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Research paper

Effect of aluminum modification on catalytic performance of Pt supported on MCM-41 for thiophene hydrodesulfurization

Yasuharu Kanda^{a,*}, Takao Kobayashi^a, Yoshio Uemichi^a, Seitaro Namba^b and Masatoshi Sugioka^a

^aDepartment of Applied Chemistry, Muroran Institute of Technology, 27-1 Muzumoto-cho, Muroran 050-8585, Japan

^bDepartment of Materials, Teikyo University of Science and Technology, 2525 Yatsusawa, Uenohara, Yamanashi 409-0193, Japan

* Corresponding author. Tel.: +81 143 46 5723; fax: +81 143 46 5733.

E-mail address: s0927029@mmm.muroran-it.ac.jp (Y. Kanda),

msugioka@mmm.muroran-it.ac.jp (M. Sugioka).

Abstract

The catalytic activities and properties of platinum supported on siliceous MCM-41 and Al-modified MCM-41, such as Al-incorporated MCM-41 (AlMCM-41) and alumina-modified MCM-41 (Al₂O₃-MCM-41), for the hydrodesulfurization (HDS) of thiophene were investigated. Al₂O₃-MCM-41 was prepared by an impregnation method using aluminum nitrate (Al(NO₃)₃·9H₂O) aqueous solution. Pt/Al₂O₃-MCM-41 catalyst showed high and stable activity for HDS of thiophene and this activity was remarkably higher than that of a commercial CoMo/Al₂O₃ HDS catalyst. The catalysts were characterized by XRD, hydrogen adsorption, ammonia-TPD, 2-propanol dehydration, cumene cracking and FT-IR. Dispersion of platinum on Al₂O₃-MCM-41 was remarkably higher than on MCM-41 or on AlMCM-41. It was revealed that the acidity of Al₂O₃-MCM-41 was higher than that of MCM-41 or of AlMCM-41. Furthermore, it was observed that there exist Brønsted acid sites on Al-modified MCM-41. FT-IR spectra of thiophene adsorbed on Al-modified MCM-41 support indicates that thiophene molecules interact with Brønsted acid sites on Al-modified MCM-41. It was found that the HDS activity of Pt/quartz mixed mechanically with Al-modified MCM-41 catalyst was higher than that calculated. This suggests that there exists spillover hydrogen on supported Pt catalysts in the HDS of thiophene. Results revealed that the high activity of Pt/Al₂O₃-MCM-41 catalyst for HDS reaction is due to good harmony of high dispersion of Pt particles and Brønsted acidity of the support.

Keywords

Hydrodesulfurization; Thiophene; Supported Pt catalyst; Alumina modification; MCM-41

1. Introduction

Hydrodesulfurization (HDS) of petroleum feedstocks is one of the important processes in the petroleum industry to produce clean fuels [1-4]. However, recently, the development of highly active HDS catalysts, which exhibit higher activity than commercial CoMo/Al₂O₃ HDS catalyst, have been claimed in the petroleum industry to produce lower sulfur content fuels [5,6]. It has been accepted that noble metal catalysts have high possibilities as new HDS catalyst for petroleum [7-12]. The authors have also investigated the development of highly active noble metal HDS catalysts supported on zeolites [13-15].

Recently, mesoporous silicate materials such as FSM-16, MCM-41 and SBA-15, which have larger pore diameter and higher surface area than zeolites, have been attracting wide attention as new materials for catalysts and catalyst supports. Some researchers have attempted to develop new HDS catalysts based on mesoporous silicates [16,17]. In the previous papers [18-22], we have reported that noble metals, especially platinum, supported on mesoporous silicates, such as FSM-16 [18], MCM-41 [19] and SBA-15 [20], showed high activity in the HDS of thiophene. Thus, noble metals supported on mesoporous silicates have high possibilities for usage with new HDS catalysts for petroleum feedstocks. Furthermore, Pt supported on alumina-modified MCM-41 (Al₂O₃-MCM-41) showed remarkably high and stable activity in the HDS of thiophene and Brønsted acid site in Pt/Al₂O₃-MCM-41 catalyst plays an important role for HDS of thiophene [22]. Generally, Brønsted acid site of mesoporous silicate is generated by incorporation of Al atom into silicate framework. It was expected that the differences between Pt/Al₂O₃-MCM-41 and Pt/Al-incorporated MCM-41 (AlMCM-41) catalysts will clarify the cause of high activity of Pt/Al₂O₃-MCM-41 for the HDS of thiophene.

In the present work, we examined the catalytic performance of platinum supported on Al-modified MCM-41 such as AlMCM-41 and Al₂O₃-MCM-41 for the HDS of thiophene in order to develop highly active platinum catalysts supported on mesoporous silicates for HDS of

petroleum feedstocks. Furthermore, we examined the effect of Al modification on the HDS activity of MCM-41-supported Pt catalysts.

2. Experimental

2.1. Preparation of Catalysts

Siliceous MCM-41 was prepared using sodium silicate (Kanto Chemical Co.) and surfactants such as $\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3\text{Br}$ (Aldrich), $(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{NBr}$ (Aldrich) and 25 wt% $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Cl}$ (Aldrich) aqueous solution. Each sample obtained was washed by water and was dried at 120 °C. The templates were removed by calcination in air at 540 °C for 10 h. Al-incorporated MCM-41 (Si/Al = 15) was prepared by the above method using sodium aluminate (NaAlO_2 , Wako Pure Chemical Industries) as an Al source. Al_2O_3 -modified MCM-41 was prepared by an impregnation method; the amount of Al_2O_3 loading was 4 wt%. Calcined siliceous MCM-41 was impregnated with aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Wako Pure Chemical Industries) aqueous solution. After impregnation of aluminum nitrate, the samples were dried at 120 °C and were calcined at 500 °C for 4 h. Addition of sodium to Al_2O_3 -MCM-41 support was also carried out by impregnation method using sodium nitrate (NaNO_3 , Wako Pure Chemical Industries) aqueous solution. Supported Pt catalysts were prepared by an impregnation method using hydrogen hexachloroplatinate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Kanto Chemical Co.) aqueous solution; the amount of Pt loading was 5 wt%. After Pt precursor impregnation, the samples were dried at 120 °C followed by calcination at 500 °C for 4 h. The supported Pt catalysts were treated by helium stream at 500 °C for 1 h and were reduced by hydrogen at 450 °C for 1 h prior to the reaction.

