Hydrogen Detection during Catalytic Surface Reactions:
Evidence for Activated Lateral Hydrogen Mobility in the Water-Forming Reaction on Pd

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By use of a Pd-SiO$_2$-Si structure as a hydrogen sensor, very small changes in the hydrogen pressure can be detected. Furthermore, such a structure can be used to detect hydrogen with perfect discrimination during a catalytic surface reaction. By using this technique, together with work-function and desorption measurements, in the study of the water-forming reaction on Pd, we conclude that hydrogen has an activated lateral mobility on Pd.

In order to understand the reaction path of a heterogeneous catalytic reaction it is important to be able to monitor the concentration of the individual reactants. In many such reactions hydrogen plays an important role but is also particularly difficult to detect and especially to discriminate from other reactants present on the active surface. It is well documented that a Pd-SiO$_2$-Si [Pd–metal-oxide-semiconductor (MOS)] structure can be used as a hydrogen sensor.[1] In this Letter we demonstrate the uniqueness of such a structure when used in a catalytic reaction. In the water-forming reaction on Pd, i.e., $O_{ads} + 2H \rightarrow H_2O$, it is straightforward to measure the water desorption rate by mass spectrometry. With the Pd-MOS structure as a sample we can also simultaneously and with perfect discrimination monitor how the amount of adsorbed hydrogen changes during the reaction. We also show that the Pd-MOS structure can be used to detect hydrogen interacting with Pd at temperatures and pressures where it is not possible to detect hydrogen with more conventional surface-sensitive methods because of low surface concentrations.

The experimental equipment consists of an UPS/XPS ultrahigh vacuum spectrometer[2] equipped with a Kelvin probe for work-function measurements and a mass spectrometer for desorption studies. The sample consists of a Pd-MOS structure, fabricated in a separate system. The thickness of both the Pd film and SiO$_2$ layer is about 1000 Å. When such a structure is exposed to hydrogen, the hydrogen molecules dissociate on the Pd surface and adsorb to a certain coverage. Because of the high diffusion coefficient for hydrogen in Pd[3] an equilibrium between the bulk and the external surface is rapidly established. This means that hydrogen atoms also adsorb at the internal Pd surface, i.e., at the Pd-SiO$_2$ interface. Thus, there exists a quasiequilibrium between the amount of

hydrogen atoms at the external and internal surfaces of the Pd film.[4] The hydrogen atoms at the internal surface are detected through the polarization-induced shift of the capacitance versus voltage $[C(V)]$ curve of the structure,[1] which is assumed to be proportional to the hydrogen concentration. The Pd film acts as a filter and lets only hydrogen atoms through and thus the shift of the $C(V)$ curve depends *only* on the amount of hydrogen at the internal surface.

The results reported in this Letter were all obtained on a Pd-MOS structure that had been Ar sputtered and oxygen-hydrogen treated in order to obtain a clean Pd surface.[5] Both x-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) indicate a clean Pd surface with the only possible contamination being that of carbon. Furthermore, the base pressure during all the experiments was of the order of 1×10^{-10} Torr and all hydrogen exposures were made with running pumps.[6] Figure 1 shows the result from $C(V)$ and work-function measurements for hydrogen pulses at two different hydrogen pressures and at a temperature of 473 K. Thus, at 473 K and with the moderate hydrogen pressures used, no variation of the work function can be detected. This is fully expected since it agrees with the adsorption-isotherm measurements on single-crystalline Pd reported by Behm, Christmann, and Ertl[7] and Conrad, Ertl, and Latta.[8] There is, however, a significant shift of the $C(V)$ signal during the hydrogen exposure. Thus, even though the presence of hydrogen cannot be seen with conventional surface-sensitive techniques such as work-function and photoemission[5] measurements because of an extremely low surface concentration, it is clearly detected with the present $C(V)$ technique. In Fig. 1 it is also shown, for reference, that for low enough temperatures hydrogen at the external surface can also be detected with
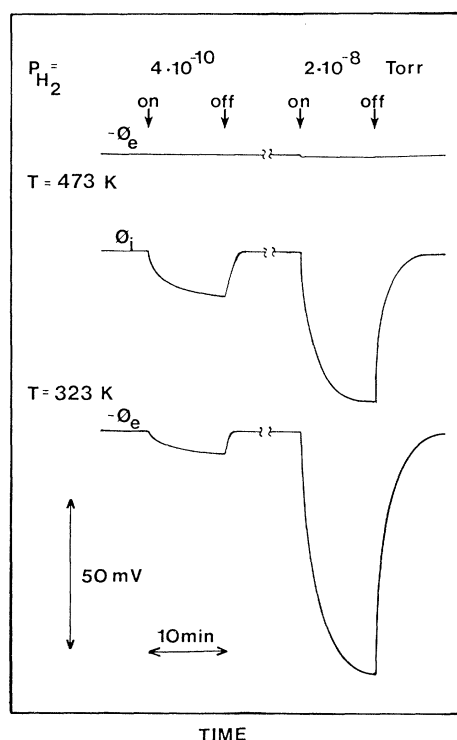
FIG. 1. The work-function shift of the external, ϕ_e, and the $C(V)$ shift of the internal, ϕ_i, surfaces of the Pd film when exposed to hydrogen. Note that different signs of the shifts; the work function of the external surface increases but that of the internal surface decreases.

