Hydration of Propene over Proton- and Metal Ion-Exchanged Zeolite Catalysts at Atmospheric Pressure

Hiroshi Mori,[†] Noritaka Mizuno, Toshihiro Shirouzu,[††] Shuichi Kagawa,[††] and Masakazu Iwamoto[*]

Catalysis Research Center, Hokkaido University,
Sapporo 060

[†] Department of Industrial Chemistry, Miyakonojo National
College of Technology, Miyakonojo 885

[††] Department of Industrial Chemistry, Faculty of Engineering,
Nagasaki University, Nagasaki 852

(Received March 1, 1991)

The gas-phase hydration of propene over proton-exchanged or metal ion-exchanged zeolites with various Si/Al ratios and structures (such as ZSM-5, mordenite, ferrierite, and Y-type) has been studied. It was found that the catalytic activity of proton-exchanged zeolites for the conversion of propene to 2-propanol did not depend on their framework structure, but showed a volcano-shaped dependence on the Al content, as was observed in the hydration of ethene. On the basis of temperature-programmed desorption experiments of NH_3 adsorbed on the zeolites, it was confirmed that the activity is controlled by the acidity of the catalysts. The catalytic activity of metal ion-exchanged Y zeolites increased with an increase in the electronegativity of the metal ion.

Hydration of lower olefins over proton-exchanged zeolites has been investigated at atmospheric and high pressures in the gas[1-5] and liquid[6] phases. Although efforts have been made to clarify the factors controlling the activity for hydration, they have been ambiguous because the conditions are complex and the activity of the catalyst depends on several factors.

We have previously reported that in the hydration of ethene over proton-exchanged zeolites at atmospheric pressure the catalytic activity of the zeolites is independent on the framework structure, showing a volcano-shaped dependence on the Al content or a SiO_2/Al_2O_3 molar ratio; a linear correlation between the activity and the number of acid sites on the zeolite was observed.[1] Further, it was suggested that the Brønsted acid site is the active site, since the temperature dependency of the activity is similar to that of a number of Brønsted acid sites. Eguchi et al.[4] as well as Kikuchi et al.[5] have, indeed, reported high catalytic activities of zeolites for the reaction. The former group has also claimed that no correlation was observed between the catalytic activity of zeolites for the hydration of propene and the number of acidic sites.[4] These results are not consistent with the correlation concerning the activity of zeolites for ethene hydration with the acid amount reported by the present group[1,3] and by Kikuchi et al.[5] This may be due to the high partial pressure of water vapor in their experiment, caused by a decrease in the number of acidic sites, owing to too much water being observed on mordenite by Kikuchi et al.[7]

In this work, therefore, catalytic hydration of propene was carried out over various zeolites including metal ion-exchanged Y zeolites in a simpler system, at both a low partial pressure of water vapor and at atmospheric pressure. We investigated how the activity for the hydration of lower olefins can be recognized by the amounts of acidic sites and tried to make the effects of the metal ion clearer on the basis of such recognition. This

paper clarifies the primary factors controlling the activity for the hydration of propene over proton-exchanged and metal ion-exchanged zeolite catalysts, and summarizes catalytic hydration over zeolites together with the previously reported results for ethene, 2-methylpropene, and 1-butene. It may be important to reveal the primary factors controlling the activity for hydration in order to design zeolite catalysts, since ion-exchange resins have disadvantages in that they decrease in catalytic activity with time and display thermal instability; alternative effective catalysts have been desired, although they are used preferentially as solid catalysts for the hydration of lower olefins.

Experimental

The parent zeolites (ZSM-5 (denoted as MFI), ferrierite (FER), and ultrastable Y-type (Y-12 and 40)) were supplied by Tosoh Corporation. Mordenite (MOR-15) and Y-type (Y-5.6) corresponding to JRC-Z-HM-15 and JRC-Z-HY-5.6, respectively, were obtained from the Catalysis Society of Japan. The number in the sample name represents the SiO_2/Al_2O_3 molar ratio in the zeolite framework, which was confirmed by ^{29}Si MASNMR (Brucker PC-250, 49.66 MHz). Proton-exchanged zeolites were prepared by the calcination (723 K, 2 h) of NH_4^+-exchanged zeolites which were supplied or prepared by three repetitions of an ion exchange of the parent Na^+-exchanged zeolites with a 2 wt% aqueous NH_4NO_3 solution at room temperature overnight. Metal ion-exchanged Y zeolites were prepared as follows: 10 g of proton-exchanged ultrastable Y zeolite ($SiO_2/Al_2O_3=12.3$) was ion-exchanged in 500 cm³ of an aqueous solution of metal nitrates or chlorides with 10 mmol cm⁻³.[#] The obtained solid was then

