AJChE 2005, Vol. 5, No. 1, 76–83

# Enhancement Effect of Hydrogen Sulfide Over Metal Ion-Exchange Mesoporous Silicate FSM-16 for Acid-Catalyzed Reactions

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The activity enhancement of metal ion-exchange mesoporous silicate FSM-16 (MeFSM-16) by sulfiding with hydrogen sulfide was studied using acid-catalyzed reactions, isomerization of 1-butene, *cis*-2-butene and cyclopropane, as model reactions. It was revealed that the catalytic activities of MeFSM-16 for the acid-catalyzed reactions were remarkably enhanced after sulfiding with hydrogen sulfide. Moreover, it was observed that the optimum enhancement effect of hydrogen sulfide was obtained at the sulfiding temperature of 200°C. Infrared spectroscopic measurement of pyridine adsorption over sulfided MeFSM-16 showed that the activity enhancement of MeFSM-16 resulted in the generation of new Brönsted acid sites.

***Keywords:*** Metal ion-exchange, mesoporous silicate, hydrogen sulfide, *and* activity enhancement.

## INTRODUCTION

Sulfur compounds are invariably present as impurities in petroleum feedstocks and considered as poisonous material in heterogenous catalytic systems.

Studies on the poisoning effect of sulfur compounds in heterogenous catalytic systems are considered important in order to gain adequate fundamental information in predicting commercial catalyst life and its behavior in practical use. The poisoning effect of hydrogen sulfide on heterogenous catalysts have been studied intensively in the past years (Bartholomew et al. 1982, Barbier et al. 1990).

More recently, for instance, the poisoning effect of hydrogen sulfide over hydrogenation catalysts (Paal et al. 1997, Rodriguez et al. 1997) and methane oxidative coupling catalysts (Campbell et al. 1992, Deng et al. 1993) had been studied. There were cases where hydrogen sulfide was used in promoting the catalysis of heterogenous catalytic systems. The activity enhancement of the industrial hydro-desulfurization catalysts $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ by pretreatment with hydrogen sulfide is a typical example. An understanding of the interaction of sulfur compounds with the catalyst surface is considered important for controlling the catalytic process as well (Ziolek and Sugioka 2000).

Mesoporous silicates, such as FSM-16 (Inagaki et al. 1993) and MCM-14 (Beck et al. 1992), are new materials with a large and regular pore structure and high surface area. They are considered as potential materials for many applications as adsorbents, catalysts, and catalyst support for treating bulky chemicals and synthesizing large molecule materials. However, these new materials show low acidity and low catalytic activity for acid-catalyzed reactions.

Previous researches had reported that the sulfiding of metal ion-exchange silica gel and zeolites with hydrogen sulfide resulted in remarkable activity enhancement for some acid-catalyzed reactions (Sugioka et al. 1994, Sugioka and Andalaluna 1997, Andalaluna and Sugioka 2001). The catalytic performance of mesoporous silicate FSM-16 might also be improved by modification using metal ion-exchange and sulfiding with hydrogen sulfide.

In the present study, the effect of sulfiding of metal ion-exchange FSM-16 (MeFSM-16, Me = Ag, Cd, Cu, Ni) with hydrogen sulfide was studied using acid-catalyzed reactions, isomerization of 1-butene, *cis*-2-butene and cyclopropane, as model reactions. Various model reactions had been applied to the present research to study the surface character of sulfided MeFSM-16. It is known that the reactants require different degrees of acidity for the reaction to proceed, where isomerization of 1-butene require relatively low acidity. Infrared spectroscopic measurements of pyridine adsorption over MeFSM-16, before and after sulfiding, were performed using FT-IR in order to study the mechanism of activity enhancement of MeFSM-16 in the sulfiding.

## EXPERIMENTAL

The mesoporous silicate material FSM-16 with a surface area 970 m$^2$/g and a channel diameter 27Å (2.7 nm) was provided by Toyota Central R&D Labs. MeFSM-16 was prepared by the ion-exchange of silicate FSM-16 using $AgNO_3$, $CdCl_2$, $CuCl_2$, and $NiCl_2$ aqueous solutions. All catalysts were calcined in air at 500°C for 4 hours.

