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Article

Synergistic effect on Au-Pd bimetallic catalyst during oxidation of benzyl alcohol to sodium benzoate

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ABSTRACT

A series of AuPd/CeO₂ bimetallic catalysts with different Au/Pd molar ratios were investigated and their catalytic performance in the oxidation of benzyl alcohol to sodium benzoate and benzoic acid under solvent-free conditions was studied. The supported catalysts were characterized by X-ray diffraction, UV-Vis diffuse reflectance spectroscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy. The Au-Pd nanoparticles were successfully deposited onto CeO₂ as a homogeneous alloy. The activity of the bimetallic catalysts was superior to that of the corresponding monometallic catalysts. This improvement was attributed to the synergistic effect between Au and Pd. The catalyst with an Au/Pd molar ratio of 3/1 showed the best catalytic performance (the yield of benzoic acid reached 92%), and it could be easily recovered and reused for more than seven successive reactions without significant loss of activity.

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1. Introduction

Supported bimetallic nanoclusters have generated much interest for decades owing to their unique bifunctional and synergistic properties [1–4]. Compared with monometallic systems, the activity and stability of bimetallic catalysts are drastically improved upon addition of the second metallic element, which can affect both the geometry and electronic properties of the pure metal clusters [5–8]. Supported Au-Pd bimetallic catalysts are used to catalyze a number of reactions with outstanding activity such as oxidative elimination of toluenes [9], nitroarene reduction to imine [10], oxidation of primary carbon-hydrogen [11–13], and oxidation of alcohols [14,15]. Recently, the beneficial effect of Au-Pd alloy exerted on Au and Pd catalysts has attracted much attention [16–18]. For example,

Goodman and co-workers [19] examined the surface structure of model catalysts, such as Pd/Au(111) and Pd/Au(100), via the synthesis of vinyl acetate, and demonstrated that Au on Pd resulted in catalysts with greatly improved activity and selectivity. Keane and co-workers [20] examined a significant increase in activity of AuPd/Al₂O₃ when compared with Au/Al₂O₃ towards the hydrogenation of *p*-chloronitrobenzene. Hao's group [21] demonstrated that the addition of Pd to Au/SBA-15 catalysts could decrease the size of the gold nanoparticles, resulting in higher activity towards the selective aerobic oxidation of benzyl alcohol. Additionally, Huang's group [22] has reported the effect of the Au/Pd molar ratio of bimetallic AuPd/MgO on the liquid phase oxidation of benzyl alcohol to benzaldehyde. Regardless, to date, the application of Au-Pd bimetallic catalysts in the oxidation of benzyl alcohol to sodium

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benzoate and benzoic acid has rarely been reported.

Cerium oxide (CeO_2) is an effective catalyst employed in various organic reactions such as transamidation of amides [23], selective synthesis of esters from nitriles and alcohols [24], preparation of organic carbamates [25], synthesis of *N*-alkyl amides [26], and reduction of NO_x [27]. Because CeO_2 has acid-base and redox properties that are expected to facilitate and promote catalysis performance [28,29], CeO_2 has been used to support Au [30,31], Cu [32], Ru [33,34], Pt [35], and Pd [36] to catalyze diverse inorganic and organic reactions. Moreover, Au/ CeO_2 catalyst has been reported to exhibit better catalytic performance than Au/ TiO_2 and Au/ Fe_2O_3 towards CO oxidation [30]. Therefore, CeO_2 is considered a promising support candidate to load gold and other noble metals.

Sodium benzoate and benzoic acid are important commodity chemicals with wide use as food additives, preservatives, spices, plasticizers, and mordants. As reported, sodium benzoate and benzoic acid can be prepared upon oxidation of benzyl alcohol in a one-pot solvent-free synthesis method that is environmentally friendly, non-toxic, and energy-efficient [37]. A novel efficient AuAg/ TiO_2 bimetallic catalyst with a high stability was employed in this reaction. The catalyst that was prepared with an Au/Ag molar ratio of 1/3 produced the best catalytic performance. To further improve the catalytic activity and evaluate the synergistic effect between Au and Pd, herein, we report the preparation of AuPd/ CeO_2 bimetallic catalysts and investigate their catalytic properties towards the oxidation of benzyl alcohol to sodium benzoate and benzoic acid. A series of AuPd/ CeO_2 catalysts with different Au/Pd molar ratios were obtained and structurally characterized by UV-Vis diffuse reflectance spectroscopy (DRS), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). It was found that the Au-Pd nanoparticles were mainly present as homogeneous alloys and the catalyst prepared with an Au/Pd ratio of 3/1 displayed optimum catalytic performance.

2. Experimental

2.1. Catalyst preparation

Au-Pd bimetallic catalyst with an Au/Pd molar ratio of 1/1 was loaded on different supports, and the synthesis process was as follows. First, Au/support catalyst was prepared by a deposition-precipitation (DP) method using urea as precipitation agent. Then, 1.0 g of support (TiO_2 , MnO_2 , SnO_2 , ZnO , or CeO_2), 9 mL of aqueous HAuCl_4 solution (24.3 mmol/L), and 2.6 g of urea were added to 80 mL of H_2O with continuous stirring. The mixture was stirred for 2 h at 353 K, during which the pH value was gradually increased from 3.0 to 8.0. The as-received precipitate was collected by filtration, washed three times with deionized water, and dried overnight at 373 K, followed by calcination for 4 h at 573 K. Then, the Pd species were loaded on the as-synthesized precursor mentioned above using an impregnation (IM) method. Typically, 1.0 g of the as-synthesized precursor was added to 7.2 mL of aqueous PdCl_2 solution (56.3 mmol/L) and mixed with 40 mL of H_2O . The resulting slurry was vigorously stirred at 353 K until complete evapora-

tion of water, and the solid material was dried at 373 K, followed by calcination for 4 h at 673 K. The as-synthesized catalyst is denoted as AuPd/MO, where MO represents the support (i.e., TiO_2 , MnO_2 , SnO_2 , ZnO , or CeO_2). It should be noted that the total metal loading and the Au/Pd molar ratio of all AuPd/MO catalysts were controlled at 8 wt% and 1:1, respectively.

