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Pd - Teflon-AF samples which are not accessible for Pd - surfactant -clusters, and that the icosahedral lattice absorbs less hydrogen for similar external pressures.
Hydrogen absorption in 3.1 nanometre sized palladium samples: does structure matter?

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In this work the hydrogen absorption behaviour of two types of Pd-clusters, different in structure but similar in size (3.1 nm), will be presented. First, icosahedral Pd clusters stabilised in surfactants; second, cubic Pd clusters stabilised in a Teflon-AF matrix. The phase transition in these samples was monitored by in-situ X-ray diffraction. It will be shown that the hydrogen uptake ability depends strongly on the lattice structure, which is affected by the type of stabilizer. Teflon AF stabilised clusters (cubic clusters) show the phase transition which is common for bulk Pd, whereas the surfactant stabilised clusters (icosahedral clusters) show only weak lattice dilatation upon hydrogen absorption. Pressure – lattice parameter Isotherms show that the cubic clusters absorb large amounts of hydrogen in comparison to the icosahedral clusters. The measured lattice expansion is 0.130 Å at 10\textsuperscript{5} Pa and 300 K, which is about 320 % the amount measured for icosahedral clusters (0.04 Å). This suggests that surface sites are available for hydrogen in the Pd – Teflon-AF samples which are not accessible for Pd – surfactant -clusters, and that the icosahedral lattice absorbs less hydrogen for similar external pressures.

Keywords: Clusters; Polymers; nanostructures; X-ray diffraction; Synchrotron radiation
1. Introduction

The palladium – hydrogen system was 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 Pd and the fact that no extensive surface treatments are required. Nowadays hydrogen absorption in metallic systems with reduced dimensions has become a very attractive research field. The physical and the chemical properties of nanometre sized materials are often size dependent and different to bulk properties [1]. Palladium nano-sized clusters have already been shown to have distinct differences in their hydrogen uptake characteristics when compared to bulk Pd. These differences are not only due to the different physical properties of the small-size system but are also affected by the type of the stabiliser used on these clusters [2] and the different structure [3]. Jisrawi et al. performing Molecular Dynamic (MD) Simulations using embedded atom potentials of Baskes et al. have shown that small cuboctahedral Pd-clusters tend to transform into the icosahedral structure [4]. For simplicity, we, therefore, assume that the two different structures we are dealing with are the cubic and the icosahedral structure.¹

The effect of the lattice structure of the clusters on the hydrogen absorption is a fundamental question. However, detailed reports on the effect of the cluster structure are very limited. Hydrogen atoms adsorbed in a metal lattice can occupy only one of two types of interstitial sites; octahedral (O_h) and tetrahedral (T_d). Bulk Pd has a face-centred-cubic lattice structure (fcc) and hydrogen atoms adsorbed in the Pd metal lattice occupies the O_h-sites [5]. Calvo and co-workers [6] recently reported that (at zero temperature) icosahedral clusters (of 147 Pd-

¹ More complicated structures than the icosahedral one are not taken into account in this paper, even though they might be present.
atoms) energetically favour hydrogen in T\textsubscript{d}-sites, while cubic clusters absorb hydrogen at O\textsubscript{h}-sites. According to Calvo and Carré [6], this should lead to greater hydrogen absorption in the icosahedral clusters, since icosahedral clusters reveal more interstitial sites. However, they find that for a moderate amount of hydrogen the cubic cluster is energetically favoured. To summarise, according to Calvo and Carrés results [6], an icosahedral cluster containing 147 Pd-atoms might transform into a cubic cluster with large hydrogen concentrations. The critical concentration for transformation is increased with increasing temperature. Such a hydrogen-induced structural transition has recently been reported by Pundt et al., however, it was for much larger clusters and there was evidence for a stabilisation of the icosahedral phase upon hydrogen loading [7].

Hydrogen adsorption studies [8 – 11] in Palladium – Hydrogen nano-sized system have shown that the amount of hydrogen uptake in nano-sized Pd-H\textsubscript{x} is higher than that for the bulk material in the solid solution region of the isotherms (i.e., c\textsubscript{H} < 0.1 H/Pd for the \(\alpha\)-phase at 300 K). However, in the hydride phase region (\(\alpha'\)-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 [3, 8].

Small nanoparticles (clusters) have been reported to have different lattice structures (e.g. icosahedral) than their coarse grained counterpart, and they possess dilated lattices [2, 4, 12]. The question which rises is if that means that they will absorb larger amounts of hydrogen.

