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Quantitative Aerobic Oxidation of Primary Benzylic Alcohols to Aldehydes Catalyzed by Highly Efficient and Recyclable P123-Stabilized Pd Nanoclusters in Acidic Aqueous Solution

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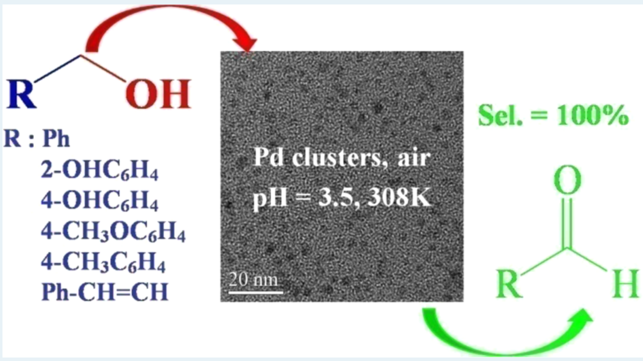
S *Supporting Information*

ABSTRACT: Quantitative oxidation of benzylic alcohols to aldehydes catalyzed by P123-stabilized Pd nanoclusters was first developed in acidic aqueous solution with air at near ambient temperature. The Pd nanocluster colloidal system showed high conversion rates for aerobic oxidation of benzylic alcohols and could easily be recovered by a simple process for multiple recycling reactions without significant loss of activity.



KEYWORDS: *Pd, nanocluster, colloid, benzylic alcohol, aerobic oxidation*

The selective oxidation of alcohols to the corresponding aldehydes or ketones is one of the fundamental transformations in the manufacture of fine chemicals and intermediates.[1,2] Oxidation of alcohols in an aqueous solution with O_2 or air, which is catalyzed by reusable metal catalysts with high activity and selectivity, is regarded as the most attractive and ideal technology from the standpoint of atom efficiency. Heterogeneous transition metal-based catalysts, mainly Pt,[3] Pd,[4] and Au,[5] have been reported to be active for aerobic oxidation of alcohols in aqueous solution under mild conditions and, thus, have received growing interest. However, in most cases, these catalysts suffered from poor activity and product selectivity due to an inherent heterogeneity of the reaction and inaccessibility of the substrates to the catalyst.[6]

Since the first report on the aerobic oxidation of glucose catalyzed by colloidal Au clusters,[7] monodisperse colloidal metal nanoclusters have attracted much attention for aerobic oxidation of various alcohols in water or an aqueous mixture at near ambient conditions because they combine the advantages of both homogeneous and heterogeneous catalysts.[8−11] The catalytic activity and product selectivity depend in large part on the structures of the metal clusters, organic stabilizers, and preparation processes of the metal cluster colloids in addition to the natures of the alcohols. However, almost all metal nanocluster colloidal systems required the presence of a base (e.g., KOH or K_2CO_3) for aerobic oxidation of alcohols in aqueous media. There are two major problems in practical applications: (i) the difficulties in separating the products and recovering the metal colloidal nanoclusters from aqueous dispersions with added base for reuse and (ii) the degradation of the catalysts due to aggregation of metal nanoclusters during the reactions or workup procedures.

So far, only very limited examples of colloidal Au nanoparticles have been reported to allow repeated reuse for aerobic oxidations in aqueous media.[12] In particular, Pd nanoclusters are known to aggregate easily and form Pd black, although they show good catalytic behavior for many useful reactions in aqueous solutions.[13−17] Herein, we report, for the first tiem,on aerobic oxidation of benzylic alcohols with high conversion rates and 100% aldehyde selectivity catalyzed by amphiphilic nonionic triblock copolymer P123 ($EO_{20}PO_{70}EO_{20}$)-stabilized Pd nanoclusters in a weakly acidic aqueous solution. The products are easily separated with diethyl ether without acidification. Furthermore, the Pd nanocluster colloids recovered by a simple decantation with diethyl ether can be reused directly without deterioration.

