Preparation of palladium nanoparticles on alumina surface by chemical co-precipitation method and catalytic applications

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ABSTRACT

The present work reports a chemical co-precipitation process to synthesize palladium (Pd) nanoparticles using alumina as a supporting material. The optimized temperature for the formation of nanocrystalline palladium was found to be 600 °C. The X-ray diffraction (XRD) and Raman spectroscopy were used to study the chemical nature of the Pd in alumina matrix. The surface morphology and properties of the nanocrystalline powders were examined using thermogravimetric analysis (TG–DTA), XRD, Raman spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The calcinations in different atmospheres including in the inert medium forms the pure nano Pd^0 while in the atmospheric air indicates the existence pure Pd^0 along with PdO nanoparticles. The catalytic activities of the as-synthesized nanocrystalline Pd nanoparticles in the alumina matrix were investigated in Suzuki coupling, Hiyama cross-coupling, alkene and alkyne hydrogenation, and aerobic oxidation reactions.

1. Introduction

Nobel metallic nanoparticles have a higher percentage of atoms on the supporting surfaces, conferring these nanoparticles with very interesting catalytic properties [1–3]. When metallic elements are in nanometer scale, their redox properties might differ from those of the bulk metal, and their redox potentials change in the presence of adsorbed foreign ions [4]. However, metal nanoparticles tend to aggregate and form larger particles since they have a very large surface area. To prepare specific disseminated metal nanoparticles, one must control the nucleation and growth processes. The use of noble transition metal nanoparticles as catalysts is confined by their scarcities and high prices. Therefore, amending their catalytic functions and decreasing their costs are important for the future applications.

The palladium can be used as catalysts for hydrogenation [5], reduction [6], oxidation [7], electro-oxidation [8,9], hydrogenolysis reactions [10], and as active membranes [11], and sensors [12]. Recently, Singh et al. reported enhancing the hydrogen storage capacity of Pd-functionalized multi-walled carbon nanotubes [13]. The catalytic properties depend on thermal treatment, doping, preparation path, and surface properties of the carrier. In particular, nanoparticles of alumina supported palladium (Pd/Al_2O_3) are widely used to catalyze the selective hydrogenation of acetylene in an ethylene rich flow [14], simultaneous NO reduction

and CO oxidation [15], enantio-selective hydrogenation [16], and in chemical and biochemical studies of traffic-related emissions [17]. Metal sintering mechanisms regenerate palladium/alumina hydrogenation catalysts [18]. Palladium nanoparticles supported by alumina nanofibers can be synthesized using an electro-spinning method [19]. However, they often suffer from low reactivity, degradation, palladium leaching, and difficult synthetic procedures. Nevertheless, reproducibly synthesizing small and stable palladium nanoparticles with a consistent size distribution is important and remains an ambitious goal.

Several methods for the synthesis of palladium nanoparticles have been reported, including UV-photoactivation [20], electrochemical reduction [21], a sol–gel process [22], pulsed laser ablation in different organic solvents [23], supercritical carbon dioxide-assisted preparation [24], and microwave plasma [25]. However, the control methods used for the physical properties of the particles, such as crystal structure, size and shape, differ from those used to control the synthesis conditions that influence nucleation and growth. Among the preparation methods, co-precipitation has been considered one of the worthy to achieve a high degree of homogenization together with a small particle size and faster reaction rates. The chemical co-precipitation also offers variety of precursor selections to choose as starting materials starting from simple salts to complicated organic–inorganic materials, cost effective and easy to set-up. The co-precipitation is one of the more successful techniques for synthesizing nanoparticles having narrow particle size distribution. The main advantage of the method is the increased homogeneity of resulting nanoparticles which lead to relatively high reactivity. The literature survey

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indicated that no methods are available to prepare the palladium nanoparticles supported on alumina surface using chemical co-precipitation method.

The present work describes the preparation of palladium nanoparticles on an alumina surface using chemical co-precipitation method which was simple, easy, less cost effective and efficient. The palladium nanoparticles were characterized by means of X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM), atomic force microscopy (AFM) and Raman spectroscopy to study the surface morphology and chemical/crystalline properties. The catalytic performances of palladium nanoparticles were evaluated in Suzuki coupling, Hiyama cross-coupling, alkene and alkyne hydrogenation and aerobic oxidation reactions.

2. Experimental

### 2.1. Preparing alumina supported palladium nanoparticles

Metallic precursors, palladium (II) chloride ($PdCl_2$) and aluminum (III) nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) (St. Louis, MO, USA) were used to prepare palladium nanoparticles. Initially, the metallic precursors were prepared separately in distilled water (Millipore Corporation, Bedford, MA, USA), and a small amount of concentrated hydrochloric acid was necessary to solubilize $PdCl_2$. Palladium nanoparticles were synthesized with different $PdCl_2$ concentrations using co-precipitation. In the preparation process, the concentration of $Al(NO_3)_3$ (0.1 M) was kept constant and various concentrations of $PdCl_2$ solutions were added, including 0.001 M, 0.005 M, 0.01 M, 0.025 M and 0.05 M which corresponds to 0.1, 0.5, 1.0, 2.5 and 5.0% by weight of Pd, respectively. Aqueous NH_4OH was added to adjust the pH to 9.0, and the suspension was stirred for 2 h to uniformly disperse the particles. The resulting suspension was centrifuged for 5 min at 3000 rpm and 25 °C. The gelatinous precipitate was washed with water and then dried at 120 °C. Finally, the dried precipitate was ground and calcined at 600 °C for 2 h to produce palladium nanoparticles on an alumina surface. Scheme 1 illustrates the co-precipitation procedure for the formation of nanocrystalline Pd powder on the alumina surface.