the Kelvin probe. No traces of hydrogen can be detected in the photoemission spectra though.[9] [A surface coverage of $\theta = 1$ on either of the Pd(111) or Pd(100) surfaces gives a work-function shift of about 0.2 eV.[7,8] Thus the coverage on the external surface at $P_{H_2} = 2 \times 10^{-8}$ Torr and $T = 323$ K (Fig. 1) corresponds to $\theta \approx 0.4$. By assuming that the adsorption is of dissociative Langmuir type, the surface coverage can be calculated to be $\theta \sim 10^{-4}$ at $P_{H_2} = 4 \times 10^{-10}$ Torr for $T = 473$ K.] The above described hydrogen adsorption-absorption behavior simply indicates that the heat of adsorption for hydrogen at the internal surface is somewhat larger than that of the external surface (22–24 kcal/mole[7,8]). The temperature dependence of hydrogen adsorption at the internal surface is, however, fairly complicated and will be discussed in a separate publication. In conclusion, Fig. 1 shows that hydrogen immediately upon exposure is absorbed by Pd and that there is no need for certain hydrogen states at the external surface to first be filled before hydrogen is allowed to enter the bulk

as has been suggested in some earlier publications.[10]

In order to study the water-forming reaction on Pd, the clean Pd surface was exposed to various amounts of oxygen. The oxygen exposure empties hydrogen sites at the internal surface. This behavior is illustrated in Fig. 2. The removed internal hydrogen probably reacts with oxygen and desorbs as water. We have not been able to identify experimentally this type of water desorption but this might simply be due to the fact that the amount is too small to be detected. The oxygen exposure has thus created empty hydrogen states at the internal surface which, when the oxygen is removed, can act as a hydrogen sink.

Figure 2 also illustrates what happens when the oxygen-covered external surface is exposed to hydrogen. The work function returns to its initial value, with its derivative for small oxygen coverages being equal to the rate at which water is produced as measured with the mass spectrometer.[5] The H_2O desorption rate shows a pronounced maximum at low oxygen coverage and has a shape similar to that measured on Pt by Kasemo and Törnqvist.[11] The internal-hydrogen signal does not respond until the H_2O desorption rate approaches its cutoff, which also corresponds to the maximum rate of change of the internal-hydrogen signal. We point out again that if there were only a very small concentration of hydrogen adsorbed on the (external) surface not interacting with the oxygen, this would immediately show up at the internal surface since that surface will act as a hydrogen sink, being far from equilibrium with the applied hydrogen pressure. Since the hydrogen signal does not respond until the oxygen coverage is very low this must inevitably mean that the incoming hydrogen molecules (or dissociated as atoms) interacting with the Pd surface have a large lateral mobility. Figure 2 thus gives direct information on how the amount of adsorbed hydrogen on the Pd surface changes during a catalytic reaction taking place at the same surface.

