# EFFECT OF COKE ON Y ZEOLITE ACTIVITY FOR CUMENE CRACKING

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ABSTRACT
    Carbonaceous deposits on a lanthanum-exchanged Y zeolite results in an
exponential relationship with catalytic activity for cumene cracking.  The
observed relationship can be attributed to several possible mechanisms.  One
mechanism that fits the experimental data involves multilayer coke formation.
Parameters from this model suggest that the rate of coke chain growth or
polymerization increases rapidly with increasing temperature.  Titration
experiments show that active sites for cumene cracking have approximately
equal strengths since initial catalyst activity was found to decrease in
direct proportion to the amount of sorbed pyridine.  Diffusivities measured by
a chromatographic technique indicate no significant difference in values
between fresh catalyst and catalyst with 5 percent coke.  Therefore, pore
blockage does not appear significant.

INTRODUCTION
    The activity of cracking catalysts declines rapidly because of the
accumulation of carbonaceous deposits on the catalyst surface.  This
phenomenon has very significant economic importance and, therefore, has been
the subject of a number of studies over the years.  Experimental studies on
lanthanum-exchanged Y zeolite for isopropylbenzene (cumene) cracking in our
laboratory demonstrated an exponential relationship between total coke
deposited on the catalyst and catalyst activity decline [1,2].  The observed
relationship between coke level and catalyst activity can be attributed to
several possible mechanisms.
    For example, if the catalytically active sites have a distribution of
strengths and the strongest sites were deactivated first, a exponential
coke-activity relationship would be found.  Another explanation, outlined by
Beeckman and Froment [3], is that a pore blockage mechanism, for certain
parameter values, provides an exponential relationship between catalyst
activity and coke content.  A third possibility, proposed by Nam and Kittrell

[4], is that both monolayer and multilayers of coke form on the surface. This model can predict linear, hyperbolic, or exponential activity-coke relationships depending on parameter values.

Acid catalysts such as zeolites can be readily poisoned by basic organic compounds. One of the earlier studies of the deactivation of amorphous silica-alumina cracking catalysts by organic compounds such as quinoline, quinaldine, pyrrole, piperidine, decylamine, and aniline was done by Mills et al [5]. A poisoning study by titration of quinoline on zeolite catalyst was investigated by Goldstein and Morgan [6]. They concluded that the amount of quinoline required to completely poison the zeolite was equal to the number of supercages in its structure.

EXPERIMENTAL

The lanthanum-exchanged Y zeolite (La Y) was made by contacting an ammonium Y (Linde type 31-200 powder) with an aqueous solution of lanthanum chloride. Approximately 60-70 percent of the ammonium ions were exchanged in the procedure. The resulting La Y powder was pressed into tablets without binder, crushed and sieved to -60+80 mesh.

A thermogravimetric analyzer was used as the reactor in this study. Coke on catalyst was measured by weight change of the catalyst and cumene conversion by chromatographic analysis of product gases. For the coking study cumene was continuously introduced into the reactor by passing helium through a sparger containing cumene. Additional details of the equipment has been previously reported [1].

For the titration study a certain amount of pyridine was injected into a stream of heated helium. After adsorption of pyridine, helium flow was continued to purge the remaining pyridine from the system and to desorb physically adsorbed pyridine from the catalyst. This purge was for 30 minutes. The final amount of pyridine loading was determined by the catalyst weight change. Then cumene was introduced to test the cracking activity of partially poisoned catalyst.

Diffusivities in fresh and coked catalysts were measured by a chromatographic technique. Chromatographic curves were measured using a constant-temperature gas chromatograph (Perkin-Elmer Model 820) with a thermal conductivity detector. Helium was used as the carrier gas, and measurements were made by injecting a small pulse of adsorbable component plus helium into the pure helium carrier. A four way, two position sampling valve was used to inject the pulse. The adsorbable component stream was prepared by passing a pure helium stream through a sparger containing the hydrocarbon. The column was 34 cm long by 0.483 cm inside diameter.

