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Decomposition of 2-Propanol Over Alkali Cation Exchanged Zeolites

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The decomposition of 2-propanol over alkali cation exchanged X and Y type zeolites was studied. Over Li and Na zeolites, most of the 2-propanol was converted to propylene and water. Over K, Rb, and Cs zeolites both dehydration and dehydrogenation of 2-propanol occurred. The dehydration and the dehydrogenation were selectively depressed by the addition of a basic reagent (pyridine) and an acidic reagent (phenol), respectively. These results showed that the K, Rb, and Cs zeolites had both acidic sites and basic sites. When the ion exchange procedure was carried out in a low pH solution, protons were introduced into the zeolite by cation exchange and these sites acted as acidic sites. The ratio of the dehydration to the dehydrogenation depended on the kind of exchanged alkali cations and the type of zeolites. It is concluded that the acidic sites of the alkali exchanged zeolites are the decationated sites, the electrostatic field, and possibly the alkali cations, and their basic sites are the lattice $(AlO_4)^-$ paired with the alkali cations.

INTRODUCTION

It is well known that the alkali cation exchanged zeolites have little activity to promote any reactions proceeding through a carbonium ion form. However, it has been found that the alkali zeolites have appreciable catalytic activity in dehydration of alcohols (*1*, *2*), methyl migration of anisole (*3*), dealkylation of cumene (*4*), and the reaction of acetic anhydride with hydrogen sulfide (*5*). It has also been reported that the Li-exchanged zeolite was always the most active catalyst among the alkali cation exchanged zeolites in the above-mentioned reactions.

Recently, Sidorenko *et al.* (*6*) found that styrene and ethylbenzene were produced by the alkylation of toluene with methanol over alkali cation exchanged zeolites. We have also reported on the alkylation of toluene with methanol and with formaldehyde over alkali cation exchanged zeolites (*7*). And it was found that xylenes were selectively formed over Li zeolites and that both styrene and ethylbenzene were produced over the other alkali cation exchanged zeolites. It has been concluded that the formation of xylenes depends on the solid acidity which was determined by the infrared measurements of pyridine adsorbed on the zeolites, and that the formation of styrene and ethylbenzene depends on the solid basicity which was detected by the indicator method.

We found that over alkali cation exchanged zeolites, 2-propanol mainly converted to propylene and acetone by dehydration and dehydrogenation, respectively. It has been known that the dehydration of 2-propanol is catalyzed by the catalyst acidity, and that the dehydrogenation depends on the catalyst basicity (*8*, *9*). We found that the yield of water decreased with the addition of pyridine and that the yield of acetone was depressed by the addition of phenol into the reaction system. These results showed that the alkali cation exchanged zeolites had both acidic and basic properties. Therefore, we studied the acidity and the basicity of alkali cation exchanged zeolites using the dehydration and the dehydrogenation of 2-propanol as a model reaction, and discussed the acidic and the basic sites of the zeolites.

EXPERIMENTAL

Material

2-Propanol, having a purity of over 99.8%, was obtained from a commercial source.

Catalyst

To examine the fundamental factors in this process, potassium-exchanged X zeolites were used as the standard catalysts. Potassium-exchanged X zeolites of varied potassium contents (KX-11–15) were prepared by a conventional ion exchange procedure, using Linde 13X and 1 *N* aqueous solution of potassium acetate. In addition, the discretionary mixture solution of potassium acetate, acetic acid, and potassium hydroxide was used to prepare the catalysts (KX-21–27) exchanged with the various pH values (pH 5.3–13.6) (Table 1).

To compare the activity of the various kinds of alkali cations or zeolites, the alkali cation exchanged zeolites were prepared using a 1 *N* aqueous solution of the corresponding alkali chloride and Linde 13X or SK-40(Y type zeolite) (Table 2).

All the exchanged zeolites were pelleted without a binder, crushed and sized in 8–14 mesh, and were calcined at a desired temperature for 2 hr in nitrogen before the reaction.

