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Effects of sulfur poisoning on hydrogen desorption from palladium

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Abstract

We present an analysis of the effect of sulfur poisoning on hydrogen desorption kinetics from palladium samples with different geometry and surface-to-volume ratios (fine powder, granules, foils and wires). The desorption process was studied by thermal desorption spectroscopy (TDS). The main effect of poisoning is a decrease of the desorption rate that shifts the TDS spectra towards higher temperatures in an amount that ranges from 30 to 80 K depending on the surface-to-volume ratio. The hydrogen storage capacity of the material remains unchanged after poisoning. The observed behavior could be well explained assuming a surface blocking effect produced by sulfur.

Keywords: Thermal desorption spectroscopy; Metal hydrogen systems; Desorption kinetics of H_2; Pd hydride; Surface contamination; Sulfur

1. Introduction

The poisoning of palladium surfaces with highly reactive species such as sulfur is of particular interest from the point of view of the catalytic properties of palladium [1] and of many applications that rely on metallic hydrides, e.g. hydrogen purification, energy storage, etc. [2,3]. Many effects induced by sulfur contamination on hydrogen absorption and desorption kinetics in palladium have been studied previously [4–7]. Bucur [4], working on the α phase region of the Pd–H system, has found that poisoning a thin palladium layer with sulfur increases the time to reach half initial hydrogen desorption rates by a factor of four. This increment occurs without any appreciable loss in the amount of hydrogen absorbed by the material. Peden et al. [5] have shown that the presence of sulfur in the (110) face of Pd produces a hydrogen absorption process initially controlled by diffusion into the bulk to change to a surface limited process. They argue that this is a consequence of a substantial reduction of the sticking coefficient. Again, no loss of the amount of hydrogen absorbed was detected. Burke and Madix [6] studied the adsorption and desorption of H on Pd(100) with and without sulfur. They found a monotonic decrease in the amount of hydrogen adsorbed as the sulfur coverage of the surface increased, and a shift towards lower temperatures in their thermal desorption spectra that produced a drop in the desorption activation energy from 85 to 49 kJ/mol. From a theoretical point of view, Gravil and Toulhoat [7] recently performed first principles calculations of sulfur and chlorine coadsorption on Pd(111). Their results show that the adsorption energy is lowered and that diffusion barriers are increased by the addition of sulfur. All these studies point to the fact that sulfur can affect hydrogen absorption and desorption kinetics by simultaneously blocking surface sites and diminishing surface mobility. From the point of view of the effect of sulfur on the properties of different metallic hydrides and its potential applications, the work of Sandrock and co-workers [8,9] has shown that sulfur in the form of hydrogen sulfide (H_2S) can dramatically affect the properties of technologically important metal alloys of the families of $LaNi_5$ and TiFe.

2. Experimental

In this work we present a study of hydrogen desorption kinetics from palladium poisoned with sulfur. The study is carried out by thermal desorption spectroscopy (TDS) measurements. We analyze desorption from palladium powders, granules, foils and wires that have been made to react previously with hydrogen to form palladium hydride (H:M>0.6). The chemical composition of the surface of

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the sample is controlled by Auger electron spectroscopy (AES).

We used high purity palladium samples (Aldrich, 99.9%) with different geometry and surface-to-volume ratios: powder (1 μm average size), granules (5–10 μm average size), foils (25 μm thickness) and wires (1 mm diameter). The samples were hydrided in a closed vessel at room temperature using two different hydrogen sources, high purity hydrogen (99.995% Air Liquide) and ultra high purity hydrogen obtained from an electrolytic hydrogen generator (99.9998%, Whatman). The hydriding pressures ranged from 0.2 to 4 bar and the hydriding times ranged from a few minutes up to 10 h. The samples with higher surface-to-volume ratios and smaller sizes required lower pressures and shorter charging times. Modifying the hydrogen gas pressure and the exposure period allowed us to control the hydrogen concentration of the specimens prior to measurement.

