JOURNAL OF CATALYSIS 6, 253-262 (1966)

Organic Reactions Catalyzed by Crystalline Aluminosilicates

V. Dehydrohalogenation and Related Reactions

P. B. VENUTO, E. N. GIVENS, L. A. HAMILTON, AND P. S. LANDIS

From the Applied Research and Development Division, and the Central Research Division, Mobil Oil Company, Inc., Paulsboro and Princeton, New Jersey

Received March 10, 1966

Crystalline molecular sieves actively catalyze the elimination of halogen acid from two-carbon haloalkanes at 1 atm and temperatures of 65–370°C. A role for polar or ionic intermediates is suggested for these dehydrohalogenation reactions. The dehydrohalogenation activity of a rare-earth-exchanged X zeolite was inhibited by nitrogenous bases.

The crystalline zeolites also catalyzed the reaction of ethanol and hydrogen chloride to form ethyl chloride at 150–250°C.

INTRODUCTION

Liquid-phase β-elimination reactions have been extensively studied, and it is generally agreed that they proceed via ionic mechanisms (*1*). While numerous pathways for decomposition exist in gas-phase eliminations, there is a class which is essentially heterolytic in character (*2*), the major factor controlling the rate being the stability of the carbonium ion formed from the alkyl halide.

Heterogeneous catalysis of dehydrohalogenation has long been of importance as a preparative method. Noller, Schwab, and co-workers have made intensive studies of the dehydrohalogenation of ethyl chloride (*3, 4*) and other haloalkanes (*5, 6*) over metals, metal oxides, nitrides, carbides, and salts. Further, considerable evidence supporting ionic mechanisms has been compiled for HCl elimination on solid catalysts such as $CaCl_2$, CaO, Al_2O_3 (*7*).

In zeolite-catalyzed eliminations, intracrystalline and molecular shape selective alcohol dehydration using zeolite catalysts has been reported by Weisz, Frilette, and co-workers (*8, 9*). Other papers on alcohol dehydration over zeolites have also recently appeared (*10–15*). Aside from some early work of Barrer and Brooks on dehydrofluorination of fluorochloromethanes over chabazite (*16*) and a patent on the dehydrochlorination of *tert*-butyl chloride over clay-bonded CaA by Milton and Breck (*17*), very little on zeolite-catalyzed dehydrohalogenation has been reported in the literature. This paper is concerned with dehydrohalogenation and related reactions in two-carbon aliphatic systems using crystalline aluminosilicates as catalysts.

EXPERIMENTAL

Materials

Catalysts. The rare earth X catalyst (REX) was prepared by exchanging Linde 13X with 5% mixed rare earth chloride ($RECl_3 \cdot 6\ H_2O$) solution until a sodium level of 0.58% wt was obtained. A typical analysis of the rare earth mixture (as % wt oxide) employed in these exchanges is La_2O_3 (24.1), CeO_2 (48.0), Pr_6O_{11} (5.9), Nd_2O_3 (19.1), Sm_2O_3 (2.0), Gd_2O_3 (0.7), and others (0.2). The rare earth Y catalyst (REY) was prepared similarly by base-exchanging a synthetic sodium Y aluminosilicate (NaY) with 5% $RECl_3 \cdot 6\ H_2O$ solution until a sodium level of 0.99% wt was obtained. The ammonium Y (NH_4Y) was obtained from a synthetic NaY zeolite by exchange with warm 10% aqueous ammonium chloride solution until a sodium level of 1.05% wt was obtained. Thermal deamination of NH_4Y gave hydrogen Y (HY) catalyst. CaX and NaX are Linde 10X and 13X, respectively. The silica-alumina was Socony Mobil Oil Company 46 AI bead cracking catalyst. Details of the analysis and activation procedures for the above catalysts were reported earlier (*18*).

The silver X (AgX) was prepared by exchanging Linde 13X with 20% aqueous silver nitrate solution until a sodium level of 0.1% was obtained; calcination was for 1 hour in air at 343°C. The Linde 5A was activated by heating 2 hours in air at 246°C. The nickel X (NiX) was prepared from Linde 13X containing 20% clay binder by exchange with aqueous nickel nitrate solution until about 25% of the sodium was replaced (about 3.68% Ni); the catalyst was activated by heating for 2 or 3 hours at 350°C in air. The alumina (Harshaw 1404) was heated for an hour at 170–270°C under a flow of nitrogen before use.

