Application of mesoporous crystalline silicates to a good catalyst support for gasoline synthesis

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Rapid synthesis of branched alkanes in the gasoline range from propene was conducted using a series reactor. Alkenes in the gasoline range produced on the MFI type H-Fe-silicate packed in the first-stage reactor were successively hydrogenated on various Pt-modified catalysts packed in the second-stage reactor. Even at high space velocity, the selectivity to branched alkanes including cycloalkanes in the gasoline range was greatly increased by adopting the Pt-modified mesoporous silicate, compared with that of Pt-modified MFI type non-metal silicate and/or silica gel having a distribution of pores in the mesoporous range. The mesoporous silicate was synthesized from kanemite by repeated ion-exchange treatment with an aqueous solution of hexadecyltrimethylammonium chloride.

Keywords: mesoporous crystalline silicate; MFI type H-Fe-silicate; Pt modification; propene conversion; gasoline synthesis

1. Introduction

Recently, Beck et al. [1,2] synthesized a new family of mesoporous materials (MCM-41) from aluminosilicate gels with a surfactant. It has regular arrays of a uniform channel size ranging from 20 to 100 Å according to the kind of surfactant. Independently, Inagaki et al. [3,4] synthesized similar mesoporous materials having a channel size of ca. 40 Å by ion-exchange treatment of kanemite with an aqueous solution of hexadecyltrimethylammonium chloride. These new mesoporous materials are expected to be useful for the reactions of high-molecular hydrocarbons because of higher diffusivities owing to their wide pore diameters.

On the other hand, we have already found that H-Fe-silicate [5–7] and H-Co-silicate [5] having MFI type framework could convert light alkenes completely into a high octane-number (research octane number of 95) gasoline fraction with an extraordinarily high space-time yield. For example, a 95.6% propene feed was converted under a gaseous hourly space velocity (GHSV) of 4500 h^{-1} and at 300°C

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to the liquid hydrocarbon product with a space-time yield as high as 8.09 kg/ℓ h. Although the product mainly consisted of iso-mono-internal alkenes and a smaller fraction of aromatics, the alkene-rich product has a potential to act as a precursor of photo-oxidants. The alkenes in the gasoline range produced on the MFI type H-Fe-silicate under GHSV of 1000 h^{-1} could be successively hydrogenated into branched alkanes and/or cycloalkanes on the Pt-modified MFI type non-metal silicate packed in the second-stage reactor connected in series [8]. Under a much higher space velocity, however, the fraction of alkenes in the final product increased because it was difficult for the gasoline-range hydrocarbons to diffuse in the MFI type silicate.

In this study, rapid propene conversion on the MFI type H-Fe-silicate was conducted under GHSV of 5000 h^{-1}, and then the product was successively and rapidly hydrogenated into branched alkanes in the gasoline range on Pt-modified catalysts. In particular, to enhance the diffusivity of gasoline-range hydrocarbons, the mesoporous silicate modified with platinum was provided to the catalyst of the second-stage reactor and the result was compared with that of Pt-modified MFI type non-metal silicate and/or silica gel having no acidity and a distribution of pores in the mesoporous range.

2. Experimental

2.1. CATALYST PREPARATION

The MFI type Fe-silicate with a silicon-to-iron atomic ratio of 100 and the non-metal silicate were prepared by the rapid crystallization method [9,10]. For the Fe-silicate synthesis, the aluminum sulfate used for ZSM-5 synthesis was replaced by ferric nitrate at the stage of gel formation. For the non-metal silicate synthesis, no metal ingredient was introduced except the contaminant in the water glass which was used as the silicon source. The synthesized crystals were washed with distilled water by using a centrifuge until no chloride ions were detected in the washing water. The crystals were then dried, and treated in air stream at 540°C for 3.5 h to burn off the organic template and to calcine. The calcined crystals were treated twice with 1 M ammonium nitrate solution at 80°C for 1 h. The crystals were washed again with distilled water and dried, again followed by calcination in an air stream at 540°C for 3.5 h.

