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Characteristics of Al-MCM-41 supported Pt catalysts: effect of Al distribution in Al-MCM-41 on its catalytic activity in naphthalene hydrogenation

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Abstract

Naphthalene hydrogenation was carried out in a high-pressure batch reactor over platinum catalysts supported on Al-MCM-41 where aluminum was incorporated through two different methods: a direct sol–gel method (Pre) and post-synthetic grafting method (Post). The catalytic reaction was also performed in the presence of dibenzothiophene to investigate the sulfur tolerance. The hydrogenation activity, selectivity and the sulfur tolerance strongly depended on the acidic nature of Al-MCM-41 support. It was suggested that the acid sites of Al-MCM-41-Post be more accessible than those of Al-MCM-Pre due to different aluminum distribution within the pore wall. The naphthalene and tetralin conversion increased with the acid amount of the supports in Pt/Al-MCM-41 catalysts. The acid sites in bifunctional catalysts seemed to contribute to alternative pathway by the spillover hydrogen in the acid–metal interfacial region for naphthalene hydrogenation, since the metal dispersions were kept constant for Pt/Al-MCM-41 catalysts. The *trans*-decalin selectivity generally increased with temperature or acid amount. The acid sites seemed to enhance the sulfur tolerance of supported platinum catalysts due to the electron-deficient state of metal.

Keywords: Supported platinum catalyst; Pt/Al-MCM-41; Al-MCM-41; Al incorporation; Naphthalene hydrogenation; Sulfur tolerance

1. Introduction

Microporous molecular sieve catalysts such as zeolites are widely used in acid-catalyzed reactions for manufacturing fuels, petrochemicals and fine chemicals [1]. However, their applications are limited due to the constraints of pore size (less than 15 Å). The discovery of MCM-41 has provided a new potential applicability in catalysis and adsorption, due to its high surface area and tunable uniform mesopores (from 20 to 100 Å). Purely siliceous MCM-41 has no Bronsted acidity. Acidity modification of MCM-41 is necessary for the applications to acid-catalyzed reactions such as cracking, isomerization and/or alkylation. Acidity could be generated through isomorphous substitution of Si by Al.

Various routes have been developed for the incorporation of aluminum into the framework of MCM-41. Even if direct mixed-gel synthesis of Al-MCM-41 has been practiced [2], not only the structures experienced unfavorable hydrothermal deterioration but also the concentration and strength of Bronsted acid

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sites were very low even at high aluminum content. Therefore, post-synthesis modifications have been developed to keep structural stability and to incorporate various metal elements easily into siliceous MCM-41 support [3–7]. These Al incorporation methods should influence the nature of Al-MCM-41 such as concentration of acid sites, pore structure, surface area and wall thickness.

High content of aromatics in diesel oil lowers fuel quality such as cetane number and coloring, and increases the hazardous emissions from diesel engines [8,9]. The more stringent environmental regulations for the reduction and limitation of aromatics in diesel fuels are being tightened in many countries. Due to the growing demand in diesel fuel of high quality, hydrotreating processes are becoming more important and playing a significant role for producing clean energy in refinery industry [10].

New diesel fuel specifications will include a reduction of sulfur (0.05 wt.% maximum) and an enhancement of the cetane number (40 minimum) [8]. It has been found that a reduction in the aromatics content lead to a positive effect on the cetane number. Many attempts have been made to develop new catalysts and processes for saturating (hydrogenating) the aromatics with improved reactivity and stability at moderate temperature.

There are two different methods for aromatics saturation, single-stage and dual-stage processes. In a single-stage operation, conventional hydrotreating catalysts such as sulfided oxides (CoMo, NiMo, NiW on γ-alumina) can only accomplish moderate levels of aromatics saturation under typical hydrotreating conditions. There are, however, thermodynamic equilibrium limitations at high temperature operation due to the exothermic nature of aromatics hydrogenation. Noble metal catalysts are preferred since they could work at a lower operation temperature but they are easily poisoned by small amount of sulfur in the feed. The dual-stage process has been introduced where the sulfur species could be removed in the first-stage reactor up to level of a few parts per million. It is necessary to develop highly active catalysts that are resistant to sulfur poison. This sulfur tolerance could be provided by supporting the noble metals on the appropriate carriers. Many works [11–19] have been reported on the noble metal hydrogenation catalysts supported on γ-alumina, activated carbon, silica–alumina, aluminum borate, TiO_2–ZrO_2, USY, beta zeolite or Al-MCM-41.