2.2. Hydrodesulfurization of thiophene

HDS of thiophene was carried out at 350 °C under 0.1 MPa using a conventional fixed bed flow reactor. Thiophene was introduced into the reactor by passing hydrogen (30 ml min^{-1}) through a thiophene trap cooled at 0 °C. Reaction conditions were as follows: catalyst weight = 0.1 g,

$\text{H}_2/\text{thiophene} = 30 \text{ mol mol}^{-1}$, $\text{W/F} = 37.9 \text{ g h mol}^{-1}$. The reaction products were analyzed with a gas chromatograph (FID) equipped with silicone DC-550 (2 m, 150 °C) and VZ-7 (4 m, 0 °C) columns, respectively.

2.3. Characterization of Catalysts

2.3.1. Nitrogen adsorption-desorption isotherm

The nitrogen adsorption-desorption isotherm at -196 °C was measured using Micromeritics ASAP 2010. The textural properties of MCM-41 and Al-modified MCM-41 were calculated by BET and BJH methods. Samples were evacuated at 400 °C for 10 h prior to nitrogen adsorption.

2.3.2. Acidities of MCM-41 and Al-modified MCM-41

Temperature programmed desorption of ammonia (NH_3 -TPD) was carried out using a glass vacuum system. The sample (0.1 g) was evacuated at 500 °C for 1 h before adsorption of ammonia. Ammonia was adsorbed at 100 °C for 30 min followed by evacuation at the same temperature for 30 min. The NH_3 -TPD profile was observed from 100 °C to 500 °C with $10 \text{ }^\circ\text{C min}^{-1}$. The pressure of desorbed NH_3 was measured with a pirani gauge. The acidities of MCM-41 and Al-modified MCM-41 were evaluated by 2-propanol (2-PA) dehydration (200 °C) and cumene cracking (400 °C) using a pulse reactor with helium carrier gas. In both reactions, catalysts (0.03 g) were charged into the reactor and were pretreated at 500 °C for 1 h before the reaction.

2.3.3. Dispersion of platinum

The dispersion of platinum on MCM-41 and Al-modified MCM-41 were evaluated by XRD analysis and by the hydrogen adsorption method. XRD analysis was carried out using a Rigaku diffractometer with Cu K_α radiation. Adsorption of hydrogen on the supported Pt catalyst was carried out using a glass vacuum system at 25 °C. The supported Pt catalysts were evacuated at 500 °C for 1 h followed by reduction with hydrogen (26.7 kPa) at 450 °C for 1 h and evacuation at the same temperature for 1 h before hydrogen adsorption.

2.3.4. Measurement of FT-IR spectra

FT-IR spectra of pyridine and thiophene adsorbed on MCM-41 and Al-modified MCM-41 were observed by using a Jasco FT-IR spectrometer. The catalysts were evacuated at 500 °C for 2 h prior to the measurement.

3. Results and Discussion

3. 1. Textural properties of MCM-41 and Al-modified MCM-41

Figure 1 shows the nitrogen adsorption-desorption isotherms of MCM-41 and Al-modified MCM-41. MCM-41 and AlMCM-41 exhibit type IV adsorption-desorption isotherms which are characteristic of mesoporous materials. Furthermore, the adsorption-desorption isotherm of Al₂O₃-MCM-41 was also type IV and was similar to that of MCM-41. This indicates that uniform pore structure of MCM-41 was maintained even after Al₂O₃ modification. Textural properties were measured by nitrogen adsorption isotherm, as shown in Table 1. MCM-41 and AlMCM-41 have high surface areas of more than 800 m² g⁻¹. Al₂O₃-MCM-41 showed slightly lower surface area, BJH average pore diameter and pore volume than MCM-41. However, these properties of Al₂O₃-MCM-41 were remained high even after Al₂O₃ modification. Furthermore, the pore size distribution of MCM-41 was shifted to more pores of smaller diameters by Al₂O₃ modification. The decrease of pore diameter by Al₂O₃ modification was approximately equivalent to the radius of Al³⁺ (0.6 Å), as shown in Fig. 2. Such results revealed that the internal pores of MCM-41 were partly modified by the impregnation method using Al(NO₃)₃ aqueous solution.

3. 2. Hydrodesulfurization of thiophene over Pt/MCM-41 and Pt/Al-modified MCM-41 catalysts

The catalytic activities of Pt supported on MCM-41 and Al-modified MCM-41 for the HDS of thiophene were examined at 350 °C. It was found that the catalytic activities of platinum supported on MCM-41 and Al-modified MCM-41 varied remarkably with the kind of support, as shown in Fig. 3. Figure 4 shows the activities of MCM-41- and Al-modified MCM-41-supported Pt catalysts for

the HDS of thiophene after 5 h reaction. Commercial presulfided CoMo/Al₂O₃ catalyst (Nippon Cyanamid Co., BET surface area 308 m² g⁻¹) was used to compare with supported Pt catalysts. The order of the activities of these catalysts was as follows: Pt/Al₂O₃-MCM-41 > Pt/AlMCM-41 > Pt/MCM-41 > CoMo/Al₂O₃. The activity of Pt/Al₂O₃-MCM-41 was very stable with time on stream and this activity was remarkably higher than that of commercial presulfided CoMo/Al₂O₃ HDS catalyst.

