

## Anomalous Behavior of Cumene Cracking in Small-Pore Catalysts

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The reaction sequence in small-pore catalysts has been postulated to be as follows: adsorption of the reactant from the gas phase to the outside surface of the catalyst to form a condensed-type phase; diffusion of the condensed molecules along the pore walls analogous to surface diffusion, then reaction on active sites, followed by diffusion of the products to the external surface of the catalyst; finally, desorption of the products. This is in contrast to the conventional diffusion, adsorption, and reaction model which is suitable for larger-pore catalysts. Kinetic data from the cumene cracking reaction over REY zeolites are used in this work. The data were obtained at a wide range of temperatures, from 225 to 575°C, sufficient to include the regions of kinetic control and strong pore diffusion. Under these conditions and using the above model, the kinetic and diffusion parameters for cumene cracking are obtained. The intrinsic reaction rate constant and diffusion coefficient over REY zeolites are  $2.5 \times 10^6 \text{ cm}^3/\text{g/s}$  and  $1.9 \times 10^{-9} \text{ cm}^2/\text{s}$  at 500°C, with activation energies of 33 and 15 kcal/mol, respectively. © 1990 Academic Press, Inc.

## INTRODUCTION

The cumene cracking reaction has a history of being used as a "test reaction" to understand the behavior of different cracking catalysts in reactor types ranging from microcatalytic to integral reactors. However, most of the work on cumene cracking is concentrated on the kinetics of the cracking and coking reactions, identifying the different products of the cracking reaction, and developing the form of the reaction rate expression. Corma and Wojciechowski (1) have summarized most of this work.

The objective of the present work is to analyze the kinetic data from the cumene cracking reaction, taking into account the reaction mechanisms in a small-pore zeolite. Riekert (2) qualitatively examined the phenomena of adsorption, diffusion, and reaction in zeolites, and analyzed some of the models representing adsorption equilibrium and reaction-rate phenomena in gas-zeolite systems. Palekar and Rajadhyaksha (3) qualitatively analyzed the role of adsorption

in various zeolite-catalyzed reactions and reviewed the principles of adsorption accompanied by chemical reaction in zeolites. Using these models, we analyze the kinetic data obtained for cumene cracking over a REY zeolite. We use a wide range of temperatures, from 225 to 575°C, sufficient to include the regions of kinetic control and strong pore diffusion. This allows us to estimate the kinetic and diffusion parameters for cumene cracking under these conditions.

## EXPERIMENT

Cumene is cracked in the microreactor of a Cahn System 113-DC Thermogravimetric Analyzer (TGA), with product analysis by a Varian 3700 Gas Chromatograph (GC). The schematic of the apparatus is shown in Fig. 1. The experiment consists of passing a stream of 2 mol% cumene in helium into the tubular quartz reactor of the TGA. The catalyst is a rare-earth-exchanged Y (REY) zeolite of particle size  $1 \mu\text{m}$ , having a pore diameter of  $9 \text{ \AA}$  and a surface area of  $620 \text{ m}^2/\text{g}$ . The catalyst is pretreated by steam treatment under atmospheric pressure and 500°C for 8 h. The catalyst sample is placed

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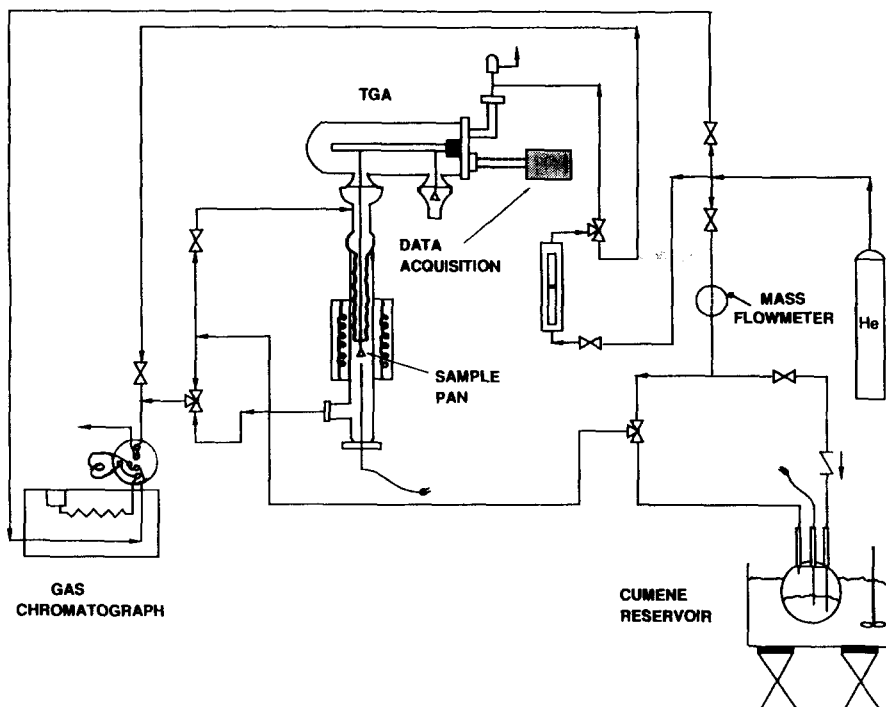


