A novel plasma reduction for the preparation of AuPd bimetallic nanocatalyst and its application in selective oxidation of benzyl alcohols

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Abstract

In this work, a low temperature plasma reduction technology is developed for the preparation of AuPd alloy nanocatalyst. The HAuCl4 and PdCl2 mixture as catalyst precursor was directly decomposed on MgO support by plasma to form AuPd nanoalloy. Results demonstrated that the final particles states of nanoalloys prepared by this technique including size, morphology, and chemical valence are highly dependent on temperature of plasma treatment. The catalytic performance of AuPd/MgO in the selective oxidation of benzyl alcohols can be tailored by optimizing the synthesis parameter. A relative low temperature in plasma process prevents particles migration and helps to maintain the small size that favors high activity. The AuPd nanoparticles with diameter about 3.5 nm by optimizing the plasma treatment condition exhibit superior conversion and TOF compared to catalyst prepared by the traditional high temperature H2 reduction method. It is believed that the low temperature plasma technology has a unique advantage for the preparation of high-quality alloy nanocatalyst and could be extended for fabricating the other alloy nanocatalysts.

1. Introduction

Selective oxidation of benzyl alcohols to benzaldehyde is one of the most versatile reactions for transforming functional groups in organic synthesis for important organic compounds including pharmaceutical, perfume, and so on [1, 2]. Traditional oxidation processes usually use strong oxidants such as permanganate and chromate that are toxic and environmentally unfriendly. In recent years, fundamental and industrial interests have been led to aerobic oxidation using noble metals as heterogeneous catalysts due to the advantages such as atomic efficiency, environmental benign, and clean byproducts [1, 3, 4]. Supported gold (Au) and palladium (Pd) nanoparticles are promising catalyst for this reaction [5–7]. Strategies have been developed to optimize the activity and selectivity of nanocatalysts, including size and shape control of nanometals [8, 9], engineering the supports [10], or composition adjustment [3]. In particular, bimetallic nanoparticles are attracting intensive interests because of the improved catalytic properties deriving from the synergetic effects between two elements. Several research groups have examined the supported Au-Pd bimetallic catalysts, which have remarkably enhanced the catalytic activity and selectivity in various alcohol oxidation reactions [2, 3, 11, 12]. Zhang et al reported the Au-Pd alloy nanocatalyst supported on Al2O3 by coimpregnation-reduction method that exhibited the high selectivity and stability for the aerobic oxidation of benzyl alcohol [12]. Enache et al reported an extraordinarily high TOF (269,000 h−1) of AuPd/TiO2 in 1-phenyl-ethanol selective oxidation, demonstrating the alloying configuration of gold and palladium generating a 25-fold improvement in catalytic activity [4].

Besides the composition and microstructure of the nanocatalyst, preparation method of nanocatalysts directly impact their catalytic performance because the preparation procedures would generate obvious
differences in particle size, morphology, structure, and even electronic properties [13–15]. Currently, most work on noble metal nanocatalyst is accomplished by bottom-up synthesis in solutions that generally contains step of reduction [10, 16] or decomposition [14, 17] of positive valent metal precursors at harsh conditions. For example, the conventional method mainly involves impregnation that usually needs thermal reduction to obtain metallic nanoparticles. The drawback of such approach is that nanoparticles would easily agglomerate and grow due to the increased surface energy and low Tamman temperature, leading to activity degradation [18, 19]. Another common approach is deposition-precipitation that could prepare the small and high monodispersed nanoparticle catalyst with improved activity. This method often brings the Cl− or other contaminants into nanocatalyst that is harmful for the catalytic activity [20, 21]. Other prepared methods, such as chemical reduction, usually require a reductant NaBH4 or hydrazine, which is environmentally unfriendly [22]. The tradeoff in activating the reduction of the precursor versus confining the growth the nanoparticle products leads to difficulties in precise control of composition and morphology of the products. A robust method for fabricating bimetallic nanocatalyst with no contamination is still a challenge. Recently, preparation of metal nanocatalyst by cold plasma techniques has attracted a lot of attention due to their unique advantages such as mild condition and free of contamination [14]. Plasma reduction is usually carried out at ambient temperature, which significantly reduces the growth and agglomeration of nanoclusters [23]. Thus, this low-temperature plasma technology has a great potential for preparing the high activity nanoparticles catalyst.

Herein, we employ the cold plasma treatment for the preparation of Au-Pd bimetallic nanoparticles supported on MgO. The solvent-free aerobic oxidation of benzyl alcohol to benzaldehyde is chosen as a model reaction to evaluate the catalytic performance of the obtained nanoparticle catalysts. Also, the parameters of plasma treatment on structure and catalytic activity of nanoparticle catalysts are carefully examined to optimize the performance of final products.

