JOURNAL OF CATALYSIS 5, 22-26 (1966)

Determination of Effective Diffusivities of Catalysts by Gas Chromatography

AMOS J. LEFFLER*

From Arthur D. Little, Inc., Cambridge, Massachusetts

Received March 23, 1965; revised May 13, 1965

The effective diffusivity of a catalyst may be determined by measuring the pulse broadenings of a nonchemically interacting gas at various flow velocities that occur in a column packed with catalyst and using the values obtained to calculate the constant in the Van Deemter equation. The C term in the equation due to mass transfer between gas and solid phases is a function of the effective diffusivity of the gas. The method was applied to H-51 alumina using nitrogen as the adsorbed gas at −78°C and reasonable agreement was found between the results obtained from this method and the Weisz-Schwartz relation.

The measurement of effective diffusivities of catalysts is of great importance in evaluating their activities in order to determine whether reaction rates are limited by chemical activity or by physical characteristics. A wide variety of procedures have been devised to measure effective diffusivities although these methods fall into two general categories. The first approach is based on the measurement of the steady state diffusion of a gas through a catalyst pellet that completely blocks a tube. Weisz (*1*) used this method in allowing streams of nitrogen and hydrogen to flow past the opposite surfaces of a pellet and measuring the rate of diffusion of the hydrogen into the nitrogen. In this measurement it is necessary to correct for the geometry of the pellet and it was found that by comparing cylindrical and spherical pellets a geometric factor of 0.78 was needed to correctly determine the diffusivity for spherical pellets. Other workers (*2*) have used similar techniques and the method is very widely used.

The second method of measuring catalyst diffusivities is based on transient phenomena. The system is saturated with a gas and the rate of desorption measured after the nonadsorbed gas is removed. This approach has been used by Bolt and Innes (*3*) to measure the rate of carbon dioxide desorption from coal and by Habgood (*4*) to measure gas desorption from molecular sieves. Recently Gorring (*5*) has measured the transient release of hydrocarbons from the porous matrix of a sphere. A modification of this technique is the introduction of a step function of pressure (*6*) to the upstream end of a bed and calculation of the diffusivity by extrapolation of the steady state portion of the downstream pressure plotted against time. A direct determination of the pressure (*7*) drop of a gas suddenly exposed to an adsorbing material in an evacuated system has been followed by high-speed techniques. Finally the nonsteady fluid diffusion rate (*8*) has been measured between two well-mixed chambers separated by a porous disc. All of these measurements are fairly complicated to carry out and frequently there is a question as to when the system has reached steady state conditions. Thus all of the previous methods of measuring diffusivity of particles have limitations and in order to overcome these difficulties the present approach was developed.

---

* Present Address: Department of Chemistry, Villanova University, Villanova, Pennsylvania.

The results of recent intensive studies of the parameters determining the column efficiencies in gas chromatography can be directly applied to the measurement of effective diffusivities of catalysts. In the gas chromatographic process a very narrow pulse of gas is sent down a packed column and the components of the gas travel at various speeds depending on their volatility and interaction with the packing. It has been shown that even when there is little interaction between the gas and the column packing, the pulse of gas will spread because of finite mass transfer due to diffusion into and out of the pores of the packing. Thus, useful information concerning effective diffusion rates can be obtained by relating the pulse spreading to the carrier gas flow rate as will be described below. In the present work the effective diffusivity of nitrogen in Alcoa H-51 alumina was measured using helium as the nonadsorbed carrier gas.

LIST OF SYMBOLS

d	Bulk density (g/cc)
d_p	Particle diameter (cm)
D_p	Effective diffusivity (cm^2/sec)
H	Plate height (cm)
F_{I}	Void fraction in packing
F_{II}	1-F_{I} = solid fraction in packing
K	Ratio of gas-phase concentration/solid-phase concentration
L	Column length (cm)
M	Molecular weight of gas being measured
p_v	Pore volume (cc/g)
r_p	Average pore radius (Å)
S	Surface area of packing (cm^2/g)
u	Interstitial gas velocity (cm/sec)
σ	Peak dispersion (sec)
τ	Retention time (sec)

EXPERIMENTAL

1. Plate height. The chromatograph used to measure the plate height was constructed in this laboratory. It was of conventional design except that the column was in the form of a helix that could be immersed in a Dewar flask. Gas injection was carried out by means of a Wilkins Six-Way Linear Gas Sampling Valve using a 0.25 ml sample. The velocity of the helium carrier gas was calibrated by means of a wet test meter attached to the outlet of the measuring cell. A Gow-Mac 9677 thermal conductivity cell with thermistor elements was used. The H-51 alumina was activated by heating the column to 350°C in a flowing stream of helium. Measurements were carried out at —78°C. For each carrier gas velocity a recording of the peak height and width was obtained and with a known chart speed it was possible to calculate the retention volume and peak width of the nitrogen gas. Peak dispersion was taken as half of the peak width at 0.606[9] of the peak height from the relation

$$H = (\sigma/\tau)^2 L \qquad (1)$$

2. Bulk density and void fraction. Bulk density measurements were made by determining the weight of a known volume of material. A value of 0.793 g/cc was found.