The rare earth silica-alumina was prepared by exchanging an amorphous silica-alumina with the 5% $RECl_3 \cdot 6\ H_2O$ solution described above. The catalyst analysis (wt %) was RE_2O_3 (19.6), Al_2O_3 (20.6), SiO_2 (59.1), and Na (0.23); its surface was 91 m^2/g after activation in air at 538°C for 1.5 hr. The rare earth oxide was prepared by ignition of rare earth hydroxides derived by treatment of the $RECl_3 \cdot 6\ H_2O$ solution with ammonium hydroxide. The quinoline-treated REX (REX-Q) was prepared by stirring 5.57 g of REX (previously calcined at 343°C) with a solution of quinoline (1.04 g) in benzene (150 ml) for 7 days at 25°C. After filtration and drying (4 hr/144°C/0.5 mm Hg), analysis of the pale yellow catalyst showed 11.30% carbon and 1.43% nitrogen.

With the exception of the NiX, all zeolite catalysts were binder-free, and were pelletted, crushed, and sized to $^8/_{14}$ mesh before activation. All other catalysts were crushed and sized to $^8/_{14}$ mesh before use.

Organic reactants. These were obtained from standard commercial sources. Liquid reactants were distilled to a purity of better than 99% in most cases. Ethyl chloride was used without further purification, and showed no impurities by gas chromatography.

Apparatus and Procedures

The apparatus, with slight modifications, has been described earlier (*18*). The general procedure consisted of placing a known weight of catalyst (0.6–2.4 g) in the electrically heated, tubular, Vycor glass reactor, fitted with an axial, glass thermocouple well. Tempered quartz chips were used as a preheater media and occasionally as diluent for the catalyst. Catalyst calcinations were either effected *in situ* immediately prior to reaction, or in separate furnaces with subsequent transfer to the reactor. The reactor was brought to initial operating temperature under a stream of dry nitrogen, and the reactants admitted. Liquid reactants were introduced at controlled rates via a motor-driven glass syringe pump. Gaseous reactants or carriers were simultaneously introduced through a T-joint at the reactor entry; rates were controlled by orifice-type flow meters. All reactions were run at 1 atm.

For time–composition studies of gaseous products, vapor samples were removed from the reactor effluent with gas-tight syringes for gas-liquid chromatography (GLC) or in glass bombs for mass spectroscopy. Liquid products were collected in an air-cooled receiver preceded by a water condenser or in a coil-type trap with a peripheral dry ice-acetone bath. In some cases, gaseous products, not condensable at the temperature of the freezing mixture, were trapped over saturated sodium chloride solution in a conventional gas collection apparatus fitted with the appropriate valve system for removing samples for analysis. Conversions were based on the total amount of material collected in the various receivers.

In a typical example (for the synthesis of ethyl chloride), ethanol (pump rate = 3.81 ml/hr) and gaseous hydrogen chloride (49 ml/min) were passed over REX catalyst (2.0 g, 3.0 ml) at 190°C for 5 hr. Ethanol and water were collected in the first trap, ethyl chloride in the second trap, which was maintained at —40° to —50°C, and ethylene and other light gases in a gas collector. For both ethanol-water and ethyl chloride, plots of the volume collected (to the nearest 0.1 ml) vs. time on stream were linear for the intervals studied (2–6 hr), indicating steady state conditions.

Analyses

Reaction mixtures were analyzed by gas-liquid chromatography (GLC) and by infrared (IR) and mass spectroscopy. Most GLC analyses were run on an F&M Model 720 dual-column chromatograph equipped with a 12-ft column packed with 20% silicone gum rubber on Chromosorb W. For each reaction system studied, the GLC injection port temperature was regulated to ensure the absence of pyrolytic reaction during sample injection. Products were identified by comparison of peak retention times with those of known standards.

Infrared analyses were run on a Perkin-Elmer 421 spectrophotometer. Liquid samples, either of total reaction product or of fractions trapped by micropreparative GLC, were run as dilute solutions in carbon disulfide using potassium bromide cells. Gas samples were run in a 10-cm potassium bromide gas cell. Mass spectra were run on a Consolidated Electrodynamics Corporation Model 21-103 spectrometer.

