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A Comparison of HY and LaY Cracking Activity in Cumene Dealkylation

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The kinetics of cumene cracking over an HY zeolite catalyst have been studied on a diffusion-free catalyst, at atmospheric pressure and at temperatures of 360, 430, and 500°C. The rate constant for dealkylation as well as the decay parameters have thus been determined. These parameters are compared with those obtained using a LaY catalyst, and the observed differences are discussed in terms of the nature and number of Bronsted sites in the two catalysts. We conclude that the nature of the active sites is identical in the two catalysts but that HY has a greater number of active sites per unit weight.

INTRODUCTION

In a catalytic reaction where the catalyst activity decays with time, the concentration of available active sites also changes with time and consequently so do the kinetic rate parameters. Several methods of calculating the initial rate parameters of the reaction have been reported in the literature. Perhaps the most commonly used are those methods which extrapolate the conversions observed at various times on stream back to time zero, in order to obtain the conversion on fresh catalyst. Other approaches commonly used, more in desperation than for cause, are

(i) leaving the catalyst to age until the decay is very slow and then assuming that the catalyst does not decay any more,
(ii) comparing conversions at the same experimental conditions, or
(iii) using a microcatalytic pulse reactor.

The difficulties connected with the use of these methods were presented in previous work (*1*, *2*) where it was shown that the most convenient method of studying the kinetics of reactions with catalyst decay is to consider the variation of the concentration of active sites with time, and to introduce this function in the general kinetic equation, as is done in the "time-on-stream theory" (*3*). The resultant kinetic parameters can then be used to compare the activities of various catalysts.

In this work the kinetics of cumene cracking over an HY zeolite catalyst have been studied using the time-on-stream theory. The kinetic parameters thus obtained are used to compare the activity of this catalyst with the activity of a LaY zeolite for the cracking of cumene.

EXPERIMENTAL

All experiments were conducted in a conventional, fixed bed, glass reactor heated by a three-zone electrical heater. The experimental method, as well as a typical run, have been described in previous work (*4*). The total liquid products col-

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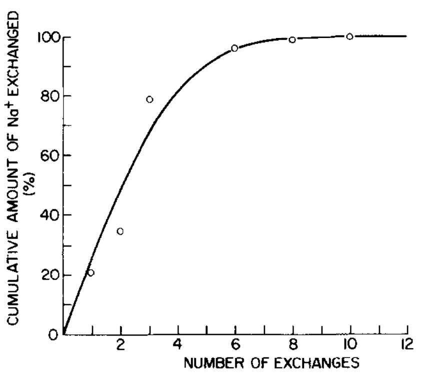

FIG. 1. Cumulative amount of Na^+ exchanged vs number of exchanges.

lected during a run were analyzed chromatographically using a Chromosorb W column. A porapak Q column was used to separate the gaseous products.

Conversion was defined as the moles of cumene reacted per mole of cumene fed while the yield was defined as the moles of product observed per mole of cumene fed. The LaY catalyst preparation has been described previously (*5*). The catalyst used in this study was an ultrastable HY obtained from the Na^+ form [Linde Co. lot No. 46972 (SK 40) with an Si/Al ratio of 2.25] by stirring the Na^+ form in a solution of ammonium nitrate for 24 hr. The solution was then filtered and the catalyst washed several times with distilled water in order to remove excess electrolyte. The filtrate was dried at 110°C for 12 hr and calcined at 500°C in a static atmosphere for 2 hr. This procedure was repeated a number of times until no more sodium ion was found in the liquid after exchange.

The sodium content in the zeolite was analyzed by atomic absorption, and a plot of the degree of exchange vs the number of exchanges is presented in Fig. 1. The sample used in this study was the one which was obtained after 10 exchanges. The measured surface area of this catalyst was 529 m^2/g.

The preparation of the La exchanged Y zeolite was reported previously (*5*).

