

The Site Density Criterion and the Mechanism of *n*-Heptane Cracking over a Rare Earth Type X Sieve

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The cracking of *n*-heptane over a rare earth X sieve was studied between 235 and 350°C up to atmospheric pressure in a flow system. The reaction is first order in reactant pressure. The catalyst deactivates rapidly. Apparent activation energies for activities obtained at 15 and 30 min are, respectively, 19.6 and 16.3 kcal/mole; the apparent initial activation energy, obtained by extrapolation of the 15- and 30-min activities, is 22.7 kcal/mole. Using transition state theory, site densities, the number of sites/cm² catalyst surface, are calculated for 0, 15, and 30 min. The calculation is made for each of several postulated slow steps. Some of the site densities calculated are physically impossible. A detailed analysis of the results indicates that adsorption is not the slow step, even though the reaction is first order, and that it is likely that the slow step is decomposition on a sparsely covered surface. Site density calculations for alkane cracking over both amorphous and crystalline catalysts were made for systems reported in the literature; the same conclusion can be made for these systems. It is suggested that a criterion for a mechanism in which one step is postulated to be slow is that the site density calculated for that step be physically possible.

INTRODUCTION

With the advent of the crystalline aluminosilicate catalysts there has been a renewed interest in the study of the mechanism of certain reactions catalyzed by solid materials. The mechanism of alkane cracking is of particular interest because it has not been as well understood as the mechanism of some other reactions. *n*-Hexane cracking over crystalline aluminosilicates has been studied by several groups (1-5). Miale *et al.* (1) reported on the cracking of *n*-octane over a rare earth zeolite; and Kibby *et al.* (6) discussed the cracking of *n*-octane and 2,5-dimethylhexane over a magnesium zeolite. For our present purpose the results given in these articles are best discussed by considering a few of those results in detail. We return to this matter in the discussion section.

We chose *n*-heptane as representative of the alkanes because there was with this compound sufficient cracking at the conditions accessible to us to enable us to carry out the reaction in a differential reactor. A differential reactor was used to minimize complications due to reverse reaction and any other effects which arise because of the presence of a large amount of product. At low conversions it is relatively easy to calculate reaction rates, rates which in turn can be related to a rate law if the reaction is not too complicated.

The pores and windows in the X sieve are large enough so that shape selectivity, often a factor in sieve studies, seemed not to be a factor.

The main purpose of this work was to calculate from kinetic data the catalyst site density, the number of active sites per

square centimeter, for each of several conceivable postulated slow steps, and to use these calculations in determining which, if any, of these steps is indeed the slow step. We have described the site density criterion in an earlier article (7).

EXPERIMENTAL METHODS

Materials

Phillips *n*-heptane, Spectro Grade, was used throughout. The catalyst was a powdered rare earth X sieve, with 27.6 wt% rare earth as RE₂O₃ and 0.29 wt% Na. The BET surface area was 538 m²/g.

Procedure

The cracking of *n*-heptane was studied in a differential flow reactor at a total pressure of 0.95 atm in the 235–350°C range. Liquid reactant was fed into the all-Pyrex reactor by a clock-driven syringe at a rate of 6.54 ml/hr. After being vaporized in a boiler, the reactant passed over a horizontal tray supporting (in the standard run) 0.1 g of the catalyst. Dry nitrogen (impurity oxygen was removed from all nitrogen used by passing it over hot copper) flowed over the catalyst for 15 min at the temperature of the run prior to the introduction of the reactant. In some runs the reactant was diluted with nitrogen before it contacted the catalyst. The product stream, in which conversion was almost always less than 10%, remained a gas as it passed into a gas chromatograph using a 6-ft Porapak Q column at 200°C. Calibration curves for most of the possible C₁ to C₆ products were prepared. At least one isomer for each of the six carbon numbers was found in the product stream. It was noted that the calibration curves for isomers were the same. The column conditions permitted analysis of all the products except for methane, not distinguishing between isomers. A few runs with the column at a lower temperature, where methane could be determined, indicated that the conversion calculated using

the 200°C column, when methane could not be determined, was at least 95% of the correct conversion, and therefore the higher temperature was used.