RESULTS AND DISCUSSION

Dehydrohalogenation

Ethyl chloride. At 260°C, REX, NaX, NiX, HY, metal-hydrogen Y, and Linde 5A zeolites all converted substantial amounts of ethyl chloride to ethylene in gas-phase reactions, while amorphous silica-alumina was considerably less active (Table 1). Moderate aging was observed, with about two-thirds to one-half of initial

TABLE 1

REACTION OF ETHYL CHLORIDE OVER ALUMINOSILICATE CATALYSTS

Catalyst[a]	Reactant flow rate (moles/g catalyst/hr)	Temp. (°C)	Mole % conversion of C_2H_5Cl to C_2H_4 (Time, Min)	
			Initial	Aged
REX[b]	0.0410	260	75.0 (10)	54.0 (120)
NaX[c]	0.0410	260	70.5 (10)	40.0 (120)
NiX	0.0410	260	62.0 (20)	41.0 (120)
HY[b,d]	0.0410	260	49.5 (10)	36.5 (120)
Linde 5A	0.0410	260	82.5 (10)	44.0 (120)
Silica-Alumina	0.0410	260	16.5 (30)	22.8 (120)
REX	0.0205	177[e]	43.5 (40)	14.5 (295)
NaX	0.0205	177	25.0 (80)	1.6 (300)
AgX[f]	0.0205	177	42.0 (40)	3.5 (150)
REX[g]	0.0205	288	18.5 (40)	6.5 (300)

[a] Under identical conditions, but using tempered quartz chips instead of catalyst, no C_2H_4 was formed at 149–260°C, with traces only at 316–371°C.

[b] Small amounts of propane, isobutane, and isopentanes were also observed in products.

[c] Similar results with NaX slurry-washed with water and filtered (14 times) until filtrate neutral to hydrion paper.

[d] Similar results observed with HY catalysts exchanged with small amounts of Ag, Cr, Fe, Ni, or Al.

[e] Under identical conditions, but in presence of ammonia (0.0041 mole/g catalyst/hr), or with quinoline-treated REX, no conversion was observed.

[f] Some ethylene formed under similar conditions at 65°C.

[g] Quinoline-treated.

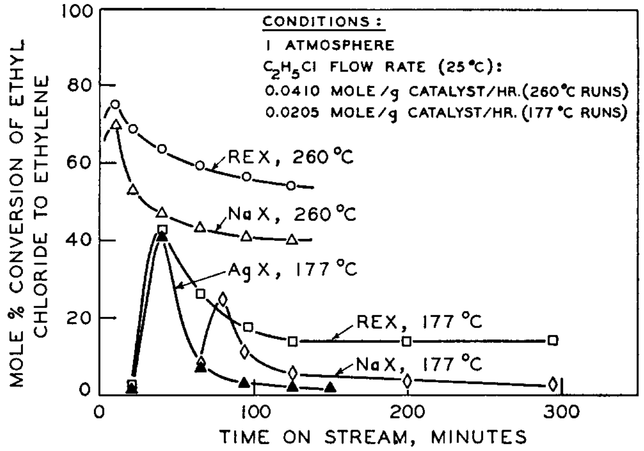


FIG. 1. Ethyl chloride dehydrohalogenation activity versus time for REX, NAX, and AgX catalysts.

activity remaining after 2 hr on stream. Typical aging profiles are shown for REX, NaX, and AgX in Fig. 1. It is apparent from Fig. 1 that at 177°C, considerably greater activity was observed with REX than with NaX. Figure 2 shows the effect of temperature on the dehydrohalogenation of ethyl chloride over REX. Conversion increased rapidly from about 5% at 149°C to nearly 100% at 316–371°C. Catalyst aging was rapid at 371°C. In Table 2 there is summarized pertinent catalyst comparisons from the literature.

TABLE 2

ELIMINATION ACTIVITY OF PRIMARY CHLORIDES AND ALCOHOLS OVER VARIOUS CATALYSTS

Reactant	Catalyst	Temperature (°C) for significant activity	Reference
C_2H_5Cl	SiO_2	520–600	*8*
C_2H_5Cl	γ-Al_2O_3	370–420	*8*
C_2H_5Cl	$CaCl_2$	360–400	*8*
C_2H_5OH	H-Mordenite	250	*10*
n-C_4H_9OH	CaA, CaX	240–260	*9*
n-$C_5H_{11}OH$	NaX	275	*15*

At 177°C, a silver-exchanged X (AgX) showed a sharp, initial peak of activity, followed by a very rapid loss of all activity (Table 1, Fig. 1). Crystalline silver chloride was detected in the discharged catalyst. Since this catalyst showed slight activity at a very low temperature (65°C),

