HETEROCYCLES, Vol 16, No 10, 1981

RING TRANSFORMATIONS OF HETEROCYCLES OVER SYNTHETIC ZEOLITES

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

Abstract —— Synthetic zeolites are found to be very effective and selective catalysts for the vapor phase ring transformations of oxygen-containing hyterocycles into nitrogen or sulfur-containing heterocycles. For example, tetrahydrofuran is converted into pyrrolidines and tetrahydrothiophene, while γ-butyrolactone is converted into pyrrolidinones and γ-thiobutyrolactone by the reactions with primary amines and hydrogen sulfide, respectively. The most effective catalysts differ with reactions. For the reaction of tetrahydrofuran with ammonia, acidic zeolites such as HL(proton form of L-type zeolite) are most effective, while for the reaction of γ-butyrolactone with hydrogen sulfide, basic zeolites like CsY(Cs^+ exchanged Y-type zeolite) are highly active. The kinetics of the ring transformations are studied and the reaction mechanisms are discussed.

INTRODUCTION

The conversion of heterocycles into compounds containing a ring system different from that of the starting substance gives a convenient route for the synthesis of some heterocycles as an alternative to the classical alicyclic intermediate as starting material. The use of heterogeneous catalysts for these important reactions has never been explored in depth except very early works by Yur'ev and coworkers.1) They used alumina as the catalyst, but the selectivities of the conversions were rather low.1)

Synthetic zeolites have very versatile properties depending on the framework structure, silica-alumina ratio, exchangeable cations and so on. Because of the versatile nature of zeolites, they work as catalysts for a very wide range of reactions. While zeolites are used as acid catalysts and have very high activities for major carbonium ion transformations such as cracking, alkylation and isomerization, they are effective also as base catalysts. Typical base-catalysed reactions include the dehydrogenation of isopropyl alcohol, the side-chain alkylations of aromatics and the aldol condensation of n-butyraldehyde. Yet for other reactions, exchangeable metal cations are responsible for the development of the catalytic activities. The author and coworkers have attempted to utilize zeolites as catalysts for the ring transformations of five- and six-membered heterocycles. Zeolites were found to be active and selective catalysts for the ring conversions. The best catalysts, however, differ from one reaction to another, indicating the change in the reaction mechanism. In this review, the catalysis by zeolites for the ring transformations is described and the reaction mechanisms are discussed.

EXPERIMENTAL

NaX(Na^+ form of X-type zeolite), NaY and KL zeolites were used as the starting materials for the most of catalysts. Various cation forms of the zeolites were prepared by the conventional cation exchange procedure using salt solutions. The cation exchanged zeolites were pelleted without a binder, crushed and sorted into grains of 9 - 16 mesh. The reactions were carried out with a continuous-flow reactor at atmospheric pressure. The catalyst (1 - 3 g) was packed in a reactor of silica-tubing (13 mm i.d.) and placed in a vertical furnace. The liquid reactants were pumped with a motor-driven syringe into a preheating zone of the reactor containing 10 ml of quartz. The gaseous materials were fed through flowmeters. The products were analyzed by gas-chromatography.

The conversion, the yield, and the selectivity are defined as follows.

$$\text{Conversion}(\%) = \frac{\text{moles of a reactant consumed}}{\text{moles of a reactant fed}} \times 100$$

$$\text{Yield}(\%) = \frac{\text{moles of a product produced}}{\text{moles of a reactant fed}} \times 100$$

$$\text{Selectivity}(\%) = \frac{\text{moles of a product produced}}{\text{moles of a reactant consumed}} \times 100$$

The contact time(W/F) is defined by

$$W/F = \frac{\text{weight of the catalyst used(g)}}{\text{total molar feed (mole } h^{-1})} .$$

RESULTS AND DISCUSSION

Ring Transformation of Tetrahydrofuran into Pyrrolidine

The reaction of tetrahydrofuran(THF) with ammonia gives a convenient route for the synthesis of pyrrolidine. Yur'ev and Prokina[2)] obtained pyrrolidine in a 43 % yield by passing THF over alumina at 400 °C. Zeolites were found to have high activity together with high selectivity for this reaction.[3, 4)] The activities of various zeolites, silica-alumina and alumina are compared in Table 1, which shows that HL(proton form of L-type zeolite) and HY are highly active and selective.[4)] Alumina and silica-alumina are also active, but the selectivity to pyrrolidine is low. Though the proton forms of L and Y-type zeolites are highly active, alkaline cation forms (KL, NaY) are not active at all, indicating that the presence of Brönsted acid is essential for the development of the catalytic activity for the ring conversion.