In this work the hydrogen absorption behaviour of 3.1 nm Pd clusters in two different lattice structures will be presented. First, icosahedral Pd clusters obtained by an electrochemical method [13] and stabilised in a surfactant shell using tetraoctylammonium bromide (TOAB). Second, cubic Pd clusters obtained by a chemical method and stabilised in a Teflon-AF matrix
[14]. The effect of the different lattice structure of each sample on the hydrogen uptake will be studied.

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) will be constructed.

The phase boundaries and the amount of hydrogen absorbed in each sample will be determined. It will be shown that the cubic clusters absorb much larger amounts of hydrogen than the icosahedral clusters.

2. Experimental

2.1. Sample preparation

The Teflon-AF stabilised Pd clusters (Pd – Teflon-AF) were prepared by a salt reduction method in which Teflon AF 2400 was used as a stabiliser [14]. Teflon AF 2400 and fluorinated Pd salts were dissolved in a proper fluorinated solvent, where a membrane was resulted by drying under argon gas. After that the Pd salt was reduced by sodium borohydride

\[ \text{NaBH}_4 \].

Determination of Pd-content in Teflon AF 2400 membranes was done as follows; 25 to 50 mg of the membrane was dissolved in Fluorinert FC-75 at 50 °C and stirred for about 1 h to obtain a black, viscous solution. 2 mL of nitrohydrochloric acid (mixture of 0.5 mL 65 % HNO₃ and 1.5 mL conc. HCl) was added and heated for 30 min. in an ultrasonic bath at 50 – 60 °C. The mixture turned from black to orange within a few minutes. After ultrasonic treatment it was cooled to RT under stirring, 40 \(\mu\)L of yttrium standard (1 g/L) was added and
further stirred for 30 min. After centrifuging for 10 min at 5000 rpm, a sample of about 10 µL was taken from the aqueous, orange top layer for further measurement by Total Reflection X-Ray Spectrometry (TXRF) described by Prage [15]. The Fluorinert layer was colourless.

The surfactant-stabilised Pd clusters (Pd-TOAB clusters) were stabilised in tetraoctylammonium bromide (TOAB). The Pd clusters were prepared by using an electrochemical technique described by Reetz et al. [13]. The clusters were prepared in a cell containing two-Pd-electrodes using a constant current density, where TOAB was used as electrolyte and stabiliser. Applying constant current to the electrodes causes dissolution of the Pd anode with the formation of Pd(II)-cations, which are reduced at the cathode forming the so-called “adatoms”. The adatoms aggregate into surfactant stabilised clusters. The electrolysis was performed at room temperature and stopped after a charge of 720 Coulomb was passed. Elemental analyses show that the amount of palladium is 75 % within the cluster stabiliser mixture.

2.2. In-situ X-ray diffraction

In-situ XRD patterns of the cluster sample were measured with 1.12 Å X-ray wavelength from the synchrotron radiation of the beam line B2 at the Hamburg synchrotron laboratory (HASYLAB) at DESY. The wavelength was selected by a Ge(111) double-crystal monochromator. The measurements were performed in a high vacuum gas loading cell, using theta –two theta geometry, which allows stepwise and controlled hydrogen loading and unloading between 10¹ Pa and 10⁵ Pa. All samples were pre-treated with hydrogen to remove any oxide layer. Each loading cycle starts at a base pressure of 10⁻³ Pa, the hydrogen pressure was increased stepwise to 10⁵ Pa. The pressure was monitored by using MKS pressure gauges with 0.01 % precision. The purity of the hydrogen gas was 99.9999 %, all the measurement
were performed at room temperature. The measurements are restricted by the time it takes to reach equilibrium pressure and the time needed to take one diffractogram at a selected $2\theta$ range (24° – 70°) with reasonable statistics. The high intensity synchrotron source makes it possible to perform such measurements and reduce enormously the time needed for such experiments.

2.3. Isotherms

Isotherms were taken after carefully pretreating the samples. To reduce any oxide surface layer each cluster sample was loaded with hydrogen at $10^5$ Pa for 24 hours and subsequently evacuated for about 36 hours. This procedure was repeated at least twice. All measurements were performed with high purity hydrogen gas (99.9999 %) at constant temperature (22 ± 0.5°C) inside a thermostatically-controlled room.

