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LEED–AES Studies of Chemisorption-Induced Sulfur Segregation from the Bulk to the Surface of Pd(100)

I. SZYMERSKA AND M. LIPSKI

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

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Auger electron spectroscopy was used to follow the surface composition of Pd(100). Exposure to hydrogen induced a migration of sulfur contaminant from the bulk to the surface of the palladium crystal. This effect was studied as a function of temperature, hydrogen pressure, and time of exposure to hydrogen.

INTRODUCTION

Auger electron spectroscopy (AES) is particularly suitable for monitoring the surface composition of solids. The Auger spectra permit a qualitative and quantitative analysis of surface species in the free surface of a solid and in any chemisorbed layer. In recent years AES has revealed its usefulness in numerous studies concerning surface chemistry, catalysis, and metallurgy.

This technique has been applied frequently to studies of the migration of dissolved elements from the bulk to the surface of a solid. Thus, the free surface composition of binary alloys has been investigated for systems such as Cu–Ni (1–3), Ag–Pd (4), Au–Ni (5), Pt–Sn (6, 7), and Au–In (8). In all cases where a difference between the surface and bulk compositions has been detected the metal of lower sublimation heat was concentrated in the surface of the alloy. The surface composition could be further changed by its contact with a chemisorbing gas (*3,5–7, 9, 10*).

The theoretical treatment of these phenomena has recently been presented by van Santen and Sachtler (11), van Santen and Boersma (11), and Williams and Nason (12).

The migration of some nonmetallic contaminants (e.g., sulfur, phosphorus) from the bulk to the surface of a metal or to its grain boundaries is of particular significance for heterogeneous catalysis, corrosion science, and metallurgy. In fundamental research, AES provides a unique tool for monitoring the surface cleanliness, as, for example in low energy electron diffraction (LEED) studies.

Metal surface contamination with sulfur has been studied particularly often and thermal diffusion of sulfur from the bulk of a metal has also been reported (*13–18*).

It seemed worthwhile to apply the AES technique to a study of the process of surface segregation of sulfur in palladium. This system was chosen by reason of its special catalytic interest. Palladium is a widely known catalyst for hydrogenation, and is particularly selective in acetylene or diene hydrogenation to mono-olefins (19).

Sulfur or phosphorus (and other elements belonging to their respective subgroups) has a drastic effect on a metal catalyst. The mechanism of the phenomenon may consist of a rearrangement of the surface structure of the metal catalyst crystals. This effect is induced by sulfur in Pt (20) and Ni (21, 22). Sulfur (and the other elements mentioned above) may alter the catalytic reaction path also by its interaction with coadsorbed molecules of reactants (*22*, *23*). Owing to an interaction of hydrogen and sulfur adatoms (also: Se, P, etc.), the process of hydrogen penetration into metals is highly accelerated. This may favour the formation of metal hydride phases (*24*) and in consequence a poisoning of an initial metal catalyst with respect to many reactions (*25*).

The general term "poisoning" is used for these phenomena the detailed nature of which has many various aspects and still needs much fundamental research (*26*). Auger electron spectroscopy is potentially of great value for the interpretation of the experimental results in this research field.

EXPERIMENTAL

The experiments were carried out in a metal ultrahigh vacuum system which was equipped with a three-grid postaccelerated LEED optics, Auger glancing incidence gun, quadrupole residual gas analyzer (Q7B), ion sputtering gun, an ion gauge of the Bayard–Alpert type, and a crystal manipulator (Vacuum Generators).

In all experiments, we have used a primary electron beam energy, E_p, of 1500 eV and a modulating voltage of 4.5 V rms. All the electronic equipment for LEED and the power supply for the Auger electron gun and argon ion gun were constructed in our Institute.

