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Application of the Single Pellet Reactor for Direct Mass Transfer Studies

II. Measurement of Composition at Center of Catalyst Pellet*

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A reactor has been designed for measuring simultaneously the bulk reaction rate and the composition at the center of a single catalyst pellet. The hydrogenolysis of cyclopropane on an alumina-supported platinum catalyst is studied. The effective diffusivity calculated from these kinetic experiments is found to be identical with the value predicted from physical measurements on the same pellet for catalysts of uniform activity. For catalysts having nonuniform activity the "kinetic" diffusivity was found to be 25% below the "physical" values.

INTRODUCTION

In Part I of this paper, the mass transfer behavior of a binary gas mixture in an inert porous medium was explored. If the solid matrix can promote a chemical reaction, one has a heterogeneous catalytic system. The coupling of the mass transfer and chemical reaction effects has been studied by many investigators since the major contribution of Wheeler (*1*). Satterfield and Sherwood (*2*) have written on the subject of diffusion and catalysis, and Petersen (*3*) has applied the theories of mass and heat transfer to problems in reactor analysis. Both of these books contain extensive lists of references which may be consulted for a more thorough understanding of many of the areas to be discussed.

Most of the experimental work has entailed measurements of only the bulk-phase conditions surrounding the catalyst. The behavior within the pellet had to be inferred. In this paper, however, a technique is presented which allows direct measurement of the concentrations of the molecular species at the center of the catalyst pellet. These data permit more accurate conclusions to be drawn concerning the mass transfer process.

One topic to be considered is the calculation of the effective diffusivity from kinetic data. In the past there have been two approaches. First, reaction rate measurements are made on catalysts which are identical except for particle size. If the smallest particle size has an effectiveness factor close to unity, then from the effectiveness factors of the larger particles and from a knowledge of the kinetic rate expression it is possible to calculate the Thiele parameter [see Eq. (6)] and then the effective diffusivity. An example of this method is the work of Johnson, Kreger, and Erickson (*4*).

The second approach is the "triangle method" discussed by Weisz and Prater

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(*5*). Again rate data on particles of differing sizes are required. However, it is not necessary to use particles with effectiveness factors of unity. Instead, the theoretical relationship between the effectiveness factor and the particle size is used to fit the data. This method is limited to situations in which the Thiele parameter is near unity. The work of Weisz and Swegler (*6*) exemplifies this technique.

Some very elaborate procedures have been developed in an attempt to predict the diffusive behavior in both reacting and nonreacting situations. Perhaps the most numerous and most useful of all the articles written on this subject are those of Smith and his co-workers (*7–13*). In their approach the pseudocapillary model discussed in Part I is applied. This requires measurements of the porosity and pore-size distribution of the catalyst. Usually different pellets and sometimes different pellet configurations are employed in the reacting and nonreacting cases. When the predicted and observed behavior of the kinetic experiments disagree, one is not certain whether this difference is due to errors in the pseudocapillary model and the predicted diffusivities or whether there really is a difference between the diffusion coefficients for diffusion alone and for diffusion with chemical reaction.

This problem is circumvented by performing all measurements on a single pellet. This necessitates a rather novel design for the reactor. In the work of Hawtin and co-workers (*14, 15*) a cylindrical shell of graphite was used to study the effect of diffusion and bulk gas flow during the thermal oxidation of the graphite. Concentrations were measured for the interior and exterior portions of the cylinder. This design is awkward for catalysts because of the difficulty in pressing a pellet into a hollow cylindrical form and then sealing the ends.

Roiter *et al.* (*16*) designed a reactor in which gas streams flowed past the two plane faces of a solid cylindrical catalyst pellet. One stream contained fresh reactants while the other was recirculated. Again, concentration gradients within the pellet were detected by direct measurements of the gas concentrations at each face. One advantage of this technique is that the one-dimensional characteristic of the pellet lends itself to the standard methods for measuring diffusion and flow in a porous medium. For this reason a modified Roiter-type reactor was chosen for the present work.

