Isomerization of n-Pentane Over Platinum Alumina Catalysts of Different Activity

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Isomerization of *n*-pentane is an ideal reaction to study to gain fundamental data on rate of reaction and on the action of catalysts. Normal pentane of high purity is easily obtained, products from the reaction are easily defined, and analysis is not difficult. Basic kinetic rate equations can be written for the reactions, and in most cases they can be integrated without resort to numerical methods.

The purpose of this work was to obtain data on the isomerization over a platinum alumina catalyst, derive a kinetic rate equation which characterizes the data obtained and also fits the data in the literature, and investigate the effect of changing the isomerization activity of the catalyst.

LITERATURE REVIEW

Perhaps the most significant theory of isomerization on a solid catalyst is the dual-site action proposed by Mills et al. (*16*), Ciapetta and Hunter (*4*), and Weisz and Swegler (*24*), among others. The dual-site action may be expressed in terms of a rate equation, with the use of a normal first-order reversible reaction rate equation with an adsorption equilibria term of the Langmuir-Hinshelwood (*9*) type. The equation for the mechanism is described by Walas (*23*), and the following is patterned after his description.

In the dual-site mechanism it is assumed that a molecule *A* which is adsorbed on one active site reacts with an adjoining vacant site. The action of both sites is needed for the reaction, and the reactant is desorbed from both sites; the mechanism is

$$A + \sigma_1 \rightarrow A\sigma_1$$

$$A\sigma_1 + \sigma_2 \rightarrow A\sigma_1\sigma_2$$

$$A\sigma_1\sigma_2 \rightleftharpoons B\sigma_1\sigma_2$$

$$B\sigma_1\sigma_2 \rightarrow B\sigma_1 + \sigma_2$$

$$B\sigma_1 \rightarrow B + \sigma_1$$

The net surface rate equation is

$$r_s = k_1\,\theta_A\theta_V - k_{-1}\,\theta_B\theta_V \tag{1}$$

The two sites in the dual-site catalyst are a hydrogenation-dehydrogenation site (metal site) and an isomerization site (acid site). If the catalyst base is alumina, the hydrogenation-dehydrogenation sites can be produced by doping the base with platinum, molybdenum, rhodium, nickel, or another similar metal. On an alumina base, isomerization sites can be produced by adding a halide. Ciapetta (*5*) shows the hydrogenation-dehydrogenation activity of several catalysts by using the dehydrogenation of cyclohexane to benzene as a yardstick. He shows the isomerization activity of a catalyst with dehydrogenating ability by using *n*-heptane as the measurement. From these two devices, it is clear that the dual functions of an acid-metal catalyst can be controlled separately. Indications are that the dehydrogenation of the normal paraffin must take place first, thus leaving an olefin to be isomerized on the second site. A measure of the isomerization activity can be made independently of the hydrogenation activity by using an olefin and a catalyst that has no dehydrogenation function. Sinfelt et al. (*19*) accomplished this by using an alumina base catalyst with only an acid function and a normal pentane.

The basic hydrogenation activity of a catalyst is generally built into the catalyst by the manufacturing technique and is not significantly changed during the catalyst's life. Isomerization, or acid activity, on the other hand, can either be built into the catalyst or, in the case of alumina, it can be added after manufacture. With alumina-base catalysts, the acid activity is generally obtained by use of a halide, although the selection of the particular type of alumina base definitely affects the catalyst's acid-site forming ability. Hydrochloric acid (*15*), fluorine (*22*), tert-butyl chloride (*8*), or, as in this work, chlorine may be used.

Alumina can exist in several different crystal structures; by means of x-ray diffraction, Stumpf et al. (*20*) identified seven different types of nearly anhydrous crystalline forms: α, γ, δ, η, θ, κ, χ. All of the forms of anhydrous alumina result from the thermal decomposition of one of

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TABLE 1. CATALYST EVALUATION DATA

(PHF-1 catalyst, ⅛-in. diameter cylindrical pellets, ⅛ in. long)

	Manufactured average PHF-1	New PHF-1 before runs 4 to 30	PHF-1 after runs 4 to 30	Chlorinated PHF-1 before runs 31 to 37	Chlorinated PHF-1 after runs 31 to 37
Wt. % platinum	0.30	0.298*	0.270	0.298	0.302
Wt. % chloride	0.25	0.26	0.33	1.69	1.70
Wt. % volatile matter	—	4.13*	—	4.32	4.14
Parts per million sulfur	—	72*	—	212	—
Surface area, S_g, sq. m./g.	240	225.2*	—	218.2	—
Pore volume, V_g, ml./g.	0.55	0.374*	—	0.34	—

* Three determinations (average).

the hydrates and will eventually go to alpha alumina (the only alumina with an established crystal structure) when they are heated. One of the most striking features, according to Stumpf, is the exceptional stability of the γ and δ aluminas obtained from the α monohydrate.

