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Noble metals supported on mesoporous silicate FSM-16 as new hydrodesulfurization catalyst

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Abstract

The Pt supported on mesoporous silicate FSM-16 showed high and stable catalytic activity for the hydrodesulfurization of thiophene at 350°C and this activity was higher than that of commercial $CoMo/Al_2O_3$ catalysts. The acid sites of FSM-16 and the spillover hydrogen formed on Pt particle in Pt/FSM-16 catalyst play an important role for the hydrodesulfurization of thiophene. © 1997 Elsevier Science B.V.

Keywords: Hydrodesulfurization; Mesoporous silicate; Pt/FSM-16 catalyst

1. Introduction

$CoMo/Al_2O_3$ catalysts have been widely used in the hydrodesulfurization process of petroleum. However, recently, the development of highly active hydrodesulfurization catalysts, which are better than commercial $CoMo/Al_2O_3$ hydrodesulfurization catalysts, has been claimed in the petroleum industry to produce lower sulfur content fuels. Such metal–zeolite catalysts have high possibilities as a new hydrodesulfurization catalyst for petroleum [1–3]. We have investigated the hydrodesulfurization of thiophene over transition metal Y zeolites (MeY) [4–7] and noble metals supported on USY and HZSM-5 zeolites [8–10]. These catalysts showed high catalytic activities for the hydrodesulfurization of thiophene. However, the pore diameter of these zeolites is too small for treating large molecular organic sulfur compounds contained in vacuum gas oil and heavy oil. Therefore, the development of new catalysts based on large pore zeolites to treat large molecular organic sulfur compounds has been desired.

Recently, mesoporous silicate materials such as MCM-41 [11] and FSM-16 (folded-sheet mesoporous material) [12,13] with large pore diameter have been developed. These new mesoporous silicate materials are attracting wide attention as catalysts and catalyst supports.

In the present work, we examined the catalytic activities of various noble metals supported on mesoporous silicate FSM-16 for the hydrodesulfurization of thiophene in order to develop highly active mesoporous zeolite-based hydrodesulfurization catalysts.

2. Experimental

Hydrodesulfurization of thiophene over noble metal/FSM-16 catalysts was carried out at 350°C

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under 1 atm by using a conventional fixed bed flow reactor. Thiophene was introduced into the reactor by passing hydrogen through a thiophene trap cooled at 0°C. The reaction products were analyzed by a gas-chromatograph.

FSM-16-supported noble metal catalysts were prepared by an impregnation method using noble metal chloride aqueous solutions; the amount of metal loading was 5 wt%. All catalysts were calcined at 500°C for 4 h in air and were reduced at 450°C for 1 h prior to the reaction. Presulfiding treatment of the catalysts was performed by 5% H_2S–H_2 mixture at 400°C for 1 h. XRD analysis of the catalysts was carried out by using Rigaku diffractometer with Cu Kα radiation.

We used mesoporous silicate FSM-16 (surface area 970 m^2/g, channel diameter 27 Å) which was provided by Toyota Central R&D Labs., Japan.

3. Results and discussion

3.1. *Catalytic activities of noble metals supported on FSM-16*

The catalytic activities of transition metals supported on FSM-16 were examined at 350°C for the hydrodesulfurization of thiophene. It was found that the catalytic activities of transition metals/FSM-16 such as Ni/FSM-16, Co/FSM-16, Fe/FSM-16, W/FSM-16, Mo/FSM-16 (5 wt% loading), 15 wt% MoO_3/FSM-16, 5 wt% NiO–15 wt% MoO_3/FSM-16 and 5 wt% CoO–15 wt% MoO_3/FSM-16 showed low activity and their activity values were lower than that of commercial CoMo/Al_2O_3 catalyst. Then we examined the catalytic activities of noble metals supported on FSM-16. Fig. 1 shows the hydrodesulfurization of thiophene over various noble metal/FSM-16 catalysts at 350°C. It was found that the catalytic activities of noble metal/FSM-16 varied remarkably with the kind of noble metals. The order of the activities of these catalysts for the hydrodesulfurization of thiophene after 2 h reaction was as follows: Pt/FSM-16>Pd/FSM-16>Rh/FSM-16≫Ru/FSM-16, Ir/FSM-16, Au/FSM-16.

