The Catalytic Activity and Selectivity of Monovalent Y-Zeolites for n-Butene Isomerization

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The catalytic activity and selectivity of Group IA Y-zeolites for n-butene isomerization were modified by substituting small amounts of Ca^{2+} for $2Na^+$, by creation of a cation deficiency by hydrolysis, and by major exchange of the original Na^+ with either K^+ or Li^+. These systems were studied with and without added H_2O as co-catalyst. The replacement of up to 5.7% of the original Na^+ by Ca^{2+} produced a linear increase in catalytic activity in the presence of excess H_2O. As the Ca^{2+} content (acidity) was increased, cis–trans isomerization of the 2-butenes was enhanced, relative to double-bond migration. At constant calcium content the activity increased with small additions of H_2O, but reached a constant maximum above 10 H_2O/Ca^{2+}.

The catalytic activity also correlated linearly with increasing cation deficiency of the catalyst (up to 0.94% of the original Na^+ extracted), both in presence and absence of added water. The activity per decationated site was higher, however, for the sites produced by the introduction of divalent cations. Major substitution of either K^+ or Li^+ for Na^+ modified the activity of the sample, but to a lesser extent than by Ca^{2+} substitution. It was concluded that a pure alkali-Y-zeolite containing no cation deficiency, no divalent cations, and therefore no decationated sites, would have negligible catalytic activity.

INTRODUCTION

Information is needed concerning the catalytic properties of X- and Y-zeolites containing only monovalent base-exchange cations. The Na–zeolite, after evacuation at 500°, is relatively inactive for carbonium ion type reactions, but the influence of proton donors on the catalytic activity of this material has not been clearly established. Habgood and co-workers (1, 2) found that the activity of Na–(X or Y)-zeolites for cyclopropane isomerization was increased by small additions of water. On the other hand, Ward (3) reported no increase in catalytic activity of these zeolites in the presence of water for cumene deal-

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kylation. Frilette and Munns (4) reported that isopropyl alcohol dehydration over Na–X-zeolite was greatly enhanced by CO_2. They found, however, that the chemisorption of CO_2 was very much smaller than the Na^+ content and suggested that the active sites originated from impurity cations such as Ca^{2+}. Recently, Matsumoto and co-workers (5) showed that HCl increased the activity of both Na- and Ca–Y-zeolite for cumene cracking; Ward (3) found that H_2O activated Ca–Y-zeolite for this reaction and Gourisetti et al. (6) reported that the catalytic activity of Ca–Y-zeolite for tert-butanol dehydration increased considerably in the presence of water. However, Topchieva and co-workers (7) found only a 10–15% increase in catalytic activity of Ca–Y-zeolite for cumene cracking on H_2O addition. Venuto et al. (8) showed that addition of proton

donors increased the catalytic activity of REX-zeolites for alkylation reactions.

The Linde workers (*9*, *10*) were the first to show that replacement of Na⁺ by

Brönsted acidity develops in divalent X- and Y-zeolites, under conditions of partial dehydration, through the following mechanism (*14–16*, *20*):
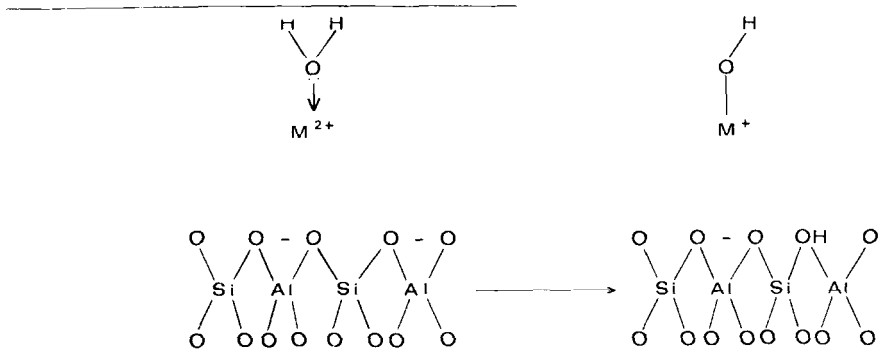
Ca²⁺ in X- or Y-zeolites did not increase markedly the hexane cracking activity until a certain *critical level* of exchange was reached. Recently, this problem has been further studied (*12*, *13*) and it has been found (*12*) that the triggering level is a function of the SiO₂/Al₂O₃ ratio.

