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Type L Zeolites as Selective Catalysts for the Ring Transformation of Cyclic Ethers into Cyclic Imines

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Type L zeolites were found to be highly selective catalysts for the ring transformation of cyclic ethers into cyclic imines. With use of the hydrogen form (HL), pyrrolidine was obtained in a 56% yield with the selectivity of 90% at 350°C by the reaction of tetrahydrofuran and ammonia. There is no sign of catalyst deactivation within 8 hr. Kinetic study revealed that the reaction rate was the first order with respect to partial pressure of ammonia and was independent of partial pressure of tetrahydrofuran. The influences of decationation and the kinds of metal cations in the zeolite on the catalytic behavior were examined, and the reaction mechanism and the origin of high selectivity were discussed. Type L zeolites are also effective catalysts for the conversion of tetrahydropyran into piperidine.

INTRODUCTION

The ring transformation of cyclic ethers by their reaction with ammonia gives a conveneient route to the synthesis of cyclic imines.

(1)

However, studies of this type of reaction are scarce. Since an old work by Yur'ev and Prokina (*1*), only a few works have been reported on the conversion of tetrahydrofuran (THF) into pyrrolidine (*2–5*). In these works, alumina or modified alumina was used as a catalyst, but the slectivity for the ring conversion was generally low. Recently, Fujita *et al.* (*6,7*) reported that, by using the hydrogen form of Type Y zeolite (HY) as a catalyst, a selectivity of 80% could be attained. Now, we report that the hydrogen form of Type L zeolite (HL) is a more selective catalyst than HY for the ring conversion of THF into pyrrolidine and also for the conversion of tetrahydropyran (THP) into piperidine.

A great number of works have been devoted to the zeolite catalysis, but the works on the catalytic properties of L-type zeolites are still few (*8–10*). Therefore, it seems of interest to investigate the catalytic behavior of Type L zeolite for these novel reactions and to compare the results with those obtained for other types of zeolites, such as Type Y zeolites.

EXPERIMENTAL

A potassium form of Type L zeolite was obtained from Strem Chemical Co. The various cation-exchanged forms were prepared by a conventional ion-exchange procedure using chloride salt solutions. The degree of cation exchange was determined by analysis for eluted potassium ions using flame photometry.

The reaction of THF (or THP) and ammonia was carried out in a reactor of fixed bed type with a continuous flow system at an atmospheric pressure. The reactor was a 13 mm i.d. silica tubing placed in a vertical furnace. Prior to the reaction, the catalyst was heated in an air stream at 460°C for 2 hr. The details of the reaction procedures have been described elsewhere (7).

THF and THP were obtained from Wako Pure Chemicals and distilled just before every run. The presence of the peroxy species as an impurity significantly lowered the selectivity for pyrrolidine or piperidine. Ammonia from a commercial cyclinder was passed through a sodium hydroxide column before entering the reactor.

The main product separated by fractional distillation was confirmed to be pyrrolidine since the infrared spectra agreed with those of authentic materials. The identification of by-products was not attempted. The reaction products were analyzed by a gas chromatograph with a hydrogen flame ionization detector.

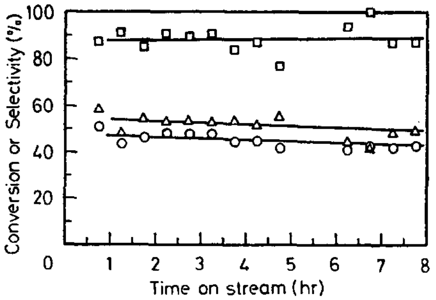

FIG. 1. Variation of the conversion of THF (△), the yield pyrrolidine (○), and the selectivity for pyrrolidine (□) with time on stream.

The conversion of THF (or THP), the yield of pyrrolidine (or piperidine), and the selectivity of the reaction are defined as follows.

$$\text{Conversion (\%)} = \frac{\text{moles of THF (or THP) reacted}}{\text{moles of THF (or THP) fed}} \times 100,$$

$$\text{Yield (\%)} = \frac{\text{moles of pyrrolidine (or piperidine) produced}}{\text{moles of THF (or THP) fed}} \times 100,$$

$$\text{Selectivity} = \frac{\text{moles of pyrrolidine (or piperidine) produced}}{\text{moles of THF (or THP) reacted}} \times 100.$$

RESULTS

Time course of the reaction. Figure 1 shows a typical time course of the reaction of THF into pyrrolidine with HL (35%). The reaction conditions are: reaction temperature, 350°C; catalyst weight, 1.5 g; reactant ratio, ammonia/THF = 7; W/F = 8.43 g-cat·hr·mol^{-1}. In these reaction conditions, a pyrrolidine yield of 45% with a selectivity as high as 90% was obtained. Moreover, there is no deactivation of the catalyst within 8 hr.