Monometallic Au/ CeO_2 catalyst was prepared by DP using urea as precipitation agent. First, 1.0 g of CeO_2 (Aldrich), 18 mL of aqueous HAuCl_4 solution (24.3 mmol/L), and 5.2 g of urea were added to 80 mL of H_2O with continuous stirring. The mixture was stirred for 2 h at 353 K, during which the pH value was gradually increased from 3.0 to 8.0. The as-received precipitate was collected by filtration, washed three times with deionized water, and dried overnight at 373 K, and calcined for 4 h at 573 K.

Monometallic Pd/ CeO_2 catalyst was prepared by IM. First, 1.0 g of CeO_2 was added to 14.5 mL of aqueous PdCl_2 solution (56.3 mmol/L) and mixed with 80 mL of H_2O . The resulting slurry was vigorously stirred at 353 K until complete evaporation of water, and the solid material was dried at 373 K, and then calcined for 4 h at 673 K.

The synthesis process of the bimetallic catalysts with different Au/Pd molar ratios was as follows. First, Au/ CeO_2 was prepared by DP (similarly to the monometallic Au/ CeO_2). Then, AuPd/ CeO_2 was prepared by IM (similarly to the monometallic Pd/ CeO_2), with Au/ CeO_2 as the support. The total metal loading was controlled at 8 wt%. The catalysts prepared at varying Au/Pd molar ratios of 3/1, 2/2, and 1/3 are denoted as 3Au1Pd/ CeO_2 , 2Au2Pd/ CeO_2 , and 1Au3Pd/ CeO_2 , respectively.

2.2. Catalyst characterization

The specific surface area of the samples was determined by nitrogen adsorption at 77 K (Micromeritics TriStar ASAP 3000) using the Brunauer-Emmett-Teller (BET) method. The Au and Pd loadings were determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo E. IRIS). The XRD patterns were recorded on a Bruker D8 advance diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154$ nm), operating at 40 mA and 40 kV. The XPS spectra were recorded under ultra-high vacuum ($<10^{-6}$ Pa) at a pass energy of 93.90 eV on a Perkin Elmer PHI 5000C ESCA system equipped with a dual X-ray source using $\text{Mg K}\alpha$ (1253.6 eV) anode and a hemispherical energy analyzer. All binding energy was calibrated using contaminant carbon ($\text{C 1s} = 284.6$ eV) as a reference. The TEM images were obtained on a JOEL JEM 2010 transmission electron microscope. The UV-Vis DRS spectra were collected using a Shimadzu UV-2450 spectrophotometer operating in the scanning range of 200–800 nm using BaSO_4 as background.

2.3. Activity test

All the experiments were carried out in a magnetically stirred glass flask under reflux; a mercury thermometer was used to monitor the reaction temperature that was maintained at 453 K using an oil bath. A predetermined quantity of benzyl alcohol (1.08 g) was introduced into the reactor, and then

AuPd/CeO₂ (0.05 g) and NaOH (0.5 g) were added. The temperature-controlled reaction mixture was stirred at 800 rpm for 8 h. Following addition of 12 mL of H₂O, the reaction mixture was centrifuged to remove the catalyst. The filtrate was evaporated and crystallized to obtain sodium benzoate (white solid) with purity of >99%.

The as-obtained filtrate was acidified with aqueous HCl solution until a pH value of 2.0 was attained. The resulting mixture was filtered, and benzoic acid (white solid) was obtained with purity of >99%. Finally, the white solid was dried and weighed. Yield (benzyl acid) = ($n_{\text{benzyl acid}}/n_{\text{benzyl alcohol}}$) × 100%. For the recycling test, the spent catalyst was washed with dilute aqueous HCl solution thrice and then calcined at 573 K for 4 h.

3. Results and discussion

3.1. Effect of support on the performance of Au-Pd bimetallic catalysts

The catalytic performance is greatly influenced by the support. The specific surface areas, surface acid-base properties, specific surface functional groups, and metal-support interactions or other structural features would affect the catalytic reaction process. In our study, oxidation of benzyl alcohol to sodium benzoate and benzoic acid was examined in the presence of a series of AuPd/MO catalysts (prepared on various supports, MO) to investigate the influence of the support on the catalyst performance. The results are shown in Fig. 1. The MnO₂- and SnO₂-supported Au-Pd bimetallic catalysts that featured higher amounts of basic sites displayed the lowest catalytic performance. The low catalytic properties could be attributed to the excessive amounts of basic sites and the small specific surface areas [38]. Both the TiO₂- and ZnO-supported Au-Pd bimetallic catalysts exhibited higher catalytic properties when compared with the MnO₂- and SnO₂-supported Au-Pd bimetallic catalysts. AuAg/TiO₂ catalysts have been reported as a promising catalyst for the transformation of benzyl alcohol to sodium benzoate [39]. However, the yield of sodium benzoate was only about 78%, and the TiO₂ loaded with the Au-Pd bimetallic catalysts was prone to aggregation in the absence of a

Fig. 1. Catalytic performance of the Au-Pd bimetallic catalysts loaded on different supports, as measured by the benzoic acid yield. Reaction conditions: temperature 453 K, reaction time 8 h, 1.08 g benzyl alcohol, 0.5 g NaOH, and 0.05 g catalyst.

protective agent. The catalytic performance of AuPd/ZnO catalyst is lower when compared with that of AuPd/CeO₂, and the poor benzoic acid yield is attributed to the low amounts of acid sites of the ZnO support [40]. In contrast, the CeO₂-supported Au-Pd bimetallic catalysts displayed higher amounts of acid sites and larger specific surface areas. Moreover, it is known that the strong metal-support interaction (SMSI) effect, first reported by Tauster et al. in 1978 [41], greatly enhances the interactions between the Au-Pd bimetallic species and CeO₂ support that subsequently would lead to extended stability of the AuPd/CeO₂ catalysts. Thus, the CeO₂ support was chosen in the subsequent studies.

