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Gold– and gold–palladium/poly(1-vinylpyrrolidin-2-one) nanoclusters as quasi-homogeneous catalyst for aerobic oxidation of glycerol

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ABSTRACT

Glycerol was oxidized catalytically under aerobic conditions in the presence of monometallic nanoclusters of gold on poly(1-vinylpyrrolidin-2-one) (PVP) to give hydroxymalonic acid (tartronic acid) as the major product, together with 2,3-dihydroxypropanoic acid (glyceric acid) and hydroxyacetic acid (glycolic acid) as minor products. In contrast, oxalic acid was selectively obtained when bimetallic Au-Pd:PVP nanoclusters were used as the catalyst.

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1. Introduction

The use of nanosized gold as a catalyst for aerobic oxidation reactions has been of considerable interest to chemists for the last two decades.^{1,2} A characteristic feature of gold nanocluster catalysts is that they show superior activity in water or water-containing solvents, which should permit the development of

environmentally sustainable systems. We have previously reported that Au nanoclusters stabilized by hydrophilic polymers, such as poly(1-vinylpyrrolidin-2-one) (PVP), behave as a quasi-homogeneous catalyst in aqueous media and that they exhibit an excellent activity toward the aerobic oxidation reactions, including the oxidation of alcohols.^{3,4} Au:PVP-catalyzed oxidation reactions of alcohols have been carried out under relatively mild conditions



Scheme 1. Reaction pathways for oxidation of glycerol under basic conditions.

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Table 1

Au:PVP-catalyzed oxidation of glycerol under open air^{15,16}

		ОН А ОН ОН	Au:PVP (x atom%) Base (x mol%) temp.(°C), time (h)	OH OH OH 1	+ 0 + 0 OH OH 2	+ OH OH OH 3			
Entry	Au:PVP (atom %	Base		Temp (°C)	Time (h)	Conversion (%)		Selectivity	
		Туре	Amount (mol %)				1	2	3
1	2.5	K ₂ CO ₃	300	30	24	0	_	_	_
2	2.5	K ₂ CO ₃	300	50	24	0	_	_	_
3	2.5	K ₂ CO ₃	300	80	24	53	25	25	21
4	5.0	K ₂ CO ₃	300	80	24	89	37	30	12
5	5.0	K ₂ CO ₃	300	80	48	100	21	29	9
6	5.0	_	_	80	48	0	_	_	_
7	5.0	NaOH	300	80	24	94	25	32	11
8	5.0	Cs ₂ CO ₃	300	80	24	96	24	40	9
9	5.0	K ₂ CO ₃	600	80	24	100	29	45	9

in basic aqueous solution at atmospheric pressure and room temperature, in the case of benzylic alcohols, or at temperatures of up to 80 °C, in the case of aliphatic alcohols. Under these conditions, carboxylic acids are obtained directly by oxidation of primary alcohols.^{4c}

Biorenewable products are attractive as raw materials because they can be produced in a sustainable fashion by agriculture or forestry. Triglycerides are typical biorenewable materials that are present as major components in vegetable oils and animal fats. Recent interest in triglycerides has focused on their reaction with methanol to produce biodiesel fuels. Each molecule of the triglyceride reacts with three molecules of methanol to produce three molecules of biodiesel and one of glycerol, so that about 10% of the product mixture consists of glycerol,⁵ which is a versatile synthon and an important biorenewable compound and is, therefore, widely used in syntheses of many useful organic derivatives. The development of environmentally benign and selective procedures for chemical transformations of glycerol into useful compounds is now a rapidly emerging field of chemistry.⁶ Here, we report our studies on the aerobic oxidation of glycerol catalyzed by Au:PVP or bimetallic Au-Pd:PVP nanoclusters.

2. Results and discussion

Several reports have appeared on oxidation reactions of glycerol catalyzed by gold nanoclusters.^{5–9} The oxidation of glycerol under basic condition follows the path shown in Scheme 1.^{5,6} In the presence of Au/C catalysts, glycerol is oxidized to 2,3-dihydroxypropanoic acid (glyceric acid) with 100% selectivity under an oxygen atmosphere in the presence of a base.⁷

The efficient conversion of glycerol into lactic acid by aerobic oxidation on a Au–Pt/TiO₂ catalyst has recently been reported.⁸ However, there are only a few reports on the use of acidic or base-free conditions for gold-catalyzed oxidation reactions of glycerol.⁹ Typical conditions for these aqueous-phase reactions generally involve temperatures in the range of 30–80 °C and oxygen pressures in the range of 1–10 atm.