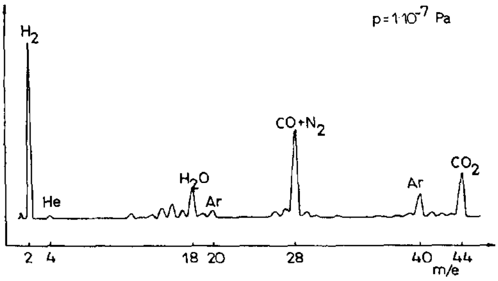

FIG. 1. Mass spectrum of the residual gas at pressure of 1×10^{-7} Pa.

With a pumping system consisting of sorption pumps and an ion sputtering diode pump (140 liter s^{-1}), an ultrahigh vacuum of 5.2×10^{-8} Pa[1] could be achieved after baking the whole apparatus at 470 K. The spectroscopically pure gases argon, hydrogen, and oxygen (VEB Technische Gase-Werke, Berlin) were introduced into the chamber through the leak valves. The cleanliness of the gas phase was checked by a quadrupole analyzer.

PROCEDURE AND RESULTS

The specimen of Pd(100) was cut from a single crystal bar of 99.99% purity (Metals Research Ltd.) by spark erosion, and orientated by X-ray Laue back-diffraction to within 1°. The surface was polished mechanically with diamond paste (<1 μm). After the sample was washed in water and in acetone, it was attached to a molybdenum foil 0.1 mm thick (99.99% purity) which could be heated resistively. The temperature was measured with a Pt/Pt-10Rh thermocouple inserted in the side of the specimen. After the specimen had been introduced into the LEED chamber the system was pumped down and baked at 470 K for 15 hr. Hydrogen, helium, water vapor, argon, carbon dioxide, nitrogen, and carbon monoxide were present in the residual gas phase, as may be seen from the mass spectrum in Fig. 1.

The Pd(100) crystal was cleaned *in situ* by ion bombardment (300 V argon ions), heat treatment up to 1170 K, and exposure to oxygen at 970 K (p_{O_2} 2.6×10^{-3} Pa), in order to obtain an atomically clean surface. The cleanliness of the surface was verified with AES. Before the cleaning, Auger peaks of sulfur 155 V ($L_{2,3}M_1M_1$) and phosphorus 122 V ($L_{2,3}M_{2,3}M_{2,3}$) were observed in addition to the palladium peaks (Fig. 2).

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[1] 1 Pa = 1 N m^{-2} = 7.5×10^{-3} Torr.

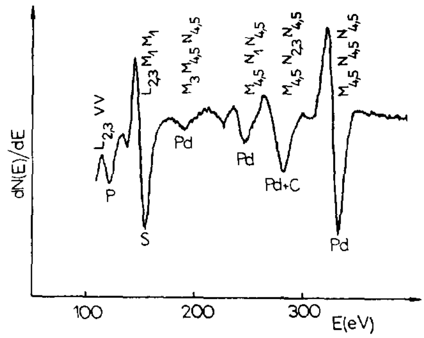

Fig. 2. Auger trace of the palladium surface before cleaning procedure.

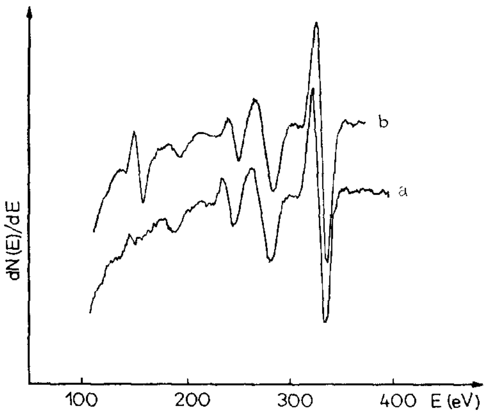

Fig. 3. Auger trace of (a) the clean surface and (b) after exposure to hydrogen at room temperature, $p_{H_2} = 4.0 \times 10^{-3}$ Pa.

