BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 51 (2), 448—452 (1978) [Vol. 51, No. 2

Ring Transformation of γ-Butyrolactone into γ-Thiobutyrolactone over Alkaline Cation Exchanged Zeolites

Kou HATADA,* Yoichi TAKEYAMA, and Yosho ONO

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

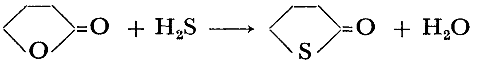
(Received August 6, 1977)

The reaction of γ-butyrolactone and hydrogen sulfide to give γ-thiobutyrolactone over zeolites was studied. Alkaline cation exchanged zeolites have high catalytic activity for the ring conversion, acidic zeolites very low activity. γ-Thiobutyrolactone was obtained in 99% yield with CsY at 330 °C. There is no decay of catalytic activity with time. The reaction kinetics over LiY, NaY, and CsY are expressed by

$$r = \frac{k(a_L P_L)(a_H P_H)}{(1+a_L P_L+a_H P_L)^2},$$

where r is the rate of reaction, P_L and P_H are the partial pressure of γ-butyrolactone and hydrogen sulfide, respectively, and k, a_L, a_H are constants. The activation energies for k are 39, 31, and 26 kcal mol^{-1} with LiY, NaY, and CsY, respectively. Catalytic activity is enhanced by addition of pyridine but almost completely depressed by addition of hydrogen chloride. It is concluded that basic sites play an important role in the ring transformation.

Synthetic zeolites usually act as acidic catalysts, having very high activity for major carbonium ion hydrocarbon transformations such as cracking, alkylation and isomerization. For these reactions, hydrogen-, rare-earth-, and alkaline earth-exchanged zeolites are the most active catalysts. However, the parent Na$^+$ and K$^+$-exchanged zeolites are inactive.[1] There are, however, some reactions in which NaY has a catalytic activity comparable with HY, *e.g.* the reactions of γ-butyrolactone with primary amines to form 1-alkyl-2-pyrrolidinone.[2] The mechanism proposed for this reaction involves the activation of primary amines on basic sites.[2] A related reaction, the conversion of γ-butyrolactone in the presence of hydrogen sulfide has been studied by Venuto and Landis.[3]



A notable feature of the reaction is that NaX was found to be the most active catalyst among the zeolites studied, HY and ReX having only a meager catalytic activity.[3] The catalytic activity for this reaction does not seem to be associated with Brönsted centers.

The kinetic behavior of the ring transformation of γ-butyrolactone into γ-thiobutyrolactone (tetrahydro-2-thiophenone) was examined over a series of alkaline Y-zeolites in order to find the mechanistic grounds of high activity of alkaline zeolites for the ring conversion reaction.

Experimental

Materials. γ-Butyrolactone (purity>99%) was distilled prior to each run. Commercial hydrogen sulfides, NaX and NaY (Linde Division of Union Carbide Corp.) were used. Various cation forms of Y-zeolites were prepared by means of the conventional cation exchange using salt solution. The cation exchanged zeolites were pelleted without a binder and crushed and made into 9—16 mesh. They were stored in a desiccator containing a saturated aqueous ammonium chloride.

Apparatus and Procedure. A continuous flow reactor was used under atmospheric pressure. The reactor was silica tubing (13 mm i.d.) placed in a vertical furnace. Prior to the reaction, the catalyst in the reactor was heated up to the reaction temperature in a nitrogen stream. Hydrogen sulfide was then fed. After 15 min, γ-butyrolactone was pumped into the preheating zone of the reactor containing 10 ml quartz powder. Nitrogen was used as diluent for regulating the initial pressure of reactants. The gaseous materials were fed through flowmeters. Reaction products collected in the receiver were withdrawn at certain intervals during the run and analyzed by gas chromatography.

Result and Discussion

Catalytic Activity of Various Forms of Zeolites. The catalytic activities of various cation forms of zeolites for the reaction of γ-butyrolactone and hydrogen sulfide were compared at 330 °C. The activities and selectivities to γ-thiobutyrolactone production on various zeolites are given in Table 1. We can see the following features of the reaction.

TABLE 1. CATALYTIC ACTIVITY OF VARIOUS ZEOLITES

Catalyst	Exchanged (%)	Conversion (%)	Yield (%)
LiY	58	27	26
NaY	—	52	51
KY	97	45	45
RbY	64	51	51
CsY	64	79	78
NaX	—	99	86
KL	—	23	22
HY	66	4	1
MgY	56	2	2

Reaction conditions; 330 °C, H_2S/lactone=6, W/F=6.26 g h mol^{-1}.

