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Ring Transformation of Tetrahydrofuran into Pyrrolidine over Synthetic Zeolite

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Synthetic zeolites were found to be effective catalysts for the ring transformation of tetrahydrofuran (THF) into pyrrolidine. With HY, the yield of pyrrolidine is 43% and the selectivity for it is over 80% at 335°C. There is no sign of catalyst deactivation within 6 hr. The kinetic study was carried out with HY to obtain the following rate equation:

$$r = \frac{k \cdot K_{\mathrm{THF}} P_{\mathrm{THF}} \cdot P_{\mathrm{NH_3}}}{1 + K_{\mathrm{THF}} P_{\mathrm{THF}}}.$$

The effect of degree of decationation of zeolite on the catalytic properties was examined and it is concluded that active centers are Brönsted sites formed at S_{II} positions in the supercage. The reaction mechanism is also proposed.

INTRODUCTION

The vapor phase reaction of tetrahydrofuran (THF) with ammonia gives the convenient route to the synthesis of pyrrolidine.

By passing THF over alumina at 400°C, Yur'ev and Prokina (*1*) obtained pyrrolidine in a 43% yield. Several patents have described the reaction conditions to improve the selectivity of the reaction over alumina (*2*, *3*). Kawaguchi *et al.* (*4*) claimed that the yield of pyrrolidine was considerably increased by treating alumina with boric acid. However, no detailed study has been made on the kinetics or the mechanism of the reaction.

The present authors and Shimada (*5*) reported in a preliminary paper that synthetic zeolites have high activities for the ring transformations of heterocycles including the reaction of THF with ammonia. The present work concerns the more extended study of this reaction. The catalytic activities of various forms of zeolites were compared and hydrogen form of Y zeolite (HY) was found to be the most effective catalyst. The kinetics of the reaction over HY was determined and the reaction mechanism was discussed.

EXPERIMENTAL METHODS

Catalyst

The starting material for all catalysts was Linde SK-40 (NaY) or Linde 13X powder. The various cation forms of zeolites were prepared by a conventional cation exchange procedure using salt solutions. The degree of exchange was estimated by gravimetric analysis for eliminated sodium ion. The degree of exchange of zeolites are listed in Table 1. The exchanged zeolites were pelleted without a

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TABLE 1
Activity and Selectivity for THF Ring Conversion over Various Zeolites[a]

Zeolite	Na^+ exchanged (%)	Conversion (%)	Yield (%)	Selectivity (%)
NaY		15	0	0
HY	49	42	29	69
CeY	65	28	13	47
MgY	65	29	19	66
CaY	65	17	5	29
SrY	65	23	8	35
BaY	65	13	9	69
MnY	36	23	9	39
CoY	67	11	3	27
NiY	52	30	0	0
CuY	65	15	8	65
ZnY	65	18	7	39
PbY	65	20	5	25
MgX	45	24	11	46
BaX	74	21	13	62
CuX	77	27	10	37

[a] W/F = 16.7 *g*-cat · hr/mole; molar ratio, NH_3/THF = 4; reaction temperature 320°C.

binder and crushed and sized into 9–16 mesh, and stored in a dessicator containing a saturated aqueous solution of ammonium chloride.

Apparatus and Procedure

Reactions were carried out in a fixed-bed-type reactor with a continuous flow system at atmospheric pressure. The reactor was a 13-mm-i.d. silica tubing placed in a vertical furnace. Prior to the reaction, 0.5–2.0 g of the catalysts were heated in an air stream at 500°C (460°C for HY) for 180 min and then heated in an ammonia stream at the reaction temperature for 30 min after air was removed by feeding nitrogen for 30 min. THF (Wako Pure Chemicals) was pumped into the preheating zone of the reactor packed with quartz or α-alumina using a microfeeder. The feed rates of ammonia and nitrogen were measured with capillary flow meters. The products were collected in an ethanol trap maintained at -100°C and analyzed by a gas chromatography with a hydrogen flame detector using a 1-m column packed with a 10% PEG-6000 on Shimalite F operating at 120°C with nitrogen as a carrier gas (25 ml/min). The conversion of THF, the yield of pyrrolidine, and the selectivity of the reaction are defined as follows:

