



References

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Principal publication and authors

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carbonyl and is thus invisible in infrared spectroscopy, is included in the refinement. It would have been very difficult using X-ray scattering alone to establish the existence of the minor intermediate $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$ because its contribution to the overall scattering curve is much smaller than

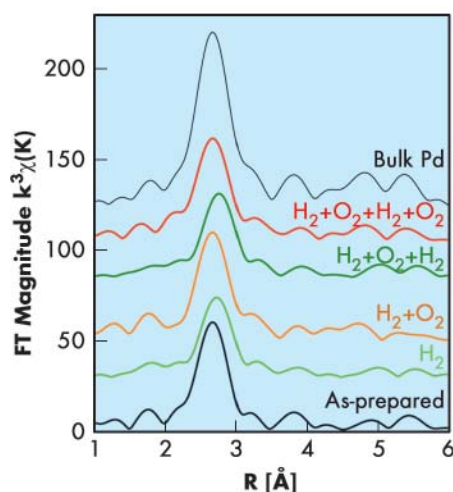
that of $\text{Ru}_3(\text{CO})_{10}$. As its existence has been unequivocally established by spectroscopy it is entirely justified to include it in the fit to the X-ray data. Together these techniques clearly indicate the existence of at least three intermediates with very different molecular structures (Figure 22).

Hydrogen-induced Ostwald ripening

The main aim in hydrogen storage research is to obtain high hydrogen concentrations in a material that possesses suitable transport properties under ambient conditions. A promising way to favourably alter the material's properties is by reducing its size to the extent that surface and quantum effects begin to play a major role. The investigation of nanocluster metal hydrides may therefore reveal novel properties. Palladium is one of the most widely studied metals with respect to hydrogen absorption. At elevated temperatures palladium nanoclusters change size due to Ostwald ripening: the larger clusters capture mobile atoms at the expense of smaller clusters [1]. As hydrogen in a metal can decrease the strength of the host metal bonding, this raises the question of how an ensemble of palladium nanoclusters will interact during and after hydrogenation. A morphological or structural change of the nanocluster ensemble may affect the hydrogenation properties as compared to a single cluster.

We investigated the effect of hydrogen exposure on a palladium cluster assembled film produced with a dual-target dual-laser vaporisation source with three different techniques: extended X-ray absorption fine structure (EXAFS), X-ray diffraction (XRD) and scanning-tunnelling microscopy (STM). These three complementary methods were used to determine the size changes of the palladium nanoclusters upon exposure to hydrogen and oxygen. The average grain size was derived both from the coordination number around palladium atoms obtained from EXAFS (Figure 23) and the width of the XRD Bragg peaks, whereas the (lateral) diameter of the nanoclusters at the sample surface was measured directly by STM. X-ray absorption data (Figure 23) collected at the DUBBLE beamline (BM26A) yielded additional parameters such as inter-atomic distances, degree of disorder and electronic information through the shift of the absorption edge; these support the observation of size changes. Upon hydrogenation, the increase in the nanocluster size measured with XRD, EXAFS, and STM is 22%, 38%, and 37%, respectively. This increase is much larger than the increase of about 8.1% in the Pd phase unit cell volume corresponding to the hydride formation. The cluster growth is due to an atomic reorganisation by three-dimensional Ostwald ripening, in which the larger clusters take up mobile atoms at the expense of smaller clusters [1]. For most materials, spontaneous Ostwald ripening is an extremely slow process at room temperature. However, the presence of a hydrogen atom in the metal reduces the binding energy, thus increasing the probability of

Fig. 23: Phase-corrected Fourier transforms of the k^3 -weighted Pd nanocluster EXAFS as a function of the atomic distance (R).





detachment of palladium atoms as shown schematically in **Figure 24**. This process can be qualitatively understood in terms of the difference between the sublimation energy of palladium metal and palladium hydride. The sublimation energy of palladium decreases with increasing hydrogen concentration and is about 50% lower at a H/Pd ratio of 0.3 [2]. The effect of hydrogen on the palladium cluster sublimation has the same result as if the temperature of the clusters was doubled. Since our experiment was performed at room temperature, a doubled temperature would correspond to approximately 600 K (327°C), a temperature at which Ostwald ripening would occur. Thus the observed cluster size increase is attributed to Ostwald ripening induced by exposure to hydrogen: the absorbed hydrogen decreases the sublimation energy of palladium, which stimulates the detachment of atoms from the clusters at room temperature.

