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Catalytic Oxidation of Polyethylene Glycol Dodecyl Ether to Corresponding Carboxylic Acid by Gold, Palladium (Mono and Bimetallic) Nanoparticles Supported on Carbon

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Abstract Mono and bimetallic catalysts based on Au and Pd nanoparticles were synthesized by sol immobilization method. The catalytic oxidation of polyethylene glycol dodecyl ether was performed using as-synthesized supported catalyst. The use of water as solvent and dioxygen as oxidant makes the reaction interesting from both an economic and environmental point of view. For 100 min, the conversion of polyethylene glycol dodecyl ether using Au–Pd/C bimetallic catalyst was 38%, showing an increase of 9% for Au/C and 15% for Pd/C respectively indicating that a synergetic effect exists between Au and Pd. For the Au–Pd/C catalyst, adding Au after the prior addition and reduction of Pd metal can form the most active catalyst.

Keywords Gold · Palladium · Nanoparticles · Bimetallic catalysts · Oxidation

1 Introduction

Gold nanoparticles (NPs) are among the oldest and best-studied nanoscale materials known [1]. Gold, as well as palladium NPs are useful in a broad range of applications [2–7], including liquid phase oxidation, hydrogenation, CO oxidation and pollution control [8]. The use of gold catalyst greatly contributes to development and use of oxidative catalytic method for its resistance to poisoning derives from overoxidation [9, 10]. Prati and co-workers has demonstrated the ability of Au/C catalysts to oxidize diols [11, 12], aldehydes [13] and carbohydrates [14].

Noble metal catalytic oxidation is often adopted to synthesize polyethylene glycol dodecyl ether carboxylic acid. However, classical Pd catalysts when dioxygen is used as the oxidant often show deactivation due to over oxidation [15]. This resulted in the destruction of the redox cycle of the Pd/C catalysts. Thus, bimetallic catalysts are studied to improve the activity and stability of catalysts in the field of liquid phase oxidation. The Au–Pd bimetallic catalysts have been given little attention until very recently [16–22]. For example, some reports are shown that supported Pd–Au catalysts are efficient for the direct synthesis of H_2O_2 from H_2 oxidation by O_2 at low temperature [23–25]. In the oxidation of polyethylene glycol dodecyl ether, many other procedures have been developed to increase the yield of the polyethylene glycol dodecyl ether carboxylic acid. Nevertheless, most reactions were performed at high temperature and high pressure [26, 27].

In the present work, we wish to report the results of a study that was aimed at the preparation, characterization and use in liquid phase oxidation, of bimetallic Au–Pd/C catalysts, comparing with Pd/C and Au/C monometallic catalysts, for the oxidation of polyethylene glycol dodecyl ether to the corresponding carboxylic acid at atmospheric pressure. This oxidation reaction using water as solvent and oxygen as oxidant produces no toxic and poisonous substance and therefore is a sort of green technology.

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2 Experimental

2.1 Materials

$PdCl_2$, $HAucl_4 \cdot 4H_2O$ (99.9% purity), $NaBH_4$ (96%), NaOH (96%), Polyvinylalcohol 87–89% hydrolyzed (PVA) (average M = 12,000) from Kuraray was used. Polyethylene glycol dodecyl ether $C_{12}H_{25}(OCH_2\,CH_2)_9OH$ (hydroxyl value = 94, averaged molecular weight = 596) were used as received. The active carbon (surface area = 1200 m^2g^{-1}) was handled with nitric acid at 300 K for 24 h to create exchangeable carboxylic acid groups and to eliminate impurities. It was filtered off and washed several times with distilled water until pH value reaches 6–6.5. Then it was dried in air at 378 K for 5–6 h.

2.2 Catalyst Preparation

Monometallic and bimetallic sols including immobilization were prepared with $NaBH_4$ as reducing agent. The solutions of $PdCl_2$(0.188 M), $HAuCl_4$(0.051 M) and PVA (2wt.%) were prepared. 0.1 M of $NaBH_4$ was freshly prepared.