Conversion (%)

$$= \frac{\text{moles of THF reacted}}{\text{moles of THF fed}} \times 100;$$

yield (%)

$$= \frac{\text{moles of pyrrolidine produced}}{\text{moles of THF fed}} \times 100;$$

selectivity (%)

$$= \frac{\text{moles of pyrrolidine produced}}{\text{moles of THF reacted}} \times 100.$$

Results and Discussion

Catalytic Activity of Various Forms of Zeolites

The catalytic activities of various forms of zeolites were examined. The reaction conditions were as follows: reaction temperature, 320°C; catalyst weight, 1.8 g; reactant ratio, ammonia/THF = 4; W/F = 16.7 *g*-cat·hr/mole, where W is the weight of the catalyst (*g*) and F is the molar flow rate (mole/hr). The conversion of THF, the yield of pyrrolidine, and the selectivity for various catalysts were summarized in Table 1. The listed values refer to the data after 3 hr running of the reaction, though the behavior of the reaction scarcely changes with time on stream as will be mentioned below.

The results in Table 1 are summarized as follows: (1) NaY has no activity for this ring transformation. (2) Transition metal forms of zeolites have low activity. (3) Zeolites which are usually known to have high acidity such as HY, CeY, or MgY have high activity. (4) HY has the best activity together with the highest selectivity.

Since HY was proved to be the best catalyst for this ring transformation, all experiments described below were made exclusively with HY.

Time Course of the Reaction

The typical time course of the reaction over HY (74%) is shown in Fig. 1. The reaction conditions are as follows: reaction temperature, 335°C; catalyst weight, 1.5 g;

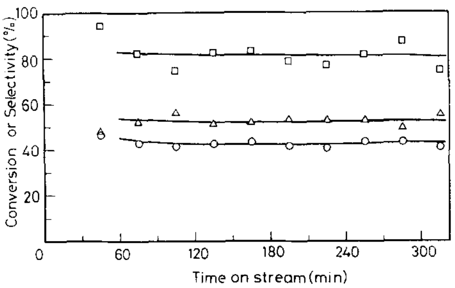


FIG. 1. Variation of the conversion of THF (△), the yield of pyrrolidine (○), and the selectivity (□) with time on stream.

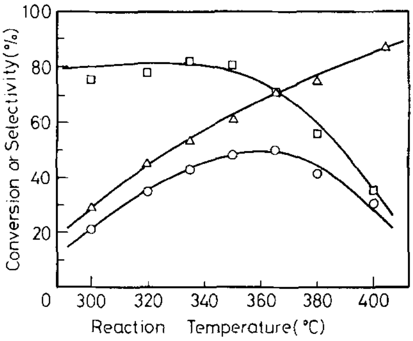


FIG. 2. Variation of the conversion of THF (△), the yield of pyrrolidine (○), and the selectivity (□) with reaction temperature. $W/F = 8.43$ g-cat·hr/mole; reactant ratio, $NH_3/THF = 7$.

reactant ratio, ammonia/THF = 7; $W/F = 8.43$ g-cat·hr/mole. In these reaction conditions, a pyrrolidine yield of 43% with a selectivity as high as 80% was obtained. Moreover, there is essentially no deactivation of the catalyst within 6 hr. X-ray diffraction patterns showed that the used catalyst retained its crystallinity.

Among byproducts, furan, 1-butene, and 1,3-butadiene were confirmed, but their amounts were too small to account for the fate of all of converted THF. No attempts were made to identify the byproducts with higher boiling points.

Effect of the Reaction Temperature

Under the constant contact time and molar ratio of the reactants, the effect of the reaction temperature on the conversion, the yield, and the selectivity were examined with HY (58%) as a catalyst. The results are shown in Fig. 2. The conversion of THF monotonously increases with the reaction temperature, while the yield of pyrrolidine increases with the reaction temperature up to 370°C and falls down over 370°C. The selectivity to pyrrolidine is a constant of 80% below 350°C, but sharply falls at higher temperatures. Thus, the optimum reaction temperature region of the reaction is 330–350°C.