---

[#] As shown in Table 2, the exchange level of Co^{2+} or Ni^{2+} was very low, indicating that the ion exchange of Co^{2+} or Ni^{2+} with H^+ is more difficult than those of the other metal ions. Similar phenomena have been reported for the ion exchange of Co^{2+} or Ni^{2+} with Na^+ in various zeolites (W. Romanowski and J. M. Jablonski, "Catalysis on Zeolites," ed by D. Kallo and K. M. Minachev, Akademiai Kiado, Budapest (1988), p. 277).

dried in air at 393 K. The ion exchange levels were determined by using atomic absorption spectroscopy after the samples were dissolved in a HF solution.

The catalytic reaction was carried out in a continuous flow reactor at atmospheric pressure using 1 g of catalysts. The reactants and products were analyzed by gas chromatography connected directly to the reaction apparatus. The flow rates of propene and water vapor were 2.6 and 5.2 cm³ min⁻¹, or 5.2 and 10.4 cm³ min⁻¹, respectively. The total flow rate was 30 cm³ min⁻¹ (N_2 balance).

Results and Discussion

Catalytic Activities of Various Proton-Exchanged Zeolites. An approximately steady formation of 2-propanol was attained within 1 h, and the conversion of propene into 2-propanol changed little with the reaction time. 2-Propanol was the main product during the steady state of all experiments; small amounts of acetone, acetaldehyde, methanol, ethyl methyl ketone, 1-propanol, and 1,5-hexadiene were observed as by-products above 413 K. Hereafter, the conversion to 2-propanol per gram of the catalyst was used as a measure of the catalytic activity. The catalytic activities of various proton-exchanged zeolites for the hydration of propene are summarized in Table 1. All of the proton-exchanged zeolites used were active for a 2-propanol synthesis. The temperature dependence of the activities of HFER-16 is shown in Fig. 1 as an example. At first, the activity increased with an increase in the reaction temperature. The reason for the decline in activities at higher temperature involves a reduction in the equilibrium conversion, indicated by the broken line in Fig. 1. The maximum yield of 2-propanol was achieved at 383—403 K. The best yield (2.2%) was obtained at 383 K upon the HFER-16 zeolite.
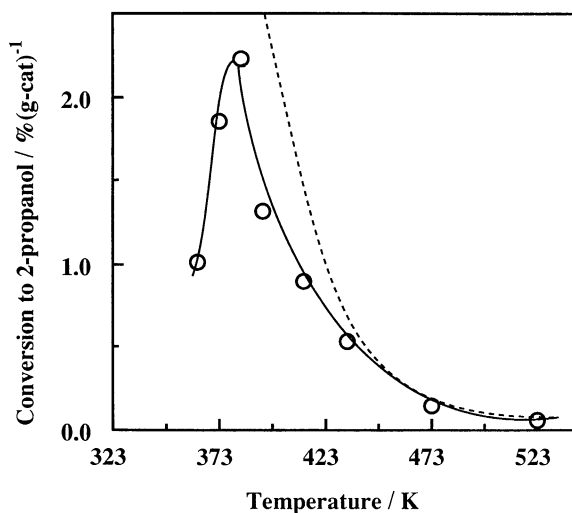

Fig. 1. Temperature dependence of the catalytic activity of HFER-16 for the hydration of propene. Reaction conditions were the same as those in Table 1. The broken line corresponds to the equilibrium conversion.