The isomerization of 1-butene, *cis*-2-butene, and cyclopropane were carried out in a conventional closed circulating reactor by employing 0.05, 0.035, and 0.035 g of catalyst at 25, 75, and 150 °C, respectively. Reaction temperature was defined considering the reactivity of the reactants that require a certain acidity at the Brönsted acid sites to proceed. For instance, since cyclopropane isomerization is known to require relatively strong Brönsted acid sites, higher reaction temperature was applied. The initial pressure of the reactant in each case was 40 Torr. The catalysts were evacuated at 500°C for 2 hours

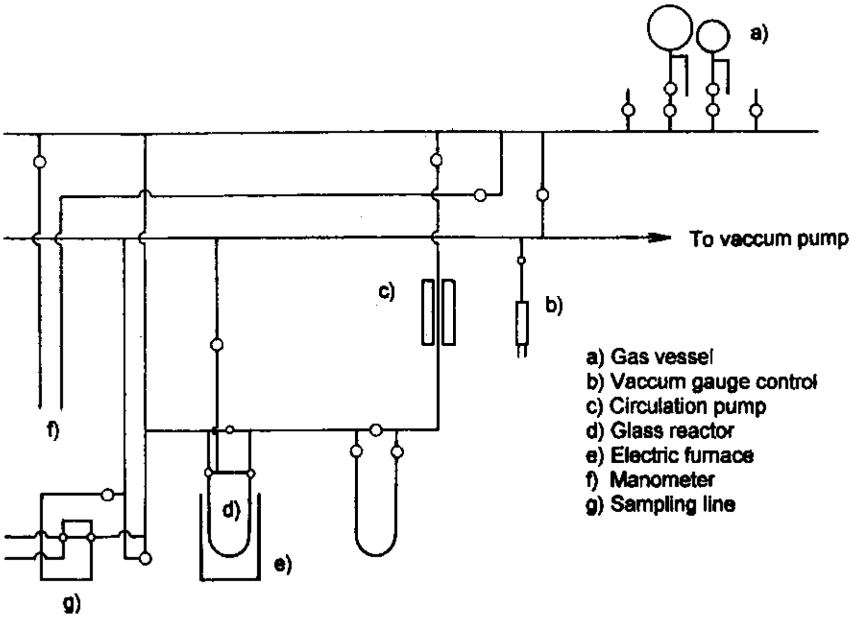

*Figure 1. Outline of the Closed Circulating Reactor System*

prior to the reaction and sulfided with 40 Torr of hydrogen sulfide at 100~500 °C for 1 hour followed by evacuation at the same temperature for 0.5 hour.

Infrared spectroscopic measurement was performed by Jasco FT-IR using an in-situ cell. Hydrogen sulfide adsorption was carried out by introducing 40 Torr of hydrogen sulfide into the cell at 200°C, followed by evacuation at the same temperature for 0.5 hour. Pyridine adsorption was performed by introducing 10 Torr of pyridine vapor into the cell at 150°C followed by evacuation at the same temperature for 0.5 hour.

## RESULTS AND DISCUSSIONS

### *Activity enhancement of MeFSM-16 in the isomerization of 1-butene*

The activity enhancement of MeFSM-16 by sulfiding with hydrogen sulfide in the isomerization of 1-butene is shown in Table 1.

On the one hand, mesoporous silicate FSM-16 and MeFSM-16 (Me = Ag, Cd, Cu) showed low activity for 1-butene isomerization before sulfiding. On the other hand, NiFSM-16 had high activity in 1-butene isomerization which was assumed due to active species of nickel oxides. The activities of MeFSM-16, except for NiFSM-16, were enhanced remarkably by sulfiding with hydrogen sulfide. The order of the activity enhancement was AgFSM-16>CdFSM-16>CuFSM-16>NiFSM-16. Furthermore, the enhanced activities of MeFSM-16 were higher than that of HY zeolite; i.e. enhanced activity of AgFSM-16 was about twice that of HY zeolite.