In selecting a reaction system an important consideration is the attainable value of the Thiele parameter. If the intrinsic rate of reaction is too low it is difficult to measure accurately the activity of the catalyst. On the other hand, if the intrinsic rate is too high there will be nearly complete conversion of the reactants at the center of the catalyst, making accurate concentration analysis difficult. A Thiele parameter of approximately unity is frequently optimal.* The hydrogenolysis of cyclopropane was chosen because of the work of Dougharty (*17*) which gives the rate of this reaction on an alumina supported platinum catalyst as a function of the platinum content. This made it relatively easy to produce a catalyst with the proper value of the Thiele parameter.

The kinetics of the reaction have been studied extensively (*18–22*). Most studies reveal that for a supported platinum catalyst the reaction is approximately first order with respect to cyclopropane if the reaction is carried out in an excess of hydrogen. The order with respect to hydrogen is much less certain and depends on the methods employed in the preparation of the catalyst as well as on the temperature of the reaction. Usually it is a fractional order between 0 and −1.

NOMENCLATURE

c_0/μ	D'Arcy flow parameter (cm^2/sec torr)
C_A	Concentration of A (g moles/cc)
$D_{AB,\mathrm{eff}}$	Effective diffusivity of A in B (cm^2/sec)

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* Although for the present study the value of unity for the Thiele parameter is optimal, in some cases it is not. The reader should consult ref. (*3*) for a general discussion of this topic.

$D_{K,A}$	Effective Knudsen diffusivity of A (cm^2/sec)
$D_{K,mix}$	$x_A D_{K,B} + x_B D_{K,A}$
$\mathfrak{D}_{AB}$	Effective molecular diffusivity of AB binary (cm^2/sec)
$\mathfrak{D}_{AB}^0$	$\mathfrak{D}_{AB}P$
F_{eff}	Effective flow parameter, defined in Eq. (11)
h	Thiele parameter, $L\sqrt{(k/D_{AB,eff})}$ for first order reaction
k	Reaction rate constant
L	Thickness of pellet (cm)
n	Reaction order
N_A	Molar flux of A (g moles/cm^2 sec)
P	Total pressure (torr)
P_A	Partial pressure of A (torr)
r	Radius of pellet (cm)
R_g	Universal gas constant
$\mathcal{R}$	Overall rate of reaction (rate of conversion of cyclopropane) (g moles/sec)
T	Temperature (°K)
x_A	Mole fraction of A
y_C	Mole fraction of cyclopropane on hydrogen-free basis, $C_C/(C_C + C_P)$
z	One-dimensional coordinate in pellet (cm)
η	z/L
μ	Gas viscosity
Ψ_A	$C_A/C_A(0)$ for binary system

Subscripts

H	Hydrogen
C	Cyclopropane
P	Propane

Other

(0)	Refers to external pellet surface
(1)	Refers to center-plane of pellet

Experimental Technique

The catalyst was prepared from η-alumina which had been impregnated with chloroplatinic acid by the Chevron Research Corporation of California. The platinum content was 0.25% by weight. The impregnated powder was pressed into support rings as described in Part I. Because Vitron O-rings in the reactor prevented the reduction of the platinum catalyst *in situ*, the pellets were activated in a separate oven as follows:

The pellet was placed in the oven and purged with nitrogen. Then hydrogen was introduced at a rate of 2 cc/min and the oven was turned on. Over a 2-hr period the temperature rose to approximately 300°C. It was allowed to remain at this temperature for 30 hrs, after which the oven was turned off and allowed to cool over a 5-hr period. Two of the pellets, C and D, were cooled in the flowing hydrogen. Two others, A and B, were cooled in flowing nitrogen after the temperature had reached 150°C. The physical dimensions and densities of the pellets are listed in Part I.

In addition to the impregnated catalysts, a pellet was prepared from a mechanical mixture of platinum black and η-alumina (1% by weight platinum). This was activated *in situ* at 45°C in hydrogen for approximately 48 hrs.

