Hydroisomerization of Normal Pentane over a Zeolite Catalyst

ALEXIS VOORHIES, JR. and PHILIP A. BRYANT

Louisiana State University, Baton Rouge, Louisiana

The most active zeolite hydroisomerization catalyst found during the course of a series of screening experiments was palladium impregnated hydrogen mordenite. The high activity of hydrogen mordenite catalyst was also reported by research workers of the Shell Oil Company. *(11)* Typical conditions used in this study were 550°F., 450 lb./sq.in. gauge, 8 g. of *n*-pentane fed /h./g. of catalyst, and a hydrogen/pentane molar ratio of 3.4.

Process variable studies have shown that neither gas to particle mass transfer, intraparticle (macro-pore) diffusion, nor the chemical reactions at the palladium sites are rate limiting. The data can be correlated by a mathematical model based on the assumptions that a first-order, reversible isomerization reaction on the mordenite acidic sites is rate-controlling, and the apparent rate constant is an Arrhenius function of the temperature of the system.

The pressure dependency of the reaction rate constant is consistent with a dual-site mechanism and Langmuir adsorption isotherms.

The isomerization of normal paraffins is a reaction which finds important applications in the octane improvement processes used in the manufacture of gasoline. Generally, these processes use solid catalysts in packed beds. The catalysts have been typically composed of a dispersed metal on conventional supports such as alumina or silica-alumina (6, 9). Recently, crystalline zeolites have been proposed as catalysts in isomerization systems (7, 8). This paper describes the results of an investigation of the isomerizing properties of synthetic mordenite, a member of the crystalline zeolite family. The pentane system was used in this work. An isomerization catalyst based on mordenite has been found to be considerably more active than a similar catalyst based on faujasite, that was employed for comparison because of its high activity.

Mordenite is a unique material in that it has a remarkable crystalline structure consisting of a three-dimensional crystalline network of silicon, aluminum, and oxygen atoms (3). This structure is such that parallel micropores, only 6 to 7Å in diameter, traverse the entire crystal (somewhat analogous to a "bundle of soda straws"). The center to center distances of the pore openings are 15 to 20Å. Inside these pores, the reactant molecules (4 to 5Å in length) are subjected to intense electrostatic fields which tend to strain, distort, and even rupture the hydrocarbon molecules. This results in an extremely reactive system, which can even be modified to some extent by impregnation with catalytic metal atoms.

EXPERIMENTAL SYSTEM

The catalysts used for this research were prepared by the Esso Research Laboratories in Baton Rouge, Louisiana. The original mordenite crystals were 1 to 5μ particles. After being pilled, the catalysts were crushed to provide particles of approximately 0.6 mm. diameter. An Inconel reactor, 8 in. high by 0.62 in. diameter was used. Figure 1 shows a sketch of the reactor system. A fluidized sand bath was used to provide an isothermal system. Liquid normal pentane (99 mole % pure) was fed by a Ruska pump, while dry electrolytic hydrogen was fed from a cylinder through a rotameter. Prior to introduction of the pentane the feed rate of hydrogen was adjusted by a wet test meter downstream of the reactor. An F & M gas chromatograph was used to analyze the product gases. Material balances, calculated by comparing the actual gram moles of product gases to the total expected gram moles, ranged from 98 to 102%.