It was observed that the activity of NiFSM-16 decreased after sulfiding with hydrogen sulfide. The decrease of activity of NiFSM-16 was attributed to the transformation of nickel from oxide form into sulfide form. It is generally known that the selectivity of product (*cis/trans* ratio) in 1-butene isomerization, which proceeds over Brönsted acid sites, is close to one. In the case of HY zeolite, which has a wide pore (0.78 nm), the selectivity of product obtained was 1.06. As shown in Table 1, it was observed that selectivities close to one were observed for sulfided MeFSM-16. Therefore, it could be inferred that Brönsted acid sites were generated over MeFSM-16 by the sulfiding with hydrogen sulfide and that these new acid sites were responsible for the activity enhancement.

Table 2 shows the activity enhancement of MeFSM-16 in the sulfiding with hydrogen sulfide for the isomerization of *cis*-2-butene. Similar results with 1-butene isomerization were observed for *cis*-2-butene isomerization. It is interesting to note that the *trans*-2-butene to 1-butene ratio (*trans/1*) increased by the sulfiding with hydrogen sulfide. These results could indicate that the acid strength of MeFSM-16 might be increased by the sulfiding treatment.

***Table 1. Activity Enhancement of MeFSM-16 by Sulfiding with Hydrogen Sulfide in the Isomerization of 1-butene***

| | **Activity (%/g. min)** | | **cis/trans ratio** | |
|---|---|---|---|---|
| **Catalysts** | *Before Sulfiding* | *After Sulfiding* | *Before Sulfiding* | *After Sulfiding* |
| | | | | |
| FSM-16 | 2.8 | 3.1 | 2.02 | 2.04 |
| | | | | |
| AgFSM-16 | 1.3 | 38.2 | 2.09 | 1.28 |
| CdFSM-16 | 10.6 | 34 | 1.36 | 1.23 |
| CuFSM-16 | 3.0 | 24.7 | 1.66 | 1.49 |
| NiFSM-16 | 47.8 | 29.4 | 0.78 | 1.17 |
| | | | | |
| HY | 19.1 | | 1.06 | |

*Catalyst weight: 0.05 g; Sulfiding temp.: 200 ℃; Reaction temp.: 25 ℃*

***Table 2. Activity Enhancement of MeFSM-16 by Sulfiding with Hydrogen Sulfide in the Isomerization of cis-2-butene***

| | **Activity (%/g. min)** | | **trans/1 ratio** | |
|---|---|---|---|---|
| **Catalysts** | *Before Sulfiding* | *After Sulfiding* | *Before Sulfiding* | *After Sulfiding* |
| | | | | |
| FSM-16 | 4.2 | 5.9 | 0.97 | 0.75 |
| | | | | |
| AgFSM-16 | 2.1 | 30.5 | 1.42 | 2.24 |
| CdFSM-16 | 13.9 | 29.3 | 1.08 | 2.21 |
| CuFSM-16 | 3.4 | 25.9 | 0.98 | 1.75 |
| NiFSM-16 | 13.1 | 20.2 | 1.23 | 1.38 |

*Catalyst weight: 0.035 g; Sulfiding temp.: 200℃; Reaction temp.: 75℃*

***Table 3. Activity Enhancement of MeFSM-16 by Sulfiding with Hydrogen Sulfide in the Isomerization of Cyclopropane***

| | **Activity (%/g. min)** | |
|---|---|---|
| **Catalysts** | *Before Sulfiding* | *After Sulfiding* |
| | | |
| FSM-16 | 2.9 | 2.1 |
| | | |
| AgFSM-16 | 1.0 | 16.5 |
| CdFSM-16 | 3.6 | 13.5 |
| CuFSM-16 | 1.4 | 11.9 |
| NiFSM-16 | 2.5 | 6.2 |
| | | |
| HY | 37.4 | |