Kinetics of the Reaction

Reaction kinetics was examined in the temperature range 300–350°C in a low W/F condition. In Fig. 3, the effect of ammonia pressure (P_{NH_3}) on the reaction rate (r) is shown. The rate is the first order with respect to ammonia in the pressure range 0.125–0.875 atm.

$$r = k \cdot P_{NH_3}. \tag{1}$$

The dependence of the rate on the THF pressure (P_{THF}) is shown in Fig. 4. The results in Fig. 4 can be expressed by the conventional Langmuir–Hinshelwood law:

$$r = \frac{k \cdot K_{THF} P_{THF}}{1 + K_{THF} P_{THF}}, \tag{2}$$

which on rearrangement gives

$$\frac{P_{THF}}{r} = \frac{1}{k \cdot K_{THF}} + \frac{1}{k}. \tag{3}$$

This equation could be checked using data of Fig. 4, as shown in Fig. 5. The slope and the intercept yielded the values of $1/k$ and $1/k \cdot K_{THF}$.

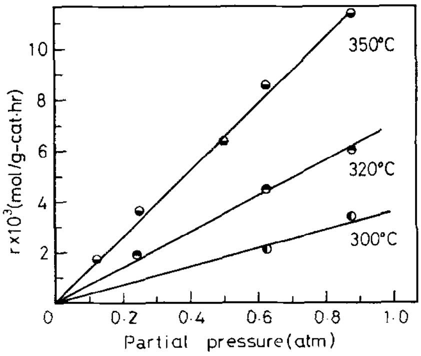


FIG. 3. The dependence of the reaction rate on the partial pressure of ammonia. $W/F = 2.81$ g-cat·hr/mole; $P_{THF} = 0.125$ atm.

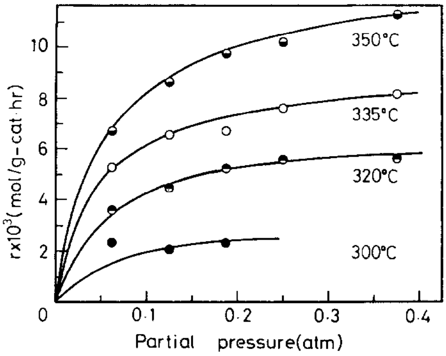


FIG. 4. The dependence of the reaction rate on the partial pressure of THF. $W/F = 2.81$ g-cat·hr/mole; $P_{NH_3} = 0.625$ atm.

By combining Eqs. (1) and (2), the rate law can be expressed by

$$r = \frac{k \cdot K_{THF} P_{THF} \cdot P_{NH_3}}{1 + K_{THF} P_{THF}}. \qquad (4)$$

The estimated values of k and K_{THF} at the reaction temperatures of 320, 335, and 350°C are summarized in Table 2. From the dependence of the values of k on the reaction temperature, the activation energy of the reaction is estimated at 17 kcal/mole, while the heat of adsorption of THF is calculated as 8 kcal/mole from the data of 320 and 350°C.

The reaction products of this reaction do not poison, nor effect the rate equation, for the addition of 10 mole% of water or pyrrolidine to the reactant THF does not change the yield of pyrrolidine or the selectivity of the reaction.

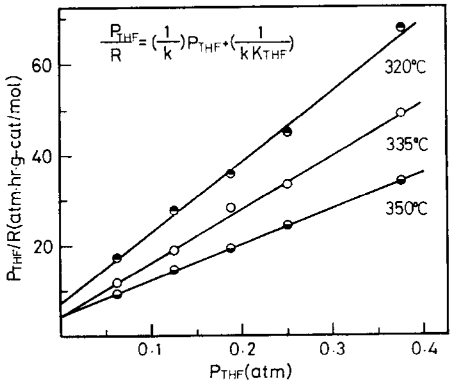


FIG. 5. P_{THF}/r-vs -P_{THF} plot.

TABLE 2

RATE CONSTANT k AND ADSORPTION EQUILIBRIUM CONSTANT K_{THF} AT VARIOUS TEMPERATURES

Temperature (°C)	k (mole/g-cat · hr · atm)	K (1/atm)
350	2.05×10^{-2}	16.4
335	1.39×10^{-2}	25.2
320	1.01×10^{-2}	22.7

$E_a = 17$ (kcal/mole) $Q = 8$ (kcal/mole)

Influence of the Extent of Cation Exchange

NH_4Y zeolites with various degrees of cation exchange of NaY with NH_4^+ were prepared and their catalytic activities on the ring transformation of THF into pyrrolidine were compared. As shown in Fig. 6, both the yield of pyrrolidine and the selectivity of the reaction increase with the increase of the degree of exchange until the latter reaches about 40%. With the exchange beyond 40%, the catalytic property does not change any more. In this region, the yield of pyrrolidine is about 43% and the selectivity is a little better than 80%. Turkevich *et al.* (*6*) have reported that the number of active centers of HY does not increase with the degree of decationization beyond 50% in cracking of cumene, in which active centers are Brönsted sites (*7*).

