

The Kinetics of Cumene Cracking on HZSM-5

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Rate expressions based on the delta mechanism of cumene cracking are applied to cumene cracking on HZSM-5. The fit is good and the resultant parameters confirm that this reaction is very strongly influenced by the steric constraints of the small pore diameter of HZSM-5. The constraints prevent the occurrence of initial bimolecular reactions and reduce the rate of dealkylation, which has a bimolecular reverse reaction, more than the rate of the monomolecular isomerization to *n*-propyl benzene. The rate of dealkylation is found to be only one order of magnitude faster than isomerization on HZSM-5 while it was found to be two orders of magnitude faster on HY, LaY, and amorphous Si/Al. The coke formed on HZSM-5 is very rich in hydrogen (H/C ratio ~2.0) and very low in poisoning activity. We believe that this too is the result of the difficulty in achieving the bimolecular transition state necessary for hydrogen transfer and the consequent "hardening" of the coke. The order of the decay reaction with respect to site concentration is ~10⁴ as compared to 2 on HY, LaY, and Si/Al, indicating that a very large number of sites are lost per deactivating event. At the same time the decay rate constant is some 10¹⁴ times smaller than that on the above catalysts. This suggests that deactivating events are rare (low rate constant) but catastrophic (many sites deactivated per event). It seems that it is the hard coke (low H/C ratio) which is primarily responsible for activity decay. In the case of HZSM-5, decay is very slow and probably takes place by pore blocking rather than site-by-site deactivation, as was clearly the case in other catalysts studied to date. © 1988 Academic Press, Inc.

INTRODUCTION

Extensive studies of cumene cracking on HY (1), LaY (2, 3), LaX (4), and amorphous Si/Al (5, 6) have been carried out in our laboratories over the past decade and a half. In these works we found the same initial products of reaction on all catalysts and showed that all the above catalysts had the same two types of sites in various relative and absolute amounts. A more recent study of cumene cracking on HZSM-5 (7) revealed that on this catalyst only the monomolecular reactions of the suite of initial reactions observed previously were present. Furthermore, coke was observed to be a primary product on HZSM-5, in contrast to all the previously studied catalysts.

In view of this, the question arises whether the same sites are present on

HZSM-5 as those on the previously studied catalysts. Since coke is now a primary product there is also the question of whether the time on stream decay function will describe the loss of activity. Finally, in view of the different product spectrum on HZSM-5, will the kinetic treatment used to explain cumene cracking on the other catalysts still be adequate?

EXPERIMENTAL

All experiments were performed using an integral, fixed-bed, gas-phase, plug-flow reactor with an independently controlled three-zone heater. The experimental apparatus and procedures used were similar to those described in previous studies (9).

Three catalyst-to-reactant weight ratios (0.0177, 0.0132, and 0.0096) were used on HZSM-5. Blank runs were carried out at 430°C to ensure that the glass used to dilute the catalyst was inert.

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Liquid products were analyzed using a Varian 6000 gas chromatograph with a 60-m SE54 capillary column. Products up to C_7 were eluted at 0°C , followed by a temperature program by $2^\circ\text{C}/\text{min}$ up to 280°C . Gaseous products were analyzed by a Carle SX 1156 gas chromatograph. The identification of all products was carried out using a Finigan 1020 automated GC/MS.

After each run the reactor was purged with dry nitrogen at a set flow rate, at the reaction temperature, for 15 min. Residual material in the reactor was regarded as coke. The reactor temperature was then increased to 500°C while dry, carbon dioxide free air was passed over the catalyst. The weight of water collected in a tube of drierite during regeneration allowed the hydrogen content of the coke to be calculated. The weight of carbon dioxide absorbed by a tube containing ascarite gave the carbon content of the coke. Complete combustion to carbon dioxide was ensured by passing the dried combustion product stream through a reactor at 350°C packed with copper oxide.

The HZSM-5 catalyst was prepared by the method described by patent (15) and repeatedly exchanged using 1 *M* ammonium nitrate solution at 80°C followed by calcination at 520°C for 2 h after the final exchange. Particles of 100–140 mesh were sieved out and used in the reactor in a mixture with crushed glass of 60–80 mesh.

The HZSM-5 was found to have a Si/Al ratio of 37 and a sodium content of <0.2 wt%. X-ray diffraction patterns identical to those reported for ZSM-5 (16) were obtained with our preparation.

Cumene supplied by Aldrich Co. was purified through a silica–alumina column to remove traces of hydroperoxide. All runs were done at ambient pressure and at 430°C over a range of times on stream at each of the catalyst/oil ratios.