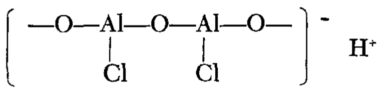
For catalyst manufacture, the intermediate anhydrous forms of alumina seem to be the most desirable. These forms exhibit a property as an active transient with structural defects. Krause (*13*) cites γ alumina as containing the radicals.

$$O = Al - \text{(electron donor)}$$

$$- O - Al = O \text{ (electron acceptor)}$$

The model form for stable α alumina may be represented as $O{=}Al{-}O{-}Al{=}O$.

In order to deposit platinum on the active alumina base, a solution of chloroplatinic acid is generally used. The catalytic properties of alumina activated with mineral acids in the isomerization of olefins have been studied by Miesserov et al. (*15*); accordingly, the activity of alumina activated with hydrochloric acid is directly related to the extent to which the surface OH groups are replaced by Cl^-. Miesserov proposes that the active centers of the catalyst have the structure



$$\left[\begin{array}{c} -O-\underset{\displaystyle Cl}{\underset{|}{Al}}-O-\underset{\displaystyle Cl}{\underset{|}{Al}}-O- \end{array} \right]^- H^+$$

This activation can be accomplished by the use of other acids, namely boric acid, hydrobromic acid, phosphoric acid, hydrofluoric acid, and sulfuric acid. Of these acids, the halides are preferable for platinum dual-function catalysts since they do not have a poisoning effect on the platinum.

EXPERIMENTAL EQUIPMENT AND MATERIALS

The reaction studies were carried out in the presence of hydrogen in a flow system with a ⅝-in. O.D. stainless steel reactor. A flow diagram of the equipment is shown in Figure 1; a detailed description of the equipment and components is presented elsewhere (*10, 14*). The equipment and flow sequence are similar to that described by Sinfelt et al. (*19*).

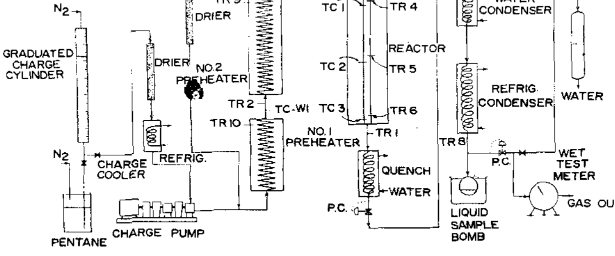


Fig. 1. Flow diagram of unit.

n-pentane and hydrogen gas, manufactured by the electrolytic process (99.91 vol. % min. purity), were used.

The catalyst is of the commercial reforming type. Typical data on the catalyst used before and after runs are presented by Table 1. The catalyst was manufactured by techniques similar to those given by Heard (*6, 7*), and Brennen et al. (*2*).

Reaction run periods were of approximately 30 min. Prior to a run period, from 1 to 2 hr. was required to achieve steady conditions. The hydrogen rate was calibrated prior to the introduction of pentane, and this rate was unchanged throughout the run.

Prior to the use of a catalyst, it was treated with an excess of oxygen to burn off any volatile matter present. Chlorination was accomplished, following the carbon burning step, with dried nitrogen as the carrier gas with a small amount of oxygen. Chlorination extended over an 8 to 10 hr. period until breakthrough was detected. A hydrogen reduction step of approximately 5 hr. followed the chlorination. Analyses of samples of catalyst from top and bottom of the reactor showed no significant variation in chloride content.

The catalyst was pretreated with hydrogen above 900°F. for at least 1 hr. before the hydrocarbon was introduced, and after a run, the unit was allowed to cool in a hydrogen atmosphere.

All gas and liquid streams were analyzed with a vapor fractometer, with helium as the carrier gas. Pentane samples were analyzed with a 20-ft. column packed with tetraisobutylene coated on C-3 firebrick. Cyclohexane samples were analyzed with a column containing di-2-ethylhexyl sebacate.