*Catalyst weight: 0.035 g; Sulfiding temp.: 200℃; Reaction temp.: 150℃*

### *Activity enhancement of MeFSM-16 in the isomerization of cyclopropane*

In order to study the nature of active sites generated over MeFSM-16 by the sulfiding with hydrogen sulfide, further study using cyclopropane isomerization, which is known to require strong Brönsted acid sites to proceed, was performed. The effect of sulfiding of MeFSM-16 in the isomerization of cyclopropane is shown in Table 3. Mesoporous silicate FSM-16 and MeFSM-16 showed low activity in the isomerization of cyclopropane before sulfiding. However, the sulfiding of MeFSM-16 with hydrogen sulfide resulted in remarkable activity enhancement in the isomerization. The enhanced activities were revealed in the order AgFSM-16>CdFSM-16>CuFSM-16>NiFSM-16. It was observed that the enhanced activities were as high as half of the activity of HY zeolite. The lower activities of sulfided MeFSM-16 than that of HY zeolite were assumed to be due to the smaller amount of active sites generated over sulfided MeFSM-16.

### *Infrared spectroscopic study on the sulfiding of MeFSM-16*

The enhancement mechanism of MeFSM-16 by sulfiding with hydrogen sulfide was studied by infrared spectroscopic measurement of pyridine adsorption. Figure 2 shows the infrared spectra of pyridine adsorbed on AgFSM-16 before and after sulfiding with hydrogen sulfide. Before sulfiding, a sharp absorption band of pyridine coordinated on silver ion was observed at 1,450 cm$^{-1}$. On the one hand, other absorption bands correlated to pyridine coordinated onto metal ion were observed at 1,606 cm$^{-1}$. On the other hand, a very small absorption band based on the Brönsted acid site was observed at around 1,550 cm$^{-1}$.

The sulfiding of AgFSM-16 resulted in the decrease of the coordinated pyridine absorption band at 1,450 cm$^{-1}$ and its disappearance at 1,606 cm$^{-1}$, which had been associated with the transformation of the metal ion into sulfide form. Furthermore, new absorption bands based on pyridinium ion (BPy) were observed at 1,548 cm$^{-1}$ for sulfided AgFSM-16. This phenomenon was accompanied by the appearance of the absorption band correlated to the pyridinium ion band at 1,639 cm$^{-1}$.

It was also noted that in the presence of gas-phase hydrogen sulfide, the IR absorption band for $\delta$(SH) vibration (~2,550 cm$^{-1}$) was observed on AgFSM-16 (spectrum not shown). This observation suggests that $H_2S$ is coordinatively adsorbed. Almost the same absorption bands as those of AgFSM-16 were observed on the other MeFSM-16. By the infrared spectroscopic measurements, it could be assumed that new Brönsted acid sites were generated on MeFSM-16 by the sulfiding with hydrogen sulfide.

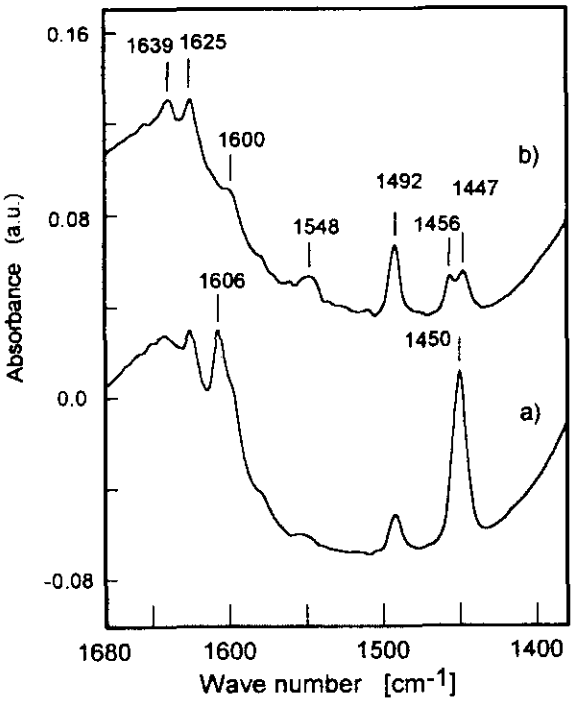

**Figure 2. Infrared Spectra of Pyridine Adsorbed on AgFSM-16 Before and After Sulfiding:**
*(a) AgFSM-16 evacuated at 500°C for 2 hours*
*(b) AgFSM-16 sulfided at 200°C*

