Acid function of Al-MCM-41 supported platinum catalysts in hydrogenation of benzene, toluene and *o*-xylene

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A series of Al-MCM-41 mesoporous materials with different Si/Al ratios are synthesized. The acidities of catalysts are measured by the temperature-programmed desorption of ammonia (NH_3-TPD) and IR spectra of pyridine. Their catalytic activities for hydrogenation of benzene, toluene and *o*-xylene are investigated on a pulse reactor system. NH_3-TPD and IR results show that only weak and medium acid sites could be observed on the catalysts, and the number of total acid sites decreases obviously with the increase of the Si/Al ratio whereas the medium acid sites are somewhat constant. The introduction of platinum onto Al-MCM-41 material decreases the total acid number by a small amount. The hydrogenation activities of the 1% Pt/HAl-MCM-41 catalysts are found to correspond well with the ratio of medium acid sites to total acid sites in the employed catalysts. It is proposed that, in addition to metal sites, the acid sites in the metal–acid interfacial regions are also the active sites for hydrogenation and the medium acid sites play important roles in the reaction.

Keywords: acidity, mesoporous material, platinum, hydrogenation, benzene, toluene, *o*-xylene

1. Introduction

Numerous studies of group VIII metals have been reported for the purpose of clarifying the correlation between the catalyst structure and its catalytic performances in hydrogenation of benzene and/or alkylbenzene [1–3]. In recent years, aromatic hydrogenation has received increased attention due to more and more stringent environmental regulations, which require refineries further to reduce the aromatic content in advanced eco-friendly transportation fuels [4–6]. To meet this requirement, it is necessary to find more efficient catalysts for the deep aromatic hydrogenation process with high liquid yield.

The novel new material Al-MCM-41, first synthesized by Mobil researchers [7], possesses a hexagonal array of uniform mesopores, very large surface area, and usually weak and/or medium acid. These peculiarities are all very important for its potential utilization as the support for hydrotreating catalysts. Song et al. [8] have reported very recently that platinum loading on Al-MCM-41 results in active catalysts for the hydrogenation of bicyclic aromatics. However, no literature is found so far to investigate catalytic properties of Al-MCM-41 supported noble metal catalysts for the hydrogenation of monoaromatics, which are more difficult to be saturated than the multicyclic aromatics [4].

Concerning the acid function of the catalysts for aromatic hydrogenation, Vannice et al. [9,10] have pointed out that the overall conversion of the aromatic over the noble metal/acid catalyst comes from two kinds of sites: one is the well known noble metal active centers, and the other is acid sites, on which the adsorbed aromatic could hydrogenate with the activated hydrogen spilt over from metal centers. The authors successfully account for the results of Pd (Pt) loading on some acidic and non-acidic supports for the hydrogenation of benzene, toluene or xylene using this model. However, the model has not dealt with the influence of different acidities on the reactivity of the aromatic in the hydrogenation reaction. Therefore, the acid function in metal-catalyzed hydrogenation reaction over metal/acid systems is still open to further study.

In this paper, a series of Al-MCM-41 mesoporous molecular sieves with different bulk Si/Al ratios are synthesized, and their acid characteristics are measured by NH_3-TPD and FT-IR techniques. The hydrogenation of benzene, toluene and *o*-xylene is studied over the series of Pt/HAl-MCM-41 catalysts. The finding that the catalytic activities rely very closely on the catalyst acidities is discussed in relation with the different acidic features of the employed catalysts.

2. Experimental

2.1. Catalysts

Al-MCM-41 materials were synthesized using water glass (Na_2O 7.40 wt%, SiO_2 25.42 wt%, H_2O 67.18 wt%) and sodium aluminate as silica and alumina source, respectively. The molar composition of the gel mixture is as follows: $(0.29 + (1/2)x)$ $Na_2O : SiO_2 : (1/2)x$ $Al_2O_3 : 0.16$ cetyltrimethylammonium bromide : 0.039 tetramethylammonium hydroxide : $(26 + 100/x)$ H_2O (x = Si/Al). The detailed synthesis procedure is according to the previous

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report [11]. By varying the x parameter in the above composition in the range of 15–200, four samples were obtained, denoted as NaAl-MCM-41-n ($n = 1, 2, 3$ and 4). HAl-MCM-41-n were given by the ion exchange reaction of NaAl-MCM-41-n with the aqueous solution of ammonium nitrate (1.0 M) at 80 °C. Pt-loading catalysts, Pt/HAl-MCM-41-n (Pt 1 wt%), were prepared by incipient wetness impregnation of HAl-MCM-41-n with the aqueous solution of chloroplatinic acid (pH = 7, adjusted by NH_3H_2O). This was followed by evaporation, drying at 120 °C for 12 h, and calcining in air at 500 °C for 8 h.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns were recorded by a Rigaku D/MAX-IIA X-ray powder diffractometer, which employed Ni-filtered Cu Kα radiation and was operated at 40 kV and 20 mA.

