ATOMIC HYDROGEN ADSORPTION DETECTOR

LESZEK STOBIŃSKI and RYSZARD DUŚ

Institute of Physical Chemistry, Polish Academy of Sciences 01-224 Warszawa, Kasprzaka 44/52, Poland

An adsorption–desorption method for the determination of atomic hydrogen concentration in an $H + H_2$ gas mixture has been proposed. Thin gold film surface at 78 K has been used as a selective adsorbent for atomic hydrogen. The experimental system, calibration and calculation procedure are described.

1. Introduction

Interaction of solids with atomic hydrogen can be important in several fields of science and technology. Generation of atomic hydrogen that is 100 % atomic has so far not been achieved, i.e. an $H + H_2$ mixture is always obtained as a result. For the determination of a low concentration of H in an $H + H_2$ gas mixture, catalytic probe [1] is not sensitive enough. Mass spectrometry is another possibility for this purpose. However, complications arise because some amount of H is generated in the gas phase due to H_2 thermal dissociation on the hot tungsten filament of the mass spectrometer [2].

In this paper we suggest the application of an adsorption–desorption method

which is particularly suitable for the determination of a low H concentration in an H + H_2 gas mixture.

It is known that molecular hydrogen does not adsorb on a clean surface of sintered thin gold films at 78 K [3-6]. However, atomic hydrogen does adsorb on a gold surface [3-6].

2. The apparatus

The apparatus and the cell were described previously [3-6]. The experiments were carried out using a Pyrex glass system capable of routinely reaching 2-4 $\times 10^{-8}$ Pa. Non-transparent thin gold films of golden colour were deposited on the inner wall of the spherical reactor, maintained in a liquid nitrogen bath at 78 K. It was reported that sintered thin gold films, which correspond well to our Au films, consist of crystallites with dominant (111) and (100) surface planes [7]. The average geometric area of the sintered thin gold films was $\approx 1.5 \times 10^{-2}$ m^2 and the roughness factor approached one [3]. The average thickness of the gold films was ≈ 70 nm. AES analysis, performed occasionally in a separate UHV apparatus, confirmed that no traces of metals, which could dissociatively adsorb molecular hydrogen, were present on the gold film surface.

Spectroscopically pure hydrogen was conventionally leaked into the apparatus by diffusion through a heated palladium thimble. During the experiments with atomic hydrogen adsorption, the reactor was disconnected from the diffusion pumps by means of greaseless Dekker valves as described previously [3-6]. The initial H_2 pressure was regulary 0.27 Pa.

3. Adsorption of atomic hydrogen

Kinetics and the uptake of atomic hydrogen on the sintered thin gold film surface, maintained at 78 K, was determined by measuring the decrease of total hydrogen pressure with the Schulz gauge in the reactor separated from the pumps [3]. During the experiments the tungsten filament used as the H generator was heated to the temperatures T_W of: 1020, 1115, 1182 or 1315 K [8]. The exposures of the thin Au film to an H + H_2 gas mixture were carried out within 1200 s. The dependence of the atomic hydrogen deposit N_{ad} on the gold film surface on the time of interaction t_{exp} of H with the Au surface for various temperatures T_W is shown in Fig. 1a. Within a limited surface hydrogen uptake, the results can be represented by a straight line in the coordinate system: dN_{ad}/dt vs. N_{ad} as shown in Fig. 1b. This indicates the following dependence of the effective rate of adsorption on population [3,6]:

$$\left(\frac{dN_{ad}}{dt}\right)_{effect.} = J_H S_0(1 - \Theta_H) - J_H \gamma_H \Theta_H \tag{1}$$

