Ring Transformation of γ -Butyrolactone into 2-Pyrrolidinone over Synthetic Zeolites

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Catalytic activities of synthetic zeolites for the ring transformation of γ -butyrolactone into 2-pyrrolidinone were compared in a flow reactor and CuY, HY, LiY, and NaY were found to have high activity. Alkaline earth forms of Y-zeolites lose their activity rapidly though their initial activities are high. For CuY, effects of the reaction temperature and the partial pressures of the reactants on the catalytic activity and the selectivity for 2pyrrolidinone were examined. At 230°-260°C, selectivity of 80-90% is easily attained. The product, 2-pyrrolidinone, works as a strong poison for the catalysis. The role of metal cations in zeolites is discussed and the reaction mechanism is proposed.

INTRODUCTION

Synthesis of 2-pyrrolidinone by the reaction of γ -butyrolactone with ammonia, has



been carried out in a liquid phase under pressure without use of catalysts (1). On the other hand, the reaction can be conveniently carried out in a vapor phase. Yur'ev et al. (2) carried out the reaction at 350°C over alumina and obtained 2pyrrolidinone in a 15.5% yield. Recent patents claim that aluminosilicates such as montmorillonite (3) or zeolite NaX (4) are effective for this reaction. Present authors and Fujita (5) reported in a preliminary paper that synthetic zeolites are potential catalysts for ring transformations of oxygen containing heterocycles into nitrogen containing heterocycles. Fujita et al. (6) studied the kinetics and the mechanism of the transformation of tetrahydrofuran into pyrrolidine. In this work, the ring transformation of γ -butyrolactone into 2-

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pyrrolidinone over synthetic zeolites has been studied. The catalytic activities of various forms of zeolites are compared and CuY is found to be the most effective catalyst. The reaction conditions were optimized in the case of CuY, 2pyrrolidinone. The correlation between the catalytic activity and the nature of metal cations is seen and the reaction mechanism is discussed.

EXPERIMENTAL

Catalyst. The starting material for all catalysts was commercial Linde SK-40(NaY), Linde 13X(NaX) or Na mordenite (obtained from Strem. Chem. Inc.) powder. In all cases, the zeolites were prepared by ion-exchange with salt solutions. The degree of exchange was estimated by a gravimetric analysis for eluted sodium using a magnesium uranyl acetate reagent. The degree of exchange of zeolites are listed in Table 1. The exchanged zeolites were dried at 110°C, pelleted without a binder, crushed and sized into 9-16 mesh, and they were stored in a desiccator containing a saturated aqueous solution of ammonium chloride.

Zeolite	Na ⁺ Ex- changed (%)	Conversion (%)	Yield (%)	Selectivity (%)	
НҮ	52	36.8	24.0	65.2	
LiY	65	30.5	17.5	57.5	
NaY		20.3	15.5	76.5	
KY	89	19.8	10.1	51.0	
RbY	61	13.3	7.9	59.4	
CsY	65	13.1	4.6	35.0	
MgY	66	14.6	9.9	67.9	
CaY	65	13.5	8.5	63.0	
SrY	65	9.0	5.2	57.8	
BaY	63	13.6	4.5	33.0	
CoY	65	22.5	10.4	46.2	
NiY	65	18.8	8.4	44.7	
CuY	65	31.1	25.1	80.0	
ZnY	65	17.5	4.0	22.0	
NaX	_	19.7	11.4	57.9	
Na Mordenite	_	1.3	0.0	—	

TABLE 1

ACTIVITY AND SELECTIVITY FOR Y-BUTYROLACTONE RING CONVERSION OVER VARIOUS ZEOLITES

W/F = 18.1 g. hr/mole, Molar ratio ammonia/ γ -butyrolactone = 5, Reaction temperature 258°C.

Material. γ -Butyrolactone with a purity of better than 99% and liquid ammonia in a high pressure cylinder were obtained from commercial sources.

