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Bimolecular Condensation of Ethanol to 1-Butanol Catalyzed by Alkali Cation Zeolites

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This study reports that ethanol is converted primarily into 1-butanol by a bimolecular condensation on alkali cation zeolites. For this base-catalyzed reaction, Rb–LiX exhibits the highest reaction activity and 1-butanol selectivity among zeolites employed. The reaction temperature and the contact time have a distinct influence on the condensation reactivity. It is also confirmed that the reaction does not proceed through aldol condensation. Thus, we propose a reaction mechanism in which one molecule of ethanol, whose C–H bond in the β-position is activated by the basic zeolite, condenses with another molecule of ethanol by dehydration.

INTRODUCTION

Base catalysis over zeolites is an area of growing interest. In recent years, some studies on zeolites have been focused on their basic properties and the reactions catalyzed by their basic sites (*1–9*). These reactions include dehydrogenation of isopropanol (*3, 4*), side-chain alkylation of toluene or *p*-xylene with methanol (*5–7*), isomerization of butene (*8*), and aldol condensation of acetone (*9*). However, the development and the utilization of base catalysis of zeolites are still limited. In this paper, a new reaction catalyzed by basic zeolites—bimolecular condensation of ethanol to 1-butanol—is reported.

1-Butanol, one of the important commercial chemicals, which is used in addition as an organic solvent, has found application as an additive to gasoline. The industrial synthesis of alcohol larger than three carbon atoms has usually been accomplished by hydrocarbonylation of alkene or alcohol. In this route, the carbon chain is extended atom by atom, and a branched product is simultaneously formed. Later, some workers found a one-step method for the preparation of 1-butanol from ethanol on solid–base catalysts such as basic oxides (*10–14*). However, no studies of the synthesis of 1-butanol in one step over zeolites have been previously reported.

It is well known that one of the traditional 1-butanol synthetic methods is aldol condensation of acetaldehyde, followed by catalytic hydrogenation of the condensation product. Aldol condensation does take place on basic zeolites (*9*), so it may be asked whether the reaction reported here proceeds by the same mechanism. We give our proposal for the reaction mechanism in this paper by investigating and answering this question.

EXPERIMENTAL

Catalyst

Lithium and potassium cation-exchanged 13X zeolites were prepared by a cation-exchange procedure. They were exchanged five times at 353–358 K using 0.5 *N* aqueous solution of lithium chloride and potassium chloride, respectively. Rb^+-impregnated zeolites were prepared by impregnating exchanged samples with rubidium nitrate solution and calcined at 573 K in air for 20 h. The cationic contents and silicon-to-aluminum ratios of these catalysts (Table 1) were ana-

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TABLE 1

Alkali Cation Content and Si-to-Al Ratio of the Catalyst

Catalyst	Alkali cation content (wt%)				Alkali cation exchange degree			Si/Al
	Li	Na	K	Rb^a	Li	Na	K	
Li*X*	1.94	2.03			62.1	19.6		1.39
Na*X*(13*X*)		9.13			—	—	—	1.38
K*X*		0.56	16.08			5.6	93.9	1.40
Rb–Li*X*	1.63	1.72		10.00				1.39
Rb–Na*X*		7.26		10.00				1.39
Rb–K*X*		0.37	10.48	10.00				1.39

[a] Calculated from impregnation.

lyzed by using inductively coupled plasma techniques and chemical methods. X-ray diffraction pattern showed that the crystal structure of the zeolites was undamaged.

Apparatus and Procedure

Experiments were carried out in a fixed-bed microreactor with a continuous-flow system at atmospheric pressure. All the catalysts were pelleted without a binder, crushed, and sized to 40–60 mesh. Before reaction, the catalyst was activated at 773 K in a nitrogen stream for 2.5 h, and then cooled to the reaction temperature *in situ*. Ethanol and acetaldehyde were fed by saturating a nitrogen stream at 308 and 277 K, respectively, and the other reactants were supplied by microfeeders. The reaction mixture was sampled periodically with a six-way valve and analyzed by on-line gas chromatography using a FID detector. The rate of product formation and the rate of ethanol conversion as well as the selectivity of product are defined, separately, as follows.

