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Heats of displacement of hydrogen from palladium by noble gases

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Abstract

It has been observed that noble gases, such as helium, neon and argon produce heat evolution when contacted with Pd powder partially saturated with hydrogen. These phenomena have been studied with flow-through adsorption microcalorimetry. The observed exothermic effects are comparable to those usually associated with the heat of sorption of hydrogen in palladium. It is suggested that the noble gases displace the adsorbed H species from the surface of Pd, causing their reabsorption in the Pd lattice with the exothermic heat of Pd–H bonds formation, or the formation of H_2, both heat evolutions being observed with a flow-through microcalorimeter.

Keywords: Palladium; Palladium hydride; Noble gases; Heat of sorption; Flow microcalorimetry

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1. Introduction

It is well known that palladium reacts with molecular hydrogen forming palladium hydrides with the evolution of heat [1–3]. The heat reflects the affinity of Pd for atomic hydrogen, which is responsible for breaking the bonds forming hydrogen molecules. Palladium hydrides decompose relatively easily producing active H atoms, which is useful in a wide range of catalytic hydrogenations. The decomposition occurs readily on evacuation of Pd hydrides, but as was found recently by the authors, the rate of the decomposition is considerably slowed down when the hydride is placed in an environment of nitrogen or that of noble gases, such as He, Ne, or Ar at atmospheric pressures. Indeed, it was found that when palladium saturated with hydrogen is placed in a flow of any of the above gases at atmospheric pressure, the metal retains about 70% of the absorbed hydrogen at room temperatures after passing as much as 8000 volumes of the inert gases through the powdered hydride.

Unexpectedly, it was found that replacing nitrogen carrier with the noble gases over the surface of palladium partially saturated with hydrogen, that is, after ca. 20 h of desorption (8000 volumes of N_2), produces high exothermic heats of sorption. The

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strong exothermic effect on contact of noble gases with palladium hydride observed in this work has not been (to our knowledge) previously detected.

In this paper, we describe thermal effects triggered by contact of He, Ar and Ne with Pd powder partly saturated with hydrogen, which produce large exothermic heat effects. Detection and measurement of these thermal absorption and desorption effects are carried out by MICROSCAL flow-through microcalorimeter in which the heats of sorption/desorption are measured concurrently with the uptake and/or release of the gases by the Pd samples.

2. Experimental

2.1. Materials

Palladium powder (purity 99.999%) was supplied by Aldrich Co., and nitrogen, He, Ar, Ne and hydrogen were provided by Linde Gas Poland S.A. The surface area of the Pd powder measured by low-temperature adsorption of nitrogen and calculated from BET was ca. 0.1 m^2/g.

2.2. Equipment

Microscal flow-through microcalorimeter, Model FMC-4110 designed for use at temperatures up to 240 °C and pressures up to 5 MPa has been applied. The use of this instrument was recently reviewed by one of the authors [4,5]. Sartorius balance S3DV, connected to a glass vacuum system, has been used for gravimetric experiments with accuracy of 1 μg.

2.3. Procedure

A sample ca. 0.2 g of palladium powder has been used to make up a volume of 0.15 cm^3 required to fill the calorimetric cell containing electrical calibrator. The sample was standardised by heating in situ for ca. 12 h at 200 °C in the flow of carrier gas prior to each experiment. Nitrogen as a carrier gas selected for the experiment was then passed through the cell after sealing it with top and bottom gas inlet and outlet, the latter connected to TC detector. The supply of gases to the inlet was controlled by mass flow controllers and the gases passed through the powder in the cell at the rate of 1 cm^3/min. Calibration has been made in situ by introducing controlled amounts of heat obtained by passing electric current through the calibrator located axially within the sample, so that the area under the peak recorded on such calibrating pulse is then used as a standard to calculate a calibration factor for the sample. After reaching thermal equilibrium of the sample with the carrier gas, its flow was replaced by the flow of hydrogen. Heat evolution in the cell was measured by a pair of thermistors and the changes in H_2 concentration in the effluent from the cell measured by TCD. All calorimetric experiments were carried out at ambient temperature and pressure in a thermostatted laboratory (± 0.1 °C). In all the experiments, the flow rates of N_2 and the noble gases were maintained at 1 cm^3/min.

The experimental procedure, which leads to the unexpectedly large thermal effects of noble gases being sorbed on the palladium partially saturated with hydrogen, can be summarised as follows:

1. Carrier gas (nitrogen) is passed through the calorimetric cell containing palladium powder until the thermal equilibrium is being reached.
2. The flow of carrier is then replaced by the flow of hydrogen, and the rate of heat evolution accompanying the process of sorption of hydrogen in palladium is being recorded.
3. After cessation of heat evolution, the nitrogen carrier is switched again and the heat of desorption is being measured.
4. After ca. 20 h period of desorption, the nitrogen carrier is replaced by the flow of noble gas (Ne, He, Ar) and the heat of sorption is being measured.

For the gravimetric experiments, the sample of 0.6586 g of palladium powder was outgassed in vacuo at 10^{-4} Torr at RT prior to admission of the adsorbed gases.

3. Results

3.1. Sorption of hydrogen in Pd powder

Fig. 1a and b represent the thermal effects and amounts of sorption and desorption of hydrogen in Pd powder. Within a second of H_2 coming into contact