtCl_6 or $Pt(NH_3)_4(NO_3)_2$ solutions.

The method using $Pt(NH_3)_4(NO_3)_2$ solution is an ion exchange technique, which is identical to the preparation of a small Pt cluster inside the supercage of NaY zeolite (Pt/NaY) using ion exchange of $Pt(NH_3)_4^{2+}$ [15]. The selectivity of the $Pt(NH_3)_4^{2+}$ ion for the AlMCM-41 phase with the solution was greater than 99% under the present experimental conditions for the ion exchange. The platinum species, adsorbed on the AlMCM-41 surface due to the ion exchange, was not removed at all upon subsequent washing with doubly distilled water at room temperature. By contrast, the platinum species was readily removed from the AlMCM-41 phase by washing with 1×10^{-3} M aqueous $Ba(NO_3)_2$ solution. This result agrees with ion exchange of $Pt(NH_3)_4^{2+}$ with Ba^{2+} at the AlMCM-41 surface.

After the ion exchange with $Pt(NH_3)_4^{2+}$, the AlMCM-41 sample was calcined in O_2 flow at 593 K and subsequently reduced with H_2 flow at 573 K. This treatment for Pt/AlMCM-41 is the same as used previously for the formation of Pt clusters from $Pt(NH_3)_4^{2+}$ in the supercages of zeolite NaY [10] and EMT [11] zeolites. The calcination before reduction is known to prevent the formation of large Pt agglomerates which occurs upon direct reduction of the $Pt(NH_3)_4^{2+}$ ion with H_2.

Fig. 2 shows two hydrogen chemisorption isotherms obtained at 300 K for the reduced Pt/AlMCM-41 sample. The upper curve in fig. 2 is a total chemisorption isotherm, which was obtained with clean Pt clusters after evacuation of the reduced sample for 1 h at 673 K. The lower curve was obtained after reversibly chemisorbed hydrogen was evacuated for 1 h at 296 K. Extrapolation of the chemisorption isotherms to zero pressure from a linear region between 10 and 40 kPa gave chemisorption of *total* 2.1 H atoms per *total* Pt and 0.8 *reversible* H per *total* Pt. These high H/Pt ratios for the Pt/AlMCM-41, compared with 1.2 H_{total}/Pt_{total} and 0.4 H_{rev}/Pt_{total} obtained for Pt/NaY [10,15], indicate a remarkably small cluster size of the Pt/AlMCM-41 sample. Hydrogen chemisorption of the Pt/MCM-41 sample was measured again after slurrying the material in aqueous solutions of NH_4NO_3, KNO_3, $Ca(NO_3)_2$, $Y(NO_3)_3$, etc. for ion exchange and subsequent reduction with H_2 flow. However, the hydrogen chemisorption did not change due to the ion exchange treatment. The result indicates that the cluster size for AlMCM-41 was not affected by the ion exchange treatment.

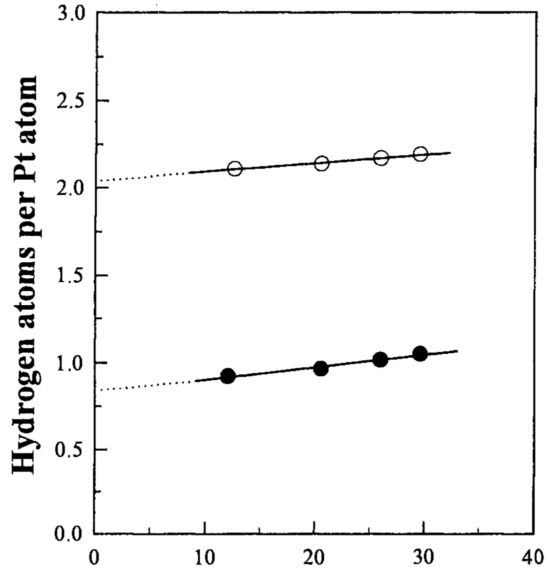


Fig. 2. Hydrogen chemisorption isotherms of 2.0 wt% Pt/Ca-AlMCM-41 at 300 K: (○) total and (●) reversible chemisorption.

We have also investigated the preparation of Pt clusters on pure-silica MCM-41 and AlMCM-41 using impregnation with H_2PtCl_6. The support materials were impregnated with H_2PtCl_6 by an incipient wetness technique using aqueous solution following the conventional method used for silica or alumina supports. The sample was then calcined in O_2 flow at 773 K and reduced with H_2 flow at 573 K. As table 1 shows, hydrogen chemisorption is very small when the impregnation method is used. Similar to NaY zeolite [16], the dispersion of platinum on AlMCM-41 is much better with the use of the ion exchange procedure than the impregnation procedure.