The rate of product formation

$$R = \frac{FY}{W}(\mathrm{mol \cdot min^{-1} \cdot g^{-1}})$$

The rate of ethanol conversion

$$-R_{\mathrm{Ethanol}} = \frac{FC}{W}(\mathrm{mol \cdot min^{-1} \cdot g^{-1}})$$

The selectivity of product

$$S\% = \frac{R}{-R_{\mathrm{Ethanol}}} \times 100,$$

where

F = feed rate of ethanol (mol · min^{-1})

Y = yield of the product $= \dfrac{\text{moles of the product}}{\text{moles of fed ethanol}}$

C = ethanol conversion $= \dfrac{\text{moles of ethanol converted}}{\text{moles of fed ethanol}}$

W = weight of the catalyst used (g).

Analysis of Liquid Products

The liquid products were cooled, collected, and then analyzed qualitatively by GC–MS and GC–IR techniques. The results of analysis are listed in Table 2.

RESULTS AND DISCUSSION

1. The Reactivity of Ethanol Condensation and the Effect of Reaction Conditions on the Reactivity

When ethanol was carried through the Rb-containing zeolites bed at 673 K or above, in addition to some gaseous light products formed by thermolysis of a part of the ethanol, a considerable amount of liquid products listed in Table 2 were observed. The changes of the rates of product formation with time over Rb–LiX are shown in Fig.

TABLE 2

MS and IR Data of Liquid Products

Product	Ms $(m/e)^a$	IR (cm $^{-1}$)	
		Product	Standard sample
1-Butanol (BO)	31, 56, 41, 43, 27	3672, 2955, 1466, 1389, 1045	3668, 2955, 1462, 1393, 1042
Acetaldehyde (AD)	29, 44, 43	2739, 1759, 1369, 1119	2739, 1759, 1369, 1126
Acetal (AC)	45, 73, 27, 103	2986, 2905, 1385, 1146, 1099, 953	2990, 2905, 1385, 1146, 1103, 953
Butyraldehyde (BA)		2970, 2897, 2812, 2712, 1747, 1400	2970, 2897, 2812, 2712, 1747, 1,400
2-Ethyl-l-butanol (EBO)	43, 70, 41, 55, 71, 27, 29, 31	3665, 2970, 2885, 1466, 1373, 1045	
Hexanal (HA)		2943, 2808, 2712, 1747, 1462	2943, 2881, 2812, 2712, 1744, 1462
1-Hexanol (HO)	56, 41, 43, 55, 31, 42, 27, 29	3661, 2939, 2878, 1462, 1389, 1053	3668, 2935, 2878, 1466, 1389, 1053
1, 1-Diethoxy-butane (BC)	103, 101, 47, 55, 29, 27, 75, 43	2974, 2885, 1454, 1385, 1138, 1103, 995	2978, 2885, 1458, 1381, 1138, 1069, 999

[a] The peaks are arranged in order of decreasing intensity of m/e values.

1. It can be seen that the reaction reaches a steady state in a short time, and the chief product is 1-butanol while acetaldehyde is the main by-product. The predominant components in the "other" in Fig. 1 and Table 3 are gaseous light products. Figure 2 gives the changes of the rate of ethanol conversion and 1-butanol selectivity with time.

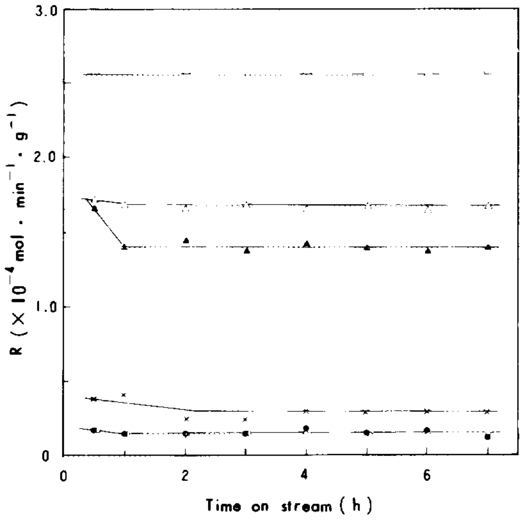


FIG. 1. Rate changes with time. Conditions: temp. = 693 K, W/F = 5.6 g · h · mol^{-1}, catalyst, Rb–LiX. (□) BO; (▲) AD; (×) EBO; (○) BA; (●) AC, (△) other.