An expression of the following form can easily be fitted to the measured H_2O rate:

$$\frac{d[H_2O]}{dt} = F(1-\theta)\{1 - \exp[-L(T)\theta^{1/2}]\}, \quad (1)$$

where θ represents the coverage of oxygen (and hydroxyl) that has not yet come off the surface as water. F is a constant. The first two factors represent the amount of hydrogen available on the Pd surface to react with oxygen, and the third factor the probability that this hydrogen will form water. Thus, the

hydrogen adsorption rate depends linearly on the noncovered surface area; that is, oxygen blocks hydrogen adsorption and only one site is needed for the incoming hydrogen molecule.[12] If the hydrogen on the Pd surface does not react with oxygen it will disappear from the external to the internal surface according to the discussion above.[5] Thus, the hydrogen adsorption rate at the internal surface will be given by

$$\frac{d[\mathrm{H}_{ai}]}{dt} = F(1-\theta)\exp[-L(T)\theta^{1/2}]. \qquad (2)$$

The above expressions require that the amount of OH on the surface is small and that the water formation is fast. From the present data we cannot exclude the possibility that water also is formed by undissociated hydrogen reacting with oxygen. We interpret $L(T)$ as being an average length over which the incoming hydrogen atoms (molecules) diffuse on the surface before they are (dissociated and) absorbed. Figure 3 shows experimental results obtained at three different temperatures. By fitting

the theoretical expression to the $\mathrm{H}_2\mathrm{O}$ rate at $T = 473$ K and $T = 323$ K we determined $L(T)$ to be equal to $L = 7.3 \times 10^3 \exp(-1.87 \times 10^3/T)$ Å, which indicates that the hydrogen diffusion is thermally activated with an activation energy of about 160 meV. $L(T)$ was then used to fit the theoretical internal hydrogen adsorption rate at all three temperatures and the $\mathrm{H}_2\mathrm{O}$ rate at 373 K to the experimental ones. As can be seen from Fig. 3 the agreement between theory and experiment is quite good. The sticking coefficient in this case is of the order of 0.7, that it, 70% of all hydrogen impinging on the bare Pd surface will have a chance to form water. At the highest temperature ($T = 473$ K) excess hydrogen is not detected until the oxygen is very small—i.e., the probability that a hydrogen atom (molecule) finding itself on the Pd surface will end up in a water molecule is close to unity. A further discussion of the water-forming reaction on Pd together with a more detailed account of the oxygen and hydrogen adsorption experiments on the Pd-MOS structure will be presented in a separate publication.[5]
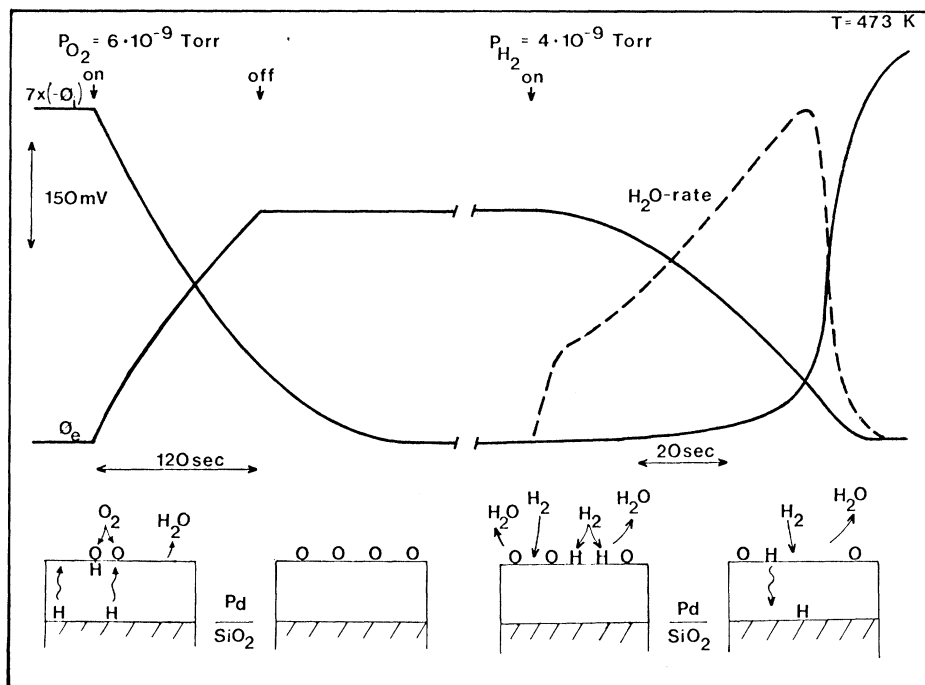

