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Characterization and catalytic activity of lead-promoted palladium nanoparticle catalysts

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ABSTRACT

A Pd–Pb/C bimetallic catalyst was prepared by the method of chemical reduction impregnation. Transmission electron microscope studies showed that metal particles were dispersed well and their size was around 10 nm, which was consistent with the calculation result of Scherrer equation and X-ray diffraction patterns. The X-ray photoelectron spectroscopy measurements were performed to illustrate the valence state of palladium and lead in the catalysts and the electron effect between these two metals. We tested the catalytic activity of 5% Pd–1% Pb/C catalyst, which exhibited higher catalytic activity than that of 5% Pd/C in the oxidation of polyethylene glycol dodecyl ether to corresponding carboxylic acid, indicating that a synergetic effect existed between Pb and Pd. A possible mechanism of aerobic oxidation was proposed based on the fact of electron transfer between Pd and Pb. Water was used as solvent and oxygen as oxidant makes the reaction interesting from both economic and environmental point of view.

1. Introduction

Polyethylene glycol dodecyl ether carboxylic acids are manufactured traditionally via monochloroacetatic sodium, vinyl cyanide addition, γ-butyrolactone addition and acrylic ester synthesis [1–3]. The products, however, prepared by these methods are impure or difficult to be separated from their by-products. On the other hand, the requirements of the reaction apparatus and conditions are very hard to satisfy. Especially in the case of the monochloroacetatic sodium method, by-product sodium chloride can be formed in the reaction and dissolved homogeneously in the reaction mixture, thus, it is very difficult to be removed. Nowadays green chemistry is strongly stressed all over the world [4]. Noble metal catalytic oxidation, therefore, is adopted to synthesize polyethylene glycol dodecyl ether carboxylic acids. The single-component palladium catalyst is reported in the liquid phase oxidation of alcohols and aldehydes to their corresponding acids [5,6] or oxidation of carbon monoxide [7]. However, the single-component catalyst is easily deactivated and self-poisoned due to excess adsorption of oxygen on the catalyst surface [8]. 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 [9–14]. And 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 [15–18].

In this study, we reported the synthesis and the catalytic characterization of lead-promoted palladium nanoparticles supported on carbon, which were used efficiently in the liquid phase oxidation of polyethylene glycol dodecyl ether under mild conditions.

2. Experimental

2.1. Materials

Palladium chloride, lead(II) acetate trihydrate (99.9% purity), formalin (37 vol.%), sodium hydroxide, polyethylene glycol dodecyl ether ($C_{12}H_{25}(OCH_2CH_2)_3OH$, hydroxyl value = 172.5, averaged molecular weight = 325.2) were used as-received. The active carbon (surface area = 1200 $m^2\,g^{-1}$) was treated 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. Preparation of the catalysts

Active carbon was dispersed in 20 mL of distilled water. The active carbon amount was calculated so that the final Pd loading

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was 5%. Three impregnation orders of palladium and lead were used: impregnation of Pd prior to Pb (preparation method A), simultaneously impregnation of Pd and Pb (preparation method B) and impregnation of Pb prior to Pd (preparation method C). In addition, the atomic ratio of Pb to Pd in catalysts varied from 0.05 to 0.5 (Pb loading varied from 0.5% to 5%). Typically, a solution of palladium chloride (1.5 mL, 0.31 M) and a suitable volume of lead acetate solution (0.094 M) were added into the above-mentioned active carbon aqueous suspension according to designed impregnation orders and atomic ratios and then stirred for 5 h. A solution of NaOH (30%) was used to adjust the pH value of the suspension to 11. Then 5 mL of formalin solution (37%) as reductant was added to the suspension with stirring. Finally catalysts were filtered and washed with distilled water until the filtrates were chlorine free with $AgNO_3$ test. Then the catalysts were ready to be used. Recycle of the catalyst can be carried out via filtration of reaction solution.