Figure 1 shows a typical time course of the reaction over HL. The reaction conditions are, reaction temperature, 350 °C; catalyst weight, 1.5 g; ammonia/THF = 7, W/F = 8.43 g h mol^{-1}. There is no deactivation of the catalyst on stream for 8 h.

The effect of the reaction temperature is shown in Fig. 2. The total conversion of THF increases gradually with the reaciton temperature, while the yield of pyrrolidine increases with the reaction temperature up to 350 °C, but sharply falls down at higher temperatures. Thus, the optimum temperature lies around 350 °C.

The reaction kinetics over HL was examined. The rate is of the first order with respect to the partial pressure of ammonia. The rate depends markedly on the partial pressure of THF when it is below 0.1 atm, but is almost independent of the THF partial pressure above 0.15 atm. In this region, the rate(r)

Table 1 Activities of various catalysts for THF conversion into pyrrolidine

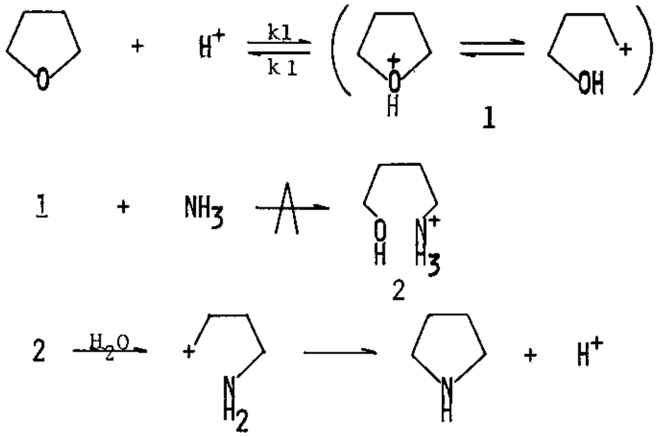
	Conversion (%)	Yield (%)	Selectivity (%)
HL	53	49	91
HY	61	50	82
H-Mordenite	25	12	48
Silica-alumina	86	36	42
Alumina	92	54	58

350 °C, NH_3/THF = 7, W/F = 8.43 g h mol^{-1}

is expressed as

$$r = k\,P_{NH_3}$$

where k is the rate constant and P_{NH_3} is the partial pressure of ammonia. From the temperature dependence of k, the activation energy was estimated to be 17 ± 1 kcal mol^{-1}. Based upon kinetics, the following reaction scheme is proposed.



The high selectivity of the conversion over zeolites could be ascribed to the structure of zeolites. Y-type zeolite has active sites in the supercages with diameter of ca. 13 Å, while L-type zeolite has active site in the straight channels with diameter of ca. 7.1 Å. The most important factor in determining

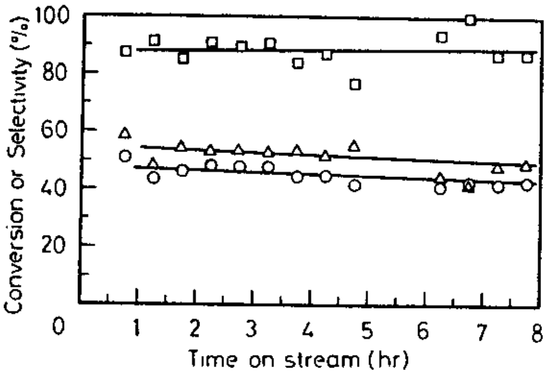


Fig. 1 Change of the conversion of THF (△), the yield of pyrrolidine (○), and the selectivity for pyrrolidine (□) with time on stream.

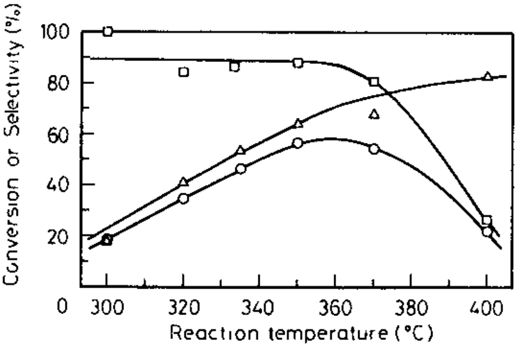


Fig. 2 Change in the conversion of THF (△), the yield of pyrrolidine (○), and the selectivity for pyrrolidine (□) with reaction temperature.

the selectivity of the reaciton may be that the intermediates 1 and 2 must have their molecular ends in close proximity. If the intermediates are in straight-chain form, they would have only a small tendency of ring closure, and would undergo further reactions like dehydration to butadiene or polymerization. Since the molecular motion of the intermediates is much restricted in the small channels of the zeolites, they have not much chance to stretch out. This is probably the reason why zeolites exhibit high selectivity for the ring conversion.

