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Comparison of Adsorption and Catalysis on Na, K and Ca Faujasite Type Zeolites

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The adsorption of cyclohexane and the cracking of isooctane have been studied on several Y zeolites containing various amounts of Ca, K or Na ions. The content and nature of cations produce opposite effects on isooctane cracking rates and cyclohexane adsorption equilibrium. Hence, it is suggested that there is a competitive adsorption of saturated molecules on acidic and cationic sites. Due to the equilibrium of this adsorption on the two centers, the high (or low) catalytic activities are correlated, respectively, to the low (or high) adsorptive properties. The hypothesis also explains the important rise in catalytic activity at low cation content and the inverse range of catalytic activities and adsorptive properties for the series CaHY, NaHY, KHY.

INTRODUCTION

Many cationic forms of zeolites are used as adsorbents and fundamental studies have related the adsorption to cation properties (*1–4*). Zeolites used as catalysts are almost in a protonic form. Hence, referring to adsorption and catalysis, molecules such as hydrocarbons are able to interact either with cations or acid centers (*5–9*). The aim of this paper is to present the changes in adsorptive and catalytic properties of zeolites with various cationic and acidic contents in order to study the simultaneous modifications which occur when both sites are present. The influences of potassium, sodium and calcium ions are compared.

EXPERIMENTAL METHODS

Materials

Samples were prepared from Union Carbide NaY zeolite. KY and CaY zeolites were obtained by exchange of Na^+ ions for K^+ or Ca^{2+} ions in chloride solutions. Partial exchange with NH_4^+ ions of K^+, Ca^{2+} and Na^+ ions give KNH_4Y, $CaNH_4Y$ and $NaNH_4Y$ materials. These zeolites were heated at 380°C in a dry air flow for 15 hr in order to evolve NH_3 and then at 550°C for the same time. Any ultrastabilizing effect due to heating conditions was avoided. Chemical compositions of the catalysts are given in Table 1. X-ray diffraction measurements showed the zeolites to be highly crystalline.

Adsorption

Nitrogen adsorption at −195°C was used in order to compare the textural properties of the samples. The micropore filling n_m is determined from a Langmuir plot for $p/p_0 \leq 0.02$ (*10*).

The adsorption of cyclohexane was studied by gas chromatography as previously described (*11,12*). Isotherms of adsorption were obtained at temperatures ranging from 70 to 180°C where no transformation of cyclohexane was observed.

The virial Eq. (1) of Bradley (*13*) and

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TABLE 1
CHEMICAL COMPOSITION OF ZEOLITES

Catalysts	Na^+/u.c.	K^+/u.c.	Equiv Ca^{2+}/u.c.
NaY	56	0	0
NaHY series	45.4, 36.4, 30.3, 24.4, 17.2, 8.7	0	0
KHY series	~0.7	46.9, 40.1, 27, 19, 8,	0
CaHY series	~0.6	0	55.4, 50.6, 40.1, 35, 22.8

Wilkins (*14*)

$$P = n \exp (C_1 + C_2 n + C_3 n^2 + \ldots), \quad (1)$$

and the virial Eq. (2) of Kiselev (*1,4*)

$$P = K'_1 n + K'_2 n^2 + K'_3 n^3 + \ldots . \quad (2)$$

were used to describe the adsorption. Coefficients C_i and K'_i ($i = 1, 2, 3 \ldots$) were determined with an IBM 370 computer. P is the pressure and n is the adsorption level.

According to Kiselev (*1,4*) Eq. (3) and (4) give the correlations between virial coefficients.

$$C_1 = -\ln K_1 = \ln K'_1 \quad (3)$$

where K_1 is the equilibrium constant and K'_1 is the Henry constant,

$$K'_2 = C_2 \exp C_1, \quad (4)$$

where K'_2 is a constant characterizing the pairwise adsorbate–adsorbate interaction depending on the zeolitic field (*4*).

Catalysis

Isooctane cracking was performed at 465°C in a microcatalytic reactor. Before catalytic measurements, the samples (20 mg) were heated at 465°C in the reactor under flowing hydrogen for 15 hr (1.8 liters/hr). Then isooctane ($p = 100$ Torr) was introduced continuously in a hydrogen stream. Activity was measured after steady state conditions were reached. Reaction products were analyzed by gas chromatography. It was shown (*15*) that isobutene was a primary reaction product and activity is expressed by the isobutene formation rate. Conversion was less than 5%.

