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Sonochemical synthesis of PdO@silica as a nanocatalyst for selective aerobic alcohol oxidation

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ABSTRACT

A sonochemical method has been employed for the synthesis of palladium oxide (PdO) nanoparticles deposited on silica nanoparticle. By sonochemical process, the PdO nanoparticles were doped on the surface of silica at room temperature and atmospheric pressure with short reaction time. Silica nanoparticles were used as a supporting material to suppress aggregation and thereby to increase surface area of PdO nanoparticles. Fabricated PdO-doped silica nanoparticle (PdO@SNP) was applied as a nanocatalyst for selective alcohol oxidation reaction in the presence of molecular oxygen. The PdO@SNP composite showed higher catalytic activity and selectivity than unsupported PdO nanoparticle for aerobic alcohol oxidation reaction.

1. Introduction

Palladium (Pd)-based nanomaterials have brought great attraction as catalyst because of its high activity and selectivity in various catalysis systems including organic chemistry and electrochemistry [1,2]. To achieve the high performance of catalyst, enhancement of the surface area of catalyst and controllability of the size and structure of active sites are important [3–5]. Various attempts have been made to synthesize and control the morphology of Pd-based nanoparticles (NP) using complicated procedures, such as polyol process and thermolysis of Pd complexes [6–9]. However, NP made by these methods usually leads to the agglomeration by van der Waals force or sintering bonds, resulting in the reduction of active sites and the limitation of catalytic activity and selectivity [10,11].

To resolve this aggregation issue, combination of solid support and Pd-based materials have been proposed since composite structure can isolate NPs on the surface of supporting material and reduce a size of NP. Consequently, such nanocomposites can provide increased surface area and high selective surface of metal NP [12–14]. As solid support, inorganic material such as alumina, zeolite and silica is commonly adopted. Among the candidates, silica has been popular due to its superior mechanical and chemical stability and easy surface modification [15,16]. With those properties, metal-decorated silica composite is generally fabricated by surface functionalization of supporting material or addition of surfactant for the preparation of possible metal deposition sites. However, these methods usually require long reaction time and complicated steps to modify the surface. Furthermore, non-uniform decoration with metal NP is observed due to the imperfect surface modification [2,17,18].

Previously, our group had applied sonochemical method for the synthesis of metal supported nanocomposites such as Au and Pt-based NP doped silica [19–22]. When ultrasound is irradiated in aqueous solution, the emitted energy reduce metal ions into metal NPs [23]. Additionally, acoustic cavitation in aqueous solution generates interparticle collision between metal NP and support material, subsequently inducing the binding of metal and support [24,25]. From this approach, metal decoration on silica can be achieved without surfactant or surface modification of silica. The ultrasonic irradiation method provides advantages of short reaction time and mild reaction condition requiring only room temperature and ambient pressure.

In the present study, we report a simple method to synthesize the PdO-doped silica NP (PdO@SNP) using an ultrasonic irradiation. Synthesized PdO@SNP nanocatalyst was applied for selective alcohol oxidation under atmospheric pressure of oxygen. Aerobic alcohol oxidation reaction is very vital, not only in the laboratory but

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also in pharmaceutical and agricultural industry to produce intermediates in various organic reactions [26]. We evaluated catalytic performance of the PdO@SNP nanocomposite by comparing with unsupported PdO NP. The nanocomposite has the following advantages in view of green chemistry: easy isolation of the catalyst from reaction mixture, low reaction temperature, no harmful oxidants, wide application to various kinds of substrates and reusability.

2. Experimental

2.1. Material

Triton X-100 (laboratory grade), tetraethyl orthosilicate (reagent grade, 98%, TEOS), ammonium hydroxide solution (28–30%, NH_4OH), n-hexanol (98%), palladium (II) nitrate hydrate, and cyclohexane (99.0%) were purchased from Sigma–Aldrich. Alcohol substrates were purchased from Sigma–Aldrich and Tokyo Chemical Industry and were used as received without further treatment.

2.2. Fabrication of catalyst

2.2.1. Synthesis of SNP

To synthesize monodispersed SNP, previously reported W/O microemulsion method was employed [22]. Briefly, 43.2 g of Triton X-100, 180 mL of cyclohexane and 38.4 mL of n-hexanol were mixed to make a solution. After vigorous stirring, 13.45 mL of deionized (DI) water was added into the solution to form microemulsion. To the mixture, 2.4 mL of TEOS and 1.44 mL of NH_4OH were added. After 24 h, the silica was separated from the mixture by ethanol and centrifugation. The synthesized SNP was washed with ethanol, acetone, and then deionized (DI) water several times and dried in air at room temperature.

2.2.2. Sonochemical synthesis of PdO@SNP

100 mg of the dried silica was well dispersed into 20 mL of DI water by ultrasound irradiation for 15 min. For the synthesis of PdO NP, 7 mL of Pd solution, prepared by dissolving palladium (II) nitrate hydrate in DI water (4 mg/mL), was added into the 20 mL of silica solution containing 100 mg of the silica. To the mixture, 4 mL of ammonium hydroxide solution was added and 80 W/cm^2 of ultrasound (SONIFIER 450, BRANSON) was applied for 15 min. The PdO@SNP was centrifuged and washed with DI water thoroughly and dried in air.

2.2.3. Characterization of SNP and PdO@SNP

Prepared SNP and PdO@SNP were characterized by field emission scanning electron microscopy (FE-SEM), field emission transmission electron microscopy (FE-TEM, 200 kV) and energy dispersive spectroscopy (EDS). Crystallinity of PdO was confirmed by high resolution TEM (HR-TEM) and X-ray Diffraction (XRD). Amount of Pd on PdO@SNP nanocatalyst was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.3. Test of composite catalyst in selective alcohol oxidation with molecular oxygen

2.3.1. Aerobic alcohol oxidation

The oxidation reaction of alcohol was performed according to the following sequence: PdO@SNP (40 mg, Pd = 3.3 mol% of substrate) with toluene (2 mL) and alcohol (0.2 mmol) was charged in the glass tube reactor. The mixture was stirred at 1000 rpm using magnetic stirrer bar under atmospheric pressure of molecular oxygen at 90 °C. The conversion and yield were obtained by taking the sample from a mixture at regular intervals and analyzing them with gas chromatography (GC, Younglin GC-6500) and at the end by GC-mass spectroscopy (GC–MS, JEOL GCMS-BU20) to

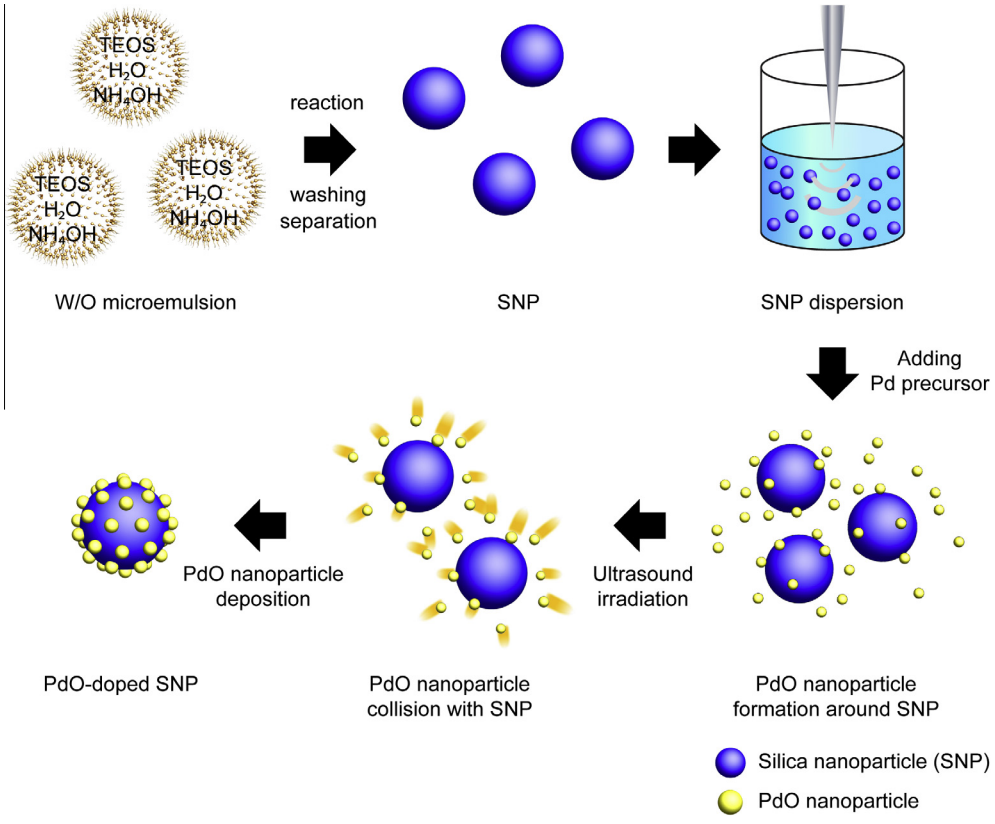

Fig. 1. Overall procedure of synthesizing SNP and PdO@SNP.