Ring Transformation of Tetrahydropyran into Piperidine

The reaciton of tetrahydropyran(THP) with ammonia to yield piperidine is also catalysed by HL and HY.[4) It has been also found that the activities of the zeolites increase by the partial removal of aluminum from the zeolitic framework as shown in Table 2.[5) The dealumination of zeolites was achieved by refluxing an aqueous solution(300 ml) of H_4EDTA with 20 g of KL(NaY). The hydrogen form of the zeolites was prepared by ion exchange of the dealuminated zeolites using ammonium nitrate followed by calcination. While hydrogen forms of zeolites increase the catalytic activity by dealumination, alkaline form(KL) is inactive whether it is dealuminated or not. This indicates that Brönsted acid sites are

Table 2 Effect of dealumination on activity and selectivity for the ring conversion of tetrahydropyran into piperidine

catalyst	Si/Al	total conversion(%)	piperidine yield (%)	selectivity (%)
KL	3.2	11	0	0
KL	4.8	15	0	0
HL	3.2	24	14	58
HL	6.0	25	20	80
HY	2.4	15	5	33
HY	4.7	26	17	65

Reaction conditions: 350 °C, NH_3/THP = 7
W/F = 26 g h mol^{-1}

essential for the catalytic activity. Infrared spectroscopic study has revealed that the number of Brönsted acid sites increases by dealumination. The acidity measurements with use of Hamett indicators led to the same conclusion. Thus, the increase in the acidity is concluded to be the cause of the enhancement of the activity by dealumination.

The rate of the reaction is of the first order with respect to the partial pressure of ammonia(P_{NH_3}). The rate depends markedly on the partial pressure of THP(P_{THP}), but is independent of P_{THP} when P_{THP} is over 0.2 atm. In this region, the rate is expressed as

$$r = k\ P_{NH_3}$$

From the temperature dependence of the rate constant k, the activation energy was estimated to be 27.7kcal mol^{-1}, far greater than that in the conversion of THF into pyrrolidine. This may be related to the stability of the ring system. Since the six-membered ring is less strained than the five membered-ring, the activation energy for the ring opening by the attack of a proton should be larger in the former case.

Ring Transformation of Tetrahydrofuran into 1-Propylpyrrolidine

The ring transformation of tetrahydrofuran into 1-alkylpyrrolidine proceeds over alumina.[6,7] Reppe and coworkers obtained 1-ethylpyrrolidine in 61 % yield by the reaction of THF and ethylamine over ThO_2 promoted alumina for 6 h at 300°C in an autoclave.[7] The catalytic activities of various cation forms of Y-type zeolites for the reaction of THF and propylamine were examined.[8] Among the zeolites studied, HY and zeolites with trivalent cations have high activity as shown in Table 3. The maximum yield of 1-propylpyrrolidine was obtained at 360°C over AlY. The yield of the pyrrolidine was about 60 % with the selectivity of 75 %. Almost same results were obtained with alumina catalyst.

The kinetics of the reaction was studied with AlY as catalyst in the temperature range of 270 - 320°C. The rate is expressed by

$$r = k \frac{K_{THF}P_{THF}}{1 + K_{THF}P_{THF}} \frac{K_A P_A}{1 + K_A P_A}$$

where k is the rate constant, P_{THF} and P_A are the partial pressures of THF and propylamine, respectively, K_{THF} and K_A being the adsorption equilibrium constants

Table 3 Activity and selectivity for the reaction of THF with propylamine over various Y-zeolites

Catalyst	Conversion of THF %	Yield of 1-propylpyrrolidine %	Selectivity %
AlY	61	46	76
FeY	58	42	72
CrY	52	40	76
HY	41	21	50
MgY	33	16	50
CuY	24	10	42
CeY	12	6	50
NaY	10	1	10

Reaction temperature, 300°C; W/F = 5.56 g h mol^{-1}, W = 1.0 g; reactant molar ratio, THF: propylamine: N_2 = 1: 5.25: 2.

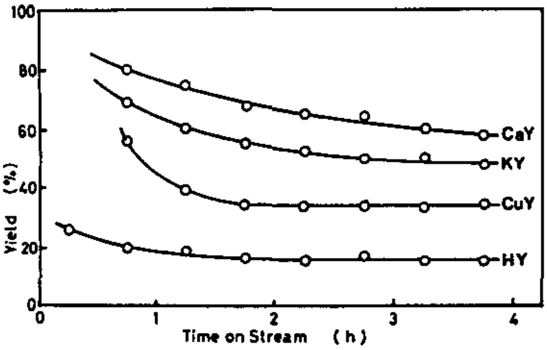


Fig. 3 Change in the yield of 1-propyl-2-pyrrolidinone with time on stream over various zeolites at 280 °C.

