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Shape-Selective Disproportionation of Xylene over Partially Cation-Exchanged H-Mordenite

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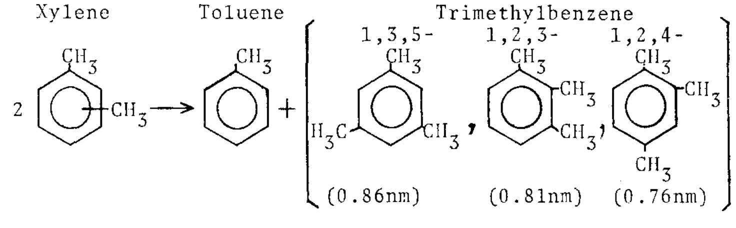
The shape-selective disproportionation of xylene to form 1,2,4-trimethylbenzene over the partially exchanged H-mordenite catalysts by various cations has been studied. The catalysts were prepared by a conventional or rapid cation-exchange method. The shape selectivity depends on the ionic radius of exchanged cation. The most suitable ionic radius is nearly 0.096 nm. The most suitable catalyst is the H-mordenite exchanged by Cu cation. This catalyst has a high selectivity, not only because there is not enough space to form the transition state leading to 1,3,5-trimethylbenzene, but also because the diffusion of 1,3,5-trimethylbenzene is inhibited. The rapid cation exchange is more effective than the conventional one, because a smaller amount of cation controls the pore dimension and provides a high selectivity without a drop in activity.

INTRODUCTION

We have reported that H-mordenite (H-M) catalyst effectively accelerates the disproportionation of toluene with a high selectivity, and the produced xylene is a mixture of three isomers in a thermodynamic equilibrium state (*1*). Therefore, it is expected that H-M catalyst will also accelerate the disproportionation of xylene [see Eq. (1)]. And the produced trimethylbenzene (TMB) will be a mixture of three isomers in equilibrium.



(1)

On the other hand, the effective pore dimension of the mordenite can be controlled by exchanged cations of the catalyst, because the pore structure of mordenite is composed of one-dimensional channels and the cations stick out from the channel walls. H-M has a large pore dimension, that is about 0.9 nm, and can absorb simple aromatic compounds in it. However, the mor-

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denites exchanged by multi-valent cations cannot always absorb easily such aromatic compounds (*2*).

Thus when the disproportionation of xylene proceeds over H-M catalyst which is partially exchanged by a cation with a suitable radius, the smallest isomer in TMB is predominantly produced. The molecular dimensions (minimum cross-section) of TMB isomers (*3*) are shown in Eq. (1). The smallest is 1,2,4-isomer and the largest is 1,3,5-isomer. So as we expected, a high selectivity for 1,2,4-isomer can be obtained using this kind of catalyst. 1,2,4-TMB is the precursor of trimellitic acid which is a raw material of the heat-resisting polymers.

A part of this work has been briefly reported in a letter in Ref. (*4*).

EXPERIMENTAL

Materials

Organic reactants. *o*-Xylene, *m*-xylene, *p*-xylene, and 1,3,5-trimethylbenzene were obtained from a commercial source with a purity of 99.5%.

Catalysts. H-Mordenite (H-M) was prepared by a conventional cation-exchange procedure at 353°K using 0.5 N aqueous solution of hydrochloric acid and Na-Mordenite (Nihon Kagaku Kogyo Co.).

The partial cation exchange of H-M was carried out by two methods. One of them was a conventional cation-exchange method using an aqueous solution of chloride or acetate of divalent metal. To obtain a desired degree of cation exchange, the concentration of cation solution was controlled. The cation exchange was carried out at least several hours at 353°K. The other was a *rapid* cation exchange method using an aqueous solution of divalent metal acetate. The cation exchange was carried out for 10 $\sim$ 30 min at room temperature. To obtain a desired degree of cation exchange, the exchange time or the concentration of the solution was controlled.

The degree of cation exchange was determined by flame photometry and atomic absorption spectrophotometry.

Analysis

The reaction mixtures were analyzed by gas chromatography, using a 4-m stainless-steel column which has a diameter of 3 mm with stationary phase Celite-545 (60–80 mesh) containing 6.3% of Benton-34 and 4.5% of DNP. The carrier gas was H_2 (60 ml/min) and the analysis temperature was 389°K.

Apparatus and Procedure

The experiment was carried out in a fixed bed-type apparatus with a continuous flow system at atmospheric pressure.