Fig. 3 shows ^{129}Xe NMR spectra of various MCM-41 samples measured with adsorbed xenon under 53.3 kPa and at 296 K. The chemical shifts are compared in table 1. The chemical shift of the Pt/Ca-AlMCM-41 sample obtained using ion exchange of $Pt(NH_3)_4^{2+}$ is 141 ppm, showing a remarkable increase from 67 ppm of the AlMCM-41. Such a large chemical shift is believed to come from the Xe–Pt interaction occurring on the surface of well dispersed Pt clusters located inside the mesoporous MCM-41 channel. Upon hydrogen chemisorption, the chemical shift decreased to 79 ppm. In good agreement with the hydrogen chemisorption in table 1, other samples obtained by impregnation of H_2PtCl_6 show very small increases from the chemical shift of the support, probably due to poor dispersion of Pt or the location of the Pt clusters at the external surface of the mesoporous materials.

In table 1, the Pt/AlMCM-41 samples prepared by the ion exchange method and the impregnation method show interesting differences in the catalytic activity for ethane hydrogenolysis. If metal dispersion of Pt is estimated based on irreversible chemisorption of hydrogen, the Pt dispersion of the ion exchanged sample exceeds that of the H_2PtCl_6-impregnated Pt/AlMCM-41 sample by only a factor of 2, but the catalytic activity per total Pt differs by a factor of 7. For the Al-free Pt/MCM-41 sample, dispersion is three times lower than that of the ion exchanged sample, but the activity per Pt atom is 44 times lower. Thus, the apparent turnover frequency (TOF) is one order of magnitude lower for the sample

Table 1
Hydrogen chemisorption, ^{129}Xe NMR chemical shift, ethane hydrogenolysis rate and BET surface area of Pt/MCM-41

Sample	$(H/Pt)_{total}$ [a]	$(H/Pt)_{rev}$ [b]	δ [c] (ppm)	$N \times 10^{-3}$ [d]	S_{BET} ($m^2 g^{-1}$)
MCM-41	–	–	77	–	927
Ca-AlMCM-41	–	–	67	–	1200
2.0 wt% Pt/Ca-AlMCM-41 [e]	2.1	0.8	141	13.2	1160
2.1 wt% Pt/AlMCM-41 [f]	1.6	0.6	130	–	1070
1.5 wt% Pt/AlMCM-41 [g]	0.9	0.4	93	2.0	1100
1.5 wt% Pt/MCM-41 [h]	0.6	0.3	77	0.3	900

[a] Total hydrogen chemisorption at 300 K, based on the total amount of Pt.

[b] Reversible hydrogen chemisorption at 300 K, based on the total amount of Pt.

[c] ^{129}Xe NMR chemical shift at 53.3 kPa and 296 K.

[d] The number of moles of ethane converted per Pt atom (based on the total amount of Pt) per second. $P_{C_2H_6} = 1.6$ kPa and $P_{H_2} = 15.1$ kPa at 570 ± 1 K.

[e] Obtained by ion exchange on calcined AlMCM-41 (Si/Al = 35) with $Pt(NH_3)_4^{2+}$ after Ca^{2+} ion exchange.

[f] Obtained by ion exchange on calcined AlMCM-41 with $Pt(NH_3)_4^{2+}$.

[g] Obtained by impregnation on calcined AlMCM-41 with H_2PtCl_6.

[h] Obtained by impregnation on pure-silica MCM-41 with H_2PtCl_6.

with supposedly larger particles. Ethane hydrogenolysis is known to be a typical structure sensitive reaction in the sense that a large Pt ensemble is required. Therefore, it is expected that the TOF should be larger for big Pt particles than for nano-clusters located inside the mesoporous channel of the ion exchanged Pt/AlMCM-41 sample, which is a trend opposite to the apparent TOF data. This discrepancy can be interpreted by multiple pore blockage of the MCM-41 channel due to the presence of large Pt particles in the impregnated samples. If the pore blockage occurs, diffusion of ethane to the Pt particles located inside the channel can be blocked and the resulting catalytic activity will be very low. By contrast, chemisorbed hydrogen atoms are expected to be small enough to migrate easily along the surface of the Pt clusters. Recombination of the hydrogen atoms occurs reversibly under the experimental conditions used for the chemisorption measurement. Then, the recombined H_2 can diffuse to other Pt particles located further inside the channel. Under this circumstance, the hydrogen chemisorption estimates metal dispersion for all the Pt particles, while the ethane hydrogenolysis occurs at the outermost particles located in the channel or the external surface.