The results of our studies on the aerobic oxidation of glycerol in the presence of Au:PVP (mean size $\phi = 1.3 \pm 0.3$ nm)⁴ catalyst are listed in Table 1. Usually, Au:PVP-catalyzed aerobic oxidations of alcohols are carried out in the presence of 300 mol % of K₂CO₃ in water under air at room temperature to 60 °C.^{4b} However, when 2.5 atom % of Au:PVP was used, no reaction was observed at 30 °C (entry 1) or at 50 °C (entry 2) after 24 h. Oxidation did, however, occur when the reaction temperature was raised to 80 °C, and a mixture of 2,3-dihydroxypropanoic acid (1), hydroxymalonic acid (2), and hydroxyacetic acid (3) was obtained with a low glycerol conversion (53%) after 24 h (entry 3). Because the products differed from those obtained under previous conditions for heterogeneous catalysis, attempts were made to achieve 100% conversion by changing the amounts of catalyst and the reaction times.¹⁰ When the amount of catalyst was increased to 5.0 atom % (entry 4), the conversion increased to 89% and when the reaction time was



Figure 1. Typical TEM images and particle size distributions of (a) Au-Pd(80:20):PVP, (b) Au-Pd(50:50):PVP, and (c) Au-Pd(20:80):PVP.

prolonged to 48 h (entry 5), the conversion reached 100% (entry 5), but the selectivity of the reaction remained unsatisfactory. In attempts to improve the selectivity of the reaction, we examined the effect of the base. As shown in entry 6, the reaction did not proceed at all in the absence of the base, showing that the presence of the base in this catalytic system is required because it initiates the reaction by abstracting a hydrogen atom from a hydroxyl group. On the basis of our results, we examined other combinations of catalysts and bases, and we found that the selectivity toward hydroxymalonic acid (2) increased to 32% or 40% when the base was changed to NaOH or Cs₂CO₃, respectively (entries 7 and 8). On the other hand, the amount of base also affected the selectivity. Quantitative conversion was observed after 24 h and the selectivity to 2 was improved to 45% when the amount of K₂CO₃ was increased to 600 mol % (entry 9). However, under these reaction conditions, it appeared to be very difficult to suppress the formation of

2,3-dihydroxypropanoic acid (1) and hydroxyacetic acid (3) as byproducts.

As a result of synergistic effects, bimetallic clusters often show superior reactivity and/or selectivity compared with the corresponding monometallic clusters.¹¹ Recently, Liu reported that Au–Pt alloy nanoclusters on TiO₂ showed a high selectivity in the conversion of glycerol into lactic acid.⁸ Among the various combinations of bimetallic systems, Au–Pd alloy catalysts has been extensively studied.¹² We were therefore encouraged to study the catalytic activity of Au–Pd:PVP in the oxidation of glycerol.

Au–Pd bimetallic catalysts containing various ratios of the two metals were prepared by rapid reduction of mixed aqueous solutions of HAuCl₄ and H₂PdCl₄ with NaBH₄.¹³ Figure 1 shows typical TEM images of a series of Au–Pd:PVPs. The average diameters of Au–Pd(80:20):PVP, Au–Pd(50:50):PVP, and Au–Pd(20:80):PVP are determined to be 3.2 ± 1.2 , 3.2 ± 0.8 , and 3.9 ± 1.2 nm, respectively.



Figure 2. Typical STEM image of Au-Pd(50:50):PVP and EDS analysis.