NH_3-TPD was tested on 100 mg of the catalyst with helium (40 ml/min) as the carrier gas and a thermoconductor as the detector. The catalyst was first calcined in helium at 540 °C for 30 min and saturated with ammonia at 120 °C, then the NH_3-TPD test was started with a heating rate of 15 °C/min. The amount of ammonia desorbed from the catalyst was quantitatively analyzed by the thermoconductor. The H_2–O_2 titration experiment was carried out in a pulsed system with Ar as the carrier gas and the thermoconductor as the detector. H_2 (or O_2) was injected into the catalyst bed through a six-port valve with a sample loop. All the gases used were properly purified.

IR spectra were obtained on a Nicolet 5SXC FTIR spectrometer. The self-supporting wafers of about 5 mg/cm^2 were first evacuated *in situ* in an IR cell at 350 °C for 4 h, and the IR spectra were recorded after the temperature decreased to room temperature. Pyridine was then admitted and, after equilibrium, pyridine was desorbed at 120, 180, 240 and 300 °C, respectively, and the spectra were recorded.

2.3. Catalytic test

The hydrogenations of benzene, toluene and o-xylene were carried out in a pulse microreactor made of stainless-steel tube with a volume of 3.2 ml at a pressure of 2.2 bar and a hydrogen flowrate of 50 ml/min. The catalyst (30 mg) with the particle size of 0.28–0.45 mm was prereduced *in situ* in hydrogen at 500 °C for 3 h followed by the injection of 0.8 μl of the reactant into the catalyst bed through a microsyringe. Reactants and products were analyzed on line by a gas chromatograph.

3. Results

3.1. Physical properties of catalysts

Table 1 displays the properties of unloaded and Pt-loaded HAl-MCM-41 samples. It can be seen that the four HAl-MCM-41 samples have very different bulk Si/Al ratios as a result of the change of Si/Al ratios in the surfactant–aluminosilicate gel mixture during synthesis. However, they possess very similar BET surface areas (around 920 m^2/g). When Pt is loaded on HAl-MCM-41, the surface areas decrease, but still have very high values (around 850 m^2/g). The Pt dispersion is observed to change from 26 to 49% with the increase of the Si/Al ratio of the support.

Table 1
Physical properties of employed catalysts.

Catalyst	Si/Al[a]	S_{BET} (m^2/g)	D^b (%)
HAl-MCM-41-1	14	909	–
HAl-MCM-41-2	23	923	–
HAl-MCM-41-3	39	923	–
HAl-MCM-41-4	73	938	–
Pt/HAl-MCM-41-1	–	873	26
Pt/HAl-MCM-41-2	–	857	35
Pt/HAl-MCM-41-3	–	862	34
Pt/HAl-MCM-41-4	–	838	49

[a] From chemical analysis.
[b] Platinum dispersion from H_2–O_2 titration.

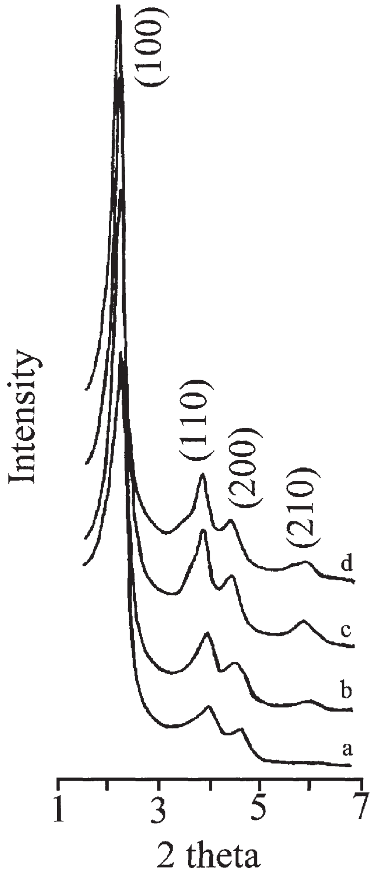

Figure 1. XRD patterns of (a) NaAl-MCM-41-1, (b) NaAl-MCM-41-2, (c) NaAl-MCM-41-3, and (d) NaAl-MCM-41-4.