The reaction studied was the hydrogenolysis of cyclopropane. The cyclopropane (Matheson, 99.0% purity) was passed over 10X molecular sieves and then was condensed and degassed. In the experiments, the hydrogen pressures ranged from 700 to 1000 torr and the cyclopropane pressures ranged from 25 to 200 torr. The temperature of reaction was usually 55°C. A diagram of the apparatus used is shown in Fig. 1.

The overall reaction rate was determined by periodically analyzing 1-cc samples of the recirculating gas. Gas analysis was performed with the Beckman GC-2A chromatograph described in Part I. Since the sampling syringe always contained small amounts of air, all experiments were carried out at pressures greater than atmospheric pressure in order to prevent contamination.

The center-plane gas was sampled by first evacuating a syringe connected to the center-plane chamber and then filling with 0.3 cc of sample. Although a batch reactor is essentially in unsteady-state operation, the rate of conversion in the experiments reported here was sufficiently small that effectively the system did operate at steady state.

THEORETICAL CONSIDERATIONS

This section will develop the operational characteristics of the single pellet-type reactor and in particular the quantitative relationships between the center-plane and the bulk-phase concentrations. The classic example of a catalytic reaction is the irreversible first order reaction in a single pore for the binary system

$$\mathrm{A} \rightarrow \mathrm{B}$$

With the assumption that the diffusion coefficient is constant, the dimensionless continuity equation becomes

$$d^2\Psi_A/d\eta^2 = h^2\Psi_A \qquad (1)$$

where k is the pseudo-first order rate constant (sec^{-1}). The boundary conditions of this equation are found by investigating the reactor geometry as depicted schematically in Fig. 2(A). At the external surface, the reactant concentration is specified

$$\Psi_A = 1 \qquad \text{at} \qquad \eta = 0$$

At the center plane the reaction rate is zero. At steady state, then, the concentration in this section must be constant, giving

$$d\Psi_A/d\eta = 0 \qquad \text{at} \qquad \eta = 1$$

Note that these boundary conditions are identical to those for the symmetric pellet depicted in Fig. 2(B). As a result, the concentrations at the center plane of reactor B and in the center-plane chamber of reactor A are identical.

The solution of Eq. (1) yields the following:

$$\mathcal{R} = \frac{\tanh(h)}{h}\pi r^2 LkC_A(0) \qquad (2)$$

$$\Psi_{A(1)} \equiv \frac{C_A(1)}{C_A(0)} = \frac{1}{\cosh(h)} \qquad (3)$$

where $\mathcal{R}$ is the overall reaction rate; r, the radius of pellet; and $C_A(1)$, the concentration of A at center plane. The value of the effective diffusivity may be determined from a *single* measurement of the overall rate and the corresponding surface and center-plane concentrations. To illustrate this procedure, h would be calculated from the measured $\Psi_A(1)$ using Eq. (3). Then k would be calculated from Eq. (2) and from the values of $\mathcal{R}$ and h. Finally,

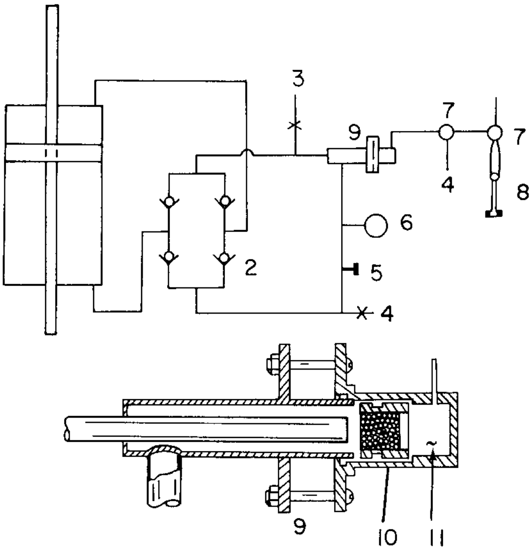

FIG. 1. Reaction apparatus. 1, Reciprocating piston pump; 2, ball check valves; 3, reactant feed inlet; 4, to vacuum pump; 5, septum for syringe sampling; 6, Bourdon-tube pressure gauge; 7, three-way valve; 8, 1-cc gas-tight syringe; 9, Roiter-type reactor; 10, sample catalyst pellet; 11, center-plane chamber.

