P123-stabilized Au–Ag alloy nanoparticles for kinetics of aerobic oxidation of benzyl alcohol in aqueous solution

Xuemin Huang [a], Xueguang Wang [a,*], Xiaoshu Wang [b], Xinxing Wang [a], Mingwu Tan [a], Weizhong Ding [a], Xionggang Lu [a,*]

[a] Shanghai Key Laboratory of Modern Metallurgy and Material Processing, Shanghai University, Shanghai 200072, China
[b] Center of Modern Analysis, Nanjing University, Nanjing 210093, China

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ABSTRACT

Colloidal Au–Ag alloy nanoparticles with various Ag/Au molar ratios were first prepared by a co-reduction method in P123 aqueous solution and characterized by UV–vis, TEM, and XPS. The prepared Au–Ag alloy nanoparticles were substantially stable and had comparable particle sizes (3–4 nm) for erobic oxidation kinetics of benzyl alcohol. The addition of Ag not only significantly enhanced the reaction rate but also increased the apparent activation energy (E_a) compared to that for monometallic Au nanocatalysts. The kinetics investigations indicated that on the pure Au sites, the oxidation of benzyl alcohol followed 1.5-order reaction kinetics, while on Au sites adjacent to Ag atoms, it followed 0.5-order reaction kinetics. The presence of Na_2CO_3 greatly improved the catalytic activity of Au–Ag nanocatalysts but decreased the selectivity to benzaldehyde.

1. Introduction

Au nanocatalysts have attracted considerable attention because of their nontoxic nature and their ability to catalyze many important chemical reactions, such as low-temperature oxidation of CO [1,2], epoxidation of alkenes [3,4], oxidation of alcohols [5–8], homocoupling of phenylboronic acid [9], and synthesis of H_2O_2 [10,11]. For practical catalytic applications, bimetallic alloy nanoparticles of Au with a second metal component have been extensively investigated to improve their catalytic properties by forming new active sites, improving the electronic structure and inducing synergistic effects. Among these bimetallic nanocatalysts, Ag-doped Au alloy nanocatalysts have been reported to show catalytic performance for oxygen transfer reactions superior to that of their monometallic counterparts, and the degree of enhancement is strongly correlated with the surface silver content [12–20]. However, these Au–Ag nanoparticles are commonly stabilized with metal oxides or activated carbon as supports, resulting in inherent heterogeneity of the reaction and inaccessibility of the substrate to the catalysts. In addition, the catalytic properties are influenced not only by the individual chemical natures of Au and the support, but also by complex interactions between them [21–23]. So, the nature of the active sites and the catalytic roles of Ag species in

Au–Ag alloy nanocatalysts for aerobic oxidation reactions are still ambiguous, which are of fundamental importance.

Monodisperse colloidal metal nanocatalysts for various reactions combining the advantages of both homogeneous and heterogeneous catalysts have received significant interest [24–28]. The active sites on the surfaces of metal nanoparticles with weak interactions with the organic stabilizers in solution can be fully exposed to the reactants and exhibit catalytic activities under mild reaction conditions. Well-dispersed colloidal Au nanoparticles in aqueous solution have been reported as catalysts for aerobic oxidation of glucose [29], dehydrogenation of formic acid [30], and aerobic oxidation of alcohols [31–35] at near-ambient temperatures, and the catalytic properties are governed by the intrinsic chemical properties of Au nanoparticles. This information will provide an ideal opportunity for us to better understand fundamental aspects of the mechanism and kinetics of the reaction and the correlation between Au and Ag species for aerobic oxidation of alcohols on Au–Ag alloy nanocatalysts.

Au–Ag alloy nanoparticles are currently synthesized in aqueous solution or organic solvents mainly through co-reduction of Au and Ag salts in the presence of a stabilizing agent [36–43]. The synthesis conditions strongly influence the reduction potentials and the effectiveness of the stabilizing agent, resulting in more complexity in size tuning for the alloy nanoparticles than for the monometallic ones. Most of the current preparation methods are unable to decouple size and composition control, that is, producing alloy

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nanoparticles with the same composition but different sizes, or the same size with different compositions. In addition, due to the propensity to form insoluble AgCl(s) ($K_{sp} = 1.6 \times 10^{-10}$), it is very hard to increase the concentration of reactants when using HAuCl$_4$ as the gold precursor. The catalytic properties of the alloy nanoparticles are also associated with the stabilizing agents. For example, thiol-stabilized metal nanocatalysts can be poisoned because of their strong interaction with the particle surface and tendency to form a monolayer with high packing density [43–45]. Tetraalkyl-ammonium-protected nanoparticles tend to aggregate, resulting in unsatisfactory long-term stability and the loss of their original properties [46]. Up to now, only a few applications of colloidal Au–Ag alloy nanoparticles in catalytic reactions have been reported, because of the difficulty of stabilizing the fragile systems without modification of their intrinsic nature. The synthesis of monodisperse Au–Ag alloy nanoparticles with controlled particle sizes and compositions is still of key importance in the study of catalytic mechanism and kinetics of the reaction. Recently, colloidal Au–Ag nanoparticles stabilized with poly(N-vinyl-2-pyrrolidone) (PVP) in aqueous solution have been reported as catalysts for oxidation of benzyl alcohol using molecular oxygen [40]. Nevertheless, PVP-stabilized Au–Ag alloy nanoparticles showed the catalytic activity only in the presence of a strong base (e.g., KOH or K$_2$CO$_3$).

