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Bimetallic Au/Pd catalyzed aerobic oxidation of alcohols in the poly(ethylene glycol)/CO_2 system

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Bimetallic Au/Pd nanoparticles were prepared and used to catalyze oxidation of alcohols in the poly(ethylene glycol) (PEG)/CO_2 biphasic system using O_2 as the oxidant without adding any base. The catalytic activity of Au/Pd bimetal with different mole ratios was studied using benzyl alcohol as the substrate. It was found that bimetallic Au/Pd nanoparticles with Au:Pd=1:3.5 had higher catalytic activity than monometallic Au, Pd and the bimetallic Au/Pd nanoparticles with other molar ratios. The effect of CO_2 pressure on the oxidation of benzyl alcohol and 1-phenylethanol in PEG/CO_2 was investigated. It was demonstrated that CO_2 pressure could be used to tune the conversion and selectivity of the reactions effectively. α,β-Unsaturated alcohols were also studied and found to be more reactive than benzyl alcohol and 1-phenylethanol. Recycling experiments showed that the Au/Pd/PEG/CO_2 catalytic system could be recycled at least four times without reducing the activity. In addition, the catalytic system is clean and the products can be separated easily.

oxidation, bimetallic Au/Pd nanoparticles, alcohols, poly(ethylene glycol)/CO_2 system

1 Introduction

Selective oxidation of alcohols to their respective aldehydes or ketones is a key process in the production of fine chemicals, and numerous approaches have been explored successfully using different oxidants [1–5]. However, it is still highly attractive to develop more satisfactory catalytic systems for the aerobic oxidation of alcohols.

Since the report of oxidation of CO and H_2 catalyzed by Au supported on metal oxides [6, 7], Au catalysts have been studied extensively. Au nanoparticles are also active for oxidation of alcohols, especially for diols and triols. However, Au catalyzed oxidation of alcohols usually occurred under base conditions. Bimetallic catalysts are of great interest and have been widely studied for many catalytic reactions due to their synergistic and tunable properties [8] compared with monometallic particles. Different groups [9–14] found that formation of Au/Pd bimetal could improve the activity of the catalyst for different reactions. It was demonstrated that supported Au/Pd nanoparticles could catalyze the synthesis of H_2O_2 from H_2 and O_2 even under low temperature [11, 12]. Furthermore, it was found that Au/Pd/TiO_2 could catalyze oxidation of alcohols without the base [13]. Dimitratos *et al*. [14] studied oxidation of alcohols with Au/Pd and Au/Pt supported on activated carbon as the catalysts and found that the Au/Pd catalysts had positive synergistic effect, but Au/Pt showed negative synergistic effect. Hou *et al*. [15] reported oxidation of alcohols with PVP-stabilized Au/Pd nanoparticles as catalysts in basic aqueous solution.

In recent years, increasing attention has been paid to the replacement of volatile organic solvents (VOS) in modern organic synthesis and practical applications. Supercritical (SC) CO_2, low volatile ionic liquids and liquid polymers are promising alternatives. CO_2 is cheap, non-toxic, non-flam-

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mable, and readily available. Liquid polymers such as PEGs are superior to ionic liquids due to low price. PEG/CO_2 biphasic system is an excellent combinative reaction medium, and reactions in the system can be conducted in the continuous mode and the products can be easily separated by the extraction with $SCCO_2$, which has been studied by several groups [16–19]. Abundant and cheap molecular oxygen is an attractive oxidant for oxidative reactions due to its apparent economic and ecological advantages, and it has been used in oxidation of alcohols with transition metals as catalysts [20, 21].

In this work, bimetallic Au/Pd nanoparticles stabilized by poly(vinylpyrrolidone) (PVP) were used as the catalyst for oxidation of alcohols in PEG/CO_2 system with O_2 as the oxidant in the absence of any base. The results indicated that the greener catalytic system was very active, and the activity and selectivity of the reactions could be tuned by CO_2 pressure. Furthermore, the separation of the product and the catalyst was easy and the catalyst could be reused.