Apparatus and procedure. A continuous flow reactor was used at an atmospheric pressure. The reactor was 20 mm id silica tubing placed in a vertical furnace. Prior to the reaction, the catalysts were heated in an air stream at 500°C for 60 min and then heated in an ammonia stream at the reaction temperature after air was removed from the reactor by feeding nitrogen for 30 min. γ -Butyrolactone was pumped into the preheating zone of the reactor by a microfeeder. The flow rate of ammonia was measured by means of a capillary flowmeter. The products were collected in a cold trap and were analyzed by gas chromatography in every 20 min. The analytical column was a 6 mm \times 2 m stainless steel tubing packed with PEG-6000 on Shimalite-F. The carrier gas was helium (40 ml/min) and the operating temperature was 200°C. The conversion of γ -butyrolactone, the yield of 2-pyrrolidinone, and the selectivity of the reaction are defined as follows:

conversion (%) =
$$\frac{\text{moles of } \gamma \text{-butyrolactone reacted}}{\text{moles of } \gamma \text{-butyrolactone fed}} \times 100$$

yield (%) = $\frac{\text{moles of } 2 \text{-pyrrolidinone produced}}{\text{moles of } \gamma \text{-butyrolactone fed}} \times 100$,
selectivity (%) = $\frac{\text{moles of } 2 \text{-pyrrolidinone produced}}{\text{moles of } \gamma \text{-butyrolactone reacted}} \times 100$.
As a measure of contact time, W/F is
defined as

 $W/F = \frac{\text{catalyst weight (g)}}{\text{feed rate of reactants(}\gamma\text{-butyrolactone} + \text{ammonia} + \text{nitrogen})(\text{mol/hr})}$

The data in figures and Table 1 are the ones taken after 3 hrs of running when the rate of catalyst deactivation becomes moderate.

RESULTS AND DISCUSSION

Catalytic activities of various forms of zeolites. The catalytic activities for the ring conversion of various forms of zeolites were compared under the following reaction conditions; reaction temperature 258°C, catalyst weight 4 g, W/F = 18.1 g·hr/mole, reactant molar ratio = ammonia/ γ -butyrolactone = 5.

The changes in the catalytic activity with time are illustrated in the cases of alkaline metal and hydrogen form (Fig. 1), alkaline earth form (Fig. 2) and transition metal forms (Fig. 3) of Y zeolites.

The catalytic activities decrease with time. For example, in the case of CuY (Fig. 4), the yield of 2-pyrrolidinone is 40.0% at the reaction time of 1 hr and it decreases to 25.1% at the reaction time at 3 hr. On the other hand, the selectivity of the reaction does not change much with time on stream. Formation of small amounts of ω -hydroxybutyronitrile is observed when hydrogen Y or a divalent metal form of zeolites are used as a catalyst, but not observed in the cases of alkaline metals.



FIG. 1. Change in the yield of 2-pyrrolidinone with time on stream in the cases of HY and alkaline metal forms of Y zeolites.



FIG. 2. Change in the yield of 2-pyrrolidinone with time on stream in the cases of alkaline earth metal forms of Y zeolites.



FIG. 3. Change in the yield of 2-pyrrolidinone with time on stream in the cases of transition metal forms of Y zeolite.

In Table 1, the activity and the selectivity for the production of 2-pyrrolidinone on various forms of zeolites are compared. From Table 1 and Fig. 1–Fig. 3, one can see the following features of the reaction:

(1) The catalytic activity strongly depends on the cation contained in the zeolites.

(2) Among the monovalent forms, HY is most active. But the activity of alkaline metal forms are also quite high. This is a great contrast to the conversion of tetrahydrofuran into pyrrolidine, in which HY has the highest activity, but NaY has no activity at all (6).



FIG. 4. Change in the catalytic behavior of CuY with time on stream; \bullet conversion of γ -butyrolactone, \bigcirc yield of 2-pyrrolidinone, \bigcirc selectivity for 2-pyrrolidinone.

(3) Activities of alkaline earth forms are very high at the beginning, but decay rapidly with time.

(4) CuY has the highest activity together with the highest selectivity.

(5) The activity of NaY is higher than that of NaX, while Na mordenite shows no activity.

Since CuY is apparently the best catalyst studied, the reaction conditions are varied to optimize the 2-pyrrolidinone yield.

Effect of reaction temperature. The effects of the reaction temperature on the yield of 2-pyrrolidinone and the selectivity of the reaction were examined with CuY as a catalyst. Fig. 5 shows the change in the yield with time at various temperatures. The higher the reaction temperature,



FIG. 5. Change in the yield of 2-pyrrolidinone with time on stream at various temperatures. Condition: W/F = 34.7 (g·hr/mole), ammonia/ γ -butyrolactone = 7. Catalyst: CuY 4 g.