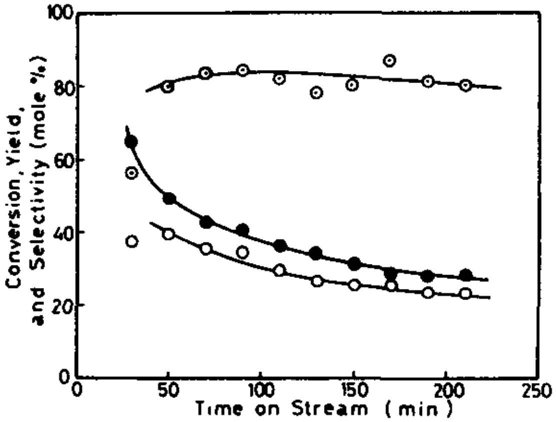


Fig. 4 Change in the catalytic behavior of CuY for the transformation of γ-butyrolactone with time on stream; (●) lactone conversion, (○) 2-pyrrolidinone yield, (⊙) selectivity to 2-pyrrolidinone.

of the two reactants. From the temperature dependence, the activation energy and the heat of adsorption of THF and propylamine were estimated to be 16, 6, and 10 kcal mol^{-1}, respectively. The kinetic expression suggests that the two reactants are activated on two different active centers. The adsorption centers for THF may be Brönsted acid sites as in the case of the conversion of THF into pyrrolidine. The active centers for propylamine are presumed to be oxygen anions in the zeolite framework. The rate determining step is concluded to be the reaction between adsorbed reactants.

Ring Transformation of Furan into Pyrrole

The activity of zeolites for the conversion of furan into pyrrole was studied using conventional pulse-reactor.8) Neat ammonia was used as a carrier gas, and 4 μl of furan was injected by a microsyringe.

In general, zeolites with high acidity give high conversion of furan, but the selectivity to pyrrole is low. Zeolites with modest acidity such as BaY show high selectivity to pyrrole. Alkaline cation exchanged zeolites have no activity. In the case of BaY, the conversion of furan is 14 % with 100 % selectivity at 330 °C, and the activity does not change with the pulse number.

Ring Transformation of γ-Butyrolactone into 2-Pyrrolidinones

Synthesis of 2-pyrrolidinone by the reaction of γ-butyrolactone with primary amines has been carried out in a liquid phase under pressure without use of catalyst.9) On the other hand, the reaction can be conveniently carried out in a vapor phase. Yur'ev et al. carried out the reaction of the lactone with ammonia at 350 °C over alumina and obtained 2-pyrrolidinone in a 15.5 % yield.10) The vapor phase synthesis of 2-pyrrolidinones by the reactions of γ-butyrolactone with ammonia or primary amines over zeolites was studied.11, 12)

Figure 3 shows the change in the 1-propyl-2-pyrrolidinone yield with time in the reaction of the lactone with propylamine over various zeolites.11) The highest yield of the pyrrolidinone was obtained by CaY, but KY and CuY are also active. The highest selectivity to the pyrrolidinone was obtained with CuY. For the reaction of γ-butyrolactone with ammonia, the highest activity was observed with CuY, but HY and alkali metal exchanged zeolites, such as LiY and NaY are also active. Figure 4 shows the time course of the reaction.12) While the catalytic activity gradually decreased with time on stream, the selectivity to 2-pyrrolidone was 80 % throughout the run. The catalytic activity is completely recovered by treating the used zeolites under air stream at 500°C.

As described above, the significant feature of the conversion of the lactone into pyrrolidinones is that alkaline cation zeolites are equally active as acidic zeolites. This indicates that the presence of the acidic sites is not a prerequisite to the catalytic activity.

Since CuY shows the most stable activity, further studies were carried out with CuY as catalyst.[11)] The reactions of γ-butyrolactone with various primary amines were studied at 280°C, and the results are summarized in Table 4. The yield of 2-pyrrolidinones depends on the nature of amines, but the selectivity of the reaction is generally high. In addition to neat amines, amines in aqueous solution can also be used for the synthesis.