The reaction products in the HDS of thiophene over Pt/Al₂O₃-MCM-41 were mainly C₄ hydrocarbons (butane 97%, butenes 3%) and a trace amounts of C₁-C₃ hydrocarbons, whereas those on Pt/MCM-41 were C₄ hydrocarbons (butane 86%, butenes 14%), as shown in Table 2. The selectivity of butane (93%) in the HDS of thiophene over Pt/AlMCM-41 was lower than that on Pt/Al₂O₃-MCM-41. These results indicate that Pt/Al₂O₃-MCM-41 catalyst has higher hydrogenating ability for unsaturated C₄ hydrocarbons formed in the HDS of thiophene than Pt/AlMCM-41 and Pt/MCM-41 catalysts.

3. 3. Dispersion of platinum on MCM-41 and Al-modified MCM-41

We performed various characterizations of Pt/MCM-41 and Pt/Al-modified MCM-41 catalysts in detail to understand the causes of the high activity of Pt/Al₂O₃-MCM-41 for the HDS of thiophene.

Figure 5 shows the XRD patterns of Pt/MCM-41 and Pt/Al-modified MCM-41 after reduction at 450 °C. It was found that peak height of Pt on MCM-41 was significant, but it decreased on AlMCM-41 compared with MCM-41. Furthermore, the peak height of Pt on Al₂O₃-MCM-41 was remarkably lower than the peak heights on MCM-41 and AlMCM-41. This indicates that the dispersion of Pt on Al₂O₃-MCM-41 was remarkably higher than those on MCM-41 and AlMCM-41. Table 2 shows the dispersion and particle size of Pt on MCM-41 and Al-modified MCM-41 measured by the hydrogen adsorption method. The particle size of Pt (d_{Pt} , assumed as spherical

shape) was calculated by dispersion of Pt, according to equation $d_{Pt} = 0.944/D$ (D = dispersion of Pt). It was also revealed that Pt dispersion (0.80) on Al_2O_3 -MCM-41 was the highest and that the particle size (1.18 nm) was lowest among supported Pt catalysts. The order of the dispersion of Pt on MCM-41 and Al-modified MCM-41 was as follows: Pt/ Al_2O_3 -MCM-41 > Pt/AlMCM-41 > Pt/MCM-41. We reported that dispersion of Pt on ZSM-5 zeolite was increased with increasing of proton content [15]. Since Pt precursors such as $[PtCl_6]^{2-}$ in aqueous solution may interact with Brønsted acid sites on AlMCM-41 and Al_2O_3 -MCM-41, dispersion of Pt was enhanced by Al modification. Furthermore, it was reported that Cl^- ligands in $[PtCl_6]^{2-}$ exchange with the hydroxyl groups on the Al_2O_3 surface [23,24]. Thus, high dispersion of Pt on Al_2O_3 -MCM-41 was due to Cl^- ligands in $[PtCl_6]^{2-}$ exchange with the hydroxyl groups of the Al_2O_3 -modified surface. Therefore, the dispersion of Pt was significantly enhanced by Al_2O_3 modification of MCM-41 and dispersion of Pt on Al_2O_3 -MCM-41 was higher than that on AlMCM-41. The order of Pt dispersion was the same as that of HDS activities.

3. 4. Acidities of MCM-41 and Al-modified MCM-41

We evaluated the acidities of MCM-41 and Al-modified MCM-41 by NH_3 -TPD, 2-PA dehydration, cumene cracking and pyridine-adsorbed FT-IR spectra. Figure 6 shows the NH_3 -TPD profiles of MCM-41 and Al-modified MCM-41. It was reported that the desorption peak at low temperature was not ammonia directly adsorbed on acid sites [26] and this ammonia was attributed to hydrogen bonding to NH_4^+ adsorbed on acid sites [27]. Thus, we evaluated the amounts of acid site between 250 °C and 500 °C. The amount of acid site on Al_2O_3 -MCM-41 was higher than that on MCM-41 and AlMCM-41. Figure 7 shows the catalytic activities of MCM-41 and Al-modified MCM-41 for 2-PA dehydration and cumene cracking. It was revealed that MCM-41 showed low activity for both acid-catalyzed reactions, whereas Al_2O_3 -MCM-41 showed high activity for these reactions. The order of the acidities of Al-modified MCM-41 was as follows: Al_2O_3 -MCM-41 >

AlMCM-41 > MCM-41. High acidity of Al₂O₃-MCM-41 was due to the exposed Al atoms on the internal pores of the Al₂O₃-modified surface. It was reported that, at low Si/Al (< 20), Al atoms in Al-incorporated MCM-41 were incorporated into inside the pore walls [25]. Thus, the acidity of AlMCM-41 was lower than that of Al₂O₃-MCM-41. The order of acidities was the same as that of the HDS activities of supported Pt catalysts.

We confirmed the existence of the Brønsted acid sites at 1547 cm⁻¹ on AlMCM-41 and Al₂O₃-MCM-41 by the observation of FT-IR spectra of pyridine adsorbed on AlMCM-41 and Al₂O₃-MCM-41, as shown in spectra (b) and (c) in Fig. 8. We have reported in previous papers [13-15,18-22] that Brønsted acid sites on the supports of noble metal catalysts act as active sites for activation of thiophene. It can be assumed that the surface silanol group (Si-OH) on support acts as a Brønsted acid site and this Brønsted acid site acts as an active site for the activation of thiophene in the HDS of thiophene.

3. 5. Reaction mechanism of thiophene hydrodesulfurization over Pt/MCM-41 and Pt/Al-modified MCM-41 catalyst

3. 5. 1 Role of Brønsted acid sites in the hydrodesulfurization of thiophene

The role of Brønsted acid sites in HDS reaction were examined by sodium addition to highly active Pt/Al₂O₃-MCM-41 catalyst. Table 4 shows the effect of sodium addition on catalytic activity for thiophene HDS and the properties of Pt/Al₂O₃-MCM-41. The dispersion of Pt was hardly changed at all by sodium addition. On the other hand, the HDS activity of the Pt/Al₂O₃-MCM-41 catalyst and the cumene cracking activity of the Al₂O₃-MCM-41 support decreased with increasing sodium addition. These results indicate that Brønsted acid sites directly participate in the HDS of thiophene.