FIG. 1. Schematic of apparatus.

on the sample pan of the TGA electrobalance. A split-shell furnace equipped with a Micricon 823 controller maintains a constant temperature in the reactor. The composition of the product stream is obtained by injecting the contents of a sampling valve into the GC at regular time intervals. The TGA is used to obtain data on coke level, not reported in this work. Only fresh catalyst data are considered here.

The major products of the cracking reaction, at all temperatures, are identified as benzene and propylene. The fractional conversion of the reaction, at all temperatures, is calculated based on the weight fraction of the unreacted cumene in the product stream. Best and Wojciechowski (4) suggest that the total disappearance of cumene is not a good measure of the extent of the cracking reaction, since cumene disproportionation becomes significant at lower temperatures. However, we find no evidence of a diisopro-

pylbenzene peak, even at the lowest temperature. Hence cumene disproportionation is not significant in our experiments. This is attributed to the low partial pressure of cumene in the reactor due to dilution of cumene by the carrier gas, helium. Moreover, the short contact time of cumene on the catalyst in the microreactor of the TGA results in relatively small conversions and negligible amounts of bimolecular reactions. We also see no evidence of *n*-propylbenzene in the chromatograms, suggesting that the monomolecular reaction of isomerization of cumene may be negligible. Under such conditions, it is reasonable to calculate the fractional conversion of the reaction based on the total disappearance of cumene.

The fractional conversion ( $X$ ) of the reaction versus time is shown in Fig. 2 for one reaction temperature (350°C) and one flow-rate (225 cc/min). The curve is extrapolated to zero times. The procedure is repeated for

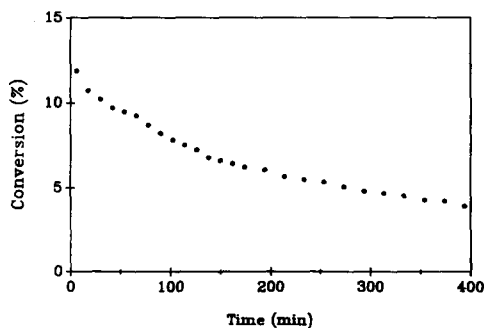


FIG. 2. Example of conversion vs time data for cumene cracking over REY zeolite.  $T = 350^{\circ}\text{C}$ ,  $W = 13$  mg,  $F_{A0} = 2.4 \times 10^{-4}$  mol/min.

different flowrates and temperatures. The observed rate constant,  $k_{\text{obs}}$ , at each temperature is calculated from a first-order kinetic model. A plot of  $-\ln(1 - X)$  versus the space time,  $\tau$  (see Appendix) is drawn, and the slope of the best-fit line passing through the origin and data points yields the observed rate constant at each temperature. The linear relationship of  $-\ln(1 - X)$  at different space times at all the temperatures, from 225 to 575°C, indicates that the first-order rate assumption of the cumene cracking reaction is reasonable.

Figure 3 shows the Arrhenius plot for the

fresh catalyst at temperatures ranging from 225°C to 575°C. Conventionally, the slope of the high-temperature asymptote should be slightly greater (in absolute magnitude) than one-half the slope of the low-temperature asymptote; see, for example Ref. (5). However, in the present case, the high-temperature slope is significantly less than one-half of the low-temperature slope. Based on these values, the activation energy for diffusion is apparently negative, which is unreasonable. In addition, the activation energy of the cumene cracking reaction would appear to be significantly lower than values reported in the literature (1). The above results can be explained by examining the effect of adsorption of cumene on REY zeolites, as shown below.