Tung and McIninch (*11a*) associated the catalytic activity of these materials with fluctuating surface electric fields, whereas Tsutsumi and Takashashi (*11b*) suggested that the action of these fields on H₂O molecules were responsible for the development of the acidity. On the other hand, Minachev et al. (*12*) argued that Brönsted sites are formed only when vacancies and Ca²⁺ ions appear at the S$_{II}$ sites. There is considerable additional evidence (*13*) that a dramatic change in properties of the zeolite occurs when more than 16 Ca²⁺ per unit cell (55% replacement of Na⁺) are introduced into NaY. The present work shows that acidity sufficient to effect the isomerization of the *n*-butenes is developed by the substitution of even trace amounts of Ca²⁺ for Na⁺.

Two important results have been established by IR spectroscopy, viz., (a) that pure Na-(X- or Y-)zeolites, either partially or totally dehydrated, show no evidence of structural hydroxyl groups (*3*, *14*, *16*); discrepancies in this regard (*17–19*) can be accounted for by either a cation deficiency or by a small impurity of divalent cations (or by both); and, (b) that

Additional support for this view has been provided by the X-ray work of Olson (*21*) and the Mossbauer results of Garten and co-workers (*22*). This mechanism also explains the ability of these zeolites to retain some H₂O even after extensive evacuation at 500°C (*10*).

Habgood and co-workers (*1*) have provided evidence for a related species formed with the Na–X-zeolite, i.e.,
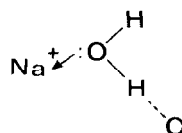
Although this interaction is apparently not strong enough to generate Brönsted sites detectable by IR (*3*, *14*, *16b*, *17*, *20*) it nevertheless could be a proton source for reaction of hydrocarbons.

The present work was undertaken to resolve the question as to whether the catalytic activity of the Na–zeolites is associated with impurities, vacancies, or both and whether H₂O interacting directly with a Group IA cation can function as a catalytic site. For this purpose the isomerization of the *n*-butenes was selected because it requires a relatively weak acidity. Thus, the function of weak sites, e.g., Na⁺ interacting with H₂O, had a chance to appear. These reactions were shown to be first-order in both conversion and time over a carefully purified Na–Y-zeolite

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TABLE 1

ANALYTICAL DATA FOR CATALYSTS[a]

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Catalyst no.	Ca^{2+} analysis (%)	H$_2$O used in washing[d] (ml)	Decationation,[e] fraction of Na$^+$ ions removed (%)	Fraction of Na$^+$ ions replaced by Ca^{2+} (%)
I[bc]	0.02 ± 0.005	—	—	0.3
II[c]	0.07 ± 0.008	—	—	1.0
III[c]	0.1 ± 0.01	—	—	1.4
IV[c]	0.2 ± 0.02	—	—	2.9
V[c]	0.4 ± 0.02	—	—	5.7
VI[c]	0.02 ± 0.005	100	0.15	0.3
VII[c]	0.02 ± 0.005	800	0.35	0.3
VIII[c]	0.02 ± 0.005	1600	0.54	0.3
IX[c]	0.02 ± 0.005	2400	0.79	0.3
X[c]	0.02 ± 0.005	4000	0.94	0.3
XI[c]	5.5 ± 0.3	—	—	77.0

[a] Emission spectroscopy was used for most of the analyses, which are reported as grams of Ca/100 g of dry zeolite. Only Na was determined spectrophotometrically, and this method was not accurate enough to show any significant variation, except for XI, for the catalysts shown above. None of these samples showed any significant variation in Fe and Ti content (∼0.1%).

[b] Catalyst I was the mother catalyst.

[c] In these cases the variation in content of B, Ba, Mg, Cr, Cu, and Mn was investigated. No significant variation was found, the values remaining constant below 20 ppm.

[d] Amount of water used to wash through 5-g aliquots of I in a Büchner funnel.

[e] The number of Na$^+$ removed was calculated from the increase in Na content of the washing water (which initially had less than 0.1 ppm of this cation). The specific conductance of the water used for washing was 1.3 μmhos/cm at 25°C corresponding to a total ion content of 0.8 ppm. The water recovered after washing was also tested for Ca, Mg, and Fe by atomic absorption. The amount found in no case exceeded 0.05 ppm.

(23). Moreover, ^{2}H and ^{14}C tracer experiments showed that the butenes react through a common intermediate and involve the intermolecular transfer of one H or D per isomerization act; thus, the intermediate is probably the sec-butyl carbonium ion (24, 25).