The catalyst was placed in the quartz reactor with an electric heater. The calcination was carried out in nitrogen stream for 2 hr at the desired temperature. The reactant was then fed into the catalyst bed by a microfeeder. Nitrogen was used as a carrier gas (N_2/reactant = 5). The liquid products were collected with an ice-water trap. The sample for gas chromatography was collected periodically.

RESULTS AND DISCUSSION

Three isomers of TMB, toluene, *o*-xylene, *p*-xylene, and a small amount of benzene and tetramethylbenzenes were obtained as the reaction products for *m*-xylene disproportionation. The distribution of the products changed with process time. A typical change of product distribution for *m*-xylene disproportionation over H(96)-M (the number in parenthese indicates percentage degree of cation exchange) is shown in Fig. 1. Not only disproportionation but also isomerization and a little secondary transalkylation were observed. Equilibrium among three xylene isomers was not established, while equilibrium between *o*- and *p*-isomers was always established. Yield of TMB decreased with process time.

The fraction of 1,2,4-isomer in TMB increased and the fraction of 1,3,5-isomer in TMB decreased with process time, while the fraction of 1,2,3-isomer in TMB was constant through the run. The TMB/toluene ratio did not differ so much from the equilibrium value (0.95) (*5*). Both yields of benzene and tetramethylbenzenes formed by the secondary transalkylation were only 0 ~ 2.5%. In the case of *p*-xylene or *o*-xylene disproportionation over the same catalyst, the yield of TMB and the fraction of 1,2,4-isomer in TMB were almost the same as those in *m*-xylene. Therefore, *m*-xylene was chosen as a reactant in the subsequent studies.

The disproportionation of *m*-xylene over H(81)-Y (prepared from SK 40) was carried out and the results are shown in Fig. 2. H(81)-Y had much less activity than H(96)-M. The fraction of 1,2,4-isomer in TMB did not change with process time and was always 64%. This value is expected to be an equilibrium one, because the same value was obtained in H(96)-M at the initial process time in Fig. 1 or at long contact time (W/F = 100 g-hr/mole) and because the large pore dimension of Y-type zeolite is not expected to have the shape selectivity. The equilibrium values calculated from API data (*6*) and reported by Hastings and Nicholson (*5*) were 62 and 68%, respectively. These three values were slightly different among them. In this paper, we have chosen 64% as the equilibrium value.

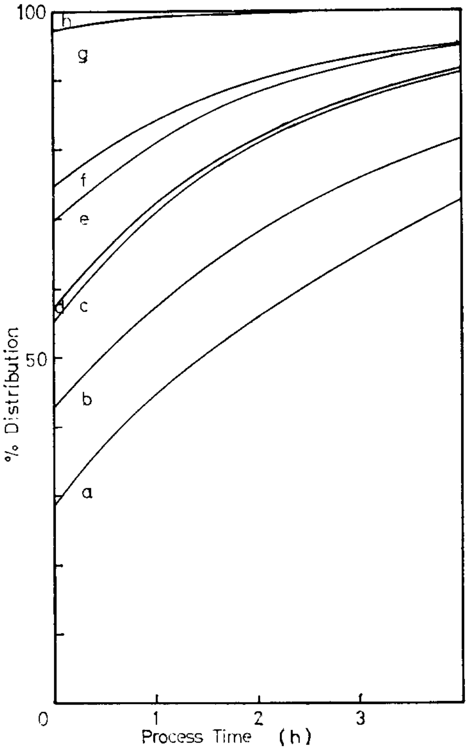

FIG. 1. Products distribution for *m*-xylene disproportionation over H(96)-M. Reaction conditions: calcination, 873°K; reaction temperature, 573°K; W/F, 15 g·hr/mole; (a) *m*-xylene, (b) *o*-xylene, (c) *p*-xylene, (d) 1,2,3-TMB, (e) 1,2,4-TMB, (f) 1,3,5-TMB, (g) toluene, (h) benzene and tetramethylbenzenes.