3.2. Catalyst characterization

3.2.1. N₂ adsorption and ICP-AES analyses

The physicochemical properties of the CeO₂-supported Au-Pd bimetallic catalysts with varying Au/Pd molar ratios are listed in Table 1. There were no obvious differences in the pore volume and average pore size, indicating that the introduction of the metal species on the support did not considerably influence the catalyst structure. A slight increase in the BET specific surface areas was observed following loading of the bimetallic species. Based on the ICP-AES analysis, the actual loading of Au or Pd was comparable with the nominal amount, indicative of the successful deposition of Au and Pd on the CeO₂ support.

3.2.2. XRD analysis

The XRD patterns of the monometallic and bimetallic catalysts are shown in Fig. 2. The CeO₂ support is well crystallized showing characteristic diffractogram of fluorite. The *fcc* peaks of Au were observed at $2\theta = 38.2^\circ$, and the intensity of the Au diffraction peak decreased with increasing amounts of Pd. The weak broad peak at $2\theta = 40.1^\circ$, which is characteristic of metallic Pd species, suggests the existence of Pd in the as-prepared Au-Pd bimetallic catalysts (Fig. 2(2)–(5)). A right shift in the Au peaks from $2\theta = 38.2^\circ$ to $2\theta = 38.9^\circ$ was observed, and all the peaks were located between the peaks corresponding to the (111) plane of metallic gold and (111) plane of metallic palladium, suggesting the formation of Au-Pd alloy [42]. Monometallic Pd/CeO₂ (Fig. 2(5)) displayed a diffraction peak corresponding to PdO species formed upon oxidation of Pd during the calcination process. The broad and weak diffraction peak suggests that the size of PdO is very small. Based on the XRD results, both the PdO nanocrystallites and metallic Pd species

Table 1

Physicochemical properties of AuPd/CeO₂ catalysts with different Au/Pd molar ratios.

Catalyst	A_{BET} (m ² /g)	Content ^a (wt%)		Au particle size ^b (nm)
		Au	Pd	
Au/CeO ₂	67.1	7.9	0	4.5
3Au1Pd/CeO ₂	70.3	5.7	1.5	4.8
2Au2Pd/CeO ₂	72.6	3.8	3.4	5.4
1Au3Pd/CeO ₂	71.6	1.9	5.5	5.7
Pd/CeO ₂	71.0	0	7.7	5.2

^a Determined by ICP.

^b The calculated Au particle size was based on the analysis of more than 200 particles from TEM images.

Fig. 2. XRD patterns of AuPd/CeO₂ catalysts with different Au/Pd molar ratios. (1) Au/CeO₂; (2) 3/1; (3) 2/2; (4) 1/3; (5) Pd/CeO₂.

were present in the bimetallic catalysts.

3.2.3. UV-Vis DRS study

Figure 3 shows the UV-Vis DRS spectra of the catalysts with different Au/Pd molar ratios. A weak absorption band at ~570 nm was observed for monometallic Au/CeO₂ catalyst that is due to the surface plasma resonance of the metallic Au particles [43]. As observed, the peak is red-shifted with increasing amounts of Pd, owing to the inter-band transitions of the bimetallic alloy nanoparticles [44–47]. Thus, this finding confirms the formation of an Au-Pd alloy rather than individual and distinct monometallic Au and Pd particles.

3.2.4. TEM results

Figure 4 shows the TEM images and particle size distributions of the AuPd/CeO₂ catalysts with different Au/Pd molar ratios. The metallic particles displayed a narrow size distribu-

Fig. 3. UV-Vis DRS spectra of AuPd/CeO₂ catalysts with different Au/Pd molar ratios. (1) Au/CeO₂; (2) 3/1; (3) 2/2; (4) 1/3; (5) Pd/CeO₂.

tion and were well dispersed on the surface of the support. The average particle sizes of the monometallic Au/CeO₂ and Pd/CeO₂ catalysts are 4.5 and 5.2 nm, respectively. The morphology of metallic particles was greatly influenced by the addition of the second metal. Compared with the monometallic Au particle, the bimetallic particle size tends to be larger with increasing Pd contents. The mean particle size of the catalysts with Au/Pd ratios of 3/1, 2/2, and 1/3 is 4.8, 5.4, and 5.7 nm, respectively. The 3Au1Pd/CeO₂ catalyst featured the smallest average particle size that is expected to improve the catalytic performance.

3.2.5. XPS analysis

The XPS spectra of the catalysts with different Au/Pd molar ratios are shown in Fig. 5. The corresponding deconvoluted Au 4f and Pd 3d XPS spectra are shown in Figs. 6 and 7. The calculated surface contents of Au and Pd species based on the XPS results are listed in Tables 2 and 3. As observed, the content of

Fig. 4. TEM images and particle size distributions of AuPd/CeO₂ catalysts with different Au/Pd molar ratios. (a) Au/CeO₂; (b) 3/1; (c) 2/2; (d) 1/3; (e) Pd/CeO₂.

Fig. 5. (a) Au 4f and (b) Pd 3d XPS spectra of AuPd/CeO₂ catalysts with different Au/Pd molar ratios. (1) Au/CeO₂; (2) 3/1; (3) 2/2; (4) 1/3; (5) Pd/CeO₂.

Au and Pd on the surface of the support is higher than that in bulk (Table 2). However, the surface Au/Pd ratio is slightly higher than the nominal Au/Pd value, implying an enrichment of Au species on the surface of the CeO₂ support. The same phenomenon was also reported and discussed in the studies on model bimetallic Pd-Au catalysts [48,49].