$$D_{AB,\mathrm{eff}} = L^2k/h^2 \qquad (4)$$

The numerical value of the effective diffusivity, calculated from kinetic runs on a given catalyst pellet, can be compared to the value of the effective diffusivity obtained on the same pellet by the direct physical measurement described in Part I. Such a calculation of course assumes a

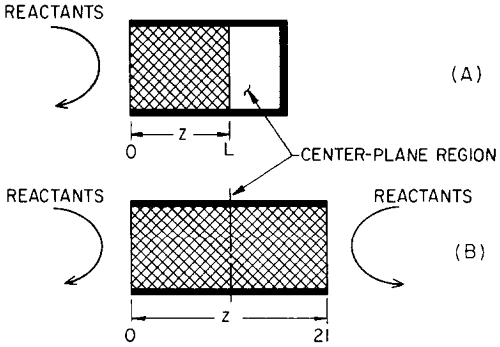

FIG. 2. Comparison of Roiter-type reactor (A) with symmetric pellet (B).

first order reaction or a complete analysis of Eq. (1) substituting the known kinetic expression.

This treatment may be extended to power-law rate expressions of the type

$$\text{local rate} = kC_A{}^n$$

The continuity equation is

$$d^2\Psi_A/d\eta^2 = h^2\Psi_A{}^n \tag{5}$$

where the Thiele parameter is defined as

$$h = L[kC_A(0)^{n-1}/D_{AB,\text{eff}}]^{1/2} \tag{6}$$

Solutions of Eq. (5) for various values of n were acquired through numerical techniques suitable for digital computers. The results are shown in Fig. 3.

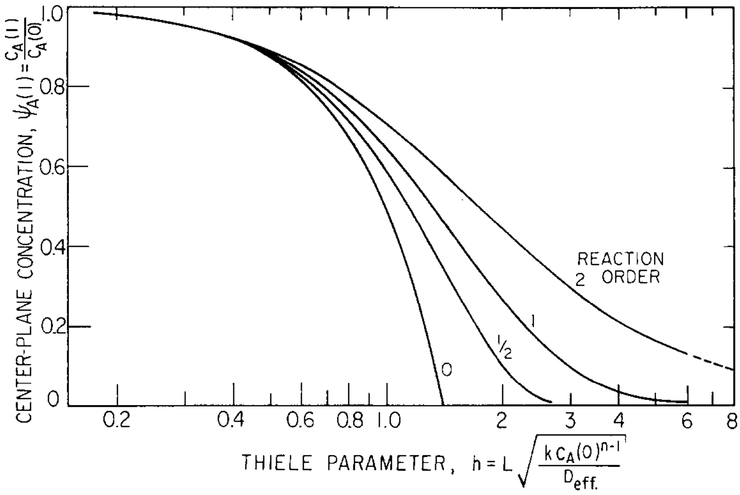

FIG. 3. Center-plane behavior for power-law rate expressions.

So far the mass transfer in the catalyst pellet has been assumed to occur by a simple diffusion mechanism which obeys Fick's law. In Part I it was shown that a more accurate mass flux equation is

$$N_A = \left[\frac{-D_{K,A}\mathfrak{D}_{AB}{}^0}{D_{K,\text{mix}}P + \mathfrak{D}_{AB}{}^0}\right]\frac{P}{R_gT}\frac{dx_A}{dz} - \left[\frac{D_{K,A}(D_{K,B} + \mathfrak{D}_{AB}{}^0)}{D_{K,\text{mix}}P + \mathfrak{D}_{AB}{}^0} + \frac{c_0P}{\mu}\right]\frac{x_A}{R_gT}\frac{dP}{dz} \tag{7}$$

Even for a first order reaction it would be difficult to find an analytical solution for the resulting continuity equation. An exception is found if the average pore radius is less than about 100 Å and the pressure is less than 1 atm. Then Knudsen diffusion predominates and Eq. (7) reduces to

$$N_A = D_{K,A}(dC_A/dz)$$

For this case, all the results previously derived are valid.