EXPERIMENTAL METHODS

Reactor. All the kinetic data were obtained using a static reactor described elsewhere (23).

Reactants. The n-butenes were Phillips Research Grade and contained less than 0.2% of the other isomers. These materials were distilled from −78 to −195° to insure removal of possible traces of H$_2$O.

Catalyst preparation. The starting material was Na–Y-zeolite furnished by the Linde Co. (Lot. No. 1280–133). Its analysis, supplied by the manufacturer, was:

This material was "purified" by successive exchanges with NaAc to remove divalent base-exchange cations. After these, the catalyst was carefully washed, using slightly alkaline water (pH ≃ 10) to minimize hydrolysis. Aliquots of this mother catalyst (I) containing 0.028% CaO underwent two kinds of treatment: (a) Catalysts II, III, IV, V, and XI were back-exchanged to increase the Ca^{2+} content; (b) five other portions were washed with increasing amounts of distilled, double-deionized, water to produce varying degrees of cation deficiency (Catalysts VI to X). The analytical data for these samples are listed in Table 1. Catalysts I and III underwent major exchange by Li (I′ and III′) or by K (I″ and III″). The data for these catalysts are presented later, together with catalytic activity results, in Table 3. Because of weight changes with cation ex-

Component	Al$_2$O$_3$	SiO$_2$	Na$_2$O	CaO	MgO	(TiO$_2$+Fe$_2$O$_3$)
%	22.4	63.2	12.6	0.7	0.2	0.1

change, some of the results are presented on the basis of *per cage of catalyst*. There are eight cages per unit cell and 3.76×10^{20} cages/g of dry Na–Y-zeolite.

Procedure. All of the catalysts were pretreated with O_2 at 500°C as described elsewhere (*23*) and evacuated overnight before each run. When this procedure was followed or repeated, the catalysts had a constant reproducible activity over many experiments, except where otherwise indicated.

Each experiment was performed at 260° using the same amount of reactant (55 ml STP), but the amount of H_2O and the type and amount of catalyst were varied. The desired amount of H_2O was transferred first to the reactor where a major fraction of it was adsorbed on the zeolite. The amounts of H_2O indicated in tables and figures are thus the total H_2O added to the reactor. After equilibrating at the desired temperature, a small side-arm trap near the top of the reactor was surrounded by a bath of liquid nitrogen and the measured amount of reactant was quickly transferred into this. The reaction was initiated by flashing the contents of the trap onto the catalyst at time zero. Samples of the gas phase were taken periodically and analyzed chromatographically (*23*). The amounts of catalyst used ($\sim$75 mg) were too small, and the gas volumes too large, to allow measurements of the amounts adsorbed. The amounts of hydrocarbon retained by the catalyst following reaction and evacuation at this temperature were estimated in some cases by a combustion method. Reactivity data were obtained from plots of log $(x_e - x)$ vs t, where x is the fraction of the reactant which has been isomerized at time t; x_e is the equilibrium value (*23*). Selectivity data were calculated by the extended Wei and Prater method (*23*).

RESULTS

Effects of cation exchange, cation deficiency, and H_2O on catalytic activity. The effect of increasing amounts of co-catalyst water on the catalytic activity was studied over Catalysts I and V, which contained 0.02 and 0.4% of Ca^{2+}, respectively. The catalytic activity invariably increased with water addition (Fig. 1), but reached a saturation point at about 10 H_2O/Ca^{2+} (2H_2O/cage for Catalyst V)
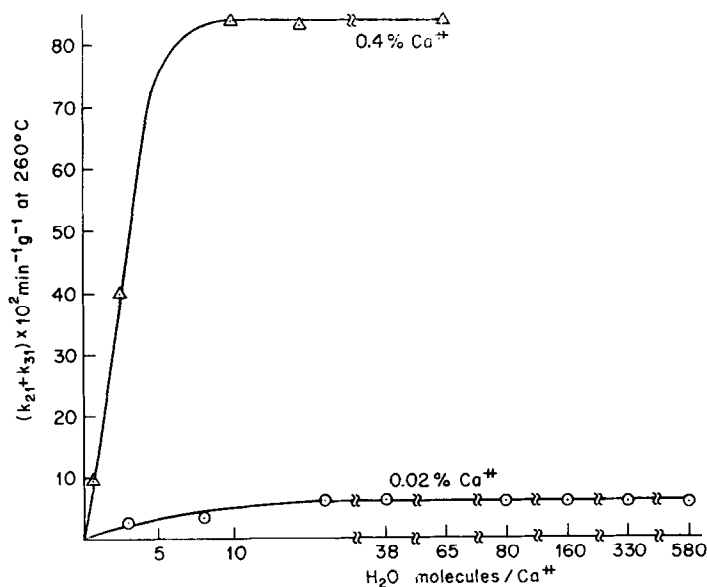

