

Communication (Special Issue on Gold Catalysis)

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



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ARTICLE INFO

Article history: Received 6 May 2016 Accepted 15 June 2016 Published 5 October 2016

Keywords: Gold cluster Poly(*N*-vinyl-2-pyrrolidone) Halogen adsorbates Aerobic alcohol oxidation Mass spectrometry

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 Au₃₄ and Au₄₃ 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 Au₃₄ and Au₄₃ 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 Au₃₄ and Au₄₃ 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 (AuCl4⁻) were adsorbed on the Au clusters. Motivated by

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This work was supported by the Elements Strategy Initiative for Catalysts and Batteries (ESICB) and a Grant-in-Aid for Scientific Research (26248003, 15H01042) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

DOI: 10.1016/S1872-2067(16)62501-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 10, October 2016

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 HAuCl₄ (30 mmol/L, 10 mL) were mixed to produce solution A, and aqueous solutions of PVP (666.6 mg in 25 mL) and NaBH₄ (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 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 Au_n⁻ clusters. These interdigitated mass peaks were assigned to Au_nCl_mbased 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 Au₃Cl₇.

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 Au₃₄ and Au₄₃, respectively. On average, 7-9 Cl atoms were adsorbed on the Au₃₄ and Au₄₃. 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 [Au11(PPh3)8Cl2]Cl, Au11(PPh3)7Cl3, and Au55(PPh3)12Cl6 [14-16]. Additionally, halide ions such as Cl⁻, Br⁻, or 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 = Cl, Br, 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).



Fig. 3. Number distributions of Cl (red bars) and Br (blue bars) adsorbates. (a) Au:PVP(X-0), (b) Au:PVP(Cl-10), (c) Au:PVP(Br-5), and (d) Au:PVP(Br-10) for Au₃₄; (e) Au:PVP(X-0), (f) Au:PVP(Cl-10), (g) Au:PVP(Br-5), and (h) Au:PVP(Br-10) for Au₄₃.

HAuCl₄. The molar ratio (x) of KX with respect to the Au clusters, calculated assuming a cluster size of 40, was varied from 5 to 20. The cluster samples obtained after deionization (achieved via centrifugal ultrafiltration with water) are referred to as Au:PVP(X-x) (X = Cl, Br, I) hereafter. According to this notation, the as-prepared Au:PVP clusters can be described as Au:PVP(X-0). The amount of halogen atoms adsorbed on the Au:PVP(X-x) was probed using MALDI mass analysis. Fig. 2 shows the negative-ion MALDI mass spectra for the Au:PVP(X-x). In addition to Au_n⁻, Au_nCl_m⁻ clusters were observed for Au:PVP(X-0) and Au:PVP(Cl-10) (Fig. 2(a) and (b)), and Cl- and Br-containing $Au_n Cl_m Br_l^-$ were observed in the mass spectra of Au:PVP(Br-x) (Fig. 2(c) and (d)). The Au_n⁻ size distributions did not change appreciably after the reaction with KCl or KBr. A close inspection of Fig. 2(a)-(d) revealed that Cl and Br were adsorbed preferentially on the Au₃₄ and Au₄₃ clusters. In contrast, the mass spectra of Au:PVP(I-5) and Au:PVP(I-10) showed significantly different patterns (Fig. 2(e) and (f)). The populations of smaller Au clusters were enhanced by the reaction with KI, suggesting that the Au clusters were converted to smaller clusters by etching with I⁻ [23,24]. These reactivity trends were consistent with the order of the bond strength with the Au surface: $I^- > Br^- > Cl^-$ [19,25]. The MALDI mass analysis indicated that the Au cluster size for Au:PVP did not change appreciably after treatment with aqueous KCl or KBr solutions (Fig. 2(a)-(d)). The size of the Au:PVP clusters before and after the treatment with aqueous KCl or KBr solutions was also examined using transmission electron microscopy (TEM) and ultraviolet-visible (UV-vis) spectroscopy. The TEM images and size distributions for Au:PVP(Cl-10) and Au:PVP(Br-10) (Fig. 4(a)) indicated that the Au:PVP(X-0) size $(1.2 \pm 0.3 \text{ nm})$ was retained during the reaction with KX (X = Cl, Br). The UV-vis spectra (Fig. 4(b)) also confirmed the retention of the Au cluster size.