Because the peaks corresponding to Au⁰ 4d_{5/2} (333.8 eV) and Pd⁰ 3d_{5/2} (334.0 eV), and Au⁰ 4f_{5/2} (87.7 eV) and Pd⁰ 4s (88.2 eV) overlap [3,50], the chemical states of the Au and Pd species were examined using the Au 4f_{7/2} and Pd 3d_{3/2} peaks. Monometallic Au/CeO₂ catalyst featured an Au 4f_{7/2} peak at 83.7 eV, corresponding to Au^{δ+} and Au⁰ species. Increasing the Pd content resulted in a negative shift of the Au 4f_{7/2} peak (Fig. 5(a)) and the surface species of Au changed to Au⁰ and Au^{δ-},

regardless of the studied bimetallic catalyst. Moreover, the amount of Au^{δ-} increased with increasing Pd amounts (Fig. 5), indicating the transfer of electrons from Pd to Au.

Monometallic Pd/CeO₂ catalyst consisted of Pd⁰, Pd²⁺, and Pd⁴⁺ species on the surface of the support. The appearance of Pd^{δ+} species is due to the oxidation of partial Pd during the calcination process. When the amount of Au increased, the Pd 3d_{3/2} peaks of the bimetallic catalysts shifted to lower binding energy when compared with that in Pd/CeO₂ (Fig. 5(b)). The Au 4f_{7/2} and Pd 3d_{3/2} peak shift to lower binding energy demonstrates the net charge flow between Au and Pd [51–54]. With increasing Au contents, the Pd^{δ+} species in the bimetallic catalysts were converted into the metallic state (Table 3). Thus, it is believed that Au tends to accept electrons, whereas Pd has

Fig. 6. Au 4f XPS spectra of AuPd/CeO₂ catalysts with different Au/Pd molar ratios. (a) Au/CeO₂; (b) 3/1; (c) 2/2; (d) 1/3.

Fig. 7. Pd 3d XPS spectra of AuPd/CeO₂ catalysts with different Au/Pd molar ratios. (a) 3/1; (b) 2/2; (c) 1/3; (d) Pd/CeO₂.

the tendency to lose electrons because of the presence of a synergistic effect between Au and Pd, alluding to the formation of an Au-Pd alloy.

3.3. Catalytic oxidation of benzyl alcohol

The catalytic oxidation of benzyl alcohol to sodium benzoate under solvent-free conditions in the presence of NaOH is known as the Cannizzaro reaction. Benzyl alcohol was oxidized to benzoic aldehyde that instantaneously transformed into sodium benzoate in an alkaline environment.

Table 4 shows the catalytic results using monometallic and bimetallic catalysts towards the oxidation of benzyl alcohol to

sodium benzoate and benzoic acid under solvent-free conditions. Because the desired product was of high purity (selectivity of 100%), the yield was used to evaluate the catalytic activity. As observed, the yields obtained in the presence of the monometallic Au/CeO₂ and Pd/CeO₂ catalysts are relatively low. Following addition of the second metal, distinctly improved catalytic activity was observed. The catalyst with an Au/Pd ratio of 3/1 displayed the best catalytic performance, with a corresponding yield of 92% achieved after 8 h of reaction. In contrast with Pd/CeO₂, the yields generated in the presence of the bimetallic catalysts decreased with increasing Pd amounts. The space time yield (STY) obtained in the presence of the AuPd/CeO₂ catalysts was also compared, and the results are shown in Table 4. The STY values markedly increased upon introduction of Pd into the monometallic Au/CeO₂ catalyst and reached maxima at an Au/Pd molar ratio of 3/1 (i.e., STY 2.81 h⁻¹), then decreased with further increase in the loading amount of Pd. This indicates the existence of a suitable Au/Pd molar ratio required to generate optimal cata-

Table 2

Surface and bulk compositions of AuPd/CeO₂ catalysts obtained from XPS and ICP-AES, respectively.

Catalyst	Surface content (%)		Au/Pd molar ratio	
	Au	Pd	Surface	Bulk
Au/CeO ₂	9.3	—	—	—
3Au1Pd/CeO ₂	8.6	2.7	3.2	2.0
2Au2Pd/CeO ₂	4.0	3.6	1.1	0.6
1Au3Pd/CeO ₂	3.2	6.4	0.5	0.2
Pd/CeO ₂	—	8.1	—	—

Table 3

Content of Au and Pd surface species of AuPd/CeO₂ catalysts calculated from the XPS results.

Catalyst	Au species (%)			Pd species (%)		
	Au ⁰	Au ^{δ-}	Au ^{δ+}	Pd ⁰	Pd ²⁺	Pd ⁴⁺
Au/CeO ₂	61	0	39	0	0	0
3Au1Pd/CeO ₂	67	33	0	48	52	0
2Au2Pd/CeO ₂	51	49	0	41	39	20
1Au3Pd/CeO ₂	42	58	0	30	31	39
Pd/CeO ₂	0	0	0	19	25	56

Table 4

Reactivity of benzyl alcohol oxidation over AuPd/CeO₂ catalysts with different Au/Pd molar ratios.

Catalyst	Conversion (%)	Yield (%)	STY ^a (h ⁻¹)
Au/CeO ₂	100	70	2.14
3Au1Pd/CeO ₂	100	92	2.81
2Au2Pd/CeO ₂	100	83	2.53
1Au3Pd/CeO ₂	100	72	2.20
Pd/CeO ₂	100	55	1.68

Reaction conditions: temperature 453 K, reaction time 8 h, 1.08 g benzyl alcohol, 0.5 g NaOH, and 0.05 g catalyst. ^a The space time yield (STY) is based on the yield of benzoic acid obtained in the presence of 1 g catalyst per hour; the results were obtained after 8 h of reaction.

lytic activity.

To examine the stability of the bimetallic catalysts, cycling experiments were conducted using the 3Au1Pd/CeO₂ catalyst, and the results are shown in Fig. 8. The bimetallic catalyst was easily recovered and reused for more than seven successive reactions without significant loss in the catalytic activity, indicating the high stability of the as-prepared AuPd/CeO₂ catalyst.

Furthermore, the activity of the AuPd/CeO₂ catalyst is higher than that of previously studied AuAg/TiO₂ (10 h, yield 82%) [37]. Moreover, the use of AuPd/CeO₂ catalyst requires lower amounts of catalyst and milder reaction conditions including a lower reaction temperature and a shorter reaction time. Therefore, the as-prepared AuPd/CeO₂ is an excellent catalyst candidate for the oxidation of benzyl alcohol to benzoic acid.