In this work, Al-MCM-41 supported platinum catalysts were used for naphthalene hydrogenation, which was carried out in a batch-type slurry reactor under high pressure of 1000 psi. Aluminums in Al-MCM-41 were introduced by two different methods; direct sol–gel method (Pre) or post-synthetic grafting method (Post). The applicability of those Al-MCM-41s as catalyst supports has previously been studied for hydrodewaxing [20,21] and for ethylene polymerization [22]. The effect of aluminum distribution in Al-MCM-41 on the catalytic activity was investigated for naphthalene hydrogenation this time. Naphthalene in *n*-hexadecane and dibenzothiophene (DBT) was used as a model compound to simulate a diesel fuel. The catalytic activity and selectivity were discussed in terms of the acidity of Al-MCM-41, together with the degree of its sulfur tolerance.

2. Experimental

2.1. Catalyst preparation

2.1.1. Al-MCM-41 by direct hydrothermal synthesis

Cetyltrimethylammonium chloride (25% CTACl, Aldrich) was dissolved in distilled water. The silica source, Ludox HS-40 (DuPont) was then added dropwise to the template solution with vigorous stirring at 70 °C in a water bath. The aluminum source, pseudoboehmite (78.2% Al_2O_3, Vista), was added into the hydrogel. The molar composition of mixture gel was 1.0 CTACl:1.0 Na_2O:4.0 SiO_2:400 H_2O, and the Si/Al ratios were taken to be 5, 10, 20 and 40. The pH of mixture was maintained at 10.0 with 5 wt.% acetic acid after heating at 100 °C for 2 days, and this pH adjustment was repeated twice more. The product was filtered, washed, dried in air and calcined at 550 °C for 10 h. To obtain proton-exchanged Al-MCM-41-Pre, the calcined Al-MCM-41-Pre was ion-exchanged twice with 1 M NH_4Cl solution at 70 °C for 10 h, and calcined at 550 °C for 10 h. Purely siliceous MCM-41 supports were prepared by the same procedure but without adding Al source to the preparation mixture.

2.1.2. Al-MCM-41 by post-synthesis modification

Al-MCM-41-Post was prepared by incorporating aluminum to siliceous MCM-41 support by post-synthetic metal incorporation method [3]. Siliceous MCM-41 was heated to remove water in a vacuum oven at 100 °C for 10 h. $AlCl_3$ (98%, Junsei) in absolute ethanol (99.8%, Merck) was added to MCM-41 in a propylene bottle and the mixture was stirred vigorously for 30 min. The mixture was filtered, washed and dried at 110 °C in air, and calcined at 550 °C for 10 h. After calcination, Al-MCM-41-Post with $Si/Al = 5$, 10, 20 and 40 was obtained.

2.1.3. Platinum impregnation

The 0.5 wt.% of platinum was loaded with $Pt(NH_3)_4Cl_2$ (98%, Aldrich) solution by excess water evaporation. After impregnation, the materials were dried at 110 °C for 5 h and calcined at 320 °C for 2 h.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns of MCM-41 supports were recorded on a Rigaku Miniflex using Cu Kα radiation at 40 kV and 45 mA. The acidic property of molecular sieves was analyzed by TPD (temperature-programmed desorption) of chemisorbed ammonia. A 0.01 g aliquot of sample was placed in a quartz tubular reactor and pretreated in a helium flow, heated to 300 °C with 10 °C/min, and remained at 300 °C for 2 h. The samples were cooled to 100 °C and ammonia pulse was injected five times. After physisorbed ammonia was purged with helium, TPD was carried out. BET surface area, pore volume and pore size distribution were calculated from N_2 adsorption/desorption isotherms at liquid N_2 temperature using a Micromeritics ASAP2000. Chemisorption of hydrogen was performed at 35 °C using the ASAP2000. Before chemisorption measurements the catalysts were reduced in H_2 at 350 °C for 2 h, followed by purging the surface at the same temperature for 1 h in He flow. The solid-state ^{27}Al MAS NMR measurements were performed at room temperature on a Bruker DSX-400 multinuclear spectrometer with 4 mm rotor at KBSI (Korea Basic Science Institute). The NMR spectra were obtained at radio-frequency of 108.27 MHz with pulse length of 0.8 mm, delay time of 1.0 s and spinning rate of 12 kHz. The chemical shifts were recorded with respect to $[Al(H_2O)_6]^{3+}$.

2.3. Model reaction

The hydrogenation of naphthalene in *n*-hexadecane was carried out in a 300 ml batch reactor (EZE-Seal, Autoclave Engineers). A 0.5 g aliquot of catalyst was loaded in the reactor and then hydrogen was introduced with 50 ml/min to reduce the platinum catalyst at 320 °C and 500 rpm for 2 h. The 5 wt.% naphthalene in *n*-hexadecane was used as a model compound. In order to investigate the reactivity in the presence of sulfur, 200 ppm (w) of sulfur as DBT were added to the naphthalene solution. The reactor was cooled to room temperature, fed with 50 ml of the model compound and pressurized to 300 psi with hydrogen. The impeller was set to 1000 rpm. The reactor was gradually heated at a rate of 5 °C/min to 200–300 °C and the pressure was set to 1000 psi. The liquid products were analyzed by a gas chromatograph (HP 6890A) equipped with a flame ionization detector and a 50 m long capillary column (HP-1) to identify the unreacted feed and the products.