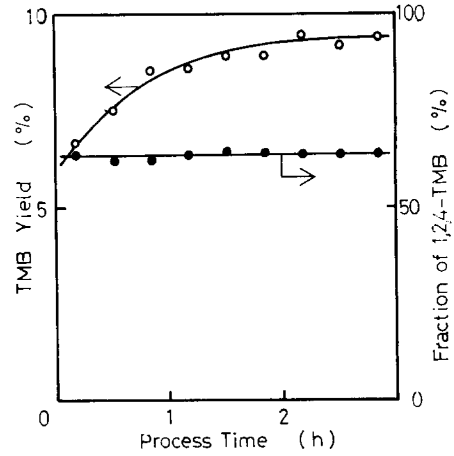

FIG. 2. Disproportionation of *m*-xylene over H(81)-Y. Reaction conditions: calcination, 723°K; reaction temperature, 573°K; W/F, 30 g·hr/mole; (○) yield of TMB, (●) fraction of 1,2,4-isomer in TMB.

To express activity and selectivity of various catalysts for xylene disproportionation, Eqs. (2) and (3) are used.

$$y \text{ (TMB Yield)} = (2 \times \text{moles of TMB produced})/(\text{moles of xylene fed}) \times 100\% \quad (2)$$

$$S = (f - f_e)/(1 - f_e) \times 100\% \quad (3)$$

TABLE 1

Activity and Selectivity of Various Catalysts[a]

Catalyst	Ionic radius (nm)	Activity y_0 (%)	Selectivity S_{20} (%)[b]
H-M	—	49	8
Be–H-M	0.033	29	8
Mg–H-M	0.062	24	17
Ni–H-M	0.065	25	28
Co–H-M	0.068	23	25
Zn–H-M	0.074	21	31
Cu–H-M	0.096[c]	26	33
Ca–H-M	0.099	9	8[d]
Sr–H-M	0.116	8	8[d]
Ba–H-M	0.136	8	8[d]

[a] Reaction conditions: calcination, 873°K; reaction temperature, 573°K; W/F, 100 g-hr/mole.

[b] Estimated by interpolation of curved S vs y plot.

[c] Ionic radius of Cu^+. The reason was described later.

[d] The value was the same as that of H-M, because the curved S vs y plot lay upon the curve of H-M.

where f is a fraction of 1,2,4-isomer in TMB and f_e is the fraction at equilibrium. $S = 0$ means that the fraction of 1,2,4-isomer in TMB is the equilibrium value. $S = 100$ means that its fraction is 100%.

Table 1 shows the initial activity (y_0) and selectivity at $y = 20\%$ (S_{20}) for *m*-xylene disproportionation over various catalysts [Me(20)–H(68)-M], which were prepared by the conventional cation-exchange method and whose cation-exchange degree was 20%.

H-M itself has a low selectivity ($S_{20} = 8\%$) and the highest activity. By a small cation (Be^{2+}), the selectivity was not increased and the activity was dropped. By a large cation (Ca^{2+}, Sr^{2+}, or Ba^{2+}) the selectivity was still not increased and the activity was remarkably dropped. In the case of H-M partially exchanged by a small cation, its effective pore dimension is large enough to freely desorb any TMB. So, the catalyst has the similar selectivity to that of H-M. In the case of the catalyst exchanged by a large cation, xylene or produced TMB is inhibited in sorbing into or desorbing from the channel, and/or these alkali earth cations reduce the acidity of the catalysts. So, the catalyst has a low activity. The catalyst exchanged by a moderate cation (especially Cu–H-M, Zn–H-M) has a moderate activity and a high selectivity. Thus the effective pore dimension of H-M can be controlled by the partially exchanged cation. Especially, the catalysts exchanged by Cu^{2+} or Zn^{2+} cation are well controlled and have the highest selectivity.

The effects of reaction temperature, calcination temperature, and W/F on activity and selectivity were studied, using Cu(25)–H(63)-M catalyst. Table 2 shows the effect of reaction temperature. In a temperature range higher than 623°K, the selectivity decreased with the increase of reaction temperature and dealkylation was observed. These results are explained in terms of the great thermal vibration of cations and oxygen atoms surrounding the apertures and the great mobility of the reaction products. These thermal behaviors of molecules prevent the molecular sieving effect of the catalyst at a high temperature. However, the catalyst has a little selectivity even at 773°K. At a temperature up to 573°K, the effect of reaction temperature on selectivity is scarcely observed. Table 3 shows the effect of calcination temperature. Activity and selectivity reach the maxima at 873°K. Table 4 shows the effect of W/F. The selectivity decreased with the increase

TABLE 2

Effect of Reaction Temperature[a]
[Catalyst: Cu(25)–H(63)-M]

Reaction temperature (°K)	Activity y_0 (%)	Selectivity S_{20} (%)
523	15	35[b]
573	20	33
623	27	25
673	29	17
773	31	7

[a] Reaction conditions: calcination, 873°K; W/F, 100 g-hr/mole.

