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CHEMISORPTION OF HYDROGEN ON A REDUCED NICKEL OVER THE MAIN COVERAGE

By

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Chemisorption isotherm for hydrogen on a reduced nickel powder was presented over coverages 0.1 to almost 0.8. The shape of isotherm as well as the heat-coverage relationship was discussed in supplement to that previously reported by one of the authors.

Introduction

Previous work by one of us¹⁾ concerned primarily with a determination of chemisorption equilibrium for hydrogen on a reduced nickel at low coverages. Under such conditions, the physical nature of the nickel surface could be discussed on statistical-mechanical grounds without complex treatment. However, it was felt desirable to extend this sort of measurement over coverages as wide as possible, because the entire shape of isotherm is not only significant for discussing interactions involved in chemisorption but also helpful for analyzing catalytic data obtained on nickel *e. g.*, in terms of the power rate law.²⁾

Thus, chemisorption isotherm has been investigated further at temperatures from 0 to 300°C and at equilibrium pressures ranging from 10^{-2} up to 630 mmHg in a manner as described before. The result was consistent with what had been obtained earlier at low coverages, and will be communicated here.

Experimental Method

Two kinds of commercial nickel sample were employed for the

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1) T. KWAN, *J. Res. Inst. Catalysis*, **1**, 81 (1949); *Advances in Catalysis* **6**, 67 (1954).

2) T. KWAN, *J. Phys. Chem.* **60**, 1033 (1956).

purpose; one is basic nickel carbonate of *guaranteed* grade supplied by *Kokusai Kagaku* Co. and the other nickel carbonate of *reagent* grade by *Kanto Kagaku* Co. containing 0.007% Fe, 0.095% Cu, 0.01% Co, less than 0.05% Zn and about 1% alkali and alkali earth. The nickel salts were heated at 550°C for 24 hours in an atmospheric air. 1 gm of the resultant oxide of *Kokusai Kagaku* (designated as Ni I) and 76.6 gm of *Kanto Kagaku* (Ni II) were then subjected to reduction at 350°C. The reduction of Ni I was carried out under 200–300 mmHg hydrogen statically for 2 weeks and Ni II for about 5 weeks by a flow method. In either case the reduction was continued till the formation of ice cloud became imperceptible when subjected to cooling the wall of the reduction vessel with liquid air.

Before chemisorption experiment the adsorbent was degassed at 350°C for 3 hours with Ni I and for 33 hours with Ni II by means of oil diffusion pump until the pressure reached down to 10^{-9} mmHg. It is supposed that about 99% surface hydrogen are removed off by such procedure.¹⁾

With Ni I, chemisorption measurement was done by using a similar apparatus to that used perviously and followed by the same procedure. With Ni II, the chemisorption vessel was connected to the BOURDON gauge and a metal cock which, in place of cold trap, served to keep mercury and grease vapour away from the adsorbent during chemisorption measurements. Pressure readings were done by the usual mercury manometer equipped on the other side of the BOURDON gauge when the tip of the gauge was adjusted to zero point.

Equilibrium pressure was determined by checking its reversibility with respect to temperature variation. In case where Knudsen correction was required the empirically determined K-values¹⁾ were adopted. Ni II required much waiting time for attaining chemisorption equilibrium especially at higher equilibrium pressures. However, a period of one week was felt sufficient to approach a *constant* equilibrium pressure.

Hydrogen used for reduction was prepared electrolytically and purified by passage thru a heated palladium asbestos and liquid air trap. For chemisorption experiment it was further passed thru a heated palladium thimble. The B.E.T. surface area of the nickel sample was 15.0 and 22.6 square meter per gm (of the sample before reduction) with Ni I and II respectively.

Results and Discussion

Chemisorption isotherm was repeatedly determined in the temperature range from 0 to 300°C and at equilibrium pressure 10^{-2} to 630 mmHg, and plotted in the logarithm of chemisorbed amount against the logarithm of equilibrium pressure in Fig. 1 and 2 respectively. The figures show that the isotherms conform a Freundlich formula quite well over the temperature range investigated except those at lower coverages which probably follow the LANGMUIR equation of dissociative type in accordance with the previous work.