XRD patterns of NaAl-MCM-41-n samples are shown in figure 1. According to the result reported by Beck et al. [7], the very typical hexagonal lattice for all the samples in figure 1 can be verified by the observation of a strong peak (100) at very low angle and the three weak peaks ((110), (200) and (210)) at comparatively higher an-

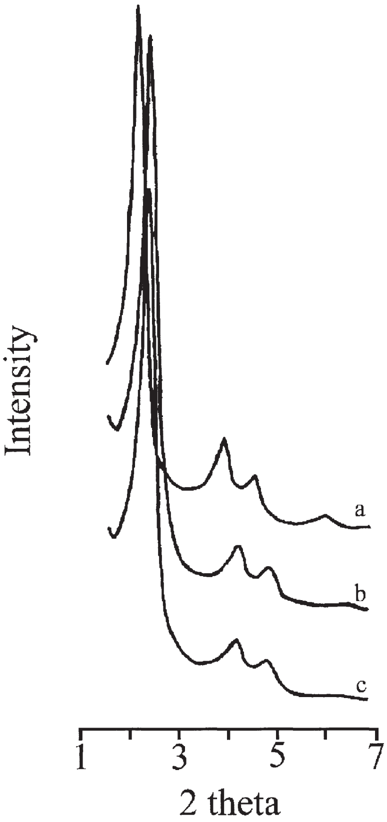

Figure 2. XRD patterns of (a) NaAl-MCM-41-3, (b) HAl-MCM-41-3, and (c) Pt/HAl-MCM-41-3.

gles. The disappearance of the (210) diffraction peak for NaAl-MCM-41-1 with high aluminum content is thought to arise from the distortion of the long-range ordering of the hexagonal structure as a consequence of the aluminum incorporation into the framework of MCM-41 [11]. Figure 2 compares the XRD result of Pt/HAl-MCM-41-3 with that of its parent samples. The (100), (110) and (210) diffraction peaks can be clearly observed for HAl-MCM-41-3, which shows explicitly its typical MCM-41 structure. However, the three peaks all shift to a higher degree of 2θ compared with those for NaAl-MCM-41-3. This indicates the occurrence of constraint of its hexagonal unit cell due to the further calcination when giving HAl-MCM-41 from the Na^+ form of Al-MCM-41. Moreover, the observation of the very similar XRD profile of Pt/HAl-MCM-41-3 to that of HAl-MCM-41-3 demonstrates that the structure of the MCM-41 material is not destroyed by the introduction of Pt. The same results as those in figure 2 are also obtained for Pt/HAl-MCM-41-n ($n = 1, 2, 4$) catalysts in other experiments.

3.2. Acid properties of catalysts

NH_3-TPD results of the series of Pt-free and Pt-loaded HAl-MCM-41-n catalysts are shown in figures 3 and 4, respectively. In figure 3, for HAl-MCM-41-2 and -3 with middle alumina contents both the low-temperature peak at about 210 °C for weak acid and the high-temperature shoulder peak at about 370 °C for medium acid are found, but no peak is detected at a temperature higher than 400 °C corresponding to strong acid sites. By contrast, for HAl-MCM-41-1 and -4 with high and very low alumina content, respectively, only weak acid can be obviously observed. The peak for medium acid might be covered up by the very broad low-temperature peak. Moreover, the total acid number of HAl-MCM-41 decreases remarkably with the increase of Si/Al ratio (see also the last column of table 2). These phenomena are in agreement with those in previous reports [11,12]. It is found in figure 4 that Pt/HAl-MCM-41 catalysts have more or less the same acid features as the corresponding Pt-free ones, i.e., weak and medium acid are observed and also the total acid number decreases with the increase of Si/Al ratio of the support. However, the total acid number of the Pt-loading sample is less than that of its parent support alone (see also the last column of table 2). It is known that MCM-41 material has a hexagonal array of uniform mesopores with one-dimensional channel. For Pt-loading catalysts obtained by the impregnation method, it is reasonable to consider that metal particles reside on the

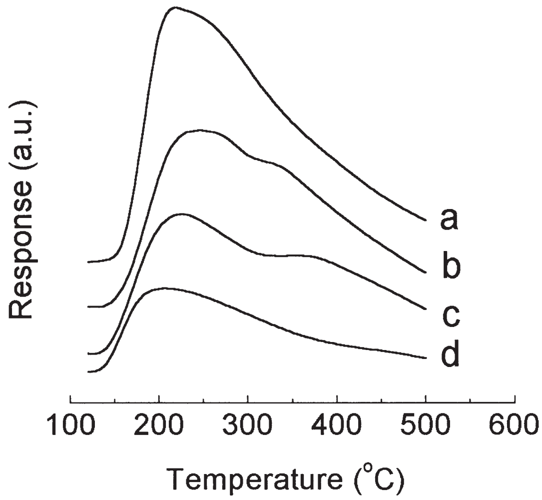

Figure 3. NH_3-TPD patterns of (a) HAl-MCM-41-1, (b) HAl-MCM-41-2, (c) HAl-MCM-41-3, and (d) HAl-MCM-41-4.