RESULTS

In the mechanism for cumene cracking proposed by Campbell and Wojciechowski (*6*), the reaction is initiated by the chemisorption of a cumene molecule on a single active site; this mechanism has also been suggested by other authors (*7*, *8*). This adsorption step is followed by the removal of the alkyl group via a carbonium ion, releasing benzene to the gas phase. This mechanism, together with its associated equilibria, is called the Delta mechanism and has been presented in full in a previous paper (*1*).

Assuming that the bond-breaking step is a controlling step, the kinetics of the dealkylation of cumene is represented by the following rate equation (*1*):

$$-r_c = \frac{k_2K_1[S][C] - k_{-2}K_3[Y][S][Z]}{1 + K_1[C] + K_3[Y] + K_4[Z]} \qquad (1)$$

where k_2 and k_{-2} are the kinetic rate constants for the dealkylation and alkylation process; K_1, K_3, K_4 are the adsorption constants for the cumene, propylene, and benzene, respectively; and [S], [C], [Y], [Z] represent the concentrations of the active sites, cumene, propylene, and benzene, respectively. Expressing Eq. (1) in terms of fractional conversion, x,

$$-r_c = \frac{k_2K_1[S][C_0]}{x_e^2}\left[\frac{x_e^2 - x^2}{px^2 + qx + s}\right] \qquad (2)$$

where

$$p = K_3[C_0] + K_4[C_0] - K_1[C_0] + 1$$
$$q = K_3[C_0] + K_4[C_0] + 2$$
$$s = K_1[C_0] + 1.$$

x_e is the equilibrium fractional conversion of cumene and can be calculated from thermodynamic data.

By substituting Eq. (2) into the design equation for a plug flow reactor and accounting for catalyst decay with the Wojciechowski decay expression (*3*), the

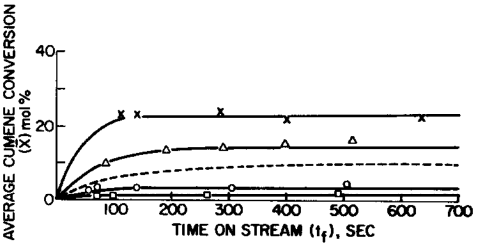

FIG. 2. Least squares fit for cumene dealkylation data on 70/80 mesh catalyst at 360°C. Solid lines represent the theoretical cumulative conversion. Experimental points: × (0.0467 cat/oil), △ (0.0173 cat/oil), ○ (0.0016 cat/oil), □ (0.0007 cat/oil). Dashed line shows conversion on LaY at 0.0163 cat/oil and 360°C.

resulting expression becomes

$$Pbt_f(1+Gt)^{-N} = -p'x + \frac{q'}{2}\ln\left[\frac{x_e^2}{x_e^2-x^2}\right] + \frac{p'x_e^2+s'}{2x_e}\ln\left[\frac{x_e-x}{x_e+x}\right] \quad (3)$$

where

$$p' = \frac{px_e^2}{k_2[S_0]K_1}, \quad q' = \frac{qx_e^2}{k_2[S_0]K_1},$$

$$\text{and} \quad s' = \frac{sx_e^2}{k_2[S_0]K_1}.$$

The average conversion $\bar{x}$ is calculated from (3) by means of Eq. (4):

$$\bar{x} = \frac{1}{t_f}\int_0^{t_f} x\,dt. \quad (4)$$

To calculate the parameters of Eq. (3), experimental average conversions at 360, 430, and 500°C were obtained, using a diffusion free catalyst of 70/80 mesh size at cat/oil ratios (P) ranging from 0.00050 to 0.047, and catalyst times on stream (t_f) of up to 700 sec. The experimental results are plotted in Figs. 2, 3, and 4.[1] The cumene cracking model was fitted to these experimental data, and the three parameters G, p', s' were calculated using a parameter optimization computer routine. The parameter N was reported previously to be equal to one for LaY, and this was also found to be the case for HY. The optimum values of the other parameters were determined using a sum of squares of residuals as the criterion of fit, with a residual being defined as the difference between the experimental average conversion and that predicted theoretically using Eq. (4). The optimum estimates for the three parameters for both catalysts at the three temperatures are listed in Table 1. The fit obtained was found to be satisfactory by the F test at 95% confidence for both catalysts. The rate constant for the reaction, k_2, can be extracted from the parameter s' using the following relationship:

$$\frac{x_e^2}{s'} = \frac{k_2[S_0]}{[C_0]} \quad (5)$$

From this equation the values for $k_2[S_0]$ have been calculated for the three temperatures, and are listed in Table 2. The kinetic rate constant for decay is obtained from the equation:

$$G = (m-1)k_{md} \quad (6)$$

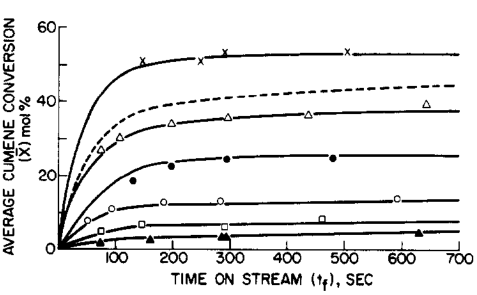

FIG. 3. Least squares fit for cumene dealkylation data on 70/80 mesh catalyst at 430°C. Solid lines represent the theoretical cumulative conversion. Experimental points: × (0.0467 cat/oil), △ (0.0173 cat/oil), ● (0.0086 cat/oil), ○ (0.0016 cat/oil), □ (0.0007 cat/oil), ▲ (0.0005 cat/oil). Dashed line shows conversion on LaY at 0.0163 cat/oil and 430°C.

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[1] Space time (τ) varies as cat/oil ratio (P) times the final time on stream (t_f), i.e., $\tau \propto Pt_f$; space time is also inversely proportional to LHSV, i.e., $\tau \propto 1/\text{LHSV}$.

TABLE 1

Computer-Derived Parameters

Catalyst	500°C			430°C			360°C		
	$G \times 10^2$ (sec^{-1})	$p' \times 10^3$ (sec)	$s' \times 10^4$ (sec)	$G \times 10^2$ (sec^{-1})	$p' \times 10^3$ (sec)	$s' \times 10^4$ (sec)	$G' \times 10^2$ (sec^{-1})	$p' \times 10^3$ (sec)	$s' \times 10^4$ (sec)
LaY	1.44	4.23	3.03	2.59	9.01	9.02	8.06	6.54	24.70
HY	3.10	3.46	1.00	3.41	9.15	3.60	8.06	6.54	11.20

where m is the order of the decay reaction and k_{md} is the kinetic rate constant for the decay process. m is related to the parameter N by the equation

$$N = \frac{1}{m - 1}$$

and since N is equal to 1 for this reaction, $m = 2$, and consequently $G = k_{md}$.

From the values of $k_2[S_0]$ in Table 2, Arrhenius plots have been generated and are shown in Fig. 5. The values for the activation energy have been calculated as 23.5 ± 1.8 kcal/mol and 25.5 ± 2.4 kcal/mol for cracking over LaY and HY, respectively.

DISCUSSION

Several authors have reported that LaY, REY,[2] REHY,[3] and similar rare earth exchanged zeolites are more active than HY for reactions such as the alkylation of toluene (*9*), cumene cracking (*10*), and *o*-xylene isomerization (*11*). In all such catalysts, the active sites for alkylation (*12*, *13*) as well as for xylene isomerization (*14*, *15*) are thought to be Bronsted acids. Cumene cracking mechanisms involving Bronsted active sites have also been proposed by some (*4*) but not by others (*16*, *17*). The rejection of a protonic mechanism for cumene dealkylation seems unjustified (*18*).

From Figs. 3 and 4 one can see that, at 500 and 430°C, conversion to benzene is higher with LaY zeolite than with HY. If we take such average conversion as a measure of catalyst activity we must conclude that LaY is a more active catalyst than HY. However, at 360°C it is clear from Fig. 2 that conversion on HY is higher than on LaY. Thus, depending on the temperature of the experiment, it is possible to arrive at different conclusions regarding the activity of the catalyst when average conversion is used as the indicator.