Hydrogen desorption was studied by TDS. The experimental set-up, presented elsewhere [10,11], uses a mass flow controller to record the amount of hydrogen desorbed from the sample. All the experiments were conducted under dynamic vacuum conditions with a linear heating rate of 0.1 K/s.

Unintentional sample poisoning occurred during the preparation stages prior to TDS measurement. The sample was hydrided in the same chamber where the TDS measurements were carried out. One of the structural components of this chamber (stainless-steel) was found to contain sulfur as an impurity in an amount close to 0.9 at.%. During sample hydriding, before TDS experiments, gaseous hydrogen reacted with sulfur contained in the component, probably forming H_2S, and traveled to the surface of the sample, where it decomposed resulting in the S covering the Pd samples. The chemical composition of the samples before and after different degrees of poisoning was monitored by AES analysis. The 'poisoning method' could not be controlled very precisely, but by repeatedly hydriding and dehydriding the samples we were able to increase the amount of sulfur in a regular and very reproducible way. The presence of S impurities in the H sources was discarded by using two different high purity H supplies and obtaining similar results.

3. Results and discussion

Fig. 1 shows typical Auger spectra obtained from palladium in a powder form as-received from the provider, after seven and ten hydrogen absorption–desorption cycles and after bombarding the sample with argon.

We see that the spectrum of the as-received sample (Fig. 1a) only shows the peaks associated with palladium. After seven hydrogen absorption–desorption cycles sulfur and carbon peaks appear on the spectra (Fig. 1b) and after ten cycles these peaks become more intense (Fig. 1c). After bombarding the surface of a poisoned sample with Ar the S and C signals almost disappear (Fig. 1d) indicating that contamination is a surface phenomena.

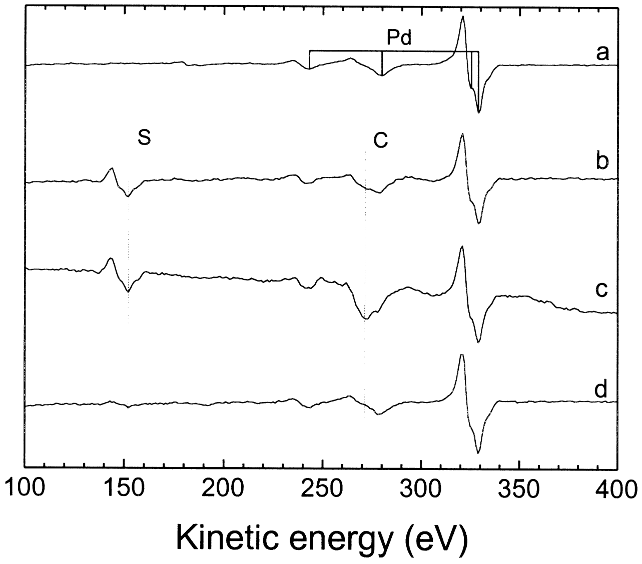

Fig. 1. Auger spectra of (a) the as received palladium powder, (b) the same sample after seven hydrogen absorption–desorption cycles, (c) after ten cycles, (d) after bombarding the surface with Ar.

By using the ratio of the Auger peaks S_{152}:Pd_{330} and C_{272}:Pd_{330} a quantitative evaluation of the amount of sulfur and carbon can be made (Table 1).

Similar results were obtained for the palladium foils and wires.

The influence of sulfur on the desorption kinetics is shown in Fig. 2. Here we present a sequence of TDS spectra of palladium powder obtained for different degrees of sulfur poisoning (increasing from top to bottom). The spectra were taken on the same sample under identical conditions.