A Pd nanocluster colloid (5.0×10^{-4} M) with a Pd/P123 molar ratio = 1: 10 was prepared as follows (see Supporting Information). An aqueous solution of H_2PdCl_4 was slowly added dropwise to a mixed aqueous solution of $NaBH_4$ and P123 ($NaBH_4$/P123 molar ratio = 1: 5) at room temperature under vigorous stirring. The colorless, clear solution turned

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dark brown, indicating the formation of a Pd nanocluster colloid. The pH value of the resulting Pd cluster colloid was ~3.5. Figure 1a presents typical images and particle size histograms of Pd nanoparticles formed in P123 aqueous solution. The spherical Pd particles with a mean diameter of 3.6 ± 0.5 nm are observed with a relatively narrow particle size distribution, and more than 95% of the nanoparticles are in the size range from 2.5−4.5 nm, also indicating a relatively high monodispersity of Pd nanoclusters in the system.

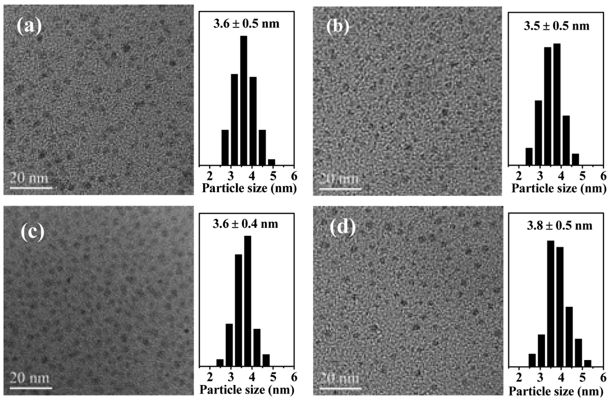


Figure 1. Typical TEM images and size distributions of Pd clusters in colloidal solutions (a) as-prepared, (b) stored for 8 months, (c) treated at 353 K for 8 h, and (d) after cycling 12 times.

Small metal nanoclusters have a strong self-aggregation tendency because of their huge specific surface area and large surface energy, which influence the stability of nanoclusters in solution for catalytic application. The Pd nanocluster colloid by the present method was found to be surprisingly stable for months (at least 8 month observation period) and to exhibit no sign of change in color or particle size after treated at 353 K for 8 h, which are confirmed by the TEM images in Figure 1b,c. The copolymer-assisted colloidal system is believed to stabilize metal nanoclusters by steric effects, and the active sites on the surface of metal clusters can be exposed to the reactants for catalytic reactions because of the weak interactions.[9,10] Thus, the prepared Pd nanoclusters with high stability provide the opportunity to explore the selective oxidation of alcohols in aqueous solution with molecular oxygen.

The oxidation of alcohols was carried out with air in a three-necked flask (see Supporting Information). Blank experiments indicated that, in all cases, $PdCl_2$ in P123 aqueous solution had no activity for aerobic oxidation of alcohols. The Pd nanocluster colloids with different Pd concentrations in the range of 10^{-4} to 5×10^{-4} M (by diluting the as-prepared Pd cluster colloid) was first examined for the aerobic oxidation reactions at the same concentration of benzyl alcohol (2.5×10^{-2} M). A linear correlation between the Pd concentration and the initial catalytic activity was observed (Supporting Information Figure S1). This result indicated that the aerobic oxidation rates were controlled by chemical reaction rather than by diffusive mass transport process.

