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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 15(3), 239-246
Issue Date	1968-02
Doc URL	https://hdl.handle.net/2115/24841
Type	departmental bulletin paper
File Information	15(3)_P239-246.pdf

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J. Res. Inst. Catalysis, Hokkaido Univ., Vol. 15, No. 3, pp. 239 to 246 (1967)

VACUUM BALANCE FOR THE MEASUREMENT OF ADSORPTION OF WATER VAPOUR ON REDUCED NICKEL

By

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(Received December 15, 1967)

Abstract

Adsorption of water vapour on reduced nickel was investigated by measuring the adsorbed amount by means of a vacuum glass beam balance. The vacuum balance was constructed as symmetric as possible and capable of operation with a load of adsorbent up to 20 g. The zero-point of balance was found steady within 0.2 mg over the whole range of relative humidity dealt with and of temperature from 30 to 120°C for many a week.

Adsorbent was about seven grams of reduced nickel, preliminarily degassed thoroughly, with which a thin glass bucket hung on the balance was charged in vacuum. Water vapour was kept at desired constant pressure over the adsorbent by keeping a reservoir of liquid water at a constant temperature. Adsorption followed by desorption of water vapour on reduced nikel was observed up to 0.8 relative humidity at 30 and 50°C and adsorption only at 70°C. The adsorption followed by desorption was found to reveal a hysteresis loop. The hysteresis decayed and finally vanished by repeating the adsorption-desorption cycle over the same range of vapour pressure except for about 2.5 mg water adsorbed per gram of reduced nickel, which remained unremovable even by immersing the water reservoir in liquid nitrogen for a week.

Introduction

Although a considerable amount of work has been done on the adsorption of water vapour on solid surface, a contribution to its adsorption on reduced nickel is not available to the best of the present author's knowledge. The present paper is concerned with observation of adsorption followed by desorption of water vapour on reduced nickel.

Gravimetric method was resorted to for measuring the adsorbed amount, lest the adsorption of water on glass surface and its hysteresis[1,2,3] should give ambiguous observations as they would be especially the case in volumetric measurement of water vapour adsorption. Adsorption and desorption were

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thus observed by means of a glass beam balance in vacuum vessel. Adsorption on the balance and the temperature change in zero-point may nevertheless affect the gravimetric observation, which is avoided as far possible by making the balance symmetric

Experimentals

Materials.

Reduced Nickel: About 15 g of nickel oxide, prepared by igniting chemical pure grade basic carbonate (Kanto Chemical Co., Tokyo) at 500°C was admitted into the reduction vessel (Fig. 1) provided with constrictions, C, and breakable joint B_1, and reduced at 380°C in a stream of hydrogen purified by filtering through a Pd-thimble. The reduction proceeded until a white spot formed on the inside wall at the point where was cooled with liquid nitrogen from outside was no more perceptible. The reduction vessel was now sealed off at the constrictions, C, after the contents of reduction vessel was degassed by evacuation to 10^{-6} mmHg at 450°C for 24 hours.

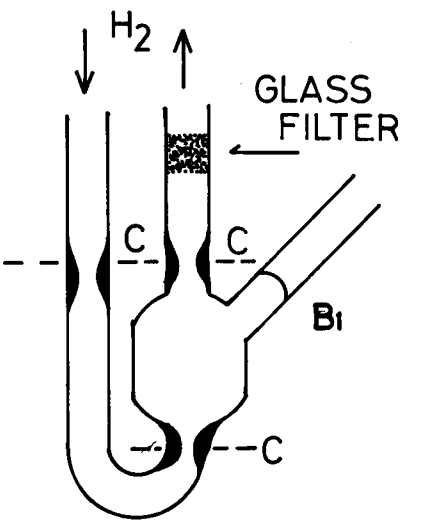

Fig. 1. Reduction vessel.
C : constrictions.
B_1 : breakable joint.

Water: A portion of redistilled water in a reservoir, provided with breakable joint and fused to the vacuum line through a constriction, was degassed by repeating evacuation to 10^{-6} mmHg with the reservoir immersed in liquid nitrogen followed by fusion of the contents; the constriction was now sealed off and the water reservoir thus finished was fused to the adsorption system desribed below with breakable joint B_2 as shown in Fig. 3 and 4.

Adsorption system.

