in the gas phase, and a Langmuir isotherm for gas mixtures to describe adsorption of these species during reaction (3), leads to a pressure dependence of the reaction rate other than that observed. This discrepancy probably arises from the irreversibility of the dissociation of adsorbed HCOOH. We prefer, therefore, to discuss the results in terms of published reaction mechanisms.

The good fit over the whole range of pressures we interpret as indicating the same rate-determining step throughout. At low pressures the order of the reaction tends to 0.5. This makes a bimolecular surface reaction unlikely (*4*, *5*), but the following scheme (*6*):

$$\mathrm{HCOOH(g)} + {*} \rightleftharpoons \underset{*}{\mathrm{HCOOH}}; \qquad \text{(a)}$$

$$\underset{*}{\mathrm{HCOOH}} \rightarrow \underset{*}{\mathrm{HCOO}} + \underset{*}{\mathrm{H}}; \qquad \text{(b)}$$

$$\underset{*}{\mathrm{HCOO}} \rightarrow \mathrm{CO_2(g)} + \underset{*}{\mathrm{H}}; \qquad \text{(c)}$$

$$\underset{*}{\mathrm{H}} + \underset{*}{\mathrm{H}} \rightarrow \mathrm{H_2(g)} \qquad \text{(d)}$$

can account for the pressure dependence of the reaction. In the above scheme, step (c) has been postulated to be rate-determining (*1*, *7*), i.e.,

$$r = k_r\theta_{\mathrm{HCOO}}.$$

If this is the case, and (i) the equilibria (a) and (b) are not appreciably disturbed, (ii) if $\theta_{\mathrm{HCOO}} \approx \theta_{\mathrm{H}} \ll \theta_{\mathrm{HCOOH}}$ so that $\theta_{\mathrm{HCOOH}} = (1/K_d)\theta_{\mathrm{HCOO}}{}^2$, then

$$r = k_rK_d{}^{1/2}\theta_{\mathrm{HCOOH}}{}^{1/2},$$

and substitution from (2) gives

$$r = k_rK_d{}^{1/2}[bp/(1 + bp)]^{1/2},$$

which is Eq. (3) with $k_0 = k_rK_d{}^{1/2}$ and $y = 0.5$, i.e., close to y_m.

REFERENCES

1. Bagg, J., Jaeger, H., and Sanders, J. V., *J. Catal.* **2,** 449 (1963).
2. Tamaru, K., *Trans. Faraday Soc.* **55,** 824 (1959).
3. Kemball, C., *Discuss. Faraday Soc.* **41,** 190 (1966).
4. Hirota, K., Kuwata, K., and Nakai, Y., *Bull. Chem. Soc. Jap.* **31,** 861 (1958).
5. Lawson, A., *J. Catal.* **11,** 295 (1968).
6. Sachtler, W. M. H., and Fahrenfort, J., *Actes Congr. Int. Catal. 2nd 1960* **1,** 831 (1961).
7. Hirota, K., and Otaki, T., *Nippon Kagaku Zasshi* **79,** 1288 (1958).

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Infrared Study of Cation-Exchanged Mordenites and Y Faujasites Adsorbed with Ammonia and Pyridine

Many reactions over synthetic zeolites as an excellent solid acid catalyst have been studied. In some cases, it has been found that the catalyst activity and the distribution of the reaction products depended on the geometric relation between the zeolite pore system and the molecular shape (*1*, *2*). Disproportionation of alkylbenzenes over synthetic zeolites has often been studied (*3*–*8*), and in the case of disproportionation of ethyltoluenes over H mordenite catalyst, it has been shown that the distribution of produced trialkylbenzenes was affected by the pore size of the catalyst (*7*, *8*).