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 and oxygen supply system. Polyethylene glycol dodecyl ether aqueous solution (5%) was added into the reactor and the desired amount of catalyst (substrate/Pd = 200 mol/mol) was suspended in the solution. The pressure of oxygen was 1 atm. Once the required temperature (338 K) was reached, 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. The produced carboxylic acids were therefore neutralized continuously. The consumption of oxygen was recorded per 15 min.

2.4. *Characterization and analysis*

X-ray diffraction (XRD) measurements were carried out with a RIGAKU D/MAX-2400 with Cu Kα (40 kV) radiation. The metal particle sizes were calculated with full width at half maximum in the XRD patterns using Scherrer equation. Electron micrographs of the samples were obtained by a JEM-3010 High-resolution transmission electron microscope. Before introduced into the instrument, 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. X-ray photoelectron spectroscopy (XPS) measurements were performed with XSAM800/SERIES 800 SIMS (Mg Kα) to estimate the oxidation state of the palladium and lead.

3. Results and discussion

3.1. *Activities of Pd–Pb/C catalysts*

The results showed that the activity increased with increasing Pb loading with Pb loading $\leq$ 1%. When Pb loading > 1%, the activity decreased drastically, indicating the inhibit effect of Pb at high loading situation. In the case of 5% Pd–1% Pb/C, impregnation of Pb prior to Pd led to the higher catalytic activity than the other two impregnation orders. The conversion of polyethylene glycol dodecyl ether reached 45.3% after 100 min. For convenience, the conversion of polyethylene glycol dodecyl ether vs. atomic ratio of Pb/Pd is plotted in Fig. 1. Here the ratio of Pb/Pd shows the effect of incorporation of Pb to Pd. When the ratio Pb/Pd was higher, the activity decreased indicating that Pb has a promotional effect as well as an inhibiting one. Actually, only a small amount of Pb drastically improved the catalytic activity.

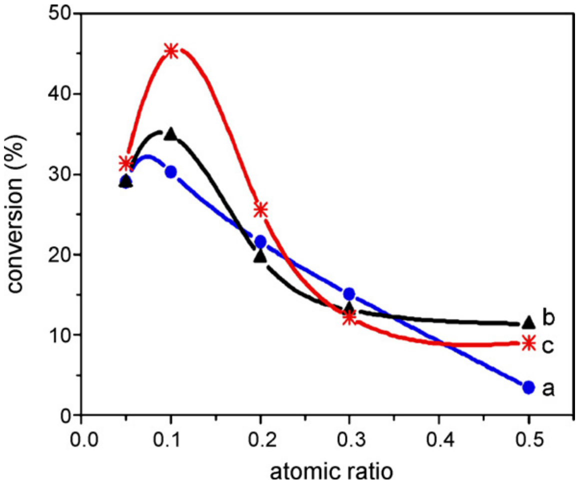

Fig. 1. The conversion of the reactant with the various atomic ratio of Pb/Pd: (a) preparation method A, (b) preparation method B, and (c) preparation method C.

The conversion of polyethylene glycol dodecyl ether vs. time by 5% Pd–1% Pb/C and 5% Pd/C is shown in Fig. 2. For the first 30 min, the activity of Pd–Pb/C catalysts was similar to Pd/C catalyst. After 60 min, however, the conversion increased very slowly for Pd/C catalyst while quickly for Pd–Pb/C catalyst. After 300 min, the catalytic activity was 77.2% and 56.9% for Pd–Pb/C and Pd/C, respectively, showing an increase of 20.3 percentage points.

3.2. *The selectivity of Pd–Pb/C catalyst*

5% Pd–1% Pb/C catalyst was reused in the catalytic oxidation of polyethylene glycol dodecyl ether under the conditions of reactant/Pd = 200 (mol/mol). The initial activity of the catalyst decreased slightly from 2.1 mL min^{-1} for the first time to 1.9 mL min^{-1} for the ninth time. The selectivity was calculated according to the equation of yield (%) = selectivity (%) × conversion (%). The data of Table 1 suggested that the average selectivity of 5% Pd–1% Pb/C catalyst was 98.9%. This may imply, from the view of the reaction, the catalytic oxidation of polyethylene glycol dodecyl ether is a high efficient reaction.