Furthermore, we observed the FT-IR spectra of thiophene adsorbed on MCM-41 and Al-modified MCM-41 in order to clarify the interaction between silanol groups and thiophene

molecules. In the background spectra of MCM-41 evacuated at 500 °C for 2 h, the silanol group was observed at 3745 cm⁻¹, as shown in spectrum (i) in Fig. 9 (a). After introduction of 2 kPa of thiophene onto the MCM-41, the absorption band of Si-OH at 3745 cm⁻¹ decreased considerably and a large and broad peak appeared at 3605 cm⁻¹, which is assigned to the silanol groups interacting with the thiophene molecules. However, the decreased absorbance of silanol groups was completely regenerated by the evacuation at 25 °C, without any shoulder peak at around 3600 cm⁻¹.

In the background spectra of AlMCM-41 evacuated at 500 °C for 2 h, the silanol group was observed at 3745 cm⁻¹, as shown in spectrum (i) in Fig. 9 (b). After introduction of 2 kPa of thiophene onto the AlMCM-41, the absorption band at 3745 cm⁻¹ decreased and shifted to 3603 cm⁻¹, as shown in spectrum (ii) in Fig. 9 (b). The decreased absorbance of silanol group was almost regenerated by the evacuation at 25 °C, but a slight shoulder peak at 3603 cm⁻¹ was observed, as shown in spectrum (iii) in Fig. 9 (b). These results indicate that the interaction between AlMCM-41 with Brønsted acid site and thiophene is stronger than that of MCM-41 without Brønsted acid site.

FT-IR spectra of thiophene adsorbed on Al₂O₃-MCM-41 was similar to those of AlMCM-41, as shown in Fig. 9 (c). However, the frequency of the shifted absorption band was observed at 3600 cm⁻¹ and a shoulder peak was clearly observed after evacuation at 25 °C. This indicates that the interaction between silanol group on Al₂O₃-MCM-41 and thiophene molecule was stronger than that of AlMCM-41. This result can be explained if the interaction between acidic silanol groups on Al₂O₃-MCM-41 and thiophene was stronger than that of AlMCM-41, since the Brønsted acidity of Al₂O₃-MCM-41 was higher than that of AlMCM-41.

Some modes of coordinated thiophene in organometallic complexes have been reported [28] and two adsorption types of thiophene on catalyst surface were proposed [29-31]; (i) via π electrons in aromatic ring and (ii) via sulfur atom. It was reported that the sulfur atom in thiophene directly interacts with the Brønsted acid site on HY zeolite [31]. Furthermore, the shift of frequency of the silanol group was due to the interaction between the sulfur atom in thiophene and hydroxyl groups

of zeolite, and these experimental results were consistent with theoretical results [32]. We also observed that frequency shifts of silanol group on MCM-41 and Al-modified MCM-41 occurred by thiophene introduction, as shown in Fig. 9. Thus, thiophene molecules may adsorb on Brønsted acid sites of Al-modified MCM-41 via sulfur atoms. These results confirmed that thiophene is adsorbed and activated on Brønsted acid site on Al-modified MCM-41 in the HDS of thiophene over Pt/Al-modified MCM-41 catalyst.

3. 5. 2 Role of spillover hydrogen in the hydrodesulfurization of thiophene

Furthermore, we tried to confirm the existence of spillover hydrogen in the HDS of thiophene over supported Pt catalysts. The catalytic activities of Pt/quartz (A, Pt dispersion = 0.05) mixed mechanically with MCM-41 and Al-modified MCM-41 (B) were examined. MCM-41, AlMCM-41 and Al₂O₃-MCM-41 catalysts (0.1 g) showed very low activities (< 0.1 % conversion) for the HDS of thiophene. It was found that the activities of mechanically mixed catalysts obtained experimentally were higher than the calculated (A+B) values, as shown in Fig. 10. The HDS activities of mechanically mixed catalysts were changed by the kind of MCM-41. The order of the HDS activities of these mechanically mixed catalysts was as follows: Al₂O₃-MCM-41 > AlMCM-41 > MCM-41. This order was the same as the order of acidities of Al-modified MCM-41. These results indicate that, since a new HDS reaction route is generated by the addition of Al-modified MCM-41, as shown in Scheme 1, mechanically mixed catalysts showed higher activity than Pt/quartz catalyst. In Scheme 1, hydrogen was activated on Pt particles in Pt/quartz to form spillover hydrogen. Spillover hydrogen attacks the thiophene adsorbed on Brønsted acid sites of Al-modified MCM-41. This suggests that there exists spillover hydrogen on supported Pt catalysts in the HDS of thiophene.

3. 5. 3 Reaction mechanism of Pt/Al-modified MCM-41 catalyst

We reported in the previous paper [33] that Pt/alumina-modified silica gel ($\text{Al}_2\text{O}_3\text{-SiO}_2$) catalyst having Brønsted acid sites and high Pt dispersion (0.76) showed remarkably higher HDS activity than Pt/ Al_2O_3 catalyst with similar Pt dispersion. Furthermore, Pt/quartz without Brønsted acid sites showed low HDS activity, but this activity was enhanced by addition of acidic MCM-41 and Al-modified MCM-41, as shown in Fig. 10. On the basis of these results, we supposed two reaction routes for thiophene HDS over the highly active Pt/Al-modified MCM-41 catalyst: (i) a monofunctional route in which HDS reaction proceeds only on Pt particles and (ii) a bifunctional route in which both Pt particle and Brønsted acid sites are involved in HDS reactions. Since the Brønsted acidity of supports remarkably affected the HDS activity of supported Pt catalysts, as shown in Table 4, both Pt particle and Brønsted acid site are important for highly active supported Pt catalyst. We propose a possible mechanism in which hydrogen is activated on Pt to form spillover hydrogen and thiophene is activated on Brønsted acid sites of Al-modified MCM-41, as shown in Scheme 2. It was reported that the C-S bond in thiophene molecules cleaves via thiophene-derived carbenium ion on Brønsted acid sites of zeolites [34-36]. Some thiophene molecules adsorbed on Brønsted acid sites of Al-modified MCM-41 are activated to form carbenium ions. The spillover hydrogen formed on Pt particles attacks the activated thiophene on the Brønsted acid sites of Al-modified MCM-41.