[b] Estimated by extrapolation of curved S vs y plot.

of W/F, while the activity increased with the increase of W/F. However, W/F slightly affected the selectivity.

From these results, we set up the standard reaction condition, i.e., calcination temperature was 873°K, reaction temperature was 573°K, and W/F was 100 g-hr/mole. Table 5 shows the effect of cation-exchange degree under the standard reaction condition using Cu-H-M catalyst. The activity decreased with the increase of the cation-exchange degree. While, in a region less than 16%, the higher cation-exchange degree provided the higher selectivity. The selectivity reached a constant in the region above 16%. So, the most effective cation-exchange degree is 16 ~ 20% in the case of the conventional Cu^{2+} exchange.

By the partially exchanged cation, the pore dimension of H-M can be controlled and the cation with a suitable ionic radius makes selectivity higher. However, a significant drop in activity is observed by this cation exchange, probably because the exchanged cations kill the active sites which are perhaps strong Brönsted acid. To avoid the drop in activity, the rapid cation exchange was tried. It was expected that most of metal cations could be located near the pore entrances and the exchanged cation could control the pore dimension more effectively and would kill less active sites.

Table 6 shows the results on the disproportionation of *m*-xylene over the rapidly exchanged H(96)-M by Cu^{2+} [Cu-H-MR (R indicates the rapid method)]. The reaction was carried out over the catalysts having various degrees of cation-exchange under the standard condition except W/F. It was cut down to 15 g-hr/mole, because these catalysts had higher activities than those of the conventionally cation-exchanged H(88)-M. The drop in activity by the exchanged cation was scarcely observed, probably because of the low cation exchange degree. The selectivity increased with the cation exchange degree and at 5.5% reached the same level as that of the conventionally prepared Cu(20)-H-M (cf.

TABLE 4

Effect of W/F[a] [Catalyst: Cu(25)-H(63)-M]

W/F (g-hr/mole)	Activity y_0 (%)	Selectivity S_{20} (%)
30	7	37
50	14	36
100	20	33
150	29	32

[a] Reaction conditions: calcination, 873°K; reaction temperature, 573°K.

TABLE 3

Effect of Calcination Temperature[a] [Catalyst: Cu(25)-H(63)-M]

Calcination temperature (°K)	Activity y_0 (%)	Selectivity S_{20} (%)[b]
673	17	22
773	18	29
873	20	33
973	12	25

[a] Reaction conditions: reaction temperature, 573°K; W/F, 100 g-hr/mole.

[b] Estimated by extrapolation of curved S vs y plot.

TABLE 5

Effect of Cation Exchange Degree (Catalyst: Cu-H-M)

Cation exchange degree (%)	Activity y_0 (%)	Selectivity S_{20} (%)
0	49	8
10	41	19
13	38	24
16	37	31
20	26	33
25	20	33
27	17	33

TABLE 6

Disproportionation of *m*-Xylene over Cu-H-MR[a]

Catalyst	Activity y_0 (%)	Selectivity S_{20} (%)
H(96)-M	37	16
Cu(0.7)-H(95)-MR	35	22
Cu(2.7)-H(93)-MR	35	33
Cu(5.5)-H(91)-MR	34	39

[a] Reaction conditions: calcination, 873°K; reaction temperature, 573°K; W/F, 15 g-hr/mole.

Table 5). Thus, the rapid cation exchange is very effective in controlling the pore dimension and provides a high selectivity without a drop in activity.

In every run made in this work, the disproportionation activity declined rapidly from the initial level with process time (e.g., Fig. 1). The effect of the regeneration on the activity and the selectivity was studied on Cu(2.7)-H(93)-MR. The regeneration was carried out at 723°K for 1.5 hr in air stream. The catalyst was regenerated twice. However, neither activity nor selectivity changed within experimental error ($y_0 = 35 \rightarrow 37 \rightarrow 38$, $S_{20} = 33 \rightarrow 32 \rightarrow 32$). Consequently, Cu cations located at the pore entrances hardly move to the interior after regenerations.

