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RING TRANSFORMATIONS OF OXYGEN CONTAINING HETEROCYCLES INTO NITROGEN CONTAINING HETEROCYCLES OVER SYNTHETIC ZEOLITES

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Synthetic zeolites are found to be effective catalysts for ring transformation of heterocycles. Furan reacts with ammonia over BaY to form pyrrole in 100% selectivity at 330°C. Tetrahydrofuran is converted to pyrrolidine in 70% selectivity over HY and MgY at 320°C, and γ-butyrolactone is converted to 2-pyrrolidone in 80% selectivity over CuY.

Transformations of heterocycles into compounds containing a ring system different from that of the starting substance over heterogeneous catalysts provide the convenient method of the synthesis of some heterocycles. Yur'ev and coworkers have extensively studied this type of reactions over alumina: Furan was converted into pyrrole in 30% yield by passing a mixture with ammonia over alumina.1) Wilson2) confirmed the results. Pyrrolidine was obtained in 43% yield from tetrahydrofuran and ammonia at 400°C.3) 2-Pyrrolidone was obtained in about 11% yield from γ-butyrolactone and ammonia at 350°C.4) Kolyer et al.6) claimed that 2-pyrrolidone could be prepared in high yield by reacting γ-butyrolactone and ammonia in the presence of montmorillonite at 250-350°C. German patent7) describes that γ-substituted γ-butyrolactones react with ammonia or primary amines over NaX zeolites to form corresponding substituted 2-pyrrolidones. The purpose of the present work is to show that synthetic zeolites are potential catalysts for the ring transformations of furan, tetrahydrofuran, and γ-butyrolactone into pyrrole, pyrrolidine, and 2-pyrrolidone.

EXPERIMENTAL All zeolites were prepared by ion-exchange of commercial Linde SK-40(NaY) or Linde 13X(NaY) powder with salt solutions. The degrees of exchange of zeolites used are listed in Table 1.

For the reaction of furan with ammonia, a conventional microreactor was used to determine catalytic activities. Neat ammonia was used as a reactant and as a carrier gas. For each pulse, 4 μl of the reactant were injected by a microsyringe. For the reactions of tetrahydrofuran and

Table 1. Conversion of Furan and Ammonia to Pyrrole over Zeolite Catalysts at 330°C *

Catalysts	Exchanged (%)	Conversion of furan (%)	Yield of pyrrole (%)	Selectivity (%)
NaY	--	trace	trace	--
MgY	73	36	16	44
CaY	93	52	12	23
SrY	98	26	20	77
BaY	--	14	14	100
MnY	66	8	8	100
CrY	90	51	9	18
CoY	83	40	12	30
NiY	89	78	6	8
CuY	93	54	10	19
ZnY	92	3	3	100
CdY	91	7	6	86
AlY	--	51	9	18
H Y	--	83	10	12
NaX	--	trace	trace	--
MgX	97	28	10	36
ZnX	100	7	4	57

* The results refer to the first pulse.

γ-butyrolactone with ammonia, a continuous flow reactor was used. The liquid reactant(tetrahydrofuran or γ-butyrolactone) was pumped into the preheating zone of the reactor by a microfeeder. The products were analyzed by gas chromatography in every 20 min.

RESULTS AND DISCUSSION

Conversion of furan to pyrrole As shown Fig.1, in the cases of HY, MgY, and the majority of other catalysts, the total conversion of furan decreased sharply with cumulative pulse number, while the yield of pyrrole remains almost unchanged. The yield of water is close to furan conversion. Since no products other than pyrrole and water were found in the gas chromatograph, high boiling point products should be formed. The difference in behavior of the pyrrole yield and the furan conversion indicates that the active

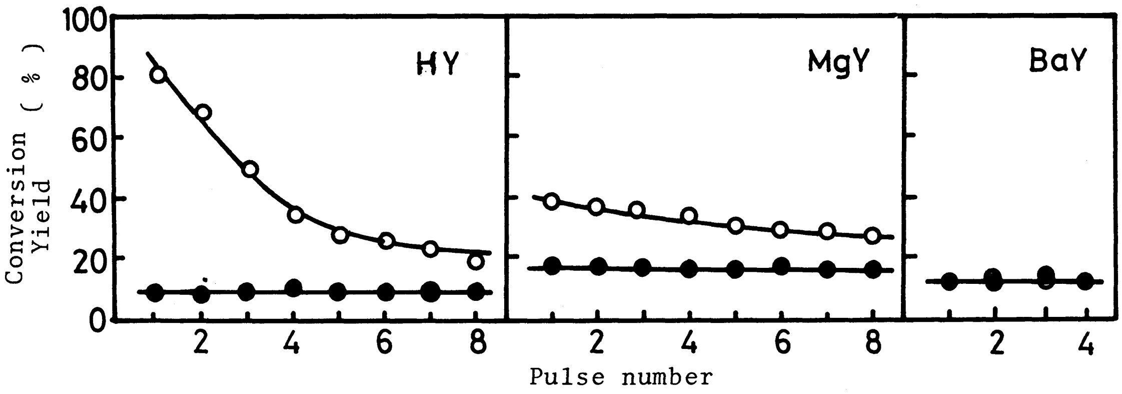

Fig. 1 Change in the catalytic activity for furan conversion with pulse number at 330°C.

o conversion of furan   catalyst 50 mg
● yield of pyrrole   ammonia 60 ml/min

centers responsible for the pyrrole formation are different from those responsible for byproducts formation, and the centers for the latter are deactivated by the reaction. In the cases of BaY, MgY, and ZnY, the selectivity to furan is almost 100%. The yield of pyrrole does not depend on pulse number, i.e., there is no deactivation of catalysts. In Table 1, the results for all the catalysts studied are summarized. NaY and NaX are inactive. In general, zeolites with high acidity[5)] such as HY or MgY seem to have high furan conversion, but to have low selectivity to pyrrole. Zeolites with modest acidity such as BaY show high selectivity to pyrrole. The temperature dependence was determined in the case of MgY. The pyrrole yield are 19.4, 15.9, 12.7, 9.2, and 0% at 360, 330,300,270,and 220°C, respectively. The selectivity of ring transformation decreased with reaction temperature. The effect of temperature of pretreatment of the catalyst was examined in the case of BaY. The yield of pyrrole does not depend on the pretreatment temperature of the catalyst in the range of 350-650°C.

