Short Notes

The Adsorption of Ethylene to Nickel; Isotherm and Heat

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Reliable equilibria for the adsorption of ethylene to a reduced nickel could be determined at 130°C and 140°C in the pressure range 10^{-3}~10^{-6} mmHg. This result and the heat of adsorption will briefly be reported here.

The nickel was prepared in a vacuum by reducing 0.5g sample of nickel oxide at 350°C with palladium-filtered hydrogen for some twenty days.[1] Adsorption measurements were made with a McLeod gauge and a Pirani gauge, the drift and sensitivity of which were carefully checked before and after each reading. The adsorbent chamber and the Pirani bulb were protected from contamination by means of traps of freezing media throughout the experiment.

Under the present experimental circumstances, the ethylene admitted to the adsorption system was almost entirely adsorbed, so that only a very small fraction (1/1,000~1/100,000) remained in the gaseous phase.** On account of this, the determination of adsorbed quantities was made with considerable accuracy or almost unaffected by the error in measuring equilibrium pressure. Under such conditions the establishment of the equilibrium could be confirmed by the following procedure (reversibility test). The volume of the adsorption system was temporarily changed to a certain extent by use of a burette filled with mercury. If equilibrium is established the pressure should not change appreciably according as the change of the volume. Because the adsorbed quantity is practically constant during the procedure of this sort. Actually it happened that after a disturbance of equilibrium for a short time the pressure was restored exactly to the original value.

The isotherms obtained at 130°C and 140°C are shown in Fig. 1.

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** The presence of impurity gas, especially adsorption inactive gas in the sample ethylene, seriously affects the value of equilibrium pressure. Therefore, special cautions were taken in the purification of ethylene.

1) T. KWAN, Advances in Catalysis, Vol. VI, 67 (1954), Academic Press, New York.

The observed points were taken in the following manner. With a definite quantity of gas the point 1 and then, by varying the temperature, the point 1′ were taken. Thereafter, the ethylene was pumped off and the nickel was washed with hydrogen and kept in the atomosphere of new hydrogen at 200°C for about 20 hours. Then, after complete evacuation, the points 2 and 2′ were taken by admitting another portion of fresh ethylene. The subsequent points were read in the same way (9′ and 10′ with the gas amount increased), the evacuation and hydrogen cleaning being interposed between every pair of points. This procedure was adopted for fear of accumulation of impurity gas as well as possible occurrence of ethylene decomposition during long contact of the gas with nickel, although preliminary experiments showed that the experimental conditions of this work were most favourable to avoid ethylene decomposition. The observed point 9 or 9′ well demonstrates the constancy of surface conditions during the experiment and the reproducibility of the isotherms.