FIG. 6. Effect of reaction temperature on the catalytic behavior of CuY; \bigoplus conversion of γ -butyrolactone, \bigcirc yield of 2-pyrrolidinone, \bigoplus yield of ω -hydroxybutyronitrile, \bigoplus selectivity for 2-pyrrolidinone. Condition: W/F = 34.7 (g-hr/mole), ammonia/ γ -butyrolactone = 7. Catalyst: CuY 4 g.

the higher the initial activity, but more rapidly was the catalyst deactivated. In Fig. 6, the catalytic properties are compared as a function of the reaction temperature. The yield of 2-pyrrolidinone increases with reaction temperature and goes through maximum at 258°C and decreases at higher temperatures.

The formation of ω -hydroxybutyronitrile is observed over 295°C. The selectivity for 2-pyrrolidinone is 85% at 210°C and 80% at 258°C, but falls down considerably at higher temperatures. Thus, the reasonable operating temperature range of the reaction is 210-260°C.

Though the catalysts are deactivated with time on stream, the original activity is completely recovered by heating the used catalyst in air at 500°C for 3 hrs. This indicates that the deactivation is caused not by the destruction of the zeolitic framework, but by poisoning caused by the products. Thus, the same catalyst was used repeatedly by treating it in the way described above after each run.

Effect of contact time. Fig. 7 shows the effect of W/F on the yield and the selectivity for 2-pyrrolidinone at 258°C. The yield increases with increasing W/F.

Effect of partial pressures of reactants. The dependence of the rate of the reaction on the partial pressure of γ -butyrolactone



FIG. 7. Change in the yield of 2-pyrrolidinone with contact time. Condition: temp. = 258° C, ammonia/ γ -butyrolactone = 7. Catalyst: CuY 4 g.

was examined at 258°C by keeping ammonia pressure at 0.5 atm. The partial pressure of nitrogen was changed to keep W/F constant (18.1 g·hr/mol). The results are illustrated in Fig. 8. The rate increases with increasing partial pressure of γ -butyrolactone (γ -BL), while the selectivity for 2-pyrrolidinone decreases, especially over 0.25 atm ($P_{\rm NH3}/P_{\gamma$ -BL} < 2).

The dependence of the rate on the partial pressure of ammonia was examined in the same manner. The partial pressure of γ -butyrolactone and W/F was kept constant of 0.125 atm and 34.7 g·hr/mol, respectively. As shown in Fig. 9, the rate increases with the partial pressure of ammonia. The selectivity as high as 90% was obtained when ammonia partial pressure is over 0.375 atm (P_{NH3}/P_{y-BL} > 3). The selectivity is much lower when the



FIG. 8. Dependence of catalytic behavior on the partial pressure of γ -butyrolactone. \bigcirc rate of 2-pyrrolidinone formation, \bigcirc yield of 2-pyrrolidinone, \odot selectivity for 2-pyrrolidinone. Condition: W/F = 18.1 (g·hr/mole), temp. = 258°C, P°_{NHa} = 0.5 atm Catalyst: CuY 4 g.



FIG. 9. Dependence of catalytic behavior on the partial pressure of ammonia, \bigcirc yield of 2-pyrrolidinone, \bigcirc selectivity for 2-pyrrolidinone. Condition: W/F = 34.7 (g·hr/mole), temp. = 258°C, P°_{γ-BL} = 0.125 atm. Catalyst: CuY 4 g.

partial pressure is below 0.25 atm ($P_{NH_3}/P_{\gamma-BL} < 2$).

From the above results, keeping molar ratio of ammonia and γ -butyrolactone over 3 seems essential to obtain the high selectivity for 2-pyrrolidinone.

As shown in Fig. 10, the dependence of the rate on the partial pressures could be expressed in a power form,

$$r = k P^{\circ} {}^{0.25}_{\gamma-B} \cdot P^{\circ} {}^{0.50}_{NH_3}$$

where $P^{\circ}_{\gamma-B}$ and $P^{\circ}_{NH_3}$ are the initial partial pressure of γ -butyrolactone and ammonia, respectively. This rate expression is only apparent, since the product, 2-pyrrolidinone was shown to have a strong inhibiting effect on the reaction.

Effect of products on rate. The inhibiting effect of the reaction products, water and 2-pyrrolidinone was examined in a fol-



FIG. 10. Dependence of the rate of 2-pyrrolidinone formation on the partial pressure of γ -butyrolactone and ammonia. $\bigcirc P^{\circ}_{\gamma,BL}, \bigoplus P^{\circ}_{NHa}$.

lowing way. The reaction was started in an ordinary manner with W/F of 34.7 g·hr/mol with the partial pressure of γ -bu-tyrolactone of 0.125 atm and that of ammonia of 0.375 atm.