RESULTS

Thermal Reaction

Conversion due to the thermal reaction was found to be 1–2% in the temperature range studied. Thus, since the total conversion was usually well under 10%, the correction due to the thermal reaction was rather large. It was difficult to make this correction properly, since reproductibility of the conversion due to the thermal reaction depended upon reproducing from run to run conditions in the entire reactor, not just in the region containing the catalyst. It was not feasible to eliminate the problem by working at a lower temperature, since the temperature coefficient of the thermal reaction is apparently smaller than that of the catalytic reaction. Nor was it possible to work at a higher temperature, where the conversion was larger than desired for a differential reactor.

Catalyst Deactivation

In a typical run the total (thermal plus catalytic) conversion at 270°C was 6.8% at 15 min and 4.1% at 30 min. In general, the total conversion at 45 min could not be distinguished from the conversion due to the thermal reaction.

Reverse Reaction

In a series of runs at 275°C it was shown for a given time during the run that the percentage conversion was proportional to the weight of catalyst at least up to 0.5 g. Therefore, it was concluded that the reverse reaction was not significant in the standard run, in which 0.1 g was used.

Order of the Reaction

Activity as a function of percentage of nitrogen diluent in the reactant stream is

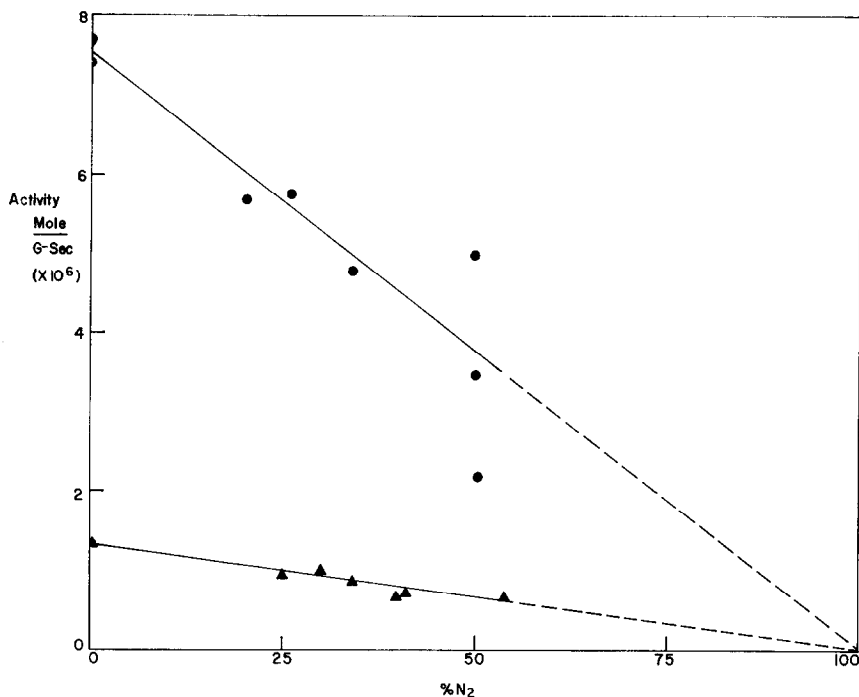


FIG. 1. Activity at 15 min for *n*-heptane cracking as a function of percentage of N₂ diluent in feed stream; (●) 275°C; (▲) 235°C.

shown for two temperatures in Fig. 1. The points for 13 of the 15 runs fall near straight lines which, when extrapolated, pass through 100% N₂. Thus, even though it was not possible to make measurements in mixtures containing more than 55% N₂, the data at both 235 and 275°C strongly suggest that the reaction is first order in partial pressure of *n*-heptane.

Temperature Coefficient

Arrhenius plots of activities at 15 min and at 30 min are given in Fig. 2. A linear extrapolation of the 15- and 30-min activities back to zero time was made; an Arrhenius plot of these initial activities is also shown. The experimental error (arising in part from difficulty in correcting for the thermal reaction) was large and therefore the plots were made neglecting a few obviously discordant points.

DISCUSSION

Mechanism of the Reaction

From the plots in Fig. 2 the apparent activation energies are found to be 16.3, 19.6, and 22.7 kcal/mole for the 30-, 15-, and 0-min activities, respectively. If poisoning of the reaction is responsible for the drift in activation energy, then the values obtained at later times are least accurate. It will be shown, however, that the conclusions which will be made are even more likely to be valid if the earlier values are used, and that the apparent activation energy would have to be much lower than the 30-min value for the conclusions to change.