#### MODEL

In order to understand the significance of adsorption, diffusion, and reaction in *smaller*-pore catalyst systems such as zeolites, we first present the analysis of diffusion, adsorption, and reaction in *larger*-pore catalyst systems. In the case of large-pore catalyst systems, the sequence of the reaction is as follows: diffusion of the reactant from the gas phase into the catalyst pore;

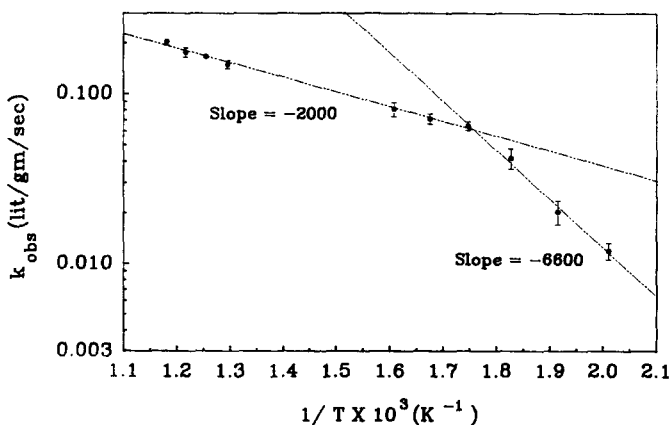


FIG. 3. Observed reaction rate for cumene cracking over fresh REY zeolite as a function of temperature, plotted in Arrhenius coordinates. Lines indicate high- and low-temperature asymptotes.

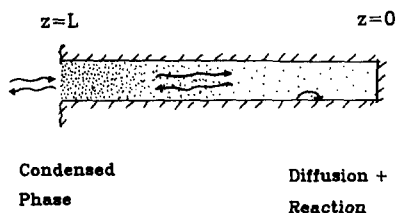


FIG. 4. Schematic of model for smaller-pore catalyst.

adsorption of the reactant at the active site, followed by reaction and the desorption of the product; and finally, diffusion of the product out from the catalyst pore. The conventional steady-state diffusion equation for this case yields

$$-r_{\text{obs}} = \rho k_{\text{int}} K_{\text{ads}} C_{\text{AS}} \eta = k_{\text{obs}} C_{\text{AS}}, \quad (1a)$$

where  $\eta$  is the effectiveness factor for a generalized pellet shape, given by

$$\eta = \frac{\tanh \phi}{\phi} \quad (1b)$$

with  $\phi$  being a Thiele-type modulus defined by

$$\phi = l \rho (k_{\text{int}} K_{\text{ads}} / D_{\text{eff}})^{1/2}. \quad (1c)$$

This treatment assumes that the intrinsic reaction rate  $r_{\text{int}}$  can be written as

$$-r_{\text{int}} = k_{\text{int}} \rho \theta_A, \quad (2a)$$

where the amount of reactant adsorbed per  $g$  catalyst,  $\theta_A$ , can be written in terms of a linear adsorption isotherm

$$\theta_A = K_{\text{ads}} C_A. \quad (2b)$$

Other symbols are conventional and are defined in the Appendix.

At temperatures low enough that the reaction is controlled by intrinsic kinetics ( $\phi \ll 1$ ), Eq. (1) reduces to

$$-r_{\text{obs}} \cong \rho k_{\text{int}} K_{\text{ads}} C_{\text{AS}} \quad (3a)$$

and

$$k_{\text{obs}} \cong \rho k_{\text{int}} K_{\text{ads}}. \quad (3b)$$

Therefore, the observed activation energy at these sufficiently low temperatures is

$$E_{\text{obs}} \cong E_{\text{int}} + \Delta H_{\text{ads}}, \quad (3c)$$

where  $\Delta H_{\text{ads}}$  is the enthalpy change of adsorption. At high temperatures, when the effect of pore diffusion is significant ( $\phi \gg 1$ ), the reaction rate can be written as

$$-r_{\text{obs}} \cong (k_{\text{int}} K_{\text{ads}} D_{\text{eff}})^{1/2} C_{\text{AS}} / l \quad (4a)$$

and

$$k_{\text{obs}} \cong (k_{\text{int}} K_{\text{ads}} D_{\text{eff}})^{1/2} / l. \quad (4b)$$

Therefore, at these sufficiently high temperatures,

$$E_{\text{obs}} \cong \frac{1}{2} (E_{\text{int}} + \Delta H_{\text{ads}} + E_d). \quad (4c)$$

For the larger-pore systems, Eqs. (3c) and (4c) indicate that, when adsorption is taken into account, the enthalpy change of adsorption,  $\Delta H_{\text{ads}}$ , is added to the observed activation energy. However, since  $E_d \ll E_{\text{int}}$ , the slope of the high-temperature asymptote in the Arrhenius plot will (still) be equal to approximately one-half the slope of the low-temperature asymptote.