When the catalyst deactivation become moderate after 3 hr of running, water or 2pyrrolidinone was added to the feed, keeping W/F constant by adjusting the feed rate of nitrogen, and the rate of 2pyrrolidinone production was followed. The addition of water to the feed had no effect on the catalytic behavior, but the addition of 2-pyrrolidinone drastically decreased the reaction rate, as illustrated in Fig. 11. The reaction was completely inhibited with an addition of 2-pyrrolidinone equal to 10 molar percent of γ -butyrolactone. The poisoning effect was found to be entirely reversible, for the rate of the reacrecovered completely when 2tion pyrrolidinone was reeliminated from the feed.

Role of metal cations. The origin of the catalytic activity of zeolites could be roughly classified into three categories.

(1) The activity is caused by the polarization of reactant molecules under the influence of the strong electrostatic field in the zeolitic cavities.

(2) The active centers are acidic sites which may be Brönsted or Lewis type.

(3) The activity depends on the coordination of the reactant to metal cations.

The first idea was originated by Rabo



FIG. 11. Effect of 2-pyrrolidinone addition to the feed. Condition: W/F = 34.7 (g·hr/mole), temp. = 258°C, $P^{\circ}_{\gamma \cdot BL} = 0.125$ atm, $P^{\circ}_{NH_{2}}$ 0.375 atm. Catalyst: 4 g.

and coworkers (7,8), who tried to explain the dependence of activity for carboniogenic reactions on the metal cations. The second is based on the observation of surface acidity by means of titration (9) or infrared spectroscopy of adsorbed bases (10). The activities for a number of reactions indicative of a carbonium ion mechanism have been explained on the basis of acidic nature. The third idea is applicable to the reactions with zeolites containing transition metal cations, such as amination of toluene (11) or chlorobenzene (1-2).

In the conversion of γ -butyrolactone into 2-pyrrolidinone, it should be noted that NaY or LiY has comparable catalytic activity with HY, though the part of HY may convert into NH₄Y in the reaction conditions. Since alkaline forms are known to have only scant amount of acidic sites, the second possibility that acidic sites are active centers, is not applicable to this particular reaction. It is of interest to note that, in the conversion of tetrahydrofuran



into pyrrolidine, HY is the most active catalyst and NaY has no activity at all (6). This indicates that the formally very similar two reactions are not similar at all in the reaction mechanism. We have concluded in the previous paper that Brönsted sites are responsible for the ring transformation of tetrahydrofuran.

The coordination of the lactone or ammonia to the metal cations does not seem essential since alkaline form has no crystal field stabilization. This may play some role in the case of CuY. The slow deactivation of CuY may be explained on this basis.

Thus, the last possibility is the electrostatic field. The catalytic activity is plotted against the electrostatic field in Fig. 12. The values of electrostatic field are taken from the works by Ward (13,14).

The catalytic activities refer to those



FIG. 12. Relation of catalytic activity to the electrostatic field of zeolite. Condition: W/F = 18.1 (g·hr/mole), temp. = 258°G, ammonia/ γ -butyrolactone = 5. Catalyst: 4 g.

after 3 hr of running. As seen in Fig. 12, the catalytic activities of alkaline metal forms and alkaline earth metal forms have a linear relationship with the electrostatic field, though the comparison of the activities of alkaline and alkaline earth forms cannot be made straightforwardly since the behavior of the catalyst deactivation is different between them. Thus, it may be concluded that the catalytic activity for the ring transformation of γ -butyrolactone is caused by the presence of the strong electrostatic field.

The activities of transition metal cations cannot be correlated with the electrostatic field. However, it is the usual observation that cations with partially filled d-orbitals do not behave as spherically charged cations (15), since the coordination or the ligand field stabilization becomes important in the former cations.

Reaction mechanism. Based on the above discussion that the electrostatic field is important, we propose the following mechanism.

The carbonyl group of γ -butyrolactone is polarized by the strong electrostatic field in the zeolites, probably in the neighborhood of the metal cation,



The polarized γ -butyrolactone (I) is attacked by an ammonia molecule to form an acid amide (II), which may quickly dehydrate and ring close.



The stronger the electrostatic field, the bigger would be the extent of polarization of the carbonyl group of γ -butyrolactone and the more readily would it be attacked by ammonia.

If M^+ was a proton, H^+ , the following competitive reaction would occur,



This explains why ω -hydroxybutyronitrile is formed only when the catalyst is a divalent cation form or HY, since multivalent forms are known to have Brönsted acidity (10).

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