PHYSICAL REVIEW B VOLUME 39, NUMBER 15 15 MAY 1989-II

X-ray-absorption study of the interaction of hydrogen with clusters of supported palladium

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(Received 10 November 1988)

The extended x-ray-absorption fine structure (EXAFS) and x-ray-absorption near-edge structure (XANES) at the Pd K edge were used to observe the interaction of hydrogen with palladium clusters, 5 nm in average size, supported on alumina. A sample was reduced in flowing dihydrogen at 573 K and atmospheric pressure. This sample was then cooled to room temperature (RT) in dihydrogen, allowing for the formation of β-phase palladium hydride. Another sample was reduced in the same way, but then evacuated at 573 K to prevent formation of the hydride. This sample was cooled to RT *in vacuo* and contacted with helium at atmospheric pressure. Analysis of the Pd EXAFS recorded at RT showed a 3.7% increase in the Pd-Pd distance and greater disorder for the hydride compared to the sample free of hydride. The XANES results were consistent with a narrowing of the $l=1$ band features for the hydride sample due to the increased Pd-Pd distance. In addition, the line shape of the edge for the hydride may result from hydrogen lowering the number of unoccupied p-like states near the Fermi level of Pd. The observed lattice expansion and modified electronic structure have been reported for bulk palladium hydride.

I. INTRODUCTION

Hydrogen is known to absorb into bulk palladium and occupy the octahedral interstices of the Pd fcc lattice. Palladium forms a β-phase hydride of composition $PdH_{0.72}$ at room temperature (RT) in H_2 at atmospheric pressure. This absorption is accompanied by an increase of 3.9% percent in the lattice parameter of Pd. In addition, the paramagnetic susceptibility of Pd decreases with H sorption and vanishes at a $PdH_{0.6}$ stoichiometry. Therefore, the presence of hydrogen modifies both the interatomic spacing and the electronic structure of the Pd lattice.[1]

Heterogeneous catalysts are often composed of supported metal clusters, 1 to 10 nm in size with 100% to 10% of their atoms exposed to the surface, respectively. The modified lattice and electronic structure resulting from interstitial hydrogen in supported Pd clusters is often similar to that observed for bulk metal. For instance, a 3% increase in the interatomic separation of Pd has been observed by x-ray-absorption spectroscopy for 1-nm Pd clusters supported inside the supercages of NaY zeolite after exposure to H_2 at 500 mbar and RT.[2] Additionally, Ladas *et al.* have shown that metal paramagnetism disappeared as hydrogen penetrated Pd clusters (1.2-nm diameter) supported on silica.[3]

We have studied the interaction of hydrogen with small palladium clusters by examining the extended x-ray-absorption fine structure (EXAFS) and the x-ray-absorption near-edge structure (XANES) at the Pd K edge.

II. EXPERIMENTAL METHODS

Two samples of palladium on alumina (5 wt.% Pd, Engelhard Industries) were used. The percentage of palladium metal exposed to the surface was measured by the titration of adsorbed oxygen with H_2.[4] A value of 21% was obtained which corresponded to a metal cluster size of about 5 nm. The samples were pressed into self-supporting wafers about 1 mm thick. Sample 1 was reduced in a controlled atmosphere x-ray-absorption cell[5] in flowing H_2 (palladium diffused) for 3 h at 573 K and atmospheric pressure. The sample was cooled to RT in flowing H_2. An x-ray-absorption spectrum was recorded at RT in static H_2 at atmospheric pressure. Sample 2 was also reduced in a cell for 3 h at 573 K in flowing H_2 but was evacuated to 10^{-6} mbar at 573 K for 1 h after the reduction. This sample was cooled to RT *in vacuo* and the cell was then filled with helium (Liquid Carbonic, 99.999%) at atmospheric pressure. This treatment was sufficient to remove hydrogen from the surface and the bulk of the Pd clusters.[4,6] An x-ray-absorption spectrum of this sample was recorded at RT.