RESULTS

Nitrogen Adsorption

For the Ca series the nitrogen adsorption capacity keeps close to 0.3 cm^3/g for all the samples. The value is the same for the K and Na series at high cation levels. At low K or Na contents the capacity is smaller. It was verified that this is not related to a decrease in crystallinity.

Cyclohexane Adsorption

Adsorption Equilibrium

It was shown (*11*) that the adsorption equilibrium constant K_1 for cyclohexane adsorption at 172°C on NaHY fitted the equation,

$$K_{1-\mathrm{Na}} = \exp (2.8 \times 10^{-2}\, x_{\mathrm{Na}} - 4.1), \quad (5)$$

where x_{Na} is the number of sodium ions per unit cell. Figure 1 compares the equilibrium constants for adsorption on NaHY, KHY and CaHY zeolites. It indicates a higher adsorption of cyclohexane on KHY zeolites, particularly at high cation level. Curves 1 and 3 of Fig. 1 which describe the adsorption on KHY and CaHY fit, respectively, the equations:

$$K_{1-K} = \exp (5.4 \times 10^{-2} x_{\mathrm{K}} - 4.1),$$
$$K_{1-\mathrm{Ca}} = \exp (1.8 \times 10^{-2} x_{\mathrm{Ca}} - 4.1) \quad (6)$$

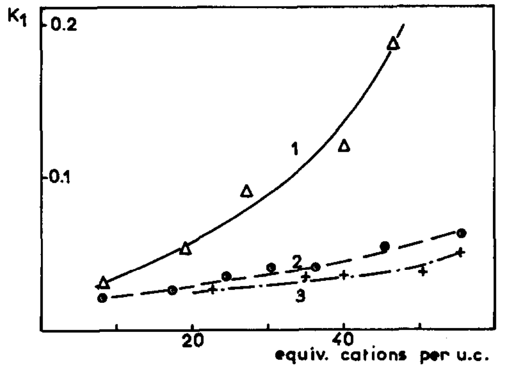

FIG. 1. Equilibrium constant of adsorption K_1 of cyclohexane as a function of cation content (T = 172°C), (+) CAHY; (O) NaHY; (Δ) KHY.

where x_K and x_{Ca} are the numbers of equivalents of cations per unit cell.

Similar results were obtained at other temperatures.

Adsorbate–Adsorbate Interactions

Figure 2 compares K_2' results over the three series of zeolites. Calcium form zeolites give the highest values in the range of calcium content studied.

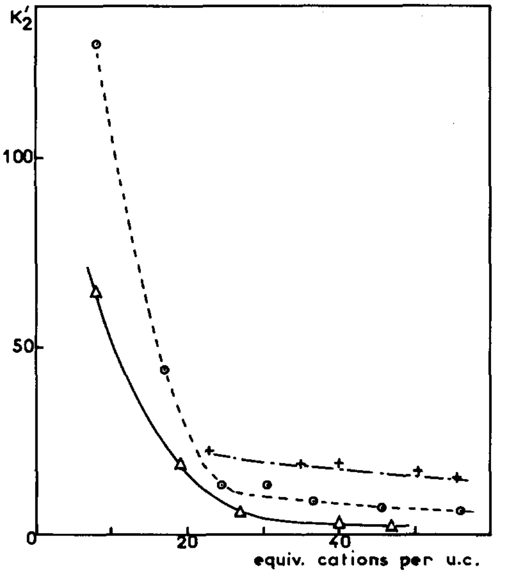

FIG. 2. Changes in viral coefficient K_2' as a function of cation content (T = 172°C). (+) CaHY; (O) NaHY; (Δ) KHY.