2 Experimental

2.1 Materials

Benzyl alcohol, 1-phenylethanol, allyl alcohol, cinnamic alcohol, ethanol, $HAuCl_4 \cdot 4H_2O$, and $PdCl_2$ were of analytical grade and supplied by Beijing Chemical Reagent Company. PEG-600, PEG-800, PEG-1000 and PEG-1500 were obtained from Beijing Yili Fine Chemical Company. $NaBH_4$ and PVP (MW=30000) were provided by Beijing Chemical Reagent Company. CO_2 (> 99.99%) and O_2 (> 99.9%) were supplied by Beijing Analytical Instrument Factory.

2.2 Preparation and characterization of the catalysts

The pre-formed bimetallic Au/Pd nanoparticles with different ratios were prepared using the reported method [22]. $HAuCl_4 \cdot 4H_2O$ aqueous solution (10^{-3} mol/L) and $PdCl_2$ ethanol solution (10^{-3} mol/L) were mixed in a 100 mL flask, and the total volume of the mixed solution was 50 mL. 0.278 g PVP (the ratio of PVP units to the metals was 50:1) was added. Then the solution was refluxed for 2 h at 100 °C.

Au nanoparticles were prepared according to the method reported by Tsukuda *et al*. [23]. In the experiment, $HAuCl_4 \cdot 4H_2O$ aqueous solution (50 mL, 10^{-3} mol/L) and PVP (0.555 g) were added to a flask (100 mL). The solution was stirred for 30 min at 0 °C. Then $NaBH_4$ aqueous solution (5 mL, 0.1 mol/L) was added under vigorous stirring.

9.72 g PEG was added to the above pre-formed nanoparticle solutions. After mixing completely, the solvents were removed by evaporation. The as-prepared catalytic system was dried at 70 °C under vacuum overnight. The metal concentration in the system was 5×10^{-3} mmol/g.

The original and used Au/Pd nanoparticles were observed by transmission electron microscopy (TEM, JEOL JEM-1011).

2.3 Oxidation of the alcohols

The oxidation reactions of the alcohols were carried out in a stainless reactor of 20 mL with a magnetic stirrer. In a typical experiment, suitable amounts of Au/Pd/PEG and alcohol were added into the reactor. After sealing, the air in the reactor was replaced by O_2. The reactor was maintained at 80 °C and then more O_2 was charged to 0.6 MPa. Then CO_2 was charged to the desired pressure, and the stirrer was started. After a suitable reaction time, the reactor was cooled down and the gases were released slowly at 0 °C. The reaction mixture was extracted by ethyl ether (3×10 mL). The extracted liquid was analyzed by GC (Agilent 4890 D) equipped with a flame-ionized detector using biphenyl as the internal standard.

3 Results and discussion

3.1 Optimization of the Au/Pd molar ratio in the catalyst

It was reported that the composition of bimetallic catalysts has great influence on the activity [14, 15, 22, 24]. In this work, the effect of the molar ratio of Au to Pd on the oxidation of benzyl alcohol was investigated in PEG/CO_2 biphasic system using O_2 as the oxidant. The results and reaction conditions are shown in Table 1. It was demonstrated that the catalytic activity for the alcohol oxidation was closely related to the molar ratio of Au to Pd. Among the catalysts investigated, the monometallic Au possessed the lowest activity, and only 2.3% yield of benzaldehyde was obtained (entry 8). Monometallic Pd gave 41.5% benzaldehyde yield under the same condition. At the Au:Pd molar ratio of 1:3.5, the catalytic activity was the highest, and 61.0% benzaldehyde was obtained. However, the catalytic activity decreased with further increasing the content of Au. When the ratio of Au:Pd was 1:1, the yield of benzaldehyde was decreased to 15.1%. Compared with monometallic Au (entry 8), addition of Pd could enhance the catalyst activity efficiently and avoid the use of bases. Compared with monometallic Pd, bimetallic Au/Pd with appropriate composition (entry 5) had higher catalytic activity for the oxidation reaction. The synergistic effect between Au and Pd has been reported by other authors [14, 15, 22, 24]. The attractive electron effect of Au atom from Pd atom enhances the interaction between Pd atom and the substrate. As reported by other authors [29], Au and Pd may form an alloy at almost any ratio. Moreover, the monometallic Au was nearly inactive for the oxidation of benzyl alcohol, suggesting that the active sites of Au/Pd nanoparticles with Au:Pd=1:3.5 should exist mainly in Pd atoms, and Au atoms can improve the activity of Pd. Au/Pd mole ratios in different Au/Pd nanoparticles could be different, and therefore the mole ratios are considered as an average value. The above results

Table 1 Effect of the Au/Pd mole ratio on benzaldehyde yield

Entry	Au/Pd (molor ratio)	Benzaldehyde yield (%)
1	1:1	15.1
2	1:2	25.9
3	1:2.5	29.2
4	1:3	50.9
5	1:3.5	61.0
6	1:4	37.0
7	0:1	41.5
8	1:0	2.3

Reaction conditions: 2.5 g Au/Pd/PEG-600, 2.5 mmol benzyl alcohol, (Au+Pd):alcohol=1:200, 80 °C, 0.7 MPa O_2, 10 MPa total pressure after adding CO_2, 8 h.

indicate that the catalytic system with Au:Pd ratio of 1:3.5 had the highest catalytic activity. Therefore, this catalyst was used to study the effect of the reaction condition on the oxidation reactions, and the results were discussed as follows.

3.2 Influence of CO_2 pressure on the reaction

The pressure usually influences the efficiency of the reactions in CO_2 considerably, which has been investigated by many researchers. In this work, the effect of CO_2 pressure on conversion and selectivity was investigated with bimetallic Au/Pd nanoparticles in PEG-600 as the catalyst using benzyl alcohol and 1-phenylethanol as the substrates. In the investigation, the pressure of O_2 was kept at 0.6 MPa and the total pressure was changed. Figure 1 shows the effect of CO_2 pressure on the conversion of benzyl alcohol. The maximum conversion occurred at about 6 MPa with changing of the pressure. This suggests that CO_2 affects the reaction rate in two opposite ways. First, the addition of CO_2 can decrease the viscosity of PEG [25], which is favorable to enhancement of the reaction rate. Second, CO_2 can dilute the solution and may occupy some active sites of the catalyst. The competition of the opposite factors resulted in the maximum in the pressure versus conversion curve.

Our experiment showed that the selectivity was only 63% in the absence of CO_2. CO_2 pressure affected the selectivity of benzaldehyde considerably, and a maximum occurred at 7 MPa, as shown in Figure 1. The selectivity at this pressure reached 93%. The reason for the occurrence of the maximum in selectivity needs to be further studied. The yield of benzaldehyde also reached the maximum at 7 MPa, indicating the yield could be optimized by pressure.

Figure 2 shows the effect of pressure on the conversion, selectivity, and yield for the oxidation of the secondary alcohol 1-phenylethanol. The pressure also considerably affected the conversion for the reaction, and the maximum also appeared at about 6 MPa. The selectivity of acetophenone was higher than 98% in the pressure range studied, indicating that the catalytic system was highly selective for the oxidation reaction.

3.3 Effect of reaction time on the reaction

The effect of reaction time on the oxidation of benzyl alcohol and 1-phenylethanol was investigated in PEG/CO_2 using the bimetallic Au/Pd nanoparticles as the catalyst. The reactions were carried out at 80 °C with O_2 pressure of 0.6 MPa and a total pressure of 7 MPa. The products were benzaldehyde and acetophenone. Figure 3 shows that the yields of the products increased with reaction time, and the apparent acceleration of the reaction rate appeared at about 6 h. A benzaldehyde yield of 90% was obtained in 9 h, and 92% acetophenone yield was achieved in 12 h. Benzyl alcohol was more reactive than 1-phenylethanol in the catalytic system.

3.4 Oxidation of α,β-unsaturated alcohols

Besides benzyl alcohol and 1-phenylethanol, oxidations of α,β-unsaturated alcohols were also carried out with the Au/Pd catalyst in PEG/CO_2 medium. The results at the optimized condition are listed in Table 2. The data indicated

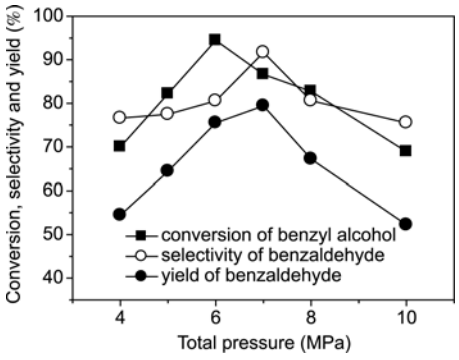


Figure 1 Effect of total pressure on the conversion, selectivity, and yield for the oxidation of benzyl alcohol to benzaldehyde. Reaction conditions: 2.5 g Au/Pd/PEG-600, 2.5 mmol benzyl alcohol, (Au+Pd):alcohol=1:200, Au:Pd=1:3.5, 80 °C, 0.6 MPa O_2, 7 h.

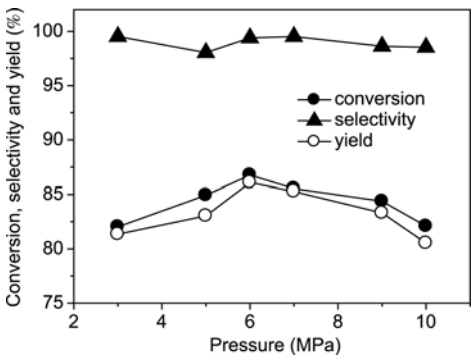


Figure 2 Effect of total pressure on the conversion, selectivity, and yield for the oxidation of 1-phenylethanol to acetophenone. Reaction conditions: 2.5 g Au/Pd/PEG-600, 2.5 mmol 1-phenylethanol, (Au+Pd):alcohol=1:200, Au:Pd=1:3.5, 80 °C, 0.6 MPa O_2, 10 h.

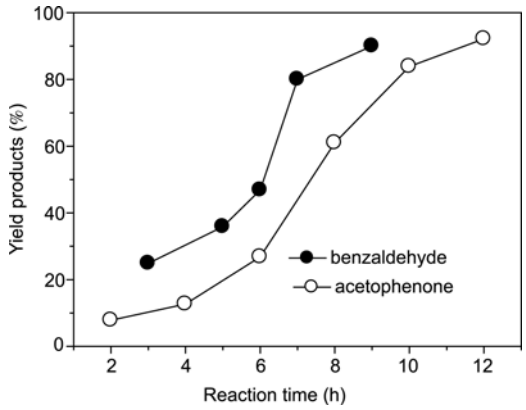


Figure 3 Dependence of product yields on the reaction time. Reaction conditions: 2.5 g Au/Pd/PEG-600, 2.5 mmol alcohol, (Au+Pd):alcohol = 1:200, Au:Pd=1:3.5, 80 °C, 0.7 MPa O_2, 7 MPa total pressure after adding CO_2.

that α,β-unsaturated alcohols were very reactive in the catalytic system. Allyl alcohol and cinnamic alcohol could be transformed completely at a lower temperature of 60 °C and in short reaction time of 1 h, and the yields of corresponding α,β-unsaturated aldehydes were 98.7% and 99.3%, respectively. The high reaction rate of α,β-unsaturated alcohols was probably due to the activation of hydroxyl by the unsaturated double bond.

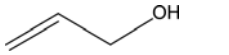
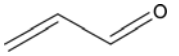
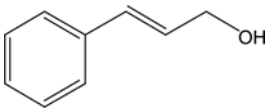
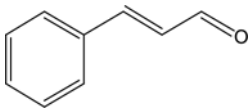
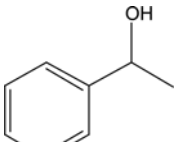
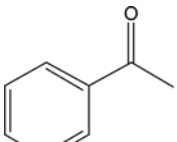
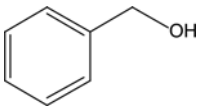
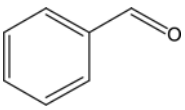
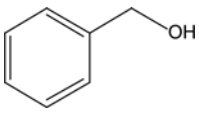
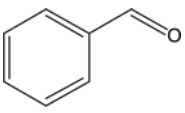
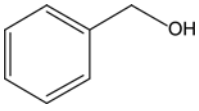
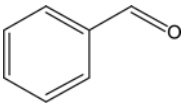
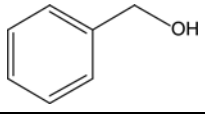
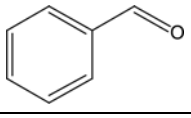
3.5 Effect of the molecular weight of PEG

The properties of PEG depends on its molecular weight. In this work, the effect of the molecular weight of PEG on the oxidation of benzyl alcohol was investigated. Our experiment demonstrated that PVP was not miscible with PEG-1500. However, PEG-600, PEG-800 and PEG-1000 could dissolve PVP to stabilize Au/Pd nanoparticles. The yields of benzaldehyde in PEGs of different molecular weights are listed in Table 2. The results in the table show that as the reaction time was long enough (9 h), a yield of 90% was reached. In order to study the effect of PEG molecular weight on the reaction, we carried out the reaction in different PEGs in a shorter reaction time. The molecular weight of PEG influenced the reaction considerably. The benzaldehyde yield increased from 48% to 79% when the molecular weight of PEG increased from 600 g/mol to 1000 g/mol with a reaction time of 6 h. Therefore, the molecular weight of PEG is a significant factor for the reaction.

3.6 Recyclability of the Au/Pd/PEG catalytic system

The recyclability of the Au/Pd/PEG catalytic system for oxidation of alcohol was examined using benzyl alcohol as the substrate. The oxidation reaction was carried out at 80 °C

Table 2 Oxidation of different substrates and effect of PEG molecular weight on the reaction

Substrate	Product	Solvent	*T* (°C)	Time (h)	Yield (%)
		PEG-600	60	1	98.7
		PEG-600	60	1	99.3
		PEG-600	80	12	92.0
		PEG-600	80	9	90.0
		PEG-600	80	6	48.0
		PEG-800	80	6	57.8
		PEG-1000	80	6	79.0

Reaction conditions: 2.5 g Au/Pd/PEG, 2.5 mmol corresponding alcohol, (Au+Pd):alcohol =1:200, Au:Pd=1:3.5, 0.6 MPa O_2, 7 MPa total pressure after adding CO_2.

with constant pressure and reaction time. In each cycle, after extraction by ethyl ether, the catalytic system Au/Pd/PEG was dried and used for the next run. In order to show the effect of run time on the reaction, we carried out the reaction in a shorter time. The yield and selectivity of benzaldehyde for the four repeated runs are shown in Figure 4. The virgin and the recycled catalytic systems showed very high selectivity at the experimental condition. The yield increased noticeably with the reusing time. This phenomenon needs to be further studied. In addition, the Au/Pd nanoparticles in the virgin Au/Pd/PEG and those in the catalytic system after used for four times were observed by transmission electron microscopy (TEM), and the images and size distributions of the Au/Pd nanoparticles are shown in Figure 5. Figures 5(b) and (d) show that the size distribution of the Au/Pd nanoparticles changed slightly after using for four times.

4 Conclusions

In this work, bimetallic Au/Pd nanoparticles stabilized by PVP have been used to catalyze oxidation of different kinds of alcohols in PEG/CO_2 biphasic system using O_2 as the oxidant without adding any base. The ratio of Au/Pd has great influence on the catalytic activity for oxidation of alcohols, and bimetallic nanoparticles with the Au/Pd molar ratio of 1:3.5 are more active than monometallic Au, Pd and the bimetallic Au/Pd nanoparticles with other molar ratios. Among the studied substrates, α,β-unsaturated alcohols are more reactive than benzyl alcohol and 1-phenylethanol. CO_2 pressure can be used to tune the conversion and selectivity for oxidation of the alcohols effectively, and at optimized conditions the yields of the desired products are higher than 90% for all the reactions. The Au/Pd/PEG can be easily separated from the products and is reusable. In addition, the Au/Pd/PEG/CO_2 system is greener. These characteristics make it a promising catalytic system.