The aerobic oxidation of benzyl alcohol was investigated at 308 K and at different pH values (3.0, 3.5, 6.0, and 8.0), which were adjusted with HCl and Na_2CO_3 aqueous solutions, and the results are shown in Figure 2. It can be seen that the Pd cluster colloids at pH = 3.0 and 3.5 show comparable catalytic activities, and benzyl alcohol can be completely converted within 540 min. As the pH of the solution is raised, the catalytic activity rapidly decreases. In all the reactions, only benzaldehyde is formed, and other byproducts, such as benzoic acid and benzyl benzoate, are not detected. The reactions at each condition were repeated more than three times to confirm the reproducibility of the results. By assuming that Pd clusters are spherical with a uniform diameter of 3.6 nm and the Pd atomic diameter is 0.276 nm, the turnover frequency (TOF, number of converted molecules per surface metal atom and hour) (see Supporting Information) at pH = 3.5 estimated by the initial conversion of benzyl alcohol during 15 min is 250 h^{-1}, which is significantly higher than those of Au or Pd nanoclusters stabilized with poly(*N*-vinyl-2-pyrrolidone) (PVP) for aerobic oxidation of benzyl alcohol in basic aqueous media under mild conditions (metal, 2.5×10^{-6} mol; metal/benzyl alcohol, 1:500; K_2CO_3, 3.75×10^{-4} mol; H_2O, 2.5 mL; 298 K).[16] To the best of our knowledge, this is the first example of smooth aerobic oxidation of alcohols over polymer-stabilized metal clusters in acidic aqueous solution at near ambient temperature.

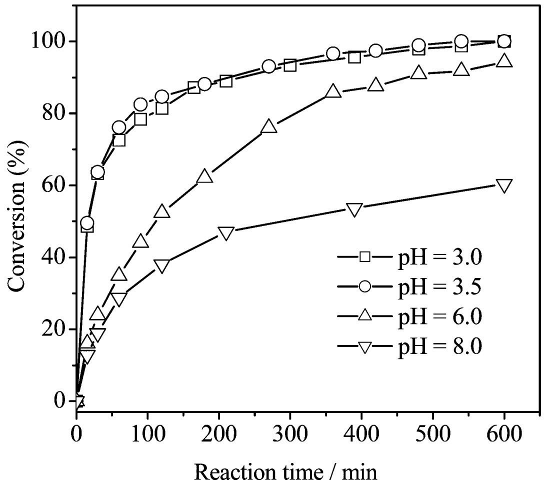
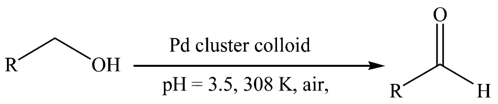


Figure 2. The activity of Pd clusters in P123 aqueous solutions with different pH values. Reaction conditions: [Pd], 5×10^{-4} M; [benzyl alcohol], 2.5×10^{-2} M; solution volume, 30 mL; air bubbling; reaction temperature, 308 K.

The colloidal Pd clusters can also efficiently catalyze the oxidation of several benzyl alcohol derivatives and aromatic allylic alcohols to the corresponding aldehydes without the formation of other byproducts (Table 1). Compared with benzyl alcohol (entry 1), lower conversion rates of its

Table 1. Aerobic Oxidation of Alcohols Catalyzed by Pd Nanoclusters in P123 Aqueous Solution[a]



entry	substrate	time (h)	conv. (%)	sel. (%)
1	benzyl alcohol	9	>99	100
2	2-hydroxybenzyl alcohol	10	>99	100
3	4-hydroxybenzyl alcohol	10	55	100
4	4-methoxybenzyl alcohol	24	68	100
5	4-methylbenzyl alcohol	17	79	100
6	3-phenyl-2-propene-1-ol	8	>99	100

[a] Reaction conditions: [Pd], 5×10^{-4} M; [benzyl alcohol], 2.5×10^{-2} M; solution volume, 30 mL; pH, 3.5; air bubbling; reaction temperature, 308 K.

derivatives with groups such as $-OH$, $-OCH_3$, and $-CH_3$ in the aromatic rings (entries 2−5) are ascribed to steric hindrance by the quasi-two-dimensional nanocluster surface,[9b] whereas 3-phenyl-2-propene-1-ol (entry 6) shows a higher conversion rate, likely due to the conjugation effect between the C=C double bond and benzene rings.