It is shown in Table 3 that the reactivities of three Rb-containing catalysts are different. The formation rates and selectivities of 1-butanol and the total formation rates and selectivities of C_4 alcohol and aldehyde on these three zeolites all decrease in the order Rb–LiX > Rb–NaX > Rb–KX. Rb–LiX possesses the best catalytic performance among the zeolites used.

Exchanged only zeolites, however, are entirely different from Rb-containing samples in catalytic behavior (see Table 3). On exchanged zeolites, especially on LiX and

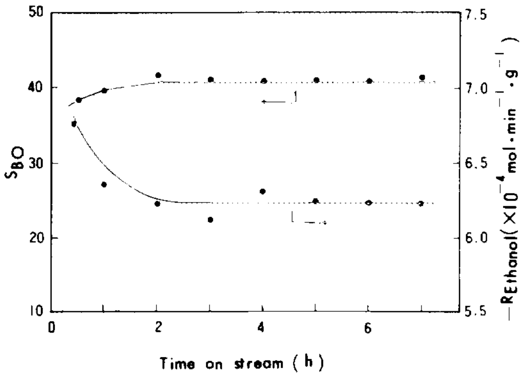


FIG. 2. Ethanol conversion rate and 1-butanol selectivity changes with time. Conditions are the same as in Fig. 1.

TABLE 3

Reactivity on Each Catalyst

Catalyst	R ($\times 10^{-4}$ mol · min^{-1} · g^{-1})										$-R_{\mathrm{Ethanol}}$ ($\times 10^{-4}$ mol · min^{-1} · g^{-1})	S_{BO} (%)	$S_{\mathrm{BO+BA}}$ (%)
	BO	AD	BA	AC	EBO	HO	HA	BC	Other	BO + BA			
LiX	0	2.10	0	0	0	0	0	0	15.41	0	17.51	0	0
NaX(13X)	0	1.74	0	0	0	0	0	0	7.88	0	9.62	0	0
KX	T[a]	1.41	0	T	T	0	0	0	3.48	T	4.89	T	T
Rb-LiX	2.55	1.41	0.15	0.15	0.30	T	T	T	1.68	2.70	6.23	40.9	43.3
Rb-NaX	2.40	1.71	0.24	0.24	0.39	T	T	T	1.59	2.68	6.56	36.6	40.2
Rb-KX	1.02	2.01	0.12	0.21	0.09	0	0	0	1.56	1.14	5.01	20.4	22.8

Note. Conditions: Temp. = 693 K; W/F = 5.6 g · h · mol^{-1}.

[a] T = Trace.

NaX, although the rates of conversion are high, most of the ethanol is converted into gaseous light products instead of condensation products. Except KX, on which a trace 1-butanol is detected, LiX and NaX do not exhibit condensation activities. The characterization of acid–base properties of these zeolites in our previous work (7) indicates that there exist weak acid sites on LiX, NaX, and KX, but no detectable acidity and only basicity exists on corresponding Rb-containing samples. The fact that the condensation of ethanol 1-butanol occurs selectively on these basic zeolites suggests that the reaction is base catalyzed.

The effect of the reaction temperature on ethanol reactivity is shown in Fig. 3. The rate of ethanol conversion increases linearly and the rates of product formation also rise with temperature, but the rate of 1-butanol formation does not change significantly at temperatures higher than 693 K and even decreases slightly at 753 K. At higher temperatures (>693 K), the 1-butanol selectivity declines linearly due to a remarkable increase of C_6 products, acetaldehyde, and gaseous light products. Thus, the temperature at which 1-butanol has both a high rate of formation and good selectivity is 693 K.