The x-ray-absorption experiments were conducted in the transmission mode on beam line IV-1 at the Stanford Synchrotron Radiation Laboratory (SSRL). The monochromator Si(220) crystals were detuned to 50% of maximum intensity to minimize the higher harmonic content of the incident beam. Intensity measurements were recorded from three ion chambers. Samples were placed between the first two chambers while a polycrystalline Pd foil was placed between the second and third chamber. This provided a reference point for the Pd K edge (24.348 keV) in the samples.

The EXAFS data were analyzed as described by Via *et al.* and the errors involved have been assumed to be the same.[7] Weighted EXAFS data $k^2\chi(k)$ were Fourier transformed to give radial structure functions (RSF's). The RSF's were backtransformed over a range of 127 to 335 pm which contained only contributions from the first coordination shell. The Pd-Pd distance R, average coordination number N, and change in the Debye-Waller factor $\Delta\sigma^2$, were calculated by a nonlinear least-squares fit of the EXAFS equation over a k range of 35–140 nm^{-1} using phase shift and amplitude functions derived from the Pd foil reference.

III. RESULTS AND DISCUSSION

A. EXAFS

Fourier transforms of the k^2 weighted EXAFS data (not corrected for phase shifts) are shown in Fig. 1. A change in the Pd-Pd distance is readily apparent from a comparison of peak positions in the transforms. The dashed curves in Fig. 2 represent the fit of the EXAFS equation to the data (solid curves). A summary of the EXAFS results is shown in Table I. The Pd-Pd distance for the clusters in He was measured at 273 pm which is slightly less than the bulk value of 275 pm. However, the Pd-Pd distance increased by 3.7% to 283 pm for the clusters in H_2. A 3.7% expansion in the lattice parameter of bulk Pd hydride compared to Pd corresponds to a stoichiometry of $PdH_{0.66}$.[1]

The value of the average coordination number was the same for both samples. This suggested that the observed differences in the spectra were due solely to the presence or absence of hydrogen in the particles. A cubo-octahedron having ~20% of its atoms exposed to the surface has an average coordination number of 11.3 which is within experimental error of 9.5 as measured by EXAFS.[8] The magnitudes of the Fourier transforms in Fig. 1 are related to N and $\Delta\sigma^2$. Since the value of N remained unchanged, the decreased peak height in Fig. 1 for the sample in dihydrogen compared to the sample in helium is due solely to an increase in $\Delta\sigma^2$.

The change in the Debye-Waller factor (referenced to Pd foil) for sample 1 was 20 pm^2 compared to 3 pm^2 for sample 2. The relatively small value for sample 2 was indicative to bulklike disorder (static and thermal) for the clusters in He. However, the sixfold increase in the Debye-Waller factor for the sample in H_2 indicated greater disorder due to the interstitial hydrogen. The change in $\Delta\sigma^2$ is expected in light of the 3.7% increase in R. The EXAFS of CuBr (Ref. 9) and NaBr (Ref. 10) under high pressure showed that the Debye-Waller factor increased (or decreased) as R increased (or decreased), independent of structure. Also, Mössbauer effect spectroscopy of ^{197}Au (Ref. 11) and ^{119}Sn (Ref. 12) impurity atoms in Pd and $\sim PdH_{0.8}$ was used to show softening of the lattice vibrational modes upon hydrogenation.

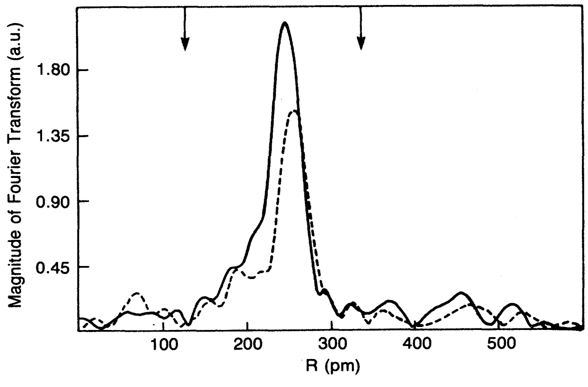

FIG. 1. Fourier transforms (not corrected for phase shifts) of k^2-weighted EXAFS data for sample 1 (dashed line) and sample 2 (solid line). The arrows depict the region of the back-transform used for curve fitting.