For the entire aerobic oxidation of alcohols, the Pd cluster colloids showed no visible change in color and no observable precipitation during the reaction or even workup procedures. To check recycling of the catalysts, the Pd cluster colloid used for the aerobic oxidation of benzyl alcohol at 308 K and pH = 3.5 for 300 min, when the conversion of benzyl alcohol was 94% and the reaction was still governed by the chemical kinetics (Figure 2), was separated by careful decantation with diethyl ether (see Supporting Information). The Pd colloid could be recovered almost quantitatively by this simple procedure and reused as a recycled catalyst for the aerobic oxidation of benzyl alcohol under identical conditions. The results are presented in Figure 3. The conversion of benzyl alcohol shows only a slight decrease from 93% to 86% after cycling 10 times, whereas the benzaldehyde selectivity is always kept unchanged at 100%. After cycling 12 times, the Pd cluster colloidal solution was still transparent, and the mean size of the Pd clusters exhibited only a slight increase from 3.6 to 3.8 nm (Figure 1d).

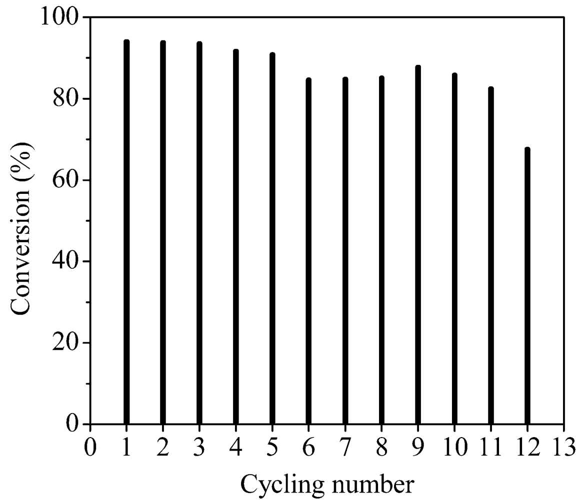


Figure 3. Recycling profiles of the Pd cluster colloid for the aerobic oxidation of benzyl alcohol. Reaction conditions: [Pd], 5×10^{-4} M; [benzyl alcohol], 2.5×10^{-2} M; solution volume, 30 mL; pH, 3.5; air bubbling; reaction temperature, 308 K; reaction time, 300 min.

In summary, we have synthesized stable and durable Pd nanoclusters in P123 aqueous solution using a simple method. The resulting Pd clusters are first reported to effectively catalyze the aerobic oxidation of benzylic alcohols to aldehydes with 100% selectivity in acidic aqueous solutions at near ambient temperature. The Pd cluster colloid is easily recovered by a simple process for cycling multiple times without significant loss of activity. The reaction kinetics and mechanism for aerobic oxidation of alcohols in acidic solution is still under investigation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Material and detailed procedures of Pd cluster colloid, catalyst characterization, catalytic reactions, and estimation of TOF. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Hudlucky, M. *Oxidations in Organic Chemistry*; ACS Monograph Series; American Chemical Society: Washington, DC, 1990.

(2) Mallat, T.; Baiker, A. *Chem. Rev.* **2004**, *104*, 3037−3058.

(3) (a) Anderson, R.; Griffin, K.; Johnston, P.; Alsters, P. L. *Adv. Synth. Catal.* **2003**, *345*, 517−523. (b) Mori, K.; Yamaguchi, K.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2002**, *124*, 11572−11573. (c) Tang, L.; Guo, X. F.; Li, Y. F.; Zhang, S.; Zha, Z. G.; Wang, Z. Y. *Chem. Commun.* **2013**, *49*, 5213−5215.

(4) (a) Zhang, H.; Liu, Y.; Zhang, X. G. *Chin. J. Catal.* **2011**, *32*, 1693−1701. (b) Uozumi, Y.; Nakao, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 194−197. (c) Ma, Z. C.; Yang, H. Q.; Qin, Y.; Hao, Y. J.; Li, G. *J. Mol. Catal. A: Chem.* **2010**, *331*, 78−85.