RESULTS

The data were interpreted using the delta mechanism and the consequent mechanis-

tic rate model. The rate of cumene conversion according to that model can be shown to be (8)

$$r = \frac{k_2 K_1 [S][C_0]}{x_e^2} \left(\frac{x_e^2 - x}{px^2 + qx + s} \right), \quad (1)$$

where k_2 is the rate constant for dealkylation; K_1 is the adsorption constant for cumene; x_e is the equilibrium conversion of cumene; x is the current conversion of cumene; $[C_0]$ is the concentration of cumene in the gas phase; $[S]$ is the current concentration of active sites; and p , q , and s are compound parameters composed of more fundamental quantities (2).

This expression must be adjusted to account for the changing concentration of active sites with time on stream, using the function (8)

$$[S] = [S_0](1 + Gt)^{-N}, \quad (2)$$

where $[S_0]$ is the active site concentration on the fresh catalyst, t is time on stream, and G and N are composite parameters which will be explained more fully in subsequent discussion.

Introducing Eq. (2) in Eq. (1) and the result into the design equation for a plug-flow reactor leads to (2)

$$\tau(1 + Gt)^{-N} = -p^1 x + \frac{q^1}{2} \ln \frac{x_e^2}{x_e^2 - x^2} + \frac{p^1 x_e^2 + s^1}{2x_e} \ln \frac{x_e - x}{x_e + x}, \quad (3)$$

where τ is the space time and p^1 , q^1 , and s^1 are composite constants containing adsorption equilibrium constants.

To make use of our experimental data we note that the space time τ depends on other process variables as

$$\tau = bPt_t, \quad (4)$$

where b is a known constant (2×10^{-3} at 430°C), P is the catalyst-to-reagent ratio (w/w), and t_t is the duration of the run at constant feed rate.

Finally, we must take into account the fact that the values of x in Eq. (3) are

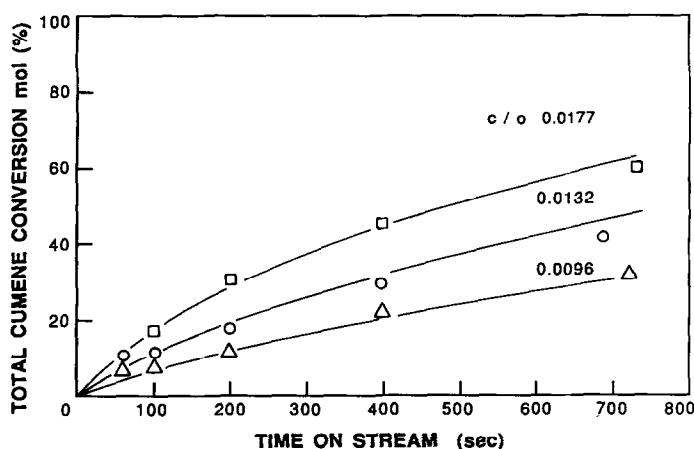


FIG. 1. Cumene conversion as a function of time on stream. Solid lines represent theoretical fit of experimental points using Eqs. (3) and (5) and parameters given in Table 1.

instantaneous fractional conversions, whereas in the laboratory one measures the average conversion at the end of the run. These two conversions are related by

$$\bar{x} = \frac{1}{t_f} \int_0^{t_f} x dt. \quad (5)$$

Fitting of the data in Fig. 1 by these equations gives the parameters shown in Table 1 and the solid curves shown in Fig. 1. A statistical analysis shows that the fit passes the *F* test at the 95% level.

A plot of the coke yield obtained on HZSM-5 is compared to that obtained on LaY (9) in Fig. 2. It is clear that coke is a primary product on this catalyst and we treat it as such in our initial mass balances. More coke is made on HZSM-5 than on LaY at any given conversion. It is also clear that the coke made on HZSM-5 is ri-

cher in hydrogen than that made on LaY (Fig. 3). The small amount of coke on HY makes studies of its H/C ratio difficult; however, for HZSM-5 we find that this ratio extrapolates back to ~ 1.85 at zero conversion. This value lies close to that of propylene (2.00), and is obviously removed from that of cumene (1.33) or benzene (1.00), as seen from Fig. 3.