2.2.1 Monometallic Sol

(a) : A solution of PVA(0.25 mL, 2wt.%) was added to a hydrogen tetrachloroaurate solution (1 mL, 0.051 M) in 100 mL of H_2O. After 5 min, under vigorous magnetic stirring, $NaBH_4$ (1.53 mL, 0.1 M) was added and immediately a ruby red sol was formed.

(b) : A solution of PVA(0.25 mL, 2wt.%) was added to a palladium chloride solution (0.5 mL, 0.188 M) in 100 mL of H_2O. The yellow-brown solution was stirred for 5 min and $NaBH_4$ (2.82 mL, 0.1 M) was added under vigorous magnetic stirring. The brown Pd (0) sol was immediately formed.

2.2.2 Bimetallic Sol

Preparation method A: PVA (0.8 mL, 2wt.%) was added to a hydrogen tetrachloroaurate solution (1 mL, 0.051 M) in 100 mL of H_2O. The yellow solution was stirred for 5 min and then $NaBH_4$ (1.53 mL, 0.1 M) was added under vigorous magnetic stirring. After further 5 min, the palladium chloride solution (1 mL, 0.188 M) and $NaBH_4$ (3 mL, 0.1 M) were added, obtaining a dark brown sol.

Preparation method B: PVA(0.8 mL, 2wt.%) was added to a palladium chloride solution (1 mL, 0.188 M) in 100 mL of H_2O. The yellow brown solution was stirred for 5 min and $NaBH_4$ (3 mL, 0.1 M) solution was added under vigorous magnetic stirring. After 5 min a solution of $HAuCl_4$ (1 mL, 0.051 M) and $NaBH_4$ (1.53 mL, 0.1 M) were added.

Preparation method C: 1 mL of the palladium chloride solution (0.188 M), 0.8 mL of PVA and 1 mL of hydrogen tetrachloroaurate solution (0.051 M) solution were added to 100 mL of H_2O. The yellow-brown solution was stirred for 5 min and $NaBH_4$ (4.53 mL, 0.1 M) was added under vigorous magnetic stirring.

2.2.3 Immobilization

The different sols were immobilized by adding active carbon into the solution. The amount of support was calculated as having a final gold loading of 1 wt.%. After 4 h, the solids were filtered out and then washed thoroughly with distilled water until the filtrates were chlorine free with $AgNO_3$ test. The ICP (Inductively Coupled Plasma Atomic Emission Spectroscopy) analysis was performed on the filtrate using Atomscan Advantage to check the total absorption of metals. The catalysts were used in the wet form. The water content was determined by drying a sample for 4 h at 120 °C in air.

2.3 Oxidation Procedures

The catalytic oxidation of polyethylene glycol dodecyl ether was carried out in a thermostat glass reactor (250 mL), equipped with heater, electromagnetic stirrer, oxygen supply system. The polyethylene glycol dodecyl ether aqueous solution (10wt.%) was added into the reactor and the desired amount of catalyst (substrate/Au(pd) = 660 mol/mol) was suspended in the solution. The pressure of the molecular oxygen was 1 atm. Once the required temperature (333 K) was reached, the monitoring of the reaction started. The pH value of the reaction mixture was precisely controlled at a constant value of 11 by adding the standard NaOH solution using Stat Titrino 718. The produced carboxylic acids were therefore neutralized continuously. The consumption of molecular oxygen was recorded per 15 min.

2.4 Characterization and Analysis

X-Ray diffraction experiments were performed on a Rigaku D/MAX-2400 with Cu Kα (40 KV) radiation. The crystallite sizes of gold were estimated from peak half-widths by using Sherrer equation with corrections for instrumental line broadening. X-ray photoelectron spectroscopy was performed on an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlKα radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C 1s line at

284.8 eV from adventitious carbon. The Au 4f region at 84.0 eV was fully investigated. In order to obtain information about the Pd species, the Pd $3p_{1/2}$ region at 556 eV was studied. The reason of choice to study Pd $3p_{1/2}$ is the classical Pd 3d peaks full in the same position of Au 4d peaks. Pd $3p_{3/2}$ peak is overlapped with the O 1s. Electron micrographs of the samples were obtained by a JEM-3010 High-resolution transmission electron microscope. Before introduction into the instrument the samples, in powder form, were ultrasonically dispersed in alcohol, and a drop of the suspension was deposited on a copper grid covered with a carbon film. Histograms of particle size distribution were obtained by counting onto the micrographs at least 300 particles, and mean particle diameter (d_m) was calculated by using the formula $d_m = \sum d_i n_i / \sum n_i$, where n_i was the number of particles of diameter d_i.