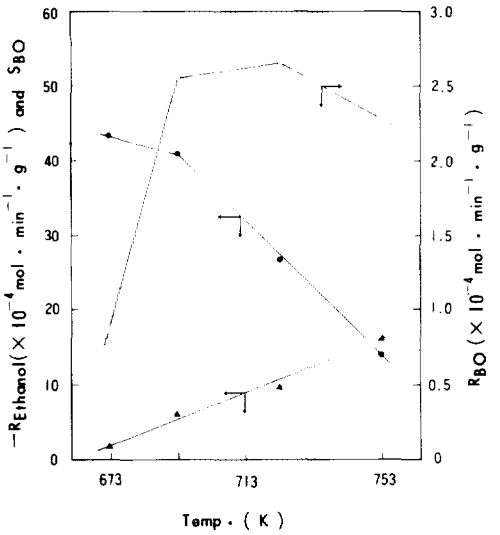


FIG. 3. Effect of temperature on the reactivity. Conditions: W/F = 5.6 g · h · mol^{-1}, catalyst, Rb–LiX. (▲) $-R_{\mathrm{Ethanol}}$, (○) R_{BO}, (●) S_{BO} %.

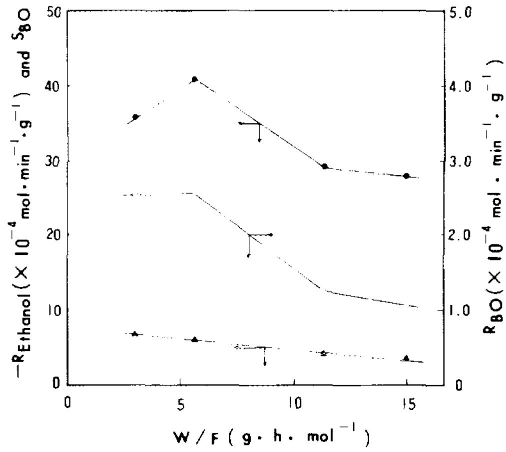


FIG. 4. Effect of contact time on the reactivity. Conditions: temp. = 693 K, catalyst, Rb–LiX. (▲) $-R_{\mathrm{Ethanol}}$, (○) R_{BO}, (●) S_{BO} %.

Changing the contact time (W/F), which is defined as the ratio of the weight of catalyst (g) to the feed rate of reactant (mol · h^{-1}), also exerts a great effect on ethanol reactivity (Fig. 4). We can conclude from Fig. 4 that the appropriate contact time for selectively forming 1-butanol is 5.6 g · h · mol^{-1}.

2. *Mechanism of Ethanol Condensation*

Since acetaldehyde, the main by-product, is a substrate for aldol condensation that can be catalyzed by basic catalysts, one may deduce readily the possible reaction scheme for extending the carbon chain and forming 1-butanol as follows:

$$CH_3CH_2OH \rightarrow CH_3CHO + H_2$$

$$2CH_3CHO \rightarrow CH_3CH = CHCHO \text{ (aldol condensation)}$$

$$CH_3CH = CHCHO + H_2 \rightarrow CH_3CH_2CH_2CHO$$

$$CH_3CH_2CH_2CHO + H_2 \rightarrow CH_3CH_2CH_2CH_2OH$$

$$C_4 \text{ alcohol or aldehyde} + CH_3CHO \rightarrow C_6 \text{ alcohol or aldehyde}$$

In this mechanism, acetaldehyde, crotonaldehyde (CA), and butyraldehyde are all reaction intermediates, and 1-butanol can also be regarded as an intermediate for the successive condensation in which C_6 alcohol and aldehyde are formed. Thus, we examined and verified the mechanism of ethanol condensation by either adding these intermediates to the reactant feed or directly taking them as reactants, and then observing the variation in reactivities. It should be explained that the mechanism referred to here is only a description of apparent reaction processes instead of elementary reaction steps.

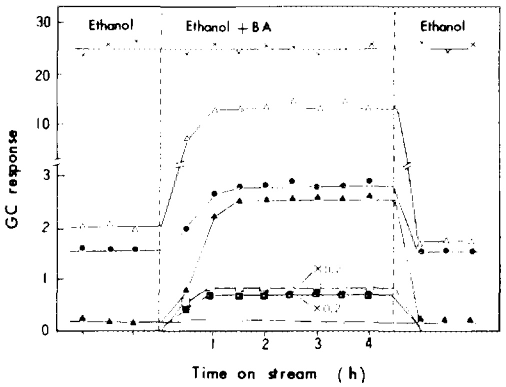


FIG. 5. Effect of butyraldehyde addition on the reactivity. Conditions: temp. = 693 K, $(W/F)_{\text{Ethanol}}$ = 4.8 g · h · mol^{-1}, $(W/F)_{BA}$ = 25.7 g · h · mol^{-1}, catalyst, Rb–LiX. (×) Ethanol, (△) BO, (●) AD, (▲) BA, (○) EBO, (□) HO, (■) HA.