2.2. Characterization techniques

The thermal decomposition and crystallization behavior of the nanopowder were studied using DTA (TA 5000/SDT 2960 DSC Q10). The XRD patterns of the calcined nanocrystalline palladium in alumina were recorded using X-ray diffraction (Philips X'pert MPD 3040) with Cu Kα radiation over a 2θ range from 20° to 80° at 2.5°/min. The voltage and the current settings were 35 kV and 30 mA, respectively. The samples were continuously scanned with a step size of 0.05° (2θ) at 1 s per step. The average crystallite sizes were measured using the XRD line profile analysis with Scherrer's equation [26].

The crystalline nature of the calcined samples was studied using transmission electron microscopy (JEM 2100F) performed at an accelerating voltage of 200 kV on a copper grid. Surface morphologies of the calcined samples of the alumina supported palladium nanoparticles were obtained using a field emission scanning electron microscope (FE-SEM-MIRA II, LMH) operated at an accelerated voltage of 20 kV.

An NRS-3300 triple monochromator Raman spectrometer (Jasco, Japan) was used to acquire Raman scattering spectra of alumina supported Pd nanoparticles in backscatter geometry. An argon laser at 532 nm and 100 mW was the excitation source. The fluorescence spectra were recorded using
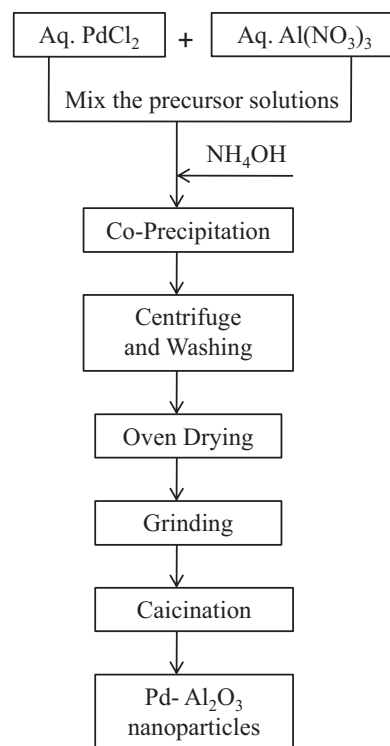
Scheme 1. Preparation process of palladium nanoparticles on alumina surface.

a spectrofluorophotometer (Shimadzu, RF-5301PC) with a xenon lamp (150 W) excitation source.

AFM measurements were carried out using a Nanoscope IV Multimode AFM (Veeco, di, USA) operated in the acoustically driven, intermittent contact ("tapping") mode. We used standard silicon AFM probes with tip sizes greater than 10 nm (Nanoworld, USA). The manufacturer estimates that the probe tip radius of curvature was no smaller than 5–10 nm. All AFM measurements were performed at ambient temperature. Dry N_2 gas was piped through the sample enclosure to maintain a relative humidity below 20 g/cm^3. All images were processed for better quality.

2.3. Catalytic reactions

2.3.1. Suzuki coupling reactions

The iodobenzene (100 mg, 0.49 mmol), Na_2CO_3 (129 mg, 1.2 mmol), different phenyl boronic acids (86 mg, 0.7 mmol), catalyst (Pd-I/Pd-A, 5 mg), H_2O (2 mL) and DMF (4 mL) were added in a 25 mL flask equipped with a condenser and the reaction mixture was stirred at 50 °C. After stirring for 6 h, the mixture was filtered through a glass filter and the filtrate was evaporated under reduced pressure. The crude residue was purified by column chromatography to give biphenyls. Three examples have performed for Suzuki coupling reaction and the ^{1}H NMR values of the corresponding products were given as follows.

Reaction 1: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.59–7.65 (m, 2H), 7.57–7.59 (m, 2H), 7.45–7.47 (m, 1H), 7.43–7.45 (m, 2H), 7.41–7.43 (m, 1H), 7.36 (t, 1H, J = 1.26 Hz), 7.34 (t, 1H, J = 2.02 Hz). Reaction 2: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.54–7.63 (m, 2H), 7.39–7.48 (m, 2H), 7.3–7.39 (m, 2H), 7.17–7.20 (m, 1H), 7.11–7.14 (m, 1H), 6.87–6.93 (m, 1H), 3.87 (s, 3H). Reaction 3: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.56 (d, J = 7.07 Hz, 2H), 7.52 (d, J = 8.33 Hz, 2H), 7.43 (t, J = 7.57 Hz, 2H), 7.29–7.37 (m, 3H), 2.52 (s, 3H).