TABLE 1
DISTRIBUTION OF CATIONS IN KX

Catalyst No.	pH of ion exchange solution	Cation content (%) Na	K	Decationated
KX-11	8.0	84	14	2
KX-12	8.0	63	32	5
KX-13	8.0	49	44	7
KX-14	8.0	34	56	10
KX-15	8.0	7	73	20
KX-21	5.3	9	57	34
KX-22	6.0	8	65	27
KX-23	8.0	11	68	21
KX-24	9.1	11	73	16
KX-25	10.9	11	76	13
KX-26	12.7	11	78	11
KX-27	13.6	12	84	4

TABLE 2
ACTIVITY OF ALKALI EXCHANGED ZEOLITE CATALYSTS

Catalyst[a]	Ion exchanged (%)	Yield[b] (mol%) Acetone	Water
LiX	70	0.9	94.0
NaX	—	1.2	89.5
KX	89	3.8	33.5
RbX	68	3.7	28.0
CsX	68	2.0	40.5
LiY	65	0.4	85.5
NaY	—	0.7	76.0
KY	89	6.5	21.0
RbY	61	7.0	15.5
CsY	80	9.3	12.5

[a] Reaction conditions: catalysts calcined at 700°C for 2 hr in N_2 before reaction. Temperature, 425°C; W/F, 5.0 g × hr/mol.

[b] The listed yield is taken at 4 hr on process time.

Analysis

The reaction mixture was analyzed by gas chromatography; for the liquid products, using a 3 mm × 2 m column with stationary phase PEG 1500 on Flusin T at 70°C, and for the gaseous products, using a 4 mm × 6 m column with stationary phase ODPN on active alumina at room temperature.

Apparatus and Procedure

Experiments were carried out in a fixed bed type apparatus with a continuous flow system under atmospheric pressure. The catalyst was placed in an electrically heated quartz reactor and calcined at a desired temperature for 2 hr in nitrogen, and then brought to the reaction temperature *in situ*. 2-Propanol was fed by the microfeeder and was carried by nitrogen to the catalyst bed. The product was cooled with a dry ice–methanol trap; liquid samples for analysis were collected periodically, and gaseous samples were collected simultaneously.

RESULTS

When the catalyst contacted with 2-propanol, its activity always changed considerably with process time. The activity change of KX-15 (Table 1), as a standard catalyst, is shown in Fig. 1. At the initial stage of this process, the activity for dehydration was stronger than that for dehydrogenation, and the products in the vapor phase contained some cracking products, such as methane, ethane, and ethylene, in addition to propylene produced by the dehydration of 2-propanol. However, after 4 hr of process time, the composition of the products scarcely changed, and little side reaction occurred. Only a small amount of diisopropyl ether was formed by the intermolecular dehydration of 2-propanol. Therefore, the yields of water and acetone after 4 hr of process time were used as the parameters of dehydration and dehydrogenation of 2-propanol, respectively.

Catalyst Preparation Conditions

Degree of ion exchange. A linear relation between the yield of acetone and potassium ion content in the KX-11–15 catalysts is shown in Fig. 2. On the other hand, the yield of water decreased with the potassium ion content. These results suggested that the rate of dehydrogenation of 2-propanol depended on the potassium ion content in the KX catalyst.

Calcination temperature. The effect of the calcination temperature of KX-15 catalyst on this process is shown in Fig. 3. The yield of acetone and water attained the maximum value at 700°C calcination temperature. At higher than 700°C, it is expected that the zeolitic framework was partially destroyed. It was suggested that the rate of dehydration and dehydrogenation were depressed by a small amount of water contained in the zeolite.

