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# Halogen adsorbates on polymer-stabilized gold clusters: Mass spectrometric detection and effects on catalysis



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## ABSTRACT

The mass spectrometry of gold clusters stabilized by poly(*N*-vinyl-2-pyrrolidone) (Au:PVP) revealed the presence of Cl adsorbates derived from synthetic precursors, mainly on the Au<sub>34</sub> and Au<sub>43</sub> clusters. Changes in the amount of Cl adsorbates on the Au clusters did not affect the catalytic properties for the aerobic oxidation of benzyl alcohol, suggesting that the Cl atoms were only weakly bound to the Au clusters. In contrast, the replacement of Cl with Br on the Au<sub>34</sub> and Au<sub>43</sub> clusters significantly suppressed activity, without any influence on the electronic structure. This result indicated that the Br atoms were strongly bound to the Au clusters and sterically blocked their active sites. The substantial reduction of the catalytic activity by the Br adsorbates suggested that the Au<sub>34</sub> and Au<sub>43</sub> clusters made a major contribution to the catalytic activity of the Au:PVP.

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The catalysis of nano-sized gold has attracted growing interest, both in academia and industry, since the discovery of the catalysis of CO oxidation by heterogeneous Au catalysts [1]. It is widely accepted that the diameter of the Au catalysts is the most important structural parameter governing the catalytic performance [2–4]. We reported previously that the catalytic activity of Au nanoparticles stabilized by poly(*N*-vinyl-2-pyrrolidone) (PVP) emerged when the particle diameter was below ~4 nm; the catalytic activity dramatically increased as the diameter decreased [5,6]. This size-specific catalysis indicated that Au clusters smaller than 2 nm might be promising candidates for active catalysts [6,7]. Another important factor for catalysis is the interaction between the Au clusters and the solid supports or polymers used for stabilization. For example,

we demonstrated that PVP played an essential role in activating the Au clusters by donating electronic charge when it is used as a stabilizer [8]. Recently, we also showed that the residual thiolates on Au clusters supported on porous carbon enhanced the selectivity in the aerobic oxidation of alcohols with some reduction in the activity [9]. This phenomenon was explained in terms of the steric hindrance and modulation of the electronic structures by the thiolate ligands. As opposed to poisoning, the catalytic activity of metal clusters can be enhanced by ligation, as recently reported for the hydrolytic oxidation of organosilanes by alkyne-protected AuAg alloy clusters [10]. During the mass-spectrometric characterization of Au:PVP, we unexpectedly found that Cl atoms derived from a gold precursor (AuCl<sub>4</sub><sup>-</sup>) were adsorbed on the Au clusters. Motivated by

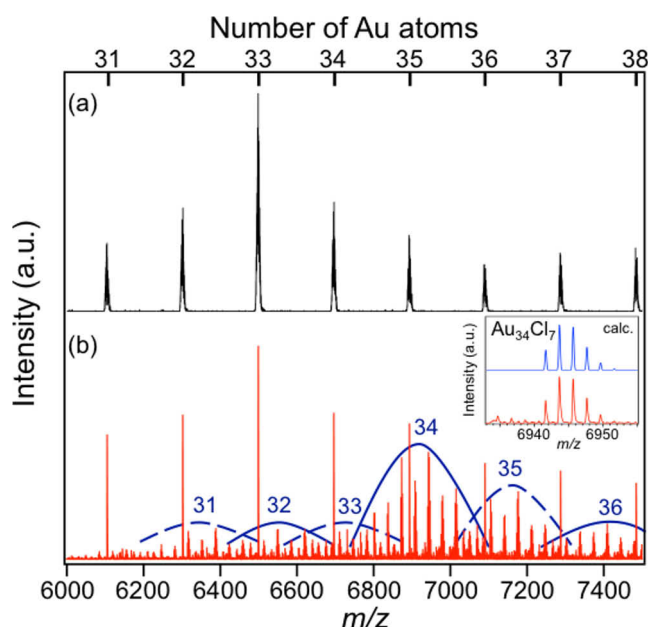
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this finding, we studied the effect of the previously overlooked halogens on the catalysis of Au clusters.