RESULTS

Cumene conversion at the low cumene partial pressures studied resulted in the formation of benzene, propylene and coke. No secondary reaction gaseous products were found. Reaction rates (r) for the differential conversion data were calculated from:

$$r = F_A X_A/W \qquad (1)$$

where $F_A$ is the moles/s of cumene flowing, $X_A$ the fractional conversion of cumene and W the catalyst mass. The initial reaction rates ($r_o$, at zero coke) fit a first order model with respect to cumene partial pressure:

$$r_o = k \; p_A \qquad (2)$$

where k is the reaction rate coefficient and $P_A$ the cumene partial pressure. Figure 1 shows an example of this relationship at 430° C.
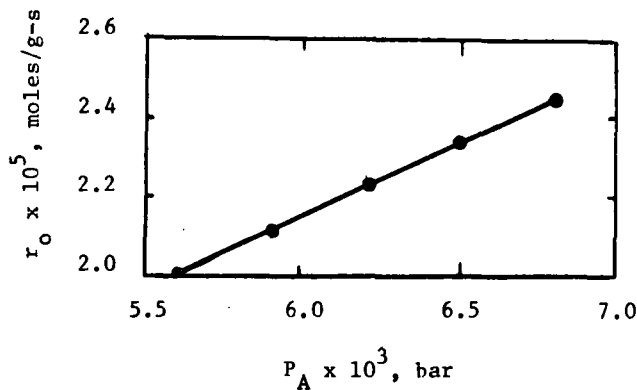


Fig. 1. Cumene cracking rate with uncoked catalyst vs. cumene partial pressure. 430°

Then the relative catalyst activity ($\phi$) was calculated from:

$$\phi = r/r_o \qquad (3)$$

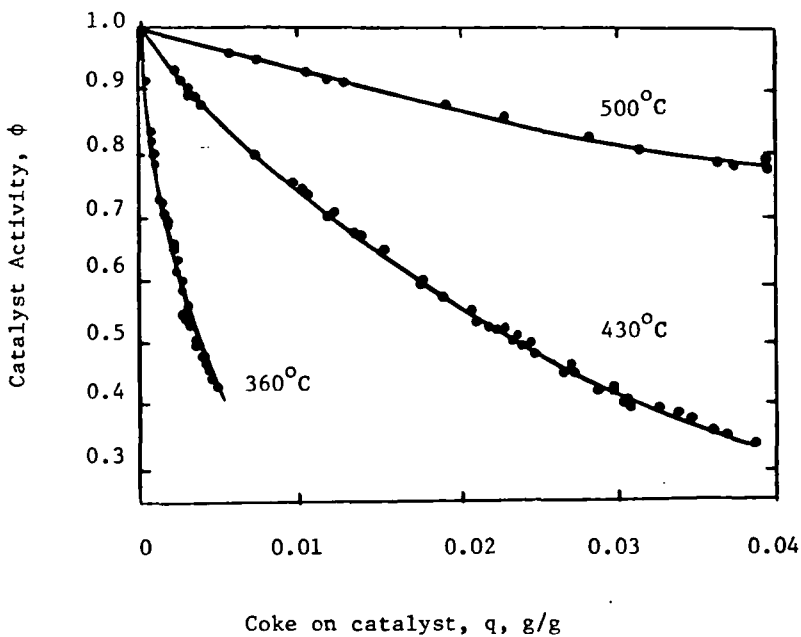Figure 2 illustrates the effect of total coke (q) on catalyst activity.

Fig. 2. Relative catalyst activity vs. total coke on catalyst.
Cumene cracking over LaY

In describing deactivation processes due to coking, it is common to
assume two independent reactions occur, the primary reaction and the coke
formation reaction [4]. Following Nam and Kittrell's deactivation model [4]
with cumene cracking kinetics [1-2], the following individual steps may be
written:

$$A + 1 = Al \qquad\qquad\qquad (4)$$
$$Al = Rl + S \qquad\qquad\qquad (5)$$
$$Rl = R + 1 \qquad\qquad\qquad (6)$$
$$Rl \geqslant coke \qquad\qquad\qquad (7)$$