Figure 2a shows the effect of the Al content on the conversion of propene. Here, conversions at 393 K are plotted, since conversions above 403 K were too close to the equilibrium conversions to compare the activities. A similar tendency was observed when conversions at 373 K were plotted against the Al constents. The optimum SiO_2/Al_2O_3 molar ratio for 2-propanol formation is about 15—16, as shown in Fig. 2a. This value is in agreement with those reported by Fajula et al.[6] as well as ours[3] for the catalytic hydration of 1-butene in an aqueous solution and a gas phase, respectively. It should be noted that the activities of the HY zeolites with

Table 1. Properties of Proton-Exchanged Zeolites Used and Their Catalytic Activities for Hydration of Propene[a]

Catalyst	$\dfrac{SiO_2{}^{b)}}{Al_2O_3}$	$\dfrac{Pore^{c)}\ diameter}{nm}$	$\dfrac{H^{+\,b,d)}}{\%}$	Temp/K and amount of β-NH_3 desorption[b,e]		% Conversion of C_3H_6 into 2-propanol Reaction temp/K				
				mmol g⁻¹		373	383	393	403	413
HY-5.6	5.6	0.74	72	729	0.57	0.10	—	0.16	0.37	0.94
HY-12	12.2	0.74	—	—	—	0.08	—	1.16	1.27	0.92
HY-40	40	0.74	—	—	—	0.96	—	1.39	1.26	—
HMOR-15	14.9	0.67×0.70	99	876	1.20	0.50	—	1.78	—	0.91
HFER-12	12.3	0.43×0.55	99	823	1.02	0.36	0.43	0.70	—	0.58
HFER-16	16.3	0.43×0.55	94	853	1.14	1.85	2.22	1.32	—	0.90
HMFI-23[f]	23.3	0.54×0.56	99	686[g]	0.28[g]	—	0.99	0.76	—	0.76
Equil.conv.[h]/%						5.09	3.40	2.29	1.57	1.10

a) Reaction conditions: C_3H_6, 2.6 cm³ min⁻¹; H_2O, 5.2 cm³ min⁻¹; N_2, 22.2 cm³ min⁻¹; catalyst=1.0 g; pressure=1 atm. b) Cited from Ref. 8.   c) Cited from G. T. Kokotairo, "Proceedings of the NATO Advanced Study Institute on Zeolites: Sciences and Technology," ed by F. R. Ribeiro, A. E. Rodrigues, L. D. Rollmann, and C. Naccache, Martinus Nijhoff Publishers, Hague (1984), p. 83.   The value indicated correspond to the diameter of larger pores if the zeolite has pores with different size.   d) Exchange level of H^+.   e) Obtained from profiles of temperature programmed desorption of ammonia. The amount and its peak temperature of β-NH_3, which well reflect the number of acid sites and its strength, respectively, as was described previously,[8] were shown.   f) Prepared with HNO_3 solution.   g) These values are uncertain owing to overlap of α- and β-NH_3 peaks.   h) Equilibrium conversion (%).
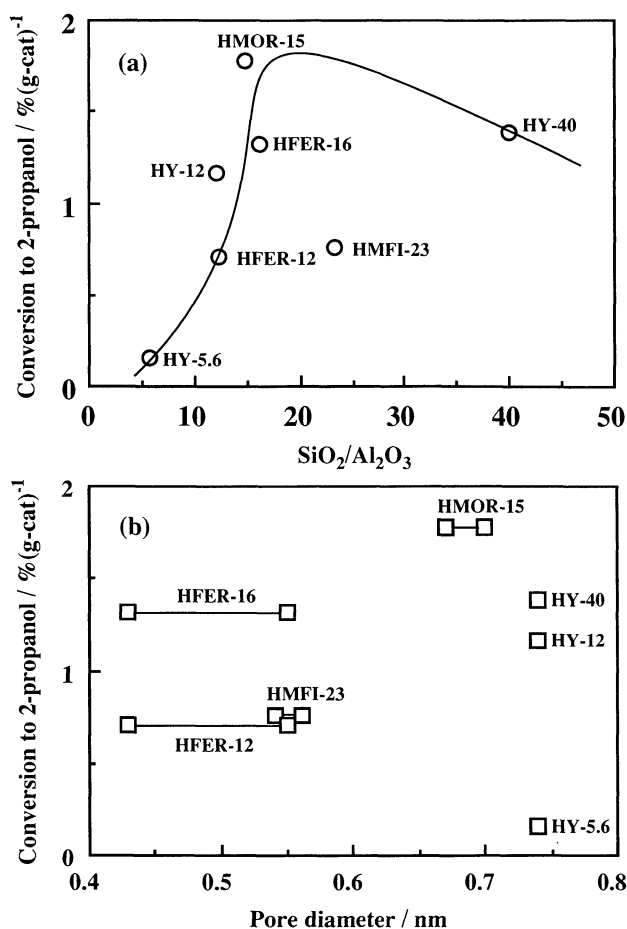
Fig. 2. Effect of Al content (SiO_2/Al_2O_3) (a) and framework (b) of zeolites on the conversion of propene to 2-propanol at 393 K. Reaction conditions were the same as those in Table 1.

various Al contents were much different from one another, as is shown in Fig. 2b. These figures indicate that the activity of the zeolites for the hydration of propene is dependent on their Al contents, not on their framework structure or pore diameter.