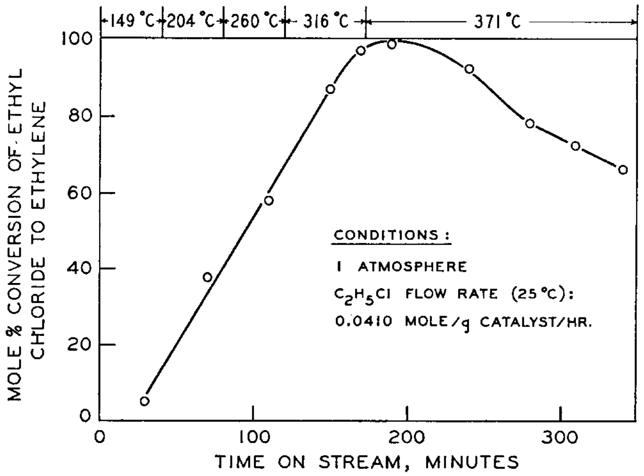
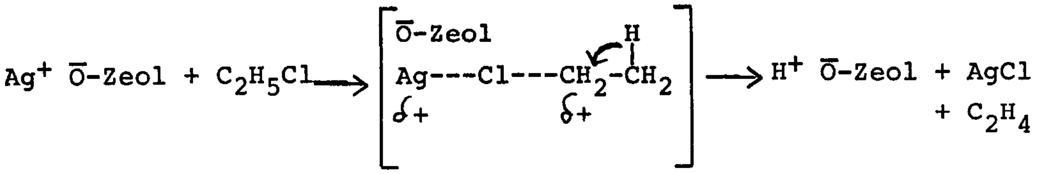


FIG. 2. Rate of reaction of ethyl chloride versus temperature for REX catalyst.

a silver-ion-assisted elimination seems probable [Eq. (1)].



$$Ag^{+}\ \bar{O}\text{-Zeol} + C_2H_5Cl \longrightarrow \left[\begin{array}{lll}\bar{O}\text{-Zeol} & & H\\ Ag\text{---}Cl\text{---} & CH_2\text{-} & CH_2\\ \delta+ & \delta+ & \end{array}\right] \longrightarrow H^{+}\ \bar{O}\text{-Zeol} + AgCl + C_2H_4 \qquad (1)$$

X-Ray analysis of NaX catalysts discharged after dehydrochlorination runs showed marked loss of lattice crystallinity and the presence of NaCl. Since only small amounts of coke were formed, it appears that the observed rapid aging with NaX catalysts (Fig. 1) is related to lattice collapse of hydrogen X (HX) formed from the reaction of NaX with hydrogen chloride. Barrer and Brooks (*16*) have reported similar breakdown of the chabazite lattice in the dehydrofluorination of occluded fluoromethanes. Acidic faujasites REX, HY, and metal-hydrogen Y, after reaction with ethyl chloride for several hours, contained large amounts of coke, but there was only slight loss in lattice crystallinity. Since small amounts of isobutane, propane, and isopentane were observed during the reactions with these catalysts, the major cause of aging is attributed to secondary intracrystalline hydrogen-transfer reactions of product ethylene (*19*).

In Table 1 data are presented to demonstrate that elimination to form ethylene over REX was inhibited by nitrogenous bases. Thus, dehydrohalogenation activity in REX may be associated with acidic sites. Yet, strong acidity, such as that required for alkylation of benzene with ethylene (*18, 19*), is not a necessary requirement for dehydrohalogenation activity at 260°C, as shown by the data for NaX and Linde 5A.

Other two-carbon reactants. Elimination reactions of other two-carbon haloalkanes

TABLE 3

REACTIONS OF TWO-CARBON HALOALKANES OVER REX CATALYST[a]

Reactant	LHSV	Temp. (°C)	Conversion of reactant (Time)[b]	Major products	(Mole %)
C_2H_5Br	0.50	66	73.5 (65)	$CH_2{=}CH_2$	(73.5%)
C_2H_5I	0.50	66	40.0 (80)	$CH_2{=}CH_2$	(100%)
$CH_2Cl{-}CH_2Cl$	0.625	288	68.9 (120)	$CH_2{=}CHCl$	(88.9%)
				C_2H_5Cl	(9.1%)
				$CHCl_2{-}CH_3$	(2.0%)
$CH_2Cl{-}CH_2Cl$[c]	0.625	288	28.0 (120)	$CH_2{=}CHCl$	(58.2%)
				C_2H_5Cl	(41.8%)
$CHCl_2{-}CH_3$	0.50	204	90.0 (120)	$CH_2{=}CHCl$	(>95%)[d]
$CCl_3{-}CH_3$	0.50	163	100.0 (260)	$CH_2{=}CCl_2$	(100%)
$CH_2{=}CHCl$[e]	[f]	260	16.3 (100)	$CH_2{=}CH_2$	(36.3%)[g]
				C_2H_5Cl	(28.0%)
				$CH_3{-}CHCl_2$	(22.3%)

[a] All reactions run at 1 atm, N_2 carrier (5 ml/min); at conditions indicated, no conversion of reactants over tempered quartz chips.

[b] Cumulative product analysis (excluding coke) after indicated time on stream.