3. Results and discussion

The XRD patterns of the calcined supports in Fig. 1 showed four characteristic peaks that can be indexed on a hexagonal lattice of a typical MCM-41 as (1 0 0), (1 1 0), (2 0 0) and (2 1 0). The intensity of the peaks decreased as aluminum was incorporated. The change of XRD intensity with the amount of aluminum was less in post-supports.

The structural properties of supports and their profiles of ammonia TPD were reported in our previous work [21] and reproduced here as Table 1 and Fig. 2, respectively. MCM-41 supports possess high surface area of 1010–1280 m^2/g, average pore diameter of ca. 30 Å and wall thickness of 10–15 Å. The surface areas of all Al-MCM-41 supports slightly decreased with Al content. As the amount of aluminum incorporated increased, the pore volume and average pore volume of Al-MCM-41-Pre generally decreased. This is probably due to partial collapse of the hexagonal structure during calcination. Al-MCM-41-Post has more uniform pore diameter and higher wall thickness than Al-MCM-41-Pre, indicating that grafting method allows the preparation of structurally well-ordered materials in high Si/Al. It was found that Al-MCM-41-Post

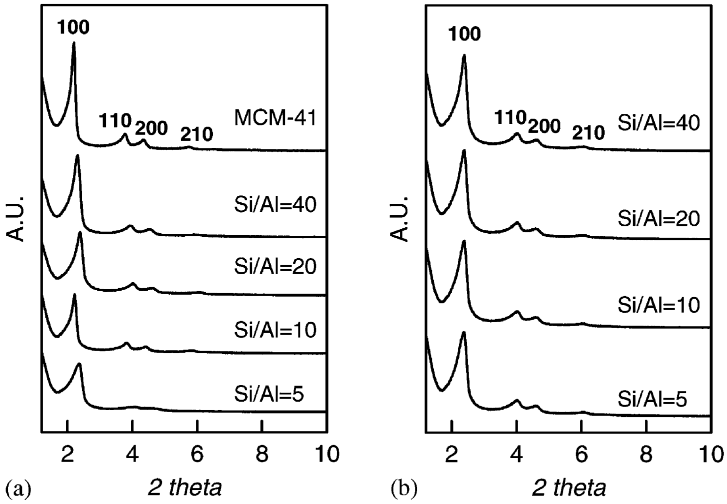


Fig. 1. XRD patterns of calcined: (a) Al-MCM-41-Pre; (b) Al-MCM-41-Post.

had higher content of acid sites than Al-MCM-41-Pre at the same Si/Al ratios, and that the amount of acid sites of Al-MCM-41 increased with decreasing Si/Al ratios as expected.

The ^{27}Al MAS NMR spectra (Fig. 3) of the supports showed signals at 50 ppm (tetrahedrally coordinated Al, Al(IV) in the framework) and 0 ppm (octahedrally coordinated Al, Al(VI) at extra-framework), respectively. The Al(IV) sites can be regarded as Bronsted acid sites. The signal appearing at 30 ppm is related to the deformation of some Al(IV) sites. Table 2 [21] shows the distribution of tetrahedral Al(IV) sites in Al-MCM-41 supports which were estimated from the peak area in ^{27}Al NMR spectra. The Al(IV) sites were predominant for Al-MCM-41-Pre, but the Al(VI) sites were formed after calcination, most probably due to some destruction of framework. For Al-MCM-41-Post, the amount of Al(IV) sites was relatively low before calcination but became significant after calcination, suggesting that Al was incorporated into the framework of MCM-41 during calcination.