To explore a more complex and more realistic situation, the hydrogenolysis of cyclopropane will be considered. The continuity equations are

$$(dN_H/dz) + \mathcal{R} = 0$$
$$(dN_C/dz) + \mathcal{R} = 0$$
$$(dN_P/dz) + \mathcal{R} = 0 \tag{8}$$

where $\mathcal{R}$ is the rate of conversion of cyclopropane to propane and the subscripts on the molar flux N are H for hydrogen, C for cyclopropane, and P for propane. The following relationships exist:

$$N_C + N_P = 0$$
$$N_{\text{total}} = N_H + N_C + N_P = N_H \tag{9}$$

To be completely rigorous, the flux equations for a ternary system should be formulated. This formidable problem is avoided by an approximation which permits the use of the binary equations. The experiments of Part I revealed that the Knudsen diffusivities, D'Arcy flow parameters, and rates of counterdiffusion are nearly identical for propane and cyclopropane. This fact, combined with Eq. (9), reduces the mass transfer problem with respect to hydrogen to the diffusion of gas A (hydrogen) into stagnant gas B (the two hydrocarbons). If, in addition, the kinetic experiments are performed in an excess of hydrogen, the diffusion of cyclopropane through the mixture of hydrogen and propane becomes, for all practical purposes, the diffusion in hydrogen only.

With the above viewpoint, approximate flux equations similar to Eq. (7) can be written for each species:

$$N_{\mathrm{H}} = -D_{\mathrm{H,eff}} \frac{dC_{\mathrm{H}}}{dz} - F_{\mathrm{eff}} C_{\mathrm{H}} \frac{dP}{dz}$$

$$N_{\mathrm{C}} = -D_{\mathrm{C,eff}} \frac{dC_{\mathrm{C}}}{dz} - F_{\mathrm{eff}} C_{\mathrm{C}} \frac{dP}{dz}$$

$$N_{\mathrm{P}} = -D_{\mathrm{C,eff}} \frac{dC_{\mathrm{P}}}{dz} - F_{\mathrm{eff}} C_{\mathrm{P}} \frac{dP}{dz} \quad (10)$$

where

$$D_{\mathrm{H,eff}} = \frac{D_{\mathrm{K,H}} \mathfrak{D}_{\mathrm{HC}}{}^{0}}{(x_{\mathrm{B}} D_{\mathrm{K,H}} + x_{\mathrm{H}} D_{\mathrm{K,C}})P + \mathfrak{D}_{\mathrm{HC}}{}^{0}}$$

$$D_{\mathrm{C,eff}} = \frac{D_{\mathrm{K,C}}}{D_{\mathrm{K,H}}} D_{\mathrm{H,eff}}$$

and

$$F_{\mathrm{eff}} = \frac{D_{\mathrm{K,H}} D_{\mathrm{K,C}}}{(x_{\mathrm{B}} D_{\mathrm{K,H}} + x_{\mathrm{H}} D_{\mathrm{K,C}})P + \mathfrak{D}_{\mathrm{HC}}{}^{0}} + \frac{c_0}{\mu}$$

where

$$x_{\mathrm{B}} = x_{\mathrm{C}} + x_{\mathrm{P}} \quad (11)$$

In this set of equations the parameters $D_{\mathrm{H,eff}}$, $D_{\mathrm{C,eff}}$, and F_{eff} are functions of the composition and total pressure. The remaining theoretical treatment will assume that these parameters do not vary with position in the catalyst pellet. For the conditions encountered in the experimental work, an excess of hydrogen and low conversion at the center plane, this assumption should be valid. However, the value of the diffusivity does depend on the partial pressures of hydrogen and hydrocarbon in the bulk phase.

