Hydrogen absorption in Palladium clusters stabilized in tetra octyl phosphonium bromide

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The palladium-hydrogen system is the first of all metal-hydrogen systems that has attracted research activities, and it has been extensively investigated. That is mainly due to the noble character of palladium and the fact that no extensive surface treatments are required. [1]. Palladium nano-sized clusters have been already shown to have distinct differences in their hydrogen uptake characteristics when compared to bulk Palladium [1-3]. These differences are not only due to the different physical properties of the small-size system but it is also affected by the type of the stabiliser used on these clusters [2] and the different structure [3]. The effect of the stabilizer and the lattice structure of the clusters on the hydrogen absorption is a fundamental question. However, detailed reports on this effect are very limited.

Hydrogen adsorption studies in Palladium-Hydrogen nano-sized system have shown that the amount of hydrogen uptake in nano-sized Pd-Hₓ is higher than that for the bulk material in the solid solution region of the isotherms (i.e., x< 0.1 for the α-phase at 300 K). However, in the hydride phase region (α´-phase), the maximum hydrogen concentration was observed to be significantly lower than that observed in bulk Pd. The increased phase solubility was attributed to the increased hydrogen absorption at the surface and in the sub-surface region. The reduced hydride solubility was attributed to 2-3 atomic layers at the surface and the sub-surface non-contributing in the hydride formation [1, 2].

In this work the hydrogen absorption behaviour of Pd clusters stabilized in tetra-octyl-phosphonium bromide (TR₆PBr) will be presented. The phase transition of these samples will be monitored by in situ synchrotron x-ray diffraction (XRD) measurements during hydrogen loading–unloading. Using the in-situ XRD measurements the pressure-lattice parameter isotherms (P-d Isotherms) can be also constructed.

The hydriding behaviour of Pd-clusters was studied in-stiu. For these measurements a special high vacuum gas loading cell was constructed that allows stepwise controlled hydrogen loading and unloading between 10 and 10⁵ Pa. Each loading cycle starts at a base pressure of about 10⁻³ Pa, the hydrogen pressure was increased stepwise. The measurements are restricted with the time it takes to reach equilibrium pressure and the time needed to take one diffractogram at a selected 2θ range (27°-65°) with reasonable statistics. The advantage of the high intensity synchrotron source makes it possible to perform such measurement and reduced enormously the time need for such experiments with a good statistics. Because of the time scale and the required statistics it will be impossible to perform such measurement using conventional x-ray, metal, source.

Figure 1 shows the XRD patterns of the cluster sample during hydrogen loading at different hydrogen gas pressures. One can see that the diffraction patterns lay at the same position expected for bulk Palladium, which indicates that the clusters have cubic structure same as
bulk. As the hydrogen pressure increases the peaks position are shifted to lower 2θ values, indicating the lattice expansion. Moreover, the maximum intensity of the peaks (peaks height) also decreases with increasing the hydrogen pressure (in range between 13 mbar and 20 mbar, Fig.1). No additional sets of Bragg reflections can be detected, only peak broadening in the pressure range 13 to 20 mbar is seen. Which can be explained by an (α-α’) phase transition, common for bulk Pd, this was checked by looking for a peak broadening during hydrogen absorption. Such phase transition has not been observed for same size icosahedral clusters [1] stabilized in tetra-octyl ammonium bromide. This indicates the important impact that the stabilizer have and hence the structure of the clusters on the hydrogen uptakes behaviours. We attributed this obvious bulk like phase transition of the 3.7nm clusters to the stabilizer and their structure, which could leads to a new way of understanding the hydrogen absorption behaviour in reduced size systems like clusters.

![Diffraction patterns of the 3.7 nm cluster sample at different hydrogen pressures.](image)

Figure 1 Diffraction patterns of the 3.7 nm cluster sample at different hydrogen pressures. The peak position of the as prepared sample matches position of those for bulk Pd, vertical lines. During hydrogen loading: the peaks positions are shifted to lower 2θ values with increasing the hydrogen pressure and the maximum intensities of the peaks is decreased in pressure range 13 to 20 mbar and peak width increase indicating the (α-α’) phase transition. At higher pressure the sample is completely in the hydride phase. \( \lambda = 1.18 \text{ Å} \)

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References

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