[CONTRIBUTION NO. 47 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Adsorption of Fatty Acids on Nickel and Platinum Catalysts

BY HILTON A. SMITH AND JOHN F. FUZEK

Several methods are available for measuring the surface of finely divided particles. Most of these methods fall into one of the following classes: (a) those methods by which the size of the particle is measured and the specific surface calculated, usually on the assumption that the particles are spherical in shape, and (b) those by which a chemical is unimolecularly adsorbed on the solid surface and the amount of adsorbed material is measured, thus permitting calculation of the specific surface after assuming the area occupied by each adsorbed molecule.

In many instances the "apparent" specific surface as measured by methods falling in group (a) and the "true" specific surface as measured by methods falling in group (b) are in good agreement. For example, Harkins and Gans[1] found that the true specific surface of titanium dioxide as calculated from experiments involving the adsorption of oleic acid on the oxide agreed with the "apparent" specific surface as calculated by the microscopic count method. Ewing[2] used the adsorption of methyl stearate and glycol dipalmitate to measure the true specific surface and particle size of several zinc oxide pigments, and found agreement with particle sizes determined by microscopic observations. Emmett and Dewitt[3] determined the true specific surfaces of a number of industrially important finely divided materials by the gas adsorption method, and found general agreement with results obtained using methods which give particle size.

There are, however, a number of finely divided materials for which the "true" specific surface differs greatly from the "apparent" value. This group includes many solid catalysts. The surface area of such materials has usually been measured by the method of Emmett and Brunauer,[4] following the modifications suggested by Brunauer, Emmett and Teller.[5] This method usually entails the adsorption of nitrogen at liquid nitrogen temperature and subsequent calculation of the volume of gas necessary to cover the solid surface with a unimolecular layer. It is then assumed that each nitrogen molecule occupies the same area as that found in the closest-packed face of solid nitrogen, and the area of the solid adsorbent calculated using the density of either liquid or solid nitrogen.

The experiments reported here involve the determination of the true specific surface of certain metal catalysts by the adsorption of normal fatty acids from liquid solution.

Experimental

Raney nickel and Adams platinum catalysts were prepared according to the directions given in "Organic Syntheses".[6,7] The Raney nickel was stored under alcohol, and samples of the settled catalyst were removed for experimentation by means of a glass tube. Capric, lauric and palmitic acids were obtained from the Eastman Kodak Company and were the best grade of acids available. They were used without further purification. The *n*-nonadecylic acid was prepared using octadecyl alcohol as the starting material. The alcohol was converted to the bromide by means of hydrobromic acid.[8] The bromide was then treated with potassium cyanide, and the product hydrolyzed to give the desired product.[9] The resulting acid was converted to the sodium salt which was extracted several times with ether in order to remove any non-acidic impurities. The salt was acidified with hydrochloric acid, and the product recrystallized from acetone. The acid used in adsorption experiments melted at 69.0–69.4° and had a neutral equivalent of 298 (theoretical 298.5). Behenic acid was prepared by hydrogenation of Eastman Kodak Co. erucic acid. The low pressure hydrogenation was carried out at 70° in acetic acid solution using Adams platinum catalyst. After hydrogenation was complete, the mixture was allowed to cool, and the solid filtered out. The acid was separated from the platinum by solution in hot acetone and subsequent hot filtration. The product was purified by the method described for *n*-nonadecylic acid. The sample used for adsorption experiments melted at 79.5–80.0° and had a neutral equivalent of 339 (theoretical, 340.6).

The benzene solvent was prepared for use by fractionation of Merck Reagent thiophene-free benzene in a five-foot, helix-packed column. It was stored over sodium wire. Du Pont methanol, Merck reagent chloroform, Baker C. P. acetone and Eastman Kodak Co. best grade cyclohexane were fractionated through the same five-foot column before use. Eastman *n*-heptane and cyclohexene were fractionated through an eight-foot Vigreux column.

For adsorption experiments on Raney nickel, two different procedures were used. These are, in general, modifications of Ewing's method.[2] In one (examples of data shown in Fig. 2), an estimated 0.5 to 1 g. of Raney nickel catalyst was placed in the adsorption tube, and the tube attached with rubber tubing to the evacuating and filling apparatus as shown diagrammatically in Fig. 1. With the stopcock closed, the tube was evacuated through the side arm until all of the ethanol had been removed from the catalyst. Then 40 ml. of benzene containing 0.1500 g. of the fatty acid was added through the stopcock. The adsorption tube was removed, tightly stoppered by means of a small cork and shaken end over end at a speed of 42 r. p. m. for a specified period of time.

The shaking was then stopped, the tube and contents centrifuged to settle the catalyst, and 5 ml. of the clear liquid withdrawn. This was delivered into a weighed bottle which was placed in an oven at a temperature just below the boiling point of the solvent. Evaporation was speeded by means of a slow stream of filtered air, and the fatty acid which remained was weighed. Blank runs established the dependability of this analytical procedure.