The results are compared with those with HY and other solid acid catalysts (Table 1). The selectivity value of 90% for HL is much higher than the value obtained for HY, while the yield of pyrrolidine is almost the same with both catalysts. Thus, it can be concluded that the HL is a very effective catalyst for the ring transformation of THF into pyrrolidine.

Effect of reaction temperature. Investigation of the influence of the reaction temperature on the catalytic properties of HL (25%) was carried out under the conditions: catalyst weight, 3 g; reactant ratio, ammonia/THF = 7; W/F = 16.7 g-cat·hr·mol^{-1}. The results are illustrated in Fig. 2. The total conversion of THF monotonously increases with the reaction temperature, while the yield of pyrrolidine increases with the reaction temperature up

TABLE 1

Catalyst used	THF → pyrrolidine[a]			THP → piperidine[b]		
	Conversion (%)	Yield (%)	Selectivity (%)	Conversion (%)	Yield (%)	Selectivity (%)
HL	53	49	91	24	14	58
HY	61	50	82	15	5	33
H-Mordenite	25	12	48	11	0	0
SiO_2–Al_2O_3 (83:17)	86	36	42	43	18	42
Activated alumina	92	54	58	60	18	30

[a] Reaction conditions: 350°C, $NH_3/THF = 7$, $W/F = 8.43$ g-cat·hr·mol^{-1}.
[b] Reaction conditions: 350°C, $NH_3/THP = 7$, $W/F = 20.8$ g-cat·hr·mol^{-1}.

to 350°C, but sharply falls down at higher temperatures. Thus, the optimum reaction temperature range lies around 350°C.

Effect of contact time. The effect of contact time was investigated at 335, 350, and 370°C by changing the catalyst weight (0.5–3 g), and keeping the total feed constant. At low W/F, the yield of pyrrolidine was higher at higher temperatures, but at high W/F, the yield is larger at 350 than at 370°C, indicating that the pyrrolidine once formed undergoes the further reaction at the higher temperature. At 350°C with $W/F = 16.9$ g-cat·hr·mol^{-1}, the pyrrolidine yield of 56% was obtained as described in the previous section (see Fig. 3).

Kinetics of the reaction. The reaction kinetics were examined in the temperature range of 310–370°C in a low W/F condition ($W/F = 2.81$ g-cat·hr·mol^{-1}). The total flow rate was kept constant by compensating the change in the partial pressure of one of the reactants by changing the partial pressure of nitrogen. In Fig. 4, the effect of the partial pressure of ammonia (P_{NH_3}) on the reaction rate is shown. It is clear that the reaction rate is of first order with respect to the partial pressure of ammonia.

Figure 5 displays the dependence of the rate on the partial pressure of THF (P_{THF}). The rate depends markedly on P_{THF} when P_{THF} is below 0.1 atm, but is almost independent of P_{THF} above 0.15 atm. Thus, the rate (r; mol·hr^{-1}·g-cat^{-1}), when $P_{THF} > 0.15$ atm, is expressed as

$$r = k \cdot P_{NH_3}. \qquad (2)$$

The values of the first-order rate constant, k, are calculated from the slope of Fig. 4 and are listed in Table 2. From the dependence of k on the reaction temperature,

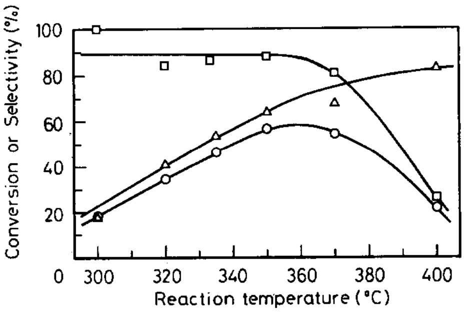

FIG. 2. Variation of the conversion of THF (△), the yield of pyrrolidine (○), and the selectivity for pyrrolidine (□) with reaction temperature.

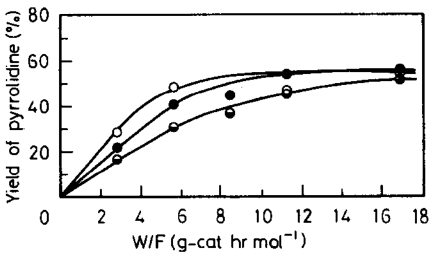

FIG. 3. Effect of contact time on the catalytic property. (◒), 335°C; (●), 350°C; (○), 370°C; reactant ratio, ammonia/THF = 7.