3.4. Synergistic effect of the Au-Pd bimetallic catalysts

Au-based bimetallic nanocatalysts have attracted considerable interest in the past decade owing to their improved sintering resistance and enhanced activity and selectivity. Because Au features a higher electronegativity (2.54) than transition metals, electron transfer from the second metal to Au may occur that will affect the catalytic performance of Au by electronic modification [55]. Wang et al. [56] reported the preparation of graphene-supported Au-Pd bimetallic nanoparticles with excellent catalytic performance towards the selective oxidation of methanol to methyl formate; additionally, their finding pointed out that electron exchange between the Au and Pd species would greatly facilitate the catalytic performance. The considerably lower binding energy of both Au and Pd in Au_{2.0}Pd_{1.0}/graphene could be attributed to the electron exchange between Au and Pd (i.e., a synergism between the Au and Pd nanoparticles). Wen et al. [57] studied Cu/TiO₂-SiO₂ catalysts and attributed the blue shift of Cu 2p_{3/2} peak and unchanged Ti 2p_{3/2} peak (which should be blue-shifted as well) binding energy to electron transfer from Ti to Cu. Deng's group [58] also studied the surface electronic characteristics of Ni-B and found that the binding energy of elemental B positively shifted by ~1.1 eV, indicating that B partially donated electrons to Ni. In our study, clear evidence from the XPS measurements was obtained as observed by the decrease in the binding ener-

Fig. 8. Recyclability of 3Au1Pd/CeO₂ towards the catalytic synthesis of sodium benzoate and benzoic acid. Reaction conditions: temperature 453 K, reaction time 8 h, 1.08 g benzyl alcohol, 0.5 g NaOH, and 0.05 g catalyst.

gy values of the Au 4f_{7/2} levels and increase in the binding energy of the Pd 3d_{3/2} levels in the AuPd/CeO₂ catalysts with varying Au/Pd molar ratios (see Table 3). These results strongly suggest the interaction of electrons between the Au and Pd species. Because the physicochemical properties of both the monometallic and bimetallic catalysts are similar, except for the surface electronic properties, with changes in the Au/Pd molar ratio, electron interaction, considered as the synergistic effect of the AuPd/CeO₂ catalysts, is believed to play important roles in the high catalytic performance towards the oxidation of benzyl alcohol to benzoic acid [59].

4. Conclusions

A systematic set of AuPd/CeO₂ bimetallic catalysts with different Au/Pd molar ratios have been successfully prepared. The catalysts efficiently catalyzed the oxidation of benzyl alcohol to benzoic acid and sodium benzoate with high yields. Compared with the monometallic catalysts, the catalytic performance of AuPd/CeO₂ catalyst was considerably improved upon addition of the second metal. This finding could be ascribed to the formation of homogeneous Au-Pd alloy and the synergistic effect between Au and Pd that influenced the size of the metal particles and their electronic states. Optimal catalytic activity was obtained at an Au/Pd ratio of 3/1. Moreover, this catalyst could be recycled by simple treatment and reused numerous times without significant loss of activity.

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A series of AuPd/CeO₂ bimetallic catalysts with different Au/Pd molar ratios were successfully prepared and applied in the catalytic oxidation of benzyl alcohol to benzoic acid and sodium benzoate with high yields. The 3Au1Pd/CeO₂ catalyst shows optimal performance and was easily recovered and reused for more than seven successive reactions without significant loss of activity, which was attributed to the synergistic effect between Au and Pd.

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苯甲醇氧化制苯甲酸钠反应中金钯双金属催化剂的协同效应

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摘要: 研究了不同Au/Pd摩尔比的AuPd/CeO₂双金属催化剂在苯甲醇氧化制苯甲酸及其钠盐反应中的催化活性, 利用XRD, UV-Vis DRS, TEM和XPS等手段对催化剂的结构进行了系统考察. 结果表明, Au-Pd纳米颗粒以合金形式分散在CeO₂载体上, 不同Au/Pd摩尔比会影响催化剂表面活性物种的粒径大小和尺寸分布, 并改变催化剂表面物种的组成. Au-Pd之间的电子效应和协同效应显著影响其催化活性. 当Au/Pd摩尔比为3时催化剂表现出最好的催化活性, 苯甲酸产率可达92%. 此外, 双金属催化剂的催化活性显著优于单金属催化剂, 主要归因于Au和Pd之间的协同效应. AuPd/CeO₂催化剂还具有良好的稳定性, Au/Pd摩尔比为3的AuPd/CeO₂催化剂使用7次后仍然具有较高的催化活性.

关键词: 金; 钯; 氧化铈; 双金属催化剂; 苯甲醇; 催化氧化; 苯甲酸盐

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1. 前言

负载型双金属催化剂由于具有独特的催化活性, 近年来在催化领域引起广泛关注^[1-4]. 与单金属催化剂相比, 双金属催化剂中第二种金属的加入可以调节和改变催化剂的形貌和电子特性, 从而提高催化剂的活性和稳定性^[5-8]. 其中, Au-Pd双金属催化剂在诸多反应体系中具有很好的活性, 如甲苯氧化消除^[9]、硝基苯还原^[10]、低碳烷烃氧化^[11-13]以及醇类氧化^[14,15]等. 目前, 关于Au-Pd合金催化剂相对于单独Au和Pd催化剂的促进作用得到了广泛关注^[16-18]. Goodman课题组^[19]研究了乙酸乙烯酯合成反应中Pd/Au(111)和Pd/Au(100)催化剂表面结构, 指出AuPd合金明显提高了催化剂的活性和选择性. Keane课题组^[20]研究发现, 在对氯硝基苯还原反应中Au-Pd/Al₂O₃催化剂比Au/Al₂O₃单金属催化剂具有更好的催化活性. Hao课题组^[21]发现将Pd加入到Au/SBA-15中可以降低纳米Au的粒径尺寸, 从而提高催化剂在苯甲醇氧化反应中的催化活性. Huang课题组^[22]报道了AuPd/MgO催化剂中Au/Pd摩尔比对苯甲醇氧化制苯甲醛的影响. 但是关于Au-Pd双金属催化剂用于苯甲醇氧化制苯甲酸盐和苯甲酸反应的报道并不多见.