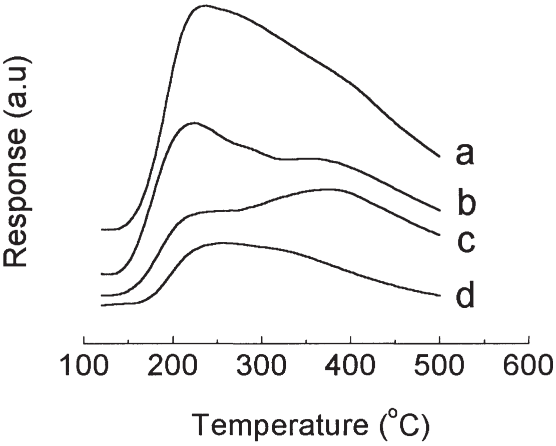

Figure 4. NH_3-TPD patterns of (a) Pt/HAl-MCM-41-1, (b) Pt/HAl-MCM-41-2, (c) Pt/HAl-MCM-41-3, and (d) Pt/HAl-MCM-41-4.

Table 2
Acid amount of HAl-MCM-41 and Pt/HAl-MCM-41 catalysts. (Pyridine adsorption number at 120, 180, 240, and 300 °C, respectively.)

Catalyst	n_B[a] ($\times 10^{19}$/g)				n_L[a] ($\times 10^{19}$/g)				n_{B+L} ($\times 10^{19}$/g)				n_m/n_t[b]	n_o[c]
	120 °C	180 °C	240 °C	300 °C	120 °C	180 °C	240 °C	300 °C	120 °C	180 °C	240 °C	300 °C		($\times 10^9$/g)
HAl-MCM-41-1	6.04	2.83	1.69	0.74	9.69	7.89	5.19	2.73	15.73	10.72	6.88	3.47	22.06	16.08
HAl-MCM-41-2	4.41	2.41	0.83	0.68	6.27	4.35	3.34	2.37	10.68	6.94	4.17	3.05	28.56	12.22
HAl-MCM-41-3	3.87	2.24	1.34	0.87	3.85	3.23	2.76	2.43	7.72	5.47	4.10	3.30	42.75	8.81
HAl-MCM-41-4	1.80	1.29	0.54	0	2.83	2.45	1.54	0.52	4.63	3.74	2.08	0.52	11.23	4.74
Pt/HAl-MCM-41-1	5.35	3.04	1.18	0.88	9.47	6.76	4.87	2.58	14.82	9.80	6.05	3.46	23.34	15.24
Pt/HAl-MCM-41-2	2.63	1.17	1.01	0.95	5.92	4.16	2.68	2.37	8.55	5.33	3.69	3.32	38.83	10.23
Pt/HAl-MCM-41-3	1.80	1.24	0.64	0.54	3.39	2.66	2.35	2.30	5.19	3.90	2.99	2.84	54.72	7.66
Pt/HAl-MCM-41-4	1.25	0.79	0.45	0	2.22	1.83	0.97	0.45	3.47	2.28	0.97	0.45	12.97	3.54

[a] From extinction coefficient by Hughes and White [20].
[b] The ratio of medium acid sites to total acid sites calculated from: $n_{B+L}(300\,^{\circ}C) \times 100/n_{B+L}(120\,^{\circ}C)$.
[c] Ammonia number desorbed out of the sample during NH_3-TPD test.

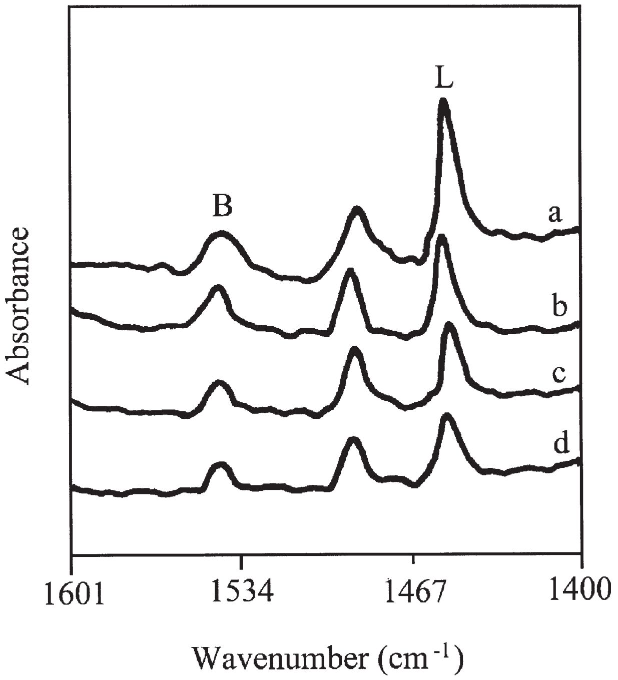

Figure 5. IR spectra of pyridine adsorbed on Pt-free catalysts and degassed at 120 °C. (a) HAl-MCM-41-1, (b) HAl-MCM-41-2, (c) HAl-MCM-41-3, (d) HAl-MCM-41-4.