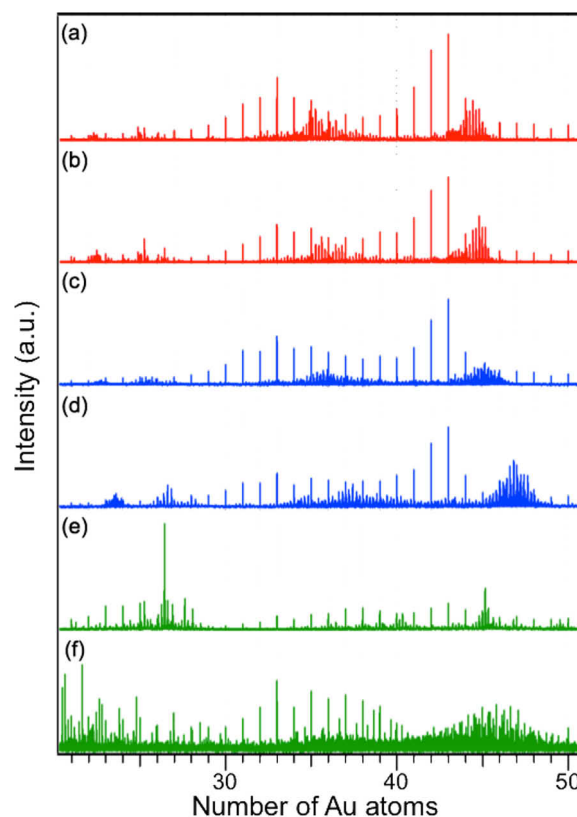
Au:PVP clusters were prepared using a microfluidic mixer as follows [11]. First, two solutions (**A** and **B**) were prepared by mixing two aqueous solutions at 273 K: aqueous solutions of PVP (666.6 mg in 20 mL) and  $\text{HAuCl}_4$  (30 mmol/L, 10 mL) were mixed to produce solution **A**, and aqueous solutions of PVP (666.6 mg in 25 mL) and  $\text{NaBH}_4$  (56.7 mg, 5 mL) were mixed to produce solution **B**. Solutions **A** and **B** were then loaded into two syringes and injected into the micromixer (SIMM-V2, Institut für Mikrotechnik Mainz GmbH) placed in an ice bath, using automatically actuated syringe pumps. Both syringe pumps were activated simultaneously, using a constant flow rate of 200 mL/h. The eluted solution was collected, and then stirred at 273 K for 1 h. Subsequent deionization of the obtained hydrosol via ultrafiltration yielded Au:PVP. Fig. 1 shows portions of the matrix-assisted laser desorption/ionization (MALDI) mass spectra of the Au:PVP, recorded using different apparatuses. Fig. 1(a) shows a negative-ion MALDI mass spectrum measured using a linear time-of-flight (TOF) mass spectrometer (AXIMA-CFR, Shimadzu) at relatively high laser fluence. We observed a series of  $\text{Au}_n^-$  clusters produced via desorption from the polymer stabilization, in agreement with previous results [12]. Fig. 1(b) shows a mass spectrum recorded using a TOF mass spectrometer with a nominal flight path of >17 m using a spiral ion trajectory (JMS-S3000, JEOL) and minimal laser fluence for the measurements. Some mass peaks were observed in addition to those attributed to the  $\text{Au}_n^-$  clusters. These interdigitated mass peaks were assigned to  $\text{Au}_n\text{Cl}_m^-$  based on the isotope pattern analysis (inset of Fig. 1(b)), although Cl was not detected in previous X-ray photoelectron spectroscopy (XPS) measurements of Au:PVP [13]. The com-



**Fig. 1.** Representative negative-ion MALDI mass spectra for Au:PVP, recorded using a lower-resolution apparatus at a relatively high laser fluence (a), and a higher-resolution apparatus at a low laser fluence (b). The inset shows the experimental (bottom) and simulated (top) isotopically resolved mass peaks for  $\text{Au}_{34}\text{Cl}_7^-$ .

plete high-resolution mass spectra are shown in Fig. 2(a). Interestingly, the Cl adsorbates were observed mainly on Au clusters with sizes of  $n = 34$  and 43. Fig. 3(a) and (e) represents the number distribution of Cl adsorbates on the  $\text{Au}_{34}$  and  $\text{Au}_{43}$ , respectively. On average, 7–9 Cl atoms were adsorbed on the  $\text{Au}_{34}$  and  $\text{Au}_{43}$ . Weak even–odd oscillations were found in the distributions. The Cl adducts did not disappear, even after repeated deionizations performed using centrifugation. These results demonstrated for the first time that Cl atoms were adsorbed on the exposed surface of PVP-stabilized Au clusters. The adsorption of Cl on Au:PVP may not be surprising, given that Cl atoms from synthetic precursors are commonly observed in phosphine-protected Au clusters such as  $[\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]\text{Cl}$ ,  $\text{Au}_{11}(\text{PPh}_3)_7\text{Cl}_3$ , and  $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$  [14–16]. Additionally, halide ions such as  $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$  can be strongly adsorbed on metal surfaces [17–19], and their adsorption onto specific facets has been used to fabricate anisotropic nanostructures such as rods, wires, and plates [20,21]. Halides may modulate the electronic structure of the Au clusters by removing electronic charges [22]. Hence, the observations reported here raised a concern that these overlooked Cl adsorbates sterically and/or electronically affected the catalysis of the Au clusters.

The effects of the halogen adsorbates on the catalysis of Au:PVP were studied using the aerobic oxidation of benzyl alcohol as a model reaction. The amount and variety of halogen adsorbates were changed by mixing an aqueous solution of KX ( $X = \text{Cl}, \text{Br}, \text{I}$ ) with the hydrosol of Au:PVP prepared from



**Fig. 2.** Representative negative-ion MALDI mass spectra for six samples of Au:PVP. (a) Au:PVP(X-0); (b) Au:PVP(Cl-10), (c) Au:PVP(Br-5), (d) Au:PVP(Br-10), (e) Au:PVP(I-5); (f) Au:PVP(I-10).

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