Figure 5 shows the effect of butyraldehyde addition on the reactivity. No change in the quantity of ethanol is found when butyraldehyde is introduced into the reactant feed, but the quantities of 1-butanol and C_6 alcohol and aldehyde increase greatly. Moreover, when the addition of butyraldehyde is ceased, the quantity of each product returns to its previous level. Similarly, adding 1-butanol to the reactant feed (Fig. 6) results in a marked increase in amounts of butyraldehyde and C_6 products. These results suggest that a reversible conversion can occur betwen butyraldehyde and 1-butanol under the reaction conditions, and the successive condensation proceeds from C_4 alcohol and aldehyde.

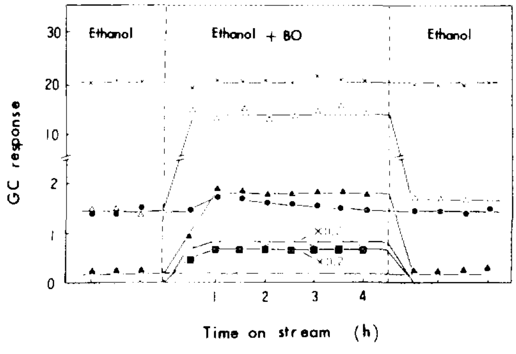


FIG. 6. Effect of 1-butanol addition on the reactivity. Conditions: temp. = 693 K, $(W/F)_{\text{Ethanol}}$ = 4.8 g · h · mol^{-1}, $(W/F)_{BO}$ = 26.7 g · h · mol^{-1}, catalyst, Rb–LiX. (×) Ethanol, (△) BO, (●) AD, (▲) BA, (○) EBO, (□) HO, (■) HA.

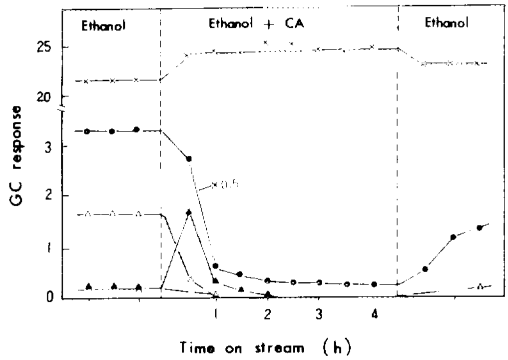
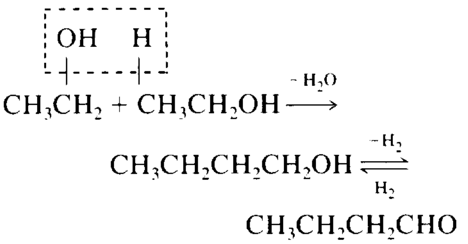


FIG. 7. Effect of crotonaldehyde addition on the reactivity. Conditions: temp. = 693 K, $(W/F)_{\text{Ethanol}}$ = 4.8 g · h · mol^{-1}, $(W/F)_{\text{CA}}$ = 24.1 g · h · mol^{-1}, catalyst, Rb–LiX. (×) Ethanol, (●) AD, (△) BO, (▲) BA, (○) EBO.

However, when crotonaldehyde is introduced into the reactant feed (Fig. 7), the quantity of ethanol increases but those of all other substances decrease. 1-Butanol and 2-ethyl-1-butanol fall rapidly to zero, and butyraldehyde also goes down after a rise. These results indicate that the conversion of ethanol is depressed by crotonaldehyde addition, and the hydrogenation of crotonaldehyde to C_4 alcohol and aldehyde take place with difficulty, but a small amount of crotonaldehyde is converted into butyraldehyde in the initial stage of crotonaldehyde addition. Therefore, crotonaldehyde cannot be the intermediate of ethanol condensation. It can also be seen from Fig. 7 that various products do not restore and only a small quantity or even none of the condensation product appears after stopping crotonaldehyde supply. This seems to suggest that crotonaldehyde has a poisoning effect on ethanol condensation on the basic zeolites.