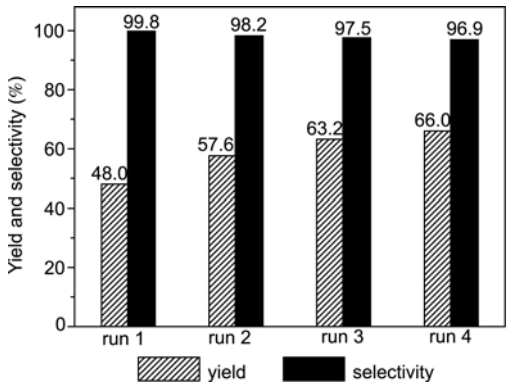


Figure 4 The yield and selectivity of benzaldehyde in the four runs of recycling experiments. Reaction conditions: 2.5 g Au/Pd/PEG-600, 2.5 mmol alcohol, (Au+Pd):alcohol=1:200, Au:Pd=1:3.5, 80 °C, 0.6 MPa O_2, 7 MPa total pressure after adding CO_2, 6 h.

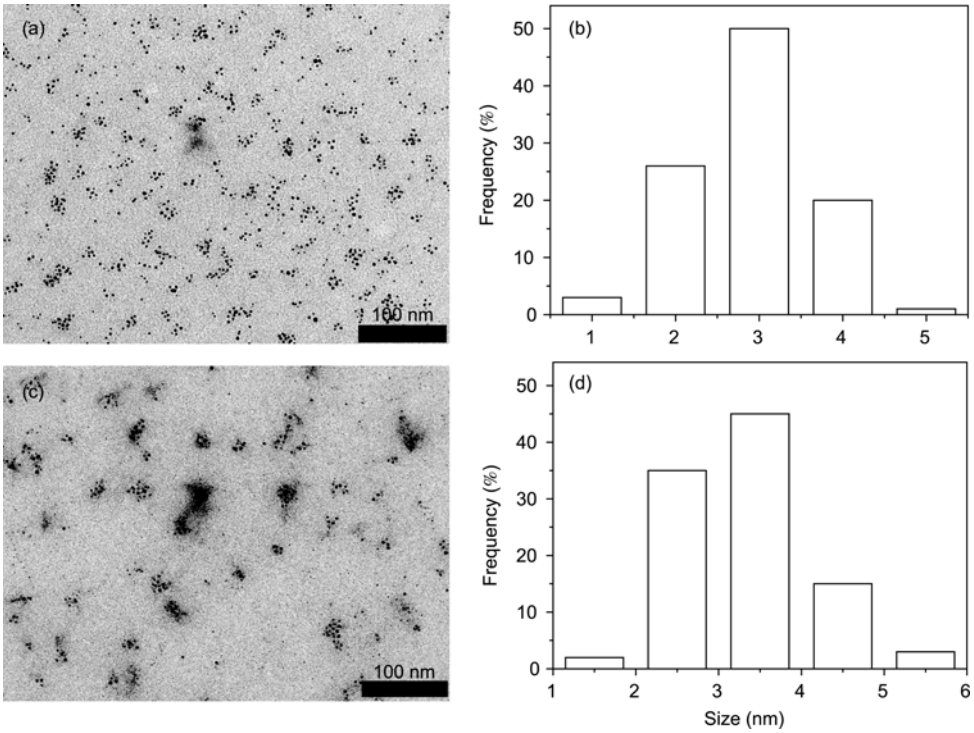


Figure 5 TEM image (a) and size distribution (b) of the Au/Pd nanoparticles in the virgin Au/Pd/PEG system, and TEM image (c) and size distribution (d) of the Au/Pd nanoparticles in the Au/Pd/PEG catalytic system after being used for four times.

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