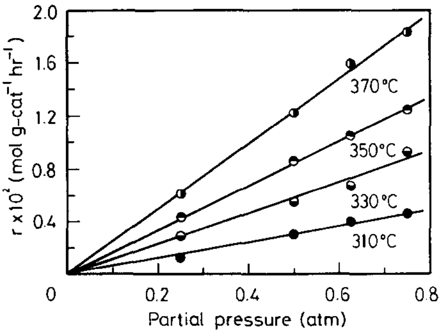

FIG. 4. The dependence of reaction rate on the partial pressure of ammonia. $P_{THF} = 0.25$ atm.

TABLE 2

Value of Rate Constant, k

Temperature (°C)	k (mol·g-cat^{-1}·hr^{-1}·atm^{-1})	
	HL	HY
310	0.61×10^{-2}	1.01×10^{-2} (320°C)
330	1.16×10^{-2}	1.39×10^{-2} (335°C)
350	1.69×10^{-2}	2.05×10^{-2}
370	2.48×10^{-2}	

the activation energy was estimated at 17 ± 1 kcal/mol.

Effect of decationization. A series of NH_4L zeolites with various degree of cation exchange of K^+ with NH_4^+ were prepared and their catalytic behavior for the ring transformation of THF was examined at 350°C for two different W/F. The results are shown in Fig. 6. The catalytic activity of NH_4L hardly depends on the degree of the exchange when the latter is beyond 10%. Exactly the same trend was observed at 335°C.

Effect of the cation species in Type L zeolites. The effect of the cation form of Type L zeolites on the catalytic properties was examined under the reaction conditions: reaction temperature, 350°C; catalyst weight, 1.5 g; reactant ratio, ammonia/THF = 7; $W/F = 8.43$ g-cat·hr·mol^{-1}. The conversion of THF, the yield of pyrrolidine, and the selectivity for pyrrolidine for various catalysts are summarized in Table 3. It is seen that the best catalyst is HL, followed by MgL and CeL. This feature of the influence of the cation species in Type L zeolite on the catalytic activity is same as that in the case of Type Y zeolites (*7*).

Conversion of THP into piperidine. Ring transformation of THP into piperidine has never been reported, except for one patent (*3*), which used alumina as a catalyst. This reaction was also studied with several acidic catalysts and the results are listed in Table 1. Again HL gave the best selectivity for piperidine among the catalysts studied.

DISCUSSION

Reaction mechanism. Since NH_4L has the best activity among the cation-exchanged Type L zeolites (Table 3), the activity for the ring transformation is expected to be

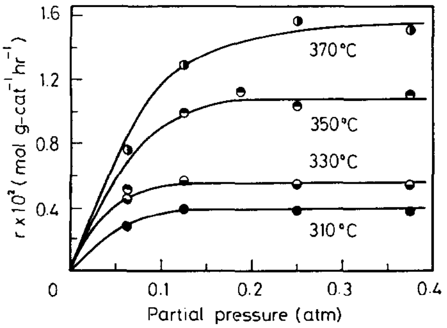

FIG. 5. The dependence of reaction rate on the partial pressure of THF. $P_{NH_3} = 0.625$ atm.

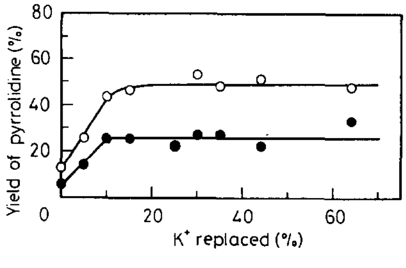

FIG. 6. Effect of decationization of KL with NH_4^+ on the catalytic behavior. (○), $W/F = 8.43$ g-cat·hr·mol^{-1}; (●), 2.81 g-cat·hr·mol^{-1}; reactant ratio, ammonia/THF = 7.

acidic sites. At the temperature of the pretreatment of this work (460°C), NH_4L is considered to be transformed into HL. It was confirmed that the transformation of NH_4L into HL is complete at 350°C and that the dehydroxylation of HL occurs above 500°C, by studying the influence of the calcination temperature of NH_4L on its catalytic activity for cracking of cumene (*11*), which is established as catalyzed by Brönsted acid sites (*12*). Thus, active sites for the reaction are concluded to be Brönsted acid sites. This is also supported by the dependence of the catalytic activity on the cation species in Type L zeolites. Table 3 shows that the Ce and Mg forms have the highest activities next to the NH_4 form. This trend is the same as that found in Type Y zeolites (*7*). Though the effect of the cation exchange on the catalytic properties of Type L zeolites has never been reported, in the case of Type Y zeolites, MgY or CeY is known as one of the best catalysts for the reactions indicative of carbonium ion mechanism (*13*). Thus, one can reasonably assume that the same reaction mechanism as the one that we have proposed for the ring transformation over Type Y zeolites (*7*) is operative also for the transformation over Type L zeolites. The scheme is written as follows.