Another characteristic of the hydrogenolysis reaction is the change in the number of moles which may create pressure gradients within the catalyst. If the mole fraction of cyclopropane is defined on a hydrogen-free basis, that is,

$$y_{\mathrm{C}} = C_{\mathrm{C}}/(C_{\mathrm{C}} + C_{\mathrm{P}})$$

it can be shown that the ratio $y_{\mathrm{C}}(1)/y_{\mathrm{C}}(0)$ is nearly independent of the convective flow and the bulk-phase concentration effects (23). For the conditions encountered in this work, the nonisothermal effects were also found to be small.

DISCUSSION OF RESULTS

The first objective of the analysis of the experimental data was to investigate the operational capabilities of the apparatus and to establish the precision of the data. The bulk rate data for the hydrogenolysis of cyclopropane would then be used to determine the kinetics of the reaction. In conjunction with the center-plane concentrations, the overall rates would provide values of the effective diffusivities, which would then be compared with the diffusivities predicted from the permeability and diffusion experiments of Part I.

For all of the impregnated platinum catalysts, a severe poisoning problem was encountered. Although it was not possible to identify the poison, a likely candidate was water. This water may have been present in the cyclopropane, or oxygen in the cyclopropane could react in the presence of hydrogen. Attempts to remove the poison using the procedure given in the experimental section failed. Since a catalyst with a relatively stable activity was required, it was necessary to permit the poisoning to occur until the amount of deactivation during an 8-hr experiment became negligible. This usually was achieved when the activity was approximately 10% of its initial value.

The bulk rate results for two pellets are shown in Fig. 4. The reaction follows first order behavior with respect to the cyclopropane. Although this order is for partially poisoned catalyst, it can be shown that if the *local* rate remains first order the possibility of nonuniform poisoning will not change the order. The center-plane results are shown in Fig. 5. Note the expanded scale on the ordinate.

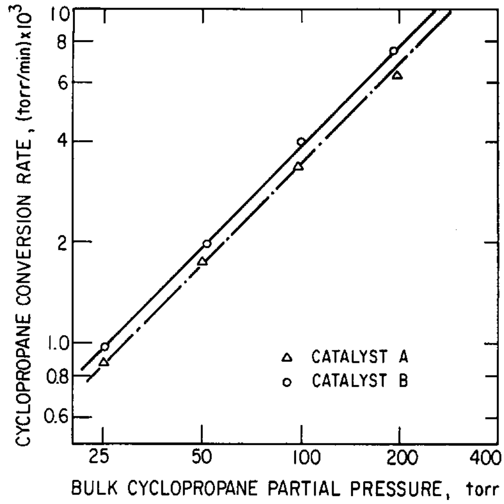

FIG. 4. Bulk rate results for pellets A and B.

TABLE 1
COMPARISON OF DIFFUSIVITIES
FOR PELLETS A AND B

"Kinetic" Diffusivity

Pellet	P_C (torr)	k (sec^{-1})	h	$D_{C,eff}$ (cm^2/sec)
A	50	0.017	0.655	0.018
B	51	0.019	0.673	0.018

"Physical" Diffusivity

Pellet	P_C (torr)	P_H (torr)	$D_{K,C}$ (cm^2/sec)	$\mathfrak{D}_{HC}^0$ (cm^2/sec)	$D_{C,eff}$ (cm^2/sec)
A	50	800	0.0308	0.14	0.024
B	51	800	0.0331	0.134	0.0248

Equation (4), developed for a first order reaction, was applied to the bulk rates and the center-plane results to evaluate the effective diffusivities for a cyclopropane pressure of 50 torr. The values are listed in Table 1. Also given are the diffusivities predicted from the Knudsen and molecular diffusivities found in Part I combined with Eq. (11). A comparison of these "kinetic" and "physical" diffusivities reveals a 25% difference. Similar differences are found for the runs at 25, 100, and 200 torr. A difference of this order is too large to be explained by experimental error. It can be shown that nonuniform catalytic activity due to poisoning can quantitatively explain such deviations (*23*). This hypothesis was also tested by preparing a catalyst pellet from a mechanical mixture of platinum black and alumina. Independent studies had shown that platinum films were more resistant to poisoning than impregnated platinum catalysts.* As anticipated, the platinum black did not deactivate. The results in Table 2 show that the reaction is slightly less than first order. The calculated values of the "kinetic" and "physical" diffusivities based on a first order reaction are in good agreement. The estimated error due to the slightly different reaction order was less than 5%. The conclusion then is that the physical measurements of the diffusion coefficient in the absence of reaction performed by the techniques developed in Part I are valid for the reaction situation. Moreover, the simplifications in the treatment of the ternary reaction system also appear to be justified.