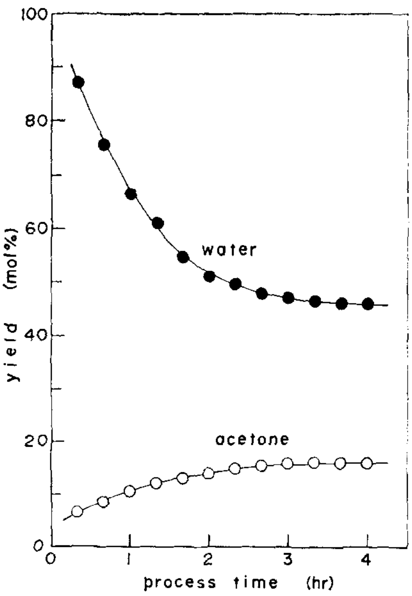

FIG. 1. Activity change with process time. Reaction conditions: catalyst, KX-15 calcined at 700°C for 2 hr in N_2; temperature, 475°C; W/F, 7.5 g × hr/mol.

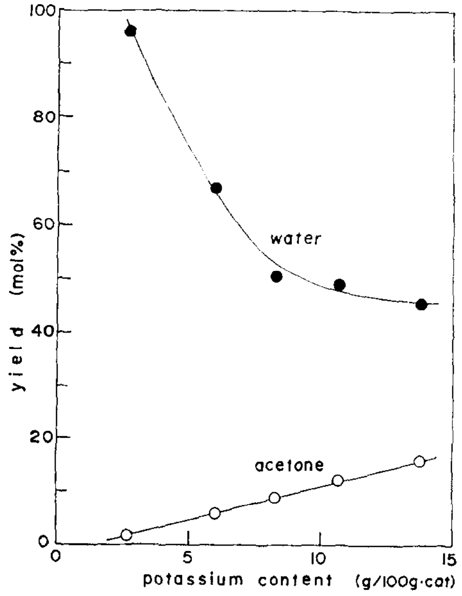

FIG. 2. Effect of potassium content in KX catalyst. Reaction conditions: catalyst, KX-11–15 calcined at 700°C for 2 hr in N_2; temperature, 475°C; W/F, 7.5 g × hr/mol.

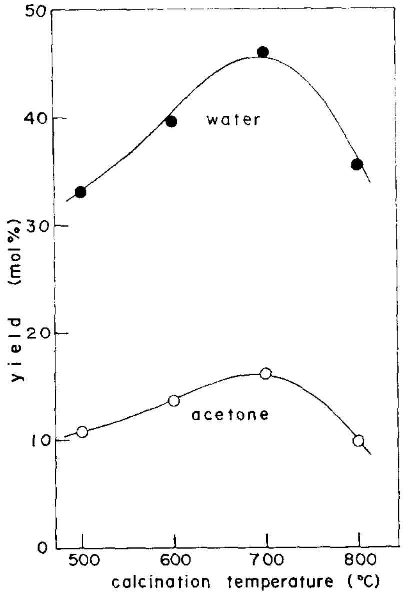

FIG. 3. Effect of calcination temperature. Reaction conditions: catalyst, KX-15; temperature, 475°C; W/F, 7.5 g × hr/mol.

Reaction Conditions

Reaction temperature. Figure 4 shows that the yield of water increased with reaction temperature, while the yield of acetone attained a maximum value at 475°C. It was suggested that in the higher reaction temperature, the rate of dehydration was faster than that of the dehydrogenation in this process, because even in the noncatalytic system, the dehydration of 2-propanol occurred considerably at a high temperature of 490°C; the yields of water and acetone were 11.0% and 0.5%, respectively.

Contact time. The effect of the contact time is shown in Fig. 5. The yields of water and acetone increased with contact time, but they did not considerably change at more than $W/F = 7.5$ g × hr/mol. From this result, it was suggested that the catalyst was poisoned by the products. Figure 6 shows that a small amount of water (0.11 mol/g × cat) sorbed on the activated KX-15 catalyst before reaction, restrained the decomposition, especially the dehydration of 2-propanol.

