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Catalytic oxidation of hydrogen at nanocrystalline palladium surfaces

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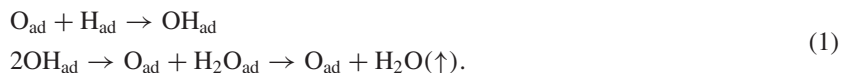
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Abstract

We studied hydrogen adsorption onto the oxidized nano-palladium surface using ¹H NMR. In the α phase, the incoming hydrogen molecules dissociate and form OH_{ad}. We confirm that the OH_{ad} → H₂O(↑) transformation occurs during the α – β phase transition by observing a decrease in OH_{ad} resonance intensity.

1. Introduction

The palladium surface is known to be a very effective catalyst. Mere contact of hydrogen with oxygen at the palladium surface forms water at room temperature. Until recently, however, few reports have been published about this interaction [1–4]. Nyberg *et al* reported that hydroxyl is produced upon water adsorption on an oxygen-covered Pd(100) surface, and they presented the following reaction path [2]:



Mitsui *et al* reported the interactions between oxygen and hydrogen co-adsorbed on a Pd(111) surface in detail [3]. Below 120 K, oxygen forms a (2 × 2) island structure. Above 120 K, co-adsorbed hydrogen increases the diffusion of oxygen and transforms the structure of oxygen into a ($\sqrt{3} \times \sqrt{3}$) structure. Above 210 K, the ($\sqrt{3} \times \sqrt{3}$) structure transforms back to (2 × 2) due to the dissolution of hydrogen into the bulk. Above 220 K, the oxygen population on the surface decreases due to H₂O_{ad} desorption.

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Johansson *et al* reported the water formation reaction on polycrystalline palladium at 1300 K [4]. They suggested that the reaction, $\text{H}_2\text{O} \rightarrow \text{H}_{\text{ad}} + \text{OH}_{\text{ad}}$, is more important for OH_{ad} formation on palladium than on platinum.

These studies, however, are confined for the most part to well-defined specific surfaces and ultrahigh vacuum (UHV) since most surface probing techniques such as scanning tunnelling microscopy (STM) and x-ray photoelectron spectroscopy (XPS) require a well-defined surface and static conditions for observation. An understanding of these reactions at high pressure ($> \sim 1$ Torr) has not yet been reached. At a certain pressure over ~ 1 Torr, the α - β phase transition occurs in the PdH_x system. The lattice of palladium crystals expands by 4% during this transition.

In this paper, we study hydrogen adsorption on the oxidized surface of Pd nanocrystals at hydrogen gas pressures over ~ 1 Torr at room temperature using ^1H nuclear magnetic resonance (NMR). We investigate how the structural phase transition of the PdH_x system is related to the surface reaction, as well as the dynamic behaviour of hydrogen at the surface. The NMR technique is suitable for the study of dynamic properties of atoms or molecules adsorbed/absorbed on/inside the particle surface/bulk. It can also be applied to a wider range of temperature and pressure.

2. Experiment

We made the nanometre size palladium particles as follows. First, we cleaned silica gels (Merck Silica gel 100 with 10 nm pores) eight times with distilled water, two times with 10 wt% aqueous HNO_3 , and eight times with distilled water again. We prepared 5 wt% PdCl_2 dissolved in 10 wt% aqueous HCl , and impregnated it into the silica gels until the incipient wetting point was reached. The wet silica gels were dried at 100°C in an oven overnight, and reduced by flowing hydrogen gas at 500°C for 3 h. In order to remove the silica gel supports, they were dissolved in a 10 wt% aqueous NaOH solution. After the dissolved solution was well stirred, the palladium particles were allowed to precipitate by coagulation. The dissolved solution was removed carefully with an aspirator pump and replaced by distilled water. This cleaning process was repeated eight times. Finally, the remaining water was pumped out slowly. Well-dispersed nanometre size palladium particles remained. We examined the particle size by transmission electron microscopy (TEM) and using x-ray diffraction (XRD). Figure 1 shows the result. In the TEM image, particles appear as dots. The particles were slightly conglomerated due to the electrical interaction between metal particles. The mean diameter of the particles can be determined from the width at the half-maximum points of a peak according to Scherrer's formula. The diameter was calculated from the left peak of figure 1(b) and was about 40 Å. In the figure we also present the spectrum of commercially available palladium particles for comparison.

If the sample is exposed to air, the surfaces of the particles are easily oxidized. We confirmed this by an elemental analysis (EA) measurement. The oxygen content of the sample was 8.83 ± 0.01 wt%. From this value we calculated the oxygen concentration, O/Pd, to be 0.55. Oxygen atoms may exist at subsurface sites [5]; thus, we cannot claim that this value corresponds solely to the oxygen adsorbed at the Pd surface.