The mesoporous silicates were prepared from kanemites according to ref. [4]. A sodium silicate solution (37% SiO_2, $SiO_2/Na_2O = 2$) was used as starting material for kanemite preparation. The sodium silicate solution was dried and calcined at 700°C for 6 h to crystallize to δ-$Na_2Si_2O_5$. The δ-$Na_2Si_2O_5$ crystals were suspended in distilled water (5 or 10 times the crystals by weight) for 3 h with stirring. The kanemite was obtained by filtration of the suspension and drying at room temperature. The formation of kanemite was confirmed by means of X-ray powder diffraction. The ion-exchange treatment of kanemite was carried out with an aqueous solution of hexadecyltrimethylammonium chloride (20 times the kanemite in weight, 0.1 mol/dm) and the mixture was heated at 70°C for 1 h and/or 3 h with stirring. The solid product was centrifuged from the mixture and then the ion-exchange treatment was repeated. The resultant product was washed with distilled water, dried at room temperature, and then calcined in air at 540°C for 6 h to remove the surfactant.

Non-acidic silica gel was prepared by repeatedly washing Kieselgel 60 (Merck) with aqua regia and distilled water.

1.0 wt% and/or 0.5 wt% Pt-modified MFI type non-metal silicate, mesoporous silicate and silica gel were prepared by impregnation with an aqueous solution of $Pt(NH_3)_3Cl_2$. The platinum ammonium complex was then thermally decomposed in an air stream of 100 ml/min by heating it up to 350°C at a constant heating rate of 3°C/min, and holding it at that temperature for 10 min. The thermally decomposed complex was then treated in a stream of 10% H_2–90% N_2 (50 ml/min) by heating it up to 400°C at a constant heating rate of 3°C/min and holding it at that temperature for 30 min.

The calcined crystals were made into tablets and crushed to 10–20 mesh to provide the catalysts for the reaction.

2.2. CATALYST CHARACTERIZATION

Powder X-ray diffraction (XRD) analysis was carried out on a Shimadzu XD-D1 with nickel filtered Cu Kα radiation at a scanning speed of 1°/min. Pore size distribution curves were calculated from the nitrogen adsorption isotherms measured on a Shimadzu Micromeritics AccuSorb 2100E at 77.4 K with the constant volume method.

2.3. REACTION METHOD

A two-stage series reactor was used in the propene-conversion reaction under atmospheric pressure. Two 1.0 g (ca. 1.5 ml) portions of the catalysts (MFI type H-Fe-silicate in the first-stage reactor and Pt-modified catalysts in the second-stage reactor) were packed in quartz tubular reactors with 8 mm inner diameter, and then they were pretreated with a nitrogen flow at 500°C for 30 min to standardize the catalyst surface state by removal of the pre-adsorbed water. Reaction temperature of the first-stage reactor was 290°C, which was the most appropriate temperature for the oligomerization of light alkenes, while that of the second-stage reactor was 100–250°C. Non-diluted propene was introduced with GHSV of 5000 h^{-1}. A number of moles of hydrogen equal to the number of moles of propene fed was added to the second-stage reactor. The products were analyzed by using three gas chromatographs. Columns of MS-5A, VZ-10 and Silicon-OV-101 were used to analyze hydrogen and the whole range of hydrocarbons produced.

3. Results and discussion

3.1. SYNTHESIS OF MESOPOROUS SILICATE

Figs. 1 and 2 show the X-ray diffraction patterns of various as-synthesized mesoporous silicates. For the synthesis of the mesoporous silicate shown in fig. 1, the kanemite was prepared by using the same amount of water as in ref. [4] (10 times of the δ-$Na_2Si_2O_5$ crystals in weight). ML1 (fig. 1a) was produced from the kanemite by ion-exchange with 0.1 M hexadecyltrimethylammonium chloride solution at 70°C for 3 h, and ML2 (fig. 1b) was produced from the air-dried ML1 by repeated ion-exchange treatment. Whereas ML1 showed only a small peak at $d = 38.7$ Å, ML2 showed four peaks which could be assigned to a hexagonal lattice with $d_{100} = 39.8$ Å. Since the sodium ion which remained in ML1 might be exchanged with hexadecyltrimethylammonium ions, a higher crystallinity of ML2 was obtained. However, the BET surface area of ML2 (930 m^2/g) was still smaller than that (1100 m^2/g) in ref. [4], and it was not improved by further ion-exchange treatment.