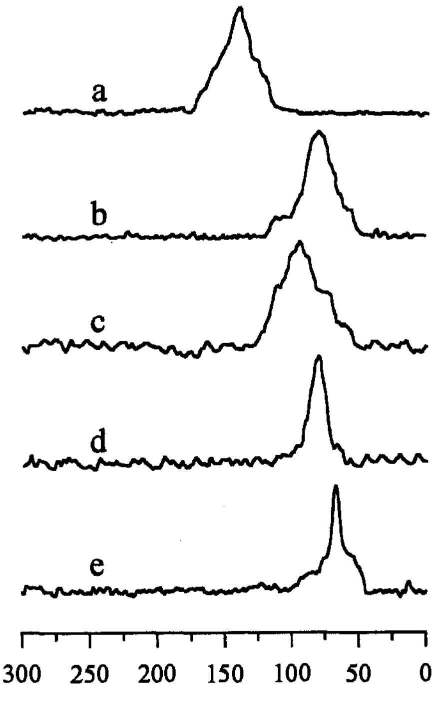


Fig. 3. ^{129}Xe NMR spectra of adsorbed xenon on various MCM-41 samples obtained at 296 K under 53.3 kPa: (a) 2.0 wt% Pt/Ca-AlMCM-41 prepared by ion exchange; (b) the same sample after hydrogen chemisorption; (c) 1.5 wt% Pt/AlMCM-41, prepared by impregnation on AlMCM-41 with H_2PtCl_6; (d) 1.5 wt% Pt/MCM-41, prepared by impregnation on pure-silica MCM-41 with H_2PtCl_6; (e) Ca-AlMCM-41 with Si/Al = 35.

We have clarified that high-quality MCM-41 materials with framework aluminum can have an ion exchange capacity high enough for supporting catalytically active transition metal ions and metal clusters inside the mesoporous channel without causing pore blockage. For ethane hydrogenolysis, the use of the ion exchange method for supporting Pt clusters has merely the advantage of high platinum dispersion. However, the Pt cluster size of about 1 nm or less and the location in the mesoporous channel of about 3 nm in diameter, as inferred from our ^{129}Xe NMR and H chemisorption data, can be very favorable for other catalytic reactions requiring shape selectivity of the MCM-41 channel as well as a supported Pt cluster.

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References

[1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli and J.S. Beck, Nature 359 (1992) 710.

[2] 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. 113 (1992) 10834.

[3] A. Corma, M.T. Navarro, J. Pérez-Pariente and F. Sánchez, J. Chem. Soc. Chem. Commun. (1994) 147.

[4] P.T. Tanev, M. Chibwe and T.J. Pinnavaia, Nature 368 (1994) 321.

[5] T. Inui, J.-B. Kim and M. Seno, Catal. Lett. 29 (1994) 271.

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

[7] A. Corma, V. Fornés, M.T. Navarro and J. Pérez-Pariente, J. Catal. 148 (1994) 569.

[8] C.-G. Wu and T. Bein, Chem. Mater. 6 (1994) 1109.

[9] J.M. Kim, J.H. Kwak, S. Jun and R. Ryoo, J. Phys. Chem., in press.

[10] R. Ryoo, S.J. Cho, C. Pak and J.Y. Lee, Catal. Lett. 20 (1993) 107.

[11] H. Ihee, T. Bécue, R. Ryoo, C. Potvin, J.-M. Manoli and G. Djéga-Mariadassou, in: *Zeolites and Related Microporous Materials: State of the Art 1994,* Studies in Surface Science and Catalysis, Vol. 84, eds. J. Weitkamp et al. (Elsevier, Amsterdam, 1994) p. 765.

[12] R. Ryoo and J.M. Kim, J. Chem. Soc. Chem. Commun. (1995) 711.

[13] C.-Y. Chen, H.-X. Li and M.E. Davis, Micropor. Mater. 2 (1993) 17.

[14] I.H. Cho, S.J. Cho, S.B. Park and R. Ryoo, J. Catal. 153 (1995) 232.

[15] R. Ryoo, S.J. Cho, C. Pak, J.-G. Kim, S.-K. Ihm and J.Y. Lee, J. Am. Chem. Soc. 114 (1992) 76.

[16] O.B. Yang, S.I. Woo and R. Ryoo, J. Catal. 123 (1990) 375.