We made an NMR probe capable of making *in situ* gas volumetric measurements. It enables us to obtain a pressure-composition isotherm and NMR spectra, simultaneously. We used a broadband pulsed NMR spectrometer (Bruker MSL200) with the ^1H resonance frequency of 200.13 MHz. In order to obtain a free induction decay (FID) signal, we used a 90° pulse of 2 μs width. Signals were accumulated 100 times to improve the signal-to-noise ratio. The time span between signals was 1 s, which is sufficiently long since the

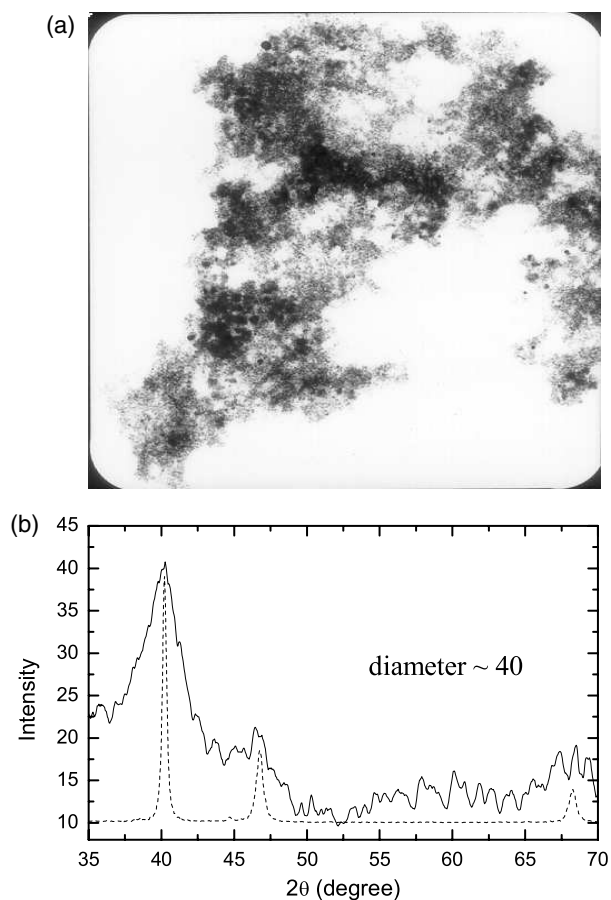


Figure 1. (a) The TEM image of palladium nanoparticles. The dimensions of the image are 121 nm \times 121 nm. (b) X-ray diffraction spectra. The dashed line denotes the spectrum of the bulk reference sample (1.0–1.5 μm).

spin–lattice relaxation time (T_1) is shorter than 100 ms. We used ~ 50 mg of nano-palladium in each measurement. All measurements were done at room temperature.

3. Results and discussion

Figure 2 shows the pressure–composition isotherms of hydrogen on nanocrystalline Pd. The open circles represent the sample with a naturally oxidized surface, while the filled circles represent the sample whose oxygens were thoroughly removed by successive hydrogen admission and evacuation. The two isotherms show an offset between their saturated H/Pd ratios. The difference is about 0.7. Considering the fact that there are two hydrogen atoms for every oxygen atom in an H_2O molecule, this difference indicates the number of hydrogen atoms used to form H_2O . One might guess that it should be 1.10 when the oxygen concentration at the surface is 0.55. We think that the difference arises from the fact that some H_2O molecules were desorbed from the surface since our experiments were performed at room temperature. The desorbed H_2O will contribute to the measured gas pressure of the sample cell which, in

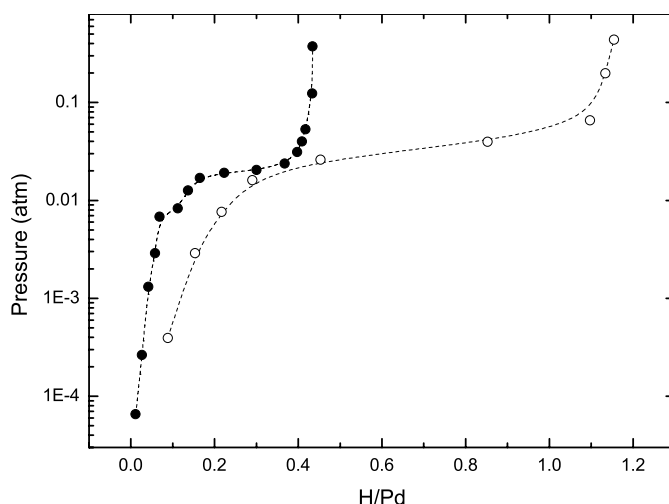


Figure 2. The pressure–composition isotherms of hydrogen in two nanocrystalline palladium samples. Open circles denote the isotherm for the sample with a naturally oxidized surface, and filled circles that for an oxygen-free surface.

turn, results in a lower calculated value of the H/Pd ratio. It is also notable that the difference between the two surfaces is limited to below 0.2 until $H/Pd = 0.4$ is reached.