EXPERIMENTAL STUDY

The *n*-pentane was isomerized with platinum on alumina catalysts with two different chloride contents, 0.26 and 1.69 wt. %; conditions were:

Temperature range, °F.	650° to 900°
Pressure range, lb./sq.in. gauge	200 to 600
n-pentane space velocity range, g. *n*-pentane/hr./g. catalyst	9 to 25
Hydrogen/*n*-pentane mole ratio range	1.8 to 5.0

Detailed data for all the runs are presented elsewhere (*14*); for the low chloride runs, 33.759 g. of catalyst (910 pellets) were used, and for the high chloride runs, 38.285 g. (1,050 pellets).

Based on the correlation of Yang and Hougen (*26*) and estimated reaction rate data, a space velocity was established above which diffusion to the catalyst surface from the bulk gas stream was negligible; calculations indicated that the critical space velocity was about 9.

Two runs were made to determine the results of hydrogenation and isomerization of pentene-2 over the low chloride content catalyst. The results indicated no pentene in the product. Temperature control was a major problem on these runs; therefore, the results can only be considered order-of-magnitude.

To provide a measure of the hydrogenation-dehydrogenation activity of the catalyst, two cyclohexane dehydrogenation runs were made, one at low chloride content and the other at high chloride content. Experimental conditions and results are shown in Table 2.* The data indicate that the catalyst was extremely active as a dehydrogenation catalyst and that the chlorination has little effect on dehydrogenation activity.

Whenever a new catalyst was placed in the reactor, it was burned off with oxygen to eliminate any volatile materials that might be present. The low chloride content catalyst was again burned off after twenty-four pentane runs, two pentene runs, and one cyclohexane run to determine the amount of carbon which had been deposited. The conditions for carbon burning were:

Temperature, °F.	900° to 950° (final temperature)
Pressure, lb./sq.in. gauge	400
Volume % oxygen	20 to 50
nitrogen	80 to 50

In order to obtain a high chloride content catalyst, it was necessary to treat with chlorine gas. This procedure was carried out immediately following the carbon burning step. The conditions used were:

Temperature, °F.	950° to 1,000°
Pressure, lb./sq.in. gauge	200
Volume % chloride	0.5
oxygen	2.3
nitrogen	97.2

PROPOSED MECHANISM AND KINETIC EQUATIONS

A dual-site mechanism can be used to explain the isomerization. To visualize the catalyst surface, the ideas of Krause (*13*) are used. The intermediate anhydrous forms of the aluminas (γ or η) are assumed to contain two types of radicals, O = Al — (electron donor) and —O — Al = O (electron acceptor). When chloroplatinic acid is added, it reacts with these surface radicals. After the addition of excess H_2PtCl_6, the catalyst is reduced with hydrogen, leaving Pt-Al complexes and either O = Al — OH and O = Al — Cl structures or O = Al — structures, depending upon the extent of the reduction. Finally, the result of chlorination yields O = Al — Cl or O = Al — O — Al = $(Cl)_2$ configurations, depending upon the extent of chlorination. The platinum-containing site represents the metal (hydrogenation-dehydrogenation) site, and the chloride-containing site represents the acid (isomerization) site.

The reaction mechanism assumes the existence of paired dual sites. When a *n*-pentane molecule approaches the sites, one of the hydrogen atoms is attracted to the metal site and then the unsatisfied carbon atom is immediately attracted to the acid site. Once on the acid site, the pentane molecule isomerizes, and the acid and metal sites are freed by the action of molecular hydrogen.

The proposed mechanism does not recognize the existence of the olefin in the gas phase even though the presence of such has been shown by Weiss and Swegler (*24*) and Sinfelt (*19*), among others. This exclusion is felt to be justified since the attraction of the olefin to the catalyst surface is great and since the isomerization step is rate controlling. The equations become very difficult to evaluate if an intermediate olefin in the gas phase is assumed, and the assumption that this olefin exists primarily on the catalyst surface simplifies the relationships.