Ammonia TPD suggested that Al-MCM-41-Post contained higher content of acid sites than Al-MCM-41-Pre, whereas ^{27}Al MAS NMR spectra indicated that the amount of tetrahedral sites (Bronsted acid sites) of Al-MCM-41-Pre was larger than that of

Table 1
Structural properties of MCM-41 and Al-MCM-41 supports [21] [a]

Supports	d_{100} (Å)	a_0 (Å)	S_{BET} (m^2/g)	Pore volume (ml/g)	Pore diameter (Å)	Wall thickness (Å)
MCM-41	40.1	46.3	1280	1.15	31.1	15.2
Al-MCM-41(5)-Pre	40.3	46.5	1010	0.96	33.6	12.9
Al-MCM-41(10)-Pre	39.6	45.7	1100	0.97	33.3	12.4
Al-MCM-41(20)-Pre	39.3	45.4	1130	1.40	34.0	11.4
Al-MCM-41(40)-Pre	38.7	44.7	1190	1.42	34.7	10.0
Al-MCM-41(5)-Post	39.9	46.1	1040	0.92	31.1	15.0
Al-MCM-41(10)-Post	40.1	46.3	1090	0.92	31.4	15.1
Al-MCM-41(20)-Post	40.1	46.3	1110	1.00	31.0	15.3
Al-MCM-41(40)-Post	39.9	46.1	1140	1.02	30.7	15.2

[a] d_{100}: d-spacing of (1 0 0), a_0: unit cell parameter.

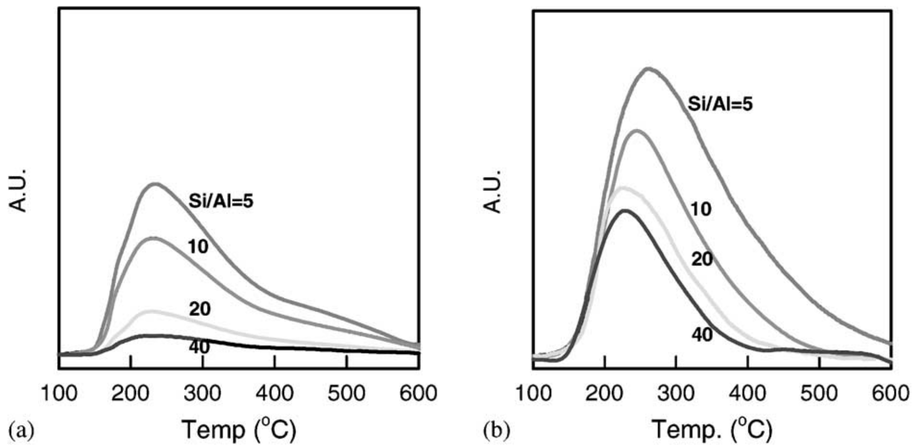


Fig. 2. NH_3 TPD of: (a) Al-MCM-41-Pre; (b) Al-MCM-41-Post [21].

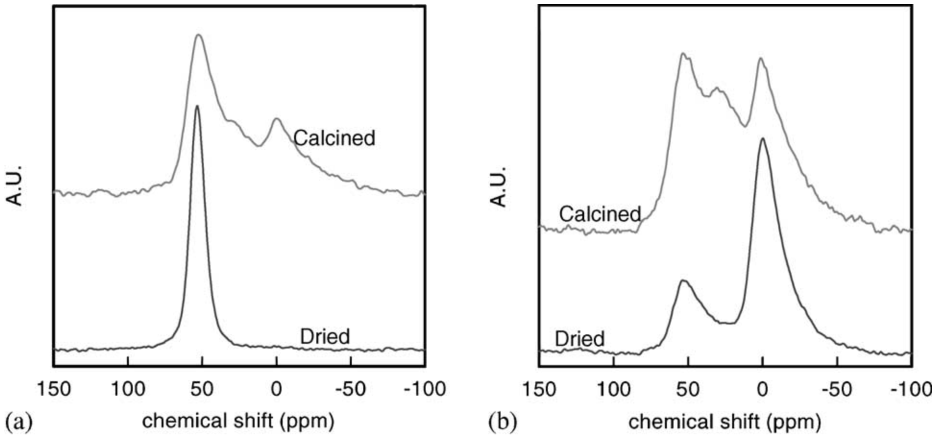


Fig. 3. ^{27}Al solid NMR spectrum of: (a) Al-MCM-41(5)-Pre; (b) Al-MCM-41(5)-Post.

Table 2
Distribution of Al(IV) sites of Al-MCM-41 from solid ^{27}Al MAS NMR [21]

Si/Al	Al-MCM-41-Pre		Al-MCM-41-Post	
	Percentage of Al(IV), dried	Percentage of Al(IV), calcined	Percentage of Al(IV), dried	Percentage of Al(IV), calcined
5	100	65.8	27.1	57.0
10	100	73.0	25.3	53.1
20	100	65.4	39.7	46.1
40	100	67.4	45.0	48.5

Al-MCM-41-Post. As aluminum of Al-MCM-41-Pre was introduced in the preparing step of hydrogel, aluminum would be located uniformly at any position (outer or inner) in the wall of Al-MCM-41, considering that the ionic radius of Al^{3+} and the bond length of Al–O are 0.57 and 1.75 Å, respectively. Significant portion of inner Al sites were buried in the framework and became inaccessible. On the other hand, Al(IV) sites in post-catalysts seem to be located mostly at the accessible outer sites. Accordingly, this difference between TPD and NMR seems to be attributed to the different accessibility of Al(IV) sites due to the thick wall (about 10–15 Å) of MCM-41.