Figure 3 displays the 1H NMR spectra obtained on increasing the hydrogen concentration, H/Pd . At low pressure there is a single resonance line in the spectrum. The intensity of the line increases gradually with increasing pressure for pressures below $H/Pd \approx 0.4$, then begins to decrease and becomes almost zero at some point between 0.85 and 1.10, but then suddenly reappears at about 1.10. At very high concentration, the spectrum becomes a double peak. We concluded elsewhere [6], by

observing the peak shift as a function of the hydrogen gas pressure and comparing to that of the bulk Pd, that the high and low frequency peaks can be attributed to the hydrogen population at the bulk and subsurface sites, respectively.

At low hydrogen coverage ($H/Pd < 0.4$), most incoming hydrogen molecules dissociate at the surface. Hydrogens at the palladium surface can be in the forms of OH_{ad} , H_2O_{ad} , or directly bonded to palladium. In order to identify the source of the resonance observed, we performed 1H NMR measurements on a sample treated as follows. First, the adsorbed oxygen layers are removed completely by hydrogen dosing and pumping out. Next, water was adsorbed into it. Figure 4 shows the result. For comparison, we also present the representative 1H NMR spectrum (dashed line) of hydrogen adsorbed at low hydrogen concentration ($H/Pd = 0.28$) on an oxidized nanocrystalline Pd surface. The dotted line denotes the spectrum of a droplet (~ 1 mg) of water. It shows a very sharp peak with the linewidth (full width at half-maximum intensity) less than 2 ppm. The true value is expected to be much smaller and it is only shown here for the purpose of demonstration. The measured value depends on hardware imperfections. But the linewidth of the adsorbed water is over 100 ppm. This difference indicates that the water molecules adsorbed on a Pd surface are very rigid. Völkening *et al* reported that the mobility of adsorbed water is much lower than that of adsorbed hydrogen atoms [7]. These facts suggest that water molecules cannot easily diffuse on transition metal surfaces since they are tightly bound to the surface atoms, which is in agreement with our experimental results.

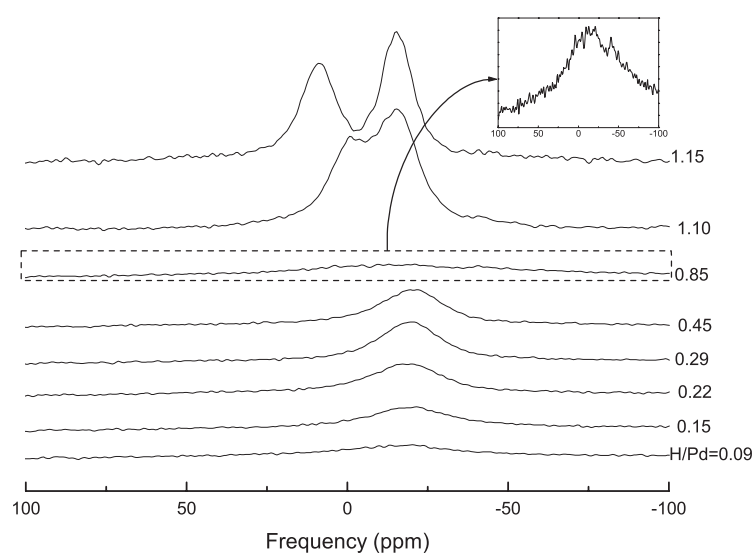


Figure 3. The ^1H NMR spectra of hydrogen adsorbed/absorbed on the nanocrystalline Pd powder with a naturally oxidized surface measured on increasing the hydrogen concentration. The inset magnifies the figure in the dashed box ($\times 10$). Zero corresponds to the proton resonance frequency of bulk water.