Beneke et al. [11] reported that about 70% of the sodium ions of the idealized formula of kanemite ($NaHSi_2O_5 \cdot 3H_2O$) can be removed by washing with water without destruction of the structure. Since the amount of sodium ions in the kanemite was also considered as an important factor for the synthesis of mesoporous silicate, the effect of an amount of water for the kanemite preparation from δ-$Na_2Si_2O_5$ on the crystallinity of mesoporous silicate was investigated. For the synthesis of the

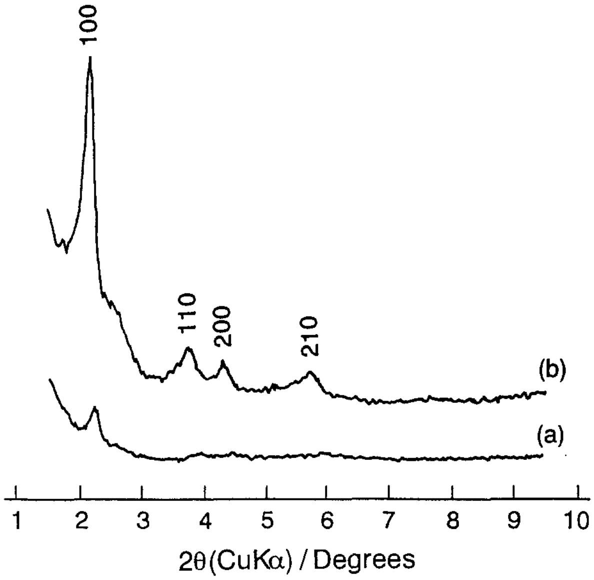

Fig. 1. X-ray diffraction patterns for mesoporous silicates. (a) ML1 synthesized by ion-exchange treatment at 70°C for 3 h, and (b) ML2 synthesized by repeated ion-exchange treatment of air-dried ML1.

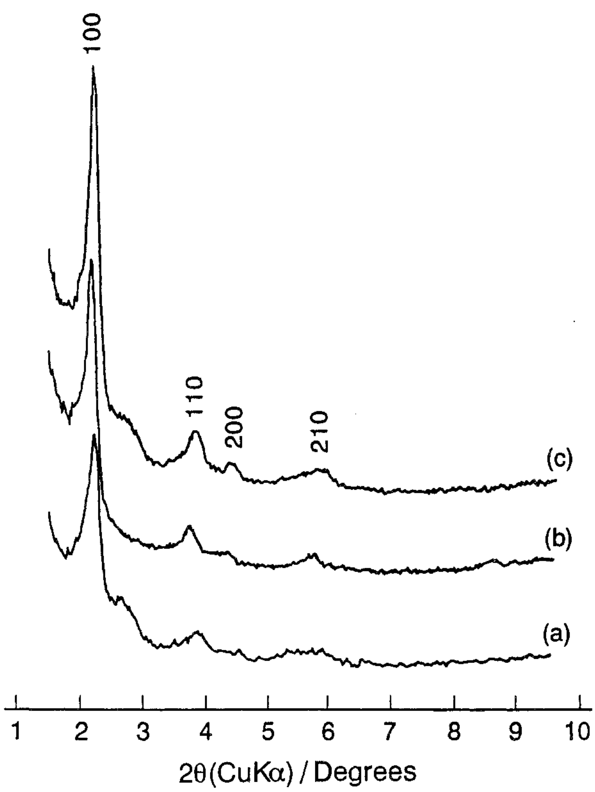

Fig. 2. X-ray diffraction patterns for mesoporous silicates synthesized by ion-exchange treatment in three steps. (a) MS1 after first ion-exchange treatment at 70°C for 1 h, (b) MS2 after second ion-exchange treatment, and (c) MS3 after third ion-exchange treatment.

mesoporous silicate shown in fig. 2, a smaller amount of water (5 times of the δ-$Na_2Si_2O_5$ crystals in weight) was used for the kanemite preparation. The ion-exchange treatment of the kanemite was carried out for 1 h and repeated three times. The MS1 (fig. 2a) produced after the first ion-exchange treatment showed stronger intensities of X-ray diffraction peaks owing to the hexagonal lattice than ML1 (fig. 1a), although the time of the ion-exchange treatment of the MS1 was shorter than that of the ML1. This result indicates that the crystallinity of mesoporous silicate could be influenced by the amount of exchangeable sodium ions in the kanemite. The final product (MS3) after the third ion-exchange treatment showed the highest crystallinity and BET surface area of 1200 m^2/g.