Using our results it is possible to make site density calculations for various possible slow steps (?). For example, if the slow step is adsorption, the site density, *L*,

in sites/cm², is given by

$$L = \frac{vF_{\text{tr}}F_{\text{rot}}e^{E/RT}}{c_0(kT/h)}, \quad (1)$$

where v is the observed rate (molecules/cm²/sec), F_{tr} and F_{rot} are the translational and rotational partition functions of the gaseous reactant, respectively, E is the activation energy, c_0 is the gas phase concentration of the reactant (molecules/cm³), and k and h are the Boltzmann and Planck constants, respectively. A small error is introduced into Eq. (1) when it is assumed that the change in vibrational partition function of the adsorbing molecule is negligible. (The rate was calculated on an area basis using the BET area of 538 m²/g. There is uncertainty in using a BET area with a sieve; but it is very likely that the error so introduced is not important enough to make a significant difference in the calculation of L .)

Log L values (rounded off to the nearest integer because of the approximations involved) are given for various possible slow steps in Table 1 for the 0-, 15-, and 30-min curves of Fig. 2. The calculations were made for 270°C, with the rates taken from the curves of Fig. 2; the *n*-heptane pressure was always 0.95 atm. (F_{rot} for *n*-heptane is a function of $(I_x I_y I_z)^{1/2}$, where the I 's are the three moments of inertia; the value of $(I_x I_y I_z)^{1/2}$ was taken to be $6 \times 10^{-57} \text{ g}^{3/2} \text{ cm}^3$, a value arrived at by comparing *n*-heptane with other molecules whose moments of inertia are known.)

We can make some conclusions about the mechanism by combining the calculations of Table 1 with what we know about the order of the reaction. Since the reaction is first order, the slow step cannot be monomolecular decomposition on a saturated surface (zero order), bimolecular surface reaction (second order), or adsorption with dissociation (one-half order). It was shown that L is the order of unity if a mobile activated complex is the activated complex

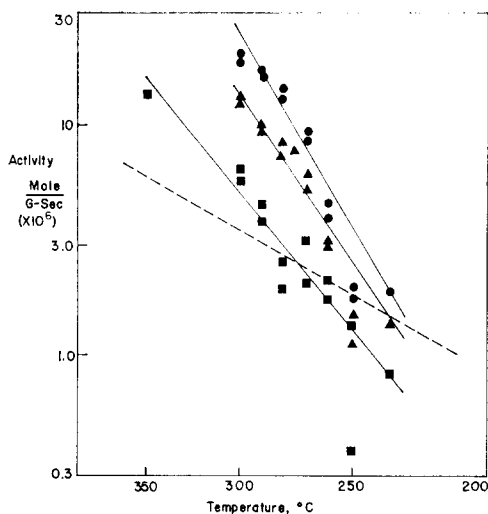


FIG. 2. Arrhenius plots; (■) activities at 30 min; (▲) at 15 min; (●) initial. (---) 30-min plot if adsorption is slow step and $L = 10^{15}$.

for the slow step (?); the results in Table 1 therefore rule out this possibility also.

If we assume that the active site is fixed and occupies at least 10 Å², the actual value of L can be no greater than 10¹⁵ sites/cm². (For a crystalline sieve, with sites possibly at only certain places in the unit cell, such an upper limit might be unrealistically large.) Therefore, even though the reaction is first order, the results in Table 1 are also inconsistent with the mechanism in which adsorption is the postulated slow step. For all three times—0, 15, and 30 min—the L values are several magnitudes larger than physically possible if adsorption is the slow step. The fourth curve in Fig. 2 is a hypothetical curve, one which would be obtained if (a) the slow step is adsorption, (b) there are 10¹⁵ sites/cm², and (c) the activity at 270°C were the same as it is on the 30-min curve. The activation energy calculated from this hypothetical curve is 7.5 kcal/mole.

Several matters should be considered in a discussion of why the calculated L values and the results concerning order are not consistent with any of the suggested slow steps. First, is it possible that experimental

TABLE 1

Site Densities for Various Postulated Slow Steps in *n*-Heptane Cracking over a Rare Earth X Sieve

Slow step	Log L^a		
	Initial	15 min	30 min
Monomolecular surface decomposition (1) ^b	8	7	5
Adsorption (2)	22	21	19
Bimolecular surface reaction (3a)	36	34	33
Adsorption with dissociation (4)	15	14	12
Mobile activated complex (5)	-3	-4	-6

^a Calculated from 270°C point on curves in Fig. 2; all at $P_{n\text{-heptane}} = 0.95$ atm.