Fig. 1. Effect of H_2O on the catalytic activity Na–Y-zeolites containing different amounts of Ca^{2+}.
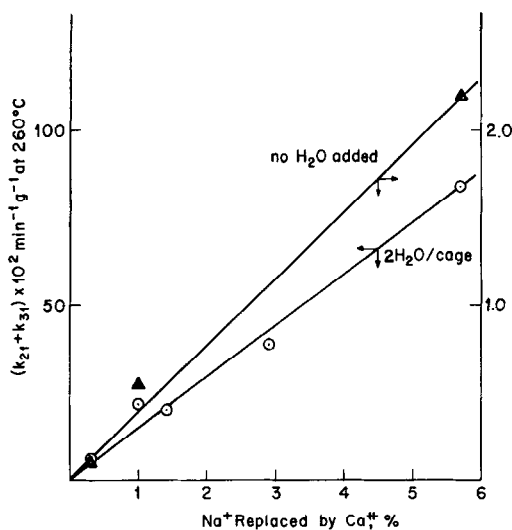
FIG. 2. Variation of catalytic activity of Na-Y-zeolite with Ca^{2+} content, with and without H_2O added as co-catalyst.

and the value $(k_{21} + k_{31})$† at these plateaus were proportional to the Ca^{2+} content. Figure 2 shows this linear relationship between maximum rates and fractional re-

placement of Na^+ with Ca^{2+} for Catalysts I to V. The data indicate that the catalytic activity for an ideally pure Na–Y-zeolite would be negligible, even in the presence of excess H_2O. When water was not added, the correlation between activity and Ca^{2+} content was still evident (Fig. 2).

Catalysts XI had 77% of the Na^+ removed; this was the only catalyst whose Ca^{2+} content was above the critical level (9, 10, 13). The reaction poisoned out very rapidly over this catalyst in presence of water, and it was difficult to obtain an accurate value of the initial reaction rate. The best estimate was 4.5 min^{-1} g^{-1}. Moreover, the reaction was no longer first-order in reactant on either a time or a conversion basis. In absence of water, the reaction was not poisoned, was first-order, and the activity was 0.83 min^{-1} g^{-1}.

Catalysts VI to X, which had increasing degrees of decationation, showed an induction period in the absence of H_2O which disappeared when H_2O was added. Figure 3 shows typical data for Catalyst X. The
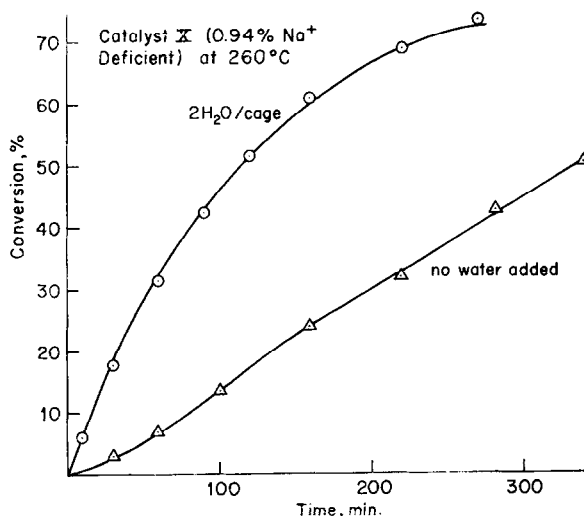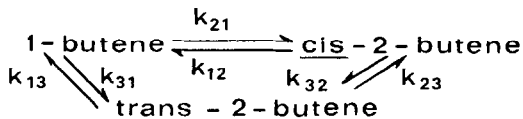

FIG. 3. Disappearance of induction period with H_2O addition.