Table 4 summarizes the results of reactions performed by directly using 1-butanol, crotonaldehyde, and acetaldehyde as the reactant, separately. 1-Butanol can be converted into butyraldehyde but no C_6 products are detected because of a lack of C_2 alcohol; this is consistent with the above results. Crotonaldehyde cannot be converted further into 1-butanol although it can be produced by aldol condensation of acetaldehyde on even LiX on which no ethanol condensation activity is observed. Consequently, it is demonstrated once again that in the condensation reaction of ethanol, the carbon chain is not extented by aldol condensation; i.e., the reaction does not undergo the scheme mentioned before.

In view of the structure of products, the formation of water in the reaction and the above-proposed elimination of the aldol condensation step, the following alternative paths for extending the carbon chain are suggested.



$$\overset{\boxed{\text{OH}\quad\text{H}}}{\text{CH}_3\text{CH}_2 + \text{CH}_3\text{CH}_2\text{OH}} \xrightarrow{-\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \underset{\text{H}_2}{\overset{-\text{H}_2}{\rightleftharpoons}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} \tag{1}$$

TABLE 4

Reactivities of Different Reactants

Reactant	Catalyst	R ($\times 10^{-4}$ mol · min^{-1} · g^{-1})			
		BO	BA	C_6	CA
1-Butanol (BO)	Rb–LiX	—	1.56	0	0
Crotonaldehyde (CA)	Rb–LiX	0	Trace	0	—
Acetaldehyde (AD)	Rb–LiX	0	0	0	7.46
	LiX	0	0	0	10.69

Note. Conditions: Temp. = 693 K; $(W/F)_{\text{BO}}$ = 26.7 g · h · mol^{-1}; $(W/F)_{\text{CA}}$ = 24.1 g · h · mol^{-1}; $(W/F)_{\text{AD}}$ = 0.67 g · h · mol^{-1}.

TABLE 5

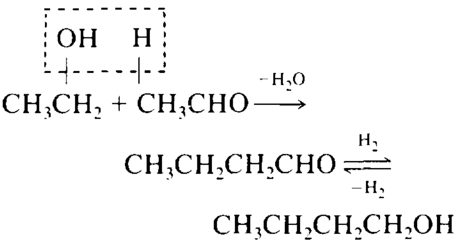
Reactivities of Different Reactants

Reactant	$-R_{\mathrm{Ethanol}}$ ($\times 10^{-4}$ mol · min^{-1} · g^{-1})	R ($\times 10^{-4}$ mol · min^{-1} · g^{-1})			
		BO	BA	C_6	CA
Ethanol	4.47	0.99	0.27	0.86	0
Ethanol + AD[a]	0.14	Trace	0.14	0	0.08

Note. Conditions: Temp. = 693 K; catalyst, Rb–NaX; $(W/F)_{\mathrm{Ethanol}}$ = 19.9 g · h · mol^{-1}; $(W/F)_{\mathrm{Ethanol+AD}}$ = 19.7 g · h · mol^{-1}.

[a] Ethanol/AD = 2 (molar ratio).

or

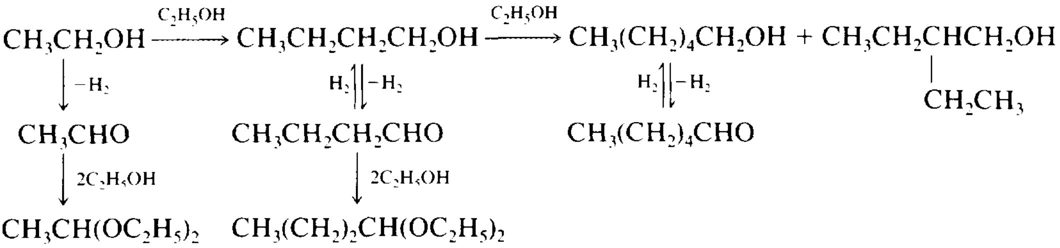


$$\overset{\boxed{OH\quad H}}{CH_3CH_2 + CH_3CHO} \xrightarrow{-H_2O} CH_3CH_2CH_2CHO \underset{-H_2}{\overset{H_2}{\rightleftharpoons}} CH_3CH_2CH_2CH_2OH \quad (2)$$