Activity of alkali cation exchanged zeolites. The results of dehydration and dehydrogenation of 2-propanol over various alkali cation exchanged zeolites prepared by the ion exchange solution of the corresponding alkali chloride are shown in

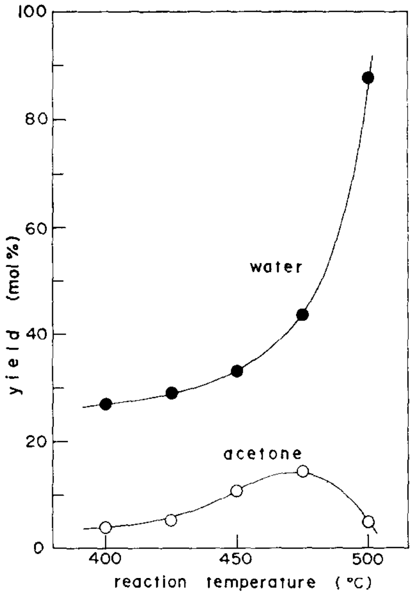

FIG. 4. Effect of reaction temperature. Reaction conditions: catalyst, KX-15 calcined at 700°C for 2 hr in N_2; W/F, 5.0 g × hr/mol.

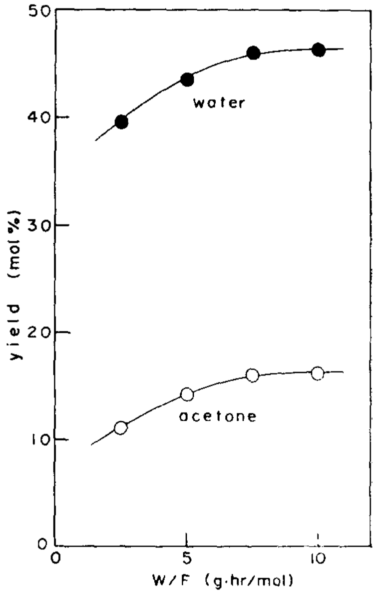

FIG. 5. Effect of contact time. Reaction conditions: catalyst, KX-15 calcined at 700°C for 2 hr in N_2; temperature, 475°C.

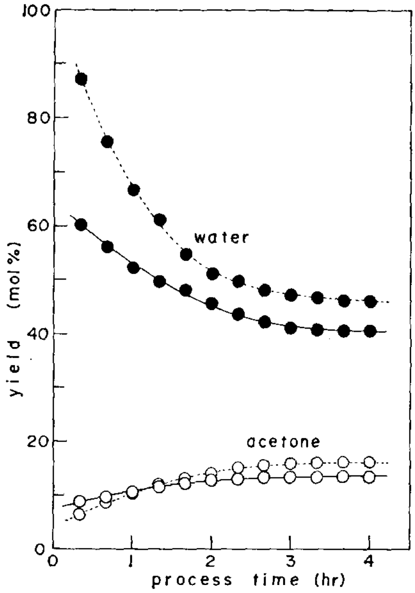

FIG. 6. Effect of water pretreatment. Reaction conditions: catalyst KX-15 calcined at 700°C for 2 hr in N_2; temperature, 475°C; W/F, 7.5 g × hr/mol. (----) Nonpretreatment, (——) water pretreatment.

Table 2. In the case of noncatalyst, the yields of water and acetone at 425°C were 0.9% and 0.4%, respectively. In Table 2, NaX and NaY were prepared by the back-exchange of 13X and SK-40 with an aqueous solution of sodium chloride, because the commercial synthetic zeolites contained a small amount of divalent cations as impurities.

On Li and Na zeolites, the dehydration was markedly far ahead of the dehydrogenation. However, on K, Rb, and Cs zeolites, the dehydrogenation proceeded and a considerable amount of acetone was formed. The yield of acetone increased with increase of ionic radius and with decrease of electron negativity of alkali cation, except CsX. On CsX, the yield of acetone was lower than that expected because the zeolitic framework was partly destroyed by the calcination at 700°C. It was due to being prepared in ion exchange solution of lower pH (pH 5.3). In the dehydration of 2-propanol, the X zeolite catalysts were more active than the corresponding cation exchanged Y zeolite catalysts. While, in the dehydrogenation, the Y zeolite catalysts showed higher activity than X zeolite catalysts.