The yield of 2-pyrrolidinone in the reaction of the lactone with ammonia was lower than that with primary amines. This may be caused by the difference in the basicity of ammonia and primary amines. The steric effect also seems to be important for the reactions; the yield of 2-pyrrolidinones depends on the starting amine in the following order.

$$CH_3NH_2 \sim C_3H_7NH_2 > C_4H_9NH_2 > C_5H_{11}NH_2 > C_6H_{13}NH_2 > PhNH_2$$

$$C_4H_9NH_2 > \text{Iso-}C_4H_9NH_2 > \text{s-}C_4H_9NH_2 > \text{t-}C_4H_9NH_2$$

Table 4 ACTIVITY AND SELECTIVITY FOR THE REACTION OF γ-BUTYROLACTONE WITH VARIOUS AMINES OVER Cu-Y

Amine	P_L (atm)	R_L ($\times 10^{-3}$ mol/h)	P_{amine} (atm)	R_{amine} ($\times 10^{-3}$ mol/h)	Yield of pyrrolidinone (%)	Selectivity (%)
Ammonia	0.098	24	0.497	122	12	68
Methylamine	0.098	24	0.497	122	98	98
Methylamine[a)]	0.052	20	0.192	73	56	—
Ethylamine[b)]	0.075	20	0.258	67	80	—
Propylamine	0.098	24	0.497	122	96	98
Butylamine	0.098	24	0.409	101	86	94
Isobutylamine	0.098	24	0.508	124	85	96
s-Butylamine	0.098	24	0.404	99	64	92
t-Butylamine	0.098	24	0.571	140	4	88
Pentylamine	0.098	24	0.522	128	60	92
Hexylamine	0.098	24	0.440	108	49	95
Aniline	0.098	24	0.446	109	8	—

Catalyst Cu-Y 3 g. Reaction temperature 280°C. Total feed($L+\text{amine}+N_2$): 245×10^{-3} mol/h. *P*: partial pressure. *R*: feeding rate. a) 40% aqueous solution. b) 70% aqueous solution.

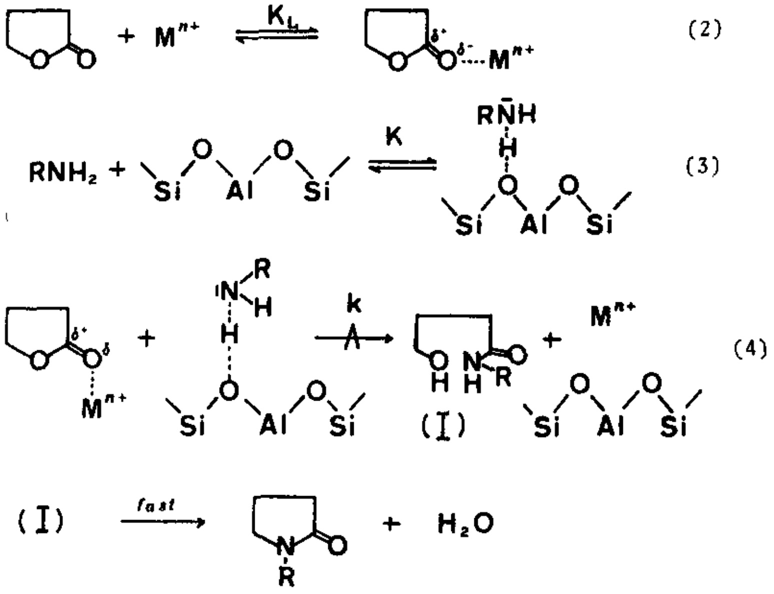
Since the basicity of alkylamines hardly depends on the kind of alkyl group, the difference in the yield of 2-pyrrolidinone seems mainly to be caused by the steric effect. The bulkier the alkyl group, the less the reactivity of amine toward the lactone.

The kinetics of the reaction of γ-butyrolactone with propylamine was examined and the following kinetic expression was established.

$$r = k \frac{K_L P_L}{1 + K_L P_L} \frac{K_A P_A}{1 + K_A P_A} \qquad (1)$$

where k is the rate constant, K_L and K_A are the adsorption equilibrium constants of the lactone and the amine, respectively, P_L and P_A being the partial pressure of the reactants. The values of k, K_L and K_A were determined at 220 - 280 °C and the activation energy, the heats of adsorption of the lactone and the amine were estimated to be 23, 9.0, and 9.9 kcal mol^{-1}, respectively.

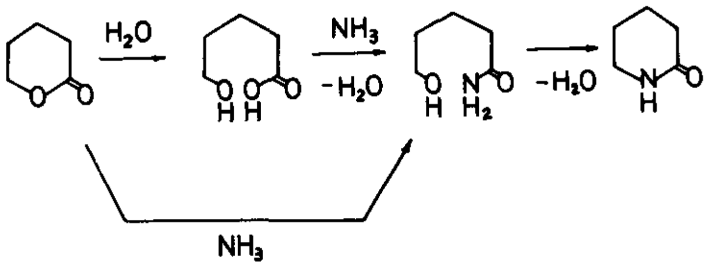
The reaction kinetics expressed by Eq.(1) suggests that there are independent adsorption sites for each reactant. It is presumed that the adsorption sites for the lactone are metal cations, which cause the strong polarization of the carbonyl groups of the lactone molecules due to the strong electrostatic field. The adsorption sites for primary amines might be oxygen ions bonded to aluminium atoms in the zeolite framework. Dissociative adsorption of ammonia has been reported on the oxide ions of alumina surface.[13] Thus, the following reaction scheme is proposed.



