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Original Research Paper

Synthesis of heterogeneous Ag-Cu bimetallic monolith with different mass ratios and their performances for catalysis and antibacterial activity

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ABSTRACT

Combination of two or more metallic particles along with high surface area and porous structure exhibits enhanced catalytic as well as antibacterial activity. Here, Ag-Cu bimetallic monoliths were synthesized by nanocasting method by strictly adjusting the molar ratio of Ag-Cu. This work is mainly focused on the effect of molar ratio (Ag:Cu) on surface area (14–110 m^2/g) and porous size of bimetallic monoliths, which has great influence on enhancement of catalytic and antimicrobial activity. The catalytic activity of bimetallic Ag-Cu monoliths was evaluated for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in the presence of excess $NaBH_4$. The reaction rate follows pseudo-first order for reduction of 4-NP with a reduction efficacy of ~95%. The effect of Ag:Cu molar ratio and reaction conditions on the rate of reaction were investigated. In comparison with novel monometallic silver monoliths, bimetallic Ag-Cu monoliths exhibit high catalytic performance on the reduction of 4-NP. These heterogeneous catalysts were effortlessly recovered and reused (up to 8 cycles) after completion of catalytic reaction. As bimetallic Ag-Cu particles are well-known for antibacterial activity, so bactericidal properties of synthesized monoliths are tested against *E. coli* and *B. subtilis* bacteria by minimum inhibitory concentration method (MIC). The calculated EC_{50} (half maximum effective concentration) after completion of incubation period, against *E. coli* and *B. subtilis* were 22.87 ± 0.015 and 23.33 ± 0.09 respectively using Ag/Cu-3 bimetallic monolith.

1. Introduction

Manufacturing of various antipyretic and analgesic drugs requires some strong transitional aromatic compounds. These compounds are also used remarkably as a photographic developer, anticorrosion-lubricant and hair-dyeing agent [1]. Thus, being a standard precursor substance for aromatic amino compounds, a novel and cost-effective process for catalytic reduction of hydrogen of nitro-aromatic compound is always in demand. Also, nitro aromatic compounds (like nitrophenols) are considered as most common organic pollutant in waste water introduced from pesticides, dyes, paper, pharmaceuticals and other chemical industries [2]. Nitrophenols has been considered as most toxic and hazardous pollutants by the US Environmental Protection Agency [3]. For removal of nitrophenols from water, an environment friendly system is required. Consequently, to convert these toxic pollutants into valuable amines, many research has been done on the synthesis of monometallic or bimetallic nanoparticles/nanocomposites [4–8]. Even if metallic particles show good catalytic activity, but their applicability on a large scale was limited due to their high cost. To overcome this problem, bimetallic nanocomposites (two different metals bound to form one composite) are formed either in core-shell structure, alloys or mixture of two metals. Bimetallic nanocomposites are more attractive than individual metallic nanocomposites mostly because of enhanced catalytic properties and they exhibit different thermal, magnetic, electrical and optical properties due to synergistic or fine-tuning effects [9–11]. Bimetallic composites can be synthesized by reduction of two different metal ions at the same time in the presence/absence of surfactant/polymer [12,13] or straight reduction of one metal ion over the nuclei of other metal [14,15]. Based on different synthesis procedures, both alloy or core-shell structures can be synthesized. Some reported bimetallic combinations (like Ag-Cu, Ag-Au, Pd-Pt and Au-Pd) have applications in heterogeneous catalysis, fuel cell electrocatalysis and sensing [16].

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Metallic elements like silver and copper are traditionally well known as bactericidal. The properties of these metal particles get amplified at nanoscale due to high surface area and volume ratio [17,18]. Metallic nanoparticles have a special potential to interact with microbial membrane, due to which they can be used as disinfectants for waste water treatment. Chen et al. have reported the synthesis of Cu-Ag core shell particles by chemical reduction of silver over commercial micrometric Cu particles to study the antioxidation and antibacterial properties [19]. Rousse et al. have studied the antibacterial properties of Cu-Ag bimetallic nanopowders using sonochemically synthesized Cu nanoparticles followed by a coating of silver ions [20].

With regard to realistic applications as a catalyst, porous materials became a hot topic for thorough study. Mesoporous metal nanoparticles as a catalyst have the advantage of very high surface area and large pore size distribution, which help in mass transfer and increase in a number of active sites on the surface of nanomaterial. For catalytic function, numerous promising procedures can be used to synthesize mesoporous materials. Even though numerous papers have been published on synthesis of noble mesoporous metal composites, but hardly some are focused on bimetallic mesoporous monoliths like sliver with copper due to difficult and complex approach needed for the synthesis [21–23].

In this work, synthesis of mesoporous Ag-Cu bimetallic monoliths with a varying molar ratio of Cu has been reported using previously synthesized silver monoliths. Synthesized porous Ag-Cu monoliths have been used as a heterogeneous catalyst to study the catalytic reduction of the nitroaromatic (4-NP) compound. Adding up to this, antibacterial activity against both gram positive and negative bacteria was also studied by minimal inhibitory concentration (MIC) using bimetallic monoliths.