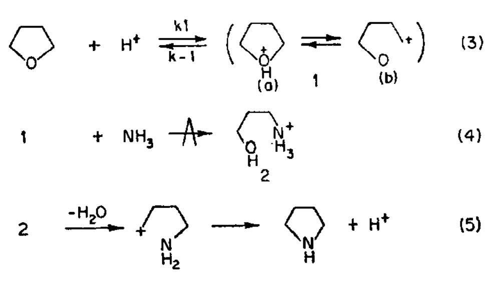

TABLE 3

Activity and Selectivity for THF Ring Conversion over Various Cation Forms of L Type Zeolites

Catalyst	Exchanged (%)	Conversion (%)	Yield (%)	Selectivity (%)
HL	30	53	49	91
KL	—	21	13	62
MgL	11	53	42	79
CaL	~10	37	23	60
BaL	~10	31	13	41
CeL	~20	45	33	73
CuL	23	20	11	55

THF molecule reacts with an acidic OH group to form protonated cation (1a) or carbocation (1b). This step (3) is fast and in equilibrium. The second step (4) is the reaction of the carbonium ion **1** with ammonia from gas phase, leading to the formation of ammonium ion **2**. This step is slow and rate determining. The ammonium ion **2** rapidly dehydrates and regenerates the protonic sites. Simple kinetic treatment for the mechanism yields the kinetic expression (*7*)

$$r = \frac{k_2K_{\mathrm{THF}}P_{\mathrm{THF}}}{1 + K_{\mathrm{THF}}P_{\mathrm{THF}}}, \qquad (6)$$

where k_2 is the rate constant of step (4) and K_{THF} is the equilibrium constant of step (3) and is equal to k_1/k_{-1}. This rate expression was found applicable to the ring transformation over HY (*7*). The values of k_2 and K_{THF} for HY are 2.05 $\mathrm{mol \cdot hr^{-1} \cdot g\text{-}cat^{-1}}$ and 16.4 $\mathrm{atm^{-1}}$ at 350°C and the activation energy for k_2 is 17 kcal/mol. The rate experimentally found for HL (2) is explained also on the basis of Eq. (6), assuming that $K_{\mathrm{THF}}P_{\mathrm{THF}}$ is much larger than unity, i.e.,

$$r = k_2P_{\mathrm{NH_3}} \quad \text{when} \quad K_{\mathrm{THF}}P_{\mathrm{THF}} \gg 1.$$

The activation energy for k_2 in the case of HL is 17 kcal/mol and is in agreement with that in the case of HY. The actual difference in the experimentally determined rate expressions for two catalysts is, thus, ascribed to the difference in K_{THF} values. The value of K_{THF} for HL is larger than that for HY. The fact that essentially the same rate equation with the same activation energy was found for both HY and HL suggests strongly the idea that the same reaction mechanism is operative in two catalytic systems for the ring transformation.

Location of active sites. It is rather surprising that the catalytic activity for the ring transformation saturates when only 10% of the potassium ions in KL are replaced by NH_4^+. This observation is a sharp contrast with the results on the cumene cracking, for which the catalytic activity increases almost proportionally with the degree of exchange up to 70% (*11*).

Type L zeolites contain nine cations at five different cation positions in their unit cells, and the most exchangeable cation positions are called D sites, which are located in the main channel (*14*). A unit cell has six D sites with the fractional occupancy of 0.6 (*14*). Thus, the exchange of 10% ($\sim\frac{1}{9}$) means that one out of six D sites is occupied by NH_4^+ cations, if one assumes that the exchange exclusively occurs at D sites. Figure 7 shows the projection of the main channel and the positions of D sites are indicated (*14*). The main channel is circumscribed by a 12-membered ring and involves six D sites. Then, we can restate the experimental results that the presence of one exchanged D site for every cross section of the main channel as drawn in Fig. 7 is enough for the saturation of the catalytic activity, and the presence of more H^+ cations at D sites is not effective at all.