### *The effect of sulfiding temperature of MeFSM-16*

The effects of the sulfiding temperature of AgFSM-16 in the *cis*-2-butene isomerization and in the infrared study are shown in figures 3 and 4, respectively. Both the activity and the selectivity of the product (*trans/1*) of *cis*-2-butene isomerization of AgFSM-16 were maximum at a sulfiding temperature of 200°C. The increase of sulfiding temperature was accompanied by the decrease of both of activity and selectivity of product.

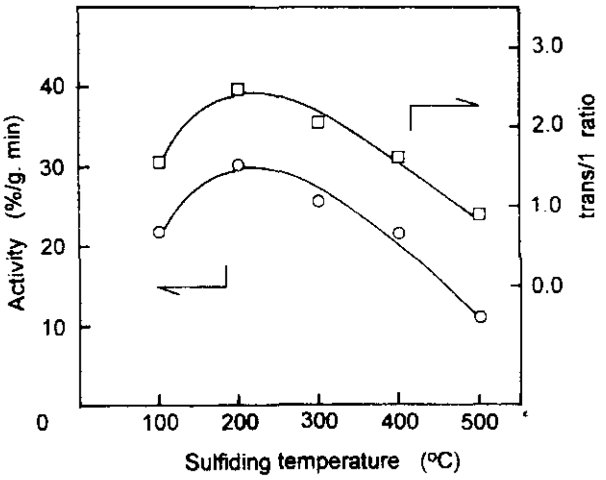

**Figure 3. Effect of Sulfiding Temperature of AgFSM-16 in cis-2-butene Isomerization**
*Catalyst weight: 0.035 g Reaction temp.: 75°C*

In the infrared study, it was revealed that at a sulfiding temperature of 200°C the coordinated pyridine absorption band was least intense. This indicated that the interaction of hydrogen sulfide with metal ion which led to the transformation to silver-sulfide species was maximum at this temperature. The increase of sulfiding temperature resulted in the increase of coordinated pyridine band, which indicated the decomposition of silver-sulfide species at higher sulfiding temperature. Moreover, the absorption band of pyridinium ion