Vacuum balance: Fig. 2 illustrates a simple glass beam balance cased in an H-shaped vacuum glass vessel. The beam, B, and its support, S, are made by grinding glass tubings of 0.8 cm diameter and 15.3 cm length, and of 3 cm diameter and 20 cm length. The beam is perpendicularly fixed at its center with AgCl seals to the tungsten wire (0.005 cm diameter) stretched tightly across the support; the fixation is strengthened by sticking the cover plate CP on to the middle of beam with AgCl seals. Two glass buckets, L_1 and

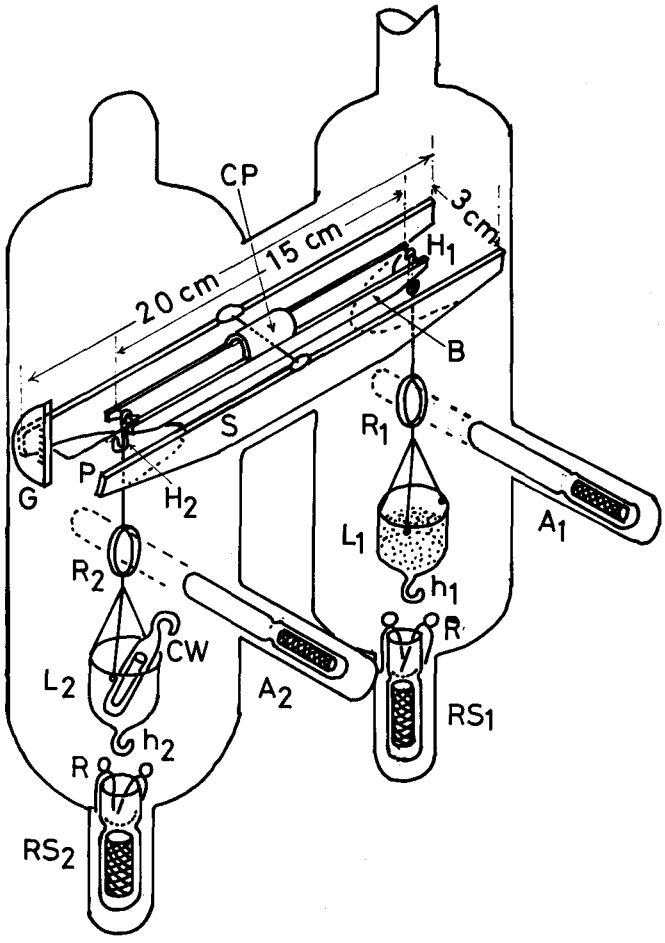

Fig. 2. Glass beam balance cased in an H-shaped vacuum glass vessel.

B : beam,
P : pointer,
S : support,
G : 0.01 cm graduated scale,
A_1, A_2 : arresters,
L_1, L_2 : glass buckets respectively for sample of adsorbent and for counterweight,
R_1 R_2 : glass rings for arrest,
H_1 H_2 : double hooks of gloss rod,
h_1 h_2 : hooks for rider,
RS_1 RS_2 : rider supports,
CW : counterweight,
CP : glass cover plate with AgCl seals,
▒▒ : soft iron enclosed in a glass bulb.

L_2, for sample of adsorbent and counterweight are hooked themselves above on tungsten wires strung perpendicularly to the beam and at equal distance from the central wire on both sides. Counterweight is a soft iron rod enclosed in a glass bulb. Pointer P is 0.05 cm diameter tungsten wire attached horizontally to the end of the beam and sharpened at its free end by electrolytic etching. The sample of adsorbent is weighed by reading the deflection of the pointer from zero point by refference to a 0.01 cm graduated scale, G, fixed to the end of the supporrt. The balance is arrested by sliding the arresters, A_1 and A_2, into the rings, R_1 and R_2, when it is not in use, or the bucket is being loaded up. The balance is calibrated with 5, 10, and 20 mg platinum riders, R, which can be hung on or removed from the hooks, h_1 and h_2 of the buckets by manipulating rider supports RS_1 and RS_2 with a magnet. The balance was checked for stability at temperatures from 30 to 120°C, over a range of vapour pressure up to 0.8 relative humidity and found to give readings accurate within 0.2 mg for weeks.

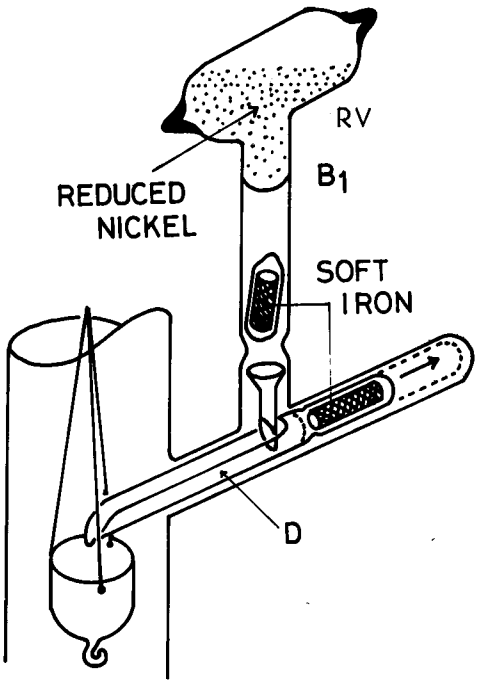

Fig. 3. Sample charging device.
RV: reduction vessel sealed at constrictions,
B_1: breakable joint,
D: conduit pipe for reduced nickel with a piece of soft iron enclosed in a glass bulb.