where $(dN_{ad}/dt)_{effect.}$ is the effective rate of H adsorption on Au, $J_H S_0(1 - \Theta_H)$ the rate of H adsorption on Au, $J_H \gamma_H \Theta_H$ is the rate of desorption of hydrogen via the Eley–Rideal mechanism (one H adatom recombines with one H atom from the gas phase), J_H is the total atomic hydrogen stream impinging the thin gold film surface per second, S_0 is the initial sticking probability for H on Au at 78 K [3] and γ_H is the probability for hydrogen recombination via the Eley–Rideal mechanism [3]. Further, Θ_H is the hydrogen coverage on the sintered thin gold film surface defined here as $\Theta_H = N_{ad}/N_{max}$, where: N_{ad} is the hydrogen population on gold film surface at 78 K and N_{max} is the maximal population of H on Au ($N_{max} = 1.3 \times 10^{19} \times A$ sites of adsorption, where A [m^2] means the geometric area of the sintered thin gold film surface [3]).
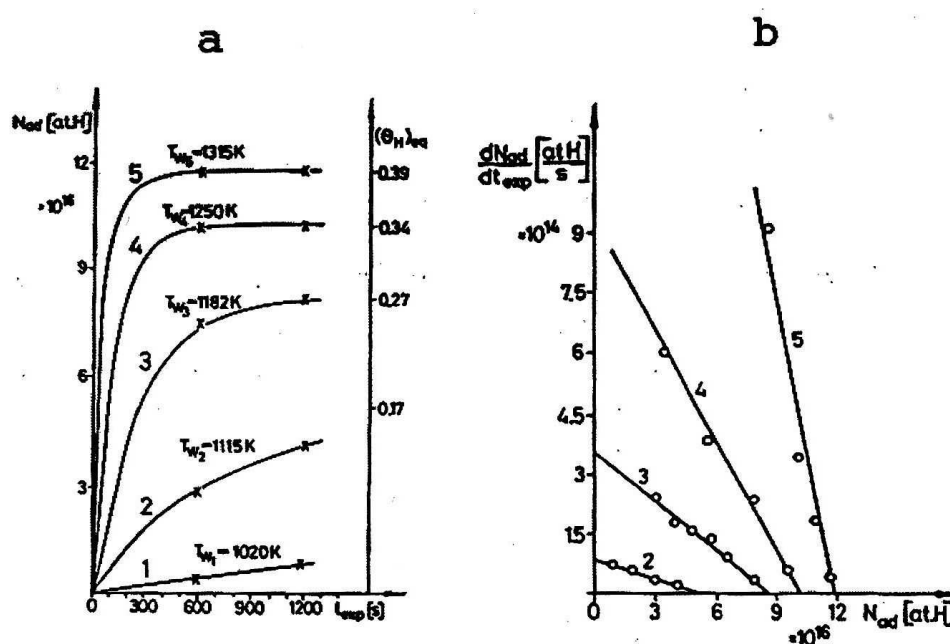

Fig. 1(a). Dependence of N_{ad} and $(\Theta_H)_{eq}$ on the time t_{exp} of exposure of the sintered thin Au film to the H + H$_2$ gas mixture for various yields (i.e. temperatures T_W) of the H generator. Corresponding p_H values calculated previously [3] were $p_H \approx 5 \times 10^{-7}$, 7×10^{-6}, 3×10^{-5}, 8×10^{-5} and 4×10^{-4} Pa corresponding to tungsten–filament temperatures $T_W = 1020$, 1115, 1182, 1250 and 1315 K, respectively, and the hydrogen pressure $p_{H_2} = 0.27$ Pa. The hydrogen uptakes determined on the basis of TD spectra analysis [3,4] are marked by crosses.

Fig. 1(b). The rate of atomic hydrogen adsorption on the sintered thin Au film surface at 78 K as a function of hydrogen uptake for various yields of the H tungsten generator (straight lines: 2,3,4 and 5 correspond to curves: 2,3,4 and 5 in part (a) of Fig. 1, respectively).

4. Desorption of hydrogen

Atomic hydrogen uptake on the sintered thin gold film surface at 78 K can be determined independently by means of the TDMS method [3]. At the end of every adsorption experiment the heating of the tungsten filament was turned off and hydrogen was quickly (in about 10 s) evacuated from the reactor, reaching a pressure of about 10^{-7} Pa. Next, the liquid nitrogen bath was removed. Increase of the temperature of the reactor (at constant evacuation) caused thermal desorption of hydrogen [3]. Hydrogen desorption from the gold surface was completed around 200 K provided that atomic hydrogen was not dissolved in a significant amount in the bulk of gold [4].

During hydrogen desorption in time t the partial pressure p_{H_2} and gold film temperature T_{Au} were continuously monitored. Thus, we obtained two relations: $p_{H_2} = f_1(t)$ and $T_{Au} = f_2(t)$. On the basis of these two functions we can obtain another relation: $p_{H_2} = f_3(T_{Au})$. This relation is shown in Fig. 2a as obtained for various yields of the H generator, i.e. for various T_W [8] and for the exposure times of 1200 s.
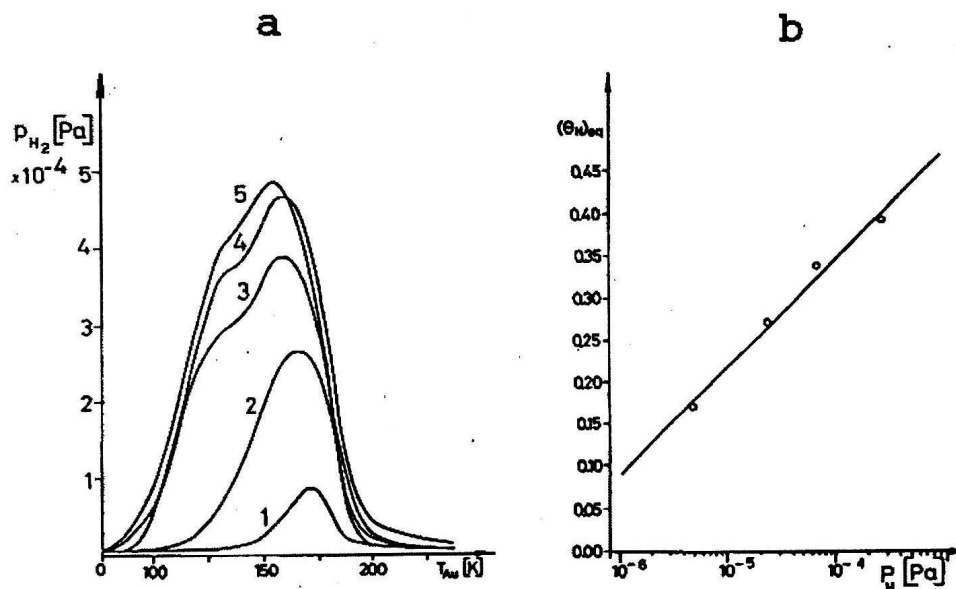