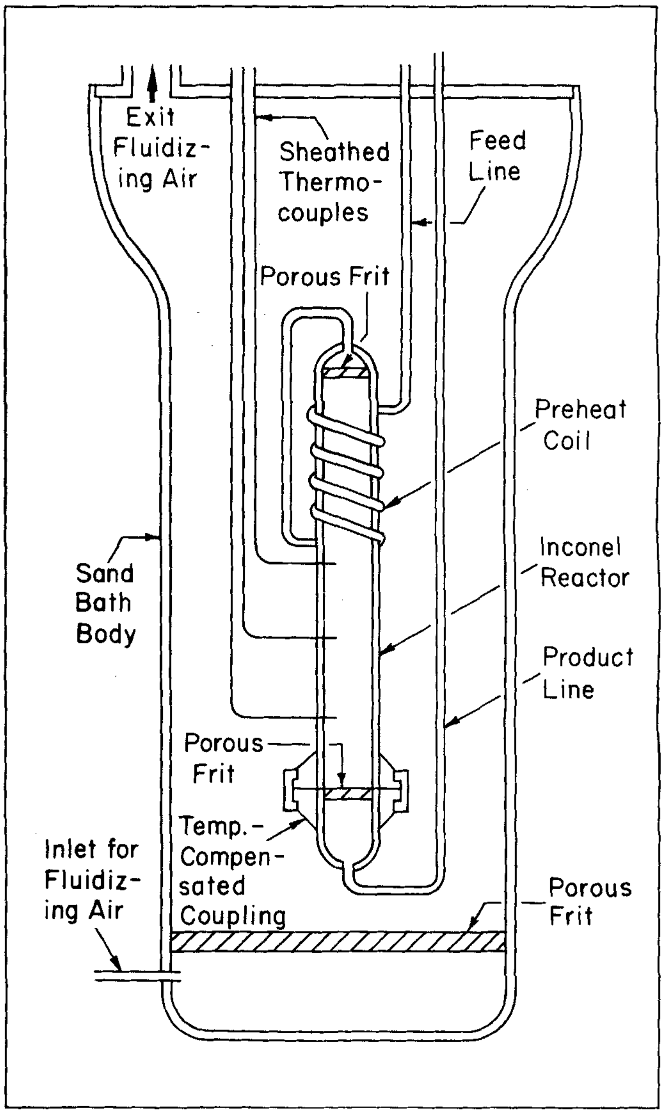

Fig. 1. Details of reactor system.

INITIAL SIMPLIFIED MODEL

In order to provide a quantitative measure of the overall isomerization activity of a given catalyst, a simplified mathematical model was used in the initial phases of this study. The rate of reaction, r, expressed as g.-moles of i-pentane produced/hr./g. of catalyst, was assumed to be

$$\frac{dN_i}{dW_c} = r = k\,[C_n - C_i/K] \tag{1}$$

This model assumed a first-order reversible isomerization reaction to be controlling. The forward rate constant, k, was assumed to be independent of the system partial pressures. All of the early runs in this study were made at a constant hydrogen/pentane ratio (3.42/1) and a constant total pressure (450 lb./sq.in.gauge). Thus, the hydrogen partial pressure and the total pentane partial pressure were also constant.

TABLE 1. COMPARISON OF MORDENITE-BASED CATALYSTS WITH FAUJASITE-BASED CATALYSTS

Catalyst Base	Hydrogen-faujasite			Hydrogen-mordenite						
Impregnated metal	Pd			None	Pd					
%	0.5			0.0	0.2	0.5				1.0
Temperature, °F.	650			550						
Pressure, lb./sq.in.gauge	450									
Feed Rate, w./hr./w*	9.49	4.91	9.82	9.73	7.95	7.50	7.56	7.56	15.86	7.66
H_2 rate, moles/mole	3.42	3.93	3.85	3.39	3.46	3.45	3.45	0.71	0.69	3.48
Product Composition										
% i-C_5 in p-C_5†	50.2	58.3	45.7	40.2	39.4	37.1	43.4	61.4	46.9	40.1
wt. % ($C_1 - C_4$)	0.4	0.7	0.3	2.4	1.0	0.75	0.8	3.0	1.0	1.0
k, cc. g.$^{-1}$ sec.$^{-1}$	0.25	0.21	0.23	0.14	0.12	0.10	0.13	0.11	0.12	0.12

* Grams of n-pentane fed per hour per gram of catalyst.
† $i-C_5$ = iso-pentane.
$p-C_5$ = total paraffinic pentanes (iso + normal).