Taking into consideration that the hydration of olefins is an acid-catalyzed reaction, a more fruitful approach would be to compare the activity of the zeolites with the number or strength of their acid sites. The correlation between the number of acid sites of proton-exchanged zeolites and the relative catalytic activity for the hydration of propene is depicted in Fig. 3b. The conversion to 2-propanol increased with an increase in the number of acid sites, which is represented in Table 1 by the amount of desorbed β-NH_3. This correlation is in good agreement with those observed in the hydration of ethene[1] (Fig. 3a), 2-methylpropene[3] (Fig. 3c), and 1-butene[3] (Fig. 3d). Although the number and strength of the acid sites on HMFI-23 zeolite have also been measured by the t.p.d method (Table 1), the results for HMFI-23 are not plotted in the figures, since it has been reported that the β-peak temperature is close to the α-

peak temperature and that separation is very difficult and ambiguous.

Next, the correlation between the acid strength and the catalytic activity is discussed. As shown in Table 1, the peak temperature of β-NH_3 varied with the zeolites, generally indicating a change in the acid strength of protons, though it has been pointed out that the peak temperature of NH_3 desorption does not always correspond to the true acid strength, but varies with the experimental conditions as well as the amount of NH_3 adsorbed.[9] Fair correlations between the activities for the hydration of propene and the peak temperature of β-NH_3 have been recognized, while a poor correlation was observed in the hydration of ethene; no conclusion was obtained with 2-methylpropene or 1-butene because of the very few plots obtained. No appearance of universality among the correlations suggests that the acid strength is not the primary factor in the hydration of olefins. It follows from Fig. 3 that the acid sites with an acid strength above a certain level would all be effective for the reaction, and that the more important factor for the hydration reaction would be the number of acid sites, compared to the acid strength. This idea is supported by a report that the acidic sites giving a β-peak well correspond to the active sites on proton-exchanged ferrierite in the hydration of ethene.[5]

Propene hydration in this work was carried out at a lower partial pressure of water vapor than those used by Eguchi et al.[4] as well as by Kikuchi et al.[5] If one takes into account that the water vapor decreases the number of strong acid sites (probably due to a decrease in the acid strength[7] or the fact that the adsorption of water inhibits the chemisorption of propene on the acidic site) the higher activity of mordenite over those reported by Eguchi et al.[4] as well as by Kikuchi et al.[5] can be readily understood; further, the hydrophobic properties of the zeolites would not much affect the present conclusion. If hydration is carried out at a higher partial pressure of water vapor, it is probable that the maximum activity is obtained at a higher SiO_2/Al_2O_3 ratio than that given in Fig. 2a, since the hydrophobic properties[10] and strong acid sites[6] of catalysts would be necessary.

Unfortunately, it was very difficult to directly compare the reactivities of olefins over the zeolites, since the equilibrium conversion and the most reactive temperature of each olefin or the most active catalyst for each olefin could not be specified.