It is expected that there will be a significant difference in activity for 1,3,5-TMB disproportionation over Cu(5.5)-H(91)-MR and H(96)-M in spite of no difference in activity for *m*-xylene disproportionation. That is, Cu(5.5)-H(91)-MR will have less activity for 1,3,5-TMB disproportionation than H(96)-M. Figure 3 shows the activities of these catalysts for this reaction and the isomerization of 1,3,5-TMB. The activities of H(96)-M for the disproportionation and the isomerization were 2 and 1.5 times, respectively, as much as those of Cu(5.5)-H(91)-MR through the run. It is concluded that the shape-selectivity of Cu-H-MR catalyst is not for xylene but for TMB.

Kasai and Bishop have reported that about a half of Cu^{2+} in mordenite is reduced to Cu^{+} by evacuation at 573°K (7). So, it was suggested that Cu^{2+} in H-M would be reduced to Cu^{+} through the pretreatment (calcination at 873°K in N_2). To check this reduction, ESR study was carried out for the sample of Cu(5.5)-H(91)-MR before and after the pretreatment, using JEOL X-band ESR spectrometer (JES-PE-1X) with 100-kHz magnetic modulation. The ESR signal of Cu^{2+} decreased through the pretreatment and showed that more than 90% of Cu^{2+} was reduced. Therefore, the pore dimension of H-M is controlled not by Cu^{2+} but by Cu^{+}.

Several cations, of which ionic radii are comparable to that of Cu^{+} (0.096 nm), were applied to control the pore dimension by the rapid method. The results are summarized in Table 7. In the case of Zn^{2+}, at 10.7% of cation-exchange degree the selectivity reached the same level as that of Zn(20)-H(68)-M with only a small drop

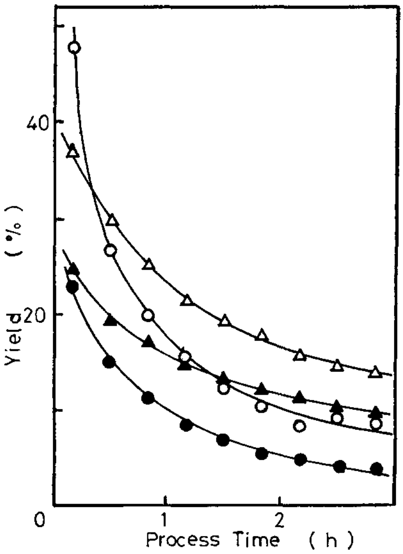

FIG. 3. Conversion of 1,3,5-TMB over H(96)-M and Cu(5.5)-H(91)-MR. Reaction conditions were the same as in Table 6. (○) Yield of xylene over H-M, (●) yield of xylene over Cu-H-MR, (△) yield of 1,2,3- and 1,2,4-TMB over H-M, (▲) yield of 1,2,3- and 1,2,4-TMB over Cu-H-MR.

in activity. The rapid method is effective in this case as well as in the case of Cu^{2+}. Cd–H-MR has a high selectivity, because the ionic radius of Cd^{2+} was almost same as that of Cu^{+}. However, at 4.6% of exchange degree the selectivity was not high enough and at 13.1% the activity drop was observed. The selectivity of Ca–H-MR was higher than that of H-M or Ca(20)–H(68)-M and lower than those of the others in Table 7. The reason why Ca(11.2)–H(85)-MR had a higher selectivity than the Ca(20)–H(68)-M prepared by the conventional method is not clear. The ionic radius of Ca^{2+} might be too large for the reaction (see Table 1). Perhaps Ca^{2+} in Ca–H-MR was not localized near the pore entrances and existed sparsely in the pore, because it took the longest time (30 min) to exchange Ca^{2+}.

In all catalysts examined in this paper, Cu(5.5)–H(91)-MR, which was prepared by the rapid cation exchange, shows the highest selectivity with a high activity. So, it is concluded that Cu^{+} has the most desirable ionic radius for the selective formation of 1,2,4-TMB in xylene disproportionation and that the rapid cation exchange is very effective. The exchanged cation except for Ca^{2+} is localized near the pore entrances of H-M, because a small amount of cation controlled the pore dimension and the drop in activity by the cation exchange was scarcely observed. To confirm the localization of the cation, the following experiments were carried out. Pure water (50 ml) was added to the catalyst (0.5 g) and the mixture was kept at 343°K for the desired time. Then, it was evaporated to dryness on a water bath. The activity and the selectivity of the catalyst so treated were measured. The results are shown in Table 8. In the case of Cu–H-MR, the water treatment for 3 hr did not affect the activity and the selectivity, while the water treatment for 5 days lowered the selectivity with only a small drop in activity. In the case of Zn–H-MR, the water treatment for 5 days also lowered the selectivity with only a small drop in activity. These facts mean that the cation localized near the pore entrances migrates to the deeper part of the pore and begins to disperse uniformly by the water treatment and that the migration of the cation is quite slow, probably because of the absence of a counterpart ion in the liquid phase.