The authors have also reported previously on the vapor phase disproportionation

TABLE 1

ACTIVITY OF VARIOUS CATION-EXCHANGED ZEOLITES IN DISPROPORTIONATION OF TOLUENE

	Ionic radius (Å)	% Exchanged	Conversion (mol %)	Yield[a] (mol %)		
				B	X	TMP[b]
HZ	—	93	57	43	42	5
BeZ	0.31	72	28	20	21	Tr
MgZ	0.65	84	Tr[c]	Tr	Tr	0
CaZ	0.99	85	0	0	0	0
CdZ	0.97	73	0	0	0	0
CeZ	1.12	79	15	4	4	0
HY	—	81	35	28	31	2
BeY	0.31	83	20	16	17	1
CaY	0.99	86	4	3	3	0
CeY	1.12	84	32	29	30	2

[a] Reaction conditions: Temperature: 400°C, W/F: 90 g·hr/mol, carrier gas: N_2 (N_2/toluene = 5/1 mol/mol). The yield listed in Table 1 is based on 2 moles of fed toluene and is taken at the highest yield on process time.

[b] B: benzene, X: xylenes and TMB: trimethylbenzenes.

[c] Tr = Trace.

of toluene over various cation exchanged mordenites and Y faujasites, and Table 1 shows the main results (*6*). It is shown that H mordenite (HZ) is the most active catalyst and divalent cation-exchanged mordenites show almost no activity, with the exception of Be which has an ionic radius of only 0.3 Å. Ce mordenite (CeZ) has a smaller activity than Be mordenite (BeZ), while Ce faujasite (CeY), shows a comparable activity to H faujasite (HY). However, it has been found that divalent cation-exchanged mordenites have a fair catalytic activity in dehydration of ethanol (*9*) and cracking of *n*-paraffins (*10*). Such selectivity based on the kind of exchanged cation might be explained by a hypothesis that the exchanged cations narrow the effective pore radius of the mordenite, and hinder a relatively large molecule, such as alkylbenzenes, from diffusing into the channel.

In order to prove this hypothesis, the interaction between the acid sites of these zeolites and ammonia, which has a small molecular dimension, or pyridine, which has a similar molecular size to the benzene ring, was measured by ir method.

All infrared measurements were made with the cation-exchanged mordenites (based on Na Zeolon) and Y faujasites (SK-40) in the form of self-supporting wafers prepared by pressing 20 mg of fine powder (dried at 110°C 48 hr) in a 20-mm diam die at 400 kg/cm^2. The wafers were electrically heated at 500°C for 1 hr while evacuated in the infrared cell. After calcination, the wafers were exposed to ammonia vapor under 40 Torr pressure at room temperature for 30 min, and were evacuated at 100°C for 1 hr, or they were exposed to pyridine vapor under 15 Torr pressure at 100°C for 30 min, and were evacuated at 200°C for 1 hr. The spectra of the wafers were recorded at room temperature.

The ir spectra of H-, Be-, Ce- and Ca-exchanged zeolites were measured. These profiles on H and Ce zeolites were shown in Figs. 1 and 2, respectively.

In the adsorption of ammonia, a strong broad absorption band at 1450 cm^{-1}, which is formed by the interaction between ammonia and Brönsted acid sites (*11*), was observed on each zeolite. Moreover, the absorbance of the ammonium ion on these mordenites (H, Be, Ce and Ca) was similar to that on the corresponding faujasites. These results suggested that cation-exchanged mordenites had a similar Brönsted acidity to the corresponding Y faujasites.