(1) Alkaline forms of zeolites are much more active than acidic zeolites (HY, MgY).

(2) The catalytic activity of alkaline forms of Y-zeolites increases in the following order.

$$\text{LiY} < \text{NaY} \simeq \text{KY} \simeq \text{RbY} < \text{CsY}$$

---

* Present address: Faculty of Education, Saitama University, Urawa, Saitama 338.

(3) NaX is a more active catalyst than NaY, but shows less selectivity.

(4) The selectivity to γ-thiobutyrolactone is essentially 100% over alkaline Y-zeolites.

It should be noted that no decay of activity with time is observed except for the case of MgY.

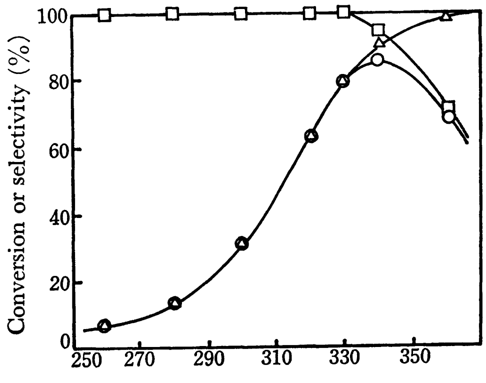


Fig. 1. Variation of the conversion (△), the yield (○) and the selectivity (□) with reaction temperature.
CsY 1.0 g, W/F=6.26 g h mol^{-1}, H_2S/lactone=6.

Influence of Reaction Temperature. The effect of reaction temperature on the yield and the selectivity to γ-thiobutyrolactone was examined with CsY as a catalyst. As shown in Fig. 1, the yield of γ-thiobutyrolactone sharply increases with temperature below 340 °C. Maximum yield is reached at 340 °C. The yield falls at higher temperatures. The selectivity to γ-thiobutyrolactone is 100% up to 330 °C, decreasing at higher temperatures.

Effect of Contact Time. The effect of contact time (W/F) on the yield of γ-thiobutyrolactone was examined at 330 °C. W/F is defined as follows:

$$W/F = \frac{\text{Weight of catalyst (g)}}{\text{Total feed } (H_2S + \text{lactone} + N_2) \text{ (mol h}^{-1})}.$$

The results are illustrated in Fig. 2. The yield increases with contact time. At W/F=18.8 g h mol^{-1}, a 99% yield can be attained. The selectivity for γ-thiobutyrolactone is always 100% at this temperature.

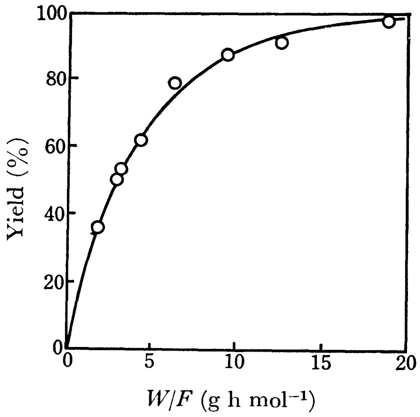


Fig. 2. Effect of contact time on γ-thiobutyrolactone yield.
CsY, 330 °C, H_2S/lactone=6.

Reaction Kinetics. The kinetics of the reaction was studied in a short contact time with LiY, NaY, and CsY as catalyst. The effect of partial pressure of γ-butyrolactone on the reaction rate was examined by keeping the partial pressure of hydrogen sulfide at 0.5 atm. The partial pressure of nitrogen was adjusted to keep the contact time constant. The results for CsY are given in Fig. 3. The rate decreases with increase in lactone partial pressure.

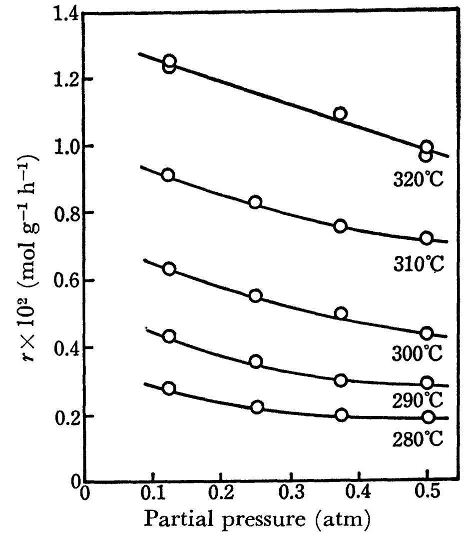


Fig. 3. Dependence of the reaction rate over CsY on the partial pressure of γ-butyrolactone.
CsY 0.5 g, W/F=2.74 g h mol^{-1}, P_H=0.5 atm.