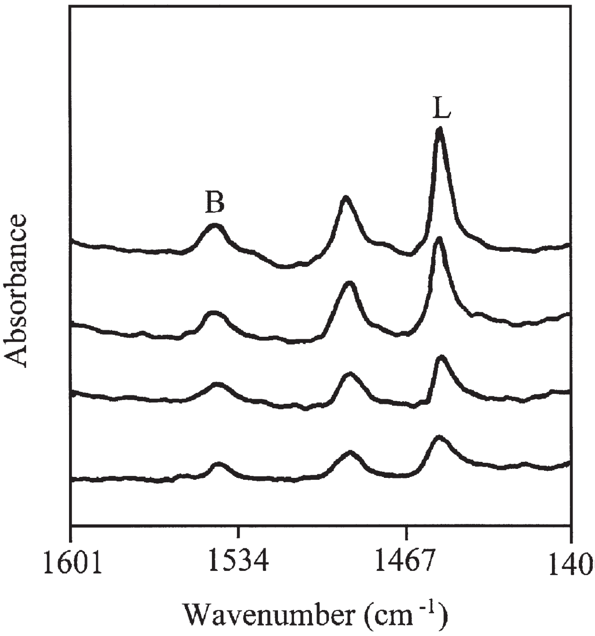

Figure 6. IR spectra of pyridine adsorbed on Pt-containing catalysts and degassed at 120 °C. (a) Pt/HAl-MCM-41-1, (b) Pt/HAl-MCM-41-2, (c) Pt/HAl-MCM-41-3, (d) Pt/HAl-MCM-41-4.

channel openings and inside channels, which could hinder the access of ammonia to acid sites and, therefore, result in the decrease of the total acid number. However, the acid number of the Pt-loading catalyst does not drop by a large amount perhaps because of the unique mesostructure of the support. This might also account for the slight decrease of surface area of HAl-MCM-41 by the introduction of platinum (table 1).

IR spectra of pyridine adsorption on HAl-MCM-41 and Pt/HAl-MCM-41 are shown in figures 5 and 6, respectively. It is revealed that all the samples exhibit both Brønsted (band at 1540 cm^{-1}) and Lewis acid sites (band at 1450 cm^{-1}). Table 2 displays the acid distribution of each catalyst quantitatively calculated from IR results of pyridine adsorption at 120, 180, 240 and 300 °C, respectively. It is clear that the total acid number (represented by n_{B+L} at 120 °C) decreases with the increase of Si/Al ratio. This trend is unaltered by the introduction of platinum onto the HAl-MCM-41 support with the total acid number being lowered by a small amount. These results are well in agreement with the NH_3-TPD results in figures 3 and 4. The larger value of the total acid number from NH_3-TPD than that from IR spectra is probably because of the stronger basicity and smaller molecular radius of ammonia than of pyridine. IR results also tell that for HAl-MCM-41-1, -2 and -3 and their Pt-loading counterparts the medium acid numbers (represented by n_{B+L} at 300 °C) are kept at somewhat the same level with the increase of the Si/Al ratio even if the total acid number decreases remarkably. As a result, the ratio of medium acid sites to total acid sites increases drastically with the increase of Si/Al ratio. As for Pt/HAl-MCM-41-4 and its support, the total acid sites and the percentage of medium acid sites are both very low owing to its too low alumina content. This result is confirmed by the explicit occurrence of the high-temperature

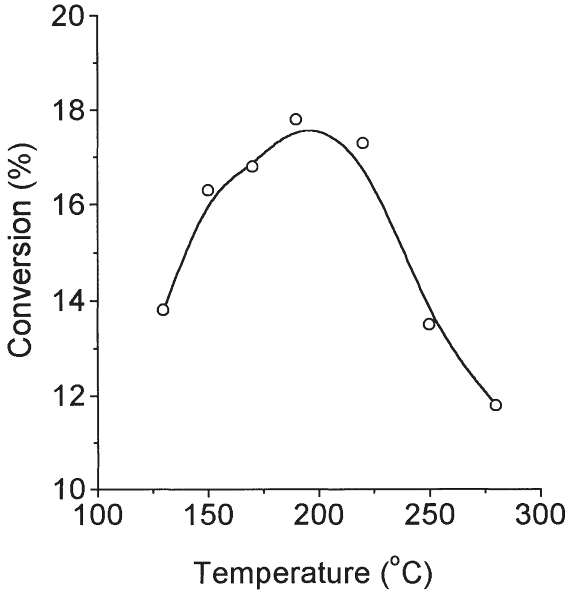

Figure 7. Conversion of benzene into cyclohexane as a function of the reaction temperature over Pt/HAl-MCM-41-3.