ОН

OН

Table 2

Glycerol oxidation on monometallic Au:PVP or bimetallic Au-Pd:PVP nanoclusters^{15,16}

	OH OH	H Au-Pd:PVP (%ratio) (5 atom%) K ₂ CO ₃ (600 mol%) 0H 80 °C, 24h			о Н ОН 5		
Entry	Au/Pd ratio ^a	Conversion (%)			Selectivity		
			1	2	3	4	5
1	100:0	100	29	45	9	_	-
2 ^b	80:20	100	5	47	4	10	_
3 ^b	50:50	100	-	9	5	57	_
4 ^b	20:80	100	-	8	4	28	_
5 ^b	0:100	82.4	28	27	22	5	17
6 ^c	2.5:2.5	100	10	27	4	10	-

^a Total Au + Pd = 0.5 mmol.

^b Precipitation occurred during the reaction and the solution became colorless.

^c Au/PVP cluster + Pd/PVP cluster.

The size of these bimetallic clusters is significantly larger than that of monometallic Au:PVP and Pd:PVP probably due to the difference of the preparative conditions. The bimetallic composition is further confirmed by STEM/EDS measurement as shown in Figure 2 as an example of the analysis of Au–Pd(50:50):PVP. EDS analysis revealed that the ratio of Au and Pd within the metal clusters is close to 1:1. The Au:Pd ratio was further confirmed by the ICP analysis.¹⁴

Representative results obtained using the resulting catalysts are shown in Table 2. All the reactions were carried out by using 5.0 atom % of metal (Au + Pd): PVP in the presence of 600 mol % of K_2CO_3 in H_2O at 80 °C for 24 h. In the case of Au-Pd(80:20):PVP, glycerol was completely consumed and several products, including unidentifiable materials, were obtained. Of the major products, the yield of 2,3-dihydroxypropanoic acid (1) was drastically decreased to 5% and, instead, oxalic acid (4) was obtained in 10% yield; however, hydroxymalonic acid (2) was still obtained as the major product in 47% yield (entry 2). A comparison of entries 1 and 2 suggests that doping with Pd could enhance the activity of the catalyst in aerobic oxidation. When the ratio of Pd was increased to 50%, the yield and the selectivity to oxalic acid (4) were significantly increased, as shown in entry 3. In contrast, when the ratio of Au/Pd was increased to 20:80, the reaction became more complicated, and a complex mixture of products was obtained (entry 4). It is noteworthy in this case that the Pd or Pd-rich catalyst immediately precipitated out at the beginning of the reaction, leading to heterogeneous conditions probably due to the poor stabilizing ability of PVP toward the Pd as well as relatively larger mean size of the clusters. In contrast, in the cases of entries 1-3, the reaction proceeded mostly under quasi-homogeneous conditions and no significant amount of precipitates was observed at the beginning. In the case of the reaction in the presence of monometallic Pd:PVP (mean size ϕ = 1.5 ± 0.3 nm),^{4a} the rate was slower than that in the presence of Au:PVP or of Au-Pd:PVP and the conversion was 82% after 24 h (entry 5). Although the product distribution was complex, formic acid (5) was obtained in 17% yield. These results showed that Pd could play some role in accelerating the oxidative C-C bond scission process in comparison with the Au catalyst. To confirm the effect of alloying the metals, a physical mixture of 2.5 atom % of Au:PVP and 2.5 atom % of Pd:PVP was examined as a catalyst (entry 6); this gave a complex mixture of products. The results, therefore, showed that the Au–Pd bimetallic structure may play an important role in relation to the high selectivity to oxalic acid in entry 3. In the case of monometallic Au:PVP, C₃ products were produced mainly, and hydroxyacetic acid (**3**), obtained in a minor amount, was the sole C₂ product. In contrast, Au–Pd bimetallic catalyst gave mainly C₂ products [oxalic acid (**4**) and hydroxyacetic acid (**3**)], together with a C₁ product (formic acid). The oxidative C–C bond scission reaction may involve H₂O₂,⁵ therefore, the bimetallic catalyst might be efficient in forming of H₂O₂ by reduction of O₂ and/or it may be efficient in catalyzing C–C bond-cleavage reactions involving H₂O₂.^{13f}

3. Conclusion

Au:PVP acted as a quasi-homogeneous catalyst for the aerobic oxidation of glycerol under relatively mild conditions and exhibited a unique selectivity for the formation of hydroxymalonic acid (**2**). A 1:1 alloy of Au and Pd showed a different selectivity, giving oxalic acid as the major product. These results suggest that the product distribution could be controlled by changing the catalyst design through an appropriate choice of the protecting polymer³ and the nature of the alloyed structure of the metals.

