JOURNAL OF CATALYSIS 4, 504–509 (1965)

Catalysis by Crystalline Aluminosilicates

III. Dehydration of Isopropyl Alcohol Catalyzed by Sodium Faujasite in the Presence of CO_2

V. J. FRILETTE AND G. W. MUNNS, JR.

From the Socony Mobil Oil Company, Central Research Division Laboratories, Princeton, New Jersey

Received November 9, 1964; revised December 29, 1964

Catalytic activity for the dehydration of isopropyl alcohol is reversibly induced in sodium faujasite (Linde 13X) by the presence of carbon dioxide.

Kinetic and sorption studies suggest that the catalytic sites are formed by chemisorption of carbon dioxide molecules. If it is assumed that the *character* of the set of sites is independent of the partial pressure of the carbon dioxide, then it can be shown that the relation between the *number* of sites and partial pressure satisfies the Langmuir equation.

Monolayer coverage by carbon dioxide is achieved when on an average of about one molecule of the gas is sorbed for each two supercages of the zeolite. This estimate was arrived at by extrapolating the sorption values observed under reaction conditions. The nonequivalence of the zeolitic supercages makes it unlikely that the chemisorption of CO_2 is associated with the sodium ions; impurity cations or defect centers are probably responsible for the sorption.

INTRODUCTION

Previous studies in our laboratories showed that the sodium salt form of synthetic faujasite is an active cracking catalyst for normal decane (*1*). However, the cracked products are free of isoparaffins, indicating that the extensive surface of this salt does not possess "acidic" centers of the type associated with silica-alumina cracking catalyst.

It seemed logical at this point to ask whether or not the sodium zeolite contained a mildly acidic form of hydrogen capable of catalyzing cracking without isomerization. For, although the idealized structure of the sodium faujasite crystal contains no hydrogen (except, perhaps, at the terminal planes of the crystals) there was some question about whether or not H_3O^+ ions were, in fact, present (*2, 3*). Should they be present, it was thought that they might be detected by examining the behavior of the zeolite as a dehydration catalyst. This reasoning was suggested by the contention that the dehydration sites of silica-alumina are distinct from the cracking sites (*4*).

Our experiments with isopropanol dehydration were not enlightening so far as the existence of H_3O^+ ions was concerned. However, in the course of conducting these experiments, it was noted that exposure to carbon dioxide converted the relatively inert sodium faujasite to a highly active, highly selective dehydration catalyst. Since there appeared to be no report in the literature of such an effect with other catalysts, it was thought of interest to investigate the mechanism for the activation. The results of this study follow.

EXPERIMENTAL METHODS

The experiments were designed to reveal the kinetic effects of carbon dioxide and minimize the involvement of other factors. An early experiment showed that the reaction was inhibited by the water produced, a characteristic often noted in catalyzed dehydrations (*5, 6*). This complication was minimized by determining decomposition rates only for aqueous isopropanol (containing 4.0 wt % H_2O) at a temperature and contact time such that only very low conversions were obtained. To permit variation of CO_2 partial pressure without changing other conditions, mixtures of helium and carbon dioxide were used at a fixed total pressure. The catalyst proved to be quite stable at the temperature and water vapor pressure used in our studies (235°C and *ca.* 50 mm). These conditions are similar to those for which Barrer reports good stability (*7*). At higher temperature or in the presence of excessive humidity it was found that both the zeolitic structure and the catalytic activity were lost.

Since the only products formed under our reaction conditions proved to be propylene, water and minor amounts of diisopropyl ether, the level of catalytic activity was determined by vapor fractometer analysis of the recovered alcohol for water content. A 15-ft, ¼-inch OD copper column containing Carbowax 1000 (10%) on Haloport F was used. The column was operated at 125°C with a helium carrier stream flowing at 70 cc/min. Precise calibration using aqueous isopropanol standards analyzed by the Karl-Fisher method showed that the peak height for water was linearly related to the weight per cent water content within 0.1% over the range up to 20% water. Small day-to-day differences in the behavior of the VPC equipment were compensated by using a sample of the aqueous alcohol charge as a secondary standard. Thus, the difference in water content of charged and recovered alcohol is believed accurate to ±0.1 wt %. The values obtained in this manner are reported in the present paper in terms of conversion of isopropanol to propylene and water from the relation:

$$\text{Mole \% Conversion} = \frac{100}{0.3 + 0.7W_f}\left[\frac{W_f - W_i}{1 - W_i}\right] - 0.1$$

in which W_i and W_f are the wt fractions of water in the charge and product, respectively; the small correction shown in the equation is required to compensate for the selective volatility loss of alcohol to the helium and carbon dioxide. Estimates of conversion under steady state conditions are believed to be accurate within ±0.3%. To achieve this accuracy, however, it is necessary to avoid upsets that alter the considerable inventory of water sorbed on the catalyst under reaction conditions (*7*).

The Pyrex reactor and auxiliary equipment are shown in Fig. 1. Alcohol was fed

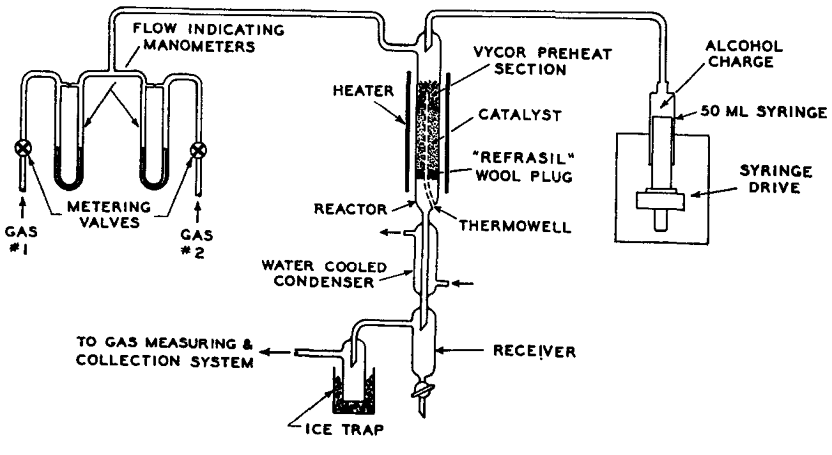

FIG. 1. Diagram of apparatus.

over the catalyst by a positive displacement syringe pump equipped with a variable-speed drive. By means of an arrangement of T-joints, it was possible to feed helium and carbon dioxide at precisely metered rates along with the alcohol-water mixture, and to recharge the syringe rapidly so as to avoid disturbance of the physical steady state.

The catalyst used was the synthetic sodium faujasite (13X) marketed by the Linde Division of Union Carbide and Carbon Corporation. It was obtained in the form of a white powder. Elementary analyses and sorption capacities of this particular batch were: Na, 15.0%; Ca, 0.45%; SiO_2, 47.4%; Al_2O_3, 33.6%; and 29.8 wt % H_2O sorption at 25°C and 20 mm. The powder was formed into ⅛ × ⅛-inch pellets and 13 g was charged to the reactor. The pellets were then dehydrated by heating to 530°C in a stream of helium.

Reagent grade isopropyl alcohol was purchased from J. T. Baker Chemical Co., Phillipsburg, N. J. (Analyzed, Lot #26503). Chromatographic analysis showed less than 0.1 wt % acetone present. It was used without further purification.

Results of Dehydration Experiments

The general character of the carbon dioxide effect is shown in Fig. 2. Fresh catalyst, pretreated as described previously, was brought to 235°C in a flow of pure helium and then a continuous flow of isopropanol was started. Samples collected during this first period showed no conversion. (Independent experiments made under similar conditions failed to show any catalytic activity even at 300°C.) On replacement of the helium by carbon dioxide, catalytic activity became evident within a very short time. The conversion initially found (~10%) decayed for the first 5 hr and stabilized at about 6%. The possible basis for this relatively long term transient will be discussed later. On reverting from carbon dioxide to pure helium, the activity fell, as shown, and in time the initial, inactive state of the catalyst was regained.