The hydrogenation of naphthalene is a consecutive reaction; naphthalene is hydrogenated to tetralin, and then tetralin hydrogenated to *cis*- and/or *trans*-decalin. The conversion of naphthalene into tetralin over Pt/Al-MCM-41 catalysts was found to be relatively fast and that of tetralin into decalins to be the rate-determining step. It would be interesting to analyze the role of acidity in the metal-catalyzed hydrogenation reaction. Bifunctional catalysts having metal sites for (de)hydrogenation and acid sites for rearrangement and/or cracking are widely used in refinery, especially hydrocracking and hydroisomerization. The activity and selectivity depends on the characteristics of the metal sites and acid sites. It is well known that the balance between metal and acid sites influences the performances in hydrocracking and hydroisomerization. Aromatic hydrogenation is known to be a metal-catalyzed reaction [23]. However, Vannice and coworkers [8,24–26] reported that acid supported noble metal catalysts showed an activity enhancement for aromatics hydrogenation compared with non-acid supported noble metal catalysts. This phenomenon seems to be attributed to the presence of another active sites in the metal–acid interfacial region. In fact, aromatic hydrogenation does not necessarily occur via a bifunctional route because it could happen on metal sites only. The hydrogen chemisorption was measured in order to investigate the state of platinum in the Pt-supported catalysts (0.5 wt.% nominal Pt content). The hydrogen irreversibly adsorbed, H_{irr}/Pt, after reduction at 350 °C for 2 h, was 67, 63 and 64% for Pt/MCM-41, Pt/Al-MCM-41(5)-Pre and Pt/Al-MCM-41(5)-Post, respectively. The Pt dispersion of Pt/Al-MCM-41 catalysts was found not to be affected by acidity of Al-MCM-41. This may lead to a better understanding on the effect of acidity rather than metal dispersion on the catalytic activity in the present work.

Fig. 4 points out that the temporal conversions over Pt/Al-MCM-41 catalysts were faster than those over Pt/MCM-41 catalysts having no Bronsted acid sites. The complete conversions of naphthalene and tetralin over Pt/MCM-41 at 200 °C and 1000 psi needed about 21 and 57 h, respectively, while those over Pt/Al-MCM-41(5)-Post needed 5 and 8 h, respectively. The tetralin conversion was faster with Pt/Al-MCM-41-Post catalysts than Pt/Al-MCM-41-Pre catalysts, while the rates of the naphthalene conversion was almost the same. Sig-

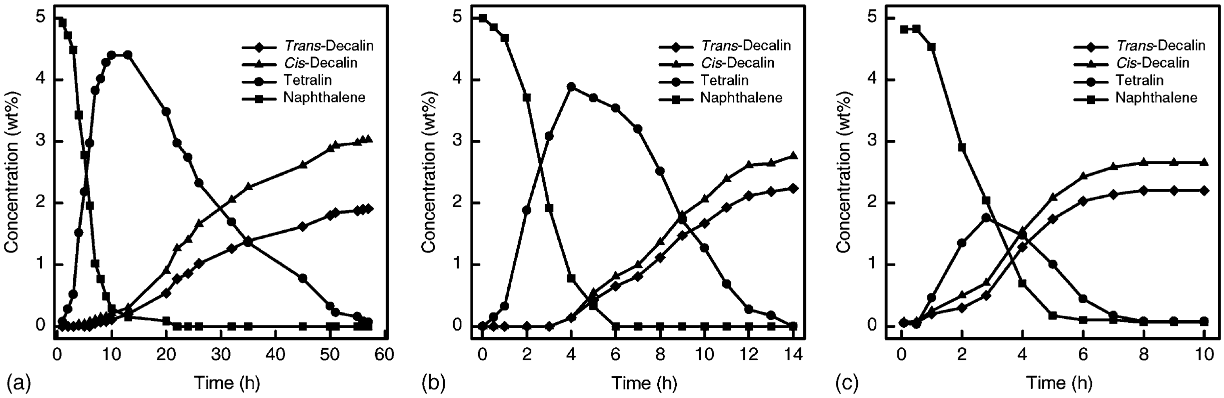


Fig. 4. Concentration change with time for conversion of naphthalene to tetralin and decalins at 200 °C and 1000 psi over: (a) Pt/MCM-41; (b) Pt/Al-MCM-41(5)-Pre; (c) Pt/Al-MCM-41(5)-Post (it is noted that the time scales are different).