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References and notes

- 1. Haruta, M.; Yamada, N.; Kobayashi, T.; Ijima, S. J. Catal. 1989, 115, 301-304.
- (a) Ketchiea, W. C.; Murayama, M.; Davis, R. J. *Top. Catal.* **2007**, *44*, 307–317;
 (b) Pagliaro, M.; Ciriminna, R.; Kimura, H.; Rossi, M.; Pina, S. D. *Angew. Chem., Int. Ed.* **2007**, *46*, 4434–4440;
 (c) Pina, C. D.; Falletta, E.; Prati, L.; Rossi, M. Chem. Soc. Rev. **2008**, *37*, 2077–2095;
 (d) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896–7936;
 (e) Hutchings, G. J. *Gold Bull.* **2004**, *37*, 3–11.
- A recent review: Tsukuda, T.; Tsunoyama, H.; Sakurai, H. Chem. Asian J. 2011, 6, 736–748.

- (a) Tsunoyama, H.; Sakurai, H.; Negishi, Y.; Tsukuda, T. J. Am. Chem. Soc. 2005, 127, 9374–9375; (b) Tsunoyama, H.; Sakurai, H.; Tsukuda, T. Chem. Phys. Lett. 2006, 429, 528–532; (c) Tsunoyama, H.; Tsukuda, T.; Sakurai, H. Chem. Lett. 2007, 36, 212–213; (d) Tsunoyama, H.; Sakurai, H.; Ichikuni, N.; Negishi, Y.; Tsukuda, T. Langmuir 2004, 20, 11293–11296; (e) Tsunoyama, H.; Ichikuni, N.; Sakurai, H.; Tsukuda, T. J. Am. Chem. Soc. 2009, 131, 7086–7093.
- (a) Prati, L.; Spontoni, P.; Gaiassi, A. *Top. Catal.* **2009**, *52*, 288–296; (b) Bianchi, C. L.; Canton, P.; Dimitratos, N.; Porta, F.; Prati, L. *Catal. Today* **2005**, *102–103*, 203– 212.
- Dimitratros, N.; Lopez-Sanchez, J. A.; Huchings, G. J. *Top. Catal.* 2009, *52*, 258–268; Villa, A.; Wang, D.; Su, D. S.; Prati, L. *Chem. Catal. Chem.* 2009, *1*, 510–514. and references cited therein..
- (a) Carrettin, S.; McMorn, P.; Johnston, P.; Griffin, K.; Hutching, G. J. Chem. Commun. (Cambridge, UK) 2002, 696–697; (b) Ketchie, W. C.; Fang, Y.-L.; Wong, M. S.; Murayama, M.; Davis, R. J. J. Catal. 2007, 250, 94–101; (c) Musialska, K.; Finocchio, E.; Sobczak, I.; Busca, G.; Wojcieszak, R.; Gaigneaux, E.; Zioleka, M. Appl. Catal., A 2010, 384, 70–77.
- Shen, Y.; Zhang, S.; Li, H.; Ren, Y.; Liu, H. Chem. -Eur. J. 2010, 16, 7368–7371. and references cited therein..
- (a) Villa, A.; Veith, G. M.; Prati, L. Angew. Chem., Int. Ed. 2010, 49, 4499–4502;
 (b) Gao, J.; Liang, D.; Chen, P.; Hou, Z.; Zheng, X. Catal. Lett. 2009, 130, 185– 191.
- In some cases, the total yield of the products based on the selectively seem to be less than 100% caused by the C–C bond scission of the products to form CO₂. See Refs. 4–8.
- (a) Daniel, M.-C.; Astruc, D. Chem. Rev. 2004, 104, 293–346; (b) Dimitratos, N.; Villa, A.; Prati, L. Catal. Lett. 2009, 133, 334–340; (c) Prati, L.; Villa, A.; Campione, C.; Spontoni, P. Top. Catal. 2007, 44, 319–324. and references cited therein.; (d) Carrettin, S.; McMorn, P.; Johnston, P.; Griffin, K.; Kielyc, C. J.; Hutchings, G. J. Phys. Chem. Chem. Phys. 2003, 5, 1329–1336.
- (a) Dimitratos, N.; Prati, L. Gold Bull. 2005, 38, 73–77; (b) Dimitratos, N.; Lopez-Sanchez, J. A.; Lennon, D.; Porta, F.; Prati, L.; Villa, A. Catal. Lett. 2006, 108, 147–153; (c) Villa, A.; Campione, C.; Prati, L. Catal. Lett. 2007, 115, 133–136; (d) Hou, W.; Delm, N. A.; Scott, R. W. J. J. Catal. 2008, 253, 22–27; (e) Mertens, P. G. N.; Vandezande, P.; Ye, X.; Poelman, H.; De Vos, D. E.; Vankelecom, I. F. J. Adv. Synth. Catal. 2008, 350, 1241–1247; (f) Edwards, J. K.; Hutchings, G. J. Angew.