The $P – d$ isotherms were constructed using X-ray diffractograms obtained from the XRD measurements at different equilibrium hydrogen pressures. Lattice parameter of each Pd sample was calculated from the position of the lower angle peak (near the bulk fcc (111) reflection). It is known that the pressure – lattice parameter isotherms are similar to those of the pressure – concentration isotherms [11] and, therefore, can be used to identify the effect of hydrogen in the samples.

The adsorption – desorption cycles were performed by loading – unloading the Pd cluster sample with hydrogen in a stepwise manner. Each loading – unloading cycle consists of ca. 20 steps, where in each step the sample is loaded–unloaded with a known amount of hydrogen.
3. Results and discussion

3.1. Samples characterisation

The size and the structure determination of the cluster samples were performed by XRD data analysis, Fig. 1a and b, and by high resolution transmission electron microscopy (HREM) image analysis, Fig. 2.

The cluster size was determined from an XRD-diffraction pattern using a Fourier transform technique (FTT) analogous to that proposed by Hall et al. [16]. Fourier transform of the XRD pattern was taken, and information related to the average distribution of the interatomic distances within the cluster was obtained. The last visible peak of the radial distribution function (r.d.f) or $P(r)$ gives a fairly accurate value of the sample diameter. In this work we have applied this technique to two types of diffraction data: model cluster, obtained by MD-simulations and cluster relaxations [7] Fig. 3, and experimental diffractograms of Pd clusters, for which independent Transmission electron microscopy (TEM) observations were made. This technique has the advantage over the Scherrer-formula because the structure has no effect on the size-determination. The good agreement between experimentally obtained Pd-cluster sizes from TEM-images and the calculated size using FTT on XRD pattern has been verified [17].

Figure 4 shows the Fourier transform of the diffraction patterns of the model cluster shown in Fig. 3. In both icosahedral and cubic structures there is a trend of decreasing oscillation in the $P(r)$ with increasing the interatomic distance. In both cases the oscillation vanishes at an interatomic distance of 3.7 nm which is also the size of this (2057 atoms) model cluster. This verifies the quality of this FFT-method for determining cluster sizes from XRD-pattern independent of the cluster structure.
The FFT-method was applied to the experimental data pattern of the samples. According to TEM measurements of about 100 clusters for each cluster type, the Pd – TOAB-stabilised clusters have a mean size of 3.2 nm (with a narrow size distribution of 0.5 nm). The Pd – Teflon-AF clusters sample has mean size of 3.1 nm. Within the experimental error both samples are of similar size.

The Fourier Transform of the XRD pattern of the Pd-TOAB sample is shown in Fig. 5. The estimated cluster size for the sample is marked with a grey rectangular region indicating uncertainty intervals around the size estimates: \(3.0 \pm 0.5\) nm. This value is fairly similar to TEM values. The FFT-method is also advantageous because it results from a large area measurement and contains the size information of numerous clusters.

Structural differentiation can also be obtained from the XRD-diffraction patterns. Recent results obtained in our group show that the XRD patterns derived from MD simulations for Pd model clusters with a cubic lattice structure or with an icosahedral structure show important and significant differences [2, 4]. These can be summarised as follows: first, the relative intensities of the cuboctahedral structure diffraction peaks are similar to those of the bulk, see Fig. 3. For example, the relative intensities are \(I_{(111)}/I_{(200)} = 1/4\). Also the positions are close to bulk values. The relative intensities of the icosahedral structure diffraction peaks (near bulk (200) and (222)) have smaller maximum amplitude in comparison to that near the bulk (111) peak. The relative intensity is \(I_{(close\ to\ (111))}/I_{(close\ to\ (200))} \approx 1/5\). Second, the separation between the peak near (111) and the peak near (220) is reduced in comparison to that of the bulk and the cubic cluster. Third, an increased intensity in the diffractogram of the icosahedral cluster between 51 and 56 degrees (for \(\lambda = 1.147\ \text{Å}\)) is also observed, as can be seen in Fig. 3.

Figure 1a and b, shows XRD patterns of (a) the Pd – Teflon-AF clusters sample, and (b) the Pd – TOAB clusters sample. The Pd – Teflon-AF clusters sample, Fig.1a, has a diffraction
pattern similar to that of bulk Pd and peaks appear at exactly those positions expected for fcc bulk Pd, whereas the Pd – TOAB clusters sample shows a different diffraction pattern. In Fig. 2b, the intensity of the diffraction peaks (near bulk (200) and (222)) has a smaller amplitude in comparison to the near bulk (111) peak. In addition, the separation between the peak near (111) and the peak near (220) is reduced compared to that of the bulk. Furthermore, an increased intensity in the diffractogram of the Pd – TOAB clusters sample between 51 and 56 degrees is also observed. Comparing the experimental XRD patterns, Fig 1, with those obtained from MD-simulated clusters, Fig. 3, shows that the Pd – Teflon-AF clusters have a cubic lattice structure, while the Pd – TOAB clusters have a predominantly icosahedral lattice structure.