If on the other hand, we use the rate and decay constants reported in Tables 1 and 2 as indicators of activity, it becomes apparent that HY is a more active catalyst than LaY zeolite, but also that it decays faster. The difference in the cracking rate constant as reported in Table 2 can

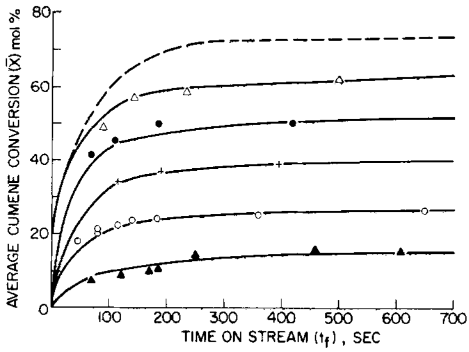

FIG. 4. Least squares fit for cumene dealkylation data on 70/80 mesh catalyst at 500°C. Solid lines represent the theoretical cumulative conversion. Experimental point: △ (0.0173 cat/oil), ● (0.0086 cat/oil), + (0.0044 cat/oil), ○ (0.0016 cat/oil), ▲ (0.0005 cat/oil). Dashed line shows conversion on LaY at 0.0163 cat/oil and 500°C.

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[2] REY is a catalyst containing mixed rare earth cations.

[3] REHY is the same as REY except that protons are also present as cations.

TABLE 2

Rate Constants for Dealkylation

Catalyst	500°C	430°C	360°C
	$k_2[S_0] \times 10^2$ (mol/g cat sec)		
LaY	4.75	1.06	0.17
HY	14.39	2.65	0.37

be attributed to a difference in the kinetic rate constants (k_2) or to a difference in the concentrations of the active sites (S_0) or to changes in both k_2 and S_0.

From Fig. 5 one can see that the activation energy is nearly the same for both catalysts, while the frequency factor is larger for HY than for LaY. Consequently, as far as the reaction is concerned, the energetic nature of the active sites in both catalysts is the same and only the entropy of activation or the total number of sites is different. It seems very unlikely that entropy differences are being observed on sites of the same strength. Rather, we believe that the difference in $k_2[S_0]$ values is entirely due to differences in active site concentrations in the two catalysts.

These results are in good agreement with those of Ward (*18*), who found that the Bronsted acid sites are similar in both the rare earth Y and HY zeolites but that the Bronsted acid concentration is higher for HY than for the rare earth Y zeolite.

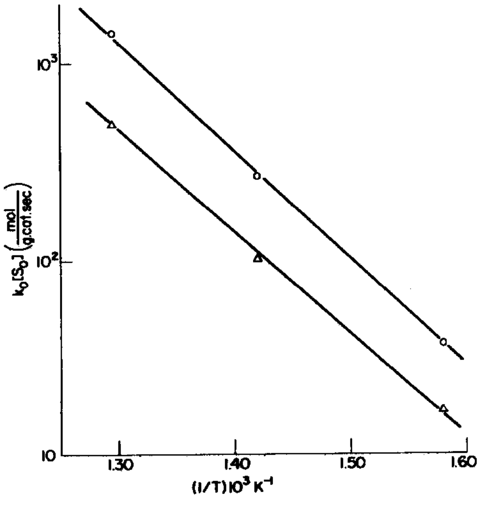

FIG. 5. Arrhenius plot for cumene dealkylation (○) HY and (△) LaY.

Because we see no difference in the energy of active sites on the two catalysts our results also support the conclusion of Novalikhina and Kuzin (*19*). They argue that even though it is possible to see a wide range of acid strengths in zeolite catalysts by titration methods, only a small portion of these sites plays a role in the cracking of cumene.

CONCLUSION

On the basis of results reported in this work, we conclude that the nature of the active sites is the same in LaY and HY zeolite catalysts as far as cumene dealkylation is concerned. The difference in the dealkylation activity of the catalysts is solely due to the total number of active Bronsted sites, which is higher in HY than in LaY. In this we agree with others (*11*) who have come to similar conclusions regarding the differences observed between molecular sieve catalysts.

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