[c] Quinoline-treated REX.

[d] Small amounts of ethyl chloride formed in early moments on stream.

[e] Under similar conditions, but in presence of HCl (2 moles), 3.5% conversion of $CH_2{=}CHCl$ occurred; a similar product distribution was observed, but more coke was formed.

[f] Gas rate: 0.0103 mole/g catalyst/hr; product analysis on 100 min sample.

[g] Large amounts of coke, small amounts of ethane and traces of acetylene, propane, and isobutane also formed.

over REX catalyst are summarized in Table 3. With ethyl bromide and ethyl iodide, elimination to form ethylene and hydrogen halide in high yield occurred at 66°C. These findings are in accord with the lower carbon–halogen bond energies in these compounds. Small amounts of iodine were formed in the ethyl iodide reaction.

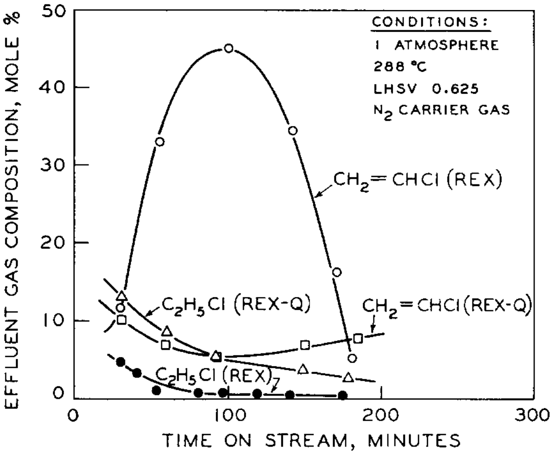


FIG. 3. Product distribution versus time for reaction of 1,2-dichloroethane over REX and quinoline-treated REX (REX-Q).

Similarly, 1,1,1-trichlorethane was smoothly converted to vinylidene chloride at 163°C, with only slight catalyst aging occurring after 4 hours on stream. Good yields of vinyl chloride were obtained from 1,1-dichloroethane at 204°C, with small amounts of ethyl chloride appearing at short times on stream. Catalyst aging was rapid, however.

A higher temperature (288°C) was required for significant conversion of 1,2-dichloroethane. Vinyl chloride was the major product, but small amounts of ethyl chloride and 1,1-dichloroethane, and traces of ethylene were also formed. As shown in Fig. 3, conversion to vinyl chloride increased to a maximum after 100 minutes on stream. The sharp decrease in conversion over the next 80 minutes was reflected by very high coke levels in the discharged catalysts. Ethyl chloride formation, which was significant in the early moments on stream, decreased rapidly with time.

To test the possibility that secondary reactions of vinyl chloride might be responsible for the side products observed in the dehydrohalogenation of 1,2-dichloroethane, this chloroolefin was passed over REX at 260°C (Table 3). The major observed products, ethylene, ethyl chloride, 1,1-dichloroethane (and coke) were the same as the side products from the 1,2-dichloride. A scheme of possible reactions of vinyl chloride at 260°C leading to the observed product distribution is shown in Fig. 4. This reaction scheme involves an intermolecular hydride ion shift. Related intramolecular hydride shifts have been reported to accompany the dehydrohalogenation of 2,3-dichlorobutane over alumina (7).

The rapid decrease in ethyl chloride formation with time (Fig. 3) probably reflects the obliteration by coke formation of very active site configurations associated with hydride transfer. As in the case of ethyl chloride, significantly lower conversion was observed when 1,2-dichloroethane was passed over quinoline-treated REX at 288°C (Fig. 3 and Table 3).

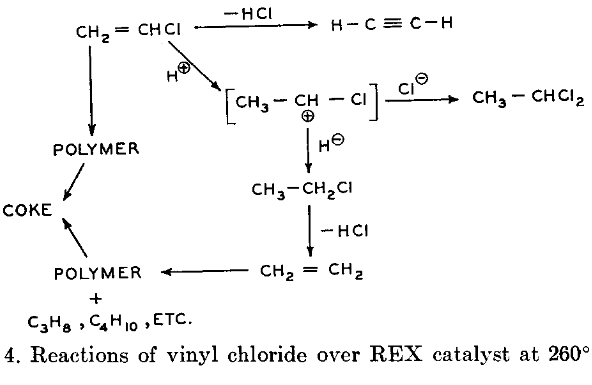


FIG. 4. Reactions of vinyl chloride over REX catalyst at 260°C.