In smaller-pore catalyst systems like REY zeolites, the critical diameter of the reactant molecule is of the same order of magnitude as the size of the pores. A free gas phase may be absent within the pores of such catalyst systems: instead, a condensed-type phase may be present at the external surface of the zeolite and within the catalyst pores. The sequence of the reaction in such catalyst systems is postulated, following Ref. (3), to be as follows: adsorption of the reactant from the gas phase as a condensed-type phase on the external surface of the catalyst; diffusion of the reactant along the pore walls, perhaps analogous to surface diffusion, followed by reaction at the active site, and the diffusion of the products to the external surface of the catalyst; and finally, the desorption of the products to the gas phase. See Fig. 3; the dots in the figure indicate a concentration profile of the adsorbed condensed-type phase inside the pore. In this model, the "condensation" of the reactant is not the conventional capillary condensation, which can occur due to curvature ef-

fects in pores which are much larger than molecular dimensions. Rather the phenomenon is due to adsorption on the surface, to an extent no greater than one monolayer, and with desorption within the pore being severely restricted, due to the molecular dimensions of the pore. Derouane *et al.* (6) have used similar arguments in describing the curvature effect in zeolites.

Based on this model, the steady-state diffusion equation can be written as

$$D_{\text{eff}} \frac{d^2 \theta_A}{dz^2} - (-r_{\text{int}}) = 0, \quad (5a)$$

where  $(-r_{\text{int}})$  is again given by Eq. (2a). The boundary conditions are

$$\frac{d\theta_A}{dz} = 0 \quad \text{at } z = 0 \quad (5b)$$

and

$$\theta_A = \theta_{\text{AS}} \quad \text{at } z = l \quad (5c)$$

In this model, equilibrium between the adsorbed phase and the gas phase exists at the external catalyst surface only, and the relationship is given by

$$\theta_{\text{AS}} = K_{\text{ads}} C_{\text{AS}}. \quad (5d)$$

The overall reaction rate for this case is written as

$$-r_{\text{obs}} = \rho k_{\text{int}} K_{\text{ads}} C_{\text{AS}} \eta = k_{\text{obs}} C_{\text{AS}}, \quad (6a)$$

where

$$\eta = \tanh \phi_1 / \phi_1 \quad (6b)$$

and

$$\phi_1 = l(\rho k_{\text{int}} / D_{\text{eff}})^{1/2}. \quad (6c)$$

Note that in the large-pore model, Eq. (1), the intrinsic rate constant  $k_{\text{int}}$  is always multiplied by the adsorption equilibrium term  $K_{\text{ads}}$ . In the small-pore model, Eq. (6), this is not the case.

At low temperatures, the small-pore model yields Eq. (3) for the observed reaction rate and the observed activation energy. However, at high temperatures, the observed reaction rate is written as

$$-r_{\text{obs}} \cong (\rho k_{\text{int}} D_{\text{eff}})^{1/2} K_{\text{ads}} C_{\text{AS}} / l \quad (7a)$$

and the observed rate constant is written as

$$k_{\text{obs}} \cong (\rho k_{\text{int}} D_{\text{eff}})^{1/2} K_{\text{ads}} / l. \quad (7b)$$

Therefore, at high temperatures,

$$E_{\text{obs}} \cong 1/2(E_{\text{int}} + E_d) + \Delta H_{\text{ads}}. \quad (7c)$$

## RESULTS

Equations (7c), (3c), and (4c) explain why the slope of the high-temperature asymptote in the Arrhenius plot is much smaller than one-half the slope of the low-temperature asymptote (in absolute magnitude).

