

The Interpretation of Pressure Dependence of Accommodation Coefficients

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are effectively non-porous. With the great majority of similar materials studied in the range of this and higher areas the nitrogen values are greater than the stearic acid values by a factor of two or more. Furthermore the nitrogen adsorption-desorption isotherm for catalyst U in the 0.4 to 0.6 relative pressure region does not show the hysteresis effect characteristic of the high area supported catalyst and generally attributed to small pores.⁵ Finally the small non-porous particle size required for an area of 91 sq.m per g is qualitatively confirmed by the extremely slow sedimentation rate in benzene observed in the stearic acid experiments. Relatively large pores are, of course, not excluded by the above observations.

CATALYST SUPPORTED ON DIATOMACEOUS EARTH

The nitrogen and stearic acid areas of the catalyst supported on diatomaceous earth, H-G,⁴ are, respectively, 270 and 46 sq.m per g (ignited weight), or expressed more significantly as area per gram of catalyst material, approximately 516 and 90 sq. m per g (see Table I). The increase in nitrogen area over that of the unsupported material is more than fivefold. Since the larger stearic acid molecules are adsorbed to the same extent as on the unsupported catalyst they evidently reach practically none of the internal surface of the high area supported material. The development of fine pore structure in the supported catalyst is also demonstrated by the marked adsorption-

catalyst material. No hysteresis is observed in the 0.4 to 0.6 relative pressure region of the nitrogen isotherm. Evidently the non-porous titanium dioxide support does not produce the high area fine pore structure obtained with the diatomaceous earth.

¹ Ries, Van Nordstrand, and Teter, *Ind. Eng. Chem.* **37**, 310 (1945).

² Brunauer, Emmett, and Teller, *J. Am. Chem. Soc.* **60**, 309 (1938).

³ Harkins and Gans, *J. Phys. Chem.* **36**, 86 (1932).

⁴ The unsupported catalyst, U, was prepared by the reaction between sodium carbonate and a salt of a heavy metal whose oxide is readily reducible. The precipitation of the supported catalyst, H-G, was similarly performed in the presence of suspended diatomaceous earth. In the preparation of catalyst T, titanium dioxide was substituted for the diatomaceous earth. All catalysts were calcined at 350°C for two hours. Catalyst material constitutes approximately fifty percent by weight of the supported samples. The catalysts were prepared by Dr. Olson of these laboratories.

⁵ Ries, Van Nordstrand, Johnson, and Bauermeister, *J. Am. Chem. Soc.* **67**, 1242 (1945).

The Interpretation of Pressure Dependence of Accommodation Coefficients

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IN a recent paper, Amdur¹ interprets the pressure dependence of the accommodation coefficients of several gases on platinum. He attributes the pressure dependence to simple Langmuir adsorption of the same gas as that of which the accommodation coefficient is being measured.

Probably this interpretation is the correct one for the gases H₂, D₂, N₂, CO, and O₂. However an alternative interpretation is possible for the inert gases He, Ne, Ar, Kr, and Xe.

In the paper giving the experimental results, Amdur, Jones, and Pearlman² report using neon of 99.9 percent purity. Thus in 0.1-mm pressure neon, there is impurity of 10⁻⁴-mm pressure.

Morrison and Roberts,³ using accommodation coefficient measurements, found that a clean tungsten surface adsorbs oxygen at pressures as low as 10⁻⁹ mm and becomes completely covered with molecular oxygen at a pressure of about 10⁻⁵ mm, always in the presence of neon at 0.1-mm pressure. Moreover, Roberts⁴ found that clean tungsten adsorbs a saturated film of hydrogen at 4×10⁻⁴-mm pressure in the presence of neon at 0.07-mm pressure.

Since the amount of impurity in each of Amdur's inert gases is directly proportional to the pressure of the inert gas, the adsorption of this impurity could account for the fitting of the Langmuir isotherm.

¹ I. Amdur, *J. Chem. Phys.* **14**, 339 (1946).

² I. Amdur, M. M. Jones, and H. Pearlman, *J. Chem. Phys.* **12**, 159 (1944).

³ J. L. Morrison and J. K. Roberts, *Proc. Roy. Soc. A173*, 1 (1939).

⁴ J. K. Roberts, *Proc. Roy. Soc. A152*, 445 (1935).

TABLE I. Nitrogen and stearic acid adsorption by supported and unsupported catalysts.

	Area, sq.m/g		Nitrogen hysteresis (0.4 to 0.6 relative pressure)
	Nitrogen (BET)	Stearic acid	
U (unsupported)	91 (91)*	93 (93)	None
H-G (on diatomaceous earth)	270 (516)	46 (90)	Marked
T (on titanium dioxide)	72 (134)	45 (82)	None

* Values in parentheses are areas per gram of catalyst material. Catalyst material constitutes approximately fifty percent by weight of the supported samples. In computing these values the maximum possible contribution of the support is subtracted (although a considerable portion of the support surface is undoubtedly covered). The nitrogen and stearic acid areas of the diatomaceous earth are, respectively, 23 and 2 sq.m/g and for the titanium dioxide, 10 and 8 sq.m/g.

desorption hysteresis effect observed with nitrogen in the 0.4 to 0.5 relative pressure region.⁵

CATALYST SUPPORTED ON TITANIUM DIOXIDE

In sharp contrast to the results obtained with a diatomaceous earth support are those found for the same catalyst supported on non-porous titanium dioxide. The nitrogen and stearic areas of this supported catalyst, T,⁴ are, respectively, 72 and 45 sq. m per g or 134 and 82 sq. m per g of