Chlorination–Dehydrohalogenation

A comparison of the product distribution obtained by the passage of ethylene and chlorine in 2:1 molar ratio over REX catalyst and quartz chips at 288°C showed marked differences (Table 4). In both cases, high conversions of ethylene were observed, and large amounts of chlorine were incorporated into the organic product. With REX, the products were 88.9% chloroethylenes (di-, tri-, and tetra- predominating); only small amounts of chlorinated ethanes were observed. Catalyst aging was severe. The data also infers the facile dehydrohalogenation of tetra- and pentachloroethane under these conditions.

TABLE 4

Comparison of Reaction of Ethylene and Chlorine over REX Catalyst and Quartz at 288°C[a]

	REX[b]	Quartz
Conversion of ethylene (%)[c]	85	79
Product distribution (Mole %)		
Vinyl chloride	2.9	Nil
trans-1,2-Dichloroethylene	11.1	1.4
cis-1,2-Dichloroethylene	20.2	2.0
1,2-Dichloroethane	4.1	7.4
Trichloroethylene	31.1	4.4
1,1,2-Trichloroethane	1.0	53.7
Tetrachloroethylene	23.6	Tr
1,1,2,2-Tetrachloroethane	6.0	16.9
1,1,1,2-Tetrachloroethane	Nil	5.7
Pentachloroethane	Tr	8.4
Hexachloroethane	Tr	Tr
	100.0	99.9

[a] Atmospheric pressure, Cl_2/C_2H_4 (molar ratio) = 2, C_2H_4 flow rate = 0.0085 mole/g catalyst/hr.

[b] Preconditioned with chlorine (10 ml/min) at 288°C for 20 min.

[c] Total conversion to other products after 180 min on stream.

With quartz, on the other hand, polychloroethanes, notably 1,1,2-trichloroethane, comprised 92.2% of the products. Di- and trichloroethylenes made up the remaining 7.8%.

The entire product distribution from the REX-catalyzed reaction is consistent with a sequence of chlorine addition followed by hydrogen chloride elimination. The presence of the zeolite is clearly associated with an acceleration of the dehydrohalogenation process; whether it has any other role, such as catalyzing chlorine addition (*20*), or inhibiting substitution reactions as in the case of other polar catalysts at higher temperatures (*21*), cannot be assessed from this data.

The large amount of 1,1,2-trichloroethane in the product from reaction over quartz probably arose via initial addition of a mole of chlorine to ethylene, followed by chlorine radical substitution. Still further substitution would afford tetra- and pentachloroethanes. Such substitution reactions are well known in the chlorine-ethylene system at these temperatures (*21, 22*). While many of the products could easily arise via other pathways, only a slight tendency toward dehydrohalogenation (thermal or chlorine-catalyzed) appears to exist in the absence of the zeolite.

Analogous experiments employing ethane instead of ethylene (in the dark) showed virtually 100% conversion of ethane to mixtures of highly chlorinated two-carbon products at temperatures of 288°C and higher. Similarly, highly chlorinated benzenes have been prepared in low yield by passing cyclohexane over sodium Y zeolite in the presence of NOCl and HCl, NO and Cl_2, or Cl_2 alone at 149–260°C (*23*).

Reaction of Ethanol and Hydrogen Chloride

Crystalline aluminosilicates show distinct catalytic activity for the gas-phase conversion of ethanol and hydrogen chloride to ethyl chloride and water at atmospheric pressure [Eq (2)]. As shown in Table 5 for this reaction at 170°C,

$$C_2H_5OH + HCl \xrightarrow{\text{Zeolite}} C_2H_5Cl + H_2O \qquad (2)$$

steady state conversion to ethyl chloride (over 3 to 6 hours in many cases) without apparent catalyst deactivation was observed for all catalysts tested. Varying amounts of ethylene were also formed, with occasional traces of diethyl ether. Under these conditions, the following order was obtained for the zeolite catalysts: HY, REX, REY > CaX, NaX > Linde 5A.

TABLE 5

Reaction of Ethanol and Hydrogen Chloride over Zeolites and other Catalysts at 170°C

Catalyst[a]	LHSV,[b] C_2H_5OH	Conversion[c] of ethanol (Mole %)		Ethyl chloride formation, steady state (ml/hr)
		Ethyl chloride	Ethylene	
HY	0.6	86	5	3.8
REX	1.3	84	0	3.8
REY	0.8	77	4	3.4
CaX	0.7	37	8	1.7
NaX	0.8	33	5	1.4
Linde 5A	0.8	10	14	0.4
Alumina	1.3	10	4	0.4
Rare earth silica-alumina	0.8	4	6	0.1
Rare earth oxide	0.9	4	7	0.2

[a] No conversion of ethanol when reactants were passed over quartz chips at 170–290°C.