4. Conclusions

It was found that the HDS activities of MCM-41- and Al-modified MCM-41-supported Pt catalysts were varied by the kind of supports. The order of the activities of these catalysts was as follows: Pt/ $\text{Al}_2\text{O}_3\text{-MCM-41}$ > Pt/AlMCM-41 > Pt/MCM-41. This order can be explained by dispersion of Pt and acidity of support. Thus, we concluded that the high activity of Pt/ $\text{Al}_2\text{O}_3\text{-MCM-41}$ catalyst for HDS of thiophene is due to good harmony of high dispersion of Pt particles and Brønsted acidity of the support.

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Table 1

Textural properties of MCM-41 and Al-modified MCM-41 supports measured by nitrogen adsorption isotherm

Support	Surface area (m ² g ⁻¹)	BJH average pore diameter (Å)	Pore volume (cm ³ g ⁻¹)
MCM-41	855	26.7	0.79
AlMCM-41	836	26.2	0.81
Al ₂ O ₃ -MCM-41	798	25.9	0.73

Table 2

Products distribution over MCM-41- and Al-modified MCM-41-supported Pt catalysts in the HDS of thiophene at 350 °C

Catalyst	HDS conv. (%)	C ₁ -C ₃ (%)	Butanes (%)	Butenes (%)
Pt/MCM-41	69.2	0.2	85.6	14.1
Pt/AlMCM-41	85.2	0.6	93.2	6.2
Pt/Al ₂ O ₃ -MCM-41	95.4	0.7	96.7	2.6

Table 3

Dispersion and particle size of Pt on MCM-41 and Al-modified MCM-41

Catalyst	Dispersion (H/Pt)	Particle size (nm)
Pt/MCM-41	0.47	2.01
Pt/AlMCM-41	0.56	1.66
Pt/Al ₂ O ₃ -MCM-41	0.80	1.18

Table 4

Effect of sodium addition on catalytic activity for thiophene HDS and properties of Pt/Al₂O₃-MCM-41

Amount of sodium addition (wt%)	HDS conv. (%)	Pt dispersion (H/Pt)	Cumene cracking (%)
0	95.4	0.80	31.2
0.1	76.4	0.83	25.1
0.5	59.4	0.74	9.3
1.0	25.7	0.79	1.6

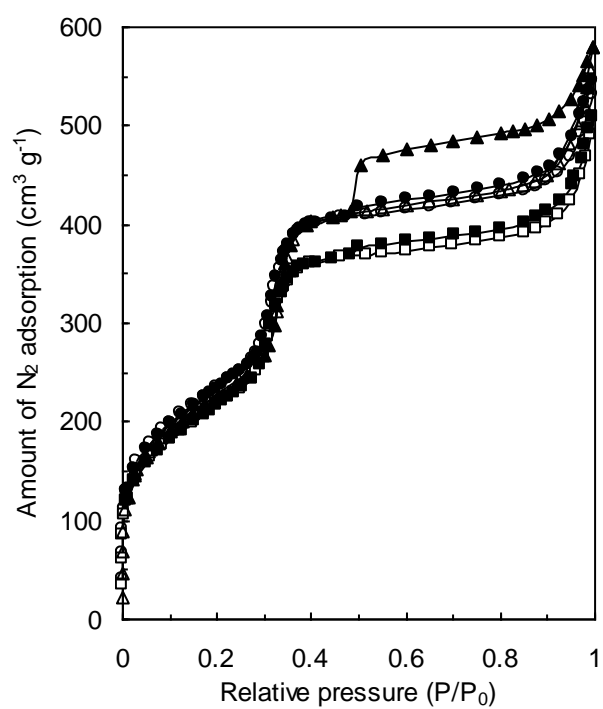


Fig. 1 Nitrogen adsorption-desorption isotherms of (●) MCM-41, (▲) AlMCM-41 and (■) Al₂O₃-MCM-41 (open: adsorption, closed: desorption).

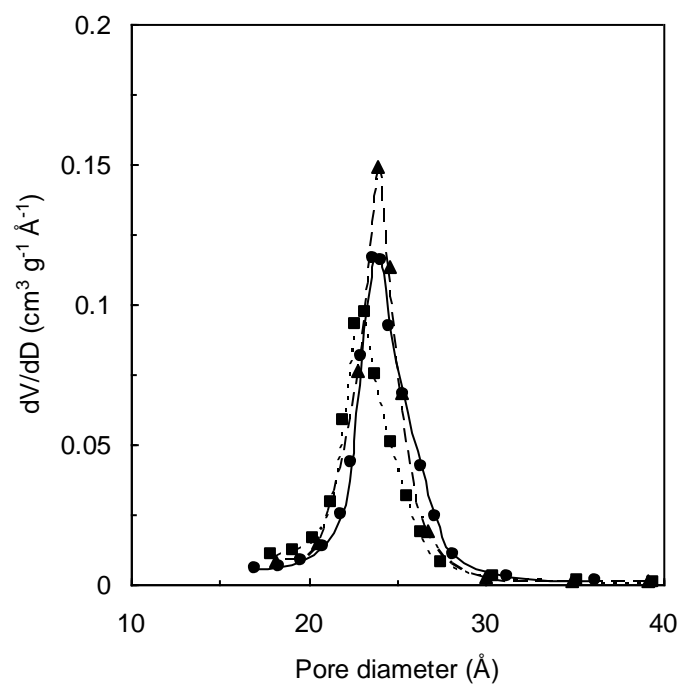
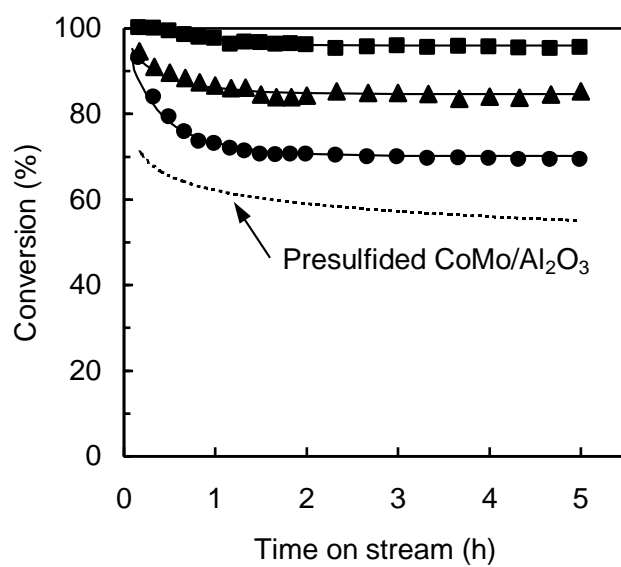


