

Correlation between Catalytic Activity and Electronic Structure of PVP Stabilized Au Clusters Probed by XAFS

We found a clear correlation between the size-specific catalysis of polymer-stabilized Au clusters and the electronic structure probed by X-ray absorption spectroscopy; the small, active clusters were negatively charged through electron donation from the polymer. The present study reveals that the stabilizing polymer, poly(vinylpyrrolidone), plays a role in the tuning of the electronic structure of Au clusters.

In contrast to the high tolerance of bulk gold materials to oxidation, the catalytic activity of gold appears for various oxidation reactions when their size was minimized below 10 nm. Au nano-catalysts supported on metal oxides have actually been applied to CO oxidation and water-gas-shift reaction in practice, and have recently been utilized for organic synthesis [1]. However, despite numerous studies on the catalysis of gold, the guiding principle for developing novel catalysts remains unclear, due to strong and complex interactions between Au cores and the supports. We have found that Au clusters weakly stabilized in a water-soluble polymer, poly(*N*-vinyl-2-pyrrolidone) (Au:PVP), act as catalysts for various oxidation reactions, such as oxidation of alcohol [2]. Through studies on the size dependence of catalytic activity, we have revealed that the activity for aerobic oxidation of alcohol dramatically increases below 2 nm as shown in Fig. 1 [3]. In order to reveal the origin of size-specific catalysis, we investigated the correlation between the electronic structure and catalytic activity of Au:PVP clusters by X-ray absorption spectroscopy.

We synthesized the smallest Au:PVP clusters by the chemical reduction of HAuCl₄ by NaBH₄ in an aqueous solution of PVP. Au:PVP clusters with 1.3±0.3 nm diameter were prepared by mixing two solutions in a conventional batch reactor. The smallest 1.1±0.2 nm clusters were obtained by using a microfluidic mixer to mix the two solutions more homogeneously. The larger clusters were prepared by growing the 1.3-nm seed clusters using a sequential reduction of HAuCl₄ by Na₂SO₃, and as a result 2.6±0.6 and 3.1±0.8 nm clusters were individually obtained at different concentration ratio between the seed cluster and HAuCl₄ [3]. Powder samples were obtained after deionization with an ultra-filtration membrane. The X-ray absorption near edge structure (XANES) was recorded at the BL-9C. Synchrotron radiation emitted from the 2.5-GeV storage ring was monochromatized using a Si(111) double-crystal monochromator. Powder samples were pressed into self-supporting disks and sealed into polyethylene bags in a glove box purged with nitrogen. All the spectra were recorded at room temperature in transmission mode using ion chambers for detection.

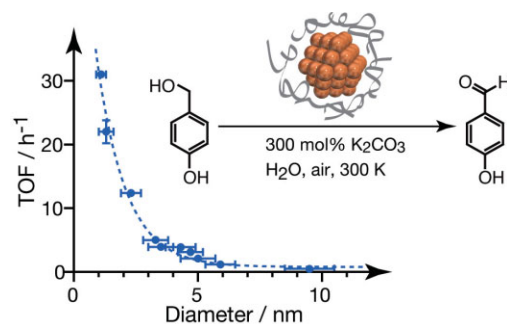


Figure 1
Size dependence of catalytic activity of PVP stabilized Au clusters for aerobic oxidation of *p*-hydroxybenzyl alcohol. Turn-over-frequency (TOF) is the initial reaction rate per unit surface atom at [*p*-hydroxybenzyl alcohol] = 16.7 mM and [Au] = 0.33 nM.

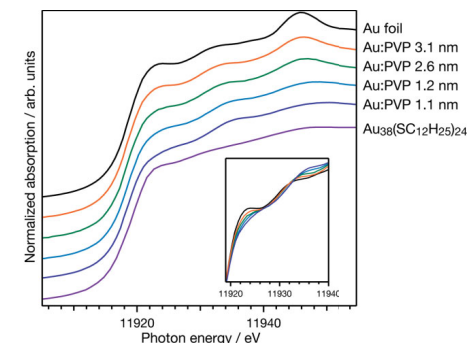


Figure 2
XANES spectra at Au L₃ edge for ligand protected Au clusters with different sizes. Inset represents superimposed spectra.

Figure 2 shows the XANES spectra of Au:PVP clusters at the Au L₃ edge. The quantitative comparison of XANES for Au:PVP samples revealed that the white line (WL) decreases with the reduction of core size as shown in the inset of Fig. 2. This observation suggests that the number of d-holes in Au:PVP clusters decreases with the reduction of core size. In order to reveal the source of electron donation, we compared XANES spectra with bulk Au and thiolate-protected Au₃₈(SC₁₂H₂₅)₂₄ clusters. The intensity of WL for all the Au:PVP clusters was lower than that of Au foil and Au₃₈(SC₁₂H₂₅)₂₄ clusters, which clearly indicates that the PVP does donate electrons to the Au core. The same trend was clearly observed in other spectroscopic measurements [4]: (i) ν_{CO} mode on the smallest, active Au:PVP was red-shifted from that of free CO in the infrared spectrum of CO molecules adsorbed on Au:PVP, which is close to that on negatively charged Au clusters [5] and (ii) the Au4f band of Au:PVP clusters in the X-ray photoelectron spectrum was shifted to lower electron binding energy from that of bulk Au surface. We conclude that the active, smallest Au:PVP clusters are negatively charged through electron donation from PVP. The molecular oxygen is probably activated through the

electron transfer from the negatively charged Au core to form superoxo-like species, which promotes the oxidation of alcohols. Based on the present findings, the activity can be tuned by controlling the interaction with ligands and/or doping of electropositive elements such as silver [6] into Au clusters.

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