Chem., Int. Ed. **2008**, 47, 9192–9198; (g) Villa, A.; Janjic, N.; Spontoni, P.; Wang, D.; Su, D. S.; Prati, L. *Appl. Catal., A* **2009**, 364, 221–228; (h) Dimitratos, N.; Lopez-Sanchez, J. A.; Anthonykutty, J. M.; Brett, G.; Carley, A. F.; Tiruvalam, R. C.; Herzing, A. A.; Kiely, C. J.; Knight, D. W.; Hutchings, G. J. *Phys. Chem. Chem. Phys.* **2009**, 11, 4952–4961; (i) Chen, Y.; Lim, H.; Tang, Q.; Gao, Y.; Sun, T.; Yan, Q.; Yang, Y. *Appl. Catal., A* **2010**, 380, 55–65; (j) Wang, D.; Villa, A.; Spontoni, P.; Su, D. S.; Proti, L. *Chem. Eur. J.* **2010**, 16, 10007–10013; (k) Kaizuka, K.; Miyamura, H.; Kobayashi, S. *J. Am. Chem. Soc.* **2010**, 132, 15096–15098.

- 13. Preparative method of Au-Pd:PVP catalysts: 278 mg (2.50 mmol of monomer unit) of PVP (K-30) was dissolved in 44 mL of MilliQ water and to the solution was added quantitative amount of HAuCl₄ (25 mM) and PdCl₂ (12.5 mM) and final concentration of metals solution was made 0.5 mM, that is, 1:100 metals to polymer ratios. The resulting solution was stirred for 30 min at 27 °C. The solution was maintained 15 °C before reduction, and an aqueous solution (5 mL) of NaBH₄ (20 mg, 0.52 mmol) was added rapidly under vigorous stirring. The color of the mixture was turned from pale yellow to brown, indicating the formation of Au-Pd bimetallic clusters. Thus obtained Au-Pd:PVP clusters were subsequently dialyzed through the membrane filter to remove the inorganic impurities such Na⁺ and Cl⁻, which is a crucial treatment to enhance the stability of the bimetallic clusters against coalescence. The dialyzed hydrosol of Au-Pd:PVP was diluted to 25 mL and stored in refrigerator for catalytic reactions and characterizations.
- 14. Detailed characterization of these Au-Pd:PVP clusters will be discussed elsewhere.
- 15. General procedure for aerobic oxidation: Glycerol (0.1 mmol) was placed in a test tube and dissolved in H_2O (10 mL). A 0.5 mM aqueous solution (0.5 mM) of the metal-containing PVP catalyst (Au or Au-Pd) was added with stirring at 1300 rpm, followed by K_2CO_3 (600 mol %). The mixture was heated at 80 °C for 24 h then cooled to room temperature. The solidified materials, including the catalyst, were separated by ultracentrifugation filtration (10,000 MWCO), and the residual solution was analyzed by HPLC.
- 16. Unfortunately, these PVP-stabilized clusters are not suitable enough for multiple reuses due to the significant aggregation during the reaction. Further studies for the pursuit of the best combination of the metals and the polymers are under investigation.