The dependence of reaction rate on the partial pressure of hydrogen sulfide was examined by keeping the lactone partial pressure at 0.125 atm. The results for CsY are given in Fig. 4.

The presence of the reaction products (water and γ-thiobutyrolactone) does not affect the reaction rate, since addition of these substances to the reactant feed does not change the yield of γ-thiobutyrolactone.

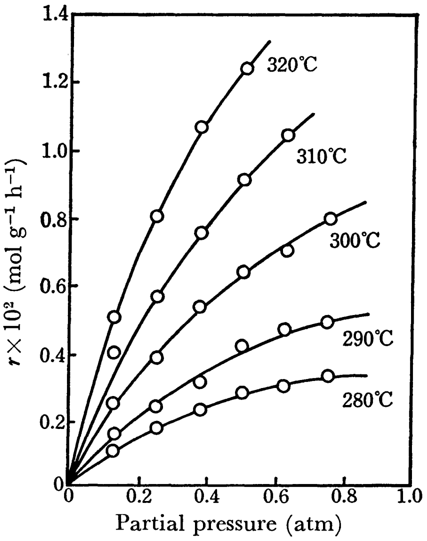


Fig. 4. Dependence of the reaction rate over CsY on the partial pressure of hydrogen sulfide.

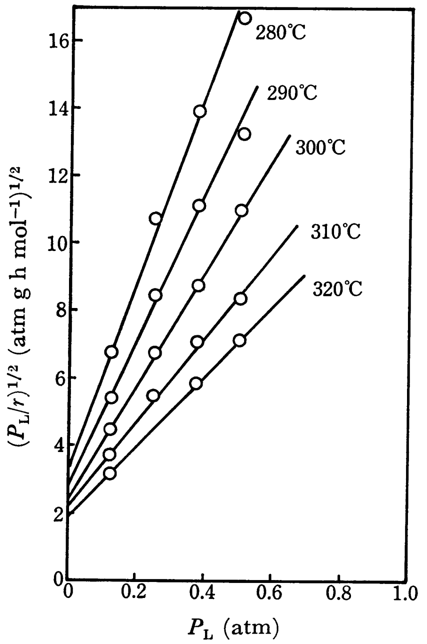


Fig. 5. $(P_L/r)^{1\,2}$ *vs.* P_L plot for CsY.

It was found that the rate of the reaction can be expressed by

$$r=\frac{k(a_LP_L)(a_HP_H)}{(1+a_LP_L+a_HP_H)^2}, \tag{1}$$

where r is the rate of reaction, P_L and P_H are the partial pressures of γ-butyrolactone and hydrogen sulfide, respectively, and k, a_L, a_H are constants.

By rearranging Eq. 1, we have

$$\left(\frac{P_L}{r}\right)^{1/2}=\frac{1+a_HP_H}{(ka_La_HP_H)^{1/2}}+\frac{a_L}{(ka_La_HP_H)^{1/2}}\cdot P_L, \tag{2}$$

or

$$\left(\frac{P_H}{r}\right)^{1/2}=\frac{1+a_LP_L}{(ka_Ha_LP_L)^{1/2}}+\frac{a_H}{(ka_La_HP_L)^{1/2}}\cdot P_H. \tag{3}$$

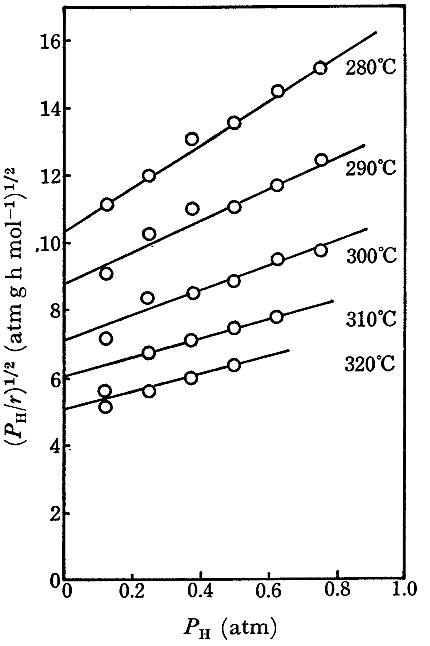


Fig. 6. $(P_H/r)^{1/2}$ *vs.* P_H plot for CsY.