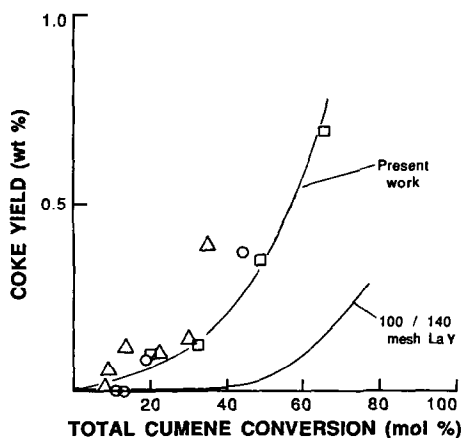


FIG. 2. Coke yield as weight percent of feed as a function of conversion. Solid curves are optimum performance envelopes and show that coke was a secondary product on LaY and is a primary product on HZSM-5. Shapes of symbols correspond to cat./oil ratios in Fig. 1.

TABLE 1

Rate Parameters Obtained by Fitting the Delta Model to the Data Shown in Fig. 1

	p^1	s^1	G	N
LaY	9.01×10^{-3}	9.02×10^{-4}	2.59×10^{-2}	1
HY	9.15×10^{-3}	3.60×10^{-4}	3.41×10^{-2}	1
HZSM-5	4.40×10^{-19}	1.42×10^{-2}	1.30×10^{-12}	7.90×10^{-5}

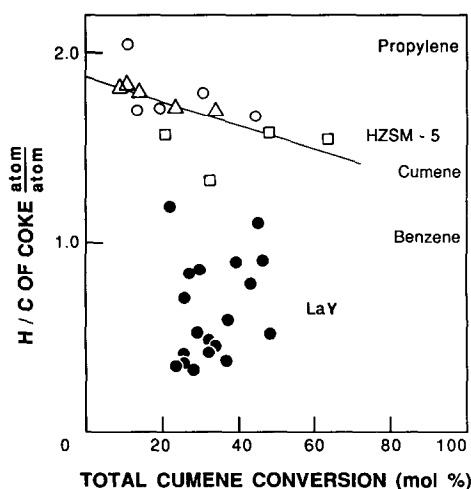


Fig. 3. H/C ratios for coke on HZSM-5 (open symbols) and LaY (closed symbols). Different shapes correspond to cat./oil ratios from Fig. 1.

DISCUSSION

The Kinetics of Dealkylation

The constants p^1 and s^1 shown in Table 1 are related to kinetic parameters (3) as follows,

$$p^1 = \frac{p x_e^2}{k_2[S_0]K_1} \quad (6)$$

$$s^1 = \frac{s x_e^2}{k_2 S_0 K_1} \quad (7)$$

where

$$p = K_3[C_0] + K_4[C_0] - K_1[C_0] + 1, \quad (8)$$

$$s = K_1[C_0] + 1, \quad (9)$$

$x_e = 0.767$ at 430°C (fraction of cumene converted at equilibrium).

k_2 is the rate constant for dealkylation; K_1 , K_3 , and K_4 are adsorption constants for cumene, propylene, and benzene, respectively; $[C_0]$ is the concentration of cumene in the feed; and $[S_0]$ is the concentration of active sites on the fresh catalyst. From Eqs. (7) and (9) we obtain

$$\frac{s^1}{x_e^2} = \frac{1}{k_2 K_1 [S_0]} + \frac{[C_0]}{k_2 [S_0]} \quad (10)$$

It was found in work on LaY and HY that the second term dominates in Eq. (10). This is equivalent to saying that

$$K_1[C_0] > 1$$

and hence that adsorption of cumene is strong and the surface is well covered. This in turn means that the reaction is zero order with respect to cumene, a fact noted in other studies as well (10). In that case our results yield

$$\frac{x_e^2}{s^1} = \frac{k_2[S_0]}{[C_0]} = 6.7 \times 10^{-4} \frac{\text{mol}}{\text{g cat. sec}}$$

This and comparable numbers for other catalysts are reported in Table 2. By multiplying the $k_2[S_0]$ value for dealkylation by the ratio of selectivities for isomerization/dealkylation (7), we obtain $k_{\text{iso}}[S_0]$ values for the same catalysts.

In terms of dealkylation activity, HZSM-5 is remarkably similar to 13% silica alumina and distinctly different from the Y zeolites. The activity for dealkylation in HZSM-5 is some 30 times smaller than that on Y catalysts while isomerization is only half that on Y zeolites. This agrees with the hypothesis that the small pore system of HZSM-5 reduces the rate of reactions which require a bulky transition state.

