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Direct Visualization of Size-Controlled Au_{39} Clusters Supported on Hydroxyapatite by AC-STEM

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In recent years, there has been growing evidence indicating that the size of gold (Au) clusters in the regime of less than 2 nm has a significant influence on their catalytic performances. Despite lively debates on the fundamental issues relating to the driving force for this size-dependent phenomenon, there is neither resolution nor consensus in general. Here we take up the challenges of synthesizing monodispersed Au clusters as well as correlating the atomic structures at atomic resolution with the catalytic properties of these clusters. A series of Au_n (n = 10, 18, 25 and 39) clusters with atomically controlled sizes on a solid support, hydroxyapatite (HAP) ($Ca_{10}(PO_4)_6(OH)_2$), were synthesized successfully by Tsukuda's group. A strong size-dependence of Au_n has been demonstrated for the aerobic oxidation, with Au_{39}/HAP showing the highest activity [1]. The goal of the present study is to link directly the catalytic properties with cluster structures at atomic-details, via high-angle annular dark field (HAADF) imaging using aberration-corrected scanning transmission electron microscopy (AC-STEM).

Fig. 1 shows a typical STEM micrograph of Au_{39}/HAP, taken by a 200 kV JEM-2100F STEM (University of Birmingham, UK), fitted with a CEOS probe corrector. To minimize e-beam influence to both the clusters and the HAP substrate, HAADF-STEM images were acquired under a medium magnification of ×10M using a pixel time of 20 μs. To gain insight into size-dependent atomic structures on these samples, we have performed detailed intensity analysis of the HAADF-STEM images. First, the background of each cluster was subtracted individually with reference to its surround areas. The integrated intensity of each cluster was then recorded and plotted in Figure 2, where evenly spaced peaks in the histogram were evident. Using single Au atoms from the micrograph as a calibrator and assuming that multiple scattering effects may be neglected [2,3], the first peak in Fig. 2 can be associated with the intensities due to ~40 Au atoms. This value is in close agreement with the core size of glutathionate-protected Au_{39} clusters used as precursor of the catalysts [4]. Consequently, the evenly spaced peaks in Fig. 2 can be associated with multiples of single clusters, indicating that a substantial fraction of clusters have aggregated by fusion. Although we cannot differentiate at this stage whether the aggregation happened during calcination at 300ºC or sample aging at room temperature, the presence of clear integer multiples suggests that the aggregation is not via an Ostwald ripening process. Together with the catalytic and optical measurements [1], the present AC-STEM study suggests that the aggregated clusters are likely to have retained the memory of initial cluster size. The work provides extremely invaluable feedback to control the dispersion and morphology of clusters, typical characteristics crucial to the performance of catalysts of oxide-supported metal catalysis, which is a primary goal of catalyst design.

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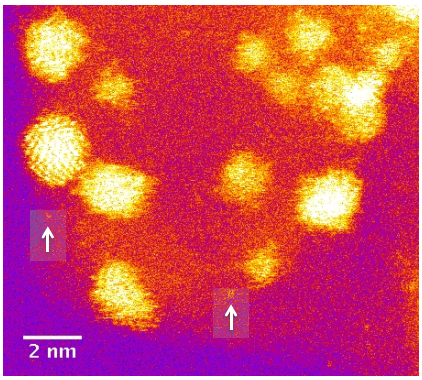

Figure 1. High-resolution STEM image of Au_{39} clusters on hydroxyapatite, where single Au atoms are visible (two of which are marked by arrows).

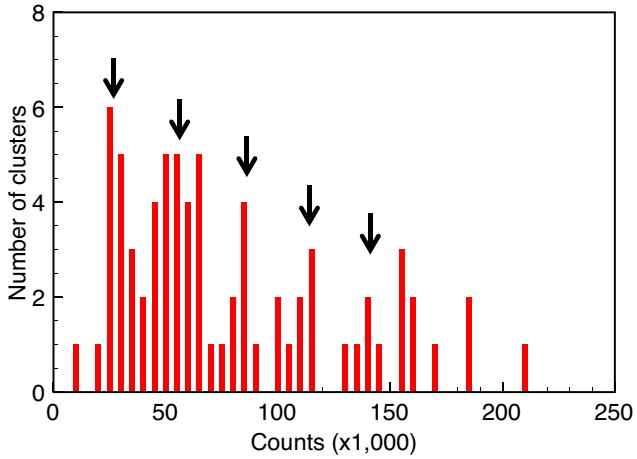

Figure 2. Histogram showing the integrated intensities of the Au_{39} clusters. The first peak (at ~27,000 count rate) was interpreted to originate from the Au_{39} monomers. The other peaks occur away from the first peak at a regular basis, due to the presence of a large number of aggregates.