^b Numbers in parentheses indicate the case number in Ref. (7).

error accounts for the difficulty? It seems certain that there is not enough experimental error in the data of Fig. 1 to invalidate the conclusion that the reaction is first order. In Fig. 2, the slope of the hypothetical curve indicates that the error would have to be very large for the observed activities to fall on the hypothetical curve. In fact, if more weight were given to the points farthest from the experimental curves, the points which were actually rejected in constructing the curves, the slopes would be larger and therefore even farther from the slope of the hypothetical curve. Also, if the calculation of activity from percentage conversion is in error where the conversion is large, the error is such that the true activity at the high temperatures is larger than reported; then the slope, the activation energy, and the calculated L value would be even larger.

Second, it is possible that unreasonable L values are obtained from the Arrhenius plots of Fig. 2 because catalyst deactivation during a run is not treated properly. Since the catalyst became completely deactivated in ~ 45 min in our runs, the activities of Fig. 2 are of necessity for a catalyst whose

activity is still decreasing. It is probable that the catalyst-reactant system achieves a steady state within the first few minutes of a run if catalyst poisoning is neglected, and that the observed deactivation is due to poisoning. If there were more rapid poisoning at low temperatures—a conceivable situation—then corrected experimental Arrhenius slopes could possibly match the slope of the hypothetical curve in Fig. 2.

Because of this inherent difficulty in using the 15- and 30-min activities, it seemed desirable to obtain the initial activity. As mentioned earlier, the initial activities which are obtained by linear extrapolation give a larger, not a smaller, Arrhenius slope and consequently a larger value for L . This raises the question as to whether it is correct to obtain initial activity by linear extrapolation of the 15- and 30-min values. The average of the 30-min activities for 12 of the runs reported in Fig. 2 (a thirteenth run was omitted from the calculation because one point is obviously in error) is 45% of the 15-min average; thus, it seems that a linear extrapolation is justified.

However, there could be enough experimental error to invalidate the calculation just made. If that were the case, what would happen if, for example, catalyst deactivation were due to poisoning by a reaction product? Let L' be the number of sites/cm² at time t ; then the activity, a , is given by

$$a = k_1 L', \quad (2)$$

where k_1 is constant for a given run. The catalytic rate drops to zero after a sufficient time; therefore, the poisoning is irreversible if deactivation is due to poisoning. The number of sites poisoned per unit time is thus proportional to the amount of product formed, or to the activity. That is, using Eq. (2),

$$-(dL'/dt) = k_2 a = k_1 k_2 L', \quad (3)$$

where k_2 is also constant for a given run. Then

$$dL'/L' = -k_1k_2dt, \quad (4)$$

$$\ln(L'/L) = -k_1k_2t, \quad (5)$$

where L is the site density at $t = 0$. Combining Eqs. (2) and (5),

$$a = k_1L \exp(-k_1k_2t). \quad (6)$$

Or,

$$\ln a = -k_1 - k_2t + \ln k_1L. \quad (7)$$

The last term is a constant during a run. Thus, if deactivation is due to product poisoning, the initial activity is obtained by linear extrapolation of $\ln a$, not a . We have carried out such an extrapolation with the 15- and 30-min activities of Fig. 2; the scatter of points in the Arrhenius plot so produced (not shown) is large and the activation energy is found to be at least 20 kcal/mole, far too large to produce an acceptable value of L if adsorption is the slow step.

Third, the trend in apparent activation energies obtained from the experimental points in Fig. 2 may explain why L values physically impossible for a slow adsorption step were obtained. The apparent activation energy decreased as the run proceeded. Conceivably, had it been possible to make activity determinations for a long enough time, the slope of the hypothetical curve in Fig. 2 could have been approached. Very likely such an hypothesis raises as many questions as it answers.

Fourth, if the number of active sites is a function of temperature, and not constant, as was supposed, then the Arrhenius plots cannot be used to calculate L values. If a curve having the slope of the hypothetical curve in Fig. 2 is drawn through the 30-min, 350°C point, then the activity indicated by the new curve at 235°C is about five times the observed activity. That is, the observed curve is accounted for if there are five times as many sites at 350°C as at 235°C at the conditions of our experiments.