Table 1
The selectivity of 5% Pd–1% Pb/C catalyst on oxidation of polyethylene glycol dodecyl ether (reaction conditions: [reactant] = 5%, reactant/Pd = 200 (mol/mol), T = 338 K, pH 11, t = 300 min).

Run	V_{O_2}[a] (mL)	V_{O_2}[b] (mL)	Conv. (%)	Reactant (g)	V_{NaOH}[c] (mL)	Yield (%)	Selectivity (%)
1	350	490	71.4	7.14	10.1	70.8	99.2
2	308	453	68.1	6.60	8.9	67.3	98.8
3	279	420	64.9	6.28	8.1	64.3	99.1
4	240	401	59.9	5.85	6.9	59.0	98.5
5	212	368	57.6	5.36	6.2	57.0	98.9

[a] Experimental value of the oxygen consumption.

[b] Theoretical value of the oxygen consumption.

[c] Volume of the sodium hydroxide solution consumption (sodium hydroxide solution neutralize the formed carboxylic acid).

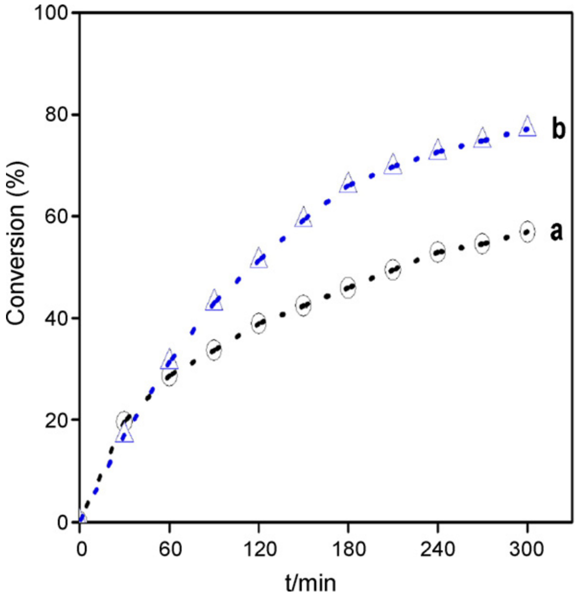

Fig. 2. The dependence of conversion on time for catalysts with different components: (a) 5% Pd/C and (b) 5% Pd–1% Pb/C.

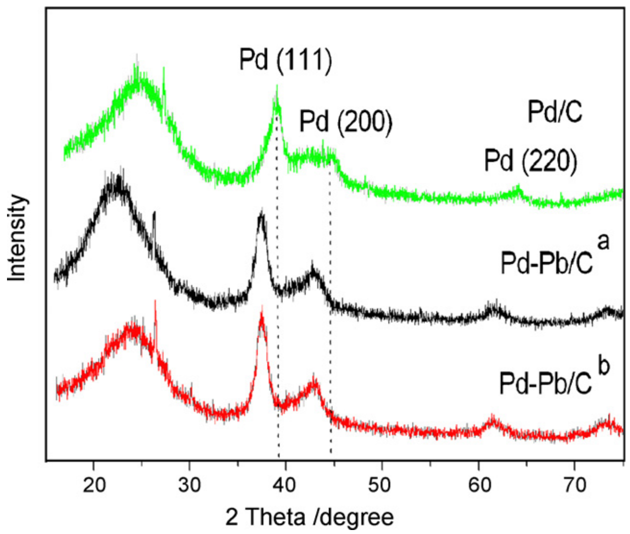

Fig. 3. XRD patterns of the Pd/C and Pd–Pb/C catalyst. (a) Fresh Pd–Pb/C and (b) Pd–Pb/C used nine times.