TABLE 2. TESTS FOR MASS TRANSFER AND DIFFUSIONAL RESISTANCES

Catalyst	½ % Pd on H-mordenite					
Temperature, °F.	550					
Pressure, lb./sq.in.gauge	450					
H_2 rate, moles/mole	3.45	3.45	3.56	3.41	3.43	3.45
Gas velocity, cm./sec.	0.49	0.99	2.02	1.00	0.98	0.99
Particle size, mm.	0.42-0.84			0.074-0.149	0.30-0.42	0.84-1.15
Feed rate, w./hr./w.	6.55	7.49	7.49	10.85	7.26	6.86
Product Composition						
% i-C_5 in p-C_5	43.6	37.1	37.4	29.4	43.5	42.5
wt. % ($C_1 - C_4$)	0.7	0.6	0.5	0.5	0.8	0.6
k, cc. g.$^{-1}$ sec.$^{-1}$	0.11	0.10	0.10	0.11	0.12	0.11

Integration of this equation led to the following relationship:

$$\frac{Y_i}{Y_i^*} = 1 - e^{\left(\frac{k\,M\rho_G}{Y_i^*\,W\,(1 + R_H)}\right)} = 1 - e^{-kt_H\,\rho_B/Y_i^*} \tag{2}$$

Thus, at constant temperature (k constant; Y_i^* constant) the conversion should be a function of the superficial holding time and the bulk density of the catalyst.

The apparent forward rate constant, k, was calculated as

$$k = -\frac{W(1 + R_H)Y_i^*}{M\rho_B}\ln\left[1 - \frac{Y_i}{Y_i^*}\right] \tag{3}$$

Table 1 shows a comparison of data taken with two different catalysts, ½% palladium on hydrogen faujasite and ½% palladium on hydrogen mordenite. These data showed that the latter catalyst could be used at approximately 100°F. lower temperature, with a conversion equivalent to the faujasite catalyst. In the light of this high activity, these initial runs were followed by a series of runs intended to shed some light on the *mechanisms* involved in the overall conversion process on a catalyst composed of palladium impregnated hydrogen mordenite.

FLUID TO PARTICLE MASS TRANSFER

In order to determine whether fluid to particle mass transfer was a limiting step in the overall conversion process, several runs were made in which the superficial velocity was varied over a four-fold range, with the other variables being maintained relatively constant (feed rates and the length of the catalyst bed were changed in the same proportions). Table 2 shows the results of these runs. As can be seen, the rate constants calculated from these data were the same (within experimental error) for all runs, showing the mass transfer from the bulk gas stream to the particle surface was not a limiting factor under these conditions.

INTRAPARTICLE DIFFUSION

In order to determine whether diffusion inside the crushed particles (normally 0.42 to 0.84 mm. diameter) was a limiting factor, a series of runs was made in which the size of the crushed particles was varied over a ten-fold range. As can be seen in Table 2, the rate constants were again constant, showing that the simple model (which assumed no significant diffusional resistance) was adequate under these conditions.

This, however, is not to say that diffusion inside the mordenite crystals was not a limiting factor in the overall conversion process. The particles whose size was varied in the above runs were actually agglomerates of the original 1 to 5μ particles. Of the two pore systems that were in series in the overall conversion process, the micropores (Figure 2) certainly offered the controlling diffusional resistance. Diffusion inside these micropores was not systematically investigated due to the lack of mordenite crystals with different particle size ranges.

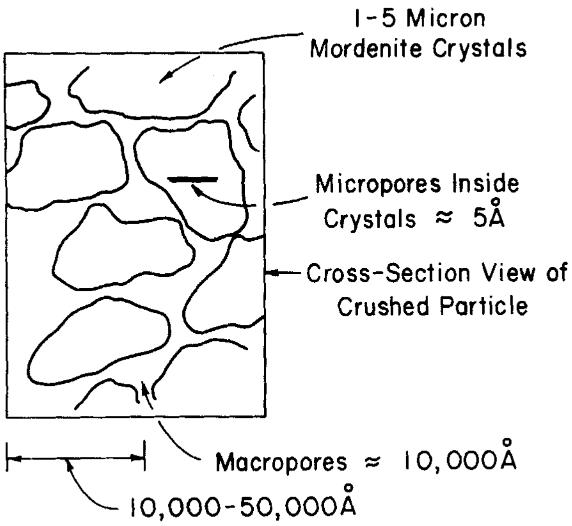

Fig. 2. Macropores vs. Micropores.