While the destination of the actual log-log plot in the region of much higher equilibrium pressures is not known, the linear extrapolation of the log-log plot, on the other hand, appears to converge at a common intersection to a good approximation. Such a pattern of the main isotherm is already familiar with hydrogen chemisorption on tungsten powder.³⁾

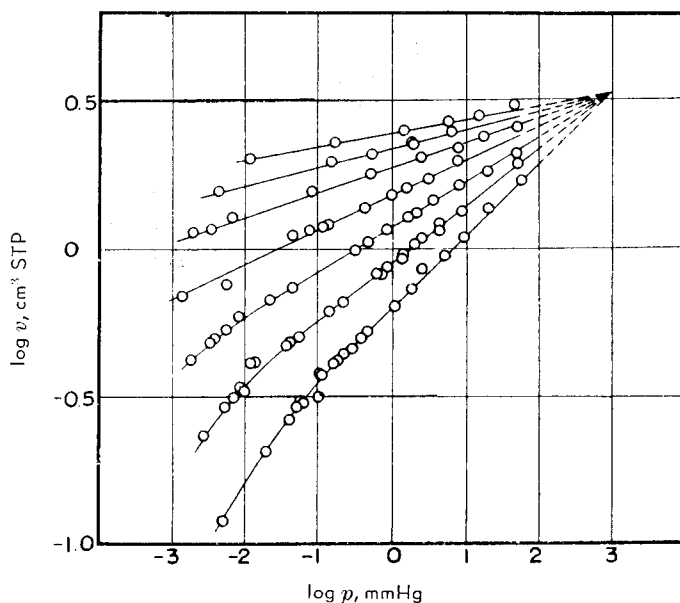


Fig. 1. Isotherm for hydrogen chemisorption on Ni I. Temperature: 0, 50, 100, 150, 200, 250 and 300°C. Ordinates represent chemisorbed amount per gm nickel (before reduction).

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

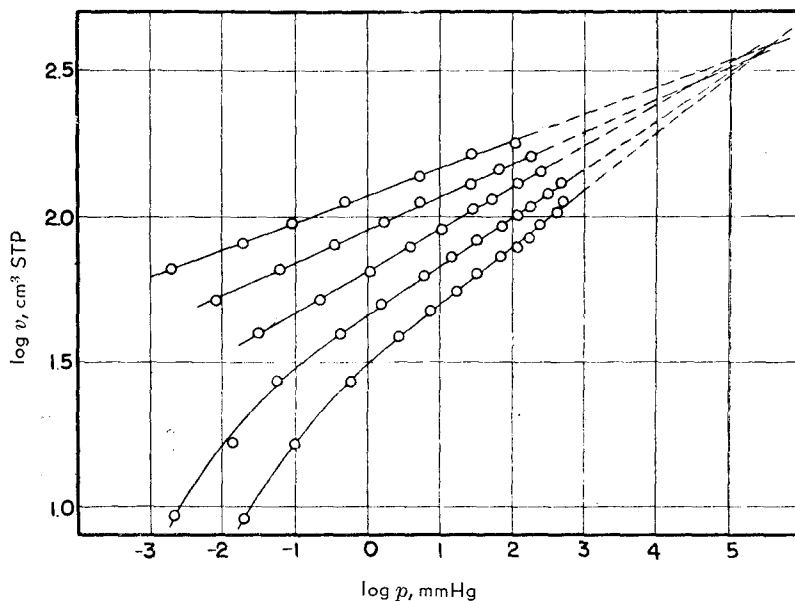


Fig. 2. Isotherm for hydrogen chemisorption on Ni II. Temperature: 100, 150, 200, 250 and 300°C. Ordinates represent chemisorbed amount per 76.6 gm nickel (before reduction).

The intersection located around 3.4 cm³ STP and 400 cm³ STP on Ni I and II respectively. The corresponding equilibrium pressures were 10³ mmHg and somewhere between 10⁵ and 10⁶ mmHg. The number of chemisorbed hydrogen atom was 1.2 × 10¹⁵ and about 1 × 10¹⁵ per square centimeter of the B.E.T. surface area respectively, indicating that a monolayer was nearly completed.

We may now have an isotherm equation of the type: $\ln \theta = \frac{1}{n} \ln \frac{p}{p_s}$ for the *main* coverage, where n is the inverse slope of the log-log linear plot and p_s the equilibrium pressure at *saturation*. In this connection reference may be made to the isotherm for hydrogen chemisorption due to SCHUIT and DE BOER⁴⁾ who used a highly dispersed nickel on silica. All of their data obtained in the temperature range -78 to 400°C also appear to follow log-log straight lines to a good approximation though some of the low temperature isotherms are expressed by

4) G. C. A. SCHUIT and N. H. DE BOER, Rec. Trav. Chim. 72, 909 (1953).

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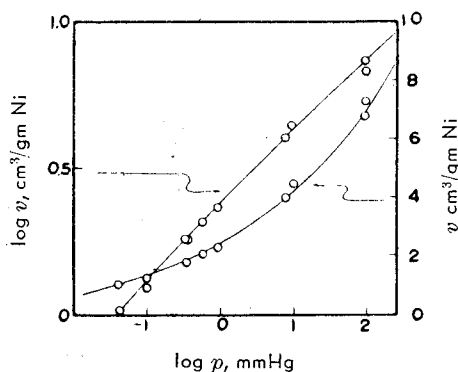


Fig. 3. Isotherm for hydrogen chemisorption on nickel supported on silica (SCHUIT and DE BOER) at 400°C.

the FRUMKIN-SYTGIN equation equally well. The latter equation is characterized by a linear variation of $\log p$ with chemisorbed amount v . In Fig. 3 are plotted their data obtained at 400°C in terms of $\log p$ against $\log v$ or v . It is evident that the $\log p-v$ relation reveals a marked deviation from linearity, while the $\log p-\log v$ gives an approximate linear relation.