Equations (2) and (3) represent the adsoption of the lactone and the amine on metal cations and oxygen anions, respectively. The adsorbed reactants react each other to form an acid amide-like intermediate (I) (Eq.(4)), the step being rate determining. The dehydration of the intermediates to the lactam is fast. This mechanism is in line with the rate expression (Eq.(1)), if one puts the adsorption constants of the lactone and the amine K_L and K_A, respectively, and the rate constant of the step (4), k.

Ring Transformation of δ-Valerolactone into 2-Piperidone

The catalytic activities of various cation forms of Y-type zeolites for the reaction of δ-valerolactone with ammonia were examined.14) Among the zeolites studied, HY was found to be most active. The optimum reaction temperature is around 285°C, since the deactivation of the catalyst is rapid at higher temperatures. As shown in Fig. 5, the activity decreases slightly at 285°C, but 80 % yield of piperidinone is obtained even after 7 h of stream time at the contact time of W/F = 50 g h mol^{-1}. At lower contact time, an intermediate, 5-hydroxypentamide ($HO(CH_2)_4CONH_2$) has been isolated. Thus, the following reaction scheme could be written for the reaction.



In conformity with this scheme, the reaction rate is enhanced by addition of water, which probably promotes the first step to occur.

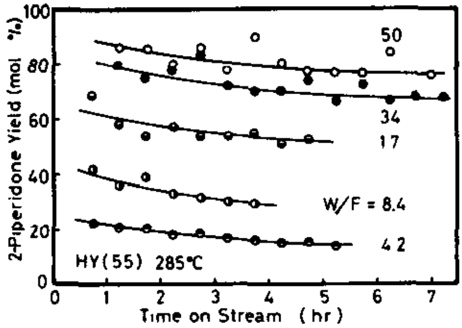


Fig. 5. Influence of contact time on the yield-time curve.

Ring Transformation of γ-butyrolactone into γ-thiobutyrolactone

The reaction of γ-butyrolactone and hydrogen sulfide to give γ-thiobutyrolactone (tetrahydro-2-thiophenone) was reported by Venuto and Landis.[15] A notable feature of the reaction is that NaX is the most active catalyst among the zeolites studied, HY and REX having only a meager activity. We have studied the kinetics of the ring transformation over a series of alkali metal cation exchanged Y-zeolites in order to find the mechanistic grounds of high activity of alkaline zeolites.[16]

The catalytic activity of various cation form of zeolites was compared at 330°C. The activities and selectivities to γ-thiobutyrolactone of various zeolites are given in Table 5, which shows the following features of the reaction.

(1) Alkali metal cation exchanged zeolites are much more active than acidic zeolites (HY, MgY).

(2) The catalytic activity of alkali metal cation exchanged Y-zeolites increases in the following order.

LiY < NaY < KY < RbY < CsY

(3) NaX is a more active catalyst than NaY.

These features are in sharp contrast with those found in ordinary carboniogenic reactions, for which HY is much more active than NaY and Y-zeolites are more active than X-zeolites, LiY being more active than CsY.

Fig. 6 shows the effect of contact time on the yield of γ-thiobutyrolactone over CsY at 330°C. At $W/F = 18.8$ g h mol^{-1}, a 99 % yield with 100 % selectivity

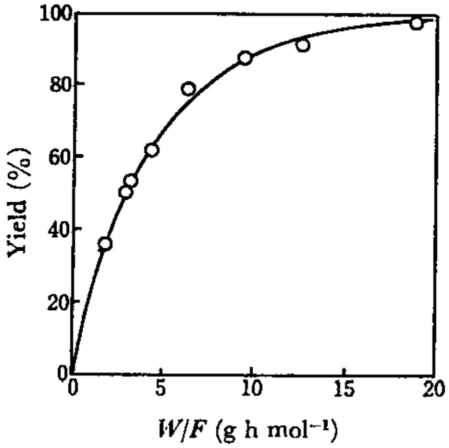


Fig. 6. Effect of contact time on γ-thiobutyrolactone yield.
CsY, 330°C, H_2S/lactone = 6.