3.2. RAPID HYDROGENATION REACTION OF ALKENES IN GASOLINE RANGE HYDROCARBONS

The iso-mono-internal alkenes produced from propene on the H-Fe-silicate were successively hydrogenated on the Pt-modified MFI type non-metal silicate and mesoporous silicate (MS3), as shown in figs. 3 and 4, respectively.

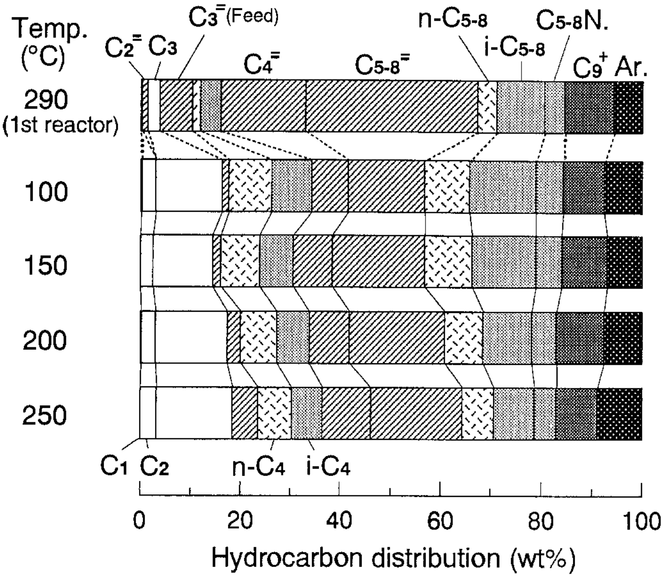

Fig. 3. Rapid gasoline synthesis from propene on the MFI type H-Fe-silicate (first stage) and on the 1.0 wt% Pt-modified MFI type non-metal silicate (second stage). Reaction conditions: GHSV of propene fed in the first stage reactor, 5000 h^{-1}; the number of moles of hydrogen added into the second-stage reactor was equal to the number of moles of propene fed.

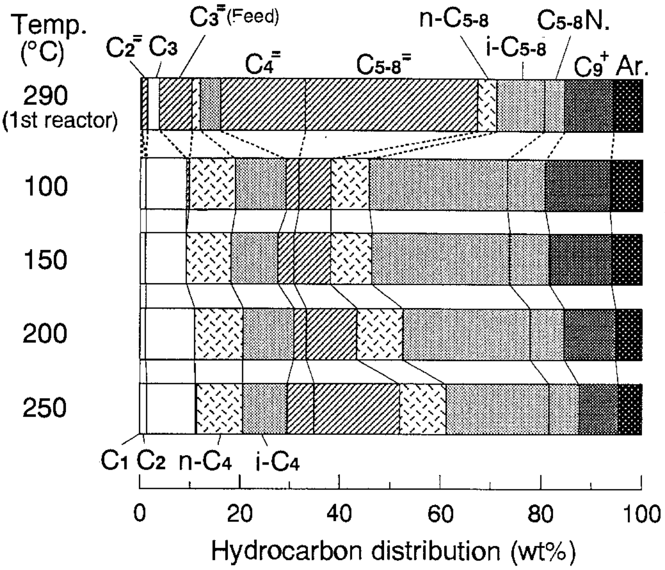

Fig. 4. Rapid gasoline synthesis from propene on the MFI type H-Fe-silicate (first stage) and on the 0.5 wt% Pt-modified mesoporous silicate (second stage). Reaction conditions as shown in fig. 3.