Table 2. Kinetic parameters for the conversion of γ-butyrolactone into γ-thiobutyrolactone over CsY

Temperature (°C)	k (mol g^{-1} h^{-1})	a_L (atm^{-1})	a_H (atm^{-1})
280	2.3×10^{-2}	14	1.8
290	4.1×10^{-2}	13	1.3
300	6.0×10^{-2}	12	1.5
310	8.0×10^{-2}	11	1.8
320	11.7×10^{-2}	10	1.6

Table 3. Kinetic parameters for the conversion of γ-butyrolactone into γ-thiobutyrolactone at 320 °C

Catalyst	k (mol g^{-1} h^{-1})	a_L (atm^{-1})	a_H (atm^{-1})	E_a (kcal mol^{-1})
LiY	4.0×10^{-2}	8	0.5	39
NaY	6.1×10^{-2}	7	0.9	31
CsY	11.7×10^{-2}	10	1.6	26

Straight lines are obtained (Fig. 5) when $(P_L/r)^{1/2}$ is plotted against P_L by using the data given in Fig. 3. Straight lines are obtained (Fig. 6) also when $(P_H/r)^{1/2}$ is plotted against P_H by using the data given in Fig. 4. From the slopes and intercepts of the plots of Figs. 5 and 6, the constants, k, a_L, a_H are determined as given in Table 2. In a similar way, the rate constants and the constants (a_L, a_H) for LiY and NaY were determined. The values at 320 °C are given in Table 3. The rate constant, k, changes with the increasing order LiY$<$NaY$<$CsY. The constant a_H also changes with the increasing order LiY$<$NaY$<$CsY, while the constant a_L does not depend much on the catalyst used. From the temperature dependence of the rate constant, the activation energy for k is determined to be 39, 31, and 26 kcal mol^{-1} for LiY, NaY, and CsY, respectively.

Nature of Active Centers. Acidic zeolites (HY and MgY) have only a limited activity for this ring transformation reaction (Table 1). However, alkaline zeolites are very effective. This clearly indicates that the active centers are not acidic sites.

Yashima *et al.*[4] found that in the alkylation of toluene with methanol or formaldehyde, xylenes were selectively formed over Li zeolite, styrene and ethylbenzene being produced over the other alkaline zeolites. They concluded that the formation of xylenes depends on the solid acidity, the formation of styrene and ethylbenzene depending on the solid basicity. The side-chain alkylation is promoted by added aniline, while the nuclear alkylation is promoted by hydrogen chloride.[4] The presence of basic sites has been further confirmed by the conversion of 2-propanol over alkaline zeolites,[5] since the dehydration and dehydrogenation of alcohols are catalyzed by the acidic and the basic sites, respectively.[6] The order of catalytic activity of alkaline Y-zeolites is as follows.[5]

For dehydration LiY$>$NaY$>$KY$>$RbY$>$CsY,
For dehydrogenation LiY$<$NaY$<$KY$<$RbY$<$CsY.

The order of catalytic activity among alkaline zeolites for the reaction of γ-butyrolactone and hydrogen sulfide suggests that the active centers for this ring conversion is basic in nature. In order to gain further insight into the active centers, the effects of addition of hydrogen chloride and of pyridine on the catalytic activity were examined.

Effect of Hydrogen Chloride. Matsumoto *et al.*[7] reported that the cracking of cumene over NaY is greatly enhanced by addition of hydrogen chloride to the system. The enhancement of the catalytic activity is ascribed to the formation of Brönsted acid sites by the interaction of hydrogen chloride with NaY.

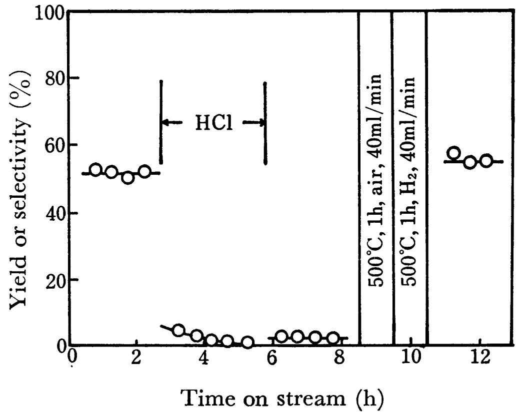


Fig. 7. Effect of hydrogen chloride on the reaction rate. CsY, 330 °C, $W/F=3.13$ g h mol^{-1}, H_2S/lactone=6.