Surface Rate Equation

Based on the foregoing mechanism, the rates of adsorption and desorption of *n*-pentane can be written as

$$r_{AD_1} = k_{A_1} a_A a_V = k_{A_1} a_A \,(1 - \theta_A - \theta_B - \theta_C) \qquad (2)$$

$$r_{AD_{-1}} = k_{A_{-1}} \theta_A \qquad (3)$$

If the surface rate is controlling (*26*), the adsorption is at equilibrium, and $r_{AD_1} = r_{AD_{-1}}$, and Equations (2) and (3) can be solved for θ_A and similarly for θ_B and θ_C. The net rate equation for the surface reaction of A is given by

$$r_s = k\left(\theta_A \theta_V - \frac{\theta_B \theta_V}{K}\right) \qquad (4)$$

$$= \frac{k\left(K_A a_A - \dfrac{K_B a_A}{K}\right)}{(1 + K_A a_A + K_B a_B + K_C a_C)^2} \qquad (5)$$

The Effect of Diffusion

The Yang and Hougen correlation approximates the flow requirement to minimize the effect of diffusion and uses a modified Reynolds number

$$N_{Re} = \frac{\sqrt{a_p}G}{\mu} \qquad (6)$$

In plant design it may be uneconomical to design at high space velocities, and thus it becomes necessary to account for diffusion to and from the catalyst surface. A method suggested by Hurt (*11*), with a height of transfer unit (HTU) and height of reaction unit (HRU) concept, appears suitable. Wheeler (*25*) suggests the use of the Hurt concept by applying a factor of $\left[\dfrac{\text{HRU}}{\text{HRU} + \text{HTU}}\right]$ to the right-hand site of the rate equation. If diffusion to the catalyst is negligible, HTU will approach zero and the factor will be equal to unity.

Unless the catalyst surface has a very high density of active sites, an important correction to the rate equation is the term which accounts for the flow of reactants into the catalyst pores. Transport into a single pore can occur by three mechanisms: ordinary or bulk diffusion, Knudsen flow, and Poiseuille flow. The total transport of a molecule A down a catalyst pore may be represented by

$$n_A = -\pi r^2 \underbrace{(D_B + D_K + D_P)}_{D_T} \frac{\partial C_A}{\partial X} \qquad (7)$$

[g. moles of A/sec.]

In ordinary diffusion a molecule of gas will move when its mean free path is not greatly restricted by the walls of the catalyst pore and when movement by pressure difference is not a factor. Reid and Sherwood (*17*) suggest the Hirschfelder et al. relationship for the bulk diffusion coefficient:

$$D_B = \frac{1.858 \times 10^{-3}\, T^{3/2} Mr^{1/2}}{P_T\, \sigma^2_{12}\, \Omega_D} = \frac{\epsilon}{P_T} \qquad (8)$$

In Knudsen flow (*12*), the molecule will, in general, strike a pore wall before it strikes a second molecule. This necessitates that the radius of the pore be much less than the mean free path of the molecule, a condition that is only satisfied at low pressures and with small pores. The Knudsen flow diffusion coefficient is

$$D_K = \frac{2r}{3}\sqrt{\frac{8RT}{M}} \qquad (9)$$

In Poiseuille flow or forced flow there is laminar movement of the molecules by virtue of pressure difference. The basic Poiseuille flow equation is, in absolute units

$$-\left(\frac{dP}{dx}\right) = \frac{32\mu G}{(2r)^2 p} \qquad (10)$$

and may be written as a Fick's law type of equation with the Poiseuille diffusion coefficient as

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Tables 2, 3, 4, and 5 have been deposited as document 8086 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

$$D_P = \left(\frac{r^2 P_T}{8\mu} \right) \tag{11}$$

Thiele (*21*) has presented equations to calculate the rate of flow of a reactant into a single catalyst pore, and his development leads to the following rate equation (nomenclature, after Wheeler):

$$\text{rate (moles/sec.)} = \pi r^2 D \frac{C_{A_0}}{L} h \tanh h \tag{12}$$

Wheeler (*25*) has shown the rate of flow of the reactant into the pore per catalyst pellet, which is equal to the rate of reaction per catalyst pellet, to be

$$\text{rate (moles/sec.)} = \frac{S_x \,\theta\, D\, C_{A_0}}{\sqrt{2}L} h \tanh h \tag{13}$$

If the reaction takes place on the surface alone, the rate would be (first-order reaction)

$$\text{rate (moles/sec.)} = \frac{2\,\theta\, v_p}{\bar{r}} C_{A_0} k_s \tag{14}$$

Dividing Equation (18) by Equation (19) and simplifying one gets

$$f = \frac{1}{h} \tanh h \tag{15}$$

where f is defined as the ratio of the observed rate to the rate which would be observed if the surface were completely available. This factor can be used in the rate equation to correct for the effect of diffusion within the pores of the catalyst. As h becomes small, $f \to 1.0$, and the effect of diffusive and forced flow into the catalyst pores becomes insignificant.