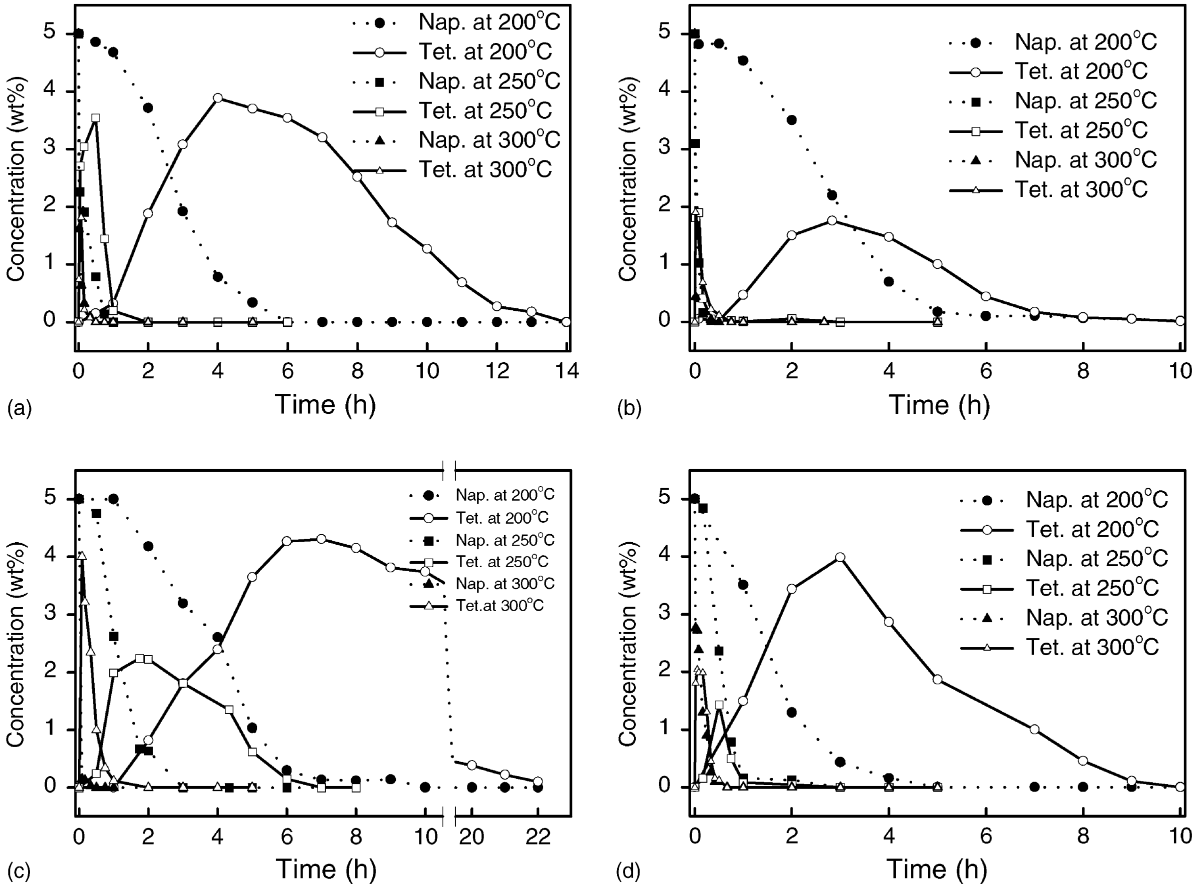
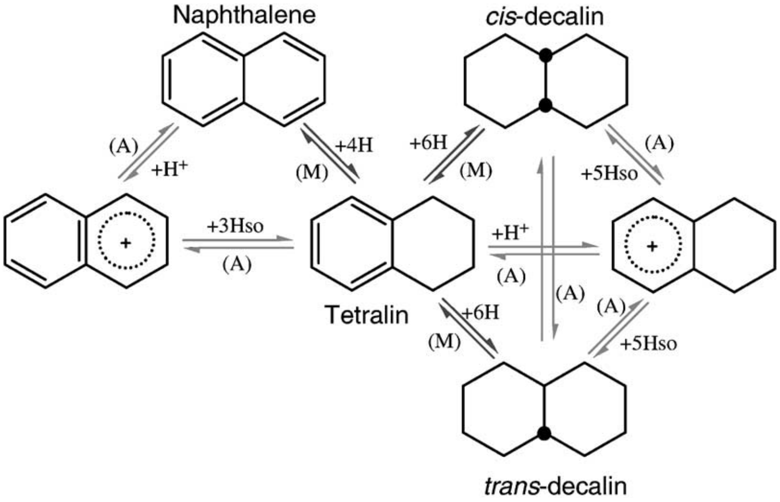


Fig. 5. Concentration change with time for conversion of naphthalene at 200, 250 and 300 °C under 1000 psi: (a) Pt/Al-MCM-41(5)-Pre; (b) Pt/Al-MCM-41(5)-Post; (c) Pt/Al-MCM-41(40)-Pre; (d) Pt/Al-MCM-41(40)-Post; Nap.: naphthalene, Tet.: tetralin.

nificant difference in the rate of tetralin conversion, which is believed to be the rate-determining step, must be due to the different amounts of acid sites. The same trend was observed for other values of Si/Al ratio and reaction temperature.