Sample charging device: Fig. 3 illustrates the device of charging the bucket with an appropriate amount of the sample of adsorbent in vacuum. Reduced nickel is led out from the reduction vessel, RV, through breakable joint B_1 opened and the conduit pipe, D, into the bucket by the aid of a magnet or a vibrator; as soon as the bucket L_1 is loaded with an amount of reduced nickel just to counterpoise the balance with CW in bucket L_2, and then the conduit pipe is withdrawn.

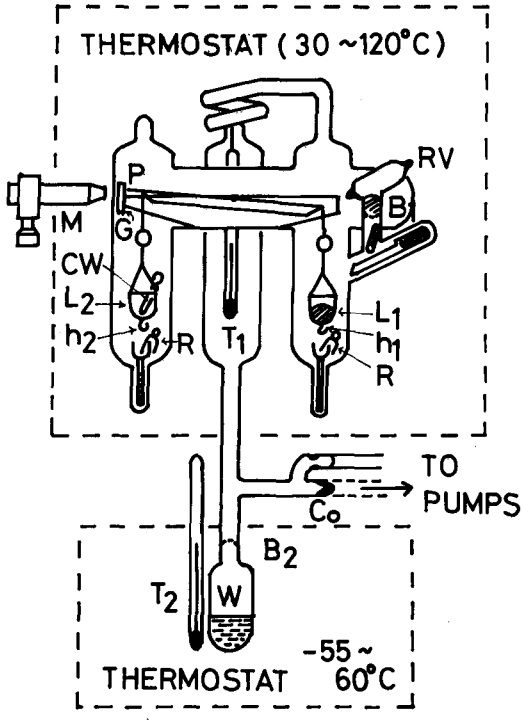

Fig. 4. Adsorption system.

RV: reduction vessel containing reduced nickel,
W: water reservoir,
B_1, B_2: breakable joints,
T_1, T_2: thermometers,
C_0: constriction,
CW: counterweight,
h_1, h_2: hooks for rider,
R: riders,
P: pointer,
G: 0.01 cm graduated scale,
M: low-powered microscope with micrometer.
L_1, L_2: glass buckets.

Adsorption system: Fig. 4 shows schematically the adsorption system to which the reduction vessel, RV, containing reduced nickel and the water reseroir, W, are fused at breakable joints, B_1 and B_2, respectively. The glass vessel of the balance is placed in an air thermostat with infrared lamp heater, which keeps temperatures from 30 to 120°C constant by means of Thermistor Temperature Regulator, Type TR-11 (Takara Kogyo Co. Ltd., Tokyo). Temperature of the water reservoir is kept constant at temperatures from −55 to 60°C by means of Sharp Thermoelectric, Model TEB-202, Hayakawa Electric Co. Ltd., Tokyo.

Procedure.

Bucket L_2 was loaded with counterweight. The adsorption system was then fused to the pumping unit through constriction C_0 and liquid nitrogen trap, evacuated to 10^{-6} mm Hg at 100°C and sealed off at C_0. Bucket L_1 was now charged with so much reduced nickel as to counterpoise the balance

