

Dehydration of Alcohols over Zeolite Catalysts

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In order to determine the influence of pore geometry on reaction rate and selectivity in dehydration, the dehydration of ethanol and *n*-butanol to olefins and ethers over various zeolite catalysts was studied. The commercial zeolites, Linde-X, Linde-A, and Norton Zeolon in sodium form were base-exchanged with lithium, potassium, magnesium, calcium, barium and, in one case, hydrogen.

Both reaction rate and selectivity were found to be strongly influenced by sieve type and by the size and charge of the exchanged cation. Selectivity between the formation of alcohol and ether was also strongly dependent on the length of the alcohol chain, and, for some sieves, on temperature.

It has been known for some time that the ordered cavities and closely sized openings of "molecular sieves" are well suited to selective adsorption and catalysis. It was the purpose of this study to investigate systematically reactivity and selectivity of several families of sieves in the vapor-phase dehydration of ethanol and *n*-butanol to olefins and ethers. The three families of zeolites studied include Linde Zeolite A (hereafter designated "A"), Linde Zeolite X or faujasite (hereafter "X"), and Norton Zeolon or mordenite (hereafter "Z"). The structures of these materials have been well defined (1, 2, 3).

Within each family the pore opening and cation character were systematically varied by exchanging the normally found sodium ion of the zeolite with lithium, potassium, magnesium, calcium, and barium. Hydrogen-exchanged Z was also studied. The much-investigated dehydration catalyst, γ -alumina, was also included as a basis for comparison.

Weisz and co-workers (4) have previously demonstrated "shape-selective" dehydration of primary and secondary butanol on the calcium-exchanged varieties of zeolites A and X. Significant conversions of both alcohols were obtained with the latter,

while Ca-A catalyst was virtually inactive in isobutanol dehydration due to pore-size considerations, but had comparable activity to the Ca-X catalyst in *n*-butanol dehydration. No information was offered regarding the relative amounts of olefin and ether formed.

The different type of "shape-selective catalysis" of interest in this investigation is described by a process where a single reactant molecule can pass through the zeolite pores and gain access to the active sites. There it is converted to two or more products, some of which can readily form in and pass out of the crystalline cavities and some of which have difficulty forming or leaving.

CATALYST PREPARATION

Ion-exchanged varieties of Linde zeolites A and X were prepared according to a procedure suggested by Linde. Before the exchange the sample was allowed to hydrate by exposure in a thin layer to the atmosphere overnight. Approximately 30 g of the hydrated pellets was placed in a glass column having an inside diameter of 15 mm. The column was mounted vertically in a tube furnace. A 1 *N* solution of the chloride salt of the exchanging cation was

passed through the zeolite column which was maintained at an elevated temperature in the 85–95°C range. A 600% excess of exchanging cation equivalents to exchange capacity of the zeolite was employed. The solution was passed at the approximate rate of 1 liter per 100 g of zeolite per hour. The exchanged molecular sieve was then washed free of soluble salts with copious quantities of distilled water until a negative test for chloride ion was obtained in the effluent wash water with 10% silver nitrate solution. In this manner the potassium-, lithium-, magnesium-, and barium-exchanged varieties of A and X were prepared.

Norton Zeolon sieves were base-exchanged in powder form beginning with the sodium form of mordenite. Thirty grams of the hydrated powder was added to 600 ml of 1 *N* solution of the chloride salt of the exchanging cation. The slurry was stirred continuously and maintained at an elevated temperature in the 80–90°C range for 2 hr. The suspension was then filtered and washed with distilled water until no chloride ion was detected in the wash water. This procedure was then repeated. Three such batch treatments were considered adequate for each exchanging cation. The powder was bonded into pellets with an organic material which was subsequently burned off.

Not all of the sodium ions are readily exchangeable (except in the case of hydrogen-exchanged mordenite). The procedures outlined above gave the percentages of original sodium ion replaced shown in Table 1. The resulting catalysts were then mixtures of sodium zeolites, bonding agents (in the case of zeolites A and X), and exchanged zeolites.

Various attempts were made in the later catalytic studies to base comparisons on an equivalent fully exchanged, pure zeolite. For example, catalytic activity of an exchanged zeolite was assumed to be made up of a portion in sodium form and a portion in exchanged form. An effective activity was calculated for the pure exchanged material by simple proportion.