To conclude, the morphological and structural changes occurring in an ensemble of palladium nanoclusters have been studied after several hydrogenation cycles with EXAFS, XRD, and STM. Initial hydrogenation

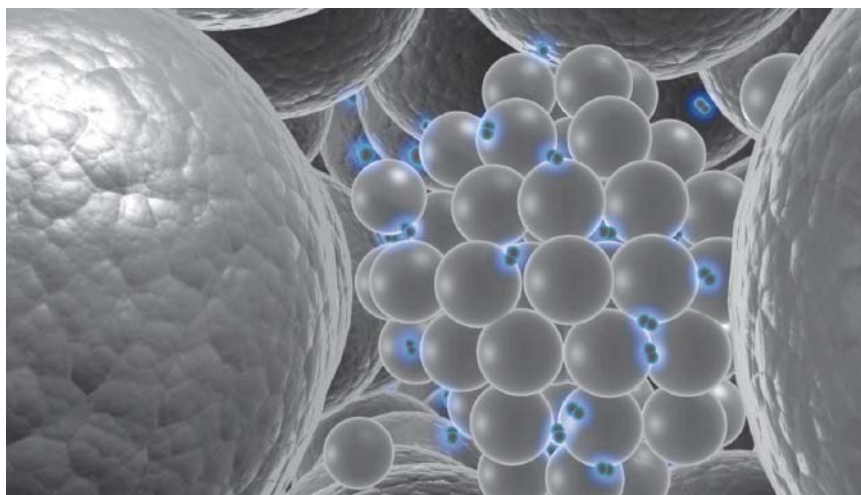


Fig. 24: A schematic impression of the palladium cluster building blocks. The palladium atoms become free to move due to the interstitial hydrogen.

increased the cluster size, a result that is attributed to hydrogen-induced Ostwald ripening. This phenomenon originates from the higher mobility of palladium atoms resulting from the low sublimation energy of palladium hydride as compared to that of the palladium metal. The universality of this phenomenon makes it important for the application of future nanostructured hydrogen storage materials.

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■ Direct observation of 3D grain growth in Al-0.1%Mn

Metals and alloys are typically polycrystalline and are processed by plastic deformation and annealing. During annealing the so-called grain growth process may occur, whereby some of the grains in the polycrystalline ensemble grow at the expense of others, resulting in a coarsening of the microstructure. This has important implications for the properties of the material; widely known applications are transformer steels and devices for power current based on T_c superconductor compounds. Grain growth has been studied extensively for decades both experimentally - mostly by optical microscopy - and theoretically, leading to the proposition of a range of grain growth models.

Here we present a 3D mapping study of an Al-0.1%Mn alloy using the three-dimensional X-ray diffraction (3DXRD) microscope situated at the material science beamline **ID11**. As a function of the treatments, the average grain volume increases from $2.9 \times 10^5 \mu\text{m}^3$ to $4.2 \times 10^6 \mu\text{m}^3$ and the number of grains within the illuminated part of the sample reduces from 483 to 32, see **Figure 25**. The volume distribution of the initial grains is shown in **Figure 26a**. Marked in red are the 27 grains that remained after annealing. As expected these are predominantly the larger grains. Notably three grains smaller than the median size were also observed to grow. As illustrated in **Figure 26b** the texture of both the initial and the final distributions are

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