Typical temporal behaviors in naphthalene hydrogenation are shown in Fig. 5 for Pt/Al-MCM-41-Pre and Pt/Al-MCM-41-Post catalysts with $\mathrm{Si/Al} = 5$ and 40 in the temperature range 200–300 °C. The conversion was higher when the acid amount was larger as in the case of *n*-hexadecane hydroisomerization [21]. The conversion of tetralin became faster at a higher temperature as expected. The difference in reactivity between Pt/Al-MCM-41-Pre and Pt/Al-MCM-41-Post catalysts was also a little pronounced at a higher Si/Al ratio.

Lin and Vannice [24–26] pointed out that the overall activity over the noble metal catalysts on acidic supports included two parts: one was the contribution of metal site, and the other was that of acid sites, where the spillover hydrogen could react with the adsorbed aromatic compound. Fujimoto and coworkers [27,28] found that protonic hydrogen of zeolite can easily be exchanged with the gaseous hydrogen, and that the spillover hydrogen was active for the paraffin isomerization. Wang et al. [29] reported the synergy effect by spillover hydrogen in benzene hydrogenation when Pt/Al_2O_3 was physically mixed with acid supports (USY and HAl-MCM-41) or n-type semiconductor (WO_3) and they [11] also proposed a concerted reaction network for benzene hydrogenation.



Scheme 1. The reaction network for hydrogenation of naphthalene over zeolite supported noble metal catalysts: M, metal sites; A, acid sites; H_{so}, spillover hydrogen.

Based on the aforementioned considerations, the reaction network for naphthalene hydrogenation can be proposed as Scheme 1. There are two reaction pathways for producing decalin from naphthalene. One is conventional metal-catalyzed hydrogenation and the other is acid site induced hydrogenation. In the latter pathway, naphthalene could be hydrogenated into tetralin, and adsorbed tetralin could be hydrogenated into *trans*- and/or *cis*-decalin through spillover hydrogen, which is formed on metal sites and migrates onto acid sites in the interfacial region between acid and metal sites. *cis*-Decalin can be converted into *trans*-decalin via isomerization on acid sites and vice versa.

The *trans*-decalin selectivity (shown in Table 3) generally increased with temperature or acid amounts in Pt/Al-MCM-41 catalysts. When naphthalene is completely converted to decalins, the isomerization of *cis*-decalin to *trans*-decalin becomes thermodynamically favored [30]. The *trans*-decalin selectivity should increase with reaction temperature. It can be seen that the dominant compound at 200 °C was *cis*-decalin, while at 300 °C the *trans*-decalin. The preference between *cis*- and *trans*-decalin depends on the acid amount of supports at 250 °C. Lower acidity showed lower *trans*-decalin selectivity. It is believed that the *cis*-decalin converted to *trans*-decalin through isomerization in Scheme 1 over acid sites of Al-MCM-41.

The naphthalene conversion in the presence of DBT (200 ppm) is shown in Fig. 6. DBT played a role of sulfur poison as expected and the conversion of naphthalene and tetralin was retarded if compared with the data without DBT shown in Fig. 5. The sulfur tolerance of supported Pt catalysts could be represented by the ratio of the naphthalene conversion rate constant, k_{1s}/k_1, between the reactions with and without DBT [14,18], where k_1 is the naphthalene conversion rate constant of pseudo-first-order kinetics

Table 3
Selectivity to *trans*-decalin in naphthalene hydrogenation under 1000 psi[a]

Catalysts	*trans*-Decalin/(*cis*- + *trans*-decalin)		
	200 °C	250 °C	300 °C
Pt/MCM-41	0.38	0.39	0.54
Pt/Al-MCM-41(5)-Pre	0.45	0.54	0.64
Pt/Al-MCM-41(40)-Pre	0.33	0.37	0.63
Pt/Al-MCM-41(5)-Post	0.46	0.59	0.82
Pt/Al-MCM-41(40)-Post	0.43	0.49	0.64

[a] The decalin selectivity was determined from the data at the time of complete conversion of tetralin.