Neither this approach nor any other modification attempted gave results which

could be defended. Accordingly it has been assumed that the catalytically active cationic sites are also those which are active in base exchange (i.e., the unexchanged sodium is relatively inactive). Activity then

TABLE 1
ION EXCHANGE OF ZEOLITES

Catalyst	Calculated % ion exchange
<i>Zeolite-A</i>	
Na-A	—
Li-A	57.3
K-A	74.8
Mg-A	53.1
Ca-A	73.9
Ba-A	Crystal structure destroyed by calcination after exchange
<i>Faujasite</i>	
Na-X	—
Li-X	52.3
K-X	64.7
Mg-X	57.8
Ca-X	74.6
Ba-X	74.0
<i>Mordenite</i>	
Na-Z	—
Li-Z	34.6
K-Z	90.6
Mg-Z	65.7
Ca-Z	76.2
Ba-Z	73.3
H-Z	99.0

has been based upon the total amount of catalyst, uncorrected for fraction exchanged or for purity. No correction has been made for the inert binder present in the Linde sieves.

APPARATUS AND PROCEDURE

All dehydration studies were made in the continuous flow, recycle, differential reactor system described by Stauffer and Kranich (5). In preliminary experiments it was established that gas flow rates were sufficiently high that bulk diffusion was not an important factor in determining reaction rate.

Prior to evaluation, each catalyst was treated in the following manner: The 3/8-

inch diameter reactor was filled with a known weight of $\frac{1}{8}$ -inch catalyst pellets. A small sample of the material charged to the reactor was subjected to calcination at approximately 1000°C. From the loss in weight on ignition the weight of the catalyst charged to the reactor could be corrected to a bone-dry basis. The loaded reactor was attached to the system and the reactor oven turned on. The catalyst was "activated" for at least 2 hr by heating to 350°C and purging with about 200 cc/min of dry helium.

The effect of temperature upon the dehydration reaction rate was investigated at three different levels for each catalyst. Because of differing activities of the catalysts and physical limitations of the equipment, these temperatures were not identical for all catalysts. For the γ alumina catalyst, temperatures of 348°, 390°, and 430°C were selected. For the hydrogen form of Z these levels were reduced to 160°, 200°, and 240°C. With the other three molecular sieve types the temperatures investigated were 270°, 310°, and 348°C. For each run the inlet and exit temperatures of the reactor gas stream were determined and maintained at the desired level for 1 hr prior to injecting a sample into a chromatograph for analysis. To check catalyst activity and aging, the middle temperature level was investigated first, followed by the low and high temperatures. Final runs were then repeated at the middle temperature.

EFFECT OF ALCOHOL CONCENTRATION

At each temperature level the relationship between the ethanol partial pressure and the rate of reaction was examined for each catalyst. The results obtained on the rate of ethylene formation can be summarized as follows: With alumina, the monovalent salts of mordenite investigated, and the entire family of faujasite investigated, the access to the active sites apparently is not hindered by product adsorption or by pore diffusion, and a constant reaction rate results for any reactant partial pressure (apparent zero order reaction). With the bivalent salts of mordenite and the members of the zeolite-A family

investigated, the olefin formation rate increases with increasing alcohol partial pressure.

In the reaction of ethanol to produce diethyl ether, the reaction rate increased with alcohol concentration for all catalysts studied except the monovalent salts in the Z series; these were essentially uninfluenced by alcohol concentration.

Since it was not the purpose of this study to determine detailed mechanisms or kinetic expressions, the data on the effect of concentration were used quantitatively only to permit evaluation of all results at a single alcohol concentration. Reaction rates at 0.6 atm average ethanol partial pressure were obtained by interpolation or limited extrapolation. These rate data are summarized in Table 2.

In addition to rate data, this table also gives the ratio of reaction rates or selectivity. Because the effect of alcohol partial pressure is frequently different on the olefin and ether reactions the tabulated selectivity applies strictly only at an alcohol partial pressure of 0.6 atm.

EFFECT OF TEMPERATURE

If the reaction rate data for ethylene and ether are treated independently, effective activation energies for the several catalysts may be obtained from Arrhenius plots. All of the ethylene data are well correlated with straight lines in this manner and activation energies are given in Table 2.

Ether data show considerable scatter when plotted in this way and are reported only as average apparent activation energies for each family. Since more diffusional effects would be anticipated for the ether molecules it is not surprising that the correlation is not so good as for ethylene.

RATE COMPARISONS

In order to permit comparison with the other substituted mordenites, H-Z data are extrapolated to 270°C. Based on this extrapolation, H-Z is shown to be the most active of the catalysts studied.