3.3. *The structure of Pd–Pb/C catalyst*

XRD measurements of the Pd–Pb/C catalysts were performed to investigate composition of the crystal phase. In Fig. 3, the diffraction peak at $2\theta = 39.5^\circ$ is ascribed to Pd(1 1 1) in Pd/C. The diffraction peaks at $2\theta = 46.2^\circ$, 68.2° are ascribed to Pd(2 0 0) and Pd(2 2 0), respectively. Compared with the graph of fresh Pd–Pb/C catalyst and Pd–Pb/C used nine times, the shape of peaks changed but their positions were not. This may be ascribed to the formation of the fine nanoparticles after catalytic oxidation. Therefore it can be concluded that the active phase did not change and the Pd–Pb/C catalyst can remain high catalytic activity. Compared with Pd/C catalyst, the diffraction peak of Pd–Pb/C shifted toward lower degree, which was consistent with the value of $PbPd_3$ phase. Thus we consider that the existence of Pb metal resulted in the formation of intermetallic compound. Devillers and co-workers [19] have also reported that the bimetallic Pb–Pd/C catalysts are characterized mainly by the presence of the intermetallic compound $PbPd_3$. In the graph of Pd–Pb/C used nine times, the peak at $2\theta = 39.1^\circ$ is also considered the diffraction peak of $PbPd_3$ [20]. The shape of broad peak at $2\theta = 39.1^\circ$ indicated that the metals were highly dispersed in the supported carbon. According to Scherrer equation, the average