FIG. 2. The left-hand part shows ϕ_e and ϕ_i during oxygen exposure. Note that the internal shift is in the opposite direction as that obtained during hydrogen exposure, i.e., the hydrogen sites (initially filled by the residual hydrogen in the chamber) at the internal surface are emptied. The right-hand part shows ϕ_e and ϕ_i during hydrogen exposure subsequent to an oxygen exposure. Also shown is the water desorption rate (dashed line) as measured by the mass spectrometer. Note the coincidence of the sharp drop in the water desorption rate with the rapidly growing hydrogen adsorption at the internal surface. The insets illustrate the different processes.
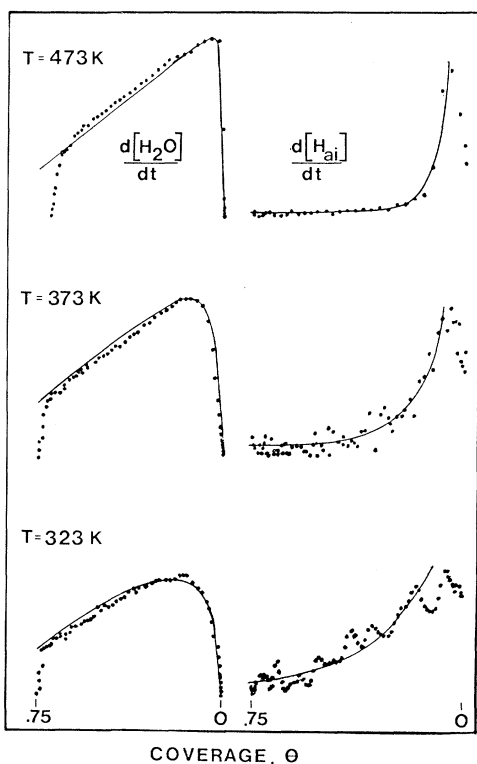
FIG. 3. The water desorption rate and the hydrogen internal adsorption rate as a function of oxygen coverage. The dotted curves represent experimental results, and the solid line, theoretical results according to Eqs. (1) and (2). The theoretical curves were fitted to the water desorption rates at $T = 473$ K and $T = 323$ K in order to obtain the temperature dependence of $L(T)$. In the other four cases only intensity adjustments have been made. The decreasing hydrogen adsorption rates at the end of the process are due to the breakdown of the assumption that the internal surface works as a hydrogen sink; i.e., hydrogen desorption will start to take place.

In conclusion, we have demonstrated two new and important features of a Pd-MOS hydrogen sensor. First, it can be used as a hydrogen detector when pressures and temperatures are such that the coverage of hydrogen on a clean Pd surface is so small that it is impossible to detect with other surface-sensitive methods. Secondly, we have shown that it can be used as a detector for free hydrogen on a Pd surface *during* a catalytic reaction. This is certainly a very important feature since hydrogen is a common element in many catalytic reactions and still is very difficult to detect and identify with conventional surface-sensitive methods. We have also shown how this new information can be utilized to gain knowledge about the water-forming reaction and, specifically, we concluded that hydrogen has an activated lateral mobility on Pd. Finally, we want to point out that the Pd-MOS structure as such is not dependent on UHV to function as a hydrogen sensor[1] and thus might be a tool that can help to bridge the gap that exists today between surface science and applied catalytic research.

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