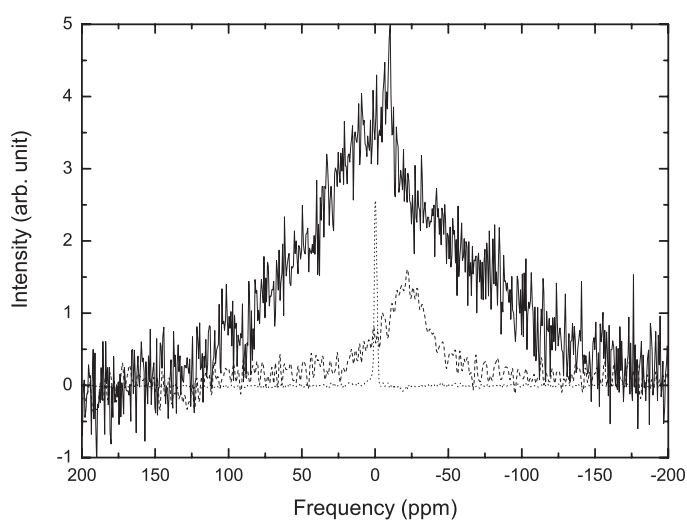


Figure 4. The ^1H NMR spectrum of water adsorbed on a nanocrystalline Pd surface without oxygen (solid line). The dashed and dotted lines denote the ^1H spectra of hydrogens adsorbed on an oxidized nanocrystalline Pd surface ($\text{H}/\text{Pd} = 0.28$) and of bulk water droplets (~ 1 mg), respectively. Note that the relative intensities are chosen for easy comparison.

The above investigation indicates that the $\text{H}_2\text{O}_{\text{ad}}$ cannot be the source of the resonance observed at $\text{H}/\text{Pd} < 0.4$. Another probable candidate is the adsorbed hydroxyl (OH_{ad}). Many investigations pointed out that water formed at the pre-oxidized surface acts as an autocatalyst

for the reaction [2, 4, 7, 11]



This reaction is important especially at low hydrogen concentrations since there are many idle oxygen atoms near $\text{H}_2\text{O}_{\text{ad}}$ that can be easily transformed into OH_{ad} . One can thus expect most hydrogen atoms to exist in the OH_{ad} form. The linewidth at $\text{H}/\text{Pd} = 0.28$ is about 50 ppm, as seen in figure 4: Rades *et al* reported that the peak due to OH_{ad} shifts to +1 ppm for the gaseous tetramethylsilane (TMS), and its linewidth is about 50 ppm, which is in surprising agreement with our results. We conclude, therefore, that the source of resonance for $\text{H}/\text{Pd} < 0.4$ is OH_{ad} .

Völkening *et al* reported that, when all the local O atoms are altered according to the equation (2), the remaining OH_{ad} is transformed into H_2O and desorbs through the following reaction [7]:



The decrease in the resonance intensity can thus be explained by the decrease in OH_{ad} .

The inset in figure 3 shows a very broad peak. Its spectral width is about 100 ppm, which is similar to that of water in figure 4. Recently, it was proposed that water adsorbed on a transition metal surface forms a 2D ice-like structure [8, 9]. The broad peak can thus be attributed to the water remaining on the Pd surface. In 3D ice, it was reported that the linewidth is about 1000 ppm [10]; however, for a 2D ice-like structure no value has been reported yet.

It is interesting that the range where the ^1H NMR peak intensity decreases coincides with the flat region of the isotherm; see figure 2. It is well known that the flat region corresponds to the α - β phase transition region, i.e., the lattice suffers an abrupt expansion within this region. This coincidence suggests that all the O_{ad} transform into OH_{ad} by the end of the α -phase region, and the process of equation (3) begins at the onset of the phase transition. This implies that the number of OH_{ad} molecules start to decrease, thus causing the ^1H resonance intensity to decrease.

Engel *et al* showed that hydrogen diffusion into the bulk sites is hindered by oxygens adsorbed on the surface [1]. This implies that, for the whole-scale phase transition to begin, surface oxygen must be removed. This fact gives further evidence useful in explaining the coincidence in our experimental data. When the process of equation (3) occurs in the phase transition region, some H_2O are desorbed from the surface. Some diffusion paths into the bulk sites are thus available. The hydrogen diffusion is no longer severely hindered which, in turn, enables the whole-scale phase transition.

4. Conclusion

We made nanometre size palladium particles whose radius is 40 Å, and performed *in situ* gas volumetric ^1H NMR measurements at hydrogen gas pressure over ~ 1 Torr and room temperature. We confirmed that hydrogen molecules dissociate and form OH_{ad} species on an oxidized Pd surface at $\text{Pd}/\text{H} < 0.4$. The spectral width of OH_{ad} is about 50 ppm. For comparison, we obtained an ^1H spectrum of water intentionally adsorbed on the Pd surface. Its spectral width is about 100 ppm in our experimental condition.

On increasing the hydrogen gas pressure, the production of OH_{ad} is saturated at $\text{Pd}/\text{H} \approx 0.4$. The ^1H NMR spectra and isotherm show that the saturation pressure coincides with the onset of the α - β phase transition. During the phase transition the resonance intensity decreases and vanishes. This implies that the population of OH_{ad} decreases, as well as the water formed desorbing from the surface.

Acknowledgments

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