[b] Ethanol input, 0.033 mole/g catalyst/hr.

[c] Steady state conversion at atmospheric pressure, C_2H_5OH:HCl (molar) ratio = 1.82.

Neutral alumina was about as active as Linde 5A, while rare-earth-exchanged amorphous silica-alumina and rare earth oxide showed only about 5% of the activity of the rare-earth-exchanged crystalline aluminosilicate.

Figure 5 shows the effect of temperature on the rate of formation of ethyl chloride for the catalysts listed in Table 5. The faujasites HY, REX, and REY show maximum activity near 200°C, while considerably higher temperatures are required to achieve comparable conversion with the other zeolites or alumina. The decreased formation of ethyl chloride (and high coke levels) observed at temperatures greater than 200°C with HY, REX, and REY reflect the increased rate of elimination of HCl to form ethylene, and ultimately, the poisoning of the catalyst due to intracrystalline hydrogen-transfer reactions of ethylene (*19*). The formation of 9.7 g ethyl chloride/g REX catalyst, in the run at 190°C, emphasizes the heterogeneous nature of this catalysis.

Slight to moderate decreases in X-ray

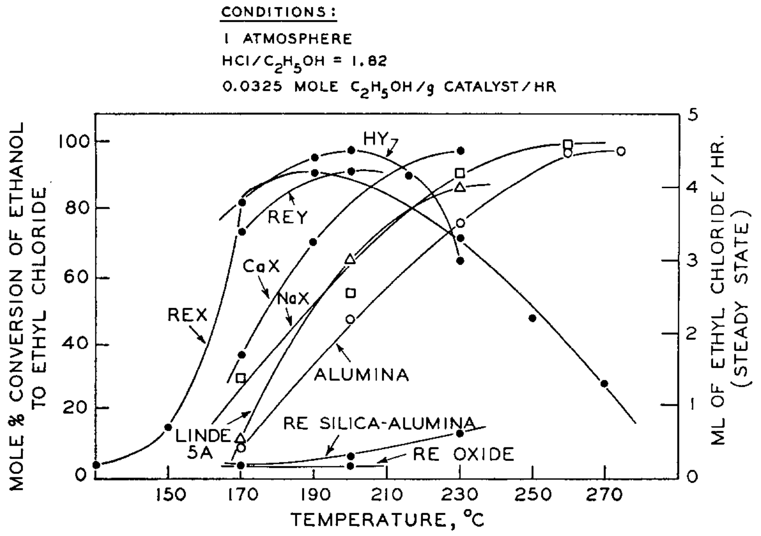


Fig. 5. Rate of ethyl chloride formation versus temperature for zeolites and other catalysts.

crystallinity were observed for REX, REY, and HY catalysts after reaction. Recovered CaX, NaX, and Linde 5A catalysts, however, showed sharp losses in crystallinity (about 80%) and the presence of large amounts of chlorine.

TABLE 6
COMPARATIVE REACTIVITIES OF ETHANOL AND ETHYLENE WITH HYDROGEN CHLORIDE OVER REX CATALYST AT 190°C

	Ethanol[a]	Ethylene[a]
Molar ratio, HCl: reactant	1.82	2.0
Ml C_2H_5Cl formed, 150 min on stream	10.4	3.8
% Carbon on discharged catalyst	2.6 (6 hr)	10.2 (2.5 hr)

[a] Input = 0.0325 moles/g catalyst/hr.

Table 6 shows that the addition of HCl to ethylene at 190°C in the presence of REX catalyst results in the formation of ethyl chloride. Ethanol, however, under similar conditions, forms about three times as much ethyl chloride and about one-fourth the amount of coke. This observation suggests that ethylene is not necessarily an intermediate in the ethanol–hydrogen chloride reaction.

CONCLUSIONS

Crystalline molecular sieves actively catalyzed the elimination of halogen acid from two-carbon haloalkanes at 1 atm and temperatures of 65–370°C. With REX catalyst, dehydrohalogenation activity was inhibited by nitrogenous bases. Crystalline zeolites also catalyzed the reaction of ethanol and hydrogen chloride to form ethyl chloride at 150–250°C.

Much of the above data suggests a possible role for polar or ionic intermediates in the dehydrohalogenation reactions. For instance, with REX catalyst, the observed order of decreasing temperature for appreciable reaction ($CH_2Cl\text{–}CH_2Cl > C_2H_5Cl > CHCl_2CH_3 > CCl_3\text{–}CH_3$) parallels the increasing stability of the corresponding carbonium ions from loss of halide ion (*7, 24*) and the decreasing ionization potentials (*24*) for the listed compounds. Similar parallels between substrate structure and carbonium ion stability have been observed in elimination over other polar solid catalysts (*5, 7*).