The main feature that we observe is the shift of the peaks towards higher temperatures. This shift ascends to about 80 K. We also identify in the spectra two main peaks, one centered at 300 K (best viewed in cycles 1–4) and the other centered at 380 K (cycles 7–10). The lower temperature peak can be associated with desorption from unpoisoned particles, whereas the higher temperature peak can be associated with desorption from poisoned particles. Between the third and sixth spectra, we observe the change from the lower to the higher temperature peak due to the increment of poisoning. Negligible changes are detected in

Table 1
Ratio of the Auger peaks S_{152}/Pd_{330}, and C_{270}/Pd_{330} for palladium powder samples in different states

Sample status	S_{152}:Pd_{330}	C_{272}:Pd_{330}
As-received Pd powder	0.00	0.00
Seven cycles	0.32	0.16
Ten cycles	0.35	0.37
Ten cycles+Ar bombardment	0.06	0.00

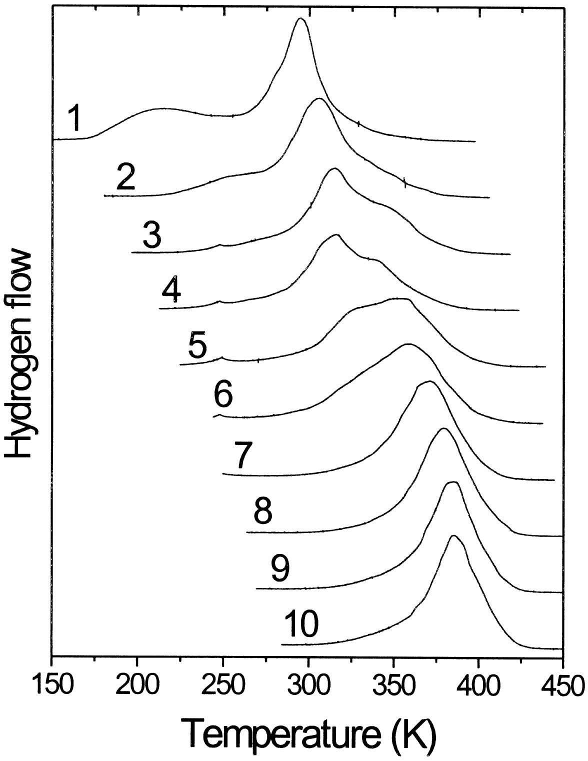

Fig. 2. Thermal desorption spectra of hydrogen desorbed from palladium powder poisoned with sulfur (the number indicates the absorption–desorption cycle).

the spectra after ~10 cycles. Because the area under the spectra (proportional to the amount of hydrogen initially absorbed in the sample) remains constant before and after poisoning we conclude that there is no loss of the hydrogen storage capacity of the material.

Fig. 3 shows the change on desorption activation energy associated with poisoning. These values were obtained by fitting the main peak of the spectra assuming a desorption process controlled by the surface [12]. Activation energy increases with poisoning from 35±3 kJ/mol (pure palladium) to 55±11 kJ/mol (sulfur saturated palladium). This increment shows that desorption kinetics is slowed down by the presence of sulfur on the surface.

When hydrogen desorption is measured by TDS experiments on Pd granules with different degrees of sulfur poisoning similar behavior is observed. As before, two peaks, separated in this case by approximately 40 K, can be associated with desorption from unpoisoned and poisoned particles (Fig. 4). Again, as the poisoning increases the high temperature peak grows at the expense of the low temperature peak, and the nearly constant area under the spectra show that the hydrogen storage capacity has not been impaired.

Different behavior is found in the spectra of palladium foils and wires (Fig. 5). Instead of two peaks there is only one peak which moves gradually towards higher temperatures as contamination of the sample increases. The shift of the spectra ascends to ~40 K for the foil and 30 K for the wire. A possible explanation for the different behavior observed is that palladium powder and granules are many-particle systems, while palladium foils and wires are one-particle systems. In many-particle systems poisoned and unpoisoned particles coexist producing two desorption peaks; on the contrary, one-particle systems progressively