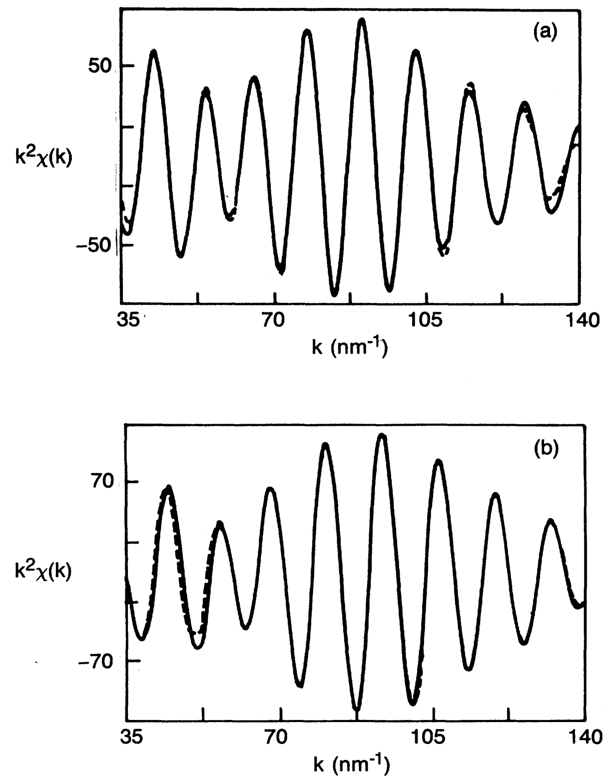

FIG. 2. Curve fits of $k^2\chi(k)$ derived from the EXAFS data (solid lines) for (a) sample 1 and (b) sample 2. The fitted function is represented by the dashed line.

B. XANES

The Pd K edge for each sample is shown in Fig. 3 on an energy scale referenced to the first inflection point of the Pd foil edge. The edge in the spectrum for sample 1 appeared at about 3–4 eV higher energy than the edge for sample 2. However, the peaks in the absorption spectra

TABLE I. EXAFS parameters. Estimated uncertainties: ±20% for N; ±10% for $\Delta\sigma^2$; ±1 pm for R.

Sample	N	R (pm)	$\Delta\sigma^2$ (pm^2)
Pd-H/Al_2O_3	9.4	283	20
Pd/Al_2O_3	9.5	273	3.2
Pd foil reference	12	275	

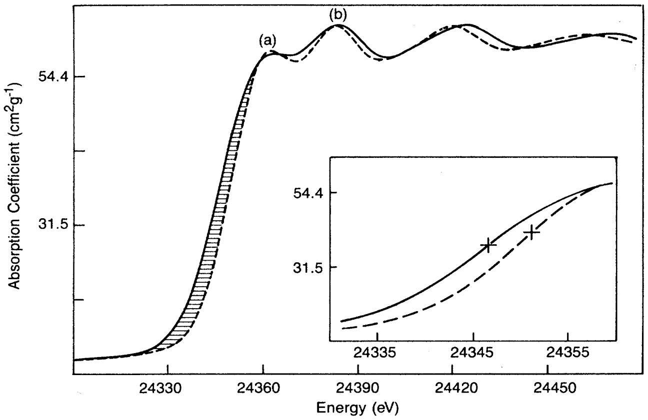

FIG. 3. Pd K near-edge spectra of sample 1 (dashed line) and sample 2 (solid line). Crosses on the inset depict the locations of the first inflection points in the edges.

at (a) and (b) in Fig. 3 coincide. The inset in Fig. 3 shows the first inflection point of the edges on an expanded energy scale. The inflection points did not occur at the same absorption value. Therefore, absolute determination of the energy at the edge was somewhat ambiguous but a decrease in area in this region of the spectrum (shaded) is easily seen.