Table 1 gives the temperature dependency of the inverse slope n of the log-log isotherm for the main coverage.

TABLE 1.

Temp. °C	0	50	100	150	200	250	300
Ni I	21.6	16.2	12.2	7.90	6.50	5.00	4.20
Ni II			11.0	8.64	6.92	6.25	4.82

If n were a linear function of reciprocal absolute temperature as expressed by $n = \frac{\gamma}{RT} - \frac{\gamma}{RT_n}$ where γ/R is the slope and $1/T_n$ the intercept on $1/T$ axis, then the heat of chemisorption q is given by $q = -\gamma \ln \theta$.^{5) 6)} However, the n -value was not linear in the present system but deviated slightly from linearity at higher temperatures. Now let γ/R be the tangent on the plot of n against $1/T$ at temperatures 100,

5) *Advances in Catalysis* 4, (1952), a chapter by G. D. HALSEY.

6) T. KWAN, *J. Phys. Chem.*, 59, 285 (1955).

200 and 300°C respectively, we find heat-coverage relationships appropriate to these temperatures as shown in Table 2 and also in Fig. 4.

TABLE 2.

Temp. (°C)	100	200	300
r (kcal)	19.8	14.9	11.5
q (kcal)	$-45.5 \log \theta$	$-34.4 \log \theta$	$-26.5 \log \theta$
θ	0.3—0.76	0.18—0.64	0.12—0.51

The general appearance of the heat curve is consistent with what had been obtained earlier in two respects. First, the heat starts at 26 kcal/mole and remains almost constant at low coverages (below 0.15) beyond which it declines monotonically. Second, this decline of the heat curve is more pronounced at higher temperature. The heat curve on Ni II indicated a similar trend although the heat was relatively low compared with that on Ni I presumably due to less cleanness of the surface.

WANG'S theoretical heat curve⁷⁾ based on lateral interactions be-

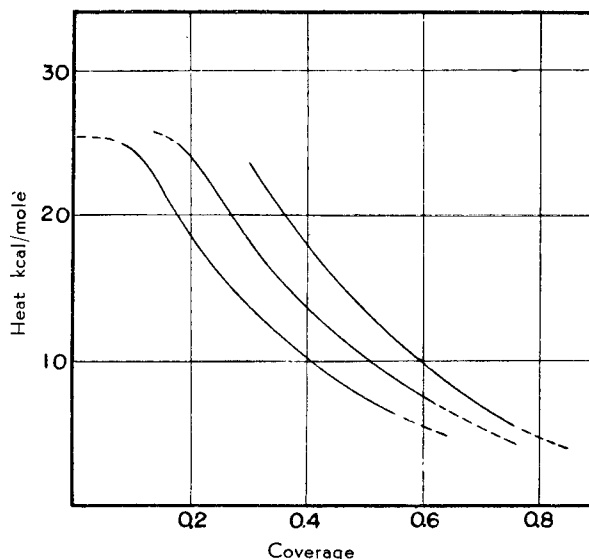


Fig. 4. Heat-coverage relationship for hydrogen on Ni I.

7) J. S. WANG, Proc. Roy. Soc. A161, 127 (1937).

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tween chemisorbed species describes qualitatively the reverse s-shaped heat curve obtained. However, it does not seem to account for the relative temperature dependency of the three heat curves as illustrated in Fig. 4. The temperature effect of this kind might first remind us an endothermic solution of hydrogen into nickel. The accepted solubility is estimated⁸⁾ however to be at most 3.7% of the total sorption, and would play only a minor role in this phenomenon.

For a possible cause of this effect the diffusivity of hydrogen atoms on the surface is attractive to us. Chemisorbed species on metal are able to migrate indeed according to the field emission microscope. If migration happens to occur to a position of lower heat and of probably greater entropy and then back to the original site, and moreover if high temperature facilitates such migration, the chemisorption heat should decrease with increasing temperature. At low coverages such migration may be inhibited due to a strong bond.

The above postulate is somewhat speculative but it seems likely to interpret also the *limited* exchangeability of chemisorbed deuterium atoms on metal with gaseous hydrogen as noticed recently by BOND⁹⁾ and others.

8) D. P. SMITH, *Hydrogen in Metal*, The University of Chicago Press (1947).

9) G. C. A. BOND, *J. Phys. Chem.*, **60**, 702 (1956).