The next most active catalyst for ether

TABLE 2
DEHYDRATION OF ETHYL ALCOHOL^a

Catalyst	Temp. (°C)	1000 × Rate of conversion (g moles/hr g catalyst) to						Selectivity (v/v%)			Energy of activation (kcal/g mole)		
		Olefin (%)			Ether (%)			270°	310°	348°	Olefin	Ether (group average)	
		270°	310°	348°	270°	310°	348°						
Mg-A	10	3.9	1.8	3.8	10	5.6	10	13	22	15	23	20	
Ca-A	2.9	18	64	3.0	8.1	21	1.0	3.1	27				
Li-A	1.7	12	54	4.3	7.0	17	0.40	3.2	30				
Na-A	0.82	5.7	30	2.1	4.9	8.8	0.39	3.4	31	—	—	—	
K-A	0	0	0	0	0	0	—	—	—				
Mg-Z	3.3	16	54	0.59	2.9	8.7	5.6	6.2	24				
Ba-Z	3.2	13	44	1.4	4.8	11.7	2.3	3.8	22	—	—	—	
Ca-Z	1.1	6.7	32	0.38	3.3	12.6	2.9	2.5	29				
Na-Z	0.73	3.9	15	0.54	1.8	6.3	1.4	2.4	26				
Li-Z	0.16	1.4	12	0.14	0.81	4.3	1.1	2.8	38	—	—	—	
K-Z	0	0	0	0	0	0	—	—	—				
Ca-X	1.4	14	67	33	92	123	.04	0.15	34				
Mg-X	0.41	4.4	31	11	35	96	.04	0.13	37	—	—	—	
Na-X	0.79	6.9	33	5.2	41	94	0.15	0.17	32				
Li-X	0.41	4.5	30	1.8	11	32	0.23	0.41	37				
Ba-X	0.02	0.07	0.94	1.3	3.7	13	—	0.02	0.07	—	—	—	
K-X	0.06	0.10	0.50	0.18	1.0	3.0	—	0.1	0.17				
	Temp. (°C)	160°	200°	240°	160°	200°	240°	160°	200°	240°	270°		
H-Z	0.49	3.2	16	45	3.0	8.9	19.5	0.16	0.36	0.82	1.5	19	10
				(extrap.)				(extrap.)					
	Temp. (°C)	348°	430°		348°	390°	430°	348°	390°	430°			
γ Alumina	1.2	7.5	28	6.6	32	83	0.18	0.23	0.34	33	27		

^a Results adjusted to ethyl alcohol partial pressure of 0.60 atm.

formation is Ca-X, and for ethylene formation is Mg-A. This is consistent with the fact that ether formation would benefit from the large cage structure of faujasite. Ethylene, on the other hand, would be able to move in the small A cages nearly as freely as in the larger structures.

The significance of pore geometry is most clearly shown by the selectivity results. The highest selectivity (r_o/r_e) is shown by the smallest pore zeolites of the A series. Apparently it is difficult for the carbon-oxygen chain to line up in the ether configuration and to escape from the small pore. Although the mordenite pores are considerably larger, their selectivity is similar to that of the A series. The long cylindrical pores of the mordenite, in contrast to the A and X roughly spherical cages, may make it difficult for the ether chain to form and move.

On the other hand the large-cage structure of the X series lends itself to about the same freedom of motion as in alumina, and ether formation is not inhibited. This leads to smaller values of the selectivity ratio.

The above explanation is based purely upon geometry; alternatively the selectivity could be explained as the result of the individual catalytic effects on the separate reactions. The geometrical explanation is appealing, however, because it follows so directly from the known pore and cage dimensions.

In practically every case the selectivity increases with increasing temperature. This most likely results predominantly from the shift in the equilibrium constant in the dehydration reaction. Higher temperatures favor the increasing formation of olefins from ethers. It should be noted, however, that selectivity in the A and X series is more sensitive to temperature than in the Z series. Least sensitive are the divalent mordenites; their selectivity is nearly independent of temperature.

BUTANOL DEHYDRATION

If the cause of differing selectivity among the zeolite series is primarily geometrical, the results should be even

more marked with longer chain alcohols. The longer chain length ethers should be extremely difficult to form and move in the A zeolites. Some production might be expected in the large-cage X series, while the Z series should lie between.

Results of somewhat limited tests on dehydration of *n*-butanol over selected zeolites are shown in Table 3. Qualitatively they confirm the above predictions. Prob-

TABLE 3
DEHYDRATION OF BUTYL ALCOHOL
OVER SELECTED CATALYSTS

Temp. (°C):	1000 × Rate of conversion (g moles/hr g catalyst) to					
	Butylene			Butyl ether		
	270°	310°	348°	270°	310°	348°
Ca-A	12	44	115	0	0	0
Na-A	2.1	5.6	9.2	0	0	0
Mg-Z	1.8	15	63	0.4	0.1	0
Ca-X	2.8	18	61	0.7	0.8	7.2
Li-X	11	46	131	3.0	3.5	0.4

ably propanol would have given better results; apparently dibutyl ether is difficult to form in even the largest cavity zeolites of Ca-X.

