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Basic Sites on Alkali Ion-added Zeolite

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The X type zeolites containing alkali ions in excess of ion exchange capacity exhibited high catalytic activity for 1-butene isomerization; the reaction proceeded at 273 K. Temperature programed desorption (TPD) of adsorbed CO_2 confirmed that strongly basic sites were generated by addition of alkali ions. Alkali metal oxides formed in the zeolite cavities are considered to possess strongly basic sites and to act as the catalytic sites.

Yashima et al. presented alkali ion exchanged zeolite X as active catalyst for side chain alkylation of toluene with methanol.1) The activity was dependent on the basicity of alkali metal element; that is, Cs > Rb > K > Na. Therefore they suggested that basic sites are active sites. Since then, a number of base-catalyzed reactions were reported to proceed on alkali ion-exchanged zeolites. Base-catalyzed reactions on basic zeolites are reviewed by Hölderich.2) However, the structure and location of the basic sites on zeolite are not clearly understood yet. The identification of the basic sites in zeolite is important subject. In addition, since the basic sites on the ion-exchanged zeolites are not so strong as those of basic metal oxides such as alkaline earth oxides, rare earth oxides, etc., preparation of zeolite possessing strong basic sites is another object to be investigated.

Recently, Hathaway and Davis reported that decomposition of the impregnated cesium acetate in the zeolite cavities resulted in the generation of catalytically active basic sites which were more active than those present in ion-exchanged zeolites.3) They proposed that the active basic sites are cesium oxide occluded in the zeolite cavities.4) In the present paper, we wish to report that strongly basic sites are generated by addition of a series of alkalis to the zeolite cavities and that the basic sites are strong enough to be capable of catalyzing 1-butene isomerization even at 273 K.

The alkali ion-exchanged zeolites and ion-added zeolites were prepared by the following procedures. Linde 13X were soaked at 333 K with 0.4 mol dm^{-3} solutions of group 1A metal acetates. The ratio of the Linde 13X to the solution was adjusted to 0.02 g Linde 13X/ml solution. The slurries were decanted and reslurried in a fresh solution. The exchange procedures were repeated four times. On completion of the four times exchange, the catalysts were separated into two parts. One part was filtered and washed with deionized water, and the other part was filtered and left unwashed to avoid decationation. Each catalyst was then dried in a vacuum desiccator at room temperature followed by calcination in O_2 at 673 K using closed circulation system with liquid N_2 trap to remove H_2O and CO_2 until no more oxygen was taken up. The color of prepared catalysts was white. The elemental analyses of catalysts by X-ray fluolecence spectroscopy were performed on RIGAKU 3080E. Surface area and X-ray diffraction pattern of each catalyst indicated that the degree of crystallinity of zeolite remained after calcination procedure.

A closed circulating system connected to a conventional vacuum line, and to a gas chromatograph was used to carry out the reaction. The reaction mixture was periodically withdrawn and analyzed by gas chromatography, a column packed with VZ-7 being operated at 273 K. Before each run of the isomerization, catalyst was evacuated under ca. 10^{-3} Pa at 673 K for 2 h.

TPD experiments were performed as follows: A sample (0.15 g) evacuated at 673 K for 2h was exposed to 1.3 kPa of CO_2 at room temperature for 30 min, followed by evacuation at room temperature for 2 h. The TPD procedure was started at a heating rate of 10 K min^{-1}. The desorbed gases were analyzed by a NEVA NAG-515 quardrupole mass spectrometer at ionization voltage of 90 eV. Peak intensities of desorbed gases were normalized to that of Ar which was constantly introduced into the system as an internal standard. CO_2 were purified by repeated freeze-thaw cycles before use.

The results of X-ray fluorescence analysis of the amounts of alkalis are given in Table 1. As expected, the amounts of alkalis in the ion-added zeolites were larger than those of the ion exchanged zeolites for all kinds of alkalis. While the oxide form is most probable as the form of excess alkalis, the formation of bulky alkali oxides on the outer surface of the ion-added zeolites is excluded since neither XRD patterns nor visual color showing alkali oxides were appreciable. They are supposed to locate in the cavities of zeolites.

Table 1. Composition and Surface area of Ion-Exchanged and Ion-Added Zeolite X

Zeolite MX[a)]		Si/Al ratio	Exchange percent M^+x100 / Al^{3+}(%)	Number of total cation (M^++Na^+) to 100Al^{3+}	Number of excess M^+ /unit cell	Surface area[b)] m^2/g
NaX	E	1.21	98	——	——	810
	A	1.23	110	——	9.9	760
KX	E	1.25	99	102	——	690
	A	1.27	112	116	11.5	660
RbX	E	1.20	76	101	——	550
	A	1.19	81	104	4.0	420
CsX	E	1.18	54	77	——	410
	A	1.20	68	93	12.8	360

a) E: Ion-exchanged, A: ion-added. b) Evacuation temp 673 K.