Carbon, which is a common impurity in metals, could not be analyzed with AES because of the coincidence of the carbon 275 V ($KL_{2,3}L_{2,3}$) and palladium 282 V ($M_{4,5}N_{2,3}N_{4,5}$) peaks. A (1 × 1) LEED pattern characteristic of the clean Pd(100) gave the only evidence that carbon was removed from the surface.

After 32 cycles of ion bombardment (total time 16 hr), 12 cycles of annealing in oxygen, and numerous heat treatments, a surface was obtained which was believed to be clean. The AES trace of this surface is shown in Fig. 3a, and the LEED pattern was (1 × 1).

The clean Pd(100) surface was then exposed to hydrogen at room temperature. At pressures up to 1.3×10^{-3} Pa, no effect on the LEED pattern was observed. However, after 3 min of exposure at a hydrogen pressure of 4.0×10^{-3} Pa, new diffraction spots appeared at positions $(h + \frac{1}{2}, k + \frac{1}{2})$; these are characteristic of a C (2 × 2) structure.

The high intensity of the extra spots made it very unlikely that the surface structure was caused by hydrogen adsorbed on the palladium surface. It therefore seemed advisable to check the surface cleanliness with AES anew after the exposure to hydrogen. The presence of a remarkable peak at 155 V on the AES trace indicated that sulfur had reappeared on the surface (Fig. 3b). The C (2 × 2) structure was therefore due to sulfur. Tracy and Palmberg have also observed a C (2 × 2) structure for a Pd(100) crystal contaminated with sulfur (*27*). Since no sulfur compounds were found mass-spectrometrically in the gas phase with the quadrupole analyzer, it was reasonable to believe that the source of sulfur was the palladium crystal itself. Therefore, a detailed study of the effect of enrichment of the palladium surface with sulfur due to hydrogen interation was undertaken.

Hydrogen at a pressure of 1.6×10^{-2} Pa was introduced to a Pd(100) crystal heated to different temperatures. After 5 min of exposure the crystal was allowed to cool

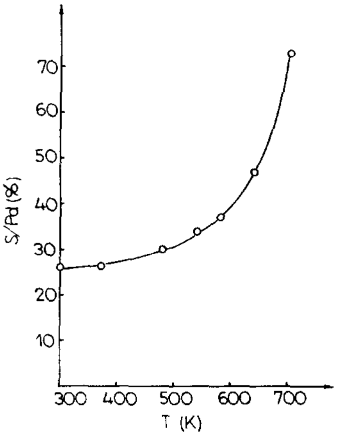

Fig. 4. The S/Pd peak-to-peak ratio as a function of heat treatment in hydrogen.

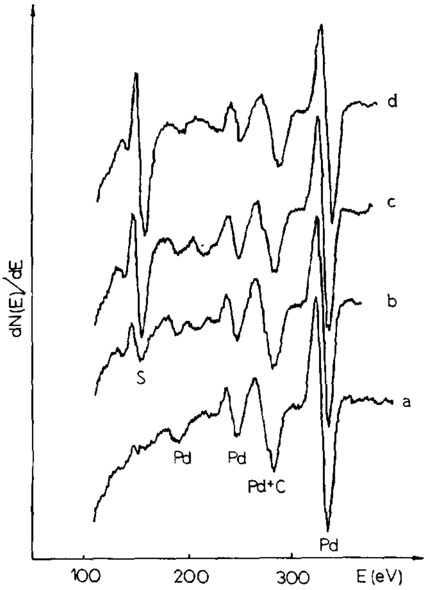

FIG. 5. Auger traces of (a) clean palladium surface, (b, c, d) after 2, 12, and 26 min of exposure to hydrogen, respectively, at 703 K, p_{H_2} = 1.6 × 10^{-2} Pa.

in hydrogen for the next 5 min. Then the hydrogen was pumped out and the Auger spectrum of the surface was monitored. Figure 4 shows the surface concentration of sulfur as a function of a heat treatment in hydrogen at different temperatures. The peak-to-peak ratio S 155 V/Pd 333 V was the measure of the surface concentration of sulfur. The predominant influence of the temperature is clearly visible.