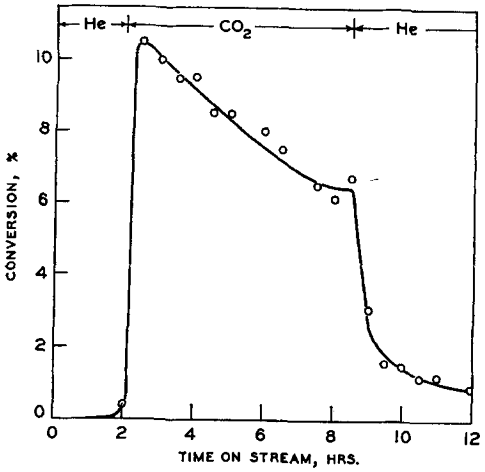

Fig. 2. Reversibility of CO_2 Activation: $t =$ 235°C, contact time, $\tau = 4.2$ sec; inlet partial pressures for alcohol, water, and gas as follows: $p_A = 360$ mm, $p_{H_2O} = 50$ mm, $p_{gas} = 350$ mm.

The same charge of catalyst used for the experiment of Fig. 2 was studied to determine the effect of varying the partial pressure of carbon dioxide. At each partial pressure, the conversion was measured periodically until no further change was noted for several hours. Figure 3 illustrates a typical determination. The assembled results of these experiments are shown in Fig. 4. The initial experiment, made at 17.5 mm, was repeated with identical results after completion of the others, indicating that the catalyst properties had not changed during the course of the study.

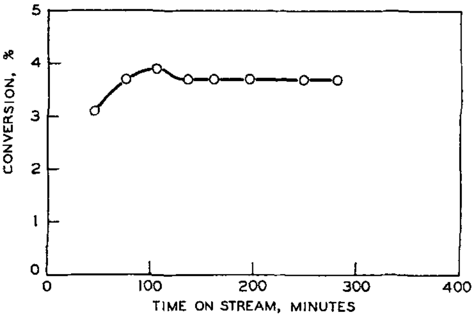

Fig. 3. Achievement of steady state: $t =$ 230°C, contact time, $\tau = 4.2$ sec; inlet partial pressures for alcohol, water, CO_2 and helium as follows: $p_A = 360$ mm, $p_{H_2O} = 50$ mm, $p_{CO_2} = 35$ mm, $p_{He} = 315$ mm.

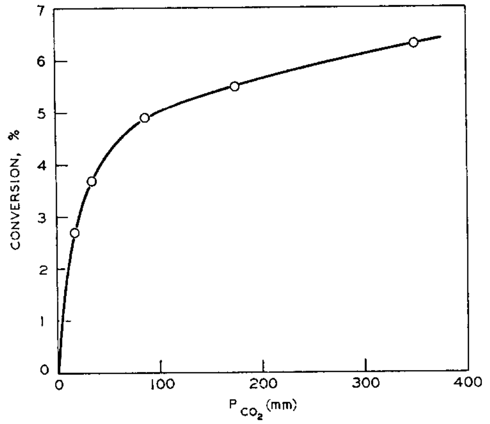

FIG. 4. Dependence of steady state conversion on partial pressure of CO_2: $t = 230°C$, $\tau = 4.2$ sec.

SORPTION OF CO_2

While it is evident that some interaction between carbon dioxide and zeolite or alcohol must be involved in the observed catalysis, the nature of this interaction is not immediately apparent. It is clear, however, that whatever mechanism is proposed must be consistent with the observed effects of partial pressure and with the relatively long-term transients. Consider, for example, the possible role of physically sorbed carbon dioxide. Although it is known that sodium faujasite is capable of sorbing 24 wt % of this gas at room temperature, equilibration is very rapid, having been observed to occur in a matter of minutes. Furthermore, the nature of the isotherm for physically held gas indicates that a nearly linear relation between the weight sorbed and partial pressure should hold under the conditions of our experiments (*8*). Since the catalytic transients require some hours to damp out, and the observed partial pressure dependence of the dehydration rate is nonlinear, it seems unlikely that the catalytic effects depend on the physically sorbed gas.