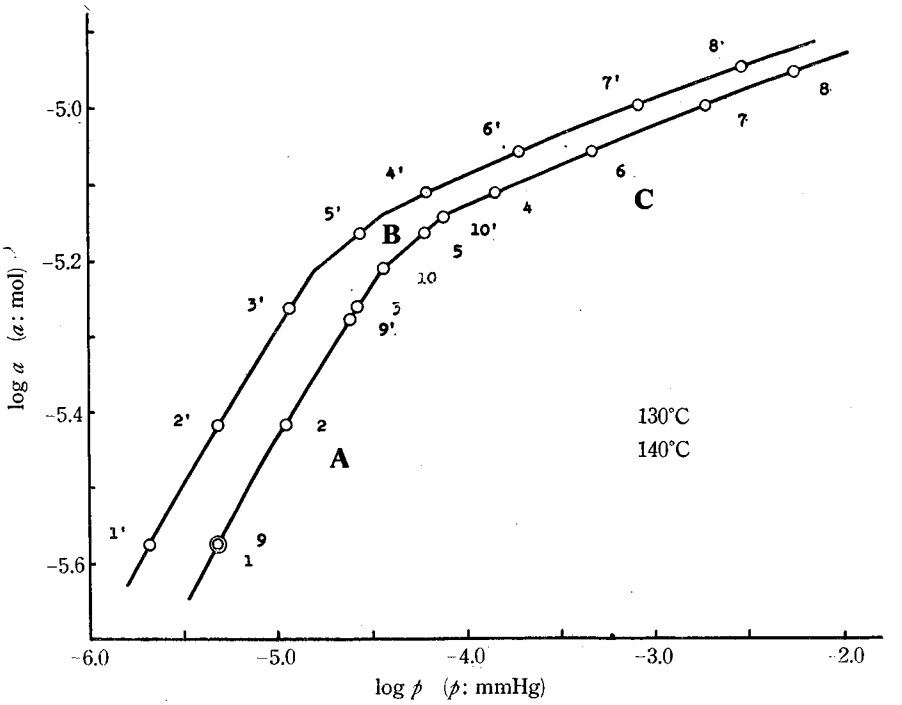

Fig. 1. The C_2H_4-Ni adsorption isotherms.

As is seen in Fig. 1, the isotherm in the log-log plot is linear separately in the lower and upper pressure regions (A and C in Fig. 1) (if carefully inspected, slightly downward concave in either). The inclinations are about 0.42 and 0.105 respectively. The heat of adsorption derived from the two isotherms is 27.3 ± 0.3 Kcal, which is constant over the coverage investigated. The BET area of the nickel was determined by use of nitrogen and of ethylene itself. The two results were in good agreement with a value of 13 m^2. If this area is uniformly available in the chemisorption and an ethylene molecule is assumed to cover two nickel atoms on the surface, the observed range corresponds to the surface coverage of *ca.* 0.02~0.08.

Of the isotherm in Fig. 1, the lower and upper straight lines (A and C) seemed to be jointed by a third short line (B) so as to give two breaks in the log-log plot. In order to confirm this, an independent experiment was carried out around this particular coverage. The result was affirmative as shown in Fig. 2 in a magnified scale. In this experiment, to know accurately the relative position of the points rather

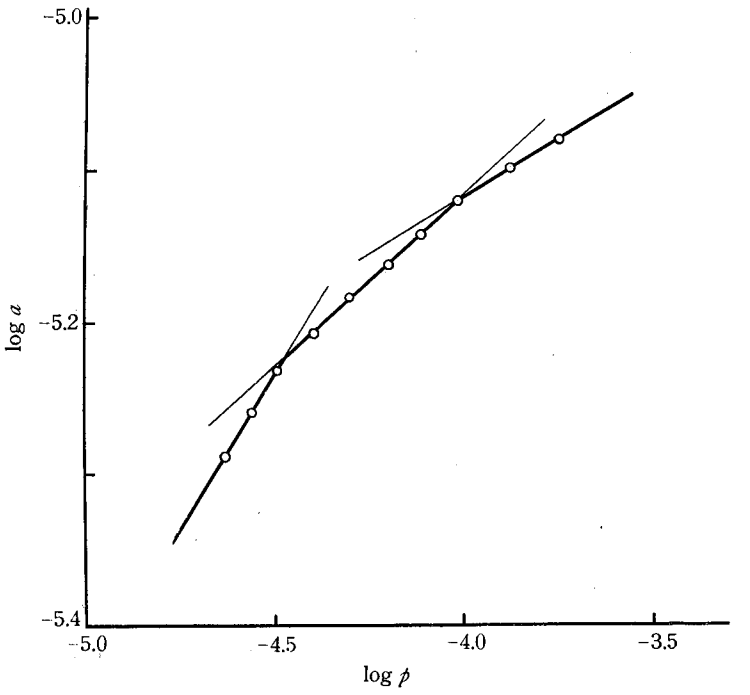

Fig. 2. The secondary discontinuity on the isotherm (140°C).

than their absolute positions, ethylene was added successively by small amounts without pumping out the presorbed ethylene.

Since the inclination of the line B is about 0.21, the inclinations of the three linear portions are fairly exactly in the ratio, 4 : 2 : 1.

The detailed discussions on this experiment will be published later.