The lattice structure of the clusters was also verified by analysing the HREM images of the cluster samples. Figure 2a and b shows the HREM-image of the clusters samples and the corresponding Fourier transfer analysis (FT). The HREM image of the Pd – Teflon-AF clusters shows lattice fringes, common for cubic lattices, and in the corresponding FT analysis two dots are visible indicating that the cluster is in the <111> orientation, Fig. 2a. The lattice structure of the Pd – TOAB clusters was also verified by analysing the HREM images of the cluster samples. Figure 2b shows the HREM-image of the TOAB stabilised cluster sample. Fourier transformation analysis (FFT) of HREM images shows that most of the particles have an icosahedral lattice structure. In Fig 2b, although there is some background noise, one can see 10 spots in the FT corresponding to the five fold symmetry. Generally, icosahedral clusters do not lie in the desired five fold symmetry direction and one has to determine the structure only from the HREM image. In this case, no straight lattice fringes are visible but an amorphous-like pattern.

These results demonstrate the important impact that the stabiliser plays on the structure of the clusters. Although the two clusters have the same size, they possess different lattice structures. The exact nature of the effect of the stabiliser is not yet fully known.
3.3. Isotherms of cubic and icosahedral clusters

During hydrogen loading one observes a shift in the diffraction patterns to lower 2θ-values, indicating a lattice expansion for the cluster. Figure 6a and b shows diffraction patterns of the two clusters samples at four different pressure steps monitoring the lattice expansion. It is clearly seen that the total lattice expansion of the Teflon stabilised cluster, Fig. 6a, is larger than that for the TOAB stabilised cluster, Fig. 6b. Additionally a phase transition is observed for the Teflon stabilised cluster.

Since the Teflon stabilised clusters have a cubic lattice structure and, also, the observed transition occurs at a pressure typical for bulk palladium, this transition is interpreted as an (α – α′)-phase transition, Fig.6a. No peak splitting was found for the icosahedral cluster sample, as shown in Fig. 6b, increasing the hydrogen pressure leads to very small dilation of the lattice, shifting the Bragg reflection to smaller 2θ. Moreover, there is no relative peak intensity change, which excludes a possible structural change.

The deduced P – d Isotherms of the two differently stabilised clusters sample are shown in Fig. 7. The P – d Isotherm of the Pd – Teflon-AF sample shows three distinct parts (I, II and III in Fig. 7). These parts are comparable to the parts found in the pressure – concentration isotherms. Part I is the solid solution (α-phase). According to our interpretation, part II represents the two-phase region (miscibility gap). In this current work it is called the lattice parameter miscibility gap, since lattice constants are presented. In contrast to bulk Pd, where ideally no pressure dependency exists, this region has, for clusters, a pressure dependency and is spread over a pressure range. This was also found in pressure – concentration isotherm measurements [9, 18]. Part III, is comparable to the metal hydride where the lattice parameter rises steeply with increasing pressure.
The initial lattice parameter of Pd – Teflon-AF is 3.90 Å which is slightly increased compared to that of bulk Pd. The initial “apparent lattice parameter” of Pd – TAOB is, at 3.940 Å, much larger. A change in the lattice parameter occurs by exceeding $2 \times 10^3$ Pa. It is rather steep for the Pd – Teflon-AF clusters, and small for the Pd – TAOB clusters. One can also see that the cubic clusters sample (Pd – Teflon-AF clusters) has a much larger total lattice expansion than the icosahedral clusters sample (Pd – TOAB clusters). The total lattice expansion $\Delta a$ of the Pd – Teflon-AF clusters is 0.130 Å is 100 % of that expected for bulk Pd, where the $\Delta a$ for the Pd – TOAB clusters is 30 % of that expected for bulk Pd. This means that the amount of hydrogen absorbed in the cubic Pd – Teflon-AF clusters is larger than that absorbed in the icosahedral Pd – TOAB clusters.