Overall Rate Equation

From the corrections outlined above, an overall rate equation may be written for the isomerization of normal pentane:

$$r_A = \underbrace{\frac{\tanh(h)}{h}}_{\substack{\text{Term to correct}\\ \text{for flow into}\\ \text{pores}}} \underbrace{\left[\frac{k\left(K_A a_A - \dfrac{K_B a_B}{K} \right)}{(1 + K_A a_A + K_B a_B + K_C a_C)^2} \right]}_{\substack{\text{Reaction equation with}\\ \text{adsorption equilibrium}\\ \text{coefficients}}} \underbrace{\frac{\text{HRU}}{\text{HTU} + \text{HRU}}}_{\substack{\text{Term to correct}\\ \text{for diffusion}\\ \text{to and from the}\\ \text{surface}}} \tag{16}$$

Equation (16) may now be integrated to yield an expression for k:

$$k = \frac{S_w}{aM_p} \left[\frac{h}{\tanh(h)} \right] \left\{ \left[\ln \frac{1}{1 - a\xi} \frac{\left[1 + bK_A \left(\nu_A c + \dfrac{K_c}{K_A} \dfrac{n_c}{n_{A_0}} \right) \right]^2}{b\, K_A\, \nu_A} + 2\xi \left(1 - \frac{K_B}{K_A} \right) \left[1 + bK_A \left(\nu_A d + \frac{K_c}{K_A} \frac{n_c}{n_{A_0}} \right) \right] \right] - \xi^2 \frac{b\, K_A\, \nu_A}{2} \left(1 - \frac{K_B}{K_A} \right)^2 \right\} \left[\frac{\text{HRU} + \text{HTU}}{\text{HRU}} \right] \tag{17}$$

CORRELATION OF THE DATA

Carr (*3*) has presented data on a designed statistical experiment to describe the rate equation for the isomerization of n-pentane in a hydrogen atmosphere at 750°F. The data were obtained at weight hourly space velocities of 60 g. n-pentane/hr./g. of catalyst, and therefore the effect of diffusion to the catalyst surface was negligible. To fit the data, it was assumed that the value of h in the pore diffusion correction was small, and thus the correction for diffusion in the catalyst pores was negligible.

From Equation (16), the data were fitted with $K = 2.18$, and the following constants were obtained

$$K_A = 1.80 \times 10^{-2},\ \frac{K_B}{K_A} = 1.5,\ \frac{K_c}{K_A} = 2.0$$

with an average value of 0.90 for ν_A, $k = 137$ g./hr./g. catalyst or 1.90 g. moles/hr./g. of catalyst. Thus the adsorption equilibrium constants for isopentane and hydrogen are 1.5 and 2.0 times, respectively, those for n-pentane. A comparison of the fit of Equation (16) with an equation suggested by Carr is shown in Table 3.*

Sinfelt et al. (*19*) present data for the isomerization of normal pentane over a platinum on alumina catalyst at 700°F. Since Sinfelt used an integral flow reactor, one might expect to fit his data using Equation (22). Sinfelt obtained his data at space velocities of 9 and 25 g. of n-pentane/hr./g. of catalyst. At the twenty-five space velocity level, no correction was needed for the effect of diffusion to the catalyst surface; however, for the space velocities of 9, $\left[\dfrac{\text{HRU} + \text{HTU}}{\text{HRU}} \right] = 1.11$ was used. As with Carr's data, the value of h in the pore diffusion correction [Equation (15)] was assumed to be small, and thus the correction for diffusive flow within the catalyst pores was negligible.

For the analysis of Sinfelt's data, the following constants were used in Equation (23): $a = 1.649$, $c = 1.303$, $d = 1.152$, $K = 2.31$; adsorption equilibrium constants were assumed the same as those obtained from Carr's data. Since all of Sinfelt's data were taken at 700°F., a constant value of k should be obtained. Table 4* shows the results of this calculation. The equation does only a fair job of fitting the data with an average variation of 27% from the average value of k; however, considering the fact that there are only nine data points and that the data were taken over a wide range of hydrogen to hydrocarbon mole ratios, the fit is acceptable. If data were available to make a complete study of the exact adsorption and pore diffusion effects existing over this wide range of hydrogen/hydrocarbon ratios, a closer fit could be obtained.