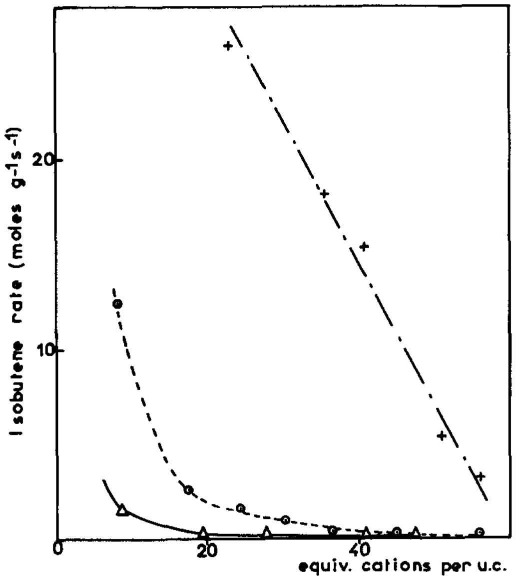

FIG. 3. Isobutene rate in isooctane cracking (T = 465°C) as a function of cation content. (+) CaHY; (O) NaHY; (Δ) KHY.

Catalysis

Isooctane cracking produces isobutene with a formation rate reported in Fig. 3 as a function of cation content. Sodium zeolite results already published (*15*) are included to allow a comparison to be made. The shapes of the K and Na curves are similar but, as is well known, potassium samples are less active. Calcium samples are much more active as expected. A similar dependence of cation content has been observed for the formation of other cracking products.

DISCUSSION

Adsorption Properties

Nitrogen adsorption changes with cation content cannot be related to other adsorption or catalytic results. Therefore these other properties do not depend to any large extent on textural modifications of the samples due to cation exchange.

The values of K_1 for cyclohexane adsorption are 10 times smaller than those obtained for benzene adsorption (*11*), indicating smaller adsorbed amounts of the saturated hydrocarbon. Furthermore, the fact that CaHY zeolites give the smallest K_1 values shows that cyclohexane is adsorbed in smallest amounts on these zeolites.

Kiselev (*4*) reported that K'_2values give the pairwise adsorbate–adsorbate interactions in the zeolite field. $K'_2$and K_1 values are linked together [Eqs. (3) and (4)] by means of the virial coefficient C_2 which may change with the zeolite. Figs. 1 and 2 show this interconnection in the experimental results since they indicate that the adsorbate–adsorbate interactions are the highest when adsorption is small at equilibrium.

Comparison of Adsorption and Catalysis

Looking at the cyclohexane equilibrium constants of Fig. 1 and the catalytic results of Fig. 3 one notes that for the same cation content, the equilibrium constants are in the range CaHY < NaHY < KHY while the cracking activities are in the reverse order. Changes with cation content also indicate an inverse behavior of the two properties. Cyclohexane adsorption decreases exponentially when lowering the amount of cation while isooctane cracking increases very rapidly. However, K'_2values which give adsorbate–adsorbate interactions vary in the same way as cracking. These remarks suggest some correlations between pure adsorption and catalysis. It is of course to be kept in mind that bivalent ions introduce new properties in zeolites (new OH groups, acidity, high thermal stability) which may modify profoundly the catalytic activity. But the results presented here show that fundamental correlations may exist independently of other new properties.

Adsorption of cyclohexane obviously means the interaction of the molecule with surface sites. It is generally accepted that these sites are cations (*11, 16*), even if the nature of the interaction is not well known (*3*), but an adsorption might also occur on acid sites. Catalytic cracking of isooctane involves firstly its adsorption and then its transformation. The adsorption step includes necessarily interaction with acid sites and adsorption on cation sites which has been shown in the adsorption of saturated hydrocarbons on zeolites (*2*). Hence, in both cases the molecules may adsorb simultaneously on two types of sites, the extent and strength of each of these adsorptions depending on the sites and on the reactivity of the molecule. This suggests that an equilibrium may exist between the reactant R, the uncovered cationic (C) and acidic (A) sites and the adsorbed molecules on each site, RA and RC.

$$\mathrm{A + C + 2R \rightleftharpoons RA + RC}. \qquad (7)$$

As the concentration of the reactant R is high it may be considered as a constant and the same for all the zeolites. The various terms of Eq. (7) have to fit Eq. (8).

$$\begin{aligned} \mathrm{RA + A} &= x_A, \\ \mathrm{RC + C} &= x_C, \qquad (8) \\ x_A + x_C &= 56, \end{aligned}$$

where x_A is the total number of acid sites per unit cell, x_C the total number of cation sites per unit cell, and 56 is number of charges to be neutralized per unit cell in Y zeolites.