† The rate constants are defined by:

$$1-\text{butene} \underset{k_{12}}{\overset{k_{21}}{\rightleftarrows}} \text{cis} - 2 - \text{butene}$$

with k_{13}, k_{31}, k_{32}, k_{23}

trans – 2 – butene

corresponding first-order plots also showed an initial curvature, indicating an acceleration of the reaction rate with time in the absence of H_2O. The relationships between the rate data on cation deficiency are

shown in Fig. 4. Three different straight lines resulted: the first corresponded to the initial rate of disappearance of the reactant in absence of water; the second, to the rate after the induction period was over; and the last to the case in which $2H_2O$/cage was added. For the last, the rate was not zero at 0% decationation, but had a finite intercept corresponding to the "saturation" value of the parent catalyst (0.02% Ca^{2+}), which is plotted as the crossed circle. A similar induction period seemed to be present with the Ca^{2+} containing catalysts in absence of water, although it was more difficult to detect. Another interesting feature is shown in Table 2. Decationated samples decreased in activity from run to run in absence of water. No variation was noticed, however, when water was present nor did the Ca^{2+} series behave this way even in the absence of H_2O.

Effect of K^+ and Li^+ on catalytic activity. The substitution of small amounts of K^+ or Li^+ for Na^+ did not produce a significant change in catalytic activity. Higher replacement levels (>50%), however, resulted in substantial effects. As shown in Table 3, the activity was increased by Li^+ and decreased by K^+ substitution.
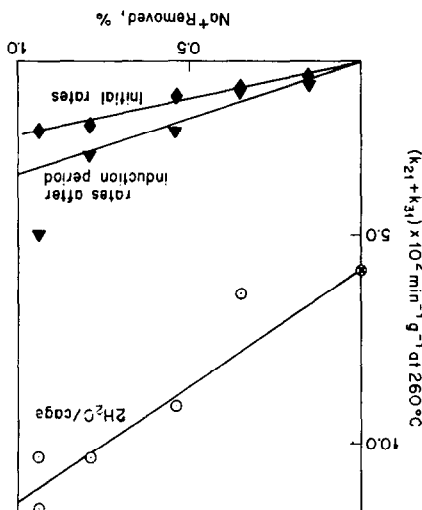

FIG. 4. The effect of decationation on the catalytic activity of Na–Y-zeolite; solid points indicate dry catalyst.

TABLE 2

Variation of Catalytic Activity of Decationated Catalysts (VI and X) in Successive Runs[a]

Catalyst	Run no.[b]	Amount of H_2O (H_2O molec/cage)	$(k_{21} + k_{31}) \times 10^2$ (min^{-1} g^{-1})
X	1	0	2.0
	2	2.0	10.4
	3	0	0.5
	4	0	0.35
	5	2.0	11.9
VI	1	0	0.45
	2	0	0.22

[a] A 300 ml static reactor was used containing 76 mg of catalyst and 55 ml (STP) of 1-butene.

[b] This column gives the number of runs with the same aliquot of catalyst.

Selectivity changes. Relative rate constants were determined for all members of the Ca^{2+} series, except for the one showing unacceptable kinetic behavior. These data, including the selectivity ratios, are listed in Table 4. The *cis/trans* ratios were unaffected by changes in calcium content, but the selectivities in the isomerization of the 2-butenes were; *cis–trans* isomerization was enhanced over the double-bond migration as the catalytic activity increased with increasing Ca^{2+} concentration.

DISCUSSION

Our results show that small amounts of impurities, as for example the divalent cations normally found in Linde zeolites, markedly affect the catalytic activity of Na–Y-zeolite. A similar effect was found when, through water washing, a slight decationation was produced. In both cases, the extrapolated catalytic activity was negligibly low for an impurity-free, nondecationated, Na–Y-zeolite. Evidently, the co-catalytic interaction of H_2O with Na^+ is relatively unimportant. Figure 1 is illustrative of this. The maximum activity was reached much before 1 H_2O/Na^+ was present in the system and the plateaus were proportional to the Ca^{2+} content. It was shown elsewhere (26) that activity cor-