The basis for involvement of *chemisorbed* carbon dioxide in the catalysis is found in a recent investigation, where it is shown by infrared absorption that a small amount of this gas is reversibly chemisorbed by the alkali metal salts of zeolite X(3). Since these studies were made at much lower temperatures than those used in our work, however, it seemed advisable to supplement them by a limited study of the sorption behavior of carbon dioxide at elevated temperature.

A fresh charge of catalyst was loaded into the reactor shown in Fig. 1. It was conditioned by heating to 530°C in a stream of helium. A mixture of 350 mm CO_2, 50 mm H_2O vapor, and 360 mm helium was then passed over the catalyst at a total flow rate of 200 cc/min for about 20 hr at 235°C. The desorption behavior of the sorbed carbon dioxide was then followed by passing a mixture of 50 mm H_2O vapor and helium at a flow rate of about 20 cc/min over the catalyst maintained at 235°C, and then through Aquasorb A. R. (supported P_2O_5, Mallincrodt), followed by Mallcosorb A. R., and finally through another Aquasorb tube. The tubes were periodically weighed to determine the amount of CO_2 desorbed. After 6 hr, at which time the rate of CO_2 removal had become very small, the residual CO_2 held was determined by raising the catalyst temperature to 550°C for 4 hr. Desorption appeared to be completed in 2 hr at this temperature. A second experiment was performed which differed from the first only in that the desorption was carried out with dry helium. The results are shown in Table 1.

TABLE 1
DESORPTION OF CO_2 AT 235°C

Desorption time (hours)	Wt % CO_2 removed	
	50 mm H_2O	Dry
1.0	0.32	0.30
2.0	0.41	0.36
3.0	0.46	0.39
4.0	0.48	0.42
5.0	0.51	0.45
6.0	0.52	0.47
Final (550°C)	1.25	1.15

Aside from the very small amount of carbon dioxide rapidly removed during the first hour, it is evident from the data that most of the gas is tightly held, i.e., chemisorbed, by the catalyst. We may assume that there is negligible readsorption along the length of the catalyst bed in view of the low partial pressure maintained by the flow of helium, and therefore that the data reflect the intrinsic desorption rate. Detailed examination of the change of rate with time suggests the existence of two varieties of chemisorbed carbon dioxide, with distinctly different rates of desorption, along with the small amount of physically adsorbed gas which comes off very quickly. The relative amounts of these three species cannot be determined precisely because of the limited scope of this study, but if it is assumed that the contribution of the most tightly held species can be neglected, an estimate of 0.55 wt % is arrived at for the sum of the physically adsorbed and more loosely chemisorbed species. The data for these two species plotted according to the first order rate law are shown in Fig. 5, from which it appears that about 0.25 wt % of carbon dioxide is physically held, the loosely and tightly chemisorbed species contributing about 0.30 and 0.65 wt % respectively to the total absorption. As shown by Fig. 5, the rate constant for the desorption is substantially increased by the presence of 50 mm H_2O vapor. This effect of water on the rate of desorption, and its reported "catalytic" effect on the rate of sorption (*3*) at lower temperatures, suggests a complex mechanism for the formation of the chemisorbed species, with rate constants which vary depending on the concentration of mechanistically participating species.

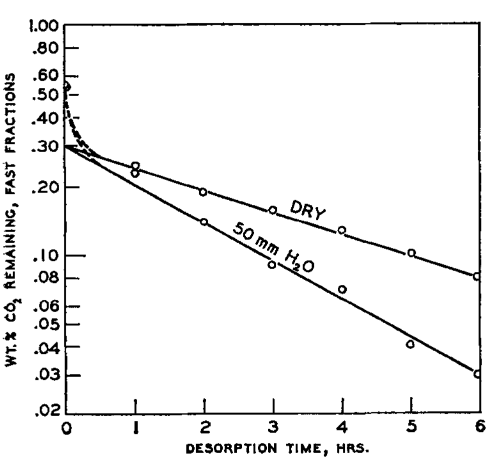

FIG. 5. Desorption of carbon dioxide: $t = 235°C$.