---

[1] Harkins and Gans, THIS JOURNAL, **53**, 2804 (1931); *J. Phys. Chem.*, **36**, 86 (1932).

[2] Ewing, THIS JOURNAL, **61**, 1317 (1939).

[3] Emmett and Dewitt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 28 (1941).

[4] Emmett and Brunauer, THIS JOURNAL, **59**, 1563 (1937).

[5] Brunauer, Emmett and Teller, *ibid.*, **60**, 309 (1938).

[6] "Organic Syntheses," **21**, 15 (1941).

[7] *Ibid.*, **8**, 92–99 (1928).

[8] *Ibid.*, **15**, 25, 35 (1935).

[9] *Ibid.*, **16**, 35 (1936).

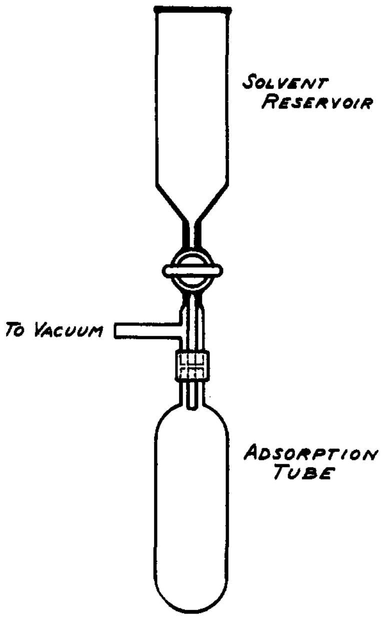

Fig. 1.—Evacuating and filling apparatus.

The adsorption tube was restoppered, shaken again for a definite interval of time, and some of the liquid removed and analyzed as just described. At the end of the experiment, the catalyst was filtered out, dried and weighed under carbon dioxide. The weight of catalyst was corrected for the weight of adsorbed acid.

The second procedure (example shown in Fig. 3) for adsorption experiments was similar to the first procedure except that 20 ml. of solvent containing a known weight (0.2–0.4 g.) of fatty acid was placed in the adsorption tube. The tube and contents were rotated for at least twenty-four hours, after which the tube was centrifuged, and ten ml. of the clear liquid removed. Ten ml. of pure solvent was added to the tube, and the shaking process repeated for at least another twenty-four hours after which the cycle was repeated. The fatty acid content of the samples removed was determined in the manner already described.

For adsorption experiments on platinum, weighed samples of platinic oxide were placed in the adsorption tube, ten ml. of methanol added, and the tube attached to a Parr low-pressure reduction apparatus. After evacuation and filling with hydrogen, the tube was shaken for about fifteen minutes. The tube was then centrifuged, and as much as possible of the methanol poured off. The tube was subsequently attached to the evacuating and filling apparatus, and adsorption experiments carried out in the same manner as for nickel.

Experimental Calculations and Results

The results as shown in Figs. 2, 3 and 4 indicate that adsorption equilibrium is obtained in twenty-four hours or less, and that the concentration of acid in the solvent does not affect the amount of the acid adsorbed. If less acid is used than that necessary to saturate the metal surface, all of the acid is removed, within experimental error. The adsorption which takes place is unquestionably of an irreversible chemisorption type. Furthermore, as Fig. 3 indicates, the number of moles of acid adsorbed is not determined by the chain length of the acid. The deviation of points from a straight line in Fig. 3 is caused by accumulated experimental error as indicated by an upward shift with one sample and a downward shift with another sample using the same acid. This error is probably due to successive sampling and dilution.

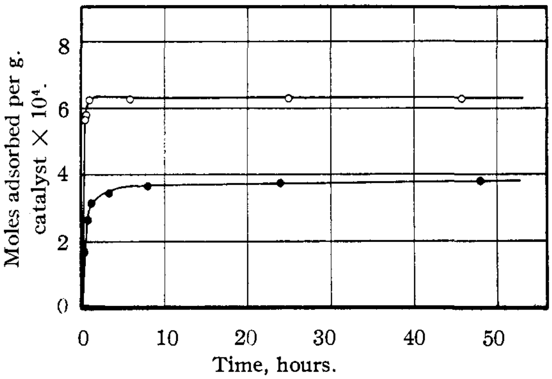

Fig. 2.—Rate of adsorption of palmitic acid on Adams platinum catalyst (○) and Raney nickel catalyst (●) from benzene solution.

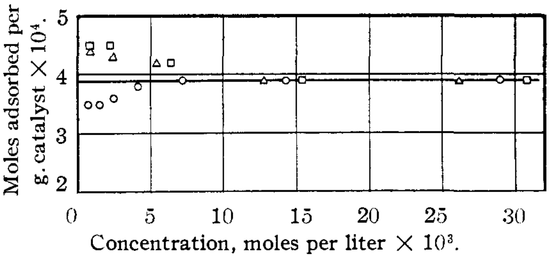

Fig. 3.—Adsorption isotherm for lauric and palmitic acids on Raney nickel catalyst from benzene solution: □, lauric acid; ○, palmitic acid #1; △, palmitic acid #2.