One molecule of ethanol or acetaldehyde, whose C–H bond in the β-position or α-position is activated by a basic zeolite, condenses with another molecule of ethanol into C_4 alcohol or aldehyde by eliminating one molecule of water. Since the C–H bond in the α-position of acetaldehyde is more easily activated than that in the β-position of ethanol, it may be considered that path (2) should be more likely than path (1). This conclusion, however, contradicts the results shown in Table 5. It can be seen from Table 5 that when an ethanol–acetaldehyde mixture is fed as reactant, the condensation activity decreases markedly in comparison with using only ethanol as reactant; the rates of 1-butanol and C_6 product formation are almost zero, ethanol is less converted, and a small amount of crotonaldehyde is observed.

Furthermore, the influence of contact time (W/F) on the ratio of butyraldehyde to 1-butanol yields (Fig. 8) was investigated to determine the relationship of formation and conversion of C_4 products. At $W/F < 11.3$ g · h · mol^{-1}, the ratio of butyraldehyde to 1-butanol yields decreases linearly with W/F. Extrapolating the line to $W/F \approx 1.5$ g · h · mol^{-1}, the ratio approaches zero. That is, the shorter the contact time, the more difficult the formation of butyraldehyde, and no butyraldehyde exists in the products when the contact time reaches a certain limit ($W/F \leq 1.5$ g · h · mol^{-1}). This indicates that 1-butanol is produced prior to butyraldehyde; in other words, the formation of 1-butanol is easier than that of butyraldehyde. It can be proposed, therefore, that the reaction proceeds by path (1) rather than path (2). Smith and Anderson (*15*) also presented this alcohol condensation scheme in their work on higher alcohol synthesis from synthesis gas.

According to the path suggested above for the growth of the carbon chain, the overall reaction scheme is:



$$\begin{tikzcd}
CH_3CH_2OH \arrow[r, "C_2H_5OH"] \arrow[d, "-H_2"] & CH_3CH_2CH_2CH_2OH \arrow[r, "C_2H_5OH"] \arrow[d, shift left, "-H_2"] & CH_3(CH_2)_4CH_2OH + CH_3CH_2\underset{CH_2CH_3}{\underset{|}{C}H}CH_2OH \arrow[d, shift left, "-H_2"] \\
CH_3CHO \arrow[d, "2C_2H_5OH"] & CH_3CH_2CH_2CHO \arrow[u, shift left, "H_2"] \arrow[d, "2C_2H_5OH"] & CH_3(CH_2)_4CHO \arrow[u, shift left, "H_2"] \\
CH_3CH(OC_2H_5)_2 & CH_3(CH_2)_2CH(OC_2H_5)_2 &
\end{tikzcd}$$

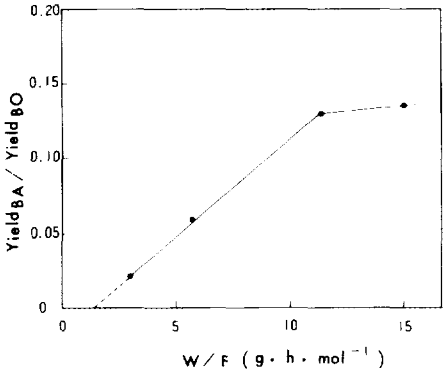


FIG. 8. Effect of contact time on $\mathrm{Yield_{BA}/Yield_{BO}}$. Conditions are the same as in Fig. 4.

In this mechanism, acetaldehyde and butyraldehyde are by-products that are not involved in the carbon chain growth process.

CONCLUSION

1. It is found that ethanol is converted mainly into 1-butanol by a bimolecular condensation on alkali cation zeolites. The activity and selectivity of the condensation reaction are higher on the Rb–LiX zeolite than on all other samples investigated. The optimum reaction temperature and contact time are 693 K and 5.6 g · h · $\mathrm{mol^{-1}}$, respectively.

2. The reaction does not proceed through aldol condensation, and acetaldehyde, a by-product, does not contribute to the extension of carbon chain. Thus, a reaction mechanism is suggested: under the effect of basic zeolite, one molecule of ethanol whose C–H bond in the β-position is activated condenses with another molecule of ethanol by dehydration; the whole reaction proceeds following this scheme for chain growth.

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