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Size-Specific Catalytic Activity of Polymer-Stabilized Gold Nanoclusters for Aerobic Alcohol Oxidation in Water

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Haruta's discovery of CO oxidation catalyzed by supported gold nanoclusters (NCs)[1] has made a great impact on both the scientific and industrial communities. Following this discovery, the literature has been inundated with reports on gold-catalyzed oxidation of CO[2] and alcohols.[3] Such great activity in this research field can be likened to a "gold rush" in modern science. As a consequence of the exhaustive experimental and theoretical studies, it is now generally accepted that adsorbed molecular oxygen, activated by electron donation from the gold cluster, plays an important role in the CO oxidation.[2,4] In contrast, the fundamental aspect of the gold-catalyzed alcohol oxidation (e.g., cluster size effect) has not been well understood mainly due to the polydisperse nature of the gold catalysts and the complex interactions with the support.[3] Here, we report on the aerobic oxidation of benzylic alcohols catalyzed by monodisperse gold NCs stabilized by the representative hydrophilic polymer, poly(*N*-vinyl-2-pyrrolidone) (PVP; $(C_6H_9ON)_n$), with a focus on the cluster size effect in catalysis. The gold NCs are known to be weakly stabilized through multiple coordination of the >N−C═O sites of PVP so that the reactants can access the NC surface.[5] Kinetic measurements show that the smaller Au:PVP NCs (1.3 nm) exhibit superior catalytic activities than the larger NCs (9.5 nm). A reaction mechanism is proposed on the basis of comparison with catalysis of Pd:PVP NCs (1.5 and 2.2 nm).

The Au and Pd NCs stabilized by PVP (K-30, 40 kDa) were prepared as follows.[6] Rapid injection of an aqueous solution of $NaBH_4$ into an aqueous solution of the $AuCl_4^-$/PVP complexes at ca. 273 K yields the brownish Au:PVP (Au:PVP-**1**) NCs with an average diameter, d_{av}, of 1.3 ± 0.3 nm (Figure 1a).[7] The Au:PVP-**1** NCs are allowed to grow in size by reducing $AuCl_4^-$ with Na_2SO_3, leading to the formation of reddish Au:PVP-**2** with $d_{av} = 9.5 \pm 1.0$ nm (Figure 1b). Reduction of $PdCl_4^{2-}$/PVP by $NaBH_4$ and ethanol[8] gives the Pd:PVP NCs with $d_{av} = 1.5 \pm 0.3$ nm (Pd:PVP-**1**) and 2.2 ± 0.4 nm (Pd:PVP-**2**) (Figure 1, c and d), respectively. The molar ratios of the metal ions to PVP monomer units were 1% for all the catalysts.

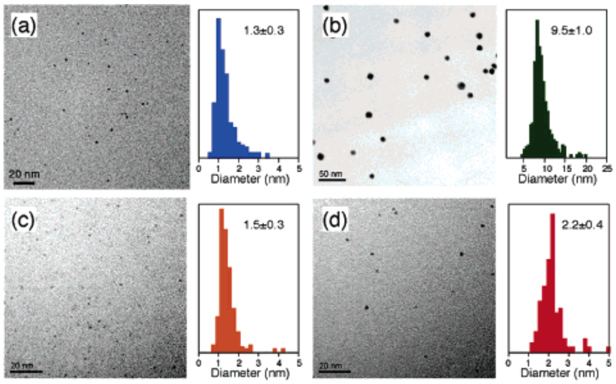
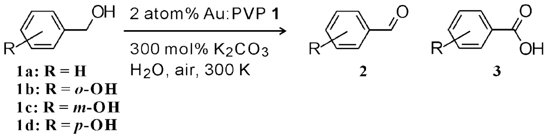


Figure 1. Typical TEM images and size distributions of (a) Au:PVP-**1**, (b) Au:PVP-**2**, (c) Pd:PVP-**1**, (d) Pd:PVP-**2**.

Table 1. Alcohol Oxidation Catalyzed by Au:PVP-**1**



entry	substrate	time (h)	yield (mol %)[a]		
			1	**2**	**3**
1[b]	**1a**	6	0	0	85
2[c]	**1b**	24	34	54	0
3	**1c**	8	3	34	52
4[c]	**1d**	8	3	91	0

[a] Estimated from GC analysis. [b] Benzyl benzoate was additionally formed in 10% yield. [c] Oligomers of **2** were formed in aqueous phase.[6,10]

We first examined the catalytic activities of Au:PVP-**1** toward aerobic oxidation of benzylic alcohols (**1a**−**1d**) in water as a test reaction. Special care was taken to conduct a batch of experiments under identical conditions;[6] an aqueous solution (15 mL) containing Au:PVP-**1** and the alcohol was stirred in a test tube ($\phi = 30$ mm) at a rate of 1300 rpm while the temperature was kept constant within an accuracy of ±1 K. Table 1 lists the yields of aldehydes and/or carboxylic acids formed in the reaction of **1a**−**1d** at 300 K. Benzoic acid and benzyl benzoate were formed from **1a** in 85% and 10% yields, respectively. In the oxidation of hydroxyl derivatives **1b**−**1d**, the corresponding aldehydes were obtained; hydroxybenzaldehydes were selectively obtained in entries 2 and 4.[9] Low conversion of **1b** is ascribed to steric hindrance by the quasi-two-dimensional NC surface[7] and/or the chelate effect by the OH group at the ortho position. The TEM and optical measurements revealed that Au:PVP-**1** NCs do not grow in size in entries 2 and 4 but coagulate into larger particles in entries 1 and 3.[6]

