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CHEMISORPTION OF HYDROGEN ON A PROMOTED IRON CATALYST UP TO THE MIDDLE RANGE OF COVERAGE

By

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Chemisorption isotherms for hydrogen on an exhaustively reduced iron catalyst were presented at temperatures 20, 200 and 300°C and at equilibrium pressures 10^{-3} to 40 mmHg. Isosteric heats were found greater than those obtained previously by one of us, and given as a logarithmic function of coverage over 0.06 to 0.55. "Saturation" of the surface covering for hydrogen was approximately twice that for nitrogen on the same catalyst.

Isobaric adsorption of hydrogen on a promoted iron has been extensively studied between −195 and 400°C by Emmett and his associates[1] who interpreted the third descending portion of the isobar above room temperature as being dissociative adsorption in "open" lattice of α-iron crystallites. Adsorption isotherm for hydrogen was determined by Kwan[2] on I. G. catalyst (Germany) at 25 and 50°C below 1 mmHg equilibrium pressure. Adsorption heats derived from the isotherms reflected the bond formation of chemical nature.

In spite of a rather patient static reduction of the I. G. catalyst over a long period at 500°C, it was thought that the surface was not still completely freed from oxide, because this catalyst was less active toward nitrogen chemisorption, and moreover it is known that nitrogen exchange on an iron catalyst is affected to a very considerable extent by the presence of a trace of water vapour.[3]

In a later investigation,[4] commercial ammonia synthetic iron catalyst supplied by *Toa Synthesis* Co. (Japan) was exhaustively reduced by a flow method and found to chemisorb nitrogen efficiently. Attempts

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1) For a compact survey, see *Catalysis* III, 1955, a chapter by W. G. Frankenburg.

2) T. Kwan, J. Res. Inst. Catalysis 1, 100 (1949).

3) J. P. McGeer and H. S. Taylor, J. Am. Chem. Soc. 73, 2743 (1951).

4) T. Kwan, J. Res. Inst. Catalysis 3, 16 (1953).

were made therefore to re-establish adsorption isotherm for hydrogen on this catalyst with special interest to the shape of isotherm as well as the magnitude of adsorption heat.

The apparatus and experimental procedure were the same as described in an earlier communication relative to nitrogen chemisorption from this Laboratory.[4,5] The catalyst, once used for nitrogen chemisorption, was re-reduced at 550°C in a stream of hydrogen purified by passage through a heated palladium thimble. The weight of the catalyst was 10.4 gm before reduction. The B.E.T. surface area of the reduced sample was 135 sq. meter per total sample, and promoters and impurities were 1.06% K_2O, 1.82% Al_2O_3, 0.41% SiO_2 and traces of MgO and CaO.

Adsorption run was started at 300°C on surfaces degassed at 550°C for 3 hours. After left standing over night, equilibrium pressures were recorded at 300, 200, 20 and again 300°C. Fresh portion of hydrogen was then admitted to the catalyst and equilibrium pressures were recorded in a similar way. Such measurements were repeated on the freshly reduced and degassed surface and found reproducable to an extent as shown in Fig. 1, in which the logarithm of adsorbed amount v is plotted against the logarithm of equilibrium pressure p.

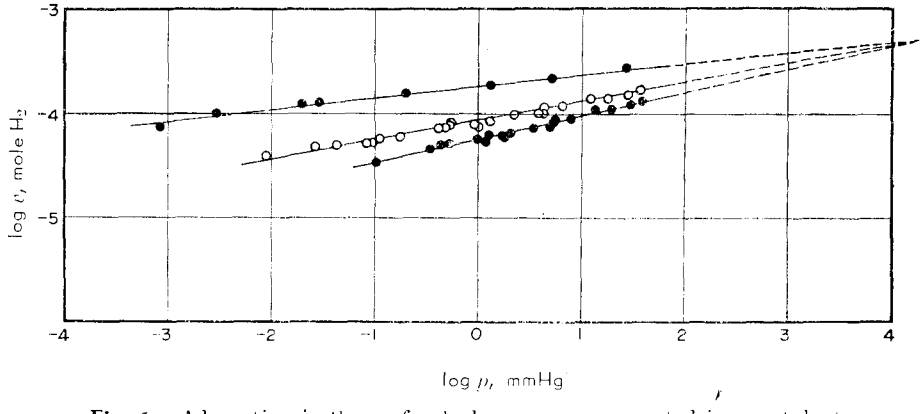

Fig. 1. Adsorption isotherm for hydrogen on a promoted iron catalyst at 20, 200 and 300 °C. Ordinates represent adsorbed hydrogen per total catalyst 10.4 gm before reduction.