Addition of hydrogen chloride was carried out by passing a hydrogen sulfide stream over the concentrated hydrogen chloride aqueous solution. The results are given in Fig. 7. Hydrogen chloride almost completely inhibits the catalytic activity. The effect is irreversible, since the activity does not recover when feeding of hydrogen chloride is interrupted. The activity can be recovered by consecutive treatment of the catalyst with air and hydrogen at 500 °C. This eliminates the possibility of deactivation being caused by the destruction of the zeolite framework. The presence of water vapor does not affect the catalytic activity. Thus, it can be assumed that the deactivation is associated with the poisoning of the active centers, presumably the basic sites, by hydrogen chloride.

Effect of Pyridine. Pyridine is often used to poison acidic center. The effect of addition of pyridine on the ring conversion was examined. The dependence of the rate of γ-thiobutyrolactone on the pyridine partial pressure is given in Fig. 8. We see that pyridine does not poison the catalysis. However, it enhances the catalytic activity; the activity increases 35 and 250% for CsY and LiY, respectively, with pyridine partial pressure$>$0.01 atm.

The effect of hydrogen chloride and pyridine indicates that the acidic sites are not responsible for the catalysis, but the active centers are associated with basic sites. The enhancement of activity by pyridine may be caused by enrichment of the electron density of the oxygen anions in $(AlO_4)^-$ unit by the induced effect of pyridine absorbed close to the basic center. A similar mechanism of the enhancement by adsorbed pyridine has been postulated for the base catalyzed butadiene formation from ethanol over SiO–MgO (75:25) catalyst.[8] Flockhart *et al.* found that the striking increase in reducing power of the decationated zeolites is caused by the addition of electron donors and suggested the existence of a strong interaction between electropositive and electronegative $(AlO_4)^-$ sites.[9]

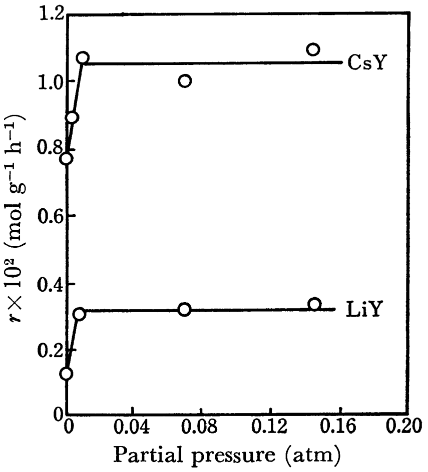


Fig. 8. Effect of pyridine partial pressure on the reaction rate.
CsY, 300 °C, $W/F=3.14$ g h mol^{-1}, $P_H=0.714$ atm, $P_L=0.143$ atm.

Catalysis by Silica–Magnesia. Niyama *et al.*[8,10] determined the acidity and basicity of SiO_2–MgO catalysts of various compositions, and found that the basicity per unit area increases with increase in MgO content, the acidity per unit area having maximum at $MgO/SiO_2=1$. The ring transformation of γ-butyrolactone into γ-thiobutyrolactone was carried out with SiO_2–MgO catalysts. The results are summarized in Table 4. The rate per unit area increases with increasing MgO content. This indicates also that the basic sites, rather than acid sites, are responsible for the ring conversion.

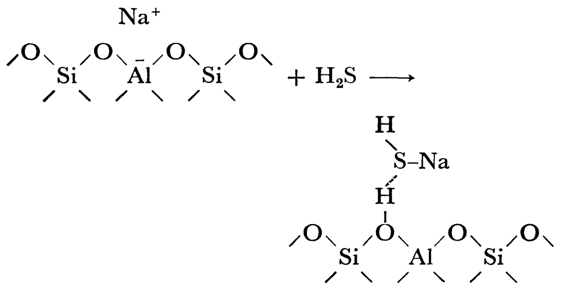
Table 4. Ring conversion of γ-butyrolactone to γ-thiobutyrolactone over SiO_2–MgO catalysts

Catalyst	Yield (%)	Surface area (m^2 g^{-1})	Rate (mol m^{-2} h^{-1})
SiO_2	1	180	1.3
SiO_2–MgO (3:1)	5	170	6.7
SiO_2–MgO (1:1)	7	150	11
SiO_2–MgO (1:3)	10	130	18
MgO	3	23	30

Reaction conditions; 330 °C, H_2S/lactone=6, $W/F=$ 6.16 g h mol^{-1}.