peak for medium acid on Pt-free and Pt-loaded HAl-MCM-41-2 and -3 samples compared with the other two (figures 3 and 4).

3.3. Catalytic performances of catalysts

The reactivity of benzene in the hydrogenation reaction is measured over Pt/HAl-MCM-41-3 in the reaction temperature range of 150–280 °C aiming at finding the optimum reaction temperature. At all reaction temperatures only cyclohexane is found. It is shown in figure 7 that benzene conversion passes through a maximum at around 200 °C with the increase of reaction temperature. This result is in good agreement with that over Pt/Al_2O_3 [9]. In another experiment, the catalyst weight is changed (10–150 mg) to test the selectivity of the Pt/HAl-MCM-41-3 catalyst at 220 °C with other reaction conditions constant. It is observed that in the obtained conversion range of 6–78% only cyclohexane is obtained. The same results are found for the hydrogenations of toluene and *o*-xylene, i.e., only the saturation products (methylcyclohexane and dimethylcyclohexane, respectively) can be observed under our reaction conditions. By contrast, no measurable product is detected over the Pt-free catalysts under the same reaction conditions.

The reaction conditions are elected so that the aromatic conversions over all catalysts are compared at a level less than 20%. Figure 8 shows very different conversions of monoaromatics over Pt/HAl-MCM-41 catalysts, depending on the reactant, reaction temperature or the Si/Al ratio of the catalyst support. By comparing the results in figure 8 (A), (B) and (C), one can see that the aromatic conversion decreases with the increase of the number of methyl substituents in the benzene cycle of the reactants on whatever the catalyst. This is consistent with the previous report [13]. Figure 8 also shows that the conversions at 220 °C are much higher than those at 280 °C for all reactants, corresponding to the observation in figure 7. A very interesting observation is the existence of a summit conversion with the increase of Si/Al ratio of the catalyst support for the hydrogenation of benzene, toluene or *o*-xylene at 220 or 280 °C, i.e., Pt/HAl-MCM-41-3 possesses the highest activity whereas Pt/HAl-MCM-41-1 and -4 exhibit very low activities.

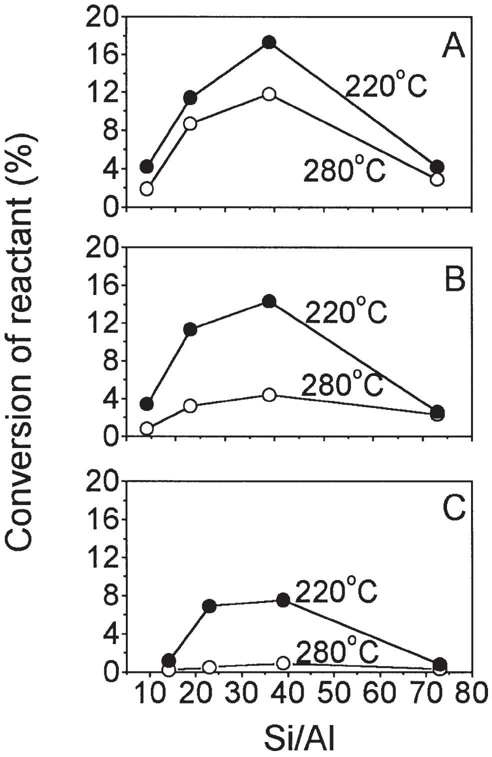

Figure 8. Effect of the Si/Al ratio of the support of Pt/HAl-MCM-41 catalysts on the hydrogenation conversion of (A) benzene, (B) toluene, and (C) *o*-xylene at the reaction temperature of 220 and 280 °C.

According to the conversion values in figure 8 together with the Pt dispersions in table 1, the flowrate through the reactor, and the reactor volume, the turnover numbers, the number of aromatic molecules converted per surface metal site per second, for each aromatic reactant on each catalyst are calculated [14,15]. These are shown as a function of the Si/Al ratio of the support of Pt/HAl-MCM-41 catalysts in figure 9. It is clear for each reactant that very different turnover numbers are observed depending on the Si/Al ratio of the catalyst support. Very similar to the conversion trend in figure 8, figure 9 reveals that Pt/HAl-MCM-41-3 is the most active catalyst whereas Pt/HAl-MCM-41-1 and -4 are the most inactive two.