Correlation of data from this work was accomplished by means of Equation (17). The effect of diffusion to the surface of the catalyst from the main bulk stream was negligible, so that $\left[\dfrac{\text{HRU} + \text{HTU}}{\text{HRU}} \right] = 1.0$. The pore radius as calculated from the pore volume V_g, and the specific surface S_g is 32.8Å. This is an average pore radius, but a distribution of pore sizes may be calculated from methods of Schull (*18*) and Barrett et al. (*1*).

When one uses the ranges of conditions of the experimental runs, values for the components of the total diffusion coefficient D_T may be calculated. The results of the evaluation show that the contributions of both Knudsen flow and Poiseuille flow are insignificant, and therefore $D_T = D_B$ and values of D_B were found from Equation (8). Since for a given gas mixture at isothermal conditions all the factors in Equation (8) are constant except P_T

$$D_T = D_B = \epsilon / P_T \tag{18}$$

If a further assumption is made that the value of h in the pore flow correction is greater than 2.0, then

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* See footnote on p. 909.

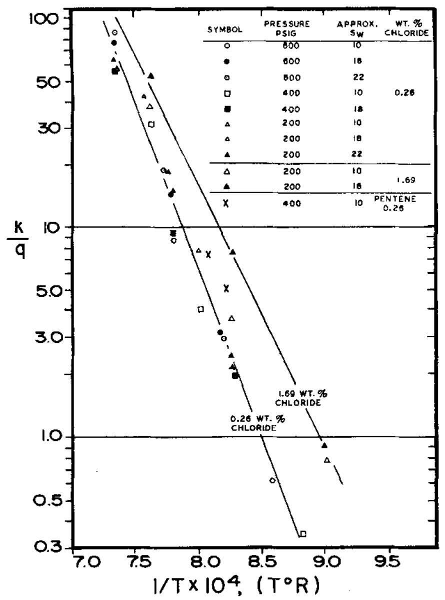

Fig. 2. Arrhenius plot of data.

$$\frac{h}{\tanh h} \simeq h \simeq \frac{2v_p}{S_x}\sqrt{\frac{k_s}{r\,D_T}} = q\sqrt{P_T} \qquad (19)$$

When one uses the above-mentioned substitutions, Equation (17) is simplified to give a relationship for k/q. The data, presented in Table 5,* obtained from the various runs were substituted into the equation and k/q obtained. Adsorption equilibrium constants from Carr's data were used in the evaluation. The results of the calculations are shown in Figure 2. As can be seen, the plot of ln (k/q) vs. $1/T$ gives a straight line indicating the Arrhenius form. The slopes of the lines in Figure 2 may be used to determine the energy of activation of each of the catalysts:

$E^* = 74{,}200$ B.t.u./lb. mole	for the catalyst containing 0.26 wt. %
$E^* = 57{,}500$ B.t.u./lb. mole	for the catalyst containing 1.69 wt. %

DISCUSSION AND CONCLUSIONS

The isomerization of normal pentane over a solid catalyst takes place on two distinct sites; a hydrogenation-dehydrogenation site, characterized by the metal component of the catalyst, and an isomerization site, characterized by the acidic component of the catalyst.

If a dual-site mechanism of the Langmuir-Hinshelwood type is used, and if the adsorption coefficients are assumed not to vary greatly with the type of acid-metal catalyst, then it is necessary to include a term in the kinetic equation to account for diffusive flow within the catalyst pores. This diffusion effect is definitely a major factor in determining the rate of reaction for some catalysts.

From the data of Carr, Sinfelt et al., and the data of this work, it is possible to compare the isomerization activities of the catalysts used, since all the data satisfy the same equation. For purposes of comparison, a temperature of 700°F. and a pressure of 200 lb./sq. in. gauge are used. Carr's data were adjusted with a relationship suggested by Carr:

$$\frac{\Delta r_A}{r_A} = \left(\frac{\Delta E^*}{RT^2}\right)\Delta T \qquad (20)$$

The results of the comparison of activities are given below:

$$\left[\frac{\tanh(h)}{h}k\right]_{\substack{\text{Sinfelt}\\700^\circ\text{F.}}} = 1.15\,\frac{\text{g. moles converted}}{(\text{g. catalyst})(\text{hr.})}$$

$$\left[\frac{\tanh(h)}{h}k\right]_{\substack{\text{Carr}\\700^\circ\text{F.}}} = \frac{1.90}{1+\left(\frac{\Delta E^*}{RT^2}\right)\Delta T} = 0.690\,\frac{\text{g. moles converted}}{(\text{g. catalyst})(\text{hr.})}$$

$$\left[\frac{\tanh(h)}{h}k\right]_{\substack{\text{This work}\\1.69\text{ wt.\% Cl}_2\\700^\circ\text{F.}}} = \frac{2.50}{(P_T)^{1/2}} = 0.171\,\frac{\text{g. moles converted}}{(\text{g. catalyst})(\text{hr.})}$$

Obviously, the catalyst used by Sinfelt was more active than Carr's and that used in this work.