POSTULATED REACTION MECHANISM

The currently accepted mechanism for the hydrosiomerization of a normal paraffin is a three-step process, with a dehydrogenation reaction occurring on a metal site and a subsequent structural rearrangement of the normal olefin on an acidic site. The resulting iso-olefin is thought to be hydrogenated to an iso-paraffin at another metal site.

This theory was tested by Weisz and Swegler (*10*) who prepared a dual-function catalyst by mechanically mixing particles of silica-alumina (isomerizing component) with particles composed of platinum (dehydrogenation component) supported on an inert base. Provided the particles were small enough (less than 1μ), this mixture was as active as were catalysts prepared with both catalytic functions on the same particle. The individual types of particles showed essentially no activity when tested alone. These experiments demonstrated that the two types of sites act independently, and that the reaction intermediates are able to diffuse, through the gas phase, from one type of catalytic site to another. Although such a step-by-step mechanism is in accord with the available experimental data, there is some disagreement in the literature as to which step in the reaction sequence controls the overall rate (*2, 5, 6, 8*).

REACTIONS AT PALLADIUM SITES

A series of runs was made with varying amounts of impregnated palladium on the crystalline catalyst. Table 1 shows the results of these runs. As can be seen, the concentration of palladium had no effect on the overall isomerization rate.

The addition of significant amounts of hydrogenation-dehydrogenation sites in the form of dispersed palladium atoms did not increase the overall reaction rate, indicating that the reactions promoted by those sites were not rate controlling. All the data taken during this study were compatible with the assumption that the isomerization sites, whose concentration was proportional to the amount of crystalline mordenite, were the sites of the rate limiting reactions.

THE EFFECT OF TEMPERATURE

Data were taken at 450 lb./sq.in.gauge over a range of temperatures, ranging from 500 to 600°F. These data, shown in Table 3, show a marked effect of temperature on the overall rate of reaction. An Arrhenius plot of the rate constants (Figure 3) shows an apparent activation energy of about 55,000 B.t.u./lb. mole, which is consistent with values reported in the literature for this isomerization reaction (*5, 6*).

TABLE 3. VARIATION OF REACTION RATE WITH TEMPERATURE

Catalyst	½ % Pd on H-mordenite				
Pressure, lb./sq.in.gauge	450				
Hydrogen, moles/mole	3.43	3.42	3.39	3.45	3.40
Feed rate, w./hr./w.	4.08	3.97	8.11	7.49	15.9
Temperature, °F.	500	500	525	550	600
Product Composition					
% i-C_5 in p-C_5	22.6	28.3	22.6	37.1	62.5
wt. % ($C_1 - C_4$)	0.1	0.4	0.2	0.7	3.7
k, cc. $g.^{-1}$ $sec.^{-1}$	0.026	0.034	0.051	0.10	0.75

THE EFFECT OF PRESSURE ON CONVERSION

As was indicated earlier, the rate constant, k, in the simplified model used thus far in the study was assumed to be independent of the partial pressures of the various gas-phase components. However, a mathematical model