One explanation for the apparent edge shift could be a change in the oxidation state of the metal due to bonding with H. We reject this for the following two reasons: (1) Experimental evidence and calculations show that the hydrogen in palladium behaves as a well-screened proton with charge very near that of the neutral atom.[13-15] For instance, only a very small positive shift (increase in binding energy of +0.17 eV) for the 3d core levels in $\sim$PdH$_{0.8}$ compared to Pd metal has been observed by XPS.[15] However, our edge shift would correspond to a large change in oxidation state which is inconsistent with the picture obtained from previous experiments and calculations. (2) The shift of 3–4 eV occurs in the edge only. If the Pd oxidation state in the hydride is different from that in the metal, other edge features would be expected to shift in the same direction by nearly the same value. For example, the first peak in the K edge of vanadium metal and its compounds shifted to higher energies in nearly identical fashion with the absorption edge as the oxidation state of V increased.[16] This has also been observed in the L_{I} edge of Pd metal and PdCl$_2$.[17] There is no shift in the first (a) or second (b) peak in Fig. 3. Therefore, we put forth other explanations for the observed spectra.

The Pd K near-edge spectrum contains structure corresponding to the $l=1$ (p-like) projected density of final states.[18,19] The Pd 5p band contributes to the observed structure at (a) in Fig. 3. However, peak (b) results from the $l=1$ projection of the tails of the 4f orbitals from adjacent Pd atoms. The shape of the absorption edge reflects the extent of 4d-5p hybridization.[18]

Two differences are seen in the spectra of Fig. 3. As mentioned earlier, the line shape of the edge is different in that the sample containing hydrogen has less area under the curve compared to the sample in helium. Second, the peak width at (a) and (b) is narrower for sample 1 compared to sample 2. Hydrogen exerts an indirect influence on the band structure of Pd by increasing the metal lattice constant. Calculations have shown qualitatively that the metal d bands narrow and become more tightly bound as the lattice constant increases.[20] Photoemission experiments revealed a decrease in the d band width of 10% for a hydride of $\sim$PdH$_{0.8}$ compared to Pd metal.[15] The narrowing of the peaks at (a) and (b) in Fig. 3 due to the hydrogen may therefore be a result of narrower band structure ($l=1$) reflecting Pd in an expanded lattice. The decrease in area at the edge (shaded area) could also result from this effect since less 4d-5p hybridization would be expected for an expanded lattice. Another possible explanation for the altered line shape at the edge is the direct influence of hydrogen on the palladium band structure through Pd—H bonding. Hydrogen-induced bonding states lower previously empty 5p-like states at the top of the Pd s-p conduction band.[21] A vanishing optical transition upon hydride formation in Pd thin films has been reported and attributed to a lowering of an s-p conduction band below the Fermi level.[22] Hydride formation also raises the Fermi level of Pd above the d band.[21] Therefore, p states previously accessible are now filled resulting in an edge shift to higher energy.

IV. CONCLUSIONS

The interaction of hydrogen with 5-nm palladium particles has been examined by x-ray-absorption spectroscopy. As for bulk palladium, the interatomic distance increased due to interstitial hydrogen. An increase in the Debye-Waller factor indicated greater disorder for the hydride sample compared to Pd clusters in helium. This increase can be attributed to the expanded Pd interatomic distance. Near-edge spectra were also consistent with an expanded Pd lattice. Alternatively, Pd—H bonding states may lower previously unoccupied 5p-like states below the Fermi level which will directly affect the K edge line shape. The EXAFS and XANES results for Pd clusters revealed a modified lattice and electronic structure which have been observed for bulk palladium hydride.

ACKNOWLEDGMENTS

The work was supported by a continuing National Science Foundation (NSF) grant, currently No. NSF CBT 85-21375, and carried out in part at SSRL which is funded by the U.S. Department of Energy under Contract No. DE-AC03-82ER-13000, Office of Basic Energy Sciences, Division of Chemical Sciences and the NIH, Biotechnology Resource Program, Division of Research Resources. One of us (S.M.L.) acknowledges support from the U.S. Department of Defense. R.J.D. acknowledges partial support from W. R. Grace and Co.

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