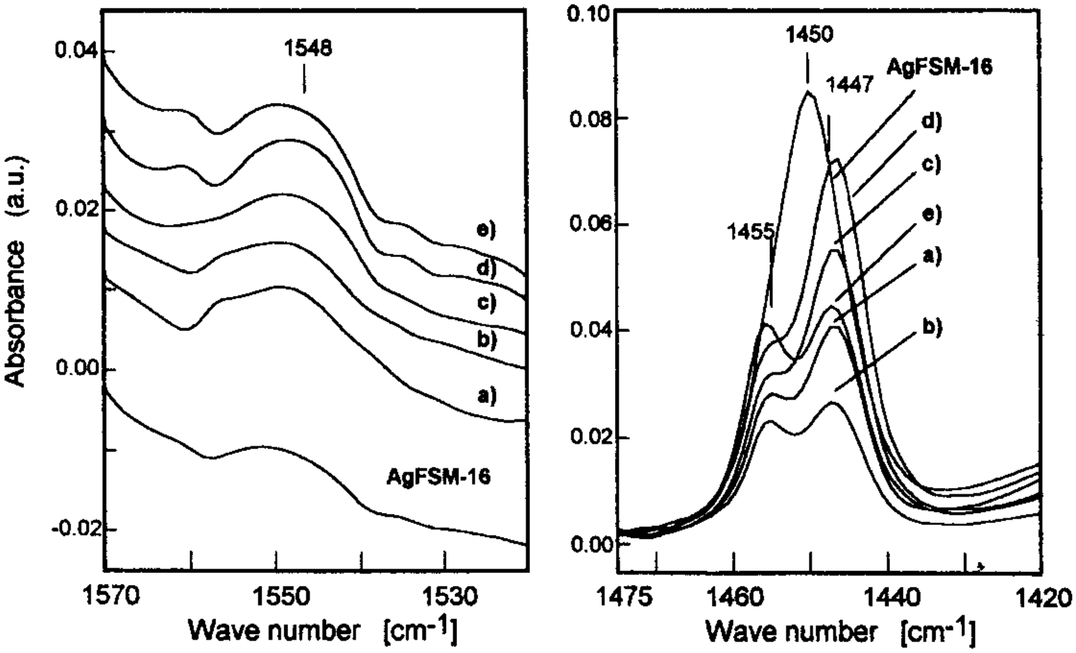

***Figure 4. Infrared Spectra of Pyridine Adsorbed on AgFSM-16 Sulfided at Various Temperatures: (a) 100°C, (b) 200°C, (c) 300°C, (d) 400°C, and (e) 500°C.***

was observed to slightly decrease and shift to a higher wave number at higher sulfiding temperature, indicating that the number of Brönsted acid sites decreased along with the increase in sulfiding temperature. From these results, it was revealed that the Brönsted acid sites formed on MeFSM-16 in the sulfiding with hydrogen sulfide were unstable and sensitive to high temperature.

### *Mechanism of activity enhancement of MeFSM-16 by sulfiding with hydrogen sulfide*

It was reported that silica gel, which was almost inactive for the acid-catalyzed reactions, could be activated by the ion-exchange of silanol group with some kind of metal ions and sulfiding with hydrogen sulfide (Sugioka, Sato, and Uchida 1994).

Thus, it had been proposed that the silanol group was regenerated by the sulfiding with hydrogen sulfide and that this regenerated silanol group was transformed into Brönsted acid sites by the electron attractive action of the metal sulfide species. Moreover, the present researchers proposed the mechanism of the formation of new Brönsted acid sites on the silver ion-exchange zeolites (MeZ) by sulfiding with hydrogen sulfide, in which silver sulfide species and acidic hydroxyl groups were formed on the MeZ surface by sulfiding (Sugioka and Andalaluna 1997, Andalaluna and Sugioka 2001).

At this point, it would be relevant to point out some observations made in the hydroxyl (OH) group region of the IR study. Typically, FSM-16 showed an intense peak assigned to an isolated silanol group at 3,744 cm$^{-1}$. On metal ion-exchanging to form AgFSM-16, the peak position slightly shifted to 3,743 cm$^{-1}$, and was found at 3,741 cm$^{-1}$ after sulfiding at 300°C. It was noted that although the shift was quite small, the change was enough to cause the activation to enhance the catalytic activity of FSM-16.

Based on the results obtained, the present researchers propose a possible mechanism of the activity enhancement of MeFSM-16 by sulfiding with hydrogen sulfide (see Figure 5).

In the sulfiding of MeFSM-16, hydrogen sulfide is coordinatively adsorbed on metal ions and then quickly dissociates leading to the regeneration of the surface silanol group and the formation of electronegatively charged metal sulfide species.

It was assumed that the regenerated surface silanol groups were strongly affected by the metal-