Fig. 2 Pore size distribution of (●) MCM-41, (▲) AlMCM-41 and (■) Al₂O₃-MCM-41 calculated by nitrogen adsorption isotherm.



$H_2/\text{thiophene} = 30, W/F = 37.9 \text{ g h mol}^{-1}$

Fig. 3 Hydrodesulfurization of thiophene over (●) Pt/MCM-41, (▲) Pt/AlMCM-41 and (■) Pt/Al₂O₃-MCM-41 catalysts at 350 °C.

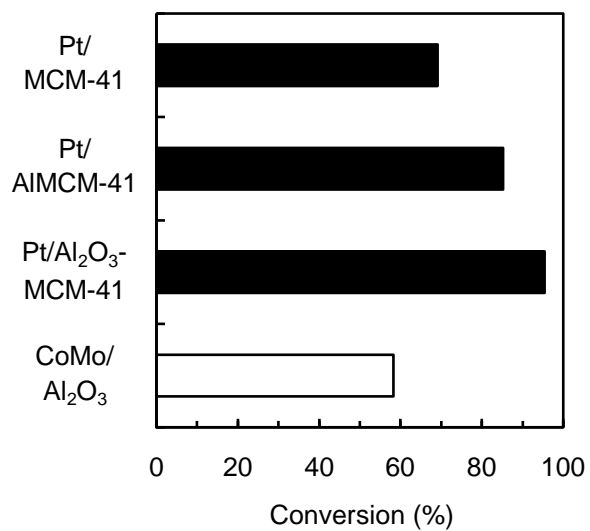


Fig. 4 Catalytic activities of Pt supported on MCM-41 and Al-modified MCM-41 for HDS of thiophene.

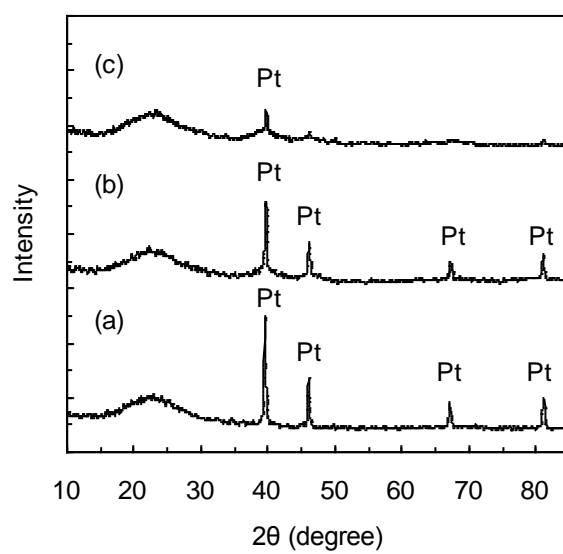


Fig. 5 XRD patterns of Pt supported on MCM-41 and Al-modified MCM-41 after reduction at 450 °C.

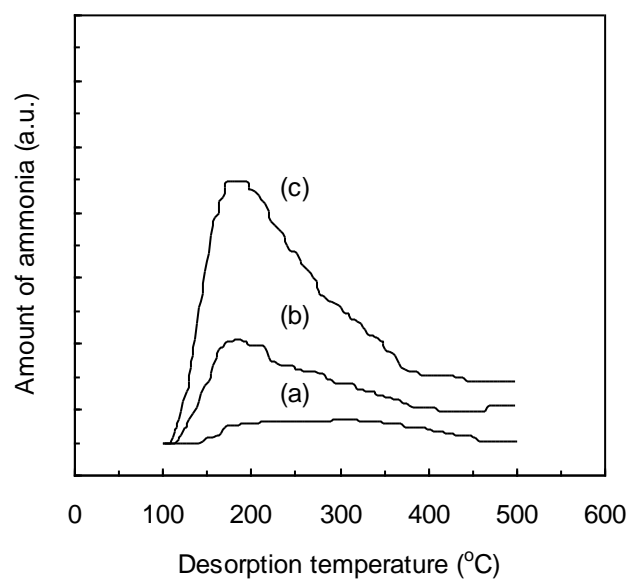


Fig. 6 NH₃-TPD profiles of (a) MCM-41, (b) AlMCM-41 and (c) Al₂O₃-MCM-41.