Fifth, it is possible that the mechanism

of the cracking of *n*-heptane does not involve just one slow step. The existence of at least one compound for each carbon number from C₁ to C₆ in the product indicates either that there were primary reactions or both primary and secondary reactions. In either case, there could be more than one slow reaction; the reaction could still be first order, but the correct rate law would then not lead to Eq. (1) or any similar equation used to construct Table 1.

Sixth, determination of which step is the slow step may possibly be obtained by reexamination of the surface decomposition step, the first step listed in Table 1. The rate is, if this step is the slow step (7)

$$v = k_s KP / (1 + KP) \quad (8)$$

where k_s is the rate constant for the surface step, K is the equilibrium constant for *n*-heptane adsorption on the active sites, and P is the partial pressure of *n*-heptane. We showed earlier (7) that

$$L = (1/KP) [ve^{E/RT} / (kT/h)], \quad (9)$$

if $1/K \gg P$. According to Eq. (8), the reaction then becomes first order. If the observed activation energy approximates E , L as calculated in the first row of Table 1 is the quantity in brackets in Eq. (9). In our case, $P = 0.95$ atm, and therefore, according to Eq. (9), L calculated for a *first order* surface decomposition is larger than the L calculated for a *zero order* surface decomposition by a factor of $1/K$. But $1/K$ is large if the slow step is a surface step and the reaction is first order. Therefore, it would not be unreasonable to add at least two or three to $\log L$ in the first row of Table 1 to obtain $\log L$ for the cracking of *n*-heptane on a sparsely covered surface.

In the analysis of the previous paragraph it was assumed that the observed activation energy approximates E . Alkanes are known to adsorb weakly on aluminosilicates, and so the heat of adsorption, associated with the temperature coefficient of K , would not be expected to make an important con-

tribution to the observed activation energy in the use of Eq. (9). The heat of adsorption is exothermic and, if it is not small, neglecting it would give an activation energy, and therefore an L value, which is too small. This is the same qualitative conclusion obtained when the heat of adsorption is actually small, providing $1/K \gg P$.

It is instructive to make calculations of L for literature results for systems somewhat similar to ours. Hatcher and Sadler (8) studied *n*-hexane cracking over various ground silicas; their lowest apparent activation energy was 26 kcal/mole. Miale *et al.* (1) reported on the cracking of *n*-hexane over amorphous silica-alumina and a wide variety of crystalline aluminosilicates, and on the cracking of *n*-octane over a rare earth faujasite; their apparent activation energies were all about 30 kcal/mole. Both groups of workers assumed cracking to be first order, although Miale *et al.* (1) indicated that they did not prove this point. With both groups, catalysts were heated before use at a temperature at least as high as the temperature of any run. Using the apparent activation energies just indicated, reactant, catalyst, temperature, and $\log L$ values for the first two cases of Table 1 are, respectively: *n*-hexane, ground silica, 582°C, 9, 25; *n*-hexane, amorphous SiO₂-Al₂O₃ (10 wt% Al₂O₃), 500°C, 7, 22; *n*-hexane, rare earth faujasite (the most active catalyst which Miale *et al.* reported), 300°C, 11, 26; *n*-hexane, Ca zeolite (least active), 500°C, 7, 22; *n*-octane, rare earth faujasite, 500°C, 8, 23. Thus, in these systems, as in ours, the apparent activation energies are too large for adsorption to be the slow step and it is strongly indicated that the slow step is decomposition on a sparsely covered surface.

CONCLUSIONS

First, it seems that the activation energy in our system is not small enough for the slow step to be adsorption. Although it is

possible that none of the steps discussed is the one slow step, it seems likely that the slow step is decomposition on a sparsely covered surface. Thus, of the two steps consistent with the first order observation, only one is consistent with the site density criterion. One referee has suggested that the slow step may be transfer of a hydride ion from *n*-heptane to a smaller carbonium ion, with the steady state concentration of carbonium ions very low. That is, the concentration of active species, the carbonium ion, would be much less than that corresponding to a saturated surface; and, since the surface concentration of the *n*-heptane is relatively large, the reaction would be pseudomonomolecular. Such an interpretation is consistent with our conclusion that the slow step is decomposition on a sparsely covered surface.

The second conclusion is more general. Calculation of L values supplement determination of the reaction order. In some cases such a calculation will indicate that no postulated slow step is satisfactory; even such a negative result, indicating either that there is a slow step not considered or that there is no single slow step, constitutes information.

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