Due to this general interaction of saturated hydrocarbons with both cationic and acidic sites and because of the known influence of cations on acidity (*17, 19*), it is proposed that while decreasing x_C and hence increasing x_A values, the competition between the adsorption of a molecule on the two types of adsorption centers is maintained and the coverage on cation sites ($\theta_c = \mathrm{RC}/x_c$) will decrease (deduced form Fig. 1) while that on acid centers ($\theta_\mathrm{A} = \mathrm{RA}/x_\mathrm{A}$) will increase. This implies that RC has to decrease and RA to increase sharply. Coverage will of course depend on the adsorbed molecule. Because of the reactivity of the molecules, in the case of isooctane at the catalytic temperature, RA formation will be favored while with cyclohexane the results presented show that RC has to be higher than RA. It is noticeable that the adsorption of cyclohexane is very small at low cation levels where acidity is high. Then it does not seem that the saturated c_6 molecule would be sufficiently reactive to be strongly linked to acid sites. This is substantiated by the adsorbate–adsorbate interaction results which indicate that at low cation content the cyclohexane molecules are not attracted much by the surface and that they can interact strongly together. Hence, with the zeolites studied, cyclohexane may be considered as being representative of a limiting case and may be used as a reference molecule to give mainly information on the interactions of saturated hydrocarbons with cations. Considering now the catalytic properties of zeolites it is proposed that the rate v of the catalytic transformation of a reactant on materials with acidic and cationic sites may be written in a general way:

$$v = k\,\mathrm{RA} + k'\,\mathrm{RC}, \tag{9}$$

where k and k' are specific rates. In the case of a reaction such as cracking which implies only acid sites, $k' \sim 0$ and the reaction rate is

$$v = k\,\mathrm{RA}. \tag{10}$$

As previously said RA depends on RC, i.e., on x_C. Bearing in mind this dependence, the results of isooctane cracking may be explained. It may be shown for example that the rate has to rise sharply at low cation content because both k and RA are increased. In fact, k becomes higher due to an increase in the number and strength of sites and from what has just been said, RA rises when the cation number decreases. It may also be deduced that KHY cracking rates have to be smaller than NaHY rates. Because of the lower polarizing power of K^+ ions the specific rate k_K is certainly smaller than k_{Na} and because of the high value for the adsorption equilibrium constant (i.e., high RC) for KHY zeolites, RA will be small. For Ca samples, similar remarks on the values of k_{Ca} and equilibrium constants explain the high catalytic activity. The similarities between K_2' and the catalytic activity shapes of curves (Figs. 2 and 3) may be explained as follows. When interactions with cations decrease (low cation content or Ca instead of Na or K), molecules not adsorbable on acid sites, like cyclohexane, begin to interact strongly together (increases in K_2') while molecules able to adsorb and to crack on acid sites, like isooctane, give a high catalytic activity.

Up to now a more elaborate mathematical model for competitive adsorption of a reactant on two different types of sites is difficult to present since many numerical values would have to be known (RA, A, RC, C concentrations). Nevertheless, the assumption made in Eq. (7) allows results of pure adsorption on cations and catalysis on acid sites to be compared. Some more general application may be attempted. For example, the rise in *o*-xylene isomerization (*20*) and cumene cracking (*21, 22*) at low cation content may be explained on the same basis. It has also to be said that the present hypothesis of competitive adsorption on cationic and acidic sites is not inconsistent with other models (*17, 23*) proposed to explain catalytic activity of Y zeolites. This assumption is also verified when cations are not only adsorption centers but when they are acting simultaneously with acid sites as in cumene cracking and dehydrogenation on Y zeolites (*17*). In this case, the general Eq. (9) $v = k\mathrm{RA} + k'\mathrm{RC}$ may be applied. Furthermore, the results also explain why KY zeolites are twice as active as NaY in the cracking of hexanes (*24*) which is described as being related to high reactant concentrations on the surface.

In conclusion, the hypothesis of a competitive adsorption of hydrocarbons between acidic and cationic sites explains the inverse changes which occur in pure adsorption on cations and catalysis on acid centers, independently of any modifications in the zeolite field which involve the changes. The correlations obtained are in agreement and complete the models which consider an interdependence of cationic and acidic centers (*17, 19*). The hypothesis also throws light on several studies in the literature which refer both to cations and to acid sites as active centers in adsorption and catalysis in faujasite.

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