3 Results and Discussion

3.1 Monometallic Catalyst

Monometallic catalyst, such as Pd or Au supported catalyst is often used in liquid phase oxidation. As shown in Table 1, The NPs obtained from PVA/Au (w/w) = 1.0 are 20–40% smaller than those obtained from PVA/Au = 0.5. That is to say, the particle size decreases as the amount of PVA increases. In fact, a too small amount of stabilizer lowers the catalytic activity due to the agglomeration, while a too high quantity leads to a heavy covering of the metal NPs that can lower the interaction between catalyst and substrate [28]. The data show that the conversion of the substrate decreases obviously with the increase of the amount of the PVA in this catalytic oxidation reaction. Actually, incomplete adsorption of metal sol on active carbon was observed during the preparation of the catalyst using high amount of the PVA. This may be due to a large amount of PVA covering on the surface of the metal sol and preventing from the adsorption on active carbon. In addition, it can be seen from the Tables 1 and 2 that a decrease in particle size was accompanied with decrease of $NaBH_4$/Au and $NaBH_4$/Pd(molar ratio) whereas the conversion of substrate was increased.

3.2 Bimetallic Catalyst

The catalytic activity and NPs size of 1%Au-2%Pd/C catalysts prepared with three different reducing orders are listed in Table 3. The results revealed that method B, namely reducing Pd prior to Au, was effective to this liquid oxidation. Moreover, the NPs sizes are correspondingly smaller than those by other reducing orders. The particle size and particle size distribution are shown in Fig. 2 (c). According to XRD (as shown in Fig. 3), catalyst prepared by method B presents the highest amount of pure palladium corresponding to almost the total Pd. Conversely gold is present only as alloy and pure gold is not present. It is clear that the diffraction peaks ($2\theta = 45.9$) of the Au alloys exhibited a slight shift from Au (200) to Pd (200). Catalyst prepared by method A and C presented almost the alloy phase. So we can conclude that method A and C are the method that allowed obtaining alloyed phase and pure palladium. The prior reduction of Pd (method B), on the contrary, prevents the formation of a palladium rich alloyed phase. Pd is almost totally presented as pure metal. In terms of XPS, Au–Pd/C prepared by method A showed the lowest ratio Au4f/Pd3p whereas Au–Pd/C (method B) the highest. These results indicate that the bimetallic system

Table 1 Oxidation of polyethylene glycol dodecyl ether using 1wt.% Au/C catalyst[a]

	Run			
	1	2	3	4
PVA/Au (w/w)	0.5	0.5	1.0	1.0
$NaBH_4$/Au (mol/mol)	3	5	3	5
d (TEM)[b] (nm)	6.3	8.8	4.8	5.6
d (XRPD)[c] (nm)	7.1	9.8	6.8	8.2
TOF[d] (h^{-1})	116	103	76	11
Conversion of substrate to acid (%)	29.3	26.1	19.1	2.7

[a] Reaction condition: [substrate] = 10wt.% (aqueous solution), substrate/Au = 660 (mol/mol), T = 333 K, pH = 11, t = 100 min

[b] Mean diameter of sol particles determined by HRTEM

[c] Particle diameter of the supported Au/C determined by XRPD

[d] TOF numbers were calculated on the polyethylene glycol dodecyl ether carboxylic acid formed per mol of total gold per hour

Table 2 Oxidation of polyethylene glycol dodecyl ether using 1wt.%Pd/C catalyst[a]

	Run			
	1	2	3	4
PVA/Pd (w/w)	0.5	0.5	1.0	1.0
$NaBH_4$/Pd (mol/mol)	3	5	3	5
d (TEM)[b] (nm)	6.9	8.4	5.2	5.8
d (XRPD)[c] (nm)	8.3	10.2	6.8	8.1
TOF[d] (h^{-1})	51	47	28	21
Conversion of substrate to acid (%)	23.4	21.8	13.3	9.6