Catalytic Activities of Metal Ion-Exchanged Zeolites. It has been reported that the activity for the hydration of ethene was increased by a metal ion exchange,[11] and it may be important to clarify the effect of metal ions on the basis of the recognition of the number of acidic sites as a primary factor which controls the activity under the present experimental conditions. The catalytic activities of metal ion-exchanged zeolites were therefore investigated on an ultrastable Y zeolite (HY-12). The change in the conversion with time was similar to that of
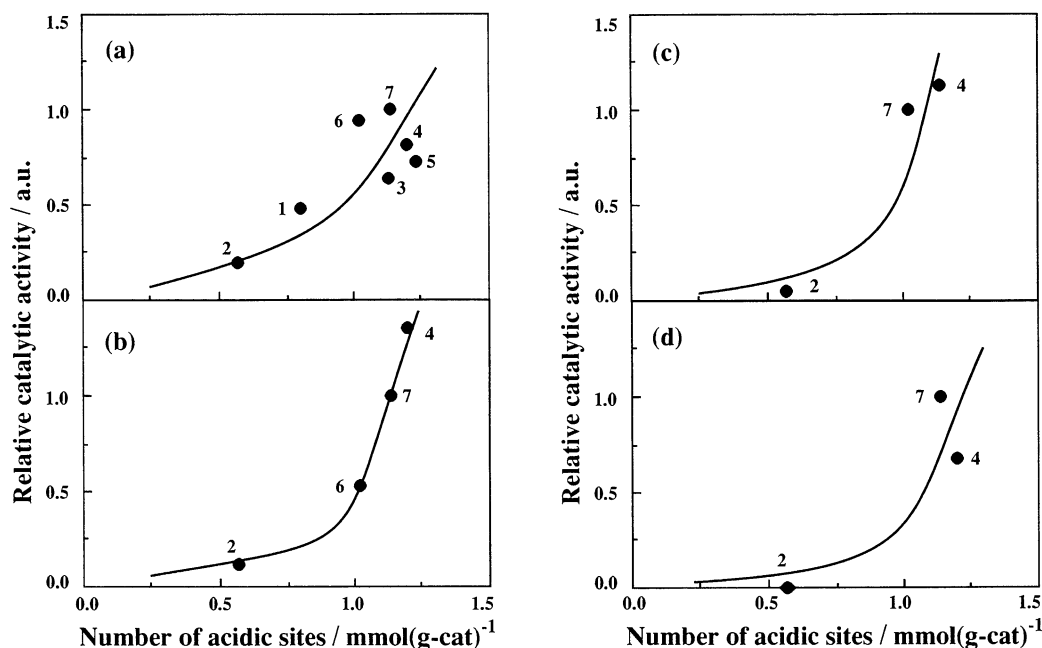
Fig. 3. Correlations between the number of acid sites of proton-exchanged zeolites and the relative catalytic activities for the hydration of ethene (a), propene (b), 2-methylpropene (c), and 1-butene (d). The catalytic activities for the hydration of ethene, 2-methylpropene, and 1-butene are cited from Refs. 1, 3, and 3, respectively. The catalytic activity of HFER-16 was taken as unity. The notations of 1, 2, 3, 4, 5, 6, and 7 in Figs. (a)—(d) correspond to the catalysts of HY-4.8, HY-5.6, HMOR-10, HMOR-15, HMOR-20, HFER-12, and HFER-16, respectively.

Table 2. Conversion of Propene to 2-Propanol over Metal Ion-Exchanged Zeolites at 393 K[a]

Catalyst	Exchange level/%	Conversion/%
HY-12		0.08
Fe^{3+}Y-12	50.9	0.92
Cr^{3+}Y-12	88.4	0.60
Zn^{2+}Y-12	52.2	0.30
Co^{2+}Y-12	21.7	0.27
Ni^{2+}Y-12	17.5	0.17
Cu^{2+}Y-12	43.0	0.61
Equi. conv./%[b]		4.44

a) Reaction conditions: C_3H_6, 5.2 cm³ min⁻¹; H_2O, 10.4 cm³ min⁻¹; N_2, 11.8 cm³ min⁻¹; O_2, 2.6 cm³ min⁻¹; catalyst=1.0 g; pressure=1 atm. b) See Table 1.

the proton-type. The rates and selectivities were little changed by the addition of oxygen to the reactant gas. The results are summarized in Table 2. The conversion was increased by the exchange of transition metal ions at 393 K, but was very low (less than one quarter of equilibrium conversion).