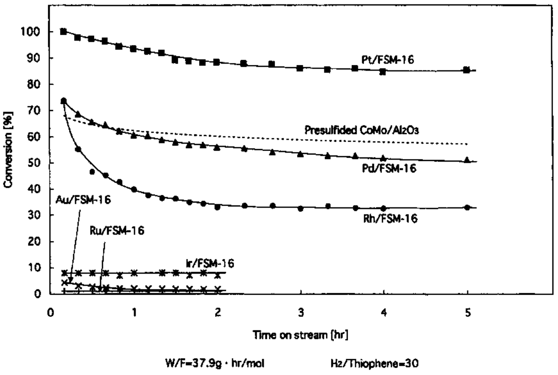


Fig. 1. Hydrodesulfurization of thiophene over noble metal/FSM-16 catalysts at 350°C.

The initial activities of Pt/FSM-16, Pd/FSM-16 and Rh/FSM-16 were higher than that of commercial CoMo/Al_2O_3 catalyst (dotted line). However, the activities of these catalysts decreased with the reaction time and Pd/FSM-16 and Rh/FSM-16 catalysts showed lower steady state activity than CoMo/Al_2O_3 catalyst. Among noble metal/FSM-16 catalysts, Pt/FSM-16 showed the highest activity for the hydrodesulfurization of thiophene and the activity of Pt/FSM-16 catalyst was higher than that of CoMo/Al_2O_3 catalyst. Pt/FSM-16 catalyst also showed higher activity than that of Pt supported on silica gel (SiO_2) in the hydrodesulfurization of thiophene. The high and stable activity of Pt/FSM-16 catalyst in the hydrodesulfurization of thiophene was kept even after it had reacted for 20 h.

Table 1 summarizes the activities of various catalysts used in this work.

As Pt/FSM-16 showed the highest catalytic activity in the hydrodesulfurization of thiophene at 350°C, we studied in detail the catalyst performance and the reaction mechanism in the hydrodesulfurization of thiophene over Pt/FSM-16 catalyst. It was found that the catalytic activity of Pt/FSM-16 was decreased slightly by the presulfiding with H_2S–H_2 mixture as shown in Table 1. Thus, we used the Pt/FSM-16 catalyst without presulfiding.

In the hydrodesulfurization of thiophene over Pt/FSM-16 catalyst, main reaction products were C_4 hydrocarbons (butane 88%, butenes 12%); trace amount of C_1–C_3 hydrocarbons was also formed. These results indicate that Pt/FSM-16 catalyst has high hydrogenating ability for unsaturated C_4 hydrocarbons and low hydrocracking activity for hydrocarbons in the presence of hydrogen sulfide.

Table 1
Catalytic activities of various metals supported on FSM-16 in the hydrodesulfurization of thiophene at 350°C (*W*/*F*=37.9 g h/mol, H_2/Thiophene=30)

Catalyst	Conversion (%)[a]	
	Reduced Catalyst[b]	Sulfided Catalyst[c]
5 wt% Ni/FSM-16	2	Trace
5 wt% Co/FSM-16	2	9
5 wt% Fe/FSM-16	Trace	Trace
5 wt% W/FSM-16	Trace	1
5 wt% Mo/FSM-16	15	19
15 wt% MoO_3/FSM-16	39	22
5 wt% NiO–15 wt% MoO_3/FSM-16	22	35
5 wt% CoO–15 wt% MoO_3/FSM-16	30	32
5 wt% Ru/FSM-16	1	Trace
5 wt% Au/FSM-16	1	Trace
5 wt% Ir/FSM-16	9	9
5 wt% Rh/FSM-16	32	31
5 wt% Pd/FSM-16	56	62
5 wt% Pt/FSM-16	90	82
5 wt% Pt/SiO_2 (JRC-SIO-1)	51	—
Commercial CoMo/Al_2O_3	—	60

[a] Reaction after 2 h.
[b] Catalysts were reduced at 450°C for 1 h.
[c] Catalysts were sulfided at 400°C for 1 h after reduced at 450°C.

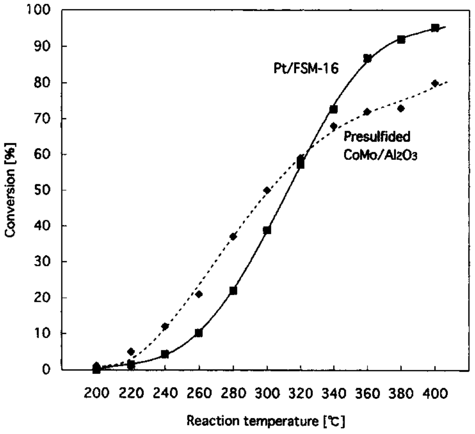


Fig. 2. Comparison of catalytic activity of Pt/FSM-16 with that of commercial CoMo/Al_2O_3 catalyst in the hydrodesulfurization of thiophene.