The hydrogen solubility in the solid phase region is significantly increased and the hydrogen solubility in the hydride phase is drastically reduced in the Pd – TOAB clusters sample compared to the Pd – Teflon-AF sample. The Pd – Teflon-AF clusters’ isotherm shows regions of significantly different slope: apparent linear fits give the correlating phase boundaries. Unloading curves (not shown here) have verified the presence of hysteresis [18], which is generally correlated to a phase transition, for both samples. Apparent linear fits were, therefore, also performed for the Pd – TAOB clusters’ isotherm. According to these results, the phase boundaries of the lattice parameter miscibility gap are significantly more narrow for the Pd – TOAB than those of the Pd – Teflon-AF sample.

Moreover the maximum lattice expansion of the hydride phase for the Pd – Teflon-AF sample is increased by almost 320 % compared to the Pd – TOAB sample. While it is about 30 % of the bulk value for the Pd – TOAB clusters at $10^5$ Pa, it is about 100% for the Pd – Teflon-AF clusters at the same hydrogen pressure. This means that fewer absorption sites are not available for hydrogen in case of the Pd – TOAB sample, and, maybe, by applying the model

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2 We note that, strictly, there is no lattice for icosahedral clusters. This $d$-value is obtained by using the Bragg-formula for the fcc-lattice, and is, therefore, named “apparent lattice parameter”.

of a Gaussian site distribution [19], that the distribution of the site energy is broadened and extends to higher energies. Thus, the icosahedral cluster can absorb less hydrogen than the cubic cluster at $10^5$ Pa and 300 K. This seems to contradict the results of Calvo and Carré, but it has to be considered that they only discussed the total amount of possible sites for the two structures, independently of the pressure conditions [6]. A broadened site distribution might explain this apparent discrepancy.

Interestingly, the measured total expansion for the cubic clusters is comparable to that of the bulk system at 300 K and $10^5$ Pa [20]. This suggests that for these clusters the surface sites are also available for hydrogen. This surface contribution will increase the total amount of hydrogen ad-and absorbed by clusters compared to that absorbed by icosahedral clusters sample.

The effect of the stabiliser on the hydrogen solubility has been noted recently and is of interest. Recently, we reported [2] on the hydrogen absorption behaviour in Pd clusters of similar structure, stabilised in either a soft surfactant matrix (TOAB) or a mechanically harder matrix poly (methyl methacrylate) (PMMA). In these studies the total hydrogen absorption and the total lattice expansion were found to be larger in the mechanically softer stabilised sample. The interpretation thus focused on the mechanical hardness of the stabiliser even though electronic effects cannot be excluded. More recently, electronic effects were discussed by Horinouchi et. al. [21] who reported that hydrogen absorbs reversibly in Isocyaine-stabilised Pd clusters samples, whereas no hydrogen storage ability at all was found for the Pd clusters stabilised by trialkylphosphine. Horinouchi et al. showed that the latter was partially oxidised because of electronegativity effects. It has been suggested that the increase in hydrogen absorption content is due to the higher electron-donation nature of the n-octyl isocyanide compared to the trialkylphosphine [21].

These examples demonstrate the important impact of the stabiliser on the hydrogen absorption properties of nano-sized clusters. The stabiliser can affect the cluster either through the
binding energy (electronic factor) [22] or through the number of the anchoring points between the stabiliser and the cluster (mechanical factor) [23]. These two factors, the electronic and the mechanical one, seem to have a huge effect on the cluster properties. As our results show, the stabiliser can also affect the lattice structure of the clusters and, consequently, influence the amount and the ability to absorb hydrogen.

In this study the difference in the hydrogen storage ability can be attributed to the fact that the absorption site number in the Pd – TOAB sample is less than that in the Pd – Teflon-AF sample. This might be due to the very low value of the dielectric constant of Teflon AF [24]. Thus, one can expect that it also has weaker binding energy to the cluster surface (electronic factor). Furthermore, the large lattice expansion upon hydride formation might hint at fewer anchoring points between the Teflon AF and the Pd-clusters. This would result in softer mechanical binding. Furthermore, Teflon AF conventionally is known to be mechanically soft. Soft binding stabilisers or those with a small number of anchoring points might offer more surface sites for hydrogen adsorption than strong binding stabilisers or those with many anchoring points would do.