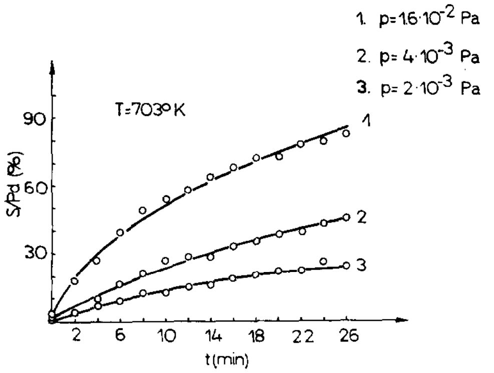

FIG. 6. The S/Pd peak-to-peak ratio as a function of exposure to hydrogen at three different pressures.

If the clean crystal was heated within the identical range of temperature (298–703 K) *in vacuo* the sulfur peak did not appear in the AES spectrum.

The changes of sulfur concentration as a function of exposure at 703 K to hydrogen at three different pressures were also determined. The results are shown in Figs. 5 and 6.

DISCUSSION

Chemisorption-induced enrichment of the surface of an alloy with one component has been reported in the literature for many systems: O_2 + Au–Ni (*5*), O_2 + Pt–Sn (*6*), CO + Au–Pt (*9*), CO + Ag–Pd (*10*). Hitherto, it has been supposed that the driving force of this effect is the difference between the heats of adsorption of the gas on the two metal components of the alloy. The partner forming the stronger chemisorption bond with the absorbate tends to aggregate in the surface (*5, 12*).

In the case of the H_2 + Pd–S system the same interpretation seems reasonable, though sulfur, here, is only a contaminant and not, of course, an alloy component. Unfortunately, there is no information about the heat of adsorption of hydrogen on sulfur. However, from the bond energy of H–S, Q_{H-S} = 363.4 kJ mol^{-1} (*28*) and of Pd–H, $Q_{Pd-H_{0.5}}$ = 38.96 kJ mol^{-1} (*29*), it can be deduced that hydrogen is much more strongly held by sulfur than by palladium.

The influence of temperature on the surface enrichment of palladium with sulfur is qualitatively the same as in the case of the O_2 + Pt–Sn system studied by Bouwman *et al.* (*6*). The adsorption of oxygen on the surface of PtSn and Pt_3Sn caused enrichment of the surface with tin. As the temperature increased this effect intensified. The oxidation of PtSn at 500°C led to the complete disappearance of Pt from the surface (*6*).

However, in the case of the hydrogen–palladium system, because of the high solubility of hydrogen in palladium, the interactions in the bulk, in addition to those at the interface, should be taken into account. We have observed an increased effect of the "extraction" of sulfur by hydrogen (from the bulk to the surface of the palladium sample) at higher temperatures. Since the solubility of hydrogen in palladium decreases with temperature, a hindering action in sulfur diffusion towards the palladium surface might be ascribed to the dissolved hydrogen. Further investigations of other metals with different characteristics of behavior with respect to hydrogen could elucidate the mechanism of the effect observed.

Whatever the ultimate explanation, the results obtained clearly point out that the exposure of a metal (even of a very high purity) to an active adsorbate, as e.g., hydrogen, can induce an accumulation of certain contaminants in the surface layer, leading to a surface concentration much higher than in the bulk. Therefore, particular care seems to be necessary in characterizing the surface composition of a metal when its surface structure or surface reactivity is investigated during or after exposure of the sample to chemisorbing gases.

On the other hand, pretreatment with a suitable adsorbate under appropriate conditions could be used as an effective step in the metal surface cleaning procedure. The impurity extracted to the surface could then be removed by other methods, e.g., by successive argon ion bombardment in the case of sulfur.

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