2. Experimental

2.1. Materials
MgO powder, Chloroauric acid (HAuCl4·4H2O) and Palladium chloride (PdCl2) were purchased from the Sinopharm Chemical Reagent Co., Ltd The bimetallic Au–Pd/MgO catalyst was first prepared using conventional incipient-wetness impregnation.

2.2. Catalyst synthesis
Typically, 1 ml (0.02 M) HAuCl4 aqueous solution and 1 ml (0.02 M) PdCl2 aqueous solution was added to 50 ml glass beaker, together with 14 ml deionized water. The glass beaker was heated in a silicon oil bath, followed by the addition of 1.98 g MgO powder. After that, the temperature was raised to 80°C accompanying with a vigorously stirring in 12 h. The obtained middle sample experienced centrifugation, washing and drying, in sequence. Finally, the sample was treated with plasma for 8 cycles (10 min per cycle), with manual mixing of the sample at intervals to ensure the homogeneous plasma effect for them [2]. The obtained catalysts were denoted as AuPd/MgO-P. For comparison, the AuPd/MgO catalyst prepared by impregnation method was reduced at 400 °C under 5% H2 in He at a flow rate of 50 ml min−1 for 4 h with a ramping rate of 1 °C min−1. The obtained catalysts were denoted as AuPd/MgO–H.

2.3. Catalyst characterizations
Transmission electron microscopy (TEM) measurements were performed on a JEOL-2100F instrument operated at 200 kV to characterize the morphology of AuPd/MgO catalysts. The mean particle diameter was calculated from the average distribution by counting ca. 200 particles. The compositions and loadings of catalysts were analyzed by an inductively coupled plasma–atomic emission spectrometer (ICP-AES). Powder x-ray diffraction (XRD) patterns were recorded on a Rigaku D/Man-2500 V/Pc diffractometer using a filtered Cu Ka radiation source (k = 1.54056 Å) operated at 40 kV and 20 mA. Diffraction data were collected from 20° to 80° (2θ) at a scanning speed of 4° min−1. X-ray photoelectron spectroscopy (XPS) was performed on a VG Escalab 250 spectrometer equipped with an Al anode (AlKa = 1486.6 eV). All binding energies were referenced to the XPS peak of carbon 1s at 284.6 eV. The atomic ratios of the different elements were estimated using the ratio of the normalized peak intensities corrected with the atomic sensitivity factors (5.240 for Au4f, 4.462 for Pd3d, 0.711 for O1s, and 0.283 for Si2p).

2.4. Catalytic activity
Solvent-free aerobic oxidation of benzyl alcohol using O2 as the oxidant was carried out in a bath–type reactor operated under atmospheric conditions. Experiments were conducted using a three-necked glass flask (capacity 25 ml) equipped with a reflux condenser. After 5 ml benzyl alcohol and 0.02 g catalyst were added, the mixture
was stirred using a magnetic stirrer (1400 rpm) and heated in a silicon oil bath. Prior to reaction, the system was charged with ultrahigh purity O₂ with a 20 ml min⁻¹ flow rate in order to remove the air. After purification process, the reaction was trigger by immersing the reactor into a silicon oil bath. Once arriving the reaction time, the products were analyzed using an Agilent gas chromatograph 6890 equipped with a HP-5 capillary column (30 m long and 0.32 mm in diameter, packed with silica-based supel cosil), and flame ionization detector (FID). O-nitrotoluene was used as the internal standard. The conversion, selectivity and quasi-turnover frequency (qTOF) was defined as follows:

\[
\text{Conversion} \, (\%) = \frac{n_1(\text{reactant converted})}{n_2(\text{reactant in feed})} \times 100\%
\]

\[
\text{Selectivity} \, (\%) = \frac{n_3(\text{product formed})}{n_1(\text{reactant converted})} \times 100\%
\]

\[
\text{qTOF} (h^{-1}) = \frac{n_1(\text{reactant converted})}{n_4(\text{active sites}) \times t(\text{reaction time})}
\]