ACKNOWLEDGMENT

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NOTATION

a = quantity defined for simplification of the rate equation, dimensionless

$$a = \left(1 + \frac{K_B}{K_A K}\right)$$

a_i = activity of a chemical species, i, dimensionless

$$a_i = \frac{\nu_i P_T}{f_o}\left(\frac{n_i}{n_T}\right)$$

a_p = surface area of a pellet, sq. ft.

b = quantity defined for simplification of the rate equation, dimensionless

$$b = \frac{P_T}{f_o}\,\frac{n_{A_o}}{n_T}$$

c = quantity defined for simplification of the rate equation, dimensionless

$$c = \frac{K_B}{K_A a}\left(1 + \frac{1}{K}\right)$$

C_{A_o} = concentration of reactant A at the pore mouth in moles/cc.

d = quantity defined for simplification of the rate equation, dimensionless

$$d = \frac{2a + K_B/K_A - 1}{2a}$$

D = diffusion coefficient in a catalyst pore, sq. cm./sec.

D_B = bulk diffusion coefficient, sq. cm./sec.

D_K = Knudsen flow diffusion coefficient, sq. cm./sec.

D_P = Poiseuille flow diffusion coefficient, sq. cm./sec.

D_T = overall or total diffusion coefficient, sq. cm./sec.

E^* = energy of activation, cal./g. mole or B.t.u./lb. mole

F = feed rate, g. moles of total feed/hr.

f = fraction of internal catalyst surface area available to a reaction; defined as the ratio of observed reaction rate to the rate which would be observed if this area was exposed on a plane surface, dimensionless

f_o = unit fugacity equal to 1.0 atm.

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* An abbreviated tabulation is presented as Table 5. For the entire table see footnote on p. 909.

G = mass velocity
h = dimensionless parameter which determines the fraction of surface available

$$h = \frac{2\,v_p}{s_x} \sqrt{\frac{k_s}{rD}}$$

k_s = reaction rate constant per unit (internal) surface area of the catalyst, volume reacted/unit time/unit surface area
k_{A_1} = adsorption rate constant for component A, weight adsorbed/unit time/unit weight of catalyst
$k_{A_{-1}}$ = desorption rate constant for component A, weight desorbed/unit time/unit weight of catalyst
k = reaction rate constant per unit weight of catalyst, g. moles/reacted/hr./g. of catalyst
K_i = adsorption equilibrium constant for component i, dimensionless
K = reaction equilibrium constant, dimensionless
L = distance from the mouth of a catalyst pore to the center of the pore, cm.
M = molecular weight of a gas or gas mixture
M_r = reduced molecular weight = $\left(\frac{M_A + M_C}{M_A\, M_C} \right)$
n_{Ao} = moles of component A per mole of total feed at the beginning of a reaction (in the equations in this paper, n_{Ao} is always equal to the total moles of pentane
n_A = moles of normal pentane per mole of total feed
n_C = moles of hydrogen per mole of total feed
n_T = 1.00 = total moles per mole of total feed
N_{Re} = modified Reynolds number, dimensionless

$$N_{Re} = \frac{\sqrt{a_p}\,G}{\mu}$$

P_T = total pressure
P_i = partial pressure of component, i, lb./sq. in. abs.
q = relationship used to group all constants in the pore diffusion relationship into one term, q has the units of (lb./sq. in. abs.)$^{-1/2}$

$$q = \frac{2v_p}{S_x} \sqrt{\frac{k_s}{\bar{r}\,\epsilon}}$$

r = pore radius, cm.
$\bar{r}$ = approximate average pore radius for a catalyst, cm.

$$\bar{r} = \frac{2V_g}{S_g}$$

r_A = reaction rate, g. moles of A converted/g. catalyst/hr.