DISCUSSION

Addition of pyridine and phenol. To examine whether the dehydration and the dehydrogenation of 2-propanol were catalyzed by the acidity and the basicity, respectively, pyridine as a basic reagent or phenol as an acidic reagent was introduced to the reaction system. Figure 7 shows the effects of addition of pyridine on this process. The dehydration was poisoned, but the activity for the dehydration could not be completely eliminated. This result shows that a part of the dehydration of 2-propanol proceeded on the sites which did not strongly interact with pyridine. Pyridine did not affect the dehydrogenation. And, stopping the addition of pyridine, the activity of KX-15 was at once completely restored.

Figure 8 shows the effects of the addition of phenol on this process. The dehydrogenation was almost perfectly depressed, while the dehydration was ac-

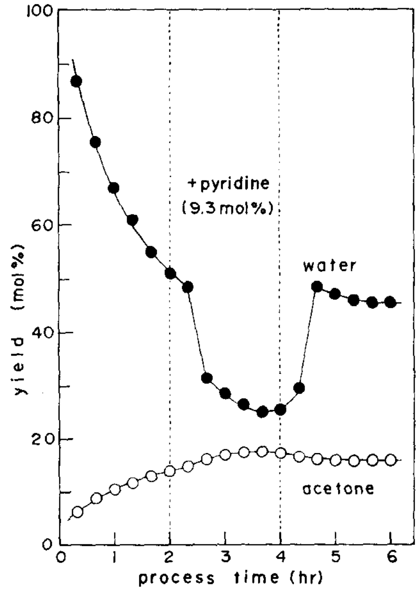

FIG. 7. Effect of pyridine addition. Reaction conditions: catalyst, KX-15 calcined at 700°C for 2 hr in N_2; temperature, 475°C; W/F, 7.5 g × hr/mol.

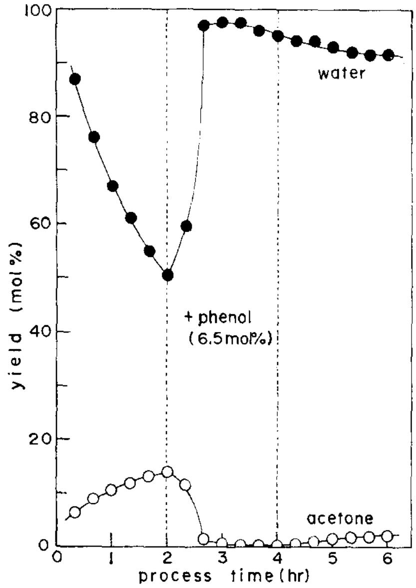

FIG. 8. Effect of phenol addition. Reaction conditions: catalyst, KX-15 calcined at 700°C for 2 hr in N_2; temperature 475°C; W/F, 7.5 g × hr/mol.

celerated. And, stopping the addition of phenol, the dehydrogenation and the dehydration were slowly restored to the non-addition state. These results clearly show that the dehydration of 2-propanol was catalyzed by the acidity of the catalyst, and the dehydrogenation of 2-propanol was catalyzed by the basicity of the catalyst.

Catalyst acidity of alkali cation exchanged zeolites. There is the electrostatic field between alkali cation and $(AlO_4)^-$ in the zeolite lattice. On Li and Na zeolites, the strength of this field is fairly large and can polarize the coordinated water. Especially, on the Li zeolites, the Lewis acid sites (three coordinated Al) and the Brønsted acid sites have been detected by the infrared measurements of pyridine adsorbed on X and Y zeolites (*7*). However, the interaction of pyridine with these acid sites of Na zeolites has never been detected (*7*). It is expected that Na zeolites have some acidic sites which do not strongly interact with pyridine, but catalyze the dehydration of 2-propanol, as mentioned above. However, on K, Rb, and Cs zeolites, the electrostatic field seemed to be very weak, because these alkali cations have a larger ionic radius than Li and Na. So, over these catalysts, the yield of water decreased with increase of the ionic radius of alkali cations.