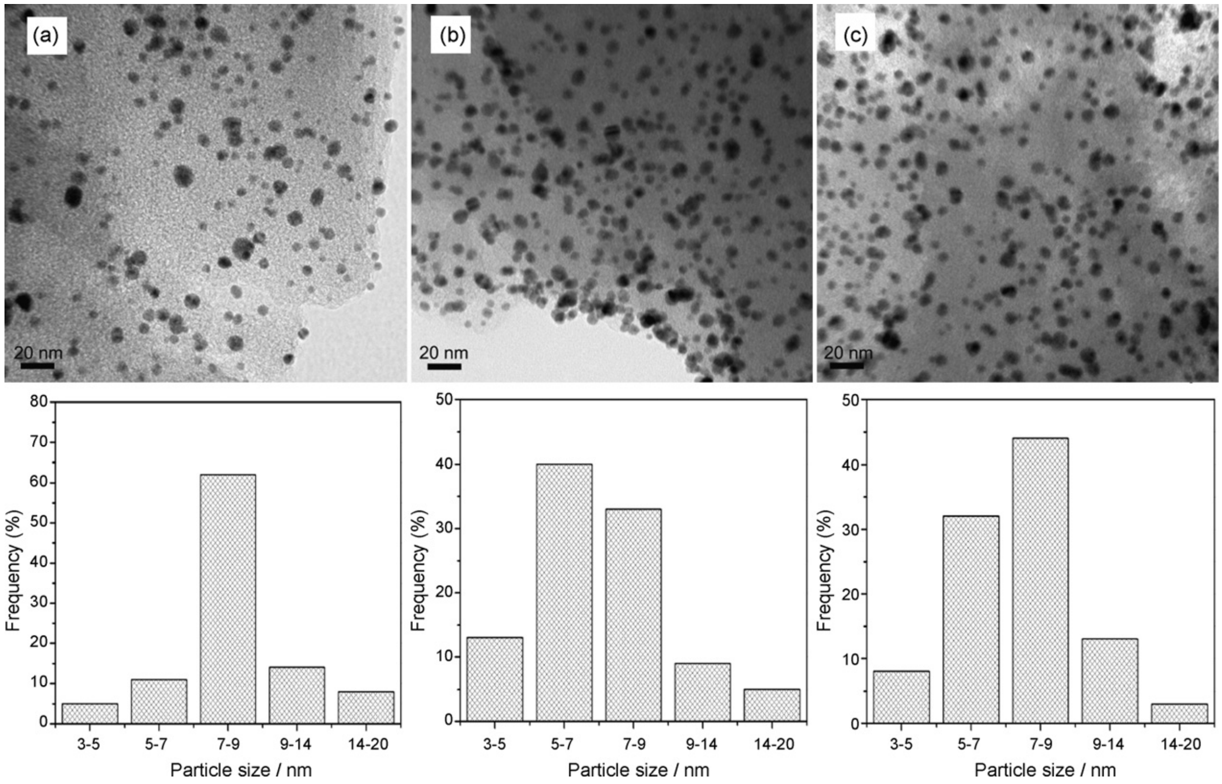

Fig. 4. TEM images and the particle size distribution histograms of (a) Pd/C catalyst, (b) fresh Pd–Pb/C catalyst and (c) Pd–Pb/C catalyst used nine times.

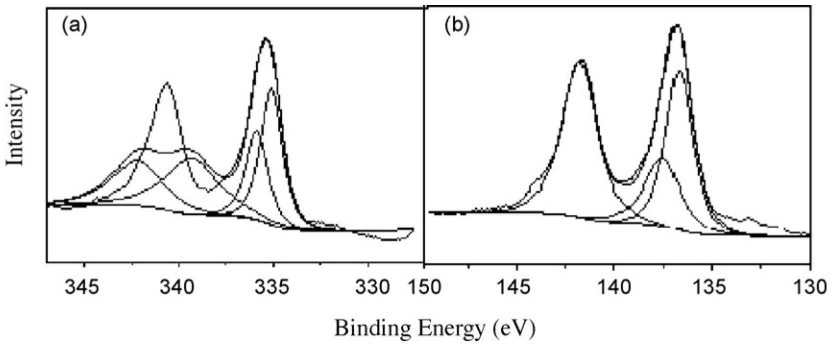

Fig. 5. XPS spectrum of the Pd–Pb/C catalyst (a) XPS spectrum of Pd_{3d} and (b) XPS spectrum of Pb_{4f}.

particle sizes were calculated that Pd/C was 8.8 nm, fresh Pd–Pb/C was 7.1 nm and Pd–Pb/C used nine times was 7.6 nm.

In the case of the 5% Pd/C the mean particle size was around 10 nm as shown in Fig. 4a. When 1% Pb was added, however, it produced very fine particles which were less than 10 nm as shown in Fig. 4b and c. These are in accordance with the results of calculating from Scherrer equation by XRD. Apparently, Pb is able to penetrate into the crystal lattice of Pd, cocrystallize together with the Pd crystals to form a fine dispersion of Pd, which is one of the reasons of the increase in catalytic activity by incorporation of Pb into Pd.

XPS studies of Pd–Pb/C catalyst were performed to investigate the relation of the valency state of Pd and Pb on the catalyst surface and their electron effect. It can be seen from Fig. 5a that Pd_{3d} spectrum is composed of two doubles, due to $Pd_{3d\,5/2}$ and $Pd_{3d\,3/2}$ both of which have contribution from Pd^0, Pd^{2+} and higher valency species (Pd^{4+}). The Pd_{3d} spectrum is fitted by four peaks components with binding energies at about 335.1, 335.9, 337.9 and 342.2 eV, which can be assigned to Pd^0, $PdO(3d_{5/2})$, PdO_2 and $PdO(3d_{3/2})$, respectively. The binding energy of 335.4 eV is higher than the lower oxidation state binding energy of 335.1 eV, whereas the binding energy of 340.6 eV is lower than the higher oxidation state binding energy of 342.2 eV. This is an indication that the presence of Pb changes the electron environment of Pd. It can be concluded that the balance between reduced and oxidized state of Pd on the catalyst surface is an important factor for controlling the catalytic activity. Ebitani et al. [21] also reported that coexistence of Pd^0, Pd^+ and Pd^{2+} is favorable for the oxidation reaction. In Fig. 5b, the Pb_{4f} spectrum consists of three peaks components with binding energies at about136.7, 137.7 and 141.7 eV, which can be attributed to $Pb(4f_{7/2})$, PbO, $Pb(4f_{5/2})$, respectively. The binding energy of Pb $4f_{7/2}$ is ~136.9 eV which is lower than the binding energy of Pb $4f_{7/2}$ in divalent state and greater than that of Pb in metallic form. Thus there might be some sort of interaction between Pd and Pb taking place during the course of reduction. Somorjai [22] believed that the oxidation states of surface atoms were also the important molecular features of an active catalyst. In addition, the charge balance on the Pd surface is an essential factor to control the adsorption equilibrium of oxygen. The electron transfer was observed with a platinum metal catalyst reported by Mallat and Baiker [23], in which a mechanism of oxidation of alcohols was proposed on the base of the electron transfer. For the Pd–Pb/C catalyzed aerobic oxidation of polyethylene glycol dodecyl ether, we proposed a similar mechanism (Fig. 6). The result can be explained in terms of a change in valence state between palladium and lead.

$$C_{12}H_{25}(OCH_2CH_2)_2OCH_2CH_2OH_{ad} \rightleftharpoons C_{12}H_{25}(OCH_2CH_2)_2OCH_2CHO_{ad} + 2H_{ad} \tag{1}$$

$$C_{12}H_{25}(OCH_2CH_2)_2OCH_2CHO_{ad} + H_2O \rightleftharpoons C_{12}H_{25}(OCH_2CH_2)_2OCH_2CH(OH)_{2,ad} \tag{2}$$

$$\begin{aligned} &Pb^{2+}\text{-}O^{2-}\text{-}Pd^{2+} + C_{12}H_{25}(OCH_2CH_2)_2OCH_2CH(OH)_{2,ad} \rightleftharpoons \\ &Pb^{2+}\text{-}O^{2-}\text{-}Pd^{0} + C_{12}H_{25}(OCH_2CH_2)_2OCH_2COOH - 2e + 2H_{ad} \end{aligned} \tag{3}$$

$$C_{12}H_{25}(OCH_2CH_2)_2OCH_2COOH + OH^- \rightleftharpoons C_{12}H_{25}(OCH_2CH_2)_2OCH_2COO^- + H_2O \tag{4}$$

$$O_2 + 2H_2O \rightleftharpoons 4OH_{ad} \tag{5}$$

$$Pb^{2+}\text{-}O^{2-}\text{-}Pd^{0} \longrightarrow Pb^{0}\text{-}O^{2-}\text{-}Pd^{2+} \tag{6}$$

$$O_2(ad) + 2Pb^0 \longrightarrow 2O^{2-}(\text{crystal lattice}) + 2Pb^{2+} \tag{7}$$

The total reaction can be described as follows.

$$C_{12}H_{25}(OCH_2CH_2)_3OH + O_2 + OH^- \longrightarrow C_{12}H_{25}(OCH_2CH_2)_2OCH_2COO^- + 2H_2O \tag{8}$$

Fig. 6. Proposed mechanism for the Pd–Pb/C catalyzed aerobic oxidation of polyethylene glycol dodecyl ether.

4. Conclusions

Pd–Pb/C bimetallic catalysts were synthesized via impregnation method. Lead has ability to produce a high dispersion of palladium on the catalyst surface and has also been in favor of electron transferring, which can decrease the binding energies of palladium. Pd–Pb/C bimetallic catalysts are more active than monometallic Pd/C catalysts, indicating that a synergetic effect exists between palladium and lead. The catalysts synthesized by impregnation method have the potential for the widely applicability in the liquid phase catalytic oxidation reaction under the conditions of ambient temperature and normal pressure instead of high temperature and high pressure.

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