Like nitrogen chemisorption isotherm on this catalyst, the isotherm appeared to follow a log-log straight line and to converge approximately at a coverage of common intersection, if extrapolated linearly at higher

5) T. KWAN, *ibid.* 3, 109 1955.

equilibrium pressures. The hydrogen adsorption at this coverage corresponded to 5×10^{-1} mole per total adsorbent or 4.5×10^{14} hydrogen atoms per sq. centimeter of the surface. This would indicate a completion of monolayer since the free iron surface which probably acts as adsorption seat is limited to 30 to 65% of the total B. E. T. surface area.*)

It is interesting to note that the corresponding "saturation" of the surface covering was 2.2×10^{14} atoms per sq. centimeter for nitrogen chemisorption on this catalyst.[5] It seems now very probable that nitrogen atom occupies two sites on iron if it is assumed that one hydrogen atom is chemisorbed for every surface iron atom exposed. The result therefore very resembles that of a set of data relative to hydrogen and nitrogen chemisorption on tungsten powder.[6,7]

The inverse slope n of the log-log linear isotherm was 10.6, 5.8 and 4.5 at 20, 200 and 300°C respectively. Within this limited range of temperature, no remarkable deviation from linearity was found, when

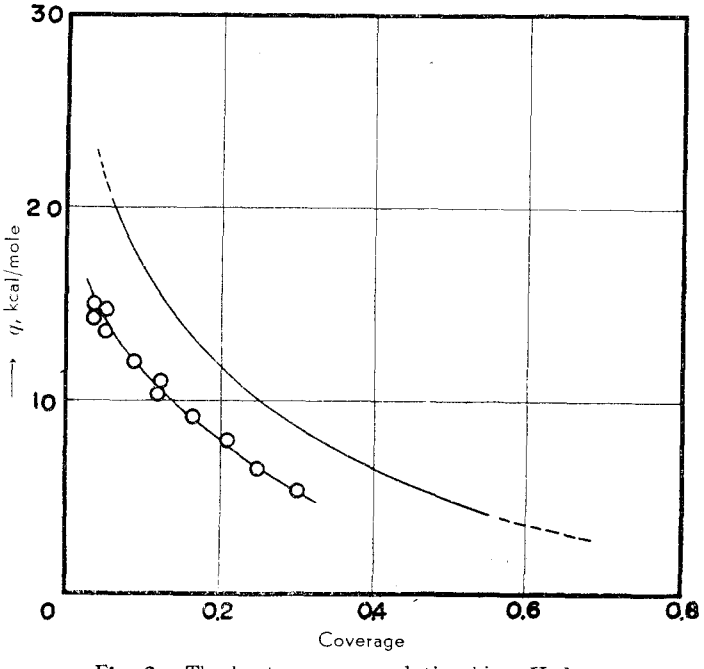

Fig. 2. The heat-coverage relationship. Hydrogen on a promoted iron catalyst.

*) See Ref. 1.

6) W. G. FRANKENBURG, J. Am. Chem. Soc., **66**, 1827 (1944).

7) R. T. DAVIS, *ibid.*, **68**, 1395 (1946).

n was plotted against $1/T$. Due to this the adsorption heat q can be given by an expression of the type: $q=-\gamma \ln\theta=-16.7 \log\theta$ kcal/mole, which is applicable over coverages 0.06 to 0.55.

This heat-coverage relationship is illustrated in Fig. 2 (full line) together with those obtained previously on I. G. catalyst (open circle). The free iron surface of the latter catalyst was assumed to be 30% of the total B. E. T. surface area. The appearance of the heat curve is similar to that on I. G. catalyst but the magnitude of adsorption heat is definitely much greater, as expectedly.

The solution of hydrogen in pure iron is estimated to be 1.73×10^{-6} mole per 10 gm at 409°C and 1 atm.[8] The square root law[9] gives 0.4×10^{-6} mole at 40 mm Hg. Since the total sorbed amount is 1.25×10^{-4} mole per 10.4 gm promoted iron at *300°C* and at 40 mm Hg, the solution of hydrogen may only be far below 0.3% of the total sorption. The solution effect to the shape of isotherm and the heat curve should substantially be negligible.

Remark may now be made to the intercept of the straight line in the plot of n against $1/T$ on the $1/T$ axis. The intercept or $1/T_n$ ($T_n\cong2000$ °K) is definitely different from that for nitrogen chemisorption on this catalyst ($T_n\cong1150$°K). Therefore, T_n is by no means related with physical or chemical characteristics inherent to the catalyst, as it is believed to be so in the Theta-Rule.[10] The small $1/T_n$ for hydrogen adsorption would mean that the degree of compensation between adsorption heats and entropies is also small.

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8) D. P. SMITH, *Hydrogen in Metal*, The University of Chicago Press 1947, p. 43.
9) See Ref. 8, p. 29.
10) *Advances in Catalysis* **2** (1950), a chapter by G. M. SCHWAB.
11) T. KWAN, J. Phys. Chem. **59**, 285 (1955).