In eq 4-7, A, R and S represent gaseous cumene, propylene and benzene
respectively, 1 represents an active site and Al and Rl represent adsorbed A
and R. The total number of active sites is the sum of the vacant sites, the
sites covered by adsorbed A or R and the sites inactivated due to coke
coverage:

$$L_c = C_v + C_{Al} + C_{Rl} + C_{cl} \qquad\qquad (8)$$

the relative activity is defined by the fraction of sites not inactivated by coke:

$$\phi = \frac{L_c - C_{cl}}{L_c} \tag{9}$$

The rate of coke formation on the active surface is assumed to be proportional to the surface concentration of the coke precursor.

$$\frac{\delta C_c}{\delta t} = \frac{k_D C_{R1}}{\rho_c} = \frac{k_D K_R P_R C_v}{\rho_c} \tag{10}$$

The parameter $\rho_c$ is used to represent the stoichrometric coefficient to convert the weight of coke on the surface to the number of sites deactivated, $C_{cl} = \rho_c C_c$, $k_D$ is the surface coke rate coefficient, $K_R$ propylene adsorption coefficient, $P_R$ the propylene partial pressure, and t time. By substitution of eq 8 and 9 into 10:

$$\frac{\delta C_c}{\delta t} = \frac{k_D K_R P_R \phi L_c}{\rho_c (1 + K_A P_A + K_R P_R)} \simeq \frac{k_D K_R P_R \phi L_c}{\rho_c} \tag{11}$$

$K_A$ and $P_A$ are the cumene adsorption coefficient and partial pressure respectively. It must be noted that $C_c$ is the coke in direct proximity to the catalyst surface. The balance of the total measured coke is described as multilayer coke. It can be envisioned as growing on top of the monolayer coke by an Eley-Rideal mechanism. The multilayer coke ($C_L$) forms as:

$$\frac{\delta C_L}{\delta t} = k_L C_c P_R \tag{12}$$

where $k_L$ is the multilayer coke rate coefficient.
The total measured coke content of the catalyst becomes

$$q = C_c + C_L \tag{13}$$

and

$$\frac{\delta q}{\delta t} = \frac{k_D K_R P_R \phi L_c}{\rho_c} + \frac{k_L L_c (1-\phi) P_R}{\rho_c} \tag{14}$$

Eq 9 can be differentiated and combined with eq 11 to yield

$$\frac{\delta \phi}{\delta t} = -k_D K_R P_R \phi \tag{15}$$

Dividing eq 15 by 14 yields the relationship between catalyst activity and total coke

$$\frac{\delta\phi}{\delta q} = \frac{- \rho_c k_D K_R \phi}{k_D K_R \phi L_c + k_L L_c (1-\phi)} \tag{16}$$

Eq 16 can be integrated to yield

$$\frac{q}{1-\phi} = \frac{L_c}{\rho_c} - \alpha - \alpha \frac{\ln\phi}{1-\phi} \tag{17}$$

where $\qquad \alpha = \dfrac{k_L L_c}{\rho_c k_D K_R}$ $\qquad\qquad$ (18)

Total coke versus catalyst activity data from cumene cracking in the thermo-balance reactor are plotted in the form of eq 17 in Fig. 3. Note that $\alpha$ should exhibit an Arrhenius temperature dependence. This effect is shown in Fig. 4.
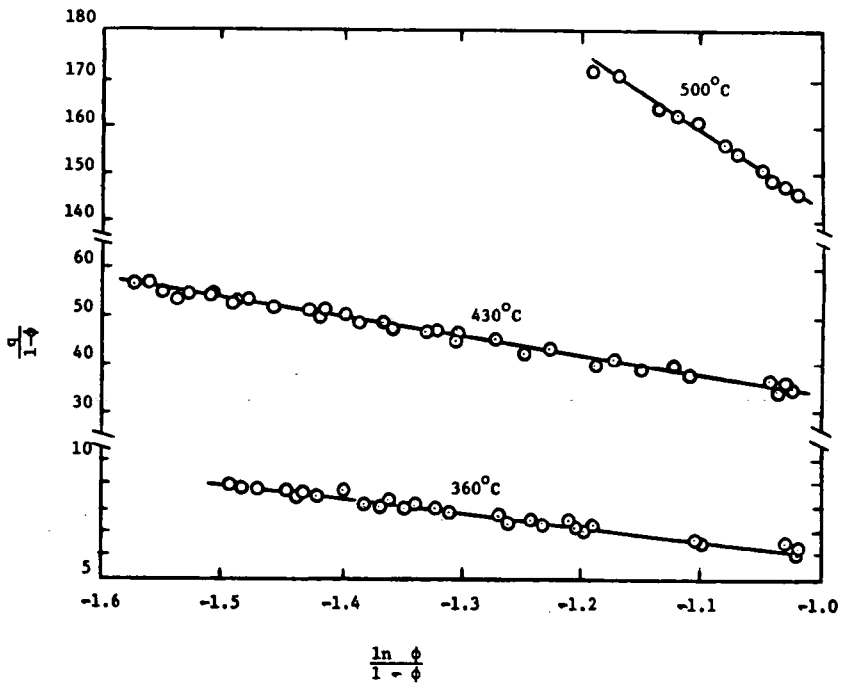