3. Results and discussion

3.1. Bimetallic AuPd/MgO catalysts
The nanocatalyst was firstly characterized by the TEM. As shown in figure 1(a), the nanoparticles (dark spot) present a uniform distribution on the surface of the support. To obtain the precise particles size, 300 particles acquired from catalyst sample was measured by the TEM calculation and the particle size distribution is illustrated at figure 1(c). The nanoparticles are spherical, with average diameter of 3.3 nm. Notable, some big particles in catalyst are unavoidable due to the various factors. In our experiment, the particle sintering might be ascribed to the electron beam irradiation in TEM operation. In addition, the catalyst precursor could not be homogeneous loaded on the support, which results in a nonuniform reduction in cold plasma treatment process, and hence generation some big particles (figure 1(b)). Compared to the traditional catalysts preparation process, the main advantage of this plasma technology focus on the 'low temperature', which can realize the reduction of nanoparticles at a mild environment, such as 30 °C (figure 1(d)), owing to the strong reduction characteristic of plasma state. Therefore, the obtained nanoparticles presents a small particles size of 3.3 nm. Also, the XRD measurements were performed to explore the catalysts that were prepared by the plasma.
reduction with different treatment duration. As shown in figure 1(d), the peak position (101) has no obvious change for the catalyst prepared by the plasma reduction and traditional thermal reduction method (250°C), while an apparent peak shift occurs for the catalyst sample prepared by the traditional impregnation that treated under 300°C. The high temperature treatment environment would decompose the original Mg(OH)$_2$ into MgO that resulted in a shift in peak position (200). In addition, the high temperature treatment also cause the particles aggregation, leading to appear a new peak at 39.8° position that could be assigned to the AuPd alloy nanoparticles [24]. Notably, there is no signal peak attributed to AuPd alloy nanoparticles for the plasma preparation samples, which derives from their small particles size.

In order to have a deep analysis for the catalyst, XPS characterization was performed to investigate the chemical valence of component elements. As shown in figure 2, the binding energy of Au 4f$_{7/2}$ in catalyst sample prepared by plasma reduction is closely to Au 4f$_{7/2}$ in sample prepared by traditional methods. Compared to the peak of Au 4f$_{7/2}$ in Au/MgO, the peak position of Au 4f$_{7/2}$ in AuPd species shifts a lower value, indicating the typical configuration of alloy AuPd on MgO support [12]. In AuPd alloy sample, the Au element receives electrons from the Pd element because of the former having a stronger electronegativity. Hence, we believe that the plasma reduction method could be used as an appropriate strategy to prepare the alloy catalyst.

3.2. Catalyst performance

The catalytic performance of the prepared AuPd/MgO catalyst was evaluated by the solvent-free aerobic oxidation of benzyl alcohol to benzaldehyde. For heterogeneous catalysis, reactions should be performed in the kinetics region [25] to obtain the real catalytic activity because reactions can be limited either by surface reactivity or diffusion of reactants. In this work, the diffusion factor (represented the mass transfer resistance) was firstly excluded by applying the different rotate speed during the catalytic reaction (1 wt% Au-Pd/MgO). As shown in figure 3(a), the conversion of benzyl alcohol almost retained unchanged when stirring speed exceeds 1500 rpm, though slight distinction could be observed. Therefore, it is believed that the reaction kinetics is fully determined by the catalytic activity of the AuPd/MgO nanocatalyst once the rotate speeds arriving 1500 rpm. In this case, the TOF of the reaction was calculated under three different rotate speeds. They present the similar variation tendency and gradually decrease with the increased reaction time, indicating the negligible mass transfer resistance. Also, the catalytic reaction results show that they possess a quite high selectivity (90%) for the benzaldehyde under the high rotate speed except for the reaction proceeds at the 1500 rpm in initial stage (75%), figure 3(b). It is worth noting that the selectivity begins to decrease with the extended reaction time, which might be ascribed to the further oxidation of benzaldehyde.

When performing the heterogeneous catalytic reaction in the kinetic regions [25], the conversion of reactants at a fixed duration is proportional to the number of reactive sites. We therefore investigate the influence of catalyst amount on the conversion of benzyl alcohol. As shown in figure 4, the conversion gradually increases with more catalyst present in the reaction system. Obviously, the more catalyst would bring the more active sites that improve the reaction conversion. Inset of the figure 4 shows the linear relationship between the
amount of added nanocatalyst and the reaction conversion, indicating no mass transfer resistance in reaction process.

