The size-dependent morphology of Pd nanoclusters formed by gas condensation

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1 Introduction

In order to fully exploit the potential applications of cluster-based nanomaterials, it is necessary to gain full control of the cluster size, shape and structure.1–7 In terms of production, both wet chemical synthesis and physical methods have their advantages. In recent years, much progress has been made in gas phase approaches,8 notably gas condensation magnetron sputtering9,10 or laser vaporization.11,12 Gas phase synthesis allows for cluster mass selection prior to deposition on a support. Whilst the size (nuclearity) of gas-phase clusters can now be selected with atomic precision in some cases,13 the control of the shape and atomic structure of the deposited clusters remains a particularly challenging task. Experimental data in this field are scarce, partly due to the limited range of characterization techniques which can provide both size and morphology information.

We reported a systematic study which employs aberration-corrected scanning transmission electron microscopy (STEM) in high angle annular dark field (HAADF) mode to explore the size, shape and atomic structure of size-selected, positively-charged, Pd clusters in the size range of \(N = 887\)–10 000 atoms produced in a magnetron sputtering gas condensation cluster source.9 The clusters were size-selected by using a lateral time-of-flight mass spectrometer14 and then deposited on amorphous carbon coated Cu mesh TEM grids. We identified key parameters affecting the morphology of the clusters and established solid correlations between the size and morphology of the Pd clusters. Pd clusters occupy a special place in industrial catalysis.7,15,16 Our ultimate goal is to gain an insight into the mechanism of the formation of Pd clusters by gas phase condensation as a basis for the applications of such clusters in catalysis and beyond.

2 Results and discussion

Fig. 1 shows two STEM images of size-selected Pd\(_{887}\) clusters co-deposited with (a) Pd\(_{3000}\) and (b) Pd\(_{4500}\) clusters. These sizes are those selected by the mass filter, with ±2.5% mass resolution.14 The smaller clusters with circular projection in both Fig. 1(a) and (b) represent Pd\(_{887}\) clusters, while the larger Pd\(_{3000}\) and Pd\(_{4500}\) clusters are visibly distinguishable from their Pd\(_{887}\) counterparts in terms of their projected 2D sizes and their relatively higher intensities. Although the cluster loading has been kept constant, there are some local coverage variations. Most clusters are well separated. Examples of low and high coverage are shown in Fig. 1(a) and (b), respectively. Fig. 1(c) highlights two Pd\(_{4500}\) clusters, showing a three-dimensional representation of the HAADF intensity profile from the marked area in (b). Two Pd\(_{4500}\) clusters can be seen with different morphologies; one is elongated and the other is more circular.

To characterize quantitatively the size and shape of the clusters, we analysed the integrated STEM intensities from individual clusters of size 2046, 2622, 3500 and 4500 atoms. It has been shown previously that the integrated STEM intensity scales with the number of atoms within the clusters.17–19 Here, the Pd\(_{887}\) clusters were used as a mass standard for internal
0.56 eV per atom for Pd887 to 0.05 eV per atom for Pd10000. Further structural investigations into Pd10000 clusters were performed to gain atomic level insight into the elongated clusters. Fig. 4(a)–(d) show typical STEM images of Pd10000 clusters with varied elongation. Fig. 4(e) shows an atomically-resolved HAADF-STEM image of one of the Pd10000 clusters. It illustrates that the cluster formation is through aggregation of smaller component clusters and reveals the distinctive local structures of the constituent clusters. This Pd10000 cluster consists of three constituent clusters with two boundaries, as pointed out by the arrows. The shapes of the individual constituents can be seen clearly, together with the different crystalline orientations across the boundaries. At the boundary region between the upper two constituent clusters, the ⟨111⟩ planes (dashed lines) were observed in both clusters with the characteristic interplanar spacing of 0.23 nm of the Pd crystal, but with different orientations. It seems likely that the component...
clusters were already crystallized when aggregation took place and these individual crystalline structures retained. Detailed analysis revealed that the angle between two {111} planes at the upper boundary was in the range of 140° to 151°. This is likely caused by incomplete re-crystallization at the boundary.

MD simulations of Pd nanoparticles showed that the interface region can melt during collision and then re-crystallize. In Fig. 4 we also see a region of low contrast circular shape in the lower part of the image, suggesting a “hollow” structure inside the cluster. We attribute this to a Kirkendall void.

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**Fig. 2** Integrated HAADF image intensity from individual (a) Pd$_{2046}$, (b) Pd$_{2622}$, (c) Pd$_{3500}$, and (d) Pd$_{4500}$ clusters as a function of their aspect ratio. Data points represent individual clusters of the respective size. The dashed lines show the average integrated HAADF intensity values for the corresponding cluster size. Histograms of cluster aspect ratios are presented in (e)-(h) for Pd$_{2046}$, Pd$_{2622}$, Pd$_{3500}$, and Pd$_{4500}$ clusters, respectively.
3 Conclusions

In summary, by a combination of mass-selected cluster deposition from an inert gas aggregation cluster source and advanced aberration corrected scanning transmission electron microscopy (STEM), a systematic study of Pd nanocluster structures has been carried out. A strongly size-dependent morphology of clusters with a size between 887 and 10,000 atoms has been unambiguously identified. The deviation from the spherical shape is much enhanced as the cluster size increases. Atomically resolved STEM images of an elongated Pd_{10000} nanocluster reveal that the cluster consists of a few smaller component clusters, which present individual crystalline structures. The re-crystallized twin structures were found to be a result from cluster-cluster collisions. The observations indicated that elongated Pd nanoclusters are mainly formed by the aggregation of component clusters due to cluster-cluster collisions in the gas phase. The work highlights the importance of the interplay between thermodynamic and kinetic factors in the morphology of clusters formed in the gas phase.

4 Experimental methods

Pd nanoclusters were synthesized using a magnetron sputtering, gas condensation cluster beam source. The gas pressure and sputtering power were fixed in this study. The positively charged Pd clusters were accelerated before size-selection with a lateral time-of-flight mass filter and deposition onto amorphous carbon coated Cu mesh TEM grids (Agar Scientific Ltd). The temperature in the condensation chamber was measured using a K-type thermocouple; this was electrically isolated, but exposed to the process gas. The temperature in the mid-position of the chamber was measured at \( \sim 90 \) K.

Pd clusters were prepared in the size range of 887 to 10,000 atoms with a kinetic energy of 500 eV and each cluster size was co-deposited with Pd_{887}, which was used as a mass standard. The mass filter resolution of \( M/\Delta M \approx 20 \), which is independent of mass, corresponds, for example, to a Pd_{2046} cluster containing 2046 ± 51 atoms. STEM images were obtained using an FEI Tecnai F20 electron microscope or a JEOL 2100F electron microscope with a spherical aberration corrector. Each microscope was operated with a field emission gun and an accelerating voltage of 200 kV. The incident probe size for the Tecnai F20 was \( \sim 4 \) Å and for the JEOL 2100F it was around 0.8 Å. The high angle annular dark field (HAADF) detectors have inner and outer detection angles of 25 mrad to 127 mrad (Tecnai) and 61 mrad to 164 mrad (JEOL), respectively. The HAADF intensity over each cluster was analyzed using the software package ImageJ. Clusters overlapped with each other were excluded in the analysis. The cluster samples were stored in a vacuum, and only exposed to air briefly when transferring into the microscope. No post-treatment of the samples was performed in the present study.

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References