Fig. 3. Test of multilayer coke model. Plot of data in form of eq 17.
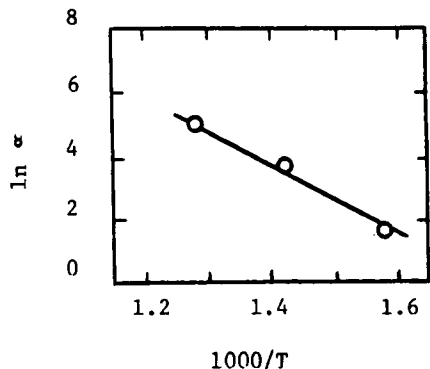
Fig. 4.  Arrhenius dependence of α.  Multilayer coke model.

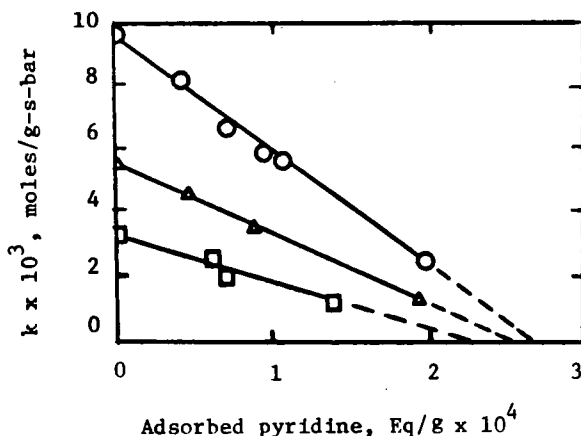Results of the pyridine titration study is shown in Fig. 5.



Fig. 5.  Pyridine loading on La-Y .  Effect on cumene cracking
rate coefficient.  Key: o 300°C, Δ 250°,□200°.

Zeolitic diffusivity was calculated from measurements of the variance and
mean of experimental chromatographic curves.  Shah and Ruthven [7] modified
equations for the variance and mean for the situation in which Reynolds number
is low, macrotransport is predominately by molecular diffusion, and the
sorption equilibrium constant is greater than one.  The modified equations
yield:

$$\frac{\sigma^2}{2\mu^2}\left(\frac{L}{U}\right) = \frac{D_L}{U^2} + \left(\frac{\epsilon}{1-\epsilon}\right)\left(\frac{1}{3} + \frac{t}{15\theta}\right)\frac{R_p^2}{D_m} + \frac{\epsilon}{1-\epsilon}\frac{r_c^2}{15K_p D_c} \qquad (19)$$

The terms on the left hand side are $\sigma^2$ the variance and $\mu$ the mean of the chromatographic curve, L the bed length and U the interstitial velocity. The terms on the right hand side represent the respective contributions of axial diffusion, film-plus-macropore resistance, and zeolitic diffusion resistance. The axial dispersion coefficient ($D_L$), molecular diffusivity ($D_m$), and tortuosity factor (t) can be estimated [7]. Therefore, the axial dispersion resistance can be calculated. Parameter $\epsilon$ is the bed porosity, $\theta$ the pellet porosity, $R_p$ the pellet radius, $r_c$ the zeolite crystal radius, $D_c$ the zeolitic diffusivity and $K_p$ the hydrocarbon sorption equilibrium constant. Since the left hand side of eq 19 can be calculated from experimentally measured quantities, the resistance due to zeolitic diffusion can be calculated by difference. A comparison of resistances for benzene diffusion in LaY with and without 5 percent coke at 30°C shown in Table 1.