[a] Reaction condition: [substrate] = 10wt.%(aqueous solution), substrate/Pd =660 (mol/mol), T = 333 K, pH = 11, t = 100 min

[b] Mean diameter of sol particles determined by HRTEM

[c] Particle diameter of the supported Pd/C determined by XRPD

[d] TOF numbers were calculated on the polyethylene glycol dodecyl ether carboxylic acid formed per mol of the total palladium per hour

Table 3 Oxidation of polyethylene glycol dodecyl ether using Au–Pd/C catalyst

	Surface atomic ratio (Au4f/Pd3p)	Conversion[a] (%)	d_m in the sol[b] (nm)	d_m on support[b] (nm)
1%Au-2%Pd/C(method B)	16.3	38.3	3.3	4.8
1%Au-2%Pd/C(method C)	1.0	33.5	4.2	7.3
1%Au-2%Pd/C(method A)	0.6	29.0	4.6	7.0

[a] Reaction condition: [substrate] = 10wt.% (aqueous solution), substrate/Au = 660 (mol/mol), T = 333 K, pH = 11, t = 100 min

[b] HRTEM measurements

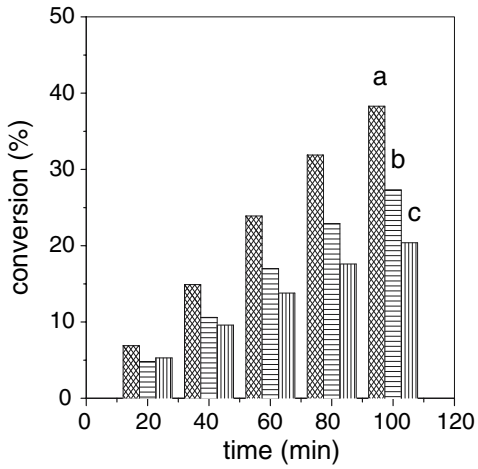

Fig. 1 Effect of the different catalysts on conversion (a) 1%Au-2%Pd/C (preparation method B), (b) 1%Au/C, and (c) 1%Pd/C. Reaction condition: [substrate] = 10wt.% (aqueous solution), T = 333 K, pH = 11, t = 100 min

with the prior reduction of Pd (method B) lead to the highest gold exposure on the surface, whereas the opposite result was observed when gold was first reduced. In previous studies, Somorjai [29] believed that the oxidation states of surface atoms were also the important molecular features of an active catalyst. In terms of activity, catalysts prepared by using method B and C possessed higher activity than catalyst prepared by method A. Comparison of the catalytic activity for Au/C, Pd/C and Au–Pd/C catalysts is shown in Fig. 1.

At atmospheric pressure and 333 K, gold on carbon showed an activity higher than palladium. This behaviour should be ascribed to higher resistance of gold to oxygen poisoning. Previous mechanistic studies revealed that as soon as the rate of oxygen supply exceeded the rate of alcohol dehydrogenation, Pd, even both promoter Bi were successively oxidized, leading to the well known overoxidation [30].

As shown in Fig. 1, for 100 min, the conversion of polyethylene glycol dodecyl ether using Au–Pd/C bime-