A fundamental question is how are the catalytic activities affected by the size and element of the cores? To answer this, a comparison was made between the oxidation rates of **1d** catalyzed by Au:PVP-**1**/**2** and Pd:PVP-**1**/**2** measured under the same conditions (2 at. %, 300 K); *p*-hydroxybenzaldehyde was selectively produced in all the systems. We monitored the conversion, *C*, from the measured yield of the product as a function of the reaction time. As shown in Figure 2a, there is a linear relationship between $-\ln(1 - C)$ and the reaction time, indicating that the reaction is first order with respect to **1d**. The rate constant, *k*, is therefore obtained from the slope and is listed in Table 2. For the sake of comparison, the *k*

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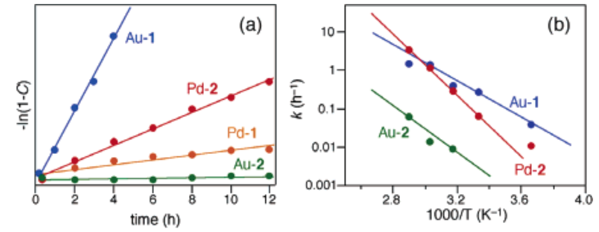

Figure 2. (a) Time course of conversion and (b) Arrhenius plots for oxidation of **1d**.

Table 2. Catalytic Activity toward Oxidation of **1d**

catalyst	d_{av} (nm)	k (h^{-1})[a]	k' [a,b]	k_H/k_D[c]	E_a (kJ mol^{-1})
Au:PVP-**1**	1.3 ± 0.3	2.7×10^{-1}	1.0	74 ± 6	20
Au:PVP-**2**	9.5 ± 1.0	9.5×10^{-5}	2.6×10^{-3}		~25
Pd:PVP-**1**	1.5 ± 0.3	1.8×10^{-2}	7.7×10^{-2}		–
Pd:PVP-**2**	2.2 ± 0.4	6.2×10^{-2}	3.8×10^{-1}	23 ± 3	33

[a] At 300 K. [b] Ratio of the rate constant normalized by surface area of the clusters. [c] At 330 K.

values are normalized by the surface areas of the corresponding NCs by assuming spherical shapes with the diameters shown in Figure 1. The k' values listed in Table 1 represent the relative rate constants thus normalized with respect to that of Au:PVP-**1**. The k' value of Au:PVP-**2** shows that the smaller (1.3 nm) Au NCs exhibit higher catalytic activity than the larger (9.5 nm) NCs. The 1.3-nm Au NCs are found to be catalytically more active than the Pd NCs of similar size at 300 K, as recently observed in the glucose oxidation catalyzed by their "naked" clusters.[3g]

To explain these findings, the mechanistic aspects of the oxidation of **1d** were studied in more detail. Kinetic measurements have shown that Au:PVP-**1** NCs cannot catalyze the oxidation in the absence of either molecular oxygen or base.[6] This result indicates that O_2 and the deprotonated form of **1d** are intimately involved in the reaction. The oxidation under air proceeds at a rate comparable to that under 1 atm of O_2, indicating that the reaction is not retarded by the concentration of O_2 dissolved in water.[6] A large kinetic isotope effect (KIE) was observed in the oxidation of α-deuterated **1d** (p-$HOC_6H_4CD_2OH$); $k_H/k_D = 74 \pm 6$ and 23 ± 3 at 330 K for Au:PVP-**1** and Pd:PVP-**2**, respectively (Table 2).[11] The primary KIE demonstrates that cleavage of the C−H bond at the benzylic position is the rate-determining step. The apparent activation energy, E_a, associated with the C−H bond cleavage is determined from the Arrhenius plots in the temperature range of 273−345 K (Figure 2b). The least-squares fit analysis yields E_a values of 20, 25, and 33 kJ mol^{-1} for Au:PVP-**1**, Au:PVP-**2** and Pd:PVP-**2**, respectively (Table 2).

The marked difference in the KIE and E_a values between Au:PVP-**1** and Pd:PVP-**2** suggests that different mechanisms are operating in their catalytic processes. It is accepted that the alcohol oxidation catalyzed by Pd(0) NCs proceeds via the following mechanism.[12] First, the alcohol is dissociatively adsorbed on the Pd NC surface, affording the alkoxide and hydride (oxidative addition). Then the H atom on the β-carbon of the adsorbed alkoxide is transferred to the Pd NC surface to form the aldehyde and a Pd-hydride species in the rate-determining step. Finally, the O_2 molecule removes the hydride species from the Pd surface to reactivate it, as well as forming H_2O_2. In contrast, the rate-determining step of the Au:PVP-**1**-catalyzed reaction may involve H-atom abstraction by a superoxo-like molecular oxygen species, which is adsorbed on Au:PVP-**1**. Within the framework of this model, the size-specific catalytic activity of Au:PVP-**1** (Table 2) is reasonably explained in terms of the efficient activation of O_2 by small-sized gold NCs.[4] Formation of similar complexes between Au NCs and O_2 has also been postulated in the homocoupling of arylboronic acid catalyzed by Au:PVP NCs.[7]

In summary, we report herein the first successful application of colloidal Au NCs toward the aerobic oxidation of benzylic alcohols in water at ambient temperatures. A size effect is clearly demonstrated, showing that O_2 adsorption onto the gold NCs is the key factor for the size-specific catalytic activities. The results reported here will contribute to the development of efficient and environmentally benign gold catalysts for alcohol oxidations, that utilize ubiquitous air (viz. molecular oxygen) as an oxidant.

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Supporting Information Available: Detailed experimental procedures of preparation and characterization of catalysts and catalytic reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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