The slopes of the asymptotes in Fig. 3 are used to calculate the observed activation energies for reaction and diffusion. The value of the enthalpy change of cumene adsorption on Y zeolites,  $\Delta H_{\text{ads}}$ , is  $-20$  kcal/mol (7). (The heat of adsorption is used, rather than that of condensation, since only about a monolayer of the species can be accommodated inside the pores, as noted earlier.) The activation energy for the cumene cracking reaction,  $E_{\text{int}}$ , is then found to be 33 kcal/mol. Then, using the slope of the high-temperature asymptote in the Arrhenius plot and Eq. (7c), the activation energy for diffusion in REY is calculated to be 15 kcal/mol.

The data of Fig. 3 can also be used to evaluate values for the intrinsic rate constant and the effective diffusivity corresponding to the fresh catalyst. This follows the procedure outlined in Ref. (8), modified by using the small-pore model of Eq. (6) in place of the conventional model. At  $500^\circ\text{C}$ , the values are

$$k_{\text{int}} = 2.5 \times 10^6 \text{ cm}^3/\text{g/s}$$

$$D_{\text{eff}} = 1.9 \times 10^{-9} \text{ cm}^2/\text{s}.$$

These values, and those of the activation energies above, are consistent with those in the literature (1, 3).

## SUMMARY AND CONCLUSIONS

In smaller-pore catalyst systems like zeolites, where the size of the reactant molecule is of the same magnitude as the pore size of

the catalyst, the mechanism of reaction may be considerably different from larger-pore catalyst systems. This is due to the absence of a free gas phase inside the pores of the zeolite-type catalysts. An adsorbed condensed-type phase is formed on the external surface of the catalyst, then diffusion (analogous to surface diffusion along the pore walls) and reaction in the zeolite-type catalysts may occur. Based on this analysis, the activation energy for cumene cracking on fresh, steamed, REY zeolites is found to be 33 kcal/mol, while the activation energy for diffusion is 15 kcal/mol. Intrinsic reaction rate constants and effective diffusivities for the catalyst are also determined. At 500°C, these values are  $2.5 \times 10^6 \text{ cm}^3/\text{g/s}$  and  $1.9 \times 10^{-9} \text{ cm}^2/\text{s}$ , respectively, for the fresh catalyst.

## APPENDIX: NOMENCLATURE

- $C_A$ : Concentration of the reactant (mol/cm<sup>3</sup>)  
 $C_{AO}$ : Concentration of the reactant at the reactor inlet (mol/cm<sup>3</sup>)  
 $C_{AS}$ : Concentrations of the reactant on the external surface of the catalyst (mol/cm<sup>3</sup>)  
 $D_{\text{eff}}$ : Effective diffusivity of the reactant (cm<sup>2</sup>/s)  
 $E_d$ : Activation energy for diffusion (kcal/mol)  
 $E_{\text{int}}$ : Activation energy for the reaction (kcal/mol)  
 $F_{AO}$ : Molar flowrate of cumene at the reactor inlet (mol/s)  
 $E_{\text{obs}}$ : Observed activation energy for the reaction (kcal/mol)  
 $\Delta H_{\text{ads}}$ : Enthalpy change of adsorption (kcal/mol)  
 $K_{\text{ads}}$ : Adsorption equilibrium constant (cm<sup>3</sup>/g)  
 $k_{\text{int}}$ : Intrinsic reaction rate constant (cm<sup>3</sup>/g/s)

- $k_{\text{obs}}$ : Observed rate constant (cm<sup>3</sup>/g/s)  
 $l$ : Characteristic length parameter of catalyst pellet, volume/external surface area (cm)  
 $r_{\text{int}}$ : Intrinsic reaction rate (mol/g/s)  
 $r_{\text{obs}}$ : Observed reaction rate (mol/g/s)  
 $W$ : Weight of catalyst in sample pan (g)  
 $X$ : Fractional conversion of the reaction  
 $z$ : Distance from the centerline to the catalyst surface (cm)  
 $\phi$ : Modified Thiele modulus, Eq. (1c)  
 $\phi_1$ : Thiele modulus, Eq. (6c)  
 $\eta$ : Effectiveness factor for generalized catalyst pellet, Eqs. (1b), (6b)  
 $\rho$ : Bulk density of the catalyst (g/cm<sup>3</sup>)  
 $\tau$ :  $C_{AO}W/F_{AO}$ , space time (s/cm<sup>3</sup>/g)  
 $\theta_A$ : Amount of adsorbed reactant per unit catalyst weight (mol/g)  
 $\theta_{AS}$ : Amount of adsorbed reactant on the external catalyst surface per unit catalyst weight (mol/g)

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