4. Discussion

It is observed that the conversion of benzene, toluene or *o*-xylene varies largely over the series of 1% Pt/HAl-MCM-41 catalysts (figure 8). Since the aromatic hydrogenation reaction on noble metal catalysts is known to be structure-

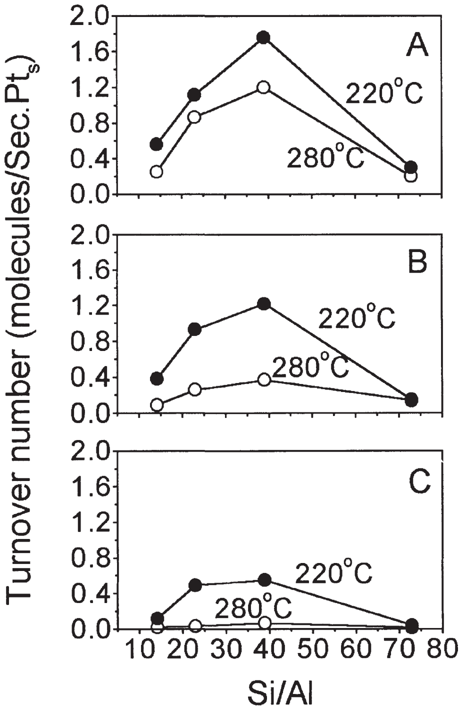

Figure 9. Effect of the Si/Al ratio of the support of Pt/HAl-MCM-41 catalysts on the turnover number of (A) benzene, (B) toluene, and (C) *o*-xylene in the hydrogenation reaction at the reaction temperature of 220 and 280 °C.

insensitive [16,17], one might think that this difference of conversions could arise from the different Pt dispersions in this catalyst system. However, very different hydrogenation activities are also obtained in figure 9 depending on the Si/Al ratio of the support when the Pt dispersion is involved. It thus appears that this catalytic behavior could most likely correlate with the different properties of catalyst supports. Considering that the change of the Si/Al ratio of the support results in very different catalyst acidities (figures 3–6), it is thought here the different activities in figure 9 might be mainly brought about by the different acidities of the support.

Vannice et al. [10] have pointed out by systematic studies that for aromatic hydrogenation the enhancement of the activities of Pt or Pd catalysts loading on acidic compared with that on non-acidic support can be attributed to the acid sites in the metal–support interfacial regions, where the aromatic molecule adsorbed on acid sites could hydrogenate with the hydrogen activated by metal sites. In other words, the overall catalytic activity of the metal/acid catalyst is distributed by metal sites as well as acid sites, even if these acid sites themselves are inactive without the neighboring metal sites. In our recent work [18] we also find the remarkable improvement of aromatic conversion on the mechanical granular mixture of Pt/Al$_2$O$_3$ and HAl-MCM-41 (or Y zeolite) compared with the bare Pt/Al$_2$O$_3$ catalyst in the hydrogenation of benzene, toluene and *o*-xylene. It is proposed that the adsorbed aromatic molecules on acid sites could be hydrogenated by the spillover hydrogen which migrates from the surface of Pt/Al$_2$O$_3$ particles to the surface of HAl-MCM-41 particles. In this work, very different catalytic activities of Pt/HAl-MCM-41 catalysts are observed for the hydrogenation of benzene, toluene and *o*-xylene and very different acid characteristics are found for the employed catalysts, but the turnover number trend in figure 9 is not simply parallel to the change of the total acid number of the catalyst in table 2. However, an interesting relationship could be achieved if attention is paid to the ratio of the medium acid to the total acid number (table 2): the change of activities in figure 9 corresponds well with the change of this ratio for all catalysts. The high percentage of medium acid sites in total acid sites implies that more platinum sites locate in the vicinity of the acid sites with medium strength if the platinum particles are thought to be averagely distributed in the support. According to the viewpoint of Vannice et al. [10] that acid sites in the metal–acid interfacial region are also active centers for hydrogenation reaction, it is believed that medium acid sites should exhibit a higher capability than the weak ones to adsorb the aromatic molecules as carbonium ions, which could be hydrogenated by the spillover hydrogen from neighboring metal sites. Moreover, the medium acid is not strong enough as the strong acid to produce hydrocracking products via the adsorbed carbonium ions and thus the loss of liquid yield is avoided. This also accounts for the observation of only saturation products on this catalyst system.