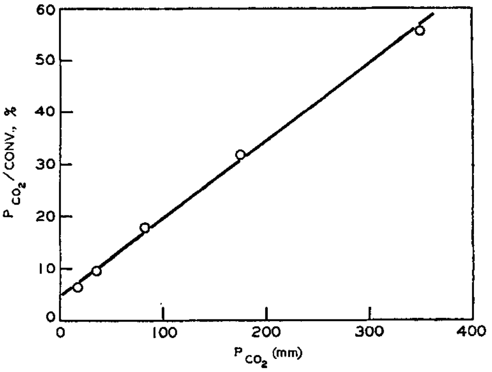

FIG. 6. Test of steady state data for conformance with Langmuir isotherm.

NATURE OF CHEMISORPTION

The sparse distribution of sorbed carbon dioxide suggested that the chemisorption sites might be noninteracting, and could show Langmuir-type behavior. That this is indeed the case is seen from Fig. 6, in which the steady state data in Fig. 4 is plotted according to the equation

$$P_{CO_2}/\% \text{ Conversion} = A + BP_{CO_2}$$

in which P_{CO_2} is the partial pressure of carbon dioxide, and A and B are simple constants or sums of constants, depending on whether or not the two chemisorbed species are interconvertible. That conversion is proportional to the fraction of surface occupied by CO_2 is implied. The linearity appears to be quite good over the range of partial pressures examined.

The previously cited infrared study indicates that bands for physically sorbed carbon dioxide are in evidence when 0.41 molecules of carbon dioxide are sorbed for each supercage of the NaX, suggesting that at this level there are very few remaining sites capable of tightly bonding the gas (*3*). This, along with other semiquantitative observations, led the authors of that study to comment that "there is little further chemisorption (with increased partial pressure), beyond approximately 0.5–1 molecule per cavity." Based on the Langmuir relation, the present investigation shows that no free sites remain when 0.4 molecules are chemisorbed per supercage. Thus, it would appear that sites are to be found on an average in less than one-half of the supercages.

The possibility that carbon dioxide is chemisorbed by reaction with the normal complement of sodium cations contained by the zeolite must be ruled out as incompatible with the sparsity of sites. Two other possibilities can be suggested, however, which are compatible with present findings. The first is that chemisorption occurs at cations, such as calcium, not shown in the empirical formula. The second possibility is that imperfections in the lattice serve as the active centers. A clear choice between these hypotheses cannot be made from presently available data.

Finally, it should be mentioned that a recent investigation reports considerable catalytic activity for the dehydration of isopropyl alcohol by sodium faujasite below 300°C (*9*). This result would appear to contradict the present study. Since we have found no such activity with several independently prepared and well-characterized specimens, it is suspected that contaminated or hydrolyzed zeolites were inadvertently used by the Russian investigators.

REFERENCES

1. FRILETTE, V. J., WEISZ, P. B., AND GOLDEN, R. L., *J. Catalysis* **1**, 301 (1962).

2. SZYMANSKI, H. A., STAMIRES, D. N., AND LYNCH, G. R., *J. Opt. Soc. Am.* **50**, 1323 (1960).

3. BERTSCH, L., AND HABGOOD, H. W., *J. Phys. Chem.* **67**, 1621 (1963).

4. TOPCHIEVA, K. V., YUN-PIN, K., AND SMIRNOVA, I. V., *Advan. Catalysis* **9**, 799 (1957).

5. FRILETTE, V. J., MOWER, E. B., AND RUBIN, M. K., *J. Catalysis* **3**, 25 (1964).

6. WINFIELD, M. E., "Catalysis" (P. H. Emmet, ed.), Vol. VII, p. 93. Reinhold, New York, 1960.

7. BARRER, R. M., AND BRATT, G. C., *J. Phys. Chem. Solids* **12**, 130 (1959).

8. CHEN, N. Y., private communication.

9. TSITSISHVILI, G. B., SIDAMONIDZE, SH. I., AND ZEDGENIDZE, A., *Dokl. Akad. Nauk SSSR* **153**, 1395 (1964).