Table 1

Comparison of Resistances for Benzene Diffusion in LaY

| $\frac{\sigma^2}{2\mu^2}(\frac{L}{U})\times 10^3, s$ | $\frac{D_L}{U^2}\times 10^3, s$ | $(\frac{\epsilon}{1-\epsilon})(\frac{1}{3}+\frac{t}{15\theta})\frac{R_p^2}{D_m}\times 10^3, s$ | $\frac{D_c}{r_c^2}, s^{-1}$ |
|---|---|---|---|
| **Coked Catalyst** | | | |
| 53.79 | 36.47 | 0.44 | 2.15 |
| 41.10 | 21.30 | 0.44 | 1.84 |
| 33.94 | 13.87 | 0.44 | 1.82 |
| 31.95 | 8.77 | 0.44 | 1.57 |
| 17.45 | 5.87 | 0.44 | 3.20 |
| 18.19 | 3.97 | 0.44 | 2.59 |
| | | Average = | 2.2 |
| **Uncoked Catalyst** | | | |
| 42.69 | 25.92 | 0.44 | 1.80 |
| 23.29 | 10.33 | 0.44 | 2.35 |
| 20.93 | 5.90 | 0.44 | 2.02 |
| 18.12 | 3.20 | 0.44 | 2.03 |
| 14.35 | 2.03 | 0.44 | 2.48 |
| | | Average = | 2.2 |

DISCUSSION

The kinetics of cumene cracking over LaY, as measured in the thermo-balance reactor, can be modeled by a mechanism based on the formation of both monolayer and multilayer coke. At the low cumene partial pressures employed, the reaction rate with fresh catalyst (no coke on the catalyst) is directly proportional to the cumene partial pressure as shown in Fig 1 and the

slope of this plot yields an intrinsic reaction rate coefficient.  Then the relative catalyst activity can be determined experimentally by the ratio of the reaction rate at any coke level to the reaction rate with fresh catalyst. The relative catalyst activity has an exponential relationship with the total coke on the catalyst as shown in Fig 2.  The effect of coke level decreases with increasing temperature.  The experimental data are well represented by the multilayer coke model as illustrated by Fig 3.  The slopes of the lines give values of $\alpha$ at each temperature.  The parameter $\alpha$ has an Arrhenius temperature dependence:

$$\ln \alpha = \ln \frac{A_L L_c}{\rho_c A_D A_R} - \frac{E_L - E_D + \Delta H_R}{RT} \tag{20}$$

The parameters $A_L$, $A_D$ and $A_R$ are the frequency factors for the multi-layer coke reaction, surface coke reaction and adsorption of R respectively, $E_L$ and $E_D$ the activation energies for the multilayer coke and surface coke formation, $\Delta H_R$ the heat of adsorption of propylene, R the gas constant and T absolute temperature.

The slope of the line in Fig 4 yields a value of 92.5 KJ/mole.  This suggests that the activation energy of the multilayer or polymerization coking reaction is greater than the monolayer coke formation.  Apparently more of the total coke is in the multilayer form at higher temperatures.

The effect of pyridine poisoning on cumene cracking activity is shown in Fig 5.  This linear relationship suggests uniform catalytic site strength. The total number of active sites estimated by extrapolation to zero activity is approximately $1.5 \times 10^{20}$ sites/g.

The zeolitic diffusivities, as measured by the gas chromatographic technique, indicated no significant difference in the values for fresh LaY and LaY with 5 percent coke.  The calculated values of diffusivity included a large degree of error because axial dispersion accounted for much of the variance in the residence time distribution curves, and the calculation method involved taking the difference of two large numbers.  Nevertheless, the actual residence time distribution curves were essentially identical for coked and fresh catalyst.  Therefore, coke appeared to have little effect on the diffusivity.  The fact that coke has little effect could be reasonable if coking occurred uniformly throughout the zeolite because the three dimensional nature of the supercages and the large number of windows into the inter-connected supercages would minimize pore plugging possibilities.

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