TABLE 3

CATALYTIC ACTIVITY OF CATION EXCHANGED Y-ZEOLITES FOR 1-BUTENE ISOMERIZATION[a]

| Catalyst | Fraction of exchange capacity occupied by ion (%) | | | | Rate of isomerization of 1-butene[b] | |
	Li^+	Ca^{2+}	Na^+	K^+	$(k_{21} + k_{31})$ $\times 10^2$ $(min^{-1} g^{-1})$	$(k_{21} + k_{31})$ $\times 10^{22}$ $(min^{-1} cage^{-1})[c]$
I	—	0.3	99.0	—	6.0	1.6
I'	60	0.3	39.0	—	18.1	4.6
I''	—	0.3	9.0	90	0.038	0.01
III	—	1.4	98.0	—	18.0	4.8
III'	32	1.3	66.0	—	17.5	4.6
III''	—	1.3	26.0	72	0.8	0.22

[a] A 300 ml static reactor was used containing 76 mg of catalyst and 55 ml (STP) of 1-butene. Reaction temperature was 260°C and $2H_2O$ molecules/cage was always present as co-catalyst.

[b] Rate constants defined in footnote†, see text.

[c] Pure Na–Y-zeolite contains 3.76×10^{20} cages/g.

related with the adsorption of 1 H_2O/Ca^{2+}. These results are consistent not only with the spectroscopic data available, but also with kinetic data reported by Gourisetti and co-workers (6) and by Frilette and Munns (4).

Habgood and George (1) reported that replacement of Na^+ with K^+ or Li^+ modified the catalytic activity of the Na–X-zeolite. They attributed their results to the presence of a small number of Brönsted sites influenced by the exchangeable cations. They were unable, however, to identify these sites with any particular property of the catalyst, e.g., with the Na/Al ratio. The present results trace the origin of the acidity to impurity Ca^{2+} or to decationated sites present because of a cation deficiency. Their experimental results are consistent

with ours. In fact they noted that a high purity sample had a much lower activity than the preparation on which they did most of their work. Moreover, they concluded that the adsorption sites were far more numerous than the catalytic sites, because no change in the retention volume of cyclopropane was detected between catalytically active and inactive materials.

If it is assumed that one Brönsted site is formed for each Na^+ removed, either by replacement with Ca^{2+} or by hydrolysis, the sites formed by the former method are more active than those by the latter. The rate increment per site (slope) of Fig. 2 ($2H_2O$/cage) is 14.7×10^{-2} compared with 3.2 to 5.7×10^{-2} min^{-1} g^{-1} %$^{-1}$ for Fig. 4. (The two figures for the decationated samples correspond to the dry zeolite fol-

TABLE 4

RELATIVE RATE CONSTANTS FOR n-BUTENE ISOMERIZATION OVER Na–Y-ZEOLITE WITH VARYING Ca CONTENT[a]

Catalyst	k_{21}	k_{31}	k_{12}	k_{32}	k_{13}	k_{23}	$\dfrac{k_{21}}{k_{31}}$	$\dfrac{k_{12}}{k_{32}}$	$\dfrac{k_{13}}{k_{23}}$
I[b]	1.0	0.86	0.55	0.20	0.28	0.12	1.2	2.7	2.3
II[c]	1.0	0.81	0.55	0.22	0.26	0.13	1.2	2.5	2.0
IV[c]	1.0	0.81	0.55	0.26	0.26	0.16	1.2	2.1	1.7
V[c]	1.0	0.82	0.55	0.30	0.27	0.18	1.2	1.8	1.5

[a] $2H_2O$/cage present as co-catalyst; reaction temperature: 260°C.

[b] Average taken from four sets of data.

[c] Computed by the extended Wei and Prater method (23) using data from cis-2-butene isomerization.

lowing the induction period and with $2H_2O$/cage added, respectively; the intercept is attributed to the Ca^{2+} impurity.) If only one site were created by substitution of Ca^{2+}, the activity per site created would be twice as large. Since it is not the number of sites alone which produces these rather large effects on catalytic activity, it is possible that the polarization effect, discussed by Richardson (27), lowers the activation energy for carbonium ion formation. Habgood and George (1) suggested that it was the *number* of Brönsted sites which was the principal factor controlling the activity although they reported a value of 35 kcal/mole for a highly pure, nearly stoichiometric Na–Y-zeolite as compared with 25 kcal/mole for a less pure sample and found the activation energy for NaX was higher than that for LiX; a value for KX was not given. Their suggestion was based mainly on results for three different lots of NaX, which may have had variable concentrations of divalent ions, and on the results from catalysts in which the major portion of the base-exchange capacity was satisfied by divalent ions. In either case, unknown factors could have affected the activation energies making it impossible to reach a firm conclusion.