The void fraction of the material was determined by mercury displacement using the apparatus shown in Fig. 1. A sample of

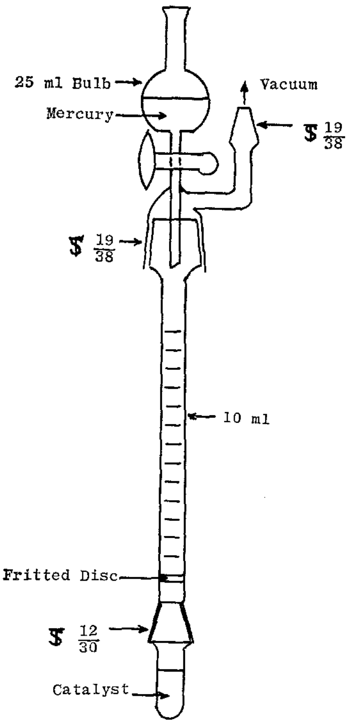

FIG. 1. Apparatus for measurement of catalyst density by mercury displacement.

catalyst was weighed into the small container by difference. Enough material was taken to fill about two-thirds of the volume. The standard taper was lightly greased, attached to the remainder of the apparatus, and the volume was then evacuated through the sidearm. In the present work, the dried but unactivated catalyst was used, since any large change in density during activation was believed unlikely. After evacuation, mercury was carefully added to the system in an amount great enough to fill the space below the fritted disc.

The level of the mercury in the column was read, and air was admitted to the system to force the mercury through the fritted disc. When the volume below the disc was filled with mercury, the level of the mercury in the column was read again; the difference between the two readings was the amount of mercury needed to fill the volume. An initial calibration with the empty system gave the empty volume below the frit, and the difference between this value and that found for a given weight of sample gave the volume occupied by the sample. The weight of the sample divided by the volume so determined gave its bulk density. The void fraction was calculated by the difference between the reciprocal of the bulk density and the reciprocal of the mercury displacement density. A value of 0.51 cc/cc volume was found for the H-51 alumina.

3. Coefficient of adsorption. Adsorption was measured using standard BET (*10*) equipment, the sample being held at —78°C. The amount of nitrogen adsorbed was measured in the usual manner and it was found that at the highest pressure of nitrogen used, the fraction adsorbed per unit volume of alumina was very high. The value of K thus determined was so small that the value of $KF_{\text{I}}/F_{\text{II}}$ was negligible.

RESULTS AND DISCUSSION

The earliest satisfactory description of the processes involved in the passage of a pulse of gas through a column was that of Lapidus and Amundson (*11*). Their description was extremely complicated mathematically and not very useful. It was greatly simplified by Van Deemter *et al.* (*12*) who showed that for any practical column where the height of a mixing stage is small compared to the column length, the output pulse has a Gaussian distribution. They were able to show that the expression for a plate height has the form

$$H = A + B/u + Cu \tag{2}$$

where A, B, and C are constants of the column, gases, and operating conditions. The A term is the so-called "eddy diffusion" term and is due to turbulence in the gas stream caused by the particles of packing. The B term is due to longitudinal diffusion of gas in the pulse both forwards and backwards in the carrier gas stream. As can be seen this term becomes unimportant at high gas velocities. Finally the C term is due to mass transfer between the gas and solid phases and is dominant at high gas velocities.

Equation (2) has been widely applied to the determination of column parameters for gas chromatographic purposes, but it has not been used to obtain catalyst data. Habgood and Hanlan (*13*) used it in their study of the adsorptive properties of a series of activated charcoals. They modified the C term of the Van Deemter equation to the form

$$C = \frac{d_p^2}{\sqrt{2}\pi^2} \cdot \frac{F_{\text{I}}}{1 - F_{\text{I}}} \cdot \frac{1}{p_v D_p} \cdot \frac{1}{(1 + KF_{\text{I}}/F_{\text{II}})^2} \tag{3}$$

The plate height of the alumina was measured by using nitrogen as the pulsed measuring gas and helium as the carrier gas. The results are given in Table 1 and plotted in Fig. 2.

Using the values of H as a function of flow velocity the values of A, B, and C were calculated and are given in Table 2.

With the value of C calculated here, the void fraction, density, and adsorption coefficient determined above, and a published value (*14*) of the pore volume, a value of D_p of 0.00664 cm^2/sec was calculated. This value is about 6% of the self-diffusion coefficient of nitrogen in the gas phase and indicates adsorption and narrow pores. In