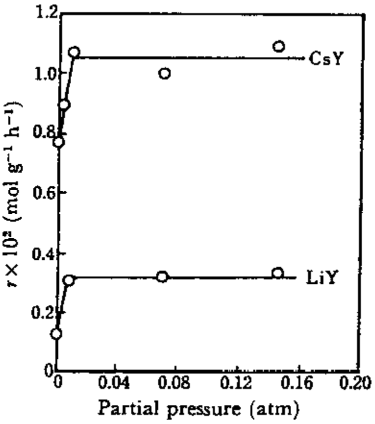


Fig. 7. Effect of pyridine partial pressure on the reaction rate. CsY, 300°C.

was attained. The decay of the catalytic activity was not observed.

The kinetics of the reaction over LiY, NaY and CsY were studied. The rate of the reaction increases with the partial pressure of hydrogen sulfide, and decreases with the partial pressure of γ-butyrolactone. The rate of the reaction over LiY, NaY and CsY can be expressed by

$$r = \frac{kK_L K_H P_L P_H}{(1 + K_L P_L + K_H P_H)^2}$$

where r is the rate of the reaction, P_L and P_H are the partial pressures of γ-butyrolactone and hydrogen sulfide, respectively. The rate constant, **k**, increases in the sequence LiY < NaY < CsY. The constant K_H also increases in the sequence LiY < NaY < CsY, while the constant K_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.

In order to gain information on the nature of the active centers, the effects of addition of hydrogen chloride and of pyridine on the catalytic activity were examined. Matsumoto et al.[17)] reported that the cracking of cumene over NaY is

Table 6. 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}.

greatly enhanced by addition of hydrogen chloride to system. The enhancement of the catalytic activity was ascribed to the formation of Brönsted acid sites by the interaction of hydrogen chloride with NaY. Addition of hydrogen chloride, however, almost completely inhibited the ring conversion. The deactivation was not caused by the destruction of the zeolite framework, since the activity was recovered by consecutive treatment of the catalyst with air and hydrogen at 500°C. Thus, it can be assumed that the deactivation is associated with the poisoning of the active centers, presumably the basic sites, by hydrogen chloride. The depencence of the reaction rate on the pyridine partial pressure is given in Fig. 7, which shows that pyridine does not poison, but enhances the catalysis. 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.

A possible candidate for the basic sites in zeolites is oxygen anions bound to aluminum cations $(AlO_4)^-$. A negative charge at the site is neutralized and shielded by an alkali metal cation. However, the results suggest that the reactant molecules are accessible to and are adsorbed on the basic oxide anions under reaction conditions. An infrared study by Karge and Rasko has shown that hydrogen sulfide is dissociatively adsorbed on Na form of faujasite-type zeolites.18) They suggest that the adsorption sites are cationic sites where the Na^+ cations are weakly bound with framework oxygen. The higher the Si/Al ratio, the smaller the population of such sites. The fact that NaX has much higher catalytic activity than NaY appears to support the idea. The order of the activity 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 for NaY and LiY, implying that the reactant molecules are more easily activated by the former catalyst.

γ-Butyrolactone molecules have an easily polarizable carbonyl group and can be activated by the electrostatic field exerted by an alkali metal cation and/or $(AlO_4)^-$ 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 M^+-(AlO_4) unit. This explains the observed Langmuir-Hinshelwood type kinetics where the adsorption of γ-butyrolactone is much easier than that of hydrogen sulfide ($K_L > K_H$).

Ring Transformation of Tetrahydrofuran into Tetrahydrothiophene

For this ring conversion, too, alkaline cation exchanged zeolites have high catalytic activities, and acidic zeolites (HY, MgY) have very low activity, alkaline cation exchanged X-zeolites being more active than the corresponding cation form of Y-zeolites.[19] Figure 8 shows the effect of the reaction temperature on the total conversion of THF and the yield of tetrahydrothiophene in the ring transformation over NaX. The activity decreased gradually with stream hours and the extent of the catalyst deactivation increases with reaction temperature. The data in Fig. 8 were obtained at stream hour of 2 - 3 h. The yield increases with reaction temperature up to 350°C, and through the maximum, decreases at higher temperatures. The selectivity to tetrahydrothiophene is almost 100 % below 350°C. The high activity of alkaline cation exchanged zeolites indicates that basic sites play an important role in the catalysis, and, in fact, hydrogen chloride inhibited the reaction completely. However, the reaction is greatly suppressed by addition of pyridine, in sharp contrast with the reaction of γ-butyrolactone and hydrogen sulfide for which pyridine does not poison but enhances the activity. This indicates the participation of acid in the catalysis. For the ring conversion of tetrahydrofuran into pyrrolidine, only acidic zeolites are effective, indicating that the presence of the Brönsted acid sites are essential for the ring opening of tetrahydrofuran.[3,4] Since there are not intrinsic Brönsted acid sites in NaX, acidic sites should have been created by the reaction itself.