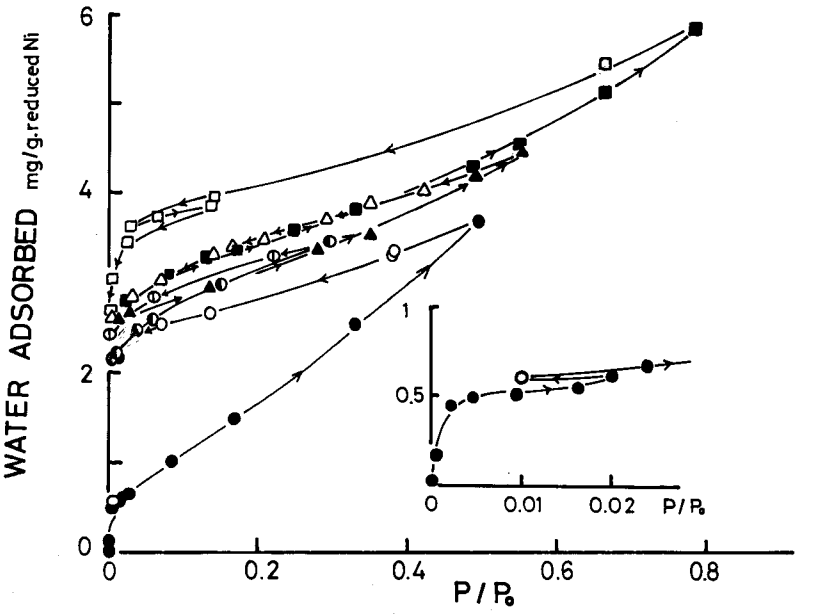

Fig. 5. Measurements of adsorption and subsequent desorption of water vapour on reduced nickel at 30°C.
Insert: separate measurement up to $P/P_0=0.025$.

run. No.	adsorption	subsequent desorption
1	●	○
2	◐	◑
3	▲	△
4	■	□

loaded with CW in L_2. Shift of the rest point of the pointer was calibrated against the 10 mg rider on hook h_2. Water vapour was now admitted by opening breakable joint B_2 and keeping W at an appropriate temperature (*cf.* Fig. 4).[4] Adsorption and subsequent desorption of water vapour on reduced nickel were followed by reading the deflection of pointer P with the adsorption system kept at a constant temperature, and with the water reservoir kept at various constant temperatures,

Results and Discussion

Adsorption and subsequent desorption of water vapour on a portion of reduced nickel were measured at 30, 50, and 70°C.

Fig. 5 summerizes the successive measurements of adsorption followed by desorption of water vapour on 6.572 g of reduced nickel at 30°C over a range of relative humidity up to 0.8. Fig. 6 shows the measurements of adsorption and subsequent desorption at 30 and 50°C, and the measurements of adsorption at 70°C. Each value was that recorded after the water reservoir was kept at constrant temperature for 6 to 12 hours, while the value was practically attained to within first 30 minutes.

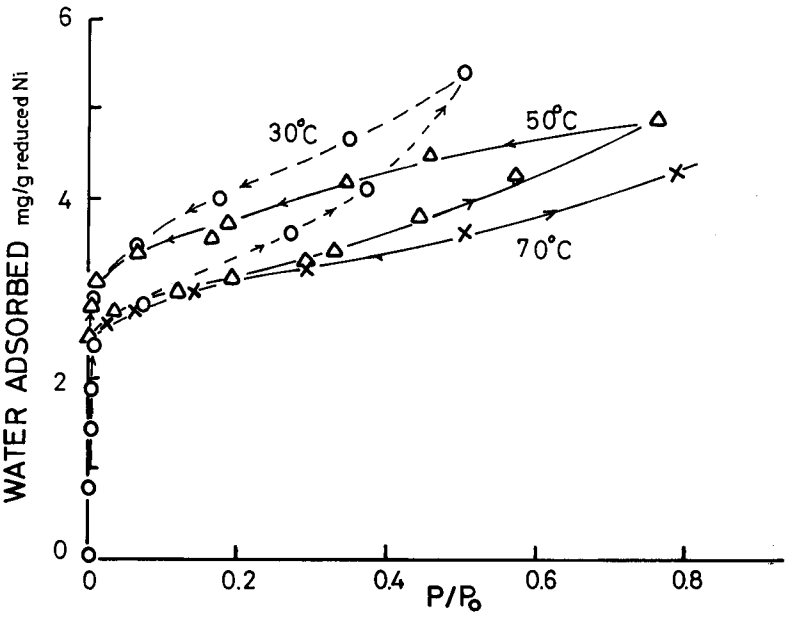

Fig. 6. Measurements of adsorption and subsequent desorption of water vapour on reduced nickel at 30 and 50 °C and that of adsorption at 70°C.

The hysteresis revealed in Figs. 5 and 6 was gradually diminished and finally vanished by the repetition of adsorption-desorption cycle over the same range of humidity except for about 2.5 mg water adsorbed per gram of reduced nickel, which was not removed even by immersing the water reservoir in liquid nitrogen for a week.*)

It is the further subject of investigation to accout for the phenomena of adsorption-desorption cycle with special reference to atomistic states of the adsorbent and adsorbate.

Acknowledgement

The author wishes to express his gratitude to Professor Emeritus Juro HORIUTI for suggesting this investigation as well as for guidance in the course of the present work.

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*) Preliminary experiment with a simple calorimeter gave the average heat of adsorption of 25–30 kcal $mole^{-1}$ for about 3 mg of water per gram of reduced nickel.