二氧化铈(CeO₂)在多种有机反应中是一种有效的催化剂, 如酰胺交换^[23]、腈类和醇类合成酯^[24]、氨基甲酸盐制备^[25]、烷基酰胺合成^[26]以及NO_x还原^[27]等反应. CeO₂由于具有酸碱性和氧化还原性能, 被广泛用作催化剂载体^[28,29], 在其上负载Au^[30,31], Cu^[32], Ru^[33,34], Pt^[35]和Pd^[36]等制备的催化剂被用在各种无机或有机反应中.

此外, 有研究指出在CO氧化反应中Au/CeO₂催化剂比Au/TiO₂和Au/Fe₂O₃催化剂具有更好的催化性能^[30]. 因此, CeO₂是一种理想的负载Au和其他贵金属的载体.

苯甲酸钠和苯甲酸是重要的精细化工产品, 主要应用于食品添加剂、防腐剂、香料、塑化剂和媒染剂. 在苯甲醇氧化合成反应中, 无溶剂、一锅法合成是一种环境友好、无毒、高效的催化路线^[37]. 我们之前的研究^[37]发现, AuAg/TiO₂双金属催化剂在苯甲醇氧化反应中表现出很好的稳定性, 并且当Au/Ag摩尔比为1/3时, 催化剂表现出最好的活性. 为了进一步提高催化活性和探讨Au与Pd之间的协同效应, 我们研究了AuPd/CeO₂双金属催化剂的制备、结构及其在苯甲醇氧化制苯甲酸钠和苯甲酸反应中的催化性能. 采用共沉淀方法制备了一系列不同Au/Pd摩尔比的催化剂, 采用紫外-可见漫反射光谱(UV-Vis DRS)、透射电镜(TEM)和X射线光电子能谱(XPS)等手段对催化剂进行了结构表征. 结果发现Au-Pd纳米颗粒主要以合金形式存在, 并且当Au/Pd摩尔比为3/1时催化剂具有最高催化活性.

2. 实验部分

2.1. 催化剂的制备

负载在不同载体上的Au-Pd (Au/Pd = 1/1)双金属催化剂的制备方法如下. 首先通过沉积-沉淀(DP)法, 以尿素为沉淀剂将Au负载在载体上. 将1.0 g载体(TiO₂, MnO₂, SnO₂, ZnO 或 CeO₂), 9 mL HAuCl₄溶液(24.3 mmol/L)和2.6 g尿素加入到80 mL蒸馏水中并不断搅拌; 然后将混合物置于353 K水浴中搅拌2 h, 溶液的pH逐渐

从3.0增加到8.0, 抽滤, 用蒸馏水洗涤3次, 得到的固体置于373 K下烘干过夜, 最后在573 K下焙烧4 h. 其次通过浸渍法将Pd负载到上述合成的前驱体上. 将1.0 g上述前驱体加入到7.2 mL PdCl₂溶液(56.3 mmol/L)中, 并加入40 mL蒸馏水, 在353 K下搅拌, 直至水分全部蒸干, 所得固体在373 K下干燥, 并在673 K下焙烧4 h. 所得催化剂即为AuPd/MO (MO = TiO₂, MnO₂, SnO₂, ZnO或CeO₂). 所有AuPd/MO催化剂中金属整体负载量为8 wt%, 并且Au/Pd摩尔比为1/1.

单金属Au/CeO₂催化剂以尿素为沉淀剂, 通过DP法制备. 将1.0 g CeO₂, 18 mL HAuCl₄溶液(24.3 mmol/L)和5.2 g尿素加入到80 mL蒸馏水中并不断搅拌. 将混合物置于353 K水浴中搅拌2 h后, 抽滤, 用蒸馏水洗涤3次, 得到的固体置于373 K下烘干过夜, 然后在573 K下焙烧4 h.

单金属Pd/CeO₂催化剂通过浸渍法制备. 将1.0 g CeO₂加入到14.5 mL PdCl₂溶液(56.3 mmol/L)和80 mL的蒸馏水中, 产生的混浊液在353 K下搅拌直到水分全部蒸干, 所得固体在373 K下干燥, 并在673 K下焙烧4 h.

不同Au/Pd摩尔比的双金属催化剂制备过程如下. 首先通过DP法制备Au/CeO₂ (与单金属Au/CeO₂制备相同), 然后通过浸渍法将Pd负载到Au/CeO₂上(类似于单金属Pd/CeO₂的制备)得到AuPd/CeO₂催化剂. 催化剂中AuPd整体负载量控制在8 wt%. Au/Pd摩尔比为3/1, 2/2和1/3的催化剂分别记为3Au1Pd/CeO₂, 2Au2Pd/CeO₂和1Au3Pd/CeO₂.

将反应后催化剂用稀HCl洗涤3次, 然后在573 K下焙烧4 h, 用于下次循环反应实验.