In AuPd catalyst preparation process, the plasma reduction temperature is fairly important for determining particles size, morphology and so on, which are closely related to their catalytic activity. In this study, we prepared the AuPd alloy catalyst under the different reduction temperatures and explored their catalytic activity including the conversion, selectivity and TOF. As shown in figure 5(a), the untreated catalyst (raw catalyst) has a relative low reaction rate compared to the plasma reduced catalyst and their catalytic activity quickly declines after reaction 4h. The AuPd catalyst prepared by plasma reduction exhibits a higher conversion of benzyl alcohol compared to the untreated catalyst. The highest conversion of benzyl alcohol for the plasma reduced catalyst arrives to 34.4% after reaction 6h while only 18% conversion using the untreated catalyst. In addition, the sample treated at 30°C shows the superior catalytic performance among the plasma reduced samples, which mainly attributes to the low temperature treatment condition that could prevent particles aggregation and sintering, leading to a relatively high catalytic conversion in identical experiment condition. Also, the selectivity of benzaldehyde in catalytic reaction was evaluated and the results showed the similar variation tendency for four AuPd catalyst samples, figure 5(b). In initial reaction stage, the untreated catalyst almost has no selectivity for the benzaldehyde and then gradually increase to 100% after reaction 7h. For the plasma reduced samples, they exhibit the high selectivity of benzaldehyde and present a different initial value due to the different reduction temperature. Especially for the AuPd catalyst prepared in 90°C plasma reduction, its initial selectivity of benzaldehyde arrives to 90% that suggests an excellent catalytic performance. Being similar the untreated
sample, the plasma reduced AuPd catalysts presents the gradual improvement for the benzaldehyde selectivity that finally reaches to 100% after reaction 7h. In fact, the selectivity of reaction is closely related to metallic state in catalyst. The untreated catalyst sample, metal salt is their primary active phase and hence has a low catalytic selectivity in initial stage. As the reaction progress, the produced benzaldehyde could reduce metal salt into corresponding metal species, which would improve the selectivity of benzaldehyde in the subsequent reaction. For other plasma reduced samples, the improved temperature would increase the reduction degree for the metal salt that leads to a high selectivity of benzaldehyde. As shown in figure 5(d), the vertical axis represents the reduction degree and horizontal axis is plasma reduction temperature. It is found that the reduction degree has a significant linear correlation with the plasma reduction temperature, suggesting the importance of plasma reduction conditions.

The catalytic activity of the prepared AuPd catalyst was characterized by calculating TOF. As shown in figure 5(c), the AuPd catalyst prepared by plasma reduction at 30 °C exhibits the highest TOF value 9871.6 h⁻¹, which is almost twice catalytic activity compared to the untreated sample. As description above, the low temperature is favorable to maintain the small particles size and high monodispersity due to the low input energy. Thus, it is obvious that the low temperature plasma reduction could prepare the high-quality AuPd nanoparticles catalysts.

All above discussion indicate that the noble metal salt could be reduced into corresponding metal nanoparticles by plasma reduction treatment, which largely decreases the reduction temperature in comparison of the traditional impregnation methods. This method could not only avoid the particles sintering but also decrease the interference of Cl⁻, which is usually introduced into the catalyst from precursor and causes the particles migration, leading to a negative effect for the catalytic activity. Therefore, this low temperature plasma reduction technology could realize the high-quality catalyst preparation and would effectively improve their catalytic activity.

In addition, we also compared the catalytic performance of the catalysts prepared by the plasma reduction and traditional high temperature H₂ reduction. The experiment results are illustrated in figure 6. Figure 6(a) shows the AuPd catalyst obtained by plasma reduction method has more superior catalytic performance both reaction conversion and TOF compared with the catalyst prepared by the traditional methods. The former reaction conversion improves about 19% and TOF value (initial 0.5h) exceeds 1.9 times than the latter. Figure 6(b) shows the selectivity of benzaldehyde by using two different AuPd catalysts. They exhibit almost
similar selectivity that indicates the low temperature plasma reduction method could achieve the highly reduction as well as the traditional high temperature method.

4. Conclusion

This work developed a novel low temperature plasma reduction technology to prepare the high quality AuPd alloy catalyst. The HAuCl4 and PdCl2 were directly decomposed reduction into the AuPd alloy nanoparticles by plasma reduction method. The low temperature treatment condition would prevent the particles migration and maintain the small particles size well that is favorable of their high catalytic activity. Compared to the traditional H2 reduction methods, AuPd catalyst prepared by this low temperature plasma reduction exhibits the higher conversion and TOF, similar selectivity and lower energy consumption. Therefore, we believe this low temperature plasma reduction technology could be used as an excellent candidate for the preparing the high-performance alloy catalyst in future.

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Figure 6. The time–activity profile for selective benzyl alcohol oxidation under aerobic conditions for (a) benzyl alcohol conversion, TOF (h−1) (b) benzaldehyde selectivity. Reaction conditions: benzyl alcohol, 5 ml; catalyst, 20 mg; O2, 20 ml min−1; temperature, 393 K; rotate speed, 1400 rpm.
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