Figure 4 shows the correlation between the conversion to 2-propanol and the electronegativity of metal ions.[13] The conversion on Fe^{3+}, Cr^{3+}, Zn^{2+} and Cu^{2+} were in the range of 0.28—0.49 mmol g⁻¹ while those on Co^{2+} (0.18 mmol g⁻¹) and Ni^{2+} (0.15 mmol g⁻¹) were much lower. A fair correlation was observed and the conversion increased with an increase in the electro-
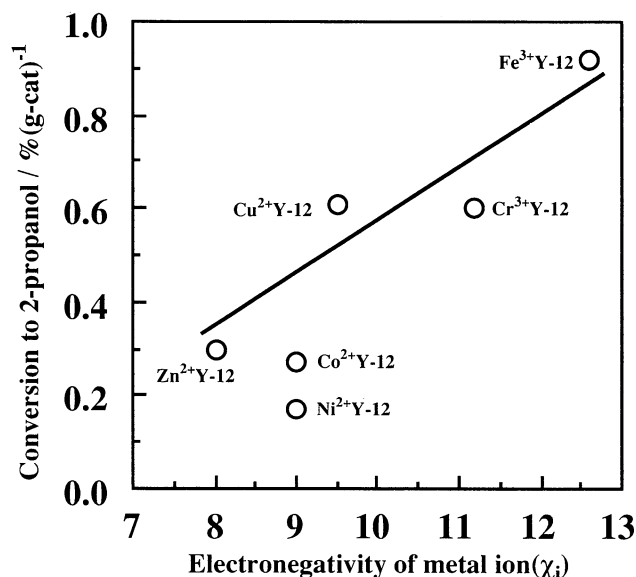

Fig. 4. Correlation between catalytic activities of metal ion-exchanged zeolites and the electronegativities of metal ions (χ_i). χ_i reported by Tanaka et al. (Ref. 12) was used. Reaction conditions were the same as those in Table 2.

negativity. The deviation of the conversions on Co^{2+}Y-12 and Ni^{2+}Y-12 to a lower extent from a linear line is probably due to the lower amounts of metal ions (or lower ion exchange levels) than those of the others. As

discussed in the previous section, the number of active centers is one of the factors which control the activity for the hydration of propene. The linear dependence in Fig. 4 shows that not only the number of acidic sites, but also the electronegativity of metal ions, controls the activity. The role of electronegativity in hydration can be explained as follows. Metal ions with a higher electronegativity would show a greater ability to coordinate olefin and/or water molecules, as has been reported for an A-type zeolite by Tanabe at al.[11] This ability may result in the higher catalytic activity.

Thus, all findings in the present work lead to the conclusion that the hydration of propene over proton-exchanged zeolites proceeds on a Brϕnsted acid site, and that the catalytic activity of zeolites is not influenced by the framework structure, but shows a volcano-shaped dependence on the Al content. Further, the activity of the Y-type zeolite was increased by a transition metal ion exchange.

References

1) M. Iwamoto, M. Tajima, and S. Kagawa, *J. Chem. Soc., Chem. Commun.,* **1985**, 228; *J. Catal.,* **101**, 195 (1986).

2) M. Nakano, K. Sekizawa, S. Fujii, and Y. Tsutsumi, *Nippon Kagaku Kaishi,* **1986**, 535.

3) M. Iwamoto, H. Mori, M. Tajima, and S. Kagawa, "Proceedings of the International Symposium on Acid-Base Catalysis," ed by K. Tanabe, H. Hattori, T. Yamaguchi, and T. Tanaka, Kodansha, Tokyo (1986), p. 453.

4) K. Eguchi, T. Tokiai, and H. Arai, *Appl. Catal.,* **34**, 275 (1987).

5) E. Kikuchi, T. Matsuda, K. Shimomura, K. Kawahara, and Y. Morita, "New Developments in Zeolite Science and Technology," ed by Y. Murakami, A. Iijima, and J. W. Ward, Kodansha, Tokyo (1986), p. 771.

6) F. Fajula, R. Ibarra, F. Figueras, and C. Gueguen, *J. Catal.,* **89**, 60 (1984).

7) E. Kikuchi, K. Shimomura, K. Kawahara, and Y. Morita, 1st Meeting of Zeolite, Zeolite Research Soc. Jpn., Tokyo, 1985, Abstr., A19.

8) M. Iwamoto, M. Tajima, and S. Kagawa, *J. Chem. Soc., Chem. Commun.,* **1986**, 598.

9) M. Niwa, M. Iwamoto, and K. Segawa, *Bull. Chem. Soc. Jpn.,* **59**, 3735 (1986).

10) S. Namba, N. Hosomura, and T. Yashima, *J. Catal.,* **72**, 16 (1981).

11) K. Tanabe and M. Nitta, *Bull. Jpn. Pet. Inst.,* **14**, 47 (1972).

12) K. Tanaka and A. Ozaki, *J. Catal.,* **8**, 1 (1967).