(5) (a) Xie, S. H.; Tsunoyama, H.; Kurashige, W.; Negishi, Y.; Tsukuda, T. *ACS Catal.* **2012**, *2*, 1519−1523. (b) Abad, A.; Concepcion, P.; Corma, A.; Garcia, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 4066−4069.

(6) Dickerson, T. J.; Reed, N. N.; Janda, K. D. *Chem. Rev.* **2002**, *102*, 3325−3344.

(7) (a) Comotti, M.; Pina, C. D.; Matarrese, R.; Rossi, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 5812−5815. (b) Comotti, M.; Pina, C. D.; Falletta, E.; Rossi, M. *Adv. Synth. Catal.* **2006**, *348*, 313−316.

(8) (a) Tsukuda, T.; Tsunoyama, H.; Sakurai, H. *Chem.—Asian J.* **2011**, *6*, 736−748. (b) Tsunoyama, H.; Liu, Y. M.; Akita, T.; Ichikuni, N.; Sakurai, H.; Xie, S. H.; Tsukuda, T. *Catal. Surv. Asia* **2011**, *15*, 230−239. (c) Tsunoyama, H.; Ichikuni, N.; Sakurai, H.; Tsukuda, T. *J. Am. Chem. Soc.* **2009**, *131*, 7086−7093.

(9) (a) Chaki, N. K.; Tsunoyama, H.; Negishi, Y.; Sakurai, H.; Tsukuda, T. *J. Phys. Chem. C* **2007**, *111*, 4885−4888. (b) Tsunoyama, H.; Sakurai, H.; Negishi, Y.; Tsukuda, T. *J. Am. Chem. Soc.* **2005**, *127*, 9374−9375.

(10) (a) Huang, X. M.; Wang, X. G.; Wang, X. S.; Wang, X. X.; Tan, M. W.; Ding, W. Z.; Lu, X. G. *J. Catal.* **2013**, *301*, 217−226. (b) Wang, X. G.; Kawanami, H.; Islam, N. M.; Chattergee, M.; Yokoyama, T.; Ikushima, Y. *Chem. Commun.* **2008**, 4442−4444.

(11) (a) Miyamura, H.; Yasukawa, T.; Kobayashi, S. *Green Chem.* **2010**, *12*, 776−778. (b) Miyamura, H.; Matsubara, R.; Miyazaki, Y.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 4151−4154.

(12) (a) Kanaoka, S.; Yagi, N.; Fukuyama, Y.; Aoshima, S.; Tsunoyama, H.; Tsukuda, T.; Sakurai, H. *J. Am. Chem. Soc.* **2007**, *129*, 12060−12061. (b) Murugadoss, A.; Sakurai, H. *J. Mol. Catal. A: Chem.* **2011**, *341*, 1−6.

(13) (a) Jiang, Y. J.; Gao, Q. M. *J. Am. Chem. Soc.* **2006**, *128*, 716−717. (b) Iwasawa, T.; Tokunaga, M.; Obora, Y.; Tsuji, Y. *J. Am. Chem. Soc.* **2004**, *126*, 6554−6555.

(14) (a) Li, Y.; Boone, E.; El-Sayed, M. A. *Langmuir* **2002**, *18*, 4921–4925. (b) Li, Y.; El-Sayed, M. A. *J. Phys. Chem. B* **2001**, *105*, 8938–8943.

(15) Yudha, S. S.; Dhital, R. N.; Sakurai, H. *Tetrahedron Lett.* **2011**, *52*, 2633–2637.

(16) Hou, W. B.; Dehm, N. A.; Scott, R. W. J. *J. Catal.* **2008**, *253*, 22–27.

(17) Baeza, J. A.; Calvo, L.; Gilarranz, M. A.; Mohedano, A. F.; Casas, J. A.; Rodriguez, J. J. *J. Catal.* **2012**, *293*, 85–93.