Most previous studies concerned with the catalytic activity of zeolites containing Ca^{2+} have been made in the absence of H_2O. In these cases, the activity increases sharply when about 50% of the Na^+ have been replaced (9, 10, 13). This behavior has been attributed to a preferential filling of the S_I sites; only after these sites are filled do large numbers of Ca^{2+} populate the S_{II} positions where they effect the formation of Brönsted sites. Consistent results were obtained in the present work. With dry catalysts the activity increased about linearly as Na^+ was removed or replaced with small amounts of Ca^{2+} (Figs. 2 and 4), although the values remained quite low relative to those found when H_2O was added. Evidently some Brönsted acidity is always introduced into the supercages on replacement of Na^+, but not on a 1:1 basis until occupation of the S_{II} sites is necessitated. Thus, a sharp up-

ward break in the activity pattern was observed with dry catalyst XI (77% Na^+ removed). This break was not found, however, when H_2O was added. This may have been due to rapid poisoning, but another factor should not be overlooked. Freeman and Stamires (28) have shown that the activation energy for cation migration decreases continuously with increasing hydration. Hence, it is possible that one function of H_2O is to effect migration of calcium ions, perhaps to the S_I' positions, with the concomitant formation of a Brönsted site. This would lead to large increases in catalytic activity with H_2O addition at low replacement levels, but to relatively much smaller increases above 50% replacement. Cation migration should be strongly influenced by temperature and might not occur in experiments carried out at temperatures much lower than those used in the present work.

Another property of the set of decationated sites is shown in Table II, viz., that they become deactivated by successive runs or by the regeneration pretreatment, when H_2O is absent. The activity was apparently restored, however, when H_2O was added as co-catalyst. These much higher values demonstrate again the much higher activity associated with the Ca^{2+} sites.

The variations in the selectivities with increasing Ca^{2+} substitution (Table 4) were similar to those reported by Misono *et al.* (29) for the same reactions over supported metal sulfates (and H_2SO_4). These workers correlated both catalytic activity and the selectivities with electronegativity of the metal ion. As shown by indicator tests, the electronegativity was a convenient measure of acid strength. The activities increased and the 1-butene/2-butene ratios decreased with the catalyst acidity. The same trends are shown in Fig. 2 and Table 4, but, whereas these ratios all exceeded unity in the present work, they fell from near unity to about 0.1 with increasing acidity of the metal sulfate catalyst. The data of Dimitrov and Leach (30) provide an additional example, this time with a catalyst having presum-

ably a still weaker acidity, viz., a Na–X-zeolite. They reported $k_{12}/k_{32} = 6.25$ at 305°C. Unfortunately, they did not give a detailed analysis of the sample used, which would have permitted a closer comparison with our results. Nevertheless, ratios between 6.25 and 2.70 were observed in the present work when (a) H_2O was omitted from Catalyst I, and (b) when K^+ was substituted for Na^+. Since the acidity of X-zeolites is generally regarded as lower than those of the Y-type, all these data form a consistent set of results. The question is, what is the explanation?

Misono et al. (29), following Brouwer (31), suggested that the catalyst selectivity stemmed from the competition of two reactions: a true carbonium ion reaction, which accounted for the cis–trans isomerization and to a minor extent the double-bond shift; and a concerted mechanism, which allowed only double-bond shift. In the latter, it was assumed the carbonium ion was not fully developed. Dimitrov and Leach (30) suggested that their results over NaX might be explained by a radical mechanism, but in view of the present results this appears unnecessary. Nevertheless, it would appear at first sight that all these results could not stem from a reaction involving only one intermediate, e.g., the sec-butyl carbonium ion. However, Hightower and Hall (32) showed that the selectivities for product formation over a silica–alumina catalyst depended principally on the differences in barrier heights between this carbonium ion and products. In this sense, the sec-butyl carbonium ion is not always the same for all catalysts, nor are the ideas of Brouwer and of Hightower and Hall mutually exclusive. Let us assume that barrier height between the carbonium ion and the 1-butene product varies directly with the catalyst acidity, relative to the barriers between the ion and cis- or trans-2-butene. (As discussed earlier (32) these latter two cannot differ much in height; hence, temperature invarient cis/trans ratios close to unity are generally observed.) Then, as the acidity decreases the reaction will appear more concerted; double-bond isomerization will

increase relative to cis–trans isomerization. Unfortunately, sufficient data are not yet available to adequately test these ideas.

ACKNOWLEDGMENT

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