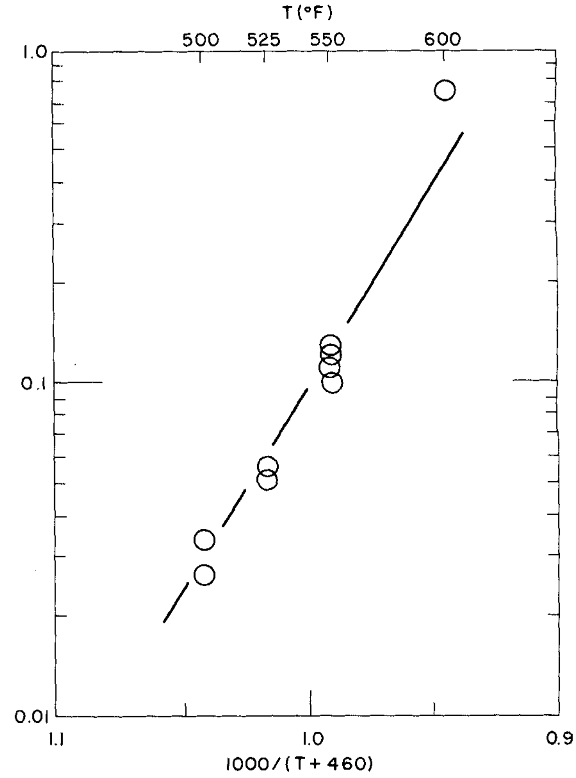

Fig. 3. Effect of temperature on rate constant at 450 lb./sq./in. gauge.

based on Langmuir-type adsorption isotherms will lead to the equation:

$$\frac{dN_i}{dW_c} = r = \left[\frac{k_o}{(1 + \Sigma K_j p_j)^n} \right] [C_n - C_i/K] \quad (4)$$

The first term in brackets, which corresponds to k, is seen to be a function of the partial pressures of the gas-phase components if the individual $K_j p_j$ terms are large compared to 1.0. In the case of a single site mechanism, wherein only one vacant site is sufficient for the isomerization reaction, $n = 1$. If a dual site mechanism prevails, $n = 2$. The latter case can arise for example, if a molecule can undergo reaction after being adsorbed on an active site only if it is adjacent to a vacant active site. If the isomerization step is governed by a dual-site mechanism, the structural rearrangement will take place only if the molecule, after being adsorbed onto one active site, can complex with an adjacent (unoccupied) active site. Only in the form of this complex (one molecule and two active sites) is the molecule sufficiently energized to react.

TABLE 4. EFFECTS OF SYSTEM PARTIAL PRESSURES ON REACTION RATE

Catalyst	½ % Pd on H-mordenite							
Temperature, °F.	525				550			
Total Pressure, lb./sq.in.abs.	465				267	465	431	235
Feed rate, w./hr./w.	8.1	7.8	7.8	8.1	7.66	7.66	3.83	3.83
Pentane partial pressure, lb./sq.in.abs.	265	237	127	106	66	67	34	34
Hydrogen partial pressure, lb./sq.in.abs.	200	228	338	359	201	398	397	201
H_2/C_5, moles/mole	0.75	0.96	2.7	3.4	3.0	5.9	11.9	6.0
Superficial holding time, sec.	20.2	18.0	9.6	8.1	4.9	5.0	5.0	5.0
Product Composition								
% i-C_5 in p-C_5	44.4	42.3	26.3	22.6	45.6	26.1	28.8	47.5
wt. % ($C_1 - C_4$)	1.3	0.8	0.8	0.2	1.2	0.4	0.4	1.3
k, cc. g.$^{-1}$ sec.$^{-1}$	0.055	0.055	0.053	0.053	0.23	0.10	0.11	0.24

In an effort to determine whether these partial pressure terms were significant, four runs were made in which the hydrogen partial pressure and the total pentane partial pressure were systematically varied. The results are shown in Table 4. As can be seen, k was definitely not a constant in these runs, indicating that the system partial pressures did affect the value of the apparent rate constant. Since all the runs were made at relatively high ratios of hydrogen/pentane (in order to prevent coking), the effects of hydrogen partial pressure and the total system pressure were confounded in these runs.