We have previously ascribed dealkylation to reactions on Brønsted sites (9) while isomerization to *n*-propyl benzene

TABLE 2
Rate Constants of Initial Reactions^a

Catalyst	Rate constant	
	Dealkylation to propylene + benzene	Isomerization to <i>n</i> -Propylbenzene
	($\frac{\text{mol}}{\text{g cat} \cdot \text{sec}}$)	
HY	2.65×10^{-2}	4.7×10^{-5}
LaY	1.06×10^{-2}	3.7×10^{-5}
Si/Al (13%)	6.79×10^{-4}	2.8×10^{-6}
HZSM-5 (Si/Al = 37)	6.70×10^{-4}	1.95×10^{-5}

^a HY, LaY, and Si/Al also exhibited a number of bimolecular primary reactions (12). HZSM-5 showed a small initial rate for coke formation as well as the above two monomolecular rates (7).

TABLE 3
Decay Constants at 430°C

Catalyst	m	k_{md} (sec ⁻¹)
HY	2	3.41×10^{-2}
LaY	2	2.59×10^{-2}
Si/Al (13%)	2	3.62×10^{-4}
HZSM-5	1.3×10^4	1.03×10^{-16}

was ascribed to reactions on Lewis sites. In keeping with this interpretation we would say here that our HZSM-5 has ~6% of the Brønsted sites of our standard LaY and ~50% of the Lewis sites. Whether our HZSM-5 under reaction conditions has in fact this ratio of Lewis to Brønsted sites we were not equipped to determine.

An alternative hypothesis is that the isomerization reaction is enhanced relative to dealkylation because isomerization is a strictly monomolecular process, whereas dealkylation results in two molecules of product after passage over the transition state. This means that the reverse reaction (alkylation) will be constrained by steric effects in keeping with all the other bimolecular processes. In order for equilibrium to be maintained, the forward reaction must also be suppressed. Which of these two explanations is correct is not clear. At this time we lean toward steric constraints as the explanation for the enhanced isomerization activity.

Our quantitative observations are consistent with our previous work on cumene cracking and are based on the fitting of the same kinetic rate expression to data on HZSM-5 as that used for HY, LaY, and amorphous Si/Al. The fact that the fit is satisfactory is an indication that the model is adequate to represent the kinetics of this reaction on all catalysts we have studied to date. We also feel justified on this basis to accept that the mechanism of reaction is similar on all these catalysts.

Catalyst Decay

The fit of the experimental data involves

the use of the time on stream decay function and the parameters derived from this are shown in Table 1. Table 3 shows various comparable values for other catalysts calculated on the basis of the relationships (12)

$$N = (m - 1)^{-1} \quad (11a)$$

$$G = k_{md}(m - 1), \quad (11b)$$

where m is the order of the decay expression and k_{md} is the rate constant in the decay expression

$$\frac{d[\theta]}{dt} = k_{md}[\theta]^m.$$

One notes immediately that the decay constant k_{md} is many orders of magnitude smaller on HZSM-5, while the order of the decay reaction indicates that catalyst poisoning involves many sites per deactivating event. The order of the decay reaction is startlingly different from that on the Y zeolites or on amorphous Si/Al. At the same time, the coke deposited on HZSM-5 is much richer in hydrogen.

Figure 4 shows the fraction of sites lost as a function of time on stream. It seems that dehydrogenated coke leads to more severe poisoning (13). The low level of dehydrogenation of coke in HZSM-5 is probably connected with the suppression of bimolecular transition states by the restricted pore diameter of HZSM-5. Those few dehydrogenation events which do occur on HZSM-5 lead to decay but, it seems, by a different mechanism than that operating on the other catalysts.

We envision the process of poisoning on HZSM-5 as follows: cumene cracks and the interior of the crystallite fills up with product propylene and perhaps its oligomers. These diffuse in and out of the catalyst, allowing a continuous flow of fresh feed and products into the pore system. Occasionally, some of the propylene molecules undergo oligomerization and cracking or a hydrogen transfer reaction, leading to propane, *i*-butane, and other saturates which

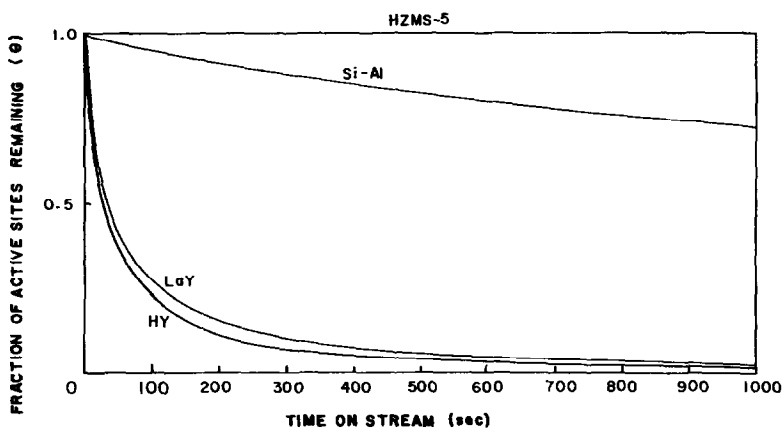


FIG. 4. Fraction of active sites left unpoisoned as a function of time on stream. Note that HZSM-5 shows essentially no decay while HY and LaY decay very rapidly.