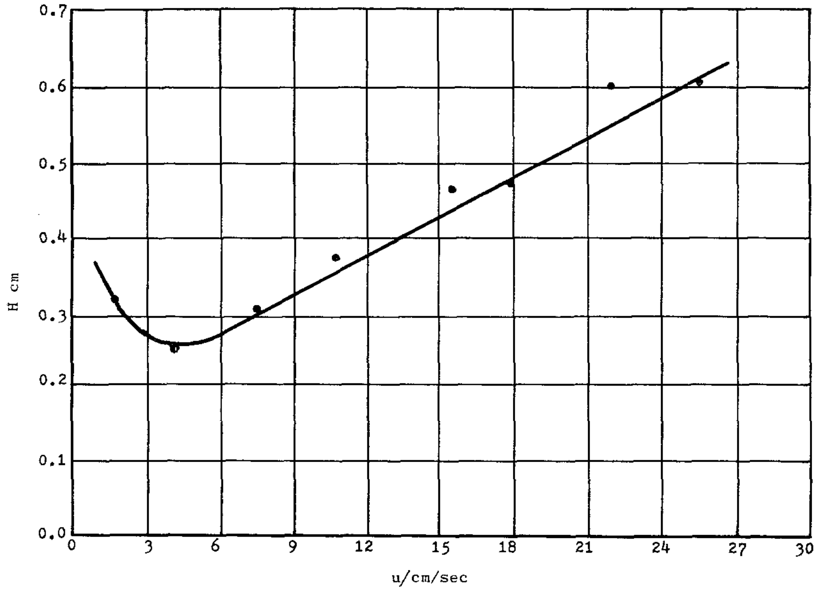

FIG. 2. Plot of plate height vs. interstitial velocity for alumina at −78°C.

TABLE 1
MEASUREMENT OF PLATE HEIGHT AS A FUNCTION OF FLOW VELOCITY AT −78°C[a]

Flow rate (cc/min)	Flow velocity (cm/sec)	τ (cm)	σ (cm)	$(\sigma/\tau)^2$	H (cm)
10	1.715	49.0	3.30	0.00455	0.324
25	4.28	24.0	1.45	0.00366	0.260
44.6	7.68	12.8	0.85	0.00441	0.313
64	10.8	8.90	0.65	0.00534	0.379
91.5	15.7	6.80	0.55	0.00654	0.464
100	17.83	6.1	0.50	0.00671	0.473
151	25.5	4.35	0.40	0.00846	0.601

[a] Column length was 71.3 cm; column diameter, 0.493 cm.

the present work, it was necessary to actually measure the adsorption coefficient; but, for materials with appreciable adsorption, the retention volume to that of air can be used, since air is not normally considered to be adsorbed. Using the relation (*15*)

$$D_p = 9700 r_p \sqrt{T/M} \tag{4}$$

we calculated an average pore radius of 26 Å.

We can compare the value of D_p measured above with that calculated from the Weisz-Schwartz (*16*) formula

$$D_p = (2.14 \times 10^5) d^2 p_v^3 / S \tag{5}$$

TABLE 2
VALUES OF A, B, AND C FROM THE VAN DEEMTER EQUATION

$A = 0.116$ cm
$B = 0.314$ cm^2/sec
$C = 0.019$ sec

where S was measured to be 4.40×10^6 cm^2/g. Substituting the values we have used for these terms, we find $D_p = 0.0038$ cm^2/sec, which is in reasonable agreement with the value determined by the gas chromatographic method described here.

ACKNOWLEDGMENT

This work was supported by the Air Force Aero Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, U. S. Air Force.

REFERENCES

1. WEISZ, P. B., *Z. Physik. Chem. (Frankfurt)* **11**, 1 (1957).
2. WICKE, E., AND KALLENBACH, R., *Kolloid Z.* **97**, 135 (1941).
VILLET, R. H., AND WILHELM, R. H., *Ind. Eng. Chem.* **53**, 837 (1961).
3. BOLT, B. A., AND INNES, J. A., *Fuel* **38**, 333 (1959).

4. Habgood, H. W., *Can. J. Chem.* **36,** 1384 (1958).

5. Gorring, R. L., and de Rosset, A. J., *J. Catalysis* 3, 341 (1964).

6. Goodknight, R. C., and Fatt, I., *J. Phys. Chem.* **64,** 1162 (1960); **65,** 1709 (1961); **66,** 760 (1962).

7. Winfield, M. E., *Australian J. Chem.* **6,** 221 (1953).

8. Gordon, A. R., *Ann. N. Y. Acad. Sci.* **46,** 285 (1945).

9. Valbert, J., Sc.D. thesis, Mass. Inst. of Technol., Dept. of Chemical Engineering, 1963.

10. Barr, W. E., and Anhorn, V. J., "Scientific and Industrial Glass Blowing and Laboratory Techniques." Instrument Publ. Co., Pittsburgh, Pennsylvania, 1949.

11. Lapidus, L., and Amundson, N. R., *J. Phys. Chem.* **56,** 984 (1952).

12. Van Deemter, J. J., Zuiderweg, F. J., and Klinkenburg, A., *Chem. Eng. Sci.* **5,** 271 (1956).

13. Habgood, H., and Hanlan, J. F., *Can. J. Chem.* **37,** 843 (1959).

14. Newsome, J. W., Heiser, H. W., Russell, A. S., and Stumpf, H. C., "Alumina Properties." Tech. Paper No. 10, Second Rev., Aluminum Co. of America, Pittsburgh, Pennsylvania, 1960.

15. Satterfield, C. N., and Sherwood, T. K., "The Role of Diffusion in Catalysis," McGraw-Hill, New York, 1964.

16. Weisz, P. B., and Schwartz, A. B., *J. Catalysis* **1,** 399 (1962).