Fig. 2 shows the comparison of the activity of FSM-16 catalyst with CoMo/Al_2O_3 catalyst. It was found that the catalytic activity of Pt/FSM-16 is higher than that of CoMo/Al_2O_3 catalyst for the reaction temperature above 320°C. The low activity of Pt/FSM-16 catalyst below 320°C might be attributed to the significant resistance of reactant diffusion into the channel of FSM-16. That is to say, the comparable size of Pt particles to the pore diameter of FSM-16 would be formed in the channel of FSM-16 after the reduction of Pt/FSM-16 by hydrogen [14] and Pt particles formed inhibit the diffusion of thiophene into the channel of FSM-16 at the reaction temperature below 320°C.

3.2. *Improvement of catalytic activity of Pt/FSM-16*

Results showed that 5 wt% Pt/FSM-16 calcined at 500°C had the highest catalytic activity for the hydrodesulfurization of thiophene. However, it is uncertain whether these preparation conditions are optimal or not. Therefore, we examined the effect of preparation conditions on the catalytic activity of Pt/FSM-16 in order to obtain the optimal activity of Pt/FSM-16 catalyst for the hydrodesulfurization of thiophene.

Fig. 3 shows the effect of Pt loading on the activity of Pt/FSM-16 catalyst. The catalytic activity increased with the increase of Pt loadings up to about 3.5 wt% and the activity became constant for loading above 3.5 wt%. Thus, it can be concluded that 5 wt% loading of Pt on Pt/FSM-16 is enough for obtaining the maximum activity.

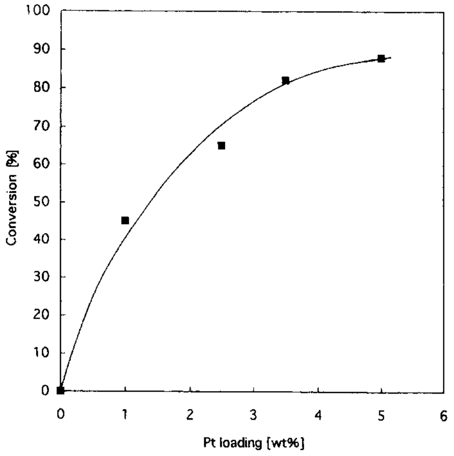


Fig. 3. Relationship between Pt loading and the catalytic activity of Pt/FSM-16 in the hydrodesulfurization of thiophene at 350°C.

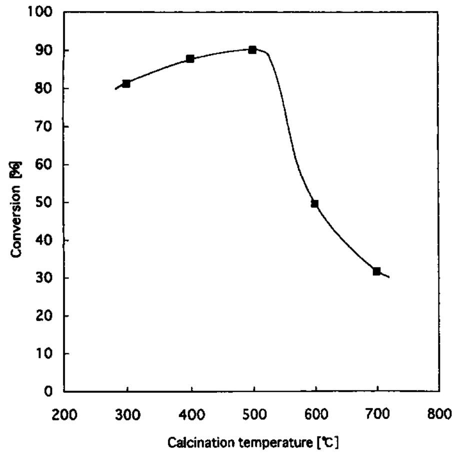


Fig. 4. Effect of calcination temperature of Pt/FSM-16 on the catalytic activity in the hydrodesulfurization of thiophene at 350°C.

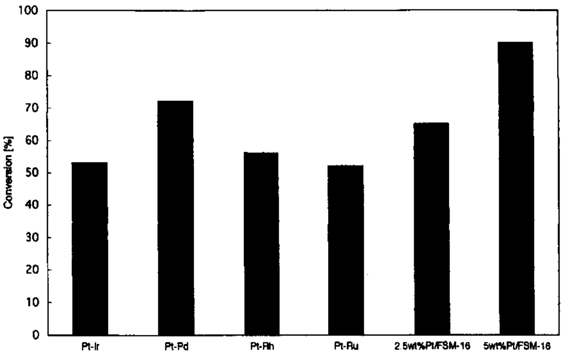


Fig. 5. Catalytic activity of Pt (2.5 wt%) combined with other noble metals (2.5 wt%) supported on FSM-16 in the hydrodesulfurization at 350°C.