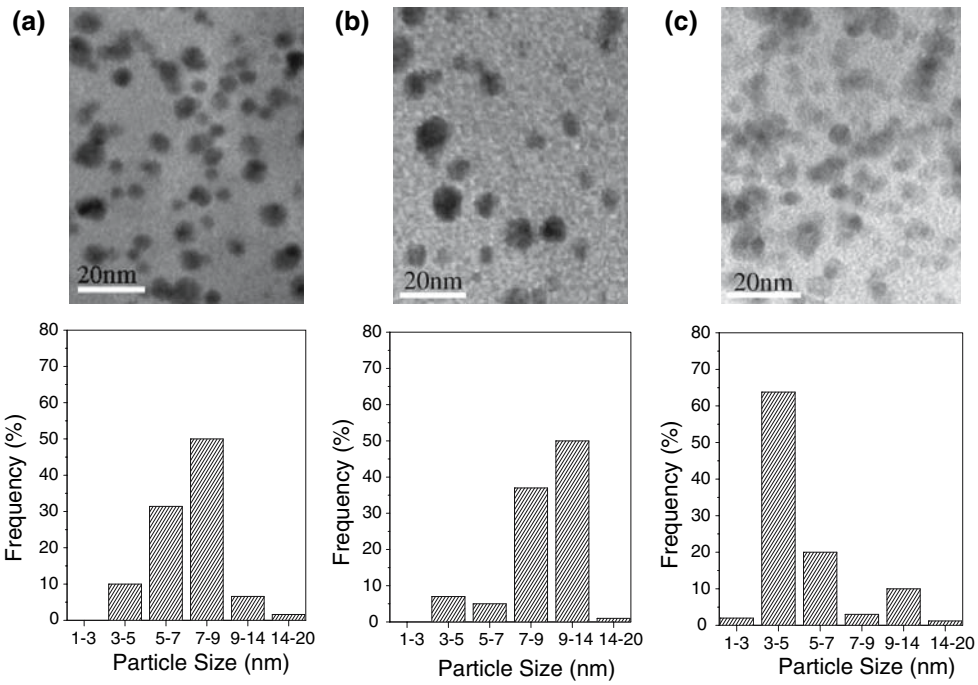

Fig. 2 HRTEM images and particle size distribution histograms of (**a**)1%Au/C, (**b**)1%Pd/C and (**c**)1%Au-2%Pd/C (method B)

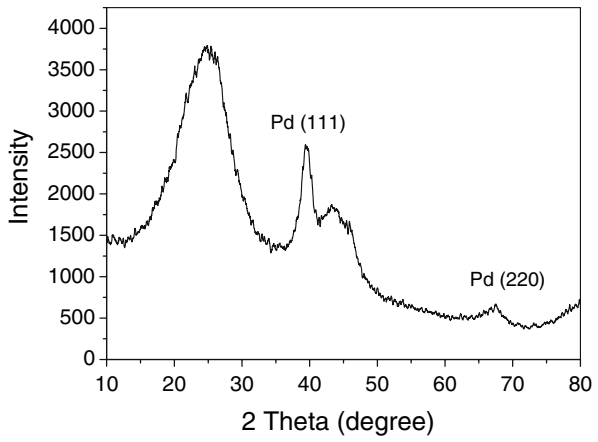

Fig. 3 XRD pattern of the Au–Pd/C bimetallic catalyst

tallic catalyst was 38.3%, showing an increase of 9% for Au/C and 15% for Pd/C respectively. It indicated that the catalytic activity of Au–Pd/C bimetallic catalyst was higher than that of both monometallic catalyst, indicating a "synergetic" effect between Au and Pd. Furthermore, a high activity of Au–Pd/C catalyst can be preserved for a long time during the oxidation reaction comparing with the Au/C and Pd/C monometallic catalyst.

HRTEM images and the particle size distribution histograms corresponding to the different catalysts are shown in Fig. 2. The histograms reveal a decrease in the particle sizes for the Au–Pd/C bimetallic catalyst comparing with the Au/C and Pd/C monometallic catalyst. The majority of the particle sizes are in range from 3 to 5 nm. This may be due to the interaction of the gold and palladium atoms resulting in the high dispersion of the Au–Pd/C. Hence, we argue that gold acts as an electronic promoter for palladium and that the active catalyst has a surface that is significantly enriched in gold. Goodman and co-workers [31], using model studies, have shown that gold can isolate palladium sites within bimetallic systems.

4 Conclusions

Polyethylene glycol dodecyl ether was oxidized with dioxygen in the presence of gold, palladium and gold–palladium bimetallic on active carbon as the catalyst at 333 K and atmosphere pressure. Au–Pd/C bimetallic catalysts are more active than monometallic catalysts, indicating that a synergetic effect exists between Au and Pd. The highest gold exposure on the surface of bimetallic catalyst plays a role in the catalytic activity. Adding Au after the prior addition and reduction of the Pd metal resulted in the most active catalyst system. The catalysts synthesized by sol immobilization method have the potential for the widely applicability in the liquid catalytic oxidation reaction under the mild conditions instead of high temperature and high pressure.

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