Nanoparticles have been reported to exhibit dilated lattices that would result in large interstitial volumes for hydrogen storage and possibly lower the hydrogen binding energy. This is not the case in our recent results, the Pd – TOAB cluster sample is more dilated than the Teflon stabilised clusters sample, but it shows lower hydrogen storage ability. It is known that nanoparticles can offer a new set of surface and subsurface sites. So far, it was assumed that surface and subsurface sites do not contribute to hydride phase formation. For the Pd – Teflon-AF sample it seems that this is not the case and a new set of surface sites contributes to the H-absorption at a pressure range which is similar to that of the hydride formation. In the Pd – Teflon-AF sample, the higher hydrogen uptake properties seem to be due to the additional contribution of the surface sites. One can assume that, as a result of the week
binding energy of Teflon AF to the cluster surface, the surface sites are more available for hydrogen absorption than in the case of TOAB stabilised clusters.

4. Conclusions

In-situ XRD measurements on Pd clusters stabilised in Teflon AF and TOAB show that the hydrogen storage ability depends strongly on the lattice structure which is affected by the type of stabiliser. The (3.1 nm) Teflon AF stabilised clusters have a cubic lattice structure and show the phase transition which is common for bulk, whereas the (3.2 nm) TOAB stabilised clusters with an icosahedral lattice structure show only weak lattice dilatation upon hydrogen absorption. $P - d$ Isotherms show that the Teflon AF stabilised clusters (the cubic clusters) absorb large amounts of hydrogen compared to the TOAB stabilised icosahedral clusters. The measured total lattice expansion of the cuboctahedral cluster is 0.130 Å at $10^5$ Pa hydrogen gas and 300 K. These results show the important impact that the stabilising matrix has on the cluster lattice structure and hence on the ability to absorb hydrogen.
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References


**Figure captions**

Figure 1: Diffraction pattern of the as-prepared samples: (a) Pd – Teflon-AF clusters sample and (b) Pd – TOAB clusters sample. The vertical dotted lines are the position of peaks for bulk Pd at \( \lambda = 1.12 \) Å.

Figure 2: HREM and FT images of single clusters of (a) Pd – Teflon-AF cluster and (b) Pd – TOAB cluster. FT analysis of image (a) gives dots indicating that the clusters is cubic while the FT of image (b) result in 10 spots indicating an icosahedral structure.

Figure 3: Diffraction patterns of a model Pd cluster:(a) shows the diffraction patterns of a cubic Pd cluster (2057 atoms, about 3.7 nm cluster diameter), (b) represents an icosahedral Pd cluster (2057 atoms, about 3.7 nm cluster diameter). The dotted vertical lines are the position of the Bragg reflections for bulk Pd with cubic lattice structure, after [4].

Figure 4: \( P(r) \) for a model Pd cluster with (a) cubic and (b) icosahedral structure. In both cases the \( P(r) \) oscillations vanish at an interatomic distance of about 3.7 nm. Since this gives the largest distance of atoms in the cluster it resembles the cluster diameter given in Fig. 3.

Figure 5: The \( P(r) \) profile show the results of inverting the diffraction patterns of Fig. 1b. The grey rectangular region indicates the uncertainty interval around the estimated Pd cluster size.

Figure 6: Diffraction patterns of (a) the Teflon stabilised and (b) the TOAB stabilised cluster samples at four different hydrogen pressures monitoring the lattice expansion. (a) Diffraction patterns of the as-prepared sample (open squares, at \( 1.6 \times 10^3 \) Pa (crossed triangles), at \( 1.8 \times 10^3 \) Pa (up triangles) and at \( 9.4 \times 10^4 \) Pa (solid squares). The \( \alpha' \)-Pd-H phase is visible at \( 1.8 \times \)
10^3 \text{ Pa}. At the largest pressure the whole sample is in the $\alpha'$-Pd-H phase. (b) Diffraction patterns of the as-prepared TOAB stabilised clusters (opened squares), at $1.6 \times 10^3 \text{ Pa}$ (solid circles), at $2.1 \times 10^3 \text{ Pa}$ (triangles) and at $8.0 \times 10^4 \text{ Pa}$ (squares). Only a small peak shift is visible. The vertical dotted lines are the position of peaks for the bulk Pd at $\lambda = 1.12 \text{ Å}$. The vertical dashed line marks the position of the hydride phase. The peak shift in the Pd – TOAB clusters has been marked with vertical lines to guide the eye.

Figure 7: Lattice parameter – pressure isotherms of the 3.0 nm cubic (Teflon stabilised) clusters and icosahedra clusters (TOAB stabilised). The lattice parameter of the cubic clusters strongly increases at $2.0 \times 10^3 \text{ Pa}$ whereas the “apparent lattice parameter” of the icosahedral clusters shows a continuous increase.