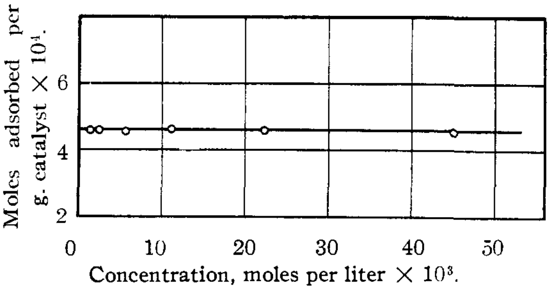

Fig. 4.—Adsorption isotherm for palmitic acid on Adams platinum catalyst from benzene solution.

The logical explanation seems to be that the acid is adsorbed on the metal in an oriented unimolecular layer, and that the true specific surface of the catalyst can, therefore, be calculated from the known cross section of fatty acid molecules. According to Adam,[10] this cross section of fatty acid molecule is 20.5 square ångström units. Table I gives the specific surfaces of the three preparations of Raney nickel used as determined by the adsorption of palmitic acid from

---

[10] Adam, "The Physics and Chemistry of Surfaces," 2nd ed., Oxford University Press, London, 1938.

benzene, by the Brunauer–Emmett–Teller method,[11] and by the microscopic count method.[11] Table II gives the specific surface of Raney nickel catalyst as determined using different solvents. Table III gives similar data resulting from the use of different fatty acids. Since a fresh sample of catalyst was used for each measurement, the variations in the individual values are probably due to sampling.

TABLE I

THE SPECIFIC SURFACE OF RANEY NICKEL AS DETERMINED BY DIFFERENT METHODS

	Specific surface (sq. meters/g.)		
Catalyst	Adsorption of palmitic acid from benzene	Brunauer–Emmett–Teller method[a]	Microscopic count method[a]
Raney nickel 1	49	49	0.045
Raney nickel 2	50	39	.045
Raney nickel 3	50	..	...

[a] See ref. 11.

TABLE II

ADSORPTION OF PALMITIC ACID ON RANEY NICKEL (SAMPLE II) FROM VARIOUS SOLVENTS

Solvent	Specific surface (sq. meters/g.)
Methanol	48
Acetone	55
n-Heptane	49
Benzene	50
Cyclohexane	52
Cyclohexene	43[a]

[a] This value is somewhat low probably because of oxidation or polymerization of cyclohexene during evaporation.

TABLE III

ADSORPTION OF VARIOUS FATTY ACIDS ON RANEY NICKEL (SAMPLE III) FROM BENZENE

Acid	No. C atoms	Specific surface (sq. meters/g.)
Capric	10	52
Lauric	12	53
Palmitic	16	50
Nonadecylic	19	48
Behenic	22	52

Discussion

The results as given by Table I indicate reasonable agreement between the true specific surfaces as calculated by the nitrogen adsorption isotherm (Brunauer–Emmett–Teller) and the fatty acid adsorption methods. Tables II and III indicate that the specific surface as determined by the fatty acid adsorption method is dependent on neither the length of the hydrocarbon chain of the fatty acid nor on the solvent used, provided that neither the solvent nor the fatty acid reacts with the catalyst. When chloroform was used as a solvent, it was found to cause reaction with the nickel.

The results with platinum indicate that the adsorption method can be used to calculate the specific surface of this catalyst. Calculations for this material gave values ranging from 50 to 75 square meters per gram depending on the individual preparation, as well as on the conditions of reduction of the oxide.

It is of considerable interest that the adsorption of fatty acids gives the same results for Raney nickel with acids varying from 10 to 22 carbon atoms and that these results also check with those found by the nitrogen adsorption method. The pores or crevices in the catalyst surface which are supposedly responsible for the difference between the true and apparent specific surface values must be uniformly large enough to accommodate these molecules whether they extend from the surface either two or three or some twenty-five ångström units.

While the fatty acid adsorption method for the determination of specific surfaces is not as generally applicable as the nitrogen isotherm method, it is experimentally much simpler. In addition, the assumption of the cross-sectional area occupied by a fatty acid chain is probably better than the assumptions made concerning the cross-sectional area of the nitrogen molecule when adsorbed on a solid surface and the necessarily arbitrary choice of liquid or solid density for the adsorbed gas.

Acknowledgment.—This research was made possible through a fellowship established and supported by the Hercules Powder Company. The authors are indebted to the Company for permission to publish the results.

Summary

The adsorption of normal fatty acids containing from ten to twenty-two carbon atoms has been studied on Raney nickel and Adams platinum catalysts. The results can be explained on the assumption that the acids are adsorbed on the metal in an oriented unimolecular film in a manner similar to that found in a compressed fatty acid film on a water surface. The specific surface of the catalyst can be calculated on the basis of this assumption, and is found to agree with values calculated by the Brunauer–Emmett–Teller method.

KNOXVILLE, TENNESSEE RECEIVED OCTOBER 15, 1945

---

[11] These measurements were made by the Hercules Powder Company of Wilmington, Delaware.