The number distributions of halogens were examined based on the MALDI mass spectra, with a focus on Au:PVP(X-0), Au:PVP(Cl-10), Au:PVP(Br-5), and Au:PVP(Br-10). It is interesting to note that Cl and Br were adsorbed preferentially on Au₃₄ and Au₄₃, as in the case of Au:PVP(X-0). The population ($I_{n,N}$) of the Au_n (n = 34 or 43) clusters containing halogens with the total number N was calculated according to the following equation:

$$I_{n,N} = \sum_{m,l}^{m+l=N} I\left(Au_n Cl_m Br_l^{-}\right) / \sum_{m,l}^{m,l\neq 0} I\left(Au_n Cl_m Br_l^{-}\right)$$

where *m* and *l* represent the number of Cl and Br, respectively, and $I(Au_nCl_mBr_l)$ indicates the intensity of the $Au_nCl_mBr_l$ mass peak. For example, $I_{34,2}$ was calculated by dividing the total ion intensities of $Au_{34}Cl_2$, $Au_{34}ClBr_{,}$ and $Au_{34}Br_2$ by those of $Au_{34}Cl_mBr_l$ with $m, l \ge 0$ and $m + l \ne 0$. The populations of $I_{34,N}$ and $I_{43,N}$ are plotted as a function *N* in Fig. 3. The reaction with KCl increased the number of Cl adsorbates (Fig. 3(b) and (f)).



Fig. 4. (a) Representative TEM images and size distributions for Au:PVP(Cl-10) and Au:PVP(Br-10). (b) UV-vis absorption spectra for Au:PVP(Cl-x) and Au:PVP(Br-x).

The addition of 5 eq. of KBr to Au:PVP caused nearly half of Cl adsorbates to be replaced with Br (Fig. 3(c) and (g)). In Au:PVP(Br-10), the originally adsorbed Cl atoms were replaced almost completely with Br (Fig. 3(d) and (h)). These results demonstrate that Br was bound more strongly to the Au clusters than Cl, as previously reported for the Au surface [19,25].

The electronic structure of Au:PVP(X-0) and Au:PVP(Br-160) was analyzed using XPS (Fig. 5). The binding energies of Au 4f7/2 for Au:PVP(X-0) and Au:PVP(Br-160) were determined to be 82.6 and 82.7 eV, respectively. These values were slightly smaller than that of bulk gold (84.0 eV) due to the electron donation from PVP [8,26], but were similar to each other. The electron affinities of the bare Au_n clusters with $n \approx$ 30-40 were determined to be in the range of 3.3-4.2 eV, using photoelectron spectroscopy [27,28]. These electron affinities of the Au_n clusters ($n \approx 30-40$) were comparable to those of the halogens (3.61, 3.36, and 3.06 eV for Cl, Br, and I, respectively). This suggested that the electronic states of the Au_n clusters ($n \approx$ 30-40) were not significantly affected by the halogen adsorbates; this was in sharp contrast to the smaller Au clusters, where the halogens acted as electron acceptors [14-16,22].

The catalytic properties of Au:PVP(X-x) (X = Cl and Br) were evaluated using the aerobic oxidation of benzyl alcohol in air as a test reaction (Table 1) to reveal the effect of the Cl and Br adsorbates on the catalysis of the Au clusters. The effect of I adsorbates was not evaluated, because the cluster sizes of Au:PVP(I-x) were significantly different from that of Au:PVP(X-0) (Fig. 2(e) and (f)). Benzyl alcohol (25.9 µL, 0.25 mmol), K₂CO₃ (103.7 mg, 0.75 mmol), and H₂O (5 mL) were mixed in a test tube. The hydrosol of Au:PVP(X-x) (0.5 mmol/L, 10 mL, 2 atom%) was then added to the mixed solution. The reaction mixture was stirred vigorously at 300 K for 1 h, and then quenched with 1 mol/L HCl. The products were extracted with ethyl acetate, and analyzed by gas chromatography. The catalysis results for Au:PVP(X-x) are summarized in Table 1, and the conversions are shown as bar graphs in Fig. 6. These results demonstrated that the effects of Cl and Br on the catalysis were very different. The catalytic activity of Au:PVP(Br-x) gradually decreased with increasing x, while that of



Fig. 5. Photoelectron spectra for Au:PVP(X-0) (a) and Au:PVP(Br-160) (b).

Table 1

Catalytic properties of Au:PVP(X-*x*) for the aerobic oxidation of benzyl alcohol.