An additional set of runs was made at a constant total pressure, with varying ratios of hydrogen/pentane. In this set of runs, the rate constants were seen to be constant in spite of the varying hydrogen and pentane partial pressures. As shown in Table 4, these data indicate that the rate constant is a function of the total system pressure, not of the individual partial pressures. Figure 4 shows the relationship between k and total pressure for all the runs in this study.

These findings are consistent with Equation (4) only if the adsorption equilibrium constants for hydrogen, normal pentane, and isopentane are approximately equal.

In this case,

$$k = \frac{k_o}{(1 + \Sigma K_j p_j)^n} = \frac{k_o}{(1 + K_o \Sigma p_j)^n} = \frac{k_o}{(1 + K_o P_T)^n} \quad (5)$$

k is seen to be a decreasing function of total pressure.

If $n = 1$,

$$\frac{1}{k} = \frac{1}{k_o} + \frac{K_o}{k_o} P_T \quad (6)$$

If $n = 2$,

$$\frac{1}{\sqrt{k}} = \frac{1}{\sqrt{k_o}} + \frac{K_o}{\sqrt{k_o}} P_T \quad (7)$$

Figures 5 and 6 show plots of the data testing Equations (6) and (7). In the former figure, the intercepts are all negative, implying that k_o is negative, which is physically unrealistic. The latter figure shows that the data are consistent with a dual-site mechanism in that the intercepts are all positive. Figure 6 indicates that the apparent rate constant will continue to increase as the

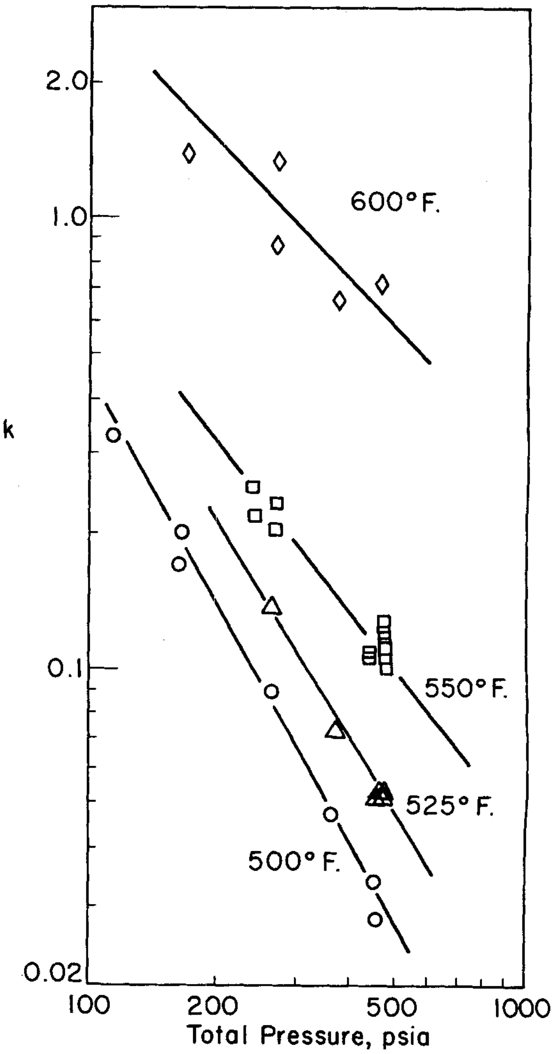

Fig. 4. Effect of temperature and pressure on rate constant.

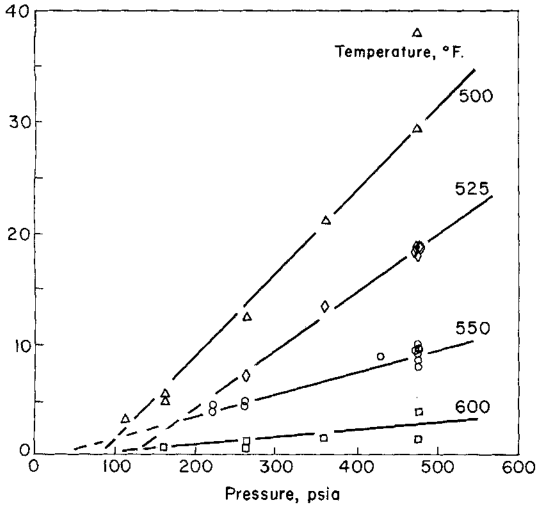

Fig. 5. Test of single site model.