appear in the secondary products. At the same time, dehydrogenated species are formed and become immobilized on the location of their formation. Since the pores are small, further bimolecular reactions are restricted. At the same time feed molecules cannot squeeze past this immobile species. Thus a whole region of the pore system becomes partly or completely unavailable. This in turn appears as the loss of many sites; if we are to believe the numbers in Table 3, $\sim 10^4$ sites are lost per deactivating event. This number may be uncertain to within an order of magnitude, but is much greater than that on other catalysts. Whereas the value of 2 clearly indicated a chemical process involving the loss of two sites per deactivating event on HY, LaY, and Si/Al, on HZSM-5 we suspect that mechanical pore plugging must be responsible for most of the sites lost.

Adsorption Modes

From the values of p^1 and s^1 in Table 1 we see that

$$\frac{p^1}{s^1} = 3.1 \times 10^{-17} \approx 0. \quad (12)$$

From Eqs. (6) to (9) we have

$$\frac{p^1}{s^1} = \frac{(K_3 + K_4 - K_1)[C_0] + 1}{K_1[C_0] + 1}. \quad (13)$$

We have already presented arguments that adsorption is strong in this system and hence all the equilibrium constants are much greater than 1. Taking Eqs. (12) and (13) this means that

$$\frac{p^1}{s^1} = \frac{K_3 + K_4 - K_1}{K_1} = 0 \quad (14)$$

and hence

$$K_3 + K_4 = K_1. \quad (15)$$

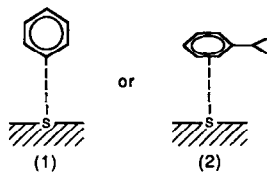
It is generally recognized that benzene is more strongly adsorbed than propylene, and therefore

$$K_4 \gg K_3. \quad (16)$$

This leads to $K_4 \approx K_1$. That is to say, the adsorption constant for benzene is very similar to that for cumene. This was not found to be so on LaY or the other large pore catalysts (9), where the ratio K_4/K_1 has a value of approximately 10. In those cases it was argued that cumene is more strongly adsorbed than benzene, as reported in the literature (14), and has a greater entropy of adsorption, since it can adsorb in more ways, as shown in Fig. 5.

On HZSM-5 it seems that the adsorption constants for those two molecules are very similar. We believe the reason for this is that modes 3, 6, and 7 for cumene adsorption are excluded by steric constraints

1. BENZENE ADSORPTION



2. CUMENE ADSORPTION

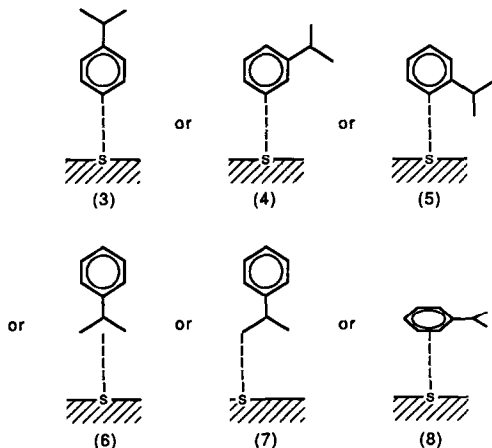


FIG. 5. Various configurations which can be assumed by a cumene molecule in the vicinity of an isolated site on a flat surface.

leaving modes 4 and 5 which are very similar to mode 1 in benzene adsorption and mode 8 which is equivalent to mode 2.

CONCLUSIONS

We find that the delta model of cumene cracking fits data obtained on HZSM-5 as well as it did for HY, LaY, and amorphous silica alumina. The kinetic parameters obtained do not allow us to say whether the active sites are or are not the same in HZSM-5 as those in the other catalysts. What we can say is that the kinetic parameters are consistent with those of previous studies when the differences observed in parameter values are explained by invoking

steric constraint within the pore system of HZSM-5.

The steric constraint prevents bimolecular reactions, leading to the elimination of all products which are formed in such reactions on larger pore catalysts. It also reduces dehydrogenation of adsorbed species, with the result that the "coke" formed is rich in hydrogen and hence presumably quite mobile. The only activity decay is that which results from pore plugging, as the chance dehydrogenation of adsorbed species blocks whole regions of the crystallite lying behind the dehydrogenated and thus immobilized residue.

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