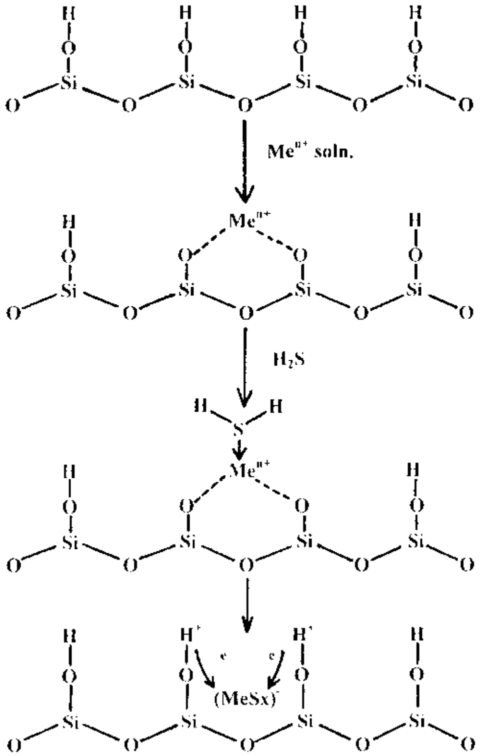

***Figure 5. A Possible Mechanism of the Activity Enhancement of MeFSM-16 by Sulfiding with Hydrogen Sulfide***

sulfide species and that the hydrogen atoms of the surface silanols were changed into protons by the electron attractive action of the metal sulfide species as well as the sulfate ion (SO$_4^{2-}$) in both SO$_4^{2-}$/Fe$_2$O$_3$ and SO$_4^{2-}$/ZrO$_2$ of solid superacid catalysts (Arata Nd).

## CONCLUSIONS

It was revealed that the catalytic activities of metal ion-exchange mesoporous silicate MeFSM-16 for some acid-catalyzed reactions were enhanced remarkably by sulfiding with hydrogen sulfide.

The optimum enhancement effect of hydrogen sulfide was observed at a sulfiding temperature of 200°C. By sulfiding MeFSM-16 with hydrogen sulfide, surface silanol groups were regenerated and transformed into Brönsted acid sites by the inductive effect of the metal sulfide cluster formed in the sulfiding which was assumed to be electronegatively charged.

## ACKNOWLEDGMENT

The authors wish to thank Dr. Yoshiaki Fukushima and Dr. Shinji Inagaki of Toyota Central R&D Labs., Japan, for kind provision of FSM-16 and valuable discussions.

## REFERENCES

Andalaluna, L., and Sugioka, M. (2001). "Activity enhancement of silver ion-exchanged sodium zeolites (AgNa-Zeolites) by sulfiding with hydrogen sulfide," *Proc. RSCE 2001,* CR17-1, Bandung, Indonesia.

Arata, K. (Year). *Advances in Catalysis, 37,* 165.

Barbier, J., Lamy-Pitara, E., Marecot, P., Boitiaux, J. P. , Cosyns, J., and Verna, F. (1990). *Advances in Catalysis, 37,* 279.

Bartholomew, H., Agrawal, P. K., and Katzer, J. R. (1982). *Advances in Catalysis, 31,* 135.

Beck, J. S., Vartulli, J. C., Roth, W. J., Leonowicz, M. E., Kresge, C. T., Smith, K. D., Chu, T. W., Olson, D. H., Sheppard, E. W., McCulleni, S. B., Higgins, J. B., and Schlenker, J. L. (1992). "A new family of mesoporous molecular sieves prepared with liquid crystal templates," *J. Am. Chem. Soc., 114,* 10834.

Campbel, I., Saricilar, S., Hoarse, I. C., and Bhargava, S. K. (1992). *Applied Catalysis A, 82,* 1, 13.

Deng, Y., Nevell, T. G., Ewen, R. J., and Honeybourne, L. (1993). *Applied Catalysis A, 101,* 1, 51.

Inagaki, S., Fukushina, Y., and Kuroda, K. (1993). "Synthesis of highly ordered mesoporous materials from a layered polysilicate," *J. Chem. Soc. Commun.*, 680.

Paal, Z., Matusek, K., and Muhler, M. (1997). *Applied Catalysis A, 149,* 1, 113.

Rodriguez, J. C., Santamaria, J., and Monzon, A. (1997). *Applied Catalysis A, 165,* 1-2, 145.

Sugioka, M., and Andalaluna, L. (1997). "Activity enhancement of H-zeolites by Ag ion-exchange and sulfiding with hydrogen sulfide," *Stud. Surf. Sci. Catal., 105,* 1995.

Sugioka, M., Sato, N., and Uchida, D. (1994). "Activity enhancement of metal in-exchanged silica by sulfiding with hydrogen sulfide," *Stud. Surf. Sci. Catal.*, *90*, 343.

Ziolek, M., and Sugioka, M. (2000). "Adsorption and dehydrosulfurization of aliphatic thiols on zeolites," *Res. Chem. Intermed., 26,* 4, 385.