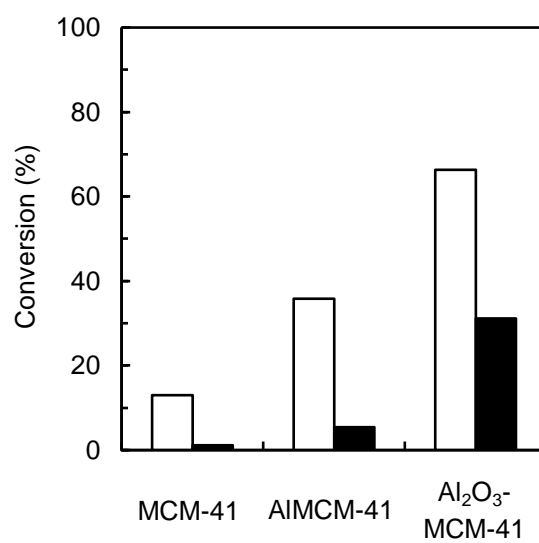


Fig. 7 Catalytic activities of MCM-41 and Al-modified MCM-41 for the (□) dehydration of 2-propanol and (■) cracking of cumene.

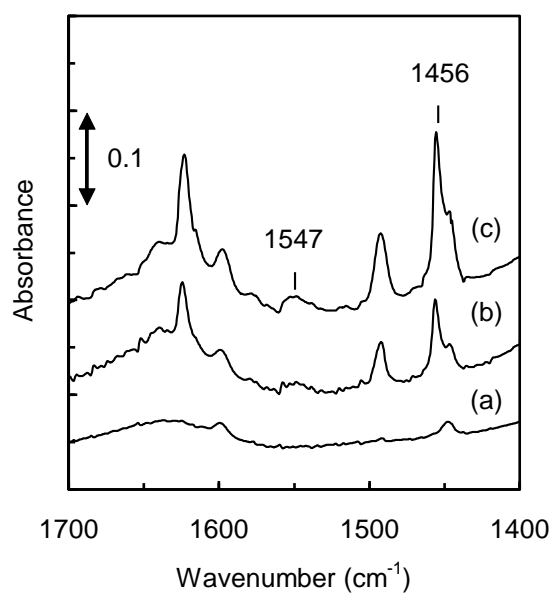


Fig. 8 FT-IR spectra of pyridine adsorbed on (a) MCM-41, (b) AlMCM-41 and (c) Al₂O₃-MCM-41. Pyridine was adsorbed at 150 °C, followed by evacuation at 150 °C for 30 min.

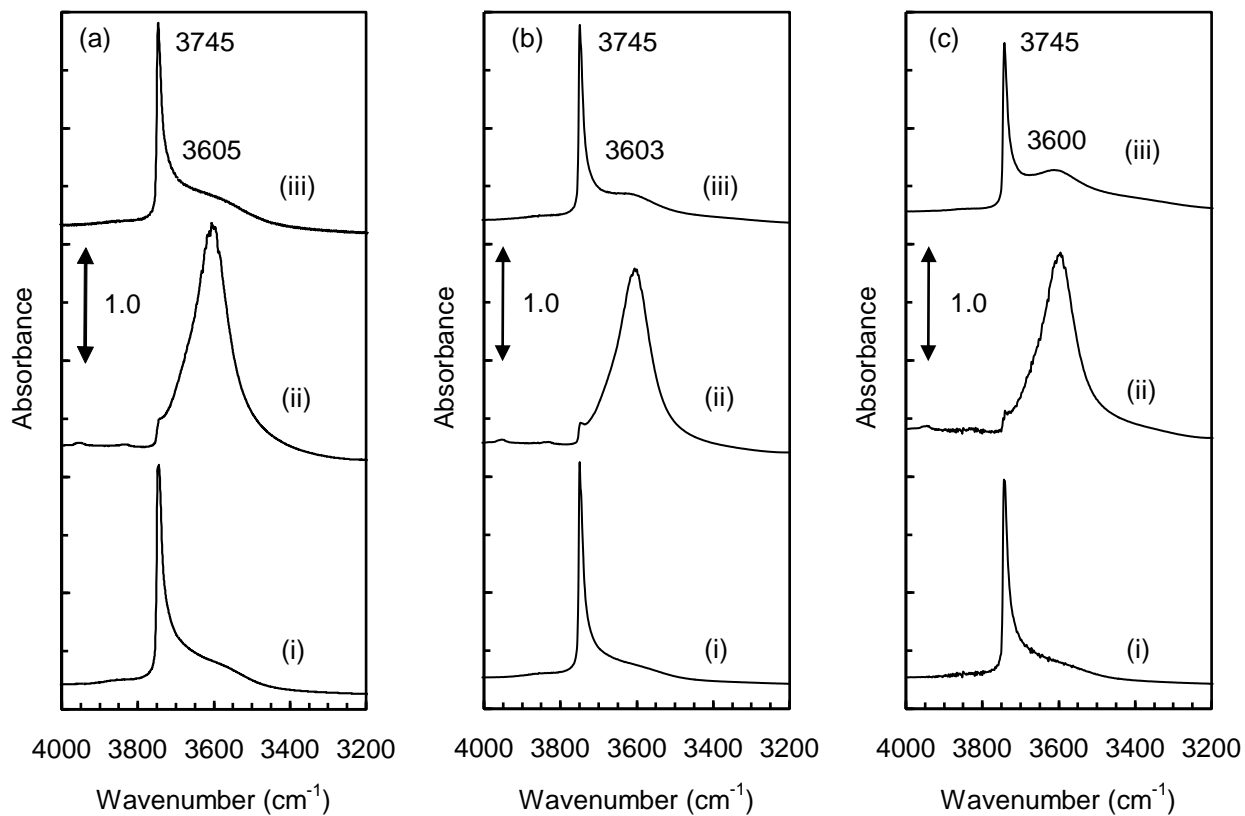


Fig. 9 FT-IR spectra of thiophene adsorbed on (a) MCM-41, (b) AIMCM-41 and (c) Al_2O_3 -MCM-41. (i) Samples evacuated at 500 °C for 2 h, (ii) Thiophene (2 kPa) introduced, (iii) After evacuation at 25 °C for 30 min.