On the H-Fe-silicate, a high selectivity to gasoline-range hydrocarbons was also obtained under GHSV of 5000 h^{-1} at 290°C and the product consisted mainly of alkenes, as shown in the top of figs. 3 and 4. Moreover, it was reconfirmed that the MFI type H-Fe-silicate was hardly deactivated [7]. Under GHSV of 1000 h^{-1}, the alkenes in the gasoline range produced on the H-Fe-silicate were effectively converted into branched alkanes and/or cycloalkanes on the Pt-modified MFI type non-metal silicate [8]. However, as shown in fig. 3, under a much higher GHSV of 5000 h^{-1}, a large amount of branched alkenes in the gasoline range remained in the final product, because it was difficult for the branched alkenes to diffuse in the microporous materials [12–14]. In the mesoporous silicate, the gasoline-range hydrocarbons would be expected to diffuse more rapidly. Actually, the selectivity to the branched alkanes in the C_5–C_8 range markedly increased on the Pt-modified mesoporous silicate, as shown in fig. 4.

On the Pt-modified MFI type non-metal silicate (fig. 3), the gasoline fraction produced from the first-stage reactor slightly decreased due to the increase of light alkanes. Since the Pt-modified MFI type non-metal silicate possesses some acid site owing to the contaminant aluminum of the sodium silicate solution used as silicon source, the hydrogenolysis and/or aromatization of the gasoline-range hydrocarbons could progress by a large amount of exothermic heat in the hydrogenation reaction. However, the Pt-modified mesoporous silicate (fig. 4) has no catalytic activity except the hydrogenation; consequently, the higher activity for the hydrogenation of branched alkenes in the gasoline range could be maintained without decrease of gasoline fraction and/or deactivation owing to the coke deposition.

In order to clarify these effects of mesoporous silicate, its performance as a support of hydrogenation catalysts was compared with silica gel, which has no acidity and a distribution of pores in the mesoporous range. The mesoporous silicate showed a narrow pore size distribution at about 25 Å, as shown in fig. 5. Although

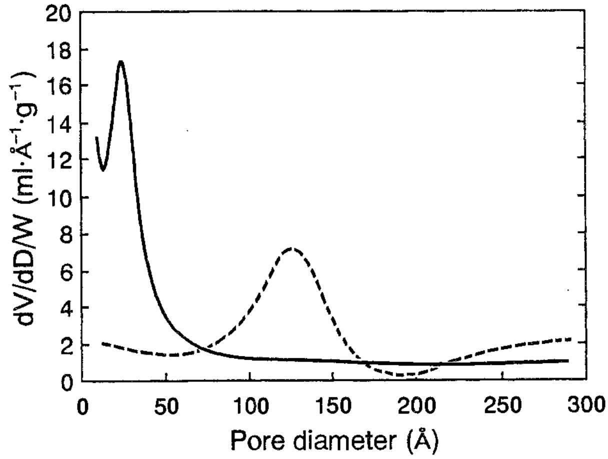

Fig. 5. Pore size distribution curves of the mesoporous silicate (solid line) and silica gel (broken line).

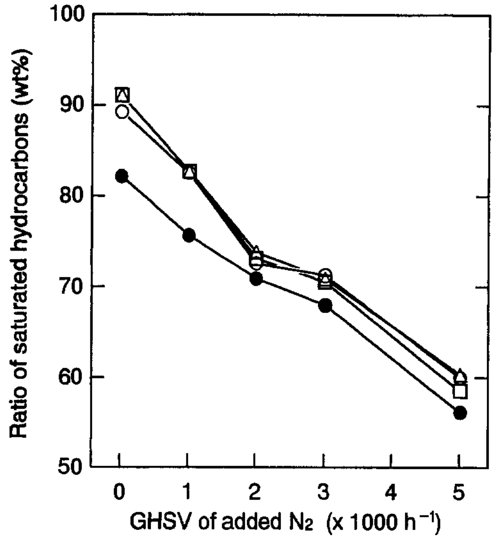

Fig. 6. Effect of the flow rate on the ratio of saturated hydrocarbons in the C_5–C_8 range when the 0.5 wt% Pt-modified silica gel was employed in the second stage. Nitrogen of GHSV 1000–5000 h^{-1} was added. Other reaction conditions as shown in fig. 3. (△) C_5, (□) C_6, (○) C_7, (●) C_8.

the silica gel showed a larger pore size and a wider distribution around 130 Å, its BET surface area of 250 m^2/g was very small, compared with that of the mesoporous silicate. Figs. 6 and 7 show the ratios of saturated hydrocarbons in the C_5–C_8 range when the 0.5 wt% Pt-modified silica gel and mesoporous silicate were