Nature of Basic Sites. All the results suggest that the active centers are basic in nature. A possible candidate for the basic sites in zeolites are oxygen anions bound to aluminum cations $(AlO_4)^-$. A negative charge at the site is neutralized and shielded by an alkaline cation. However, our results suggest that the reactant molecules are accessible to and are adsorbed on the basic oxygen anions at reaction conditions. A recent infrared study by Karge and Raskó[11] has shown that hydrogen sulfide is dissociatively adsorbed on Na form of faujasite-like zeolites. They suggest that the adsorption sites are cationic sites of low coordination, where the Na^+ cations are weakly bound. The higher the Si/Al ratio, the smaller the population of such sites. This explains why hydrogen sulfide dissociates quite easily over NaX, but not over NaY.[11] Our result showing that NaX has higher catalytic activity for the ring transformation than NaY appears to support the idea. The order of reactivity among Y-zeolites (LiY$<$NaY$<$KY$<$RbY$<$CsY) may be associated with the ionic radius of the cations. The larger cations are bound more weakly to the basic sites, which, in turn, are more readily attacked by foreign molecules. The observed activation energy values can be understood on this basis. Thus, the activation energy for CsY is much smaller than that for NaY and LiY, which implies that the reactant molecules are more easily activated by the former catalyst.

Mechanism of the Reaction. The above discussion indicates that the active center involves the basic $(AlO_4)^-$ tetrahedron. Thus, hydrogen sulfide may be activated by the following scheme.



Karge and Raskò[11] showed that hydrogen sulfide dissociates on NaX. They found no evidence of the dissociation of hydrogen sulfide on NaY. It is very plausible, however, that H_2S molecules dissociate at reaction conditions ($\approx$300 °C) on NaY.

γ-Butyrolactone molecules have an easily polarizable carbonyl group and can be activated by the electrostatic field exerted by a Na^+ cation and/or a $(AlO_4)^-$ unit. The reaction may proceed through the reaction between adsorbed hydrogen sulfide and adsorbed γ-butyrolactone, which may compete for the adsorption sites made up of the combination of Na^+-$(AlO_4)^-$ unit.[12] This explains the observed Langmuir-Hinshelwood type kinetics where the adsorption of γ-butyrolactone is much easier than that of hydrogen sulfide ($a_L < a_H$).

The authors are very grateful to Prof. Tominaga Keii for many fruitful discussions.

References

1) M. L. Poustma, in "Zeolite Chemistry and Catalysis," ed by J. A. Rabo, American Chemical Society, Washington (1977), p. 437.

2) K. Hatada and Y. Ono, *Bull. Chem. Soc. Jpn.*, **50**, 2517 (1977).

3) P. B. Venuto and P. S. Landis, *Adv. Catal.*, **18**, 259 (1968).

4) T. Yashima, K. Sata, and N. Hara, *J. Catal.*, **26**, 303 (1972).

5) T. Yashima, H. Suzuki, and N. Hara, *J. Catal.*, **33**, 486 (1974).

6) G. V. Krylov, in "Catalysis by Nonmetals," Academic Press, New York (1970), p. 116.

7) H. Matsumoto, K. Yasui, and Y. Morita, *J. Catal.*, **12**, 84 (1968).

8) H. Niyama, S. Morii, and E. Echigoya, *Bull. Chem. Soc. Jpn.*, **45**, 655 (1972).

9) B. D. Flockhart, M. C. Meggarry, and R. C. Pink, *Adv. Chem. Ser.*, **121**, 509 (1973).

10) H. Niyama and E. Echigoya, *Bull. Chem. Soc. Jpn.*, **45**, 938 (1972); H. Niyama and E. Echigoya, *Bull. Petro. Inst.*, **14**, 83 (1972).

11) H. G. Karge and J. Raskò, private communication.

12) K. Hatada, M. Shimada, Y. Ono, and T. Keii, *J. Catal.*, **37**, 166 (1973).