2. Materials

Silver nitrate, ammonia (28–30%), cupric nitrate, nitric acid (69%), sodium hydroxide and sodium borohydride were purchased from Merck. Polyethylene glycol (MW 35,000 g/mol) and cetyltrimethyl ammonium bromide were purchased from Sigma Aldrich. Tetraethoxysilane and 4-nitrophenol (4-NP) were purchased from Alfa Aesar. All the chemicals and reagents used in this study are of analytical grade and used without further purification.

2.1. Preparation of Ag-Cu monolith

The detailed procedure for the synthesis of silver monolith has been discussed in our previous paper [24]. Cupric nitrate was used as precursor for Ag-Cu monolith synthesis. Cupric nitrate sol (in different molar ratios, which is defined in Table 1) along with a 0.1 M $NaBH_4$ was impregnated into silver monoliths in the presence of nitrogen atmosphere. Later, wet impregnated monoliths were dried for 10 h at 80 °C with a heating rate of 1 °C/min. Impregnation procedure was repeated for at least five times to get homogeneous impregnation of cupric solution into the pore of silver monoliths and to get solid Ag-Cu monoliths. At the time of drying, oxidation of Cu may result in the formation of Cu_2O in a little amount on monolithic surface which is confirmed by UV–Vis spectroscopy and XRD analysis. Afterwards, composites of Ag-Cu monoliths were finally calcined at 200 °C for 6 h at the heating ramp of 1 °C/min.

2.2. Instrumentations

X-ray diffraction analysis (XRD) was analyzed using Pan Analytical (X'Pert-pro) diffractometer using Cu Kα radiation (λ = 1.5406 Å). The sample morphology and elemental analysis were studied by FESEM and EDS by Hitachi SU 8010 field emission scanning electron microscope operating at 30 kV. Detailed structural analysis of bimetallic nature of Ag-Cu monolith was done using a high-resolution transmission electron microscope (HRTEM) (FEI TECHNAI-G2 operating at 200 kV). The oxidation state of Ag-Cu monolith was determined from PHI 5200 mode X-ray photo- electron spectroscopy (XPS) system. Surface area and pore-size distributions were evaluated through Brunauer–Emmett–Teller (BET) method and Barrett–Joyner–Halenda (BJH) model by using BELSORP MINI-II (Bel, Japan) surface area and pore size analyzer. Before each set of measurements, samples were degassed at 200 °C in vacuum for more than 3 h. The excitation of 4-NP and kinetic parameters were stately studied using a Champion UV- 500 spectrophotometer.

2.3. Antibacterial studies

The antimicrobial activity of synthesized mesoporous Ag-Cu bimetallic monolith (with varying molar ratio) was evaluated by minimum inhibitory concentration (MIC) method against *E. coli* (MTCC-77) and *B. subtilis* (MTCC-441). Luria broth (LB) was taken as a medium for growing and preserving the bacterial liquid cultures. 10 ml of bacterial culture was developed from a single colony. 5 ml of LB was used to inoculate the bacterial cells in glass test tubes. Different Ag-Cu bimetallic monoliths (0–660 μg) was added to the bacterial culture and the cultures were transferred to the incubator with constant agitation (130 rpm) for 24 h at 37 °C (under aerobic conditions). Optical density of bacterial culture was noted at 600 nm after completion of action. The outcomes were drew by mean of 3 mutually independent experiments. EC_{50} (half maximum effective concentration), was also determined to measure the concentration of bimetallic monolith required to attain the 50% reduction in bacterial growth.

2.4. Catalytic reduction of nitro compound

A catalytic stability and activity of heterogeneous Ag-Cu bimetallic catalyst was evaluated for reduction process of 4-NP. The standard procedure for reduction reaction as used by Pradhan et al. [25] was performed in a quartz cuvette (3 ml). Initially, 200 μL of 0.1 M freshly prepared $NaBH_4$ solution was mixed to a solution containing 30 μL of 0.01 M 4-NP and 2 mL of deionized water. The reaction process does not start at all without addition of catalyst. But with the addition of catalyst, it drives to accomplish to conversion 4-AP. The solution was mixed by frail shaking after addition of catalyst and excitation of 4-NP was investigated by UV–Vis spectrophotometer.

Table 1
Textural properties of Ag-Cu monoliths.

Monolith	Ratio (Ag:Cu)	S_{BET} ($m^2\ g^{-1}$)	Mesopore diameter (nm)	Micropore diameter (nm)	Mesopore volume ($cm^3\ g^{-1}$)	Micropore volume ($cm^3\ g^{-1}$)
Ag/Cu-0	1:0	14 ± 5	25.06	–	0.04	–
Ag/Cu-1	1:0.5	39 ± 5	21.2	1.2	0.27	0.038
Ag/Cu-2	1:0.75	52 ± 5	12.4	1	0.13	0.055
Ag/Cu-3	1:1	110 ± 5	8.3	1.3	0.25	0.050

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