TPD plots of the adsorbed CO_2 on both ion-exchanged and ion-added zeolites are shown in Fig. 1. The amounts of desorbed CO_2 were larger for the ion-added zeolites than for ion-exchanged zeolites, though quantitative correlation between the amounts of desorbed CO_2 and the number of excess ions for each alkali ion-added zeolite was not clear. This lack of quantitative correlation is considered to be due to many factors such as retention of CO_2 on the zeolites at 673 K, existence of various species and geometrical differences of pore resulting from size and location of added ions. In addition to the larger amounts of desorbed CO_2, two peaks were distinctly observed for K and Rb ion-added zeolites. The peaks appearing at higher temperatures were not appreciable for the ion-exchanged zeolites. This demonstrates that new basic sites generate on the ion-added zeolites. The newly generated basic sites are stronger than the basic sites possessed by the simply ion-exchanged zeolites.

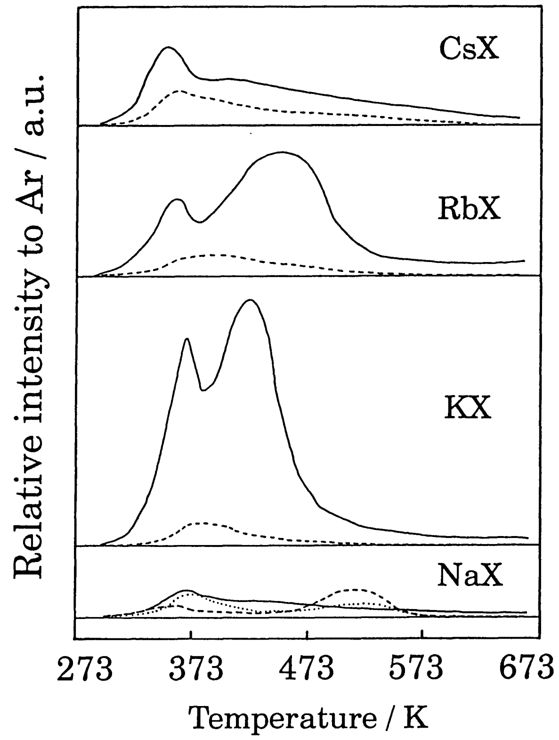

Fig. 1. TPD plots of CO_2 adsorbed on various zeolites; 13X • • • , ion-exchanged - - - , ion-added —— .

The catalytic activities of the alkali ion-exchanged and ion-added zeolites for 1-butene isomerization are listed in Tables 2 and 3 for reaction temperature of 273 K and 423 K, respectively. At the reaction temperature of 273 K, all ion-exchanged zeolites showed practically no activity, while ion-added zeolites exhibited considerable activities. The activities of the different alkali ion-added zeolites was in the following order; $Cs^+/CsX \approx Rb^+/RbX > K^+/KX > Na^+/NaX$. The appreciable activities for 1-butene isomerization at 273 K have never reported before for any basic zeolites, alkali oxides, and alkali hydroxides. Considering the generation of the strong basic sites on the ion-added zeolites evidenced by TPD of adsorbed CO_2, the active sites of the ion-added zeolites for 1-butene isomerization are suggested to be those basic sites. The basic sites existing on the simple ion-exchanged zeolites are not able to act as active sites at 273 K.

At the reaction temperature of 423 K, the activity of the Cs ion-exchanged zeolite became appreciable. The other ion-exchanged zeolites did not show activity. The ion-added zeolites showed much higher activities than the ion-exchanged zeolites. The cis/trans ratio in the product 2-butenes reflects the reaction intermidiates.[5)] By anionic mechanisms in which basic sites are active, a high cis/trans ratio is normally observed. The observed cis/trans ratios were more than 3 at the reaction temperature of 273 K, suggesting that the basic sites on the ion-added zeolites are active sites for 1-butene isomerization at 273 K. At 423 K, the cis/trans ratios were lower than those observed at 273 K. It is interesting to note that the cis/trans ratios obtained for the ion-added zeolites in the present study are close to those obtained for alkali metal oxides.6,7) Noumi et al.6) reported that the initial ratio obtained for potassium oxide at 423 K was about 1 which is close to the value obtained for potassium ion-added zeolite in this study. They also reported the dependence of the initial ratio for potassium oxide and sodium oxide on the reaction temperature, which coincide with those observed for potassium and sodium ion-added zeolites. The ratio 11 obtained in this study for Rb ion-added zeolite at 423 K is also close to the values observed7) for rubidium oxide at 413 K.

The similarity of the cis/trans ratios for ion-added zeolites to those for alkali metal oxides suggests that the active sites of the ion-added zeolites are alkali metal oxide clusters present in the zeolite cavities.

Table 2. Activity for 1-butene isomerization at 273 K

Catalyst[a)]		Reaction rate[b)] mmol/g • min	cis/trans[c)] ratio
13X		0	——
NaX	E	0	——
	A	0	——
KX	E	0	——
	A	2.4×10^{-2}	3
RbX	E	0	——
	A	3.2×10^{-2}	11
CsX	E	8.6×10^{-4}	——
	A	1.4×10^{-1}	10

a) E: Ion-exchanged, A: ion-added. b) Initial rate. c) Reaction time=0.

Table 3. Activity for 1-butene isomerization at 423 K

Catalyst[a)]		Reaction rate[b)] mmol/g • min	cis/trans[c)] ratio
13X		0	——
NaX	E	0	——
	A	1.1×10^{-2}	2
KX	E	0	——
	A	7.8×10^{-2}	1
RbX	E	0	——
	A	1.3	12
CsX	E	1.3×10^{-1}	5
	A	1.1	9

a),b),c) See Table 2.

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