pressure is reduced. This effect, however, cannot be extrapolated to lower pressures. At hydrogen partial pressures below 100 lb./sq.in.abs., coking becomes excessive, causing the catalyst to lose activity.

DISCUSSION OF MATHEMATICAL MODEL

Although the data can be fitted with a simplified mathematical model of the form of Equation (4), no definite statements can be made concerning the true nature of the intracrystalline adsorption, diffusion, or reaction mechanisms. These occur in an environment totally different from those normally assumed in the derivations of the equations governing catalytic processes in conventional porous catalysts. For example, the pore diameters are only about 20% larger than the reacting molecules! The adsorption constants in this equation would normally be expected to be functions of the type of catalyst used, the specific methods of preparation and activation, and the type of reactions occurring on the active sites.

The measured effects of the various process variables (which are dependent upon the catalysts being used and their methods of preparation and activation) are specific for the particular catalysts used and their methods of preparation and activation, and for the particular catalysts used in this study. Although similar zeolite catalysts would not be expected to show quantitatively the same characteristics, they should show qualitatively similar responses.

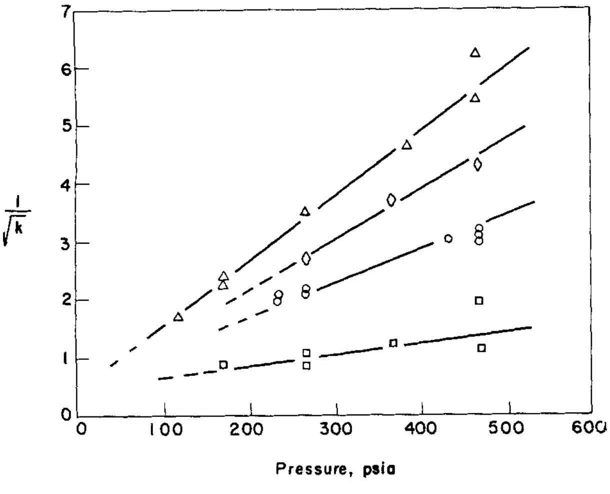

Fig. 6. Test of dual site model.

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NOTATION

C_i = concentration of iso-pentane, moles/unit volume
C_n = concentration of normal pentane, moles/unit volume
k = apparent forward rate constant (in general, a function of temperature and system partial pressures)
k_o = hypothetical apparent forward rate constant at zero pressure (in general, a function of temperature only)
K = thermodynamic equilibrium constant
K_j = adsorption equilibrium constant for component j
K_o = mean adsorption equilibrium constant for hydrogen, *i*-pentane and *n*-pentane.
M = molecular weight of pentane
N_i = molar flow rate of iso-pentane
n = exponent, 1.0 for single-site mechanisms; 2.0 for dual-site mechanisms.
P_T = total pressure
p_j = partial pressure of component j
R_H = molar ratio of hydrogen/pentanes
r = rate of reaction, g. moles iso-pentane produced per unit time per unit mass of catalyst
T_F = temperature, °F.
t = time
t_H = superficial holding time
W = pentane feed rate, g./hr./g. catalyst
W_c = weight of catalyst in reactor
Y_i = hydrogen-free mole fraction of iso-pentane
Y_i^* = hydrogen-free mole fraction of iso-pentane at equilibrium, ($Y_i^* = 79.46 - 0.026428\ T_F + 2125/T_F$; $500 \leq T_F \leq 600$)
ρ_B = bulk density of catalyst
ρ_G = molar density of reactor gases at reactor conditions

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