Fig. 2(a). TD spectra obtained as a result of Au exposure to the H + H_2 gas mixture for $t_{exp} = 1200$ s. Spectra: 1,2,3,4 and 5 correspond to curves: 1,2,3,4 and 5 in Fig. 1a, respectively.

Fig. 2(b). Dependence of the equilibrium atomic hydrogen coverage, $(\Theta_H)_{eq}$, on the sintered thin gold film surface at 78 K on atomic hydrogen pressure p_H.

The TDMS method provides the possibility to compare the amount N_{des} of desorbed hydrogen (marked by crosses in Fig. 1a), calculated on the basis of Fig.

2a [3,4], with the amount N_{ad} of hydrogen adsorbed on a sintered thin gold film surface, determined by means of the Schulz gauge during adsorption experiments. The obtained agreement for the adsorption and desorption process was within ± 5 %.

5. Results and discussion

The adsorption method and the desorption method described above allow the determination of the equilibrium amount $(N_{ad})_{eq}$ of atomic hydrogen adsorbed on a sintered thin gold film surface at 78 K, corresponding to the plateaus of each curve in Fig. 1a. On the basis of $(N_{ad})_{eq}$ and N_{max} one can calculate the equilibrium coverage $(\Theta_H)_{eq}$ for various atomic hydrogen yields of the H generator (i.e. for various temperatures T_W of the tungsten filament).

Taking into account the dependence represented in Fig. 1b, the initial sticking probability $S_0 \simeq 6 \times 10^{-3}$ for atomic hydrogen on the sintered thin gold film surface at 78 K was determined [3]. Hence, the total atomic hydrogen stream J_H impinging the thin gold film surface per second was calculated [3]. Atomic hydrogen pressure, p_H, corresponding to given T_W and $(\Theta_H)_{eq}$ was obtained using the expression presented in our previous paper [6].

On the basis of atomic hydrogen pressure, p_H, and the corresponding equilibrium coverage $(\Theta_H)_{eq}$, one can derive the relation $p_H = f(\Theta_H)_{eq}$, which is the fundamental calibration graph in the procedure of determining atomic hydrogen concentration in an H + H$_2$ gas mixture. We can directly read p_H on the basis of Fig. 2b for every known equilibrium atomic hydrogen coverage $(\Theta_H)_{eq}$ obtained on the sintered thin gold film surface at 78 K.

The straight line dependence, shown in Fig. 2b, can be expressed by the equation:

$$p_H \text{ [Pa]} = \exp\left(\frac{(\Theta_H)_{eq} - 1.0}{0.0625}\right). \qquad (2)$$

The concentration of atomic hydrogen C_H in the (H + H$_2$) gas mixture can be calculated by the relation: $C_H = p_H/p_{H_2}$, where p_{H_2} is the molecular hydrogen pressure in the reactor measured by any conventional method.

6. Conclusions

The proposed adsorption or desorption method can be applied for the determination of atomic hydrogen concentration in an H + H$_2$ gas mixtures. The method is particularly useful for measurements of low concentration of atomic hydrogen ($p_H < 10^{-3}$ Pa in an H + H$_2$ gas mixture).

References

1) F. Breceli, M. Mozetič and K. Zupan, Vacuum **44** (1993) 459;

2) A. G. Sault, R. J. Madix and C. T. Campbell, Surf. Sci. **169** (1986) 347;

3) L. Stobiński and R. Duś, Surf. Sci. **269/270** (1992) 383;

4) L. Stobiński and R. Duś, Appl. Surf. Sci. **62** (1992) 77;

5) L. Stobiński and R. Duś, Surf. Sci. **298** (1993) 101;

6) L. Stobiński and R. Duś, Vacuum **45** (1994) 299;

7) H. von Geiger, K. Haupl, P. Wissmann and E. Wittmann, Vac.-Tech. **34** (1985) 135;

8) L. Stobiński and R. Duś, Vacuum **46** (1995) 433.

ADSORPCIJSKI DETEKTOR ATOMA VODIKA

Predložena je adsorpcijsko–desorpcijska metoda za određivanje koncentracije vodikovih atoma u smjesi plina H + H$_2$ primjenom tankog Au sloja. Opisana metoda osobito je prikladna za mjerenje u smjesama s malom koncentracijom vodikovih atoma.