Applied Catalysis B: Environmental 160–161 (2014) 514–524

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

# Carbon supported trimetallic PdNiAg nanoparticles as highly active, selective and reusable catalyst in the formic acid decomposition

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A R T I C L E I N F O

*Article history:*
Received 20 April 2014
Received in revised form 20 May 2014
Accepted 6 June 2014
Available online 13 June 2014

*Keywords:*
Formic acid
Dehydrogenation
Nanoparticles
Palladium
Nickel
Silver
Alloy
Carbon

A B S T R A C T

Trimetallic PdNiAg nanoparticles supported on activated carbon were simply and reproducibly prepared by wet-impregnation followed by simultaneous reduction method without using any stabilizer at room temperature. The characterization of the resulting material was done by the combination of complimentary techniques and the sum of their results shows that the formation of well-dispersed 5.6 ± 2.2 nm PdNiAg nanoparticles in alloy form on the surface of activated carbon. These carbon supported PdNiAg nanoparticles were employed as heterogeneous catalyst in the catalytic decomposition of formic acid, which has great potential as a safe and convenient hydrogen carrier for fuel cells, under mild conditions. It was found that PdNiAg/C can catalyze the dehydrogenation of formic acid with high selectivity (∼100%) and activity (TOF = 85 $h^{-1}$) at 50 °C. More importantly, the exceptional stability of PdNiAg nanoparticles against to agglomeration, leaching and CO poisoning make PdNiAg/C reusable catalyst in the formic acid dehydrogenation. PdNiAg/C catalyst retains almost its inherent activity (>94%) even at 5th reuse in the dehydrogenation of formic acid with high selectivity (∼100%) at complete conversion. The work reported here also includes the compilation of kinetic data for PdNiAg/C catalyzed dehydrogenation of formic acid depending on catalyst [PdNiAg], substrate [HCOOH], promoter [HCOONa] concentrations and temperature to determine the rate expression and the activation parameters (Ea, $\Delta H^{\#}$, and $\Delta S^{\#}$) of the catalytic reaction.

## 1. Introduction

Hydrogen has been considered as a clean energy carrier [1,2], since only water and small amounts of heat are the byproducts when it is utilized in proton exchange membrane fuel cells (PEMFC) [3,4]. Today, there have been serious efforts to achieve safe and efficient chemical hydrogen storage as it remains one of the most difficult problems in the transition from fossil fuels to hydrogen-based fuel cells energy technologies [1–4]. At this concern, formic acid (FA, HCOOH), which is one of the major products formed in biomