Applied Catalysis B: Environmental 203 (2017) 505–514

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Random alloy nanoparticles of Pd and Au immobilized on reducible metal oxides and their catalytic investigation

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ARTICLE INFO

Article history:
Received 20 July 2016
Received in revised form 13 October 2016
Accepted 18 October 2016
Available online 19 October 2016

Keywords:
Dendrimer
Metal nanoparticles
Mesoporous metal oxide materials
Oxidation
Activity

ABSTRACT

Well-dispersed, random alloy, palladium-gold nanoparticles (2.66 ± 0.51 nm) were immobilized onto several reducible mesoporous transition metal oxide materials. The composites (palladium-gold nanoparticles immobilized onto mesoporous transition metal oxide (PdAu–MTMO)) were characterized through several analytical methods such as UV–vis spectroscopy, BET, XRD, FT-IR, ICP-OES, TEM and TPR analyses. Catalytic oxidation of morin (quercetin) was performed as a model reaction in the presence of hydrogen peroxide to investigate the synergic catalytic activity of the composite. Silica was used as inert support to isolate the catalytic activity of the metal nanoparticles (32.69 ± 9.93 kJ mol^{-2}). Synergistic interaction of PdAu–MTMO was mechanically described according to Langmuir-Hinshelwood and Mars-van Krevelen approaches. The TOF of PdAu–Co_3O_4 (6073.23 ± 85.01 s^{-1} mol^{-1}) was considerably larger than that of random alloy nanoparticles (PdAu–SiO_2 (25.71 ± 2.35 s^{-1} mol^{-1})). The Arrhenius-type plot was constructed to determine the synergistic activity of the composite, where PdAu–Co_3O_4 described the best synergistic interaction.

1. Introduction

Since the Mobil Oil Corporation's discovery over 20 years ago, countless mesoporous materials were produced and considerable effort was applied to improve its physicochemical features [1,2]. Several types of mesoporous materials were reported based on the synthesis methods [3,4], the doping materials [5], and the composite materials [6]. The use of mesoporous materials expanded to a large scientific field based on their features [7,8]. The thermal stability described by most of the mesoporous materials increase their application in several industries such as manufacturing [9]. The tunable structural properties of mesoporous materials justified their interest in catalysis [10,11]. The mesoporous transition metal oxide (MTMO) materials demonstrated a wide catalytic potential in diverse oxidation and reduction reactions due to the multiple oxidation states of the transition metal [12].

A common synthesis approach of MTMO materials is conducted in an aqueous medium, which results in thermally unstable and amorphous wall materials [13,14]. Suib's group recently reported the synthesis approach of several mesoporous transition metal oxide materials using sol-gel chemistry in a non-aqueous solvent [15]. The hydrolysis and condensation of oxo-clusters were controlled by NO_x chemistry taking place *in situ* due to the thermal decomposition of nitrate ions [16,17].

The catalytic activity of palladium-gold random alloy nanoparticles encapsulated into dendrimer cavities was recently reported by our group [18]. The catalytic activity was investigated through morin oxidation as a model reaction in the presence of hydrogen peroxide. The adsorption isotherm of the reactants onto the alloy nanoparticles surfaces were investigated through the Langmuir-Hinshelwood mechanism which described the alloy nanoparticle activities relative to the alloy ratio and the optimization of their activities through the performed model reaction [18].

Here, we report the synthesis of several mesoporous transition metal oxide materials through the inverse micelle approach using nitrate ions to prevent condensation. It was reported that the heat treatment resulted in pore expansion of those mesoporous materials [15]. Therefore, the heat cycling was subdivided into four steps where 450 °C will be the last heat treatment temperature. The catalytic activity shown by mesoporous transition metal oxide materials was reported in a large number of investigations [19–22]. The synthesis of CeO_2, NiO, Fe_2O_3, Co_3O_4, MnO_2, and SiO_2 will be performed. The encapsulated random alloy (PdAu) nanoparticles will be immobilized on these mesoporous transition metal oxides. The catalytic oxidation of morin (natural flavonoid) will be performed as a model reaction [23,24]. A comparative evalu-

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http://dx.doi.org/10.1016/j.apcatb.2016.10.053
0926-3373/

ation related to the catalytic activity of the mesoporous transition metal oxide materials and their supported alloy nanoparticles will be described to identify the most active combination. The catalytic process will be monitored through UV–vis spectroscopy by recording the absorbance peak at λ 410 nm (morin maximum absorbance) [25].

2. Experimental section

2.1. Mesoporous metal oxide materials

A generic inverse micelle approach developed by Suib's group was followed to synthesize the mesoporous metal oxide materials [15]. Tetraethyl orthosilicate (≥99.0%), manganese (II) nitrate tetrahydrate (≥99.0%), iron (III) nitrate nonahydrate (≥98.0%), cobalt (II) nitrate hexahydrate (≥98.0%), nickel (II) nitrate hexahydrate (≥99.0%), and cerium (II) nitrate hexahydrate (≥99.0%) (Sigma-Aldrich), were used as metal precursors. The oxo-cluster aggregation was prevented using the surfactant, Pluronic® P-123 (Sigma-Aldrich), as a nanoreactor. The surfactant was mixed with 1-butanol (Rochelle chemical, ≥99.5%) and nitric acid (Rochelle chemical, ≥55.0%). The metal salt was added to an acidified alcoholic solution of P-123 while stirring. The synthesis of cobalt oxide was conducted using 4.08×10^{-4} mol (2.37 g) of P-123 mixed with 0.23 mol (21.04×10^{-3} L) of 1-butanol. The mixture was acidified with 0.038 mol (2.29×10^{-3} L) nitric acid. Exactly, 0.02 mol (5.82 g) of cobalt nitrate hexahydrate was added to the acidified alcoholic solution. The gel solution was heated to 120 °C for 4 h under air. The obtained powder was washed with an excess of ethanol (Associated Chemical Enterprises, ≥95.0%), centrifuged and dried in a vacuum oven overnight at 60 °C. The heating cycle was subdivided into four steps proceeding to different temperatures 150 °C (12 h), 250 °C (4 h), 350 °C (3 h), and 450 °C (2 h), respectively. Prior to proceeding with the next heating cycle, the powder was cooled to room temperature. The reactant amounts used for the synthesis of CeO_2, NiO, Fe_2O_3, MnO_2, and SiO_2 is shown in Supporting information (Table 1S). Silica was calcined directly at 450 °C for 4 h, however, all the other materials were subjected to heating cycles.

2.2. Dendrimer encapsulated random alloy (PdAu) metal nanoparticles

The synthesis approach of the encapsulated random palladium-gold nanoparticles was adapted based on Crooks's report [26]. In light of our previous investigation, an optimal molar ratio of palladium-gold (alloy) nanoparticles ($Pd_{75}Au_{35}$/DENs-OH) was used to prepare the random alloy nanoparticles [18]. The fifth generation hydroxyl terminated poly(amido-amine) dendrimer was used as a template for the encapsulated random alloy nanoparticle synthesis. A stock solution of 10^{-4} M dendrimer (Dendritech®, 4.98 wt.% solution in methanol) contained in 15×10^{-3} L of deionized water was used as a template to encapsulate the random alloy nanoparticles. The methanol solution was removed *in vacuo* at room temperature. Exactly, a 75 molar ratio of palladium (potassium tetrachloropalladate, ≥98.0% (Sigma-Aldrich)) and a 35 molar ratio of gold (chloroauric acid, ≥99.9% (Sigma-Aldrich)) ions were added into the dendritic solution, respectively. To assure the interaction of palladium ions with the internal tertiary amine groups, the mixture was subjected to stirring for 30 min. An alkaline solution of sodium borohydride (≥98.0%, Sigma-Aldrich) was added to initiate the metal ion reduction. For an efficient reduction of the metal ions, the sodium borohydride was added in excess. The reduction of both metal ions complexed in the dendrimer structure resulted in the encapsulated random alloy nanoparticles [26]. Dialysis membrane (Snakeskin® Dialysis Tubing (10,000 MWCO)) was used to remove the excess reducing agent.

2.3. Immobilization of random alloy nanoparticles onto mesoporous metal oxide

The immobilization of the encapsulated metal nanoparticles on the mesoporous metal oxide materials was performed following the Somorjai group's report [27]. The mesoporous metal oxide material was mixed with the encapsulated random alloy nanoparticle solution. The mixture was stirred for 30 min prior to sonication for 3 h using a digital ultrasonic cleaner (Celsius Scientific cc). The slurry was centrifuged at 15,000 rpm for 10 min (Lasec (HERMLE Labortechnik GmbH)). The precipitate was dried at room temperature for 2 days and heated at 100 °C in an oven for 4 h. The percentage of the palladium-gold nanoparticles immobilized onto the metal oxide pores were estimated through inductively coupled plasma optical emission spectrometry (ICP-OES) analysis in *aqua regia* medium [28]. The amount of alloy on mesoporous metal oxide materials range $(10–30) \times 10^{-3}$ g was mixed with 4×10^{-3} L of *aqua regia* ($HCl/HNO_3 = 3/1$ (v/v)) and diluted at 50×10^{-3} L of deionized water. The solution was filtered prior to analysis.

The mesostructure of the mesoporous transition metal oxide materials was evaluated through X-ray diffraction (XRD) analysis (Rigaku Mini Flex 600). The surface area, pore volume, and pore diameter were investigated by Brunauer–Emmett–Teller (BET) analysis (Micromeritics Tristar) based on isothermal adsorption and desorption of nitrogen gas onto the mesoporous metal oxide materials surface. Amounts of 0.1–0.3 g of each synthesized mesoporous material were degassed overnight prior to analysis. The metal-oxygen stretching vibration was analyzed through Fourier transformed infrared (FT-IR) analysis using FT-IR spectroscopy (Bruker Tensor 27). The micrograph analysis of mesoporous metal oxide materials was conducted using a high-resolution transmission electron microscopy (HR-TEM) (JOEL JEM–2100F electron microscope). Small quantities of mesoporous materials were diluted in ethanol and sonicated for 30 min. A copper grid was used to sample the solution and dried at room temperature prior to transmission electron microscopy analysis. The reducibility of the synthesized mesoporous metal oxide materials was evaluated by temperature programmed reduction (Micromeritics AutoChem II). Approximately 0.03-0.04 g of the synthesized materials (MTMO and PdAu–MTMO) was weighted and placed in the reactor to perform the temperature programmed reduction (TPR) analysis. The TPR analysis was performed using a gas composition of H_2-He, the temperature range was 50–900 °C where the heat flow rate was 10 °C min^{-1}.

2.4. Catalytic investigation

An aqueous morin (≥98.0%, Sigma-Aldrich) solution of 2.5×10^{-3} M was prepared in an alkaline medium using a carbonate buffer as a stock solution. Exactly, 60×10^{-6} M of morin was used to perform all the investigations. The morin adsorption and hydrogen peroxide stability during the reaction process were assured by using 1×10^{-3} M of carbonate buffer consisting of sodium carbonate (Merck laboratories, ≥98.0%) and sodium bicarbonate (Merck laboratories, ≥99.5%) maintaining the solution pH at 10. The mesoporous metal oxide slurry was mixed with morin solution and allowed to stir for 300 s. The desired amount of hydrogen peroxide (Merck laboratories, 30–35%) was added last to initiate the process. The hydrogen peroxide concentration was determined by titration [29]. Time intervals of 180 s were allocated to the reaction prior to the measurements. Deionized water from an in-house Milli-Q system (18 MΩ cm) was used to prepare all solutions.