This could probably happen because of the steric restriction in the narrow channel of Type L zeolites (7.1 Å). A tetrahydrofuran molecule may adsorb at D sites to form the intermediate **1** (~5 Å in diameter) in such a way that a preadsorbed **1** prevents the second THF molecule from adsorbing another OH group on the same cross section of the main channel. Strong adsorption of THF is supported from the reaction kinetics, which indicates that the adsorption equilibrium of THF is established during the reaction.

Origin of selectivity. The most fascinating feature of Type L zeolite in this ring transformation is its high selectivity. At 350°C, the selectivity for pyrrolidine is 90%, while is is about 80% with HY. The difference in the selectivity with the two zeolites is probably caused by the difference in the pore structure; Type Y zeolites have active sites in supercages with diameter of ca. 13 Å, while Type L zeolites have straight channels of diameter of ca. 7.1 Å. The most important factor in determining the selectivity of the reaction could be that the intermediates **1** and **2** must have their molecular ends in very close positions. If the intermediates are in straight-chain form, they would have only a small chance of ring closure, and would undergo further reactions such as dehydration to butadiene or dimerization. Since in small channels on Type L zeolites, the molecular motion of the intermediate **1** or **2** is much restricted, they have only a small chance to stretch out. This is probably the main reason why Type L zeolite exhibits high selectivity. The above idea is supported by a comparison of activities and selectivities of various acid catalyts. As seen in Table 3, amorphous silica–alumina or activated alumina shows very small selectivity though the total conversion is high. Except for mordenite, the order of selectivity, HL > HY > amorphous silica–alumina or activated alumina, is just the reverse order of their pore diameters. In the case of mordenite, the pore diameter is so small that the larger fraction

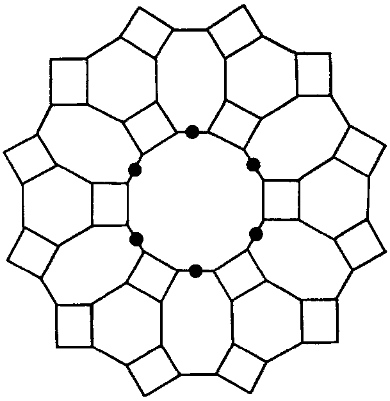

FIG. 7. Projection of framework of zeolite L parallel to *c* axis and position of D sites (●).

of the reaction may take place at the external surface. The same discussion can be applied to the dependence of the selectivity on catalysts for the ring conversion of a six-membered ring, tetrahydropyran into piperidine.

REFERENCES

1. Yur'ev, Yu. K., and Prokina, M. N., *J. Gen. Chem. USSR* **7**, 1868 (1938); *Chem. Abstr.* **32**, 548 (1938).
2. Reppe, W. *et al.*, *Annalen* **596**, 103 (1955).
3. Bordner, C. A., and Kamin, C. G., U. S. Patent No. 2,525,584 (1950).
4. Bordner, C. A., U. S. Patent No. 2,600,289 (1952).
5. Kawaguchi, T., Kita, T., and Naito, H., Japan Patent No. 6,819,940 (1969).
6. Hatada, K., Shimada, M., Fujita, K., Ono. Y., and Keii, T., *Chem. Lett.*, 439 (1974).
7. Fujita, K., Hatada, K., Ono, Y., and Keii, T., *J. Catal.* **35**, 325 (1974).
8. Nishimura, Y., and Takahashi, H., *Bull. Jap. Petro. Inst.* **13**, 201 (1971).
9. Shirinskaya, L. P., Ermolenko, N. F., Bokhau, N. P., and Pryakhina, N. P., *Neftekhimiya* **12**, 833 (1972); *Chem. Abstr.* **78**, 10011 (1973).
10. Shirinskaya, L. P., Piguzova, L. I., Ermolenko, N. F., and Nikolina, V. Ya., *Vestsi Akad. Navuk Belarus. SSR, Ser. Khim. Navuk 1* **5** (1973): *Chem. Abstr.* **78**, 126,537 (1973).
11. Ono, Y., unpublished work.
12. Turkevich, J., and Ono, Y., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 20, p. 135 (1969); *Advan. Chem. Ser.* **102**, 315 (1971).
13. Hansford, R. C., and Ward, J. W., *J. Catal.* **13**, 316 (1968).
14. Barrer, R. M., and Villiger, H., *Z. Kristallogr.* **128**, 352 (1969).