TABLE 2
REACTION AND DIFFUSIVITY RESULTS
FOR PELLET E

"Kinetic" Diffusivity

P_C (torr)	k (sec^{-1})	h	$D_{C,eff}$ (cm^2/sec)
26	0.076	1.16	0.032
99	0.066	1.14	0.028

"Physical" Diffusivity

P_C (torr)	P_H (torr)	$D_{K,C}$ (cm^2/sec)	$\mathfrak{D}_{HC}^0$ (cm^2/sec)	$D_{C,eff}$ (cm^2/sec)
26	800	0.0477	0.111	0.0313
99	800	0.0477	0.111	0.0277

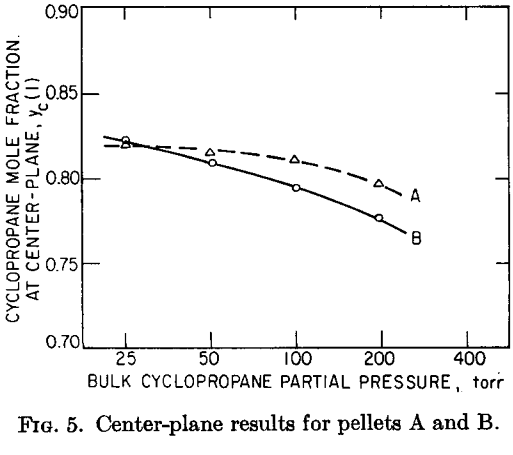

FIG. 5. Center-plane results for pellets A and B.

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* Work of R. D. Clay, this laboratory.

The concentration dependence of the "physical" diffusivity is predicted from the theory developed in Part I using Eq. (11) and the values of $D_{K,C}$ and $\mathfrak{D}_{HC}{}^0$. Table 3 has been prepared for the reaction conditions used with Catalyst B. There is a definite reduction in the effective diffusivity as the cyclopropane concentration increases. The effect of this reduction on the center-plane behavior can be examined by choosing the Thiele parameter for a first order reaction so that $y_C(1)$ would be equal to 0.81 for a cyclopropane pressure of 50 torr. The $y_C(1)$ value, 0.81, is obtained from Fig. 5. The dependence of the Thiele parameter on the diffusivity is employed to predict the Thiele parameters at cyclopropane pressures of 25, 100, and 200 torr. The corresponding center-plane concentrations are evaluated by means of Eq. (3) and were used to draw the theoretical curve in Fig. 6. The experimental results are well explained by the concentration dependence of the diffusivity. Similar behavior is found for Pellet A.

TABLE 3

PREDICTED CONCENTRATION DEPENDENCE OF "PHYSICAL" DIFFUSIVITY FOR PELLET B

P_C (torr)[a]	$D_{C,eff}$ (cm²/sec)	h
25	0.0255	0.665
50	0.0248	0.673
100	0.0234	0.693
200	0.0211	0.730

[a] P_H = 800 torr.

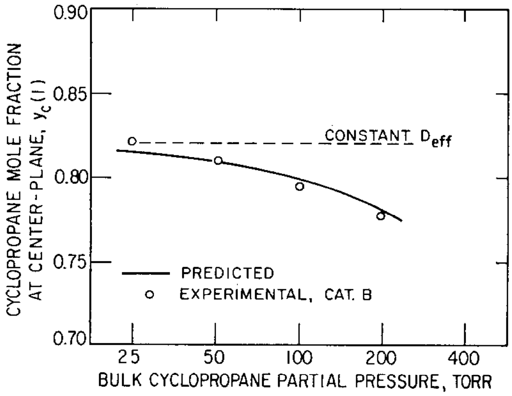

FIG. 6. Comparison of predicted and observed center-plane behavior for pellet B.