The results indicate that only the decationated sites produced by the replacement of Na^+ in NaY easily accessible to

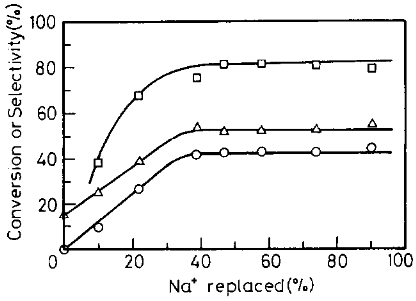


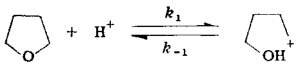
FIG. 6. Effect of cation exchange of NaY with NH_4^+ on the catalytic behavior: (△) conversion of THF; (○) yield of pyrrolidine; (□) selectivity for pyrrolidine. $W/F = 8.43$ g-cat·hr/mole; reaction temperature, 335°C; reactant ratio = 7.

NH_4^+ are catalytically effective for these reactions. In other words, the active centers are acidic sites located in the supercage, probably in S_{II} sites.

Reaction Mechanism

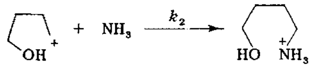
Since the temperature of pretreatment of NH_4Y in this work (460°C) is high enough to convert NH_4Y completely to HY and too low to cause the dehydroxylation of HY (*8, 9*), the acidic sites of the catalyst are considered to be exclusively Brönsted acid sites. The fact that zeolites which are known to have high Brönsted acidity such as MgY (*10*) show high activity supports the idea that active centers are Brönsted acid sites.

Taking the observed reaction kinetics into account, we propose the following mechanism for the reaction: THF is attacked by a protonic acid and opens the ring to form a carbonium ion [I]. This step is fast and in equilibrium in the reaction condition.



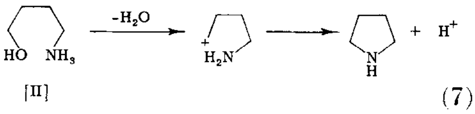
[I] (5)

The carbonium ion [I] thus formed reacts with ammonia from gas phase to form an ammonium ion [II]. This step is slow and rate determining.



[I] [II] (6)

The ammonium ion [II] dehydrates rapidly and closes the ring to produce pyrrolidine and to regenerate a protonic acid.



[II] (7)

The rate law of the reaction can be derivated from the above mechanism. Since step (5) is in equilibrium, the following relationship holds:

$$k_1 P_{THF} C_{H^+} = k_{-1} C_I, \tag{8}$$

where k_1 and k_{-1} are the rate constants of the forward and the reverse reaction of step (5), C_{H^+} and C_I are the surface concentrations of the Brönsted acid site and the intermediate carbonium ion [I] in the reaction condition. The sum of C_{H^+} and C_I is equal to surface concentrations of the effective Brönsted acid site originally present in the catalyst $(C_{H^{+0}})$:

$$C_{H^{+0}} = C_I + C_{H^+}. \tag{9}$$

From Eqs. (8) and (9), one obtains

$$C_I = C_{H^{+0}} \frac{K_{THF} P_{THF}}{1 + K_{THF} P_{THF}}, \tag{10}$$

in which $K_{THF} = k_1/k_{-1}$. Since the overall rate is determined by the rate of step (6), the rate law is given by

$$r = k_2 C_I P_{NH_3}. \tag{11}$$

Insertion of Eq. (10) into Eq. (11) results in

$$r = \frac{k_2 C_{H^{+0}} K_{THF} P_{THF} P_{NH_3}}{1 + K_{THF} P_{THF}}. \tag{12}$$

The rate law Eq. (12) is in agreement with experimentally obtained rate law Eq. (3), by putting $k_2 C_{H^{+0}} = k$.

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