TABLE 7

Disproportionation of *m*-xylene over Various Catalysts Prepared by Rapid Method[a]

Catalyst	Ionic radius (nm)	Activity y_0 (%)	Selectivity S_{20} (%)
H(96)-M	—	37	16
Zn(3.2)–H(93)-MR	0.074	33	25
Zn(10.7)–H(85)-MR		32	36
Cu(5.5)–H(91)-MR	0.096	34	39
Cd(4.6)–H(92)-MR	0.097	32	28
Cd(13.1)–H(83)-MR		23	37
Ca(11.2)–H(85)-MR	0.099	29	28

[a] Reaction conditions were the same as in Table 6.

TABLE 8

Effect of Water Treatment[a]

Catalyst	Treatment	Activity y_0 (%)	Selectivity S_{20} (%)
Cu(5.5)–H(91)-MR	None	34	39
	3 hr	35	38
	5 days	31	30
Zn(10.7)–H(85)-MR	None	32	36
	5 days	30	26

[a] Reaction conditions were the same as in Table 6.

Csicsery has reported beautiful works on the shape-selective disproportionation of methylethylbenzene over H-M (*3*, *8*). The disproportionation to form 1,3,5-trialkylbenzene over H-M is inhibited because there is not enough space to form the large 1,1-diphenylalkane-type intermediate. Transition states leading to the other trialkylbenzene isomers are relatively smaller, and, therefore, their formation is uninhibited. On the other hand, disproportionation and isomerization of 1,3,5-TMB over H-M proceed similarly to those of 1,2,3-

TMB. Consequently, the diffusion of 1,3,5-TMB is not seriously inhibited in H-M.

In the disproportionation of xylene, H-M has a slight selectivity at low yield of TMB. The formation of 1,3,5-TMB is slightly inhibited, because the transition state leading to 1,3,5-isomer requires more space than is available as in the disproportionation of methylethylbenzene reported by Csicsery. On the other hand, Me–H-M has the high selectivity. The partial cation exchange reduces the effective pore dimension, which affects not only the transition state leading to 1,3,5-TMB but also the diffusion of 1,3,5-TMB because of the following two facts: (i) The rapid cation-exchange method, by which the cation is localized near the pore entrances, is very effective. (ii) The activities of not only disproportionation but also isomerization in 1,3,5-TMB conversion over Cu–H-MR are lower than those over H-M (Fig. 3).

CONCLUSION

The effective pore dimension of H-M can be controlled by the partially exchanged cation.

H-M catalyst has a slight selectivity for the selective formation of 1,2,4-TMB in the disproportionation of xylene, while the partially exchanged H-M by the cation with a suitable ionic radius has a high selectivity, not only because there is not enough space to form the transition state leading to 1,3,5-TMB, but also because the diffusion of 1,3,5-TMB is inhibited.

The most suitable cation is Cu^+ whose ionic radius is 0.096 nm.

The rapid cation exchange is more effective than the conventional one, because a smaller amount of cation controls the pore dimension and provides a high selectivity without drop in activity.

REFERENCES

1. Yashima, T., Moslehi, H., and Hara, N., *Bull. Japan Petrol. Inst.* **12**, 106 (1970).
2. Yashima, T., and Hara, N., *J. Catal.* **27**, 329 (1972).
3. Csicsery, S. M., *J. Catal.* **19**, 394 (1970).
4. Yashima, T., Iwase, O., and Hara, N., *Chem. Lett.* **1975**, 1215.
5. Hastings, S. H., and Nicholson, D. E., *J. Chem. Eng. Data* **6**, 1 (1961).
6. "Table of Selected Value of Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Thermodynamics Research Center, Texas A & M University, College Station, Texas, 1977.
7. Kasai, P. H., and Bishop, R. J., Jr., *J. Phys. Chem.* **81**, 1527 (1977).
8. Csicsery, S. M., *J. Catal.* **23**, 124 (1971).