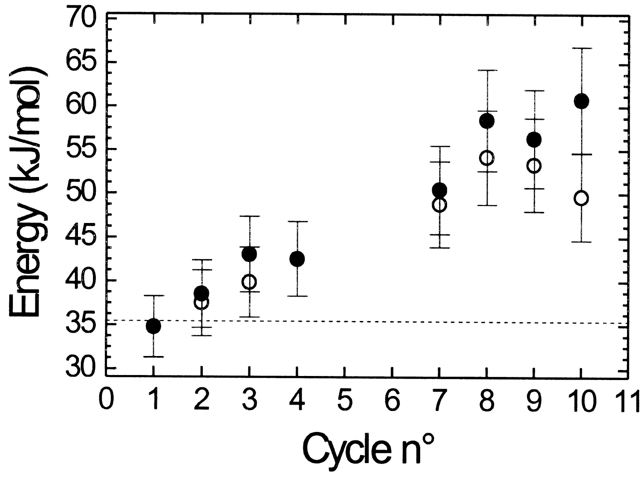

Fig. 3. Activation energies obtained from the TDS measurements performed on palladium powder as a function of the number of absorption–desorption cycles (solid and open symbols correspond to different samples showing reproducibility).

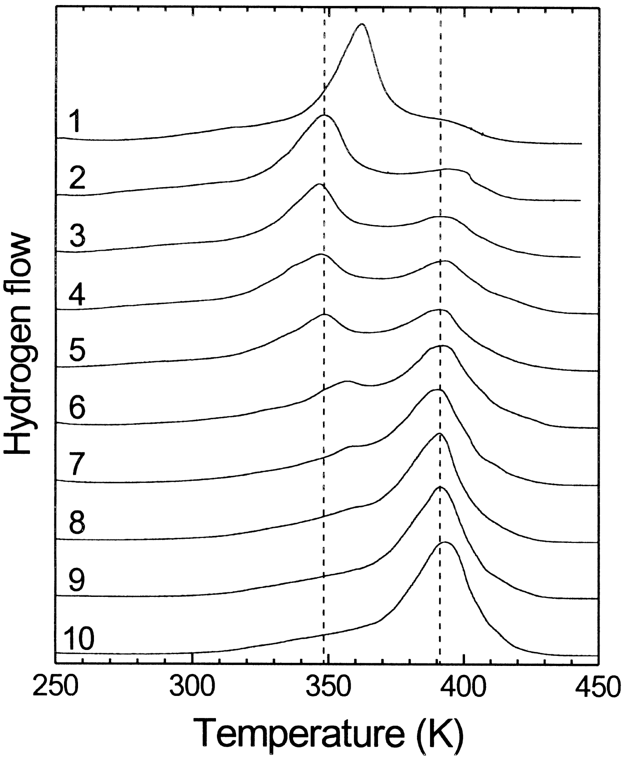

Fig. 4. Thermal desorption spectra of hydrogen desorbed from palladium granules poisoned with sulfur. Poisoning increases from top to bottom.