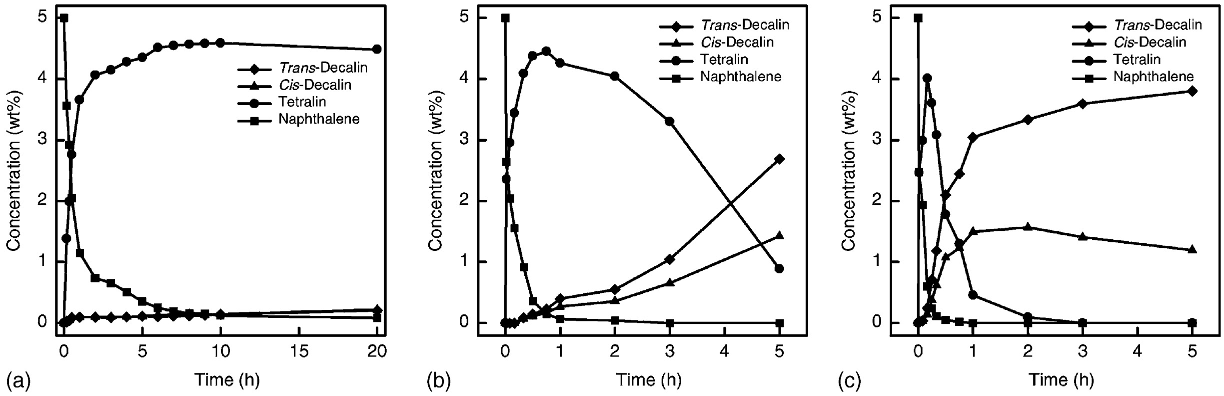


Fig. 6. Concentration change with time for conversion of naphthalene to tetralin and decalins in the presence of 200 ppm DBT at 300 °C and 1000 psi over: (a) Pt/MCM-41; (b) Pt/Al-MCM-41(5)-Pre; (c) Pt/Al-MCM-41(5)-Post.

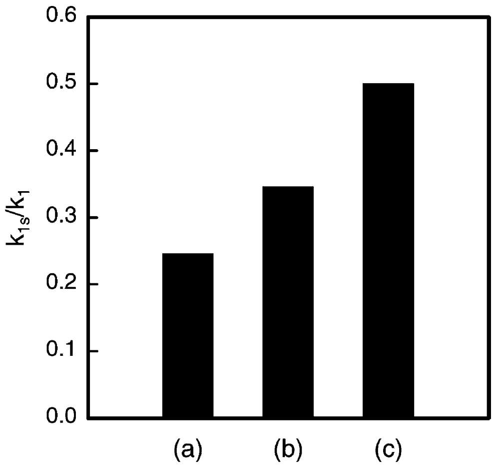


Fig. 7. Relative hydrogenation activity at 300 °C and 1000 psi after addition of 200 ppm DBT over: (a) Pt/MCM-41; (b) Pt/Al-MCM-41(5)-Pre; (c) Pt/Al-MCM-41(5)-Post.

and k_{1S} the corresponding rate constant in the presence of DBT. Fig. 7 shows that the value of k_{1S}/k_1 was the highest with Pt/Al-MCM-41(5)-Post. This may indicate that the supported platinum catalysts with higher acidity showed not only better activity and selectivity but also better sulfur tolerance. Schultze and Koppitz [31] reported that a charge or partial charge transfer of electron is possible when a sulfur species comes in close contact with a metal. Barbier et al. [32] reported that more acidic support makes more electron-transfer from the metal to the support, which makes the metal electron-deficient. Therefore, the electron deficiency reduces the chances of adsorbing acceptor compounds such as sulfur. This effect seemed to contribute to the increase of sulfur tolerance in naphthalene hydrogenation over Pt/Al-MCM-41 catalysts.

4. Conclusions

Mesoporous Al-MCM-41 prepared through direct sol–gel (Pre) or post-synthetic method (Post) was used as effective supports for platinum catalysts in naphthalene hydrogenation at 200–300 °C. Under hydrogen pressure of 1000 psi, the catalytic activity was higher in the order of Pt/Al-MCM-41-Post > Pt/Al-MCM-41-Pre > Pt/MCM-41. Al-MCM-41-Post showed higher activity than Al-MCM-41-Pre due to the better accessibility of their acid sites, which could explain the difference in acid amounts between ammonia TPD and ^{27}Al MAS NMR. The acidity of Al-MCM-41 resulted in the improvement of catalytic activity, which seemed to be attributed to alternative pathway induced by spillover hydrogen in the metal–acid interfacial region. The sulfur tolerance represented by the ratio of rate constants between the reactions with and without DBT as sulfur poison was the highest for the Pt/Al-MCM-41-Post catalyst due to the more electron-deficient state of metal.

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