$$r_A = F\,\frac{dx}{dw}$$

r_s = reaction rate at the catalyst surface, g. moles converted/g. catalyst/hr.
r_{AD} = rate of adsorption, g. adsorbed/g. catalyst/hr.
R = gas constant
S_x = external geometrical surface area per catalyst pellet
S_g = internal or total surface area per gram of catalyst, sq. cm./g.
S_w = weight hourly space velocity, g. of pentane feed/hr./g. of catalyst
t = time
T = temperature
v_p = geometrical volume of a single catalyst pellet, including pore space, cc.
V_g = catalyst pore volume per gram of catalyst, cc./g.
w = weight of catalyst, g.
x = moles of pentane converted per mole of total feed
X = distance down a catalyst pore, $X = 0$ at mouth of pore

$$\alpha = \frac{n_{Ao}}{n_T}$$

Greek Letters

ϵ = $D_B\, P_T$, (sq. cm./sec.) (lb./sq. in. abs.)
θ = fraction of voids within the catalyst pellet
θ_i = fraction of active catalyst sites occupied by component i
λ = mean free path, cm.
μ = viscosity
ν_i = fugacity coefficient of component i
ξ = fraction of pentane converted, x/n_A
π = 3.1416
ρ = density, lb./cu. ft. or g./cc.
σ_{12} = $\frac{1}{2}\,(\sigma_1 + \sigma_2)$
σ = symbol used to indicate an active catalyst surface site
Ω_D = collision integral, used in the Hirschfelder relationship for the bulk diffusion coefficient

Subscripts

A = n-pentane
B = iso-pentane
C = hydrogen
V = vacant
i = any component
1 = forward
-1 = reverse

LITERATURE CITED

1. Barett, E. P., L. G. Joyner, and P. P. Halenda, *J. Am. Chem. Soc.*, **73**, 373 (1951).
2. Brennan, H. M., H. S. Sellig, and R. W. Vander Harr, *U.S. Pat. 2,840,514* (1958).
3. Carr, N. L., *Ind. Eng. Chem.*, **52**, 5 (1960).
4. Ciapetta, F. G., and J. B. Hunter, *ibid.*, **45**, 147 (1953).
5. ———, *Petro./Chem. Eng.*, **5**, C-19 (1961).
6. Heard, L., *U.S. Pat. Reissue 22, 196* (1942).
7. ———, and M. J. Den Herder, *U.S. Pat. 2,659,701* (1953).
8. Heinemann, H., and G. A. Mills, *U.S. Pat. 2,798,105* (1957).
9. Hinshelwood, C. N., "Kinetics of Chemical Change," Oxford University Press, New York, New York (1941).
10. Hobbs, J. L., M.S. thesis, University of Houston, Houston, Texas (1961).
11. Hurt, D. M., *Ind. Eng. Chem.*, **35**, 522 (1943).
12. Knudsen, M., "The Kinetic Theory of Gases," Methmen's Monograph Series, Wiley, New York (1950).
13. Krause, A., *Nature*, **183**, 1615 (1959).
14. Lyster, W. M., M.S. thesis, University of Houston, Houston, Texas (1962).
15. Miesserov, K. G., O. E. Morozova, and A. A. Petrov, *Chem. Abs.*, **50**, 4611i (1956).
16. Mills, G. A., H. Heinemann, T. H. Milliken, and A. G. Oblad, *Ind. Eng. Chem.*, **45**, 134 (1953).
17. Reid, R. C., and T. K. Sherwood, "The Properties of Gases and Liquids," pp. 268-71, McGraw-Hill, New York, New York (1958).
18. Shull, C. G., *J. Am. Chem. Soc.*, **70**, 1405 (1948).
19. Sinfelt, J. H., H. Hurwitz, and J. C. Rohrer, *J. Phys. Chem.*, **64**, 892 (1960).
20. Stumpf, H. C., A. S. Russell, J. W. Newsome, and C. M. Tucker, *Ind. Eng. Chem.*, **42**, 1398 (1950).
21. Thiele, E. W., *ibid.*, **31**, 916 (1939).
22. Universal Oil Products Co., British Pat. 823,010 (1959).
23. Walas, S. M., "Reaction Kinetics for Chemical Engineers," p. 157, McGraw-Hill, New York, New York (1959).
24. Weisz, P. B., and E. W. Swegler, *Science*, **126**, 31 (1957).
25. Wheeler, A., "Advances in Catalysis, III," p. 249, Academic Press, New York, New York (1951).
26. Yang, K. H., and O. A. Hougen, *Chem. Eng. Progr.*, **46**, No. 3, p. 146 (1950).

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