Fig. 4 shows the effect of calcination temperature on the catalytic activity of Pt/FSM-16. The catalytic activity of Pt/FSM-16 increased slightly up to the calcination temperature at 500°C and it decreased above 500°C. It was found that the calcination of the catalyst at 500°C is the optimal condition.

In the previous paper [10], we showed that the steady state activity of Pt/USY catalyst in the hydrodesulfurization of thiophene was remarkably improved by the combination with other noble metals. Combination of Pt with Pd was the most effective. Thus, we tried to enhance the steady state activity of Pt/FSM-16 by combining Pt (2.5 wt%) with other noble metals (2.5 wt%). It was found that the steady state activity of Pt/FSM-16 was not improved by the combination of Pt with other noble metals and the activity of 2.5 wt% Pt/FSM-16 was decreased by the addition of 2.5 wt% other noble metals except Pd as shown in Fig. 5.

3.3. Properties of Pt/FSM-16 catalyst

Pt/FSM-16 catalyst showed high and stable activity for the hydrodesulfurization of thiophene among the noble metals supported on FSM-16. We also studied in more detail concerning the catalytic properties of Pt/FSM-16 in the hydrodesulfurization of thiophene.

The effect of introduction of hydrogen sulfide on the catalytic activity of Pt/FSM-16 was examined in order to learn more about the origin of high and stable activity of Pt/FSM-16 catalyst. The introduction of hydrogen sulfide (3 ml/min) was performed using a microfeeder with a glass syringe; the concentration of hydrogen sulfide in the hydrogen stream was ca. 5 vol%. The catalytic activity of Pt/FSM-16 was remarkably decreased by the introduction of hydrogen sulfide in the course of hydrodesulfurization reaction. However, the decreased activity was almost restored after cutting off the introduction of hydrogen sulfide as shown in Fig. 6. This shows that hydrogen sulfide is reversibly adsorbed on Pt/FSM-16.

Furthermore, the activity of Pt/FSM-16 catalysts was slightly decreased after the presulfiding with 5% H_2S–H_2 mixture at 400°C as shown in Fig. 6. These results indicate that the Pt/FSM-16 catalyst has high

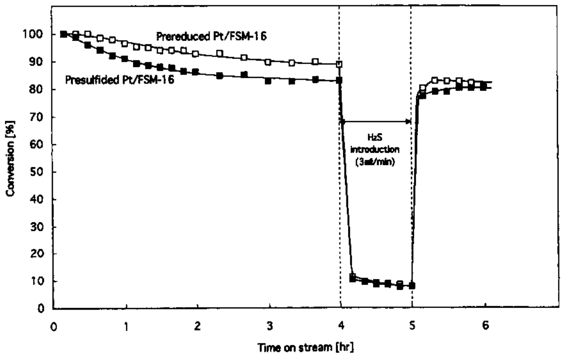


Fig. 6. Reversible inhibition of hydrogen sulfide in the hydrodesulfurization of thiophene at 350°C.

sulfur tolerant properties for the hydrodesulfurization of thiophene as well as Pt/HZSM-5 catalyst described in the previous paper [9].

On the other hand, as mentioned in the previous papers [7–9], the acid site, especially Brønsted acid site, of H-zeolites (HY, USY, HZSM-5) as support in noble metal/H-zeolite catalysts plays an important role for the hydrodesulfurization of thiophene. In this study, we examined the effect of introduction of ammonia on the catalytic activity of Pt/FSM-16 in the hydrodesulfurization of thiophene in order to clarify the role of acidic properties of Pt/FSM-16 in the hydrodesulfurization of thiophene. The introduction of ammonia (3 ml/min) was carried out using microfeeder with glass syringe as well as the introduction of hydrogen sulfide. It was revealed that the catalytic activity of Pt/FSM-16 was decreased by the introduction of ammonia (ca. 5 vol%) in the course of hydrodesulfurization reaction and decreased activity was completely regenerated after cutting off the introduction of ammonia as shown in Fig. 7. The catalytic activity of Pt/FSM-16 was remarkably decreased by the addition of small amount (1 wt%) of sodium using sodium hydroxide aqueous solution to Pt/FSM-16 catalyst. Furthermore, FSM-16 also showed the catalytic activities for the isomerization of 1-butene (25°C) and cyclopropane (150°C) and the dehydration of 2-propanol (250°C), which are typical acid-catalyzed reactions. These results indicate that the acid sites exist on Pt/FSM-16 catalysts and the acid sites play an important role for the hydrodesulfurization of thiophene over Pt/FSM-16 catalyst.