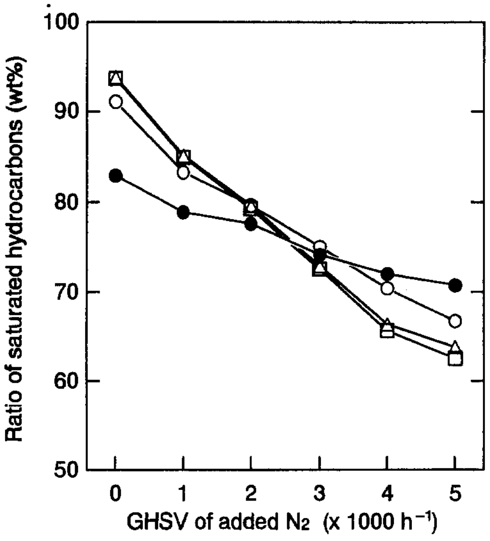

Fig. 7. Effect of the flow rate on the ratio of saturated hydrocarbons in the C_5–C_8 range when the 0.5 wt% Pt-modified mesoporous silicate was employed in the second stage. Reaction conditions and marks as shown in fig. 6.

employed in the second stage. Moreover, nitrogen of GHSV 1000–5000 h^{-1} was added to raise the flow rate and clear the differences between silica gel and mesoporous silicate. On the whole range of hydrocarbons, Pt-modified mesoporous silicate was more effective in the hydrogenation of olefins as fist-stage products compared with Pt-modified silica gel. This tendency was more clarified by raising the flow rate with the addition of nitrogen. In particular, higher molecular alkenes were more selectively hydrogenated on the Pt-modified mesoporous silicate under the higher flow rate conditions.

4. Conclusions

It was possible to synthesize a highly crystallized mesoporous silicate from kanemite containing a larger amount of sodium ions by repeated ion-exchange treatment with an aqueous solution of hexadecyltrimethylammonium chloride. The higher activity for the hydrogenation of branched alkenes in the gasoline range was obtained by adopting the mesoporous silicate modified with platinum, especially under higher flow rate conditions. This result indicates the high potential of mesoporous silicate as a new catalyst support for the rapid reaction.

References

[1] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins and J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.

[2] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli and J.S. Beck, Nature 359 (1992) 710.

[3] S. Inagaki, Y. Fukushima, A. Okada, T. Kurauchi, K. Kuroda and C. Kato, in: *Proc. 9th Int. Zeolite Conf.*, eds. R. von Ballmoos, J.B. Higgins and M.M.J. Treacy (Butterworth–Heinemann, Boston, 1992) p. 305.

[4] S. Inagaki, Y. Fukushima and K. Kuroda, J. Chem. Soc. Chem. Commun. (1993) 680.

[5] T. Inui, J. Tarumoto, F. Okazumi and H. Matsuda, Chem. Express 1 (1986) 49.

[6] T. Inui, React. Kinet. Catal. Lett. 35 (1987) 227.

[7] T. Inui, F. Okazumi, J. Tarumoto, O. Yamase, H. Matsuda, H. Nagata, N. Daito and A. Miyamoto, J. Japan. Petrol. Inst. 30 (1987) 249.

[8] J.-B. Kim, T. Takeguchi and T. Inui, in: *Preprints Int. Symp. on Zeolites and Microporous Crystals*, Nagoya 1993, p. 341.

[9] T. Inui, O. Yamase, K. Fukuda, A. Itoh, J. Tarumoto, N. Morinaga, T. Hagiwara and Y. Takegami, in: *Proc. 8th Int. Congr. on Catalysis*, Berlin, 2 July 1984, Vol. III (Verlag-Chemie, Weinheim, 1984) p. 569.

[10] T. Inui, in: *Zeolite Synthesis*, ACS Symp. Ser., Vol. 398, eds. M.L. Occelli and H.E. Robinson (Am. Chem. Soc., Washington, 1989) p. 479.

[11] K. Beneke and G. Lagaly, Am. Mineral. 62 (1977) 763.

[12] N.Y. Chen and W.E. Garwood, J. Catal. 52 (1978) 453.

[13] V.Y. Frillette, W.O. Haag and R.M. Lago, J. Catal. 67 (1981) 218.

[14] R.M. Dessau, J. Catal. 89 (1984) 520.