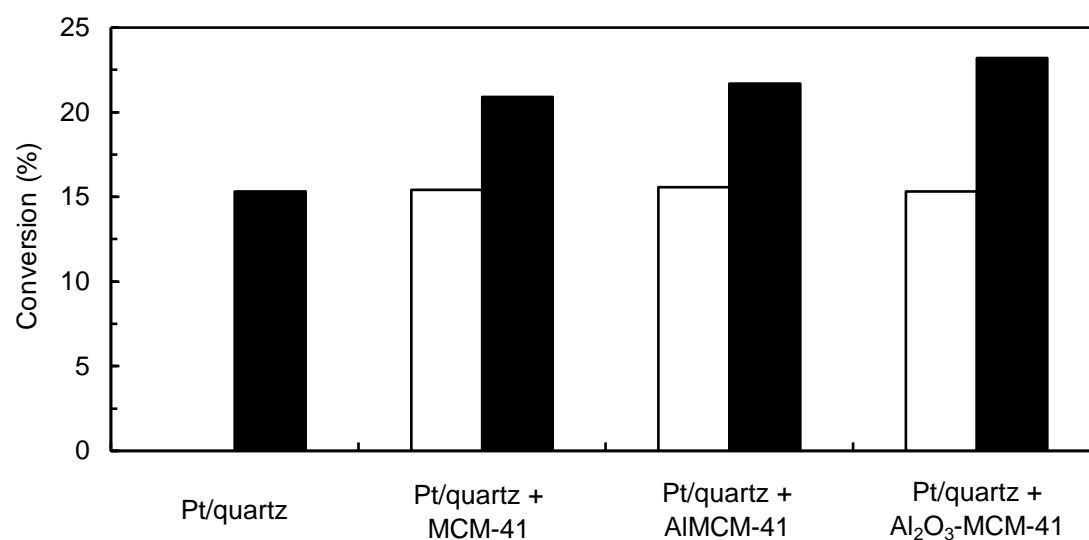
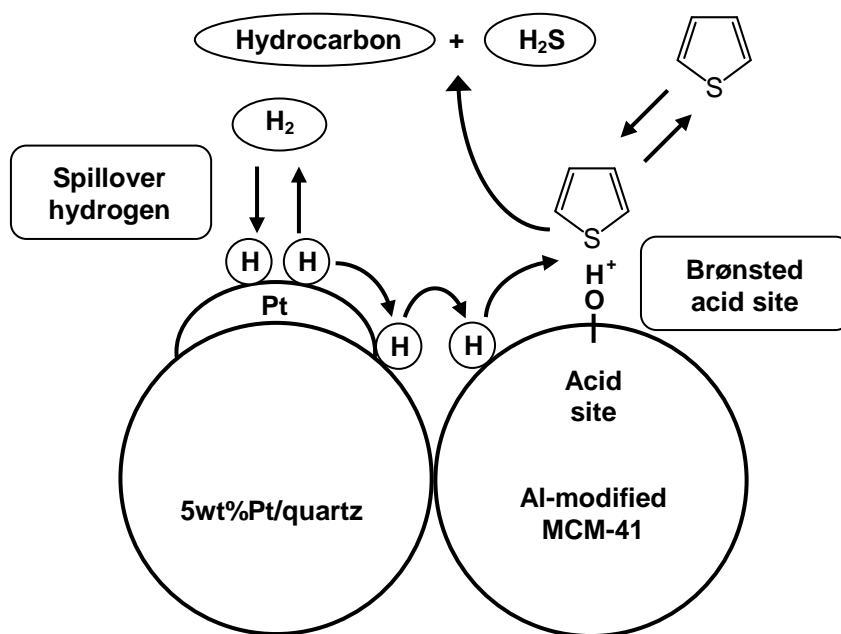
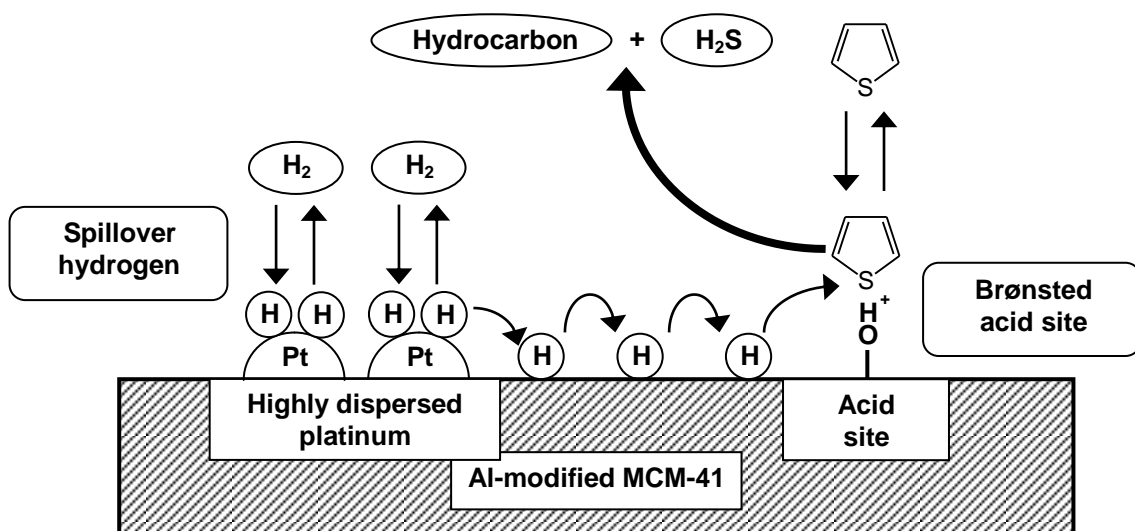


Fig. 10 HDS activities of physically mixed Pt/quartz and various MCM-41 catalysts at 350 °C.

(□) HDS activities of mechanically mixed catalysts obtained by calculation, (■) HDS activities of mechanically mixed catalysts obtained by experiment.



Scheme 1 New reaction route of HDS of thiophene over physically mixed Pt/quartz and Al-modified MCM-41 catalyst.



Scheme 2 A possible mechanism of HDS of thiophene over highly active Al-modified MCM-41-supported Pt catalysts with Brønsted acid sites.