EFFECT OF THE CATION

It was desired to correlate the activities of members of a family of zeolite catalysts with some property of the cation located within the intracrystalline voids. The results indicated that both the size and the valence of the exchanging cation had pronounced effect on the catalytic activities of the zeolite-A and mordenite families. This is expected since the cations do occupy space in the cages or channel, and only one bivalent ion is required per two monovalent sodium ions removed by exchange. In general divalent cations produced increased activity within a family.

Ethylene formation rates were plotted versus the radius of the cation in the exchanged position for zeolite-A. Within experimental error, straight lines which intersected at a common point could be drawn through two points for each temperature. Figure 1 predicts that replace-

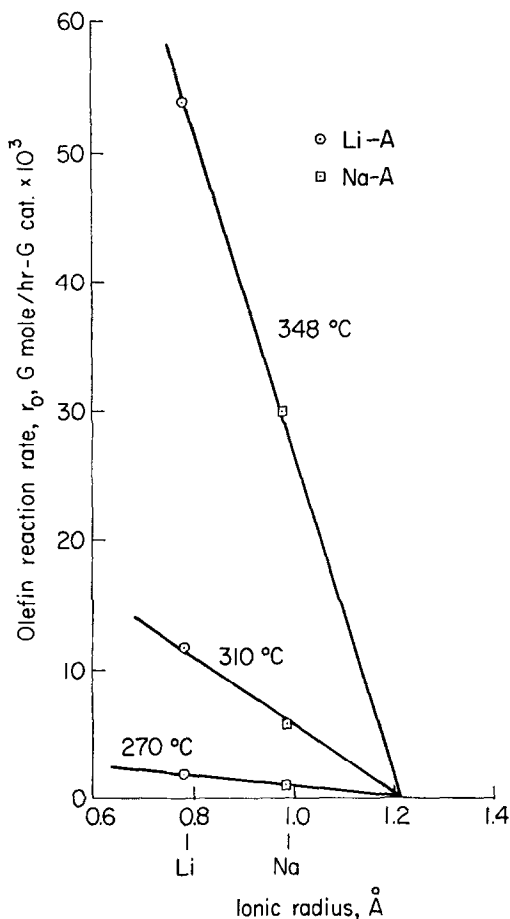


FIG. 1. Effect of cation radius on ethylene reaction rates—monovalent salts of Zeolite-A.

ment of sodium ions by a monovalent ion of radius greater than 1.21 Å would result in a catalyst having no activity in the dehydration of ethanol to ethylene. This conclusion was verified experimentally when potassium-exchanged zeolite-A was found to be inactive. Figure 2 indicates that exchange with a bivalent ion having a radius larger than 1.32 Å would result in no catalytic activity. Thus if the crystal structure of barium-exchanged A had been stable it should not have produced ethylene from ethanol. Similar correlations were neither expected nor obtained with the mordenites and faujasites since the olefin activities of these large-pore sieves would be less influenced by cation size alone. The simple straight-line relationship found here cannot be expected to hold for all geometry-controlled situations.

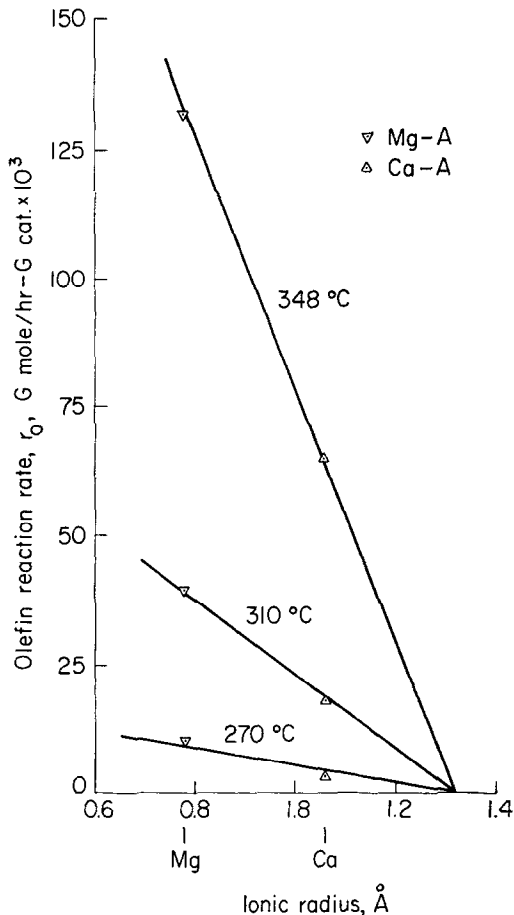


FIG. 2. Effect of cation radius on ethylene reaction rate—divalent salts of Zeolite-A.

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