Conversion of tetrahydrofuran to pyrrolidine The catalytic activity for this reaction was examined for 15 catalysts with the continuous flow reactor. Time course of the reaction in the case of HY is shown in Fig.2. The

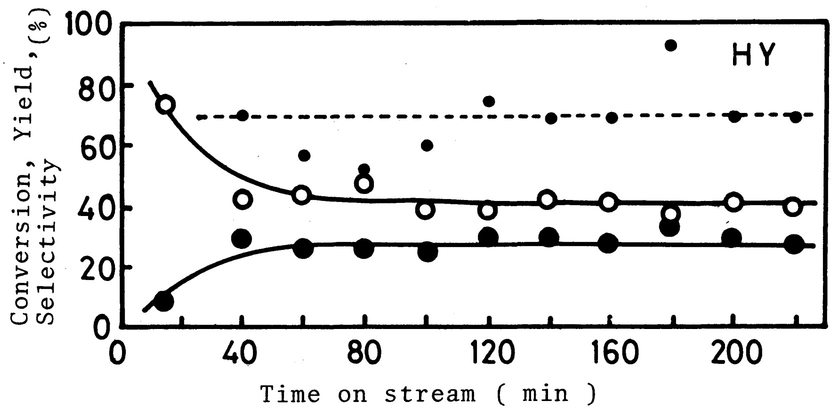

Fig.2 Changes in the catalytic activity and selectivity for tetrahydrofuran conversion with reaction time at 320°C.

○ conversion of tetrahydrofuran
● yield of pyrrolidine
• selectivity of pyrrolidine

catalyst 1.84 g
NH_3 /tetrahydrofuran = 4
W/F = 16.7 g·h/mole

yield and the selectivity do not change with reaction time, that is, there is no deactivation of the catalyst. The best results are obtained with HY which shows 30% yield of pyrrolidine in about 70% selectivity. The order of pyrrolidine yield is, HY(30%) > Mgy(19%) > BaY(13%) ≃ CeY(13%) > MgX(11%) > CuX(10%) > MnX(9%) ≃ BaY(9%) > SrY(8%) ≃ CuY(8%) > ZnY(7%) > PbY(5%) ≃ CaY(5%) > CoY(3%) > NiY(0%) ≃ NaY(0%). The best selectivity to pyrrolidine was obtained in the cases of HY, MgY, BaY(70%), and BaX(65%). Sodium form has no activity for this reaction and transition metal forms show low selectivity.

Conversion of γ-butyrolactone to 2-pyrrolidone This reaction was also examined with the continuous flow reactor. Typical time course of the reaction is shown in Fig.3. In contrast with previous two reactions, alkaline forms of zeolites show good activity for this reaction. Alkaline earth forms are less active than alkaline forms. The yield and the selectivity to 2-pyrrolidone decrease with reaction time. For example, in the case of NaY, the yieldsof 2-pyrrolidone are 57%, 27%, and 16% at the reaction time of 1, 2, and 3 hrs, respectively. Original activity is regained by the reactivation of the catalysts at 450°C for 2 hrs in an air stream. The best results are obtained with CuY, which shows 25% yield of 2-pyrrolidone in 80% selectivity at the reaction time of 3 hrs.

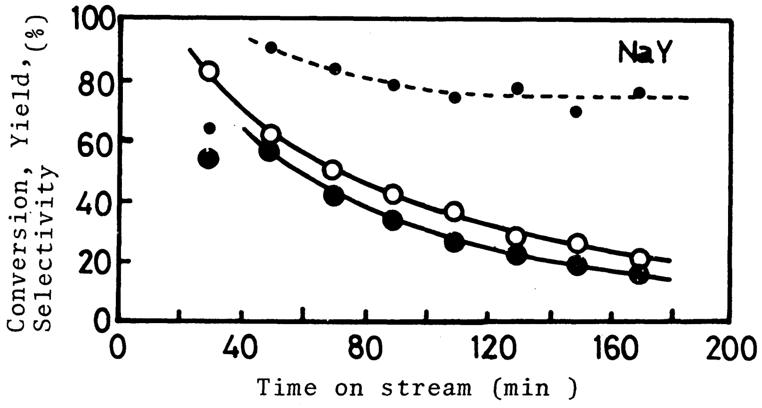

Fig.3 Changes in the catalytic activity and selectivity for γ-butyrolactone conversion with reaction time at 258°C.

○ conversion of γ-butyrolactone	catalyst 4 g
● yield of 2-pyrrolidone	NH_3 /γ-butyrolactone = 5
• selectivity of 2-pyrrolidone	W/F = 18.1 g·h/mole

In conclusion, it is clearly demonstrated that synthetic zeolites are the effective catalysts for the ring transformations of furan, tetrahydrofuran, and γ-butyrolactone into pyrrole, pyrrolidine, and 2-pyrrolidone.

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