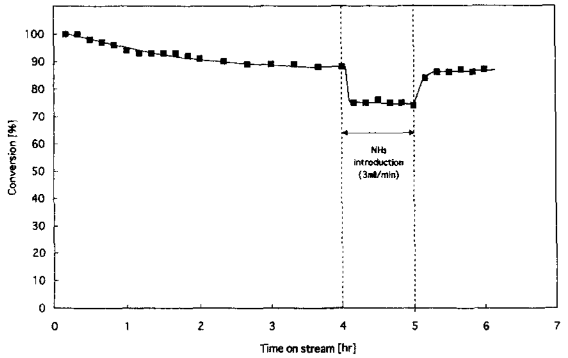


Fig. 7. Effect of introduction of ammonia on the catalytic activity of Pt/FSM-16 in the hydrodesulfurizatrion of thiophene at 350°C.

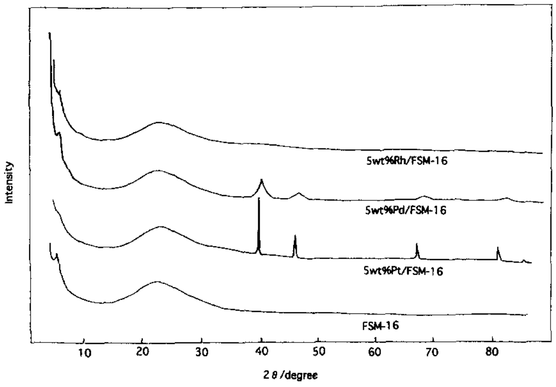


Fig. 8. XRD patterns for various noble metal/FSM-16 catalysts before reduction.

3.4. *XRD analysis of Pt/FSM-16 catalyst*

Fig. 8 shows the XRD patterns of FSM-16 and noble metal/FSM-16 before reduction. Almost the same XRD patterns as that of FSM-16 were obtained before and after loading of noble metals. This indicates that the structure of FSM-16 was maintained after loading of noble metals on FSM-16. No peaks of Rh were observed on Rh/FSM-16 catalyst. On the other hand, broad and sharp peaks of Pd and Pt were observed in the XRD analysis of Pd/FSM-16 and Pt/FSM-16 catalysts. The same XRD pattern of Pt/FSM-16 was observed for Pt/FSM-16 after reduction at 450°C. These results infer that Rh is loaded on FSM-16 with high dispersion but Pd and Pt are loaded on FSM-16 with relatively large particle size. The order of the dispersion of noble metals on FSM-16 is assumed to be Rh/FSM-16>Pd/FSM-16>Pt/FSM-16. This order is reverse to that of the steady state activity of noble metal/FSM-16 catalysts in the hydrodesulfurization of thiophene. It is interesting that the lower dispersion of noble metals on FSM-16, especially Pt/FSM-16, showed higher catalytic activity for the hydrodesulfurization of thiophene.

3.5. *Mechanism of hydrodesulfurization of thiophene on Pt/FSM-16 catalyst*

Pt/FSM-16 showed higher catalytic activity than commercial $CoMo/Al_2O_3$ catalyst in the hydrodesulfurization of thiophene. We also studied the mechanism of hydrodesulfurization of thiophene over Pt/FSM-16 catalyst. As mentioned above, the acid site of FSM-16 in Pt/FSM-16 catalyst plays an important role for the hydrodesulfurization of thiophene. That is, it is assumed that the acid site of FSM-16 in the Pt/FSM-16 catalyst acts as active sites for the activation of thiophene, whereas Pt particles on FSM-16 act as active sites for the activation of hydrogen in the hydrodesulfurization of thiophene. Furthermore, we supposed the existence of spillover hydrogen in the hydrodesulfurization of thiophene over Pt/FSM-16 catalyst. Hence, we tried to confirm the existence of spillover hydrogen in the hydrodesulfurization of thiophene. The catalytic activity of Pt/SiO_2 (quartz) mixed mechanically with FSM-16 was examined. It was found that the activity of mixed catalyst obtained experimentally was higher than that of the calculated one (A+B) as shown in Fig. 9.