In the case of pyridine adsorption, the

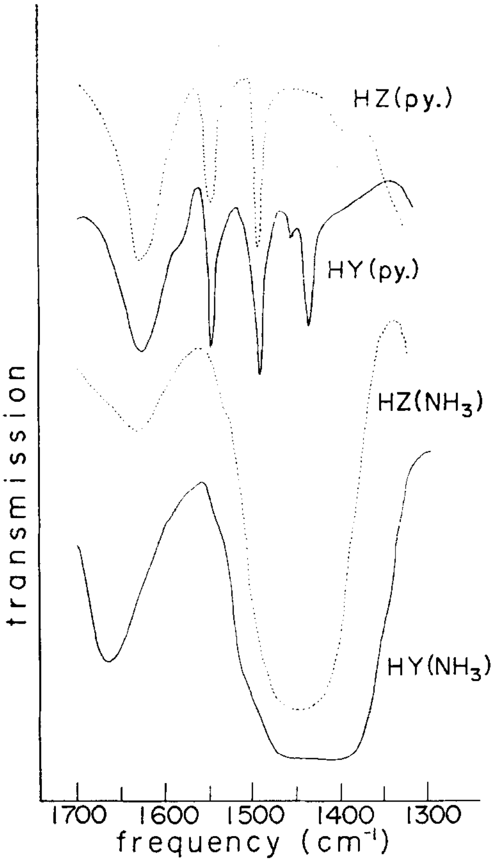

FIG. 1. Infrared spectra of pyridine and ammonia adsorbed on HZ and HY.

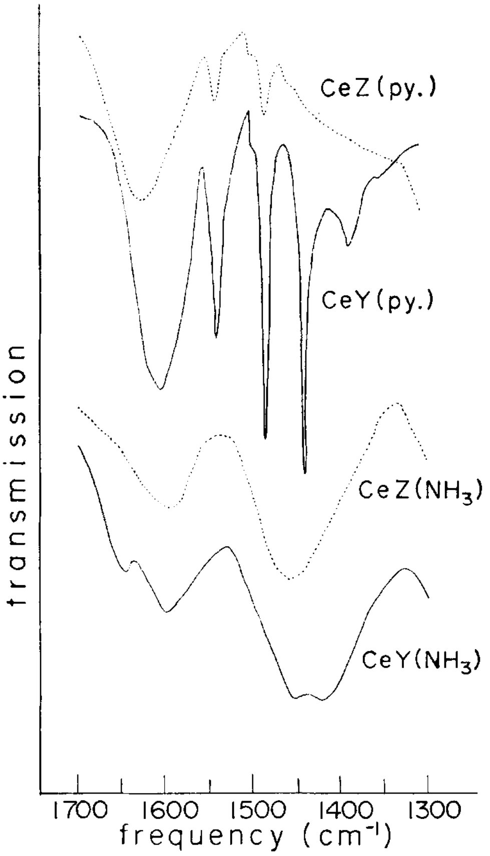

FIG. 2. Infrared spectra of pyridine and ammonia adsorbed on CeZ and CeY.

main three peaks, which were formed by the interaction between pyridine and the acid sites of zeolites at 1445 (Lewis acid site), 1490 (Brönsted and Lewis acid sites) and 1540 cm^{-1} (Brönsted acid site), were observed on each Y faujasite. On HZ and BeZ, the absorbances at 1490 and 1540 cm^{-1} were comparable to those on HY and BeY, respectively. However, the absorption band at 1445 cm^{-1} did not appear on HZ and BeZ. These results showed that the Brönsted acid sites on HZ and BeZ did not convert to Lewis acid sites under heating at 500°C, and that a Brönsted acid site of cation-exchanged mordenite was more stable toward dehydration to a Lewis acid site than the corresponding cation-exchanged faujasite. On the other hand, on CeZ and CaZ, the absorbances at these bands were much smaller than those on CeY and CaY, and these absorbances on CaZ were still smaller than those on CeZ. These phenomena suggested that pyridine was restrained from diffusing to the acid sites in the channel of CeZ and CaZ, and they corresponded to the small activity of these catalysts in disproportionation of toluene. It was proved that the effective pore radius of metal cation exchanged mordenite was smaller than that of proton-exchanged mordenite. Compared with CaZ (ionic radius of Ca 0.99 Å), CeZ (ionic radius of Ce 1.1 Å) had more activity and more sites possible to interact with pyridine. These results could be explained by two reasons. One is that a trivalent cation (Ce^{3+}) produces stronger Brönsted acid sites in a zeolite framework than a divalent cation (Ca^{2+}), and another is that the number of trivalent cation would be less in the mor-

TABLE 2
REACTION OF *o*-XYLENE OVER CATION-EXCHANGED MORDENITES[a]