The common denominator in these zeolite-catalyzed dehydrohalogenations is the presence of a high-surface-area, rigid, ordered, polar (*25*) surface. It seems probable that a major function of the zeolite surface is to give assistance to ionization or heterolytic bond cleavage in the adsorbed haloalkane, as has been commonly observed with other polar catalysts (*7*). Thus, electron-deficient sites such as protons or metal cation fields (of which the $C_2H_5Cl\text{–}AgX$ case may be a specific example) may be involved, as well as the negative $AlO_4^{\ominus}$ sites in the oxygen-rich anionic lattice. Our data does not exclude the possibility that traces of chlorine, from Ce^{4+} oxidation of hydrogen chloride, may be exerting a catalytic effect in the reactions over rare earth zeolites.

ACKNOWLEDGMENTS

We wish to thank Mr. R. M. Buckingham and Mr. F. E. Harvey for their excellent technical assistance, and Prof. G. A. Russell of Iowa State University for very helpful discussions.

REFERENCES

1. BUNNETT, J. F., *Angew. Chemie* **74,** 731 (1962).
2. MACCOLL, A. *In* "The Chemistry of Alkenes" (S. Patai, ed.), p. 203. Interscience, New York, 1964.
3. SCHWAB, G.-M., AND NOLLER, H., *Z. Elektrochem.* **58,** 762 (1954).
4. NOLLER, H., AND OSTERMEIER, K., *Z. Elektrochem.* **60,** 921 (1956).
5. NOLLER, H., AND OSTERMEIER, K., *Z. Elektrochem.* **63,** 191 (1959).
6. ANDRÉU, *P.*, LETTERER, R., LÖW, W., NOLLER, H., AND SCHMITZ, E., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **2,** 857 (Wiley, New York, 1965).
7. NOLLER, H., HANTSCHE, H., AND ANDRÉU, P., *J. Catalysis* **4,** 354 (1965).
8. WEISZ, P. B., AND FRILETTE, V. J., *J. Phys. Chem.* **64,** 382 (1960).
9. WEISZ, P. B., FRILETTE, V. J., MAATMAN, R. W., AND MOWER, E. B., *J. Catalysis* **1,** 307 (1962).
10. KEOUGH, A. H., AND SAND, L. B., *J. Am. Chem. Soc.* **83,** 3536 (1961).

11. Gourisetti, B., Cosyns, J., and Leprince, P., *Compt. Rend.* **258,** 4547 (1964).

12. Minachev, Kh. M., Garanin, V. I., and Isakov, Ya. I., *Izv. Akad. Nauk SSSR, Ser. Khim.* p. 1722 (1964); *Chem. Abstr.* **61,** 15965 (1964).

13. Frilette, V. J., and Munns, G. W., Jr., *J. Catalysis* **4,** 504 (1965).

14. Rapoport, I. B., Itsikson, L. B., Kheifets, E. M., and Sidyakova, G. V., *Neftekhimiya* **5,** 738 (1965); *Chem. Abstr.* **64,** 1941 (1966).

15. Rapoport, I. B., Itsikson, L. B., Kheifets, E. M., and Sidyakova, G. V., *Neftekhimiya* **5,** 549 (1965); *Chem. Abstr.* **63,** 16199 (1965).

16. Barrer, R. M., and Brook, D. W., *Trans. Faraday Soc.* **49,** 940 (1953).

17. Milton, R. M., and Breck, D. W., U. S. Patent 2,920,122, January 5, 1960.

18. Venuto, P. B., Hamilton, L. A., Landis, P. S., and Wise, J. J., *J. Catalysis* **5,** 81 (1966).

19. Venuto, P. B., Hamilton, L. A., and Landis, P. S., *J. Catalysis* **5,** 484 (1966).

20. Eng, J., and Baker, S. B., U. S. Patent 2,956,084, October 11, 1960.

21. Sherwood, P. W. *in* "Chlorine: Its Manufacture, Properties and Uses" (J. S. Sconce, ed.), p. 564. Reinhold, New York, 1962.

22. Steacie, E. W. R., "Atomic and Free Radical Reactions," Vol. II, p. 673. Reinhold, New York, 1954.

23. Miale, J. N., Central Research Division, Mobil Oil Company, private communication.

24. Maccoll, A., *in* Ref. 2, pp. 232–234.

25. Barrer, R. M., Bultitude, F. W., and Sutherland, J. W., *Trans. Faraday Soc.* **53,** 1111 (1957).