Based on the above consideration, it is proposed that for Pt/HAl-MCM-41-3 with the largest ratio of medium acid sites to total acid sites there are more amounts of metal centers with medium acid sites as their neighbors than in other catalysts, and, as a consequence, the aromatic hydrogenation on acid sites could take place more efficiently. Thus, the interpretation of the high activities of Pt/HAl-MCM-41-3 and -2 could be achieved by the more contributions of acid sites to the overall activities if the catalytic performances of the accessible Pt sites are assumed to be identical for the series of Pt/HAl-MCM-41 catalysts. By contrast, for Pt/HAl-MCM-41-1 and -4, both with very low percentages of medium acid sites, a large part of platinum particles are surrounded by weak acid sites in the metal–acid regions, the hydrogenation reaction on weak acid sites could not take place so efficiently as that on medium acid sites owing to its poor ability to adsorb aromatic molecules. This results in their low hydrogenation activities. Therefore, the contribution of acid sites to the overall activity is not simply parallel to the total acid number of the catalyst, but relates closely to the acid strength in the metal–acid interfacial region.

The above discussion has not considered the formation of the strong interaction phase of metal and support, as what Vannice et al. [10] have proposed that the hydrogenation performances of metal sites themselves are not affected by acid sites. On the other hand, the reaction result for the methylcyclopentane hydroconversion over Pt/HY catalysts [9] leaves little room for speculations on metal/zeolite interactions. Moreover, we recently find the enhancement of the overall hydrogenation activity of the mechanical granular mixture of Pt/Al_2O_3 with HAl-MCM-41 (or Y zeolite) over the Pt/Al_2O_3 alone. This excludes the possibility that the metal–oxide interaction phase is responsible for the enhanced activity. Thus, we tend to think that the acid sites in the metal–acid interfacial regions are the active sites for aromatic hydrogenation. It is further found here that the medium acid sites play important roles in this reaction.

5. Conclusions

The catalytic activities of a series of 1% Pt/HAl-MCM-41 catalysts in the hydrogenation of either benzene, toluene, or *o*-xylene are found to be parallel to the ratio of medium acid sites to total acid sites, rather than to the total acid number of the catalyst. It is proposed that both metal sites and acid sites are responsible for the overall aromatic conversion. On the catalyst with high percentage of medium acid sites there are more Pt active sites surrounded by medium acid sites in the metal–acid interfacial regions, and the aromatic hydrogenation on medium acid sites could more efficiently take place than that on weak ones. This results in its high catalytic activity.

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References

[1] J.L. Garnett, Catal. Rev. 5 (1971) 229.
[2] J.M. Orozco and G. Webb, Appl. Catal. 6 (1983) 67.
[3] P. Reyes, I. Concha, M.E. Konig and J.L.G. Fierro, Appl. Catal. 103 (1993) 5.
[4] A. Stanislaus and B.H. Cooper, Catal. Rev. Sci. Eng. 36 (1994) 75.
[5] B.H. Cooper and B.B.L. Donnis, Appl. Catal. A 137 (1996) 203.
[6] L.P. Poslovina, V.G. Stepanov, L.V. Malysheva, E.A. Paukshtis, L.A. Vostrikova and K.G. Ione, Stud. Surf. Sci. Catal. 105 (1997) 997.
[7] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli and J.S. Beck, Nature 359 (1992) 710.
[8] K.M. Reddy and C.S. Song, Catal. Today 31 (1996) 137.
[9] S.D. Lin and M.A. Vannice, J. Catal. 143 (1993) 539.
[10] S.D. Lin and M.A. Vannice, J. Catal. 143 (1993) 563.
[11] X.Y. Chen, L.M. Huang, G.Z. Ding and Q.Z. Li, Catal. Lett. 44 (1997) 123.
[12] A. Corma, V. Fornes, M.T. Navarro and J. Perez-Pariente, J. Catal. 148 (1994) 569.
[13] P. Dufresne, P.H. Bigeard and A. Billon, Catal. Today 1 (1987) 367.
[14] K.M. Sancier, J. Catal. 20 (1971) 106.
[15] K.M. Sancier, J. Catal. 23 (1971) 404.
[16] J.M. Basset, G. Dalmai-Imelik, M. Primet and R. Mutin, J. Catal. 37 (1975) 22.
[17] F. Figueras, R. Gomez and M. Primet, Adv. Chem. Ser. 121 (1973) 480.
[18] J. Wang, L.M. Huang and Q.Z. Li, Appl. Catal. A, accepted.
[19] M. Chow, S.H. Park and W.M.H. Sachtler, Appl. Catal. 19 (1985) 349.
[20] T.R. Hughes and H.M. White, J. Phys. Chem. 71 (1967) 2192.