Catalyst	HZ		BeZ		CeZ		CaZ
Reaction temperature (°C)	250	300	250	300	250	300	300
Product composition (mol%)							
Benzene	0.78	2.52		0.14			
Toluene	18.12	24.51	0.10	0.80	0.04	0.10	
Xylenes	61.23	41.73	98.63	96.55	98.83	98.10	99.01
Trimethylbenzenes	18.53	25.61		0.60		0.11	
Tetramethylbenzenes		2.65					
Gas + residue	1.29	2.98	1.27	1.91	1.13	1.69	0.99
Isomer distribution (%)							
Xylene							
o-	21.5	22.2	98.2	73.7	99.94	99.61	99.96
m-	54.8	54.9	1.7	21.8	0.06	0.39	0.04
p-	23.7	22.9	0.1	4.5			
Trimethylbenzene							
1,3,5-		33.9		3.3		2	
1,2,4-		60.0		91.7		95	
1,2,3-		6.1		5.0		3	

[a] Reaction conditions; W/F: 90 g·hr/mol, carrier gas: N_2 (N_2/xylene = 5/1 mol/mol). The listed value in Table 2 is taken at the highest conversion of *o*-xylene on process time.

denite framework than that of divalent cation, and therefore, on the trivalent cation-exchanged mordenite, toluene would be less hindered from diffusing into the channel than on the divalent cation-exchanged mordenite.

Recently, Csicsery (*8*) discussed the points that in disproportionation of alkylbenzenes over HZ, the shape selectivity of the products depended on the geometric relation between the pore system and diphenylmethane-type intermediate. Therefore, the disproportionation of toluene over metal cation exchanged mordenites may also depend on the effect between the pore system and the intermediate. In order to make this possibility clear, isomerization of *ortho*-xylene, which is regarded as a monomolecular reaction, over various cation-exchanged mordenites was studied. The results were shown in Table 2. The catalytic activity of each cation-exchanged mordenite in isomerization of *ortho*-xylene showed a similar tendency to that in disproportionation of toluene. It was found that the isomerization over HZ and BeZ proceeded readily, but only very slowly, over CeZ and CaZ. These results suggested that the selective activity of cation-exchanged mordenites in disproportionation of toluene did not depend on the geometric effect between the pore system of mordenite and any intermediate, but on the effect that the diffusion of a raw material into the channel was prevented by the exchanged cation.

From these results, it was concluded that the exchanged cation narrowed the effective pore radius by sticking out from the channel walls of mordenite, and on the mordenite catalyst exchanged by a cation which had the relatively large ionic radius, toluene molecules were hindered from diffusing to the active sites in the channel, resulting in little activity in the disproportionation reaction.

REFERENCES

1. YASHIMA, T., AHMAD, H., YAMAZAKI, K., KATSUTA, M., AND HARA, N., *J. Catal.* **16**, 273 (1970).
2. YASHIMA, T., YAMAZAKI, K., AHMAD, H., KATSUTA, M., AND HARA, N., *J. Catal.* **17**, 151 (1970).
3. BENESI, H. A., *J. Catal.* **8**, 368 (1967).
4. MORITA, Y., AND MATSUMOTO, Y., *Kogyo Kagaku Zasshi* **70**, 1363 (1967).
5. WARD, J. W., *J. Catal.* **10**, 34 (1968).

6. Yashima, T., Moslehi, H., and Hara, N., *Bull. Japan Petrol. Inst.* **12**, 106 (1970).
7. Csicsery, S. M., *J. Catal.* **19**, 394 (1970).
8. Csicsery, S. M., *J. Catal.* **23**, 124 (1971).
9. Bryant, D. E., and Kranich, W. L., *J. Catal.* **8**, 8 (1967).
10. Keough, A. H., *Amer. Chem. Soc.*, Div. Petrol. Chem., Los Angeles Meeting, Preprints **8**, (1), 65 (1963).
11. Eischens, R. P., and Pliskin, W. A., "Advances in Catalysis," Vol. 10. Academic Press, New York, 1958. p. 28.

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