In this paper, we first report a facile method for preparing highly stable monodisperse Au–Ag alloy nanoparticles of varied Ag/Au molar ratios with a high total metal concentration of 5×10^{-4} M by simultaneous reduction of HAuCl$_4$ and AgNO$_3$ mixtures with NaBH$_4$ in an aqueous solution of a typical amphiphilic triblock copolymer, poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (P123; EO$_{20}$PO$_{70}$EO$_{20}$). The copolymer-assisted nanoparticles are known to be stabilized through weak steric force, so that the reactants can access the particle surface for catalytic reactions [19,47]. The prepared Au–Ag nanoparticles have comparable particle sizes of 3–4 nm and show a certain activity for benzyl alcohol as a model reaction with molecular oxygen in the absence of base. This is highly desirable as a way to measure the aerobic oxidation kinetics of benzyl alcohol and to investigate the roles of Ag in Au–Ag alloy nanocatalysts.

2. Experimental

2.1. Chemicals and preparation of Au–Ag nanoparticles

P123 (EO$_{20}$PO$_{70}$EO$_{20}$, M_{av} = 5800) and NaBH$_4$ were purchased from Aldrich and other chemicals of reagent grade were from Sinopharm Chemical Reagent Co., Ltd. All chemicals and solvents were used as received without further purification.

The Au$_{1-x}$Ag$_x$ alloy nanoparticles (x: Ag mole fraction) with various Ag/Au molar ratios (0::1–0.50::0.50) were prepared through the simultaneous reduction of HAuCl$_4$ and AgNO$_3$ in a P123 aqueous solution at room temperature (293 K) using NaBH$_4$ as the reducing agent. Typically, an appropriate amount of AgNO$_3$ aqueous solution (1.5×10^{-3} M) was first introduced into P123 aqueous solution (25 mL) and stirred vigorously for 5 min. Then, HAuCl$_4$ aqueous solution (1.5×10^{-3} M) was added to the AgNO$_3$/P123 solution under vigorous stirring. At this time, the solution became clear and light yellowish, and no flocculation due to the formation of AgCl was observed. Immediately, 1 g/L NaBH$_4$ aqueous solution (15 mL) was added very slowly to the mixture of HAuCl$_4$ and AgNO$_3$ in the P123 aqueous solution under vigorous stirring within 15 min. Finally, the solution was exactly adjusted at 100 mL with deionized water and stirred for 60 min further. The ratios of molar concentrations of P123 monomer units to total metal atoms, [P123]/[Au + Ag], were in the range of 5–20.

2.2. Characterization

UV–vis absorption spectra were recorded with a UV-2501 spectrophotometer at ambient temperature, with P123 aqueous solution as a standard for background correction. Before measurement, 1 mL of the colloidal solution was diluted five times with deionized water.

Transmission electron microscopy (TEM) images were obtained with a JEM-2010F transmission electron microscope operating at 200 kV. The specimens for TEM measurements were prepared by dropping the colloidal dispersion onto carbon-coated copper grids and dried for 1 day in a desiccator. Size distributions of the particles were obtained by counting ca. 200–250 particles in TEM images.

X-ray diffraction (XRD) was carried out on a Rigaku D/MAX-2500 apparatus using Cu Kα radiation (λ = 0.15418 nm) at a voltage of 40 kV and a current of 40 mA. The nanoparticle colloid was dropped on the glass substrate and dried to form a uniform film and finally was washed with deionized water to remove inorganic salts and parts of the surfactant.

X-ray photoelectron spectra (XPS) of the particles were measured using a PHI 5000 VersaProbe spectrometer equipped with monochromatized Al Kα radiation (hv = 1486.6 eV) operated at a pressure of ca. 1×10^{-9} Torr. The samples for the XPS measurements were prepared on an aluminum sheet by centrifuging the colloids and washed to remove some of the excess P123 with deionized water. The spectra for the nanoparticles were calibrated using the most intense C1s peak of P123 as an internal standard [32,40].

2.3. Oxidation reaction of benzyl alcohol

The oxidation of benzyl alcohol was carried out with O$_2$ in a three-necked flask of 50 mL with a reflux condenser, and the flask was placed in a thermostatic bath with a magnetic stirrer. In a typical experiment, metal nanoparticle colloid (20 mL) was heated at the set temperature with an accuracy of ±0.1 K and bubbled with pure O$_2$ for 60 min. Then, an appropriate amount of benzyl alcohol was added into the reaction mixture, and the oxidation reaction was started under vigorous magnetic stirring by bubbling O$_2$. The reactions were monitored by sampling the reaction mixture (0.5 mL) at fixed intervals. The reaction mixture was immediately quenched with 2 M HCl aqueous solution (0.5 mL) and extracted three times with ethyl acetate (5 mL). The obtained organic layer was dried with Na$_2$SO$_4$ and analyzed by a CP-3800 gas chromatograph with an FID detector using the external standard method.

3. Results and discussion

3.1. Preparation of Au–Ag nanoparticles

The Au–Ag alloy nanoparticles were prepared through the simultaneous reduction of HAuCl$_4$ and AgNO$_3$ in a P123 aqueous solution with NaBH$_4$ as reducing agent. It is well known that in preparing Au–Ag bimetallic particles in aqueous solution, the most troublesome problem is the precipitation of AgCl when the two metallic solutions are mixed [48]. To solve it, AgNO$_3$ was first introduced into P123 aqueous solution to stabilize Ag$^+$. As a result, no precipitation or turbidity was observed when HAuCl$_4$ precursor solution was added into AgNO$_3$/P123 aqueous solution, although [Ag$^+$][Cl$^-$] was much higher than K_{sp} of AgCl(s). This result was also confirmed by UV–vis spectra of the mixture solutions (not shown), in which no absorption band appeared at about 295 nm [49]. Very importantly, once HAuCl$_4$ precursor is introduced into the AgNO$_3$/P123 aqueous solution and appears homogeneous, dropping of