All sorts of alkali cations can interact with pyridine in the zeolite as observed in the infrared measurements (*10*). It was found that the X zeolite, which contained more alkali cations than Y zeolite, showed higher catalytic activity in dehydration of 2-propanol than the Y zeolite. Therefore, it can be expected that the alkali cations act as Lewis acid sites and can catalyze the dehydration of 2-propanol. And the strength of this Lewis acid site depends on the electron negativity of alkali cations. The results shown in Table 2 agreed with this relation.

When Na cation in the parent zeolites was exchanged by the other cation in an aqueous solution, a part of Na cation might be exchanged by proton in the solution. The degree of the proton exchange depends on its concentration in the solution; i.e., pH value. Therefore, the catalyst activity for both dehydration and dehydrogenation of 2-propanol depended on the pH value of the ion exchange solution for KX preparation, as shown in Fig. 9. Over KX catalysts

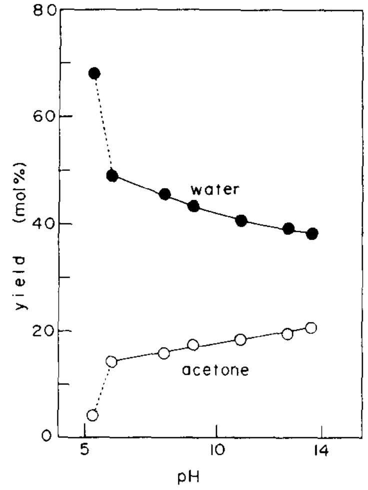

FIG. 9. Effect of pH value of ion exchange solution. Reaction conditions: catalyst, KX-21–27 calcined at 700°C for 2 hr in N_2; temperature 475°C; W/F, 7.5 g × hr/mol.

prepared in the pH range of the solution between 6.0 and 13.6 (KX-22–27), the yield of acetone increased and that of water decreased with increase of the pH value. These results could be explained by the fact that the concentration of potassium ion increased with the pH value at the same degree of ion exchange as shown in Table 1. The cation sites, which were not occupied by either sodium or potassium ions, are believed to be occupied by protons. These proton sites formed the decationated sites by the calcination at a high temperature and catalyzed the dehydration of 2-propanol. When there were so many decationated sites, the zeolitic structure became more unstable. X-Ray diffraction showed that the zeolitic structure of KX prepared in the pH 5.3 solution was destroyed when it was calcined at 700°C for 2 hr in nitrogen. Over this KX-21 catalyst, the yield of acetone considerably decreased, but that of water increased. These results suggested that the catalytic sites for dehydration were not lost by the destruction of zeolitic framework.

Thus, the acidic sites of alkali-exchanged zeolites are the decationated sites, the electrostatic field, and possibly the alkali cations.

Catalyst basicity of alkali cation exchanged zeolites. The yield of acetone depended on the content of potassium ion in KX catalyst (Figs. 2 and 9), and it increased with the increase of ionic radius and with the decrease of electron negativity of the exchanged alkali cations (Table 2). It was suggested that the lattice $(A1O_4)^-$ was expected to act as a basic site on the alkali zeolites. This site is ordinarily neutralized and sealed by the hydrated cation. However, in the case of alkali cation, especially K, Rb, or Cs, the acidity of these cations is very weak, and moreover these cations have only weak interaction with water molecules. Therefore, it is believed that the basicity of lattice $(A1O_4)^-$ paired with these alkali cations is still effective, and these sites can catalyze the dehydrogenation of 2-propanol. It is expected that the basicity of $(A1O_4)^-$ was also affected by the adjacent alkali cations, so that the basicity of the alkali exchanged Y zeolite was stronger than that of the corresponding X zeolite, because the Y zeolite contained less alkali cations than the X zeolite. This explanation satisfied the fact that the Y zeolite showed higher catalytic activity for the dehydrogenation of 2-propanol than the corresponding X zeolite.

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