This suggests that there exists spillover hydrogen on Pt/FSM-16 in the hydrodesulfurization of thiophene. Therefore, we propose a possible mechanism for the hydrodesulfurization of thiophene over Pt/FSM-16 catalyst as shown in Scheme 1. In the proposed mechanism, thiophene is activated on the acid site of FSM-16 and hydrogen is activated on Pt to form spillover hydrogen. The spillover hydrogen formed on Pt particle attacks the activated thiophene formed on the acid site on FSM-16.

On the basis of the proposed mechanism, it would be possible to develop much more highly active mesoporous zeolite-based hydrodesulfurization catalyst for petroleum feedstocks.

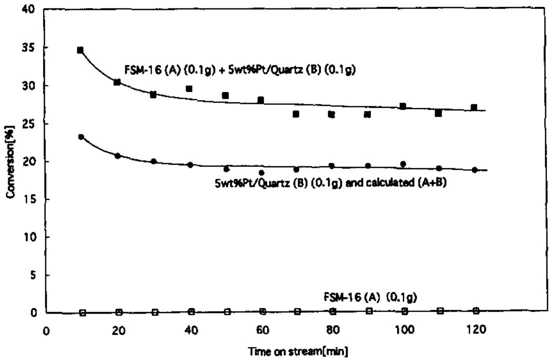
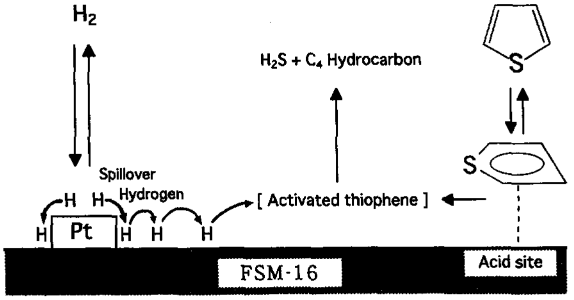


Fig. 9. Hydrodesulfurization of thiophene over FSM-16 (A), Pt/quartz (B), and mechanically mixed (FSM-16(A)+Pt/quartz (B)) at 350°C.



Scheme 1. The possible mechanism of thiophene hydrodesulfurization over Pt/FSM-16 catalyst.

4. Conclusion

It was found that the Pt/FSM-16 catalyst showed high and stable activity for the hydrodesulfurization of thiophene. Therefore, it is concluded that Pt/FSM-16 might be a promising new hydrodesulfurization catalyst for the petroleum feedstocks.

Acknowledgements

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References

[1] S. Gobolos, M. Breysse, M. Cattenot, T. Decamp, M. Lacroix, J.L. Portefaix, M.L. Vrinat, Stud. Surf. Sci. Catal. 50 (1989) 243.
[2] R. Cid, J.L.G. Fierro, A.L. Agudo, Zeolites 10 (1991) 95.
[3] M. Laniecki, W. Zmierczak, Zeolites 11 (1991) 95.
[4] M. Sugioka, J. Japan Petrol. Inst. 33 (1990) 280.
[5] M. Sugioka, Y. Takase, K. Takahashi, Proceedings of JECAT'91, 1991, p. 224.
[6] M. Sugioka, Zeoraito (Zeolite) 10 (1993) 121.

[7] M. Sugioka, Erdol and Kohle, Erdgas Petrochemie 48 (1995) 128.

[8] M. Sugioka, C. Tochiyama, F. Sado, N. Maesaki, Stud. Surf. Sci. Catal. 100 (1996) 441.

[9] M. Sugioka, C. Tochiyama, Y. Matsumoto, F. Sado, Stud. Surf. Sci. Catal. 94 (1995) 544.

[10] M. Sugioka, F. Sado, Y. Matsumoto, N. Maesaki, Catal. Today 29 (1996) 255.

[11] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kreage, K.D. Smitt, T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCulleni, J.B. Higgions, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.

[12] T. Yanagisawa, T. Shimizu, K. Kuroda, C. Kato, Bull. Chem. Soc. Jpn. 62 (1990) 763.

[13] S. Inagaki, Y. Fukushima, K. Kuroda, J. Chem. Soc., Chem. Comm. (1993) 680.

[14] S. Inagaki, K. Fukumoto, Y. Fukushima, Shokubai (Catalyst) 37 (1995) 191.