The hydrogen concentration should not vary significantly within the catalyst for the experimental conditions in this work. This is the reason that the order of reaction with respect to hydrogen has not been a factor in evaluating the diffusivities.

CONCLUSION

A single pellet diffusive reactor has been designed to measure simultaneously the bulk reaction rates and the compositions at the center of a single catalyst pellet. The hydrogenolysis of cyclopropane on alumina-supported platinum catalysts was studied in this reactor. The effective diffusivity calculated from these kinetic experiments was about 25% below the value determined from the physical measurements of Part I. This difference was attributed to the nonuniform catalytic activity of the pellet due to poisoning. There was good agreement between the "kinetic" and "physical" diffusivities for a platinum black catalyst which was not subject to poisoning. To interpret accurately the center-plane behavior, it was necessary to take into account the concentration dependence of the effective diffusivity. This was accomplished by simplifying the ternary hydrogenation problem so that the binary flux equations developed in Part I could be applied.

REFERENCES

1. WHEELER, A., *Advan. Catalysis* **3**, 249 (1951).
2. SATTERFIELD, C. N., AND SHERWOOD, T. K., "The Role of Diffusion in Catalysis." Addison-Wesley, Reading, Massachusetts, 1963.
3. PETERSEN, E. E., "Chemical Reaction Analysis" Prentice-Hall, Englewood Cliffs, New Jersey, 1965.
4. JOHNSON, M. F., KREGER, W. E., AND ERICKSON, H., *Ind. Eng. Chem.* **49**, 283 (1957).
5. WEISZ, P. B., AND PRATER, C. D., *Advan. Catalysis* **6**, 143 (1954).
6. WEISZ, P. B., AND SWEGLER, E. W., *J. Phys. Chem.* **59**, 823 (1955).
7. HENRY, J. P., CHENNAKESAVAN, B., AND SMITH, J. M., *A. I. Ch. E. J.* **7**, 10 (1961).
8. OTANI, S., AND SMITH, J. M., *J. Catalysis* **5**, 332 (1966).

9. Rao, M. R., and Smith, J. M., *A. I. Ch. E. J.* **9,** 485 (1963).
10. Rao, M. R., and Smith, J. M., *A. I. Ch. E. J.* **10,** 293 (1964).
11. Rao, M. R., Wakao, N., and Smith, J. M., *Ind. Eng. Chem. Fundamentals* **3,** 127 (1964).
12. Wakao, N., Otani, S., and Smith, J. M., *A. I. Ch. E. J.* **11,** 435 (1964).
13. Wakao, N., and Smith, J. M., *Ind. Eng. Chem. Fundamentals* **3,** 123 (1964).
14. Hawtin, P., Gibson, J. A., Murdoch, R., and Lewis, J. B., *Carbon* **2,** 299 (1964).
15. Hawtin, P., and Murdoch, R., *Chem. Eng. Sci.* **19,** 819 (1964).
16. Korneichuk, G. P., Zhilailo, Ya. V., Roiter, V. A., and Garkavenko, I. P., *Zhur. Fiz. Khim.* **29,** 1073 (1955).
17. Dougharty, N. A., Dissertation, University of California, Berkeley, 1960.
18. Bond, G. C., *"Catalysis by Metals,"* p. 270, Academic Press, New York, 1962.
19. Bond, G. C., and Addy, J., *Advan. Catalysis* **9,** 44 (1957).
20. Bond, G. C., and Newham, J., *Trans. Faraday Soc.* **56,** 1501 (1960).
21. Bond, G. C., and Sheridan, J., *Trans. Faraday Soc.* **48,** 713 (1952).
22. Newham, J., *Chem. Rev.* **63,** 123 (1963).
23. Balder, J. R., Dissertation, University of California, Berkeley, 1967.