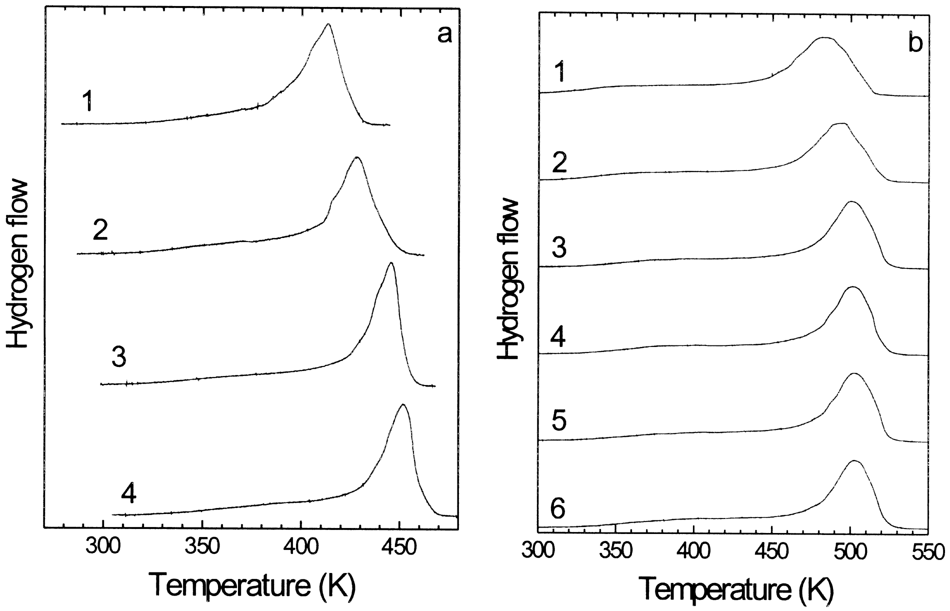

Fig. 5. Thermal desorption spectra of hydrogen desorbed from palladium foil (a) and wire (b) poisoned with sulfur. Poisoning increases from top to bottom.

become poisoned producing only one peak that gradually moves towards higher temperatures.

The observed effects point to the blocking of surface sites produced by sulfur atoms. This blocking, already suggested in the literature, might make difficult the transfer of hydrogen atoms from the bulk to the surface and vice versa, and could diminish surface mobility of hydrogen atoms hindering the H recombination previous to desorption.

Our results are consistent with the work of Bucur [4] because we also observe a decrease in the desorption rate without any appreciable loss in the amount of hydrogen absorbed. However, our work has been carried out in the hydride phase of the palladium hydrogen system. A comparison with the work of Burke and Madix [6] is more difficult, because they worked with hydrogen adsorbed on a well-characterized monocrystalline palladium surface. Although they measured TDS spectra that shift towards lower temperatures with increasing poisoning, and observed no hydrogen adsorption on a sulfur saturated surface, we believe that our results agree well with theirs. They are measuring desorption of surface adsorbed hydrogen whereas we are measuring desorption of hydrogen absorbed in the bulk. The blockage of surface sites that hinders hydrogen adsorption and shifts the Burke spectra towards lower temperatures (also diminishing adsorption energy) shifts our spectra towards higher temperatures by blocking transfer channels between the bulk and the surface (and also increasing desorption energy). From the point of view of the applications of the metallic hydrides, taking into account the different categories proposed by Sandrock and co-workers [8,9], we can identify the effects of sulfur on hydrogen desorption from palladium as a retardation effect: a decrease in the desorption rate without loss of hydrogen storage capacity.

4. Summary

We have presented a study of hydrogen desorption kinetics from palladium samples poisoned with sulfur. The samples studied have different geometry and sizes. Gas desorption was analyzed by TDS and the poisoning of the surface was monitored by AES. Our main results are summarized below.

1. AES analysis of the samples shows that sulfur is located on the surface of the samples. The maximum ratio of the Auger S_{152} and Pd_{330} peaks obtained during this work was 0.35.
2. Sulfur poisoning induces a delay on hydrogen desorption kinetics that appears in the TDS spectra as a shift of the desorption peaks towards higher desorption temperatures. The shift is greater for samples with greater surface-to-volume ratios. The measured shifts are ~80 K for Pd powder, ~40 K for Pd granules, ~40 K for Pd foil and ~30 K for Pd wire.
3. Fitting the main desorption peak of the powder spectra (assuming a surface controlled desorption), we obtain desorption activation energies that increase from 35±3 kJ/mol for the pure palladium to 55±11 kJ/mol for the sulfur saturated palladium.
4. The desorption spectra of the samples composed of many small particles show the coexistence of a desorp-

tion peak associated with desorption from uncontaminated particles and a higher temperature desorption peak associated with desorption from poisoned particles. On the contrary, the spectra of the samples composed of only one particle show a desorption peak that gradually moves to higher temperatures when poisoning increases.

5. The results obtained are consistent with previous works and could be explained by the blocking of surface sites produced by sulfur atoms. This blocking could make difficult the passage of hydrogen atoms from the bulk to the surface and reduce mobility of the hydrogen atoms located on the surface of the sample.

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