2.2. 催化剂的表征

催化剂的比表面积和孔分布采用美国Micromeritics公司Tristar 3000型自动物理吸附仪测定, 在液氮温度77 K下获得样品的N₂吸附/脱附等温线. Au和Pd的负载量使用电感耦合等离子体发射光谱测定, 采用的仪器型号为IRIS Intrepid (美国Thermo Elemental公司). 采用德国Bruker公司D8 Advance型X射线粉末衍射仪进行催化剂样品的物相分析, 射线源采用波长为0.154 nm的Cu K_α线, 采用Goebel镜将发散X光束汇聚为平行光, 管电压为40 kV, 管电流为40 mA. XPS采用PerkinElmer PHI 5000C ESCA System X射线光电子能谱仪, 以Mg K_α射线(1253.6 eV)作为光源, 分析器通能为93.9 eV, 分析室的压力 < 10⁻⁶ Pa. 样品压片后测试, 所有结合能均以污染碳(C 1s = 284.6 eV)进行校正. TEM仪器型号为JEOL

2011 TEM. 紫外-可见漫反射光谱测试采用Shimadzu UV-2450型紫外-可见分光光度计, 将粉末样品装入样品池中, 以BaSO₄为参比测定, 扫描范围200–800 nm.

2.3. 催化剂活性测试

所有实验均在装有冷凝回流装置的圆底烧瓶中进行. 反应温度为453 K, 称取1.08 g苯甲醇、0.05 g催化剂和0.5 g NaOH于圆底烧瓶中, 然后置于油浴中搅拌, 453 K加热回流8 h. 然后加入12 mL水, 离心分离除去催化剂, 滤液蒸发结晶得到苯甲酸钠, 纯度 > 99%.

另外, 将上述滤液用HCl进行酸化至pH < 2.0, 有白色固体出现, 静置后抽滤, 获得白色的苯甲酸固体, 在空气中干燥后称重. 苯甲酸得率 = (苯甲酸摩尔量/苯甲醇摩尔量) × 100%.

3. 结果与讨论

3.1. 载体对AuPd双金属催化剂的影响

载体效应是影响催化剂活性的重要因素. 载体的比表面积、表面酸性、特殊的表面官能团以及载体与金属之间的相互作用等都会影响催化反应的活性. 不同载体负载的AuPd催化剂在苯甲醇氧化制苯甲酸和苯甲酸钠反应中的催化活性示于图1. 可以看出, 具有较多碱性位的MnO₂和SnO₂负载的AuPd双金属催化剂, 催化活性最差, 这可能是由于催化剂中具有较多的碱性位和较小的比表面积^[38]. 以TiO₂和ZnO为载体的催化剂的催化活性比MnO₂和SnO₂负载的催化剂好. 我们先前研究发现AuAg/TiO₂催化剂对于苯甲醇制苯甲酸钠反应是一种优良的催化剂^[39], 但是苯甲酸钠得率只有78%左右, 并且该催化剂在没有保护剂的作用下很容易发生聚集. 而AuPd/ZnO催化剂的活性比AuPd/CeO₂低, 这可能是由于ZnO载体缺乏一定量的酸性位^[40]. 而对于AuPd/CeO₂, 催化剂中存在较多的酸性位和具有较大的比表面积, 并且金属与载体之间存在着强相互作用, 使得该催化剂具有较好的活性和稳定性^[41]. 因此, CeO₂被选作载体进行深入研究.

3.2. 催化剂的表征结果

3.2.1. N₂吸附和ICP-AES结果

各催化剂的物理化学性质如表1所示. 负载双金属后的催化剂的比表面积有稍许增加. 不同催化剂的孔体积和平均孔径没有明显区别, 说明金属物种的引入对催化剂结构没有造成影响. 从ICP测试结果可以看出, 实际的Au和Pd负载量和其理论值相近, 说明Au和Pd都有效负载在CeO₂载体上.

3.2.2. XRD结果

不同Au/Pd摩尔比的AuPd/CeO₂双金属催化剂的XRD结果如图2所示。可以看出,在 $2\theta = 38.2^\circ$ 处可以观察到Au的衍射峰,并且随着Pd含量的增加,Au的衍射峰强度逐渐减弱。在 $2\theta = 40.1^\circ$ 处可以观察到金属Pd的微弱且宽化的衍射峰(图2(2)–(5)),说明Pd成功负载在AuPd双金属催化剂上。对于双金属AuPd/CeO₂,Au的衍射峰从 $2\theta = 38.2^\circ$ 偏移至 38.9° ,并且衍射峰位于单独的Au和单独的Pd的衍射峰值之间,这说明有部分Au和Pd在制备过程中形成了合金^[42]。在单金属Pd/CeO₂(图2(5))中出现了PdO的微弱衍射峰,该峰非常微弱且宽化,说明PdO的粒径非常小;PdO的出现可能是催化剂在制备过程中,在空气中焙烧时少量的Pd被氧化形成的。由XRD结果可以看出,在双金属催化剂中同时存在着PdO和Pd物种。

3.2.3. UV-Vis DRS结果

不同Au/Pd摩尔比的AuPd/CeO₂双金属催化剂的紫外-可见漫反射光谱如图3所示。Au在570 nm左右有一个微弱的宽吸收峰,对应的是金属态金(Au⁰)的等离子共振峰(SPR)^[43]。加入Pd形成双金属催化剂以后,等离子共振吸收峰有一个明显的红移。这可能是由于形成双金属AuPd合金后能带间发生了电子跃迁^[44–47]。这一现象说明催化剂中的金属以AuPd合金的形式存在,而不是以单独的Au和Pd存在。AuPd合金的形成能很好地加强电子之间的相互作用,这可能是催化剂活性提高的一个重要原因。

3.2.4. TEM结果

不同Au/Pd摩尔比的AuPd/CeO₂催化剂的透射电镜照片和金属的粒径分布如图4所示。可以看出,金属颗粒均匀分散在载体表面。单金属的Au/CeO₂催化剂中金属的平均粒径是4.5 nm,粒径分布较窄。单金属Pd/CeO₂催化剂上金属的平均粒径是5.2 nm,粒径分布较宽。然而在双金属催化剂中,随着Pd含量的增加,金属颗粒的平均粒径逐渐增加,从4.8 nm增加到5.7 nm。其中,3Au1Pd/CeO₂催化剂的平均粒径最小,这可能是其活性好的原因之一。

3.2.5. XPS结果

不同Au/Pd摩尔比的AuPd/CeO₂的XPS谱如图5–7所示,催化剂表面Au和Pd的元素组成列于表2和表3。从表2可以明显看出,Au和Pd的表面含量明显高于体相中的含量,但是表面Au/Pd摩尔比只是稍高于化学计量的Au/Pd摩尔比,说明AuPd/CeO₂是表面富Au。文献^[48,49]在