	2 atom% Au:F 300 mol% K ₂ 0 ₂ O, air, 300 K	(1 PVP) $(1 Ph)$ $(1$	о он 3	Ph	0 Ph 4
Catalyst	v	Conversion ^{a,b} (%)	Selectivity ^{a,c} (%)		
	X		2	3	4
Au:PVP(X-0)	0	64	16	73	11
Au:PVP(Cl-x)	10	66	22	64	14
	20	65	21	65	14
Au:PVP(Br-x)	5	42	51	37	12
	10	19	46	51	3
	20	13	50	48	2

Reaction conditions: PhCH₂OH (25.9 μ L, 0.25 mmol), K₂CO₃ (103.7 mg, 0.75 mmol), Au:PVP (0.5 mmol/L, 10 mL, 2 atom%), H₂O (5 mL), air pressure 1 atm, temperature 300 K, reaction time 1 h.

^a Determined by gas chromatography.

 $^{\rm b}$ Defined as the ratio of the amount of 1 consumed in the oxidation reaction to the amount of 1 at the initial time.

^cDefined as the ratio of **1** converted to the corresponding products.

Au:PVP(Cl-x) did not change with respect to x. This result reflected the different adsorption strengths of Cl and Br. Although the Cl adsorbates could not be removed, even using repeated centrifugal ultrafiltration, they were desorbed during the catalytic reaction; elemental analysis showed that the amount of Cl for Au:PVP(X-0) was reduced from 0.32 to <0.01 wt% after catalytic usage under the conditions shown in Table 1. This result suggested that benzyl alkoxide produced under basic conditions replaced the Cl adsorbate for the subsequent oxidation reaction. Therefore, the catalytic activity was retained even when the amount of Cl adsorbates is increased. In contrast, the reaction was retarded significantly by the Br adsorbates, suggesting that they were not removed efficiently by the benzyl alkoxide. Because the electronic state of the Au clusters was not altered appreciably (Fig. 5) by the adsorption of Br, the decreased conversion at larger amounts of Br adsorbates could be explained by the steric blocking of the active sites.



Fig. 6. Catalytic activity of Au:PVP(X-0) (a), Au:PVP(CI-10) (b), Au:PVP(CI-20) (c), Au:PVP(Br-5) (d), Au:PVP(Br-10) (e), and Au:PVP(Br-20) (f).

The determination of the distribution of cluster compositions in the original Au:PVP(X-0) sample based on the MALDI mass spectra (Figs. 1(b) and 2(a)) was a formidable task. This was because MALDI mass spectra are typically affected by the distribution of the cluster compositions in the sample, and by their ionization efficiency and fragmentation process, which depend on the composition of the clusters. Nevertheless, the preferential observation of Au₃₄Cl_m⁻ and Au₄₃Cl_m⁻ suggested that the Au₃₄Cl_m and Au₄₃Cl_m clusters in their neutral form dominated in the Au:PVP(X-0) sample. The special stability of $Au_{34}X_m$ could be explained by the closure of the electronic shell with 34 valence electrons [27,28] if we assumed that the electron transfer from Au₃₄ to Cl was negligibly small. However, the origin of the efficient formation of Au₄₃X_m is currently an open question [12]. The significant reduction in the catalytic activity when Cl was replaced with Br indicated that magic Au_nCl_m clusters (n = 34, 43) in Au:PVP(X-0) made an essential contribution to the catalytic activity. Further investigation is needed to determine why the magic-sized Au clusters were catalytically reactive.

In summary, we demonstrated the adsorption of Cl atoms on Au clusters stabilized by PVP using mass spectrometry, and investigated their effect on the catalytic properties. The catalytic activity of Au:PVP was not affected by the presence of Cl, but it was significantly suppressed by the Br adsorbates. This difference was attributed to the different binding strengths to gold. A substantial reduction in the catalysis was observed when the Cl was replaced with Br on the Au clusters, suggesting that magic-sized Au_n clusters (n = 34, 43) dominantly acted as catalysts.

Acknowledgments

We thank Prof. Hiroshi Nishihara (The University of Tokyo) for providing us with access to the TEM apparatus.

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Graphical Abstract

Chin. J. Catal., 2016, 37: 1656–1661 doi: 10.1016/S1872-2067(16)62501-9

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The effect of halogen adsorbates on the oxidation catalysis of gold clusters was studied by monitoring the number and variation of halogens adsorbed using mass spectrometry.



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