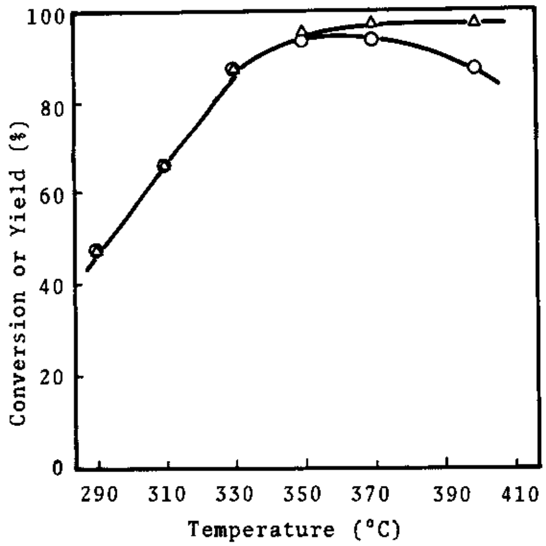
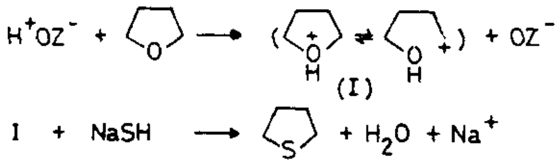


Fig. 8 Effect of the reaction temperature on the conversion(△) and the yield of tetrahydrothiophene(○).
W/F = 15.9 g h mol^{-1}

Infrared study revealed that hydrogen sulfide dissociates on NaX, producing an acidic OH group (3650 cm^{-1}) and a SH group (2560 cm^{-1}).[18,19] Thus, the interaction of basic sites produces acidic OH group, which in turn reacts with tetrahydrofuran. The reaction scheme can be summarized as

$$Na^+OZ^- + H_2S \longrightarrow NaSH + H^+OZ^-$$


(I)

REFERENCES

1. H. C. Van der Plus, 'Ring Transformation of Heterocycles', Vol. 1, Akademic Press, London, 1973.
2. Yu. K. Yur'ev and M. N. Prokina, J. Gen. Chem. USSR, 1938, 7, 1868; Chem. Abstr. 1938, 32, 548.
3. K. Fujita, K. Hatada, Y. Ono, and T. Keii, J. Catal., 1974, 35, 325.
4. Y. Ono, K. Hatada, K. Fujita, A. Halgeri, and T. Keii, J. Catal., 1976, 41, 322.
5. Y. Ono, A. Halgeri, M. Kaneko, and K. Hatada, Amer. Chem. Soc., Symp. Ser. No. 40, 1977, p. 569.
6. Yu. Yur'ev, V. I. Bazan, A. N. Esfova, S. M. Seliverstova, and S. I. Chernyakhover, J. Gen. Chem. USSR, 1940, 10, 1839; Chem. Abstr., 1941, 35, 4377.
7. W. Reppe and co-worker, Ann., 1955, 596, 143.
8. K. Hatada, K. Fujita, and Y. Ono, Bull. Chem. Soc. Jpn., 1978, 51, 2419.
9. E. Spath and J. Linter, Chem. Ber., 1936, 69, 2727.
10. Yu. Yur'ev, E. G. Vendel'shtel, and L. A. Zinov'eva, J. Gen. Chem. USSR, 1952, 22, 509; Chem. Abstr., 1953, 47, 2747.
11. K. Hatada and Y. Ono, Bull. Chem. Soc. Jpn., 1978, 51, 448.
12. K. Hatada, M. Shimada, Y. Ono, and T. Keii, J. Catal., 1975, 37, 166.
13. J. B. Peri, J. Phys. Chem., 1969, 69, 231.
14. Y. Ono, Y. Takeyama, K. Hatada, and T. Keii, Ind. Eng. Chem., Prod. Res. Dev., 1976, 15, 180.

15. P. B. Venuto and P. S. Landis, 'Advances in Catalysis' Vol. 18, eds. by D. D. Eley, H. Pines, and P. B. Weisz, Academic Press, New York, 1968, p. 311.

16. K. Hatada, Y. Takeyama, and Y. Ono, Bull. Chem. Soc. Jpn., 1977, 50, 2517.

17. H. Matsumoto, Y. Yasui, and Y. Morita, J. Catal., 1968, 12, 84.

18. H. G. Karge and J. Rasko, J. Colloid Interface Sci., 1978, 64, 522.

19. Y. Ono, T. Mori, and K. Hatada, Acta Phys. Chem., 1978, 24, 233.

Received, 27th May, 1981