研究Pd-Au催化剂时也发现了Au在催化剂表面富集的现象。

此外,由于Au⁰ 4d_{5/2} (333.8 eV)和Pd⁰ 3d_{5/2} (334.0 eV)以及Au⁰ 4f_{5/2} (87.7 eV)和Pd⁰ 4s (88.2 eV)有部分重叠^[3,50],因此我们通过Au 4f_{7/2}和Pd 3d_{3/2}来确定金属的化合态。在单金属Au/CeO₂催化剂中,Au 4f_{7/2}的结合能是83.7 eV,对其进行分峰拟合后发现,Au物种有Au^{δ+}和Au⁰两种存在形式。随着Pd含量的增加,Au 4f_{7/2}峰位置向低结合能方向移动,并且在双金属催化剂中Au^{δ+}消失,表面Au的存在状态变为Au⁰和Au^{δ-},并且Au^{δ-}的含量随着Pd含量的增加而增加。这可能是由于Pd的加入增加了电子之间的相互作用,催化剂表面Pd的部分电荷转移到Au簇上面,造成Au表面电荷富集,从而导致Au^{δ-}物种的生成。

对于单金属Pd/CeO₂催化剂,Pd的物种为Pd⁰,Pd²⁺和Pd⁴⁺。Pd^{δ+}的形成可能是由于在制备过程中,在空气中焙烧时有部分Pd被氧化。当Au含量增加时,Pd 3d_{3/2}峰出现明显的位移,Pd 3d_{3/2}的结合能逐渐降低(图5(b))。Au 4f_{7/2}和Pd 3d_{3/2}结合能位置的改变表明了电子在Au和Pd之间的流动^[51–54]。此外,我们发现随着Au含量的增加,Pd^{δ+}物种的含量逐渐降低,转变为金属态的Pd(见表3)。这可能是由于Au和Pd之间的协同效应,Au倾向于获得电子,而Pd容易失去电子。

3.3. 催化剂的活性

在无溶剂的碱性条件下,苯甲醇氧化合成苯甲酸钠属于Cannizzaro反应。在这一反应中,苯甲醇首先被氧化生成苯甲醛,苯甲醛在碱性条件下立即转化形成苯甲酸钠。

不同Au/Pd摩尔比的AuPd/CeO₂催化剂在苯甲醇氧化制苯甲酸和苯甲酸钠反应中的活性测试结果见表4。可以看出,用单金属催化剂Au/CeO₂和Pd/CeO₂催化该反应体系时,产物得率均较低。当加入第二种金属后,催化剂活性得到明显提高,并且当Au/Pd摩尔比为3/1时催化活性最好,得率可达92%;但是再增加Pd的含量时,催化剂活性开始明显下降。AuPd/CeO₂催化剂的时空产率也列于表4。当Pd加入到Au/CeO₂催化剂中时,时空产率明显增加,并且当Au/Pd摩尔比为3/1时达到最大值,为2.81 h⁻¹,进一步增加Pd的负载量导致时空产率降低,说明Au/Pd摩尔比对催化剂的催化活性有很大影响。

除此之外,以3Au1Pd/CeO₂催化剂为例,对催化剂的稳定性进行了测试(图8)。结果发现,催化剂循环使用7次后依然具有良好的催化活性(>79%),说明AuPd/CeO₂

双金属催化剂具有良好的稳定性.

另外, 与之前我们报道的AuAg/TiO₂ (时间10 h, 得率82%)催化剂相比, AuPd/CeO₂催化剂具有更好的催化活性, 并且反应过程中催化剂用量较少, 反应条件更温和. 因此, AuPd/CeO₂催化剂是苯甲醇氧化制备苯甲酸的优良催化剂.

3.4. AuPd双金属的协同效应

由于Au基双金属催化剂具有抗烧结能力, 并在许多反应中表现出高活性和高选择性, 因此得到了广泛关注. 在Au基双金属催化剂中, 由于Au具有很高的电负性, 因此电子容易从另一种金属向Au上转移, 从而影响Au的催化性能^[55]. Wang等^[56]合成了以石墨烯为载体的Au-Pd催化剂, 该催化剂对甲醇选择性氧化合成甲酸甲酯具有很好的活性, Au和Pd之间的电子转移能够提高催化剂的催化活性; 并且Au_{2.0}-Pd_{1.0}/石墨烯催化剂中Au和Pd电子结合能均较低的原因可能是Au和Pd之间电子转移的结果, 即Au和Pd之间存在协同作用. Wen等^[57]在研究Cu/TiO₂-SiO₂催化剂时发现, 由于Cu和Ti之间存在电子转移, 使得Cu 2p_{3/2}的结合能向低处偏移. Deng课题

组^[58]在研究Ni-B的表面电子特性时发现, 在Ni-B中B的结合能向高处移动了大约1.1 eV, 说明B贡献出电子转移给合金中的Ni. 在我们的研究中发现, 不同Au/Pd摩尔比的AuPd/CeO₂催化剂中Au 4f_{7/2}和Pd 3d_{3/2}的结合能发生变化(表3), 也证实了Au和Pd之间电子的相互作用. 由于不同Au/Pd摩尔比的双金属催化剂的物理化学性质类似, 因此电子效应是影响AuPd/CeO₂催化剂在苯甲醇氧化制苯甲酸反应中催化活性的重要因素^[59].

4. 结论

制备了一系列不同Au/Pd摩尔比的AuPd/CeO₂催化剂, 并应用到苯甲醇氧化制苯甲酸钠和苯甲酸反应中, 获得了较好的催化活性. 与单金属催化剂相比, 双金属催化剂催化性能更好. 这主要归因于AuPd/CeO₂催化剂中AuPd合金的形成以及Au和Pd之间的协同作用, 它们影响了粒径尺寸和电子状态. 当Au/Pd摩尔比为3/1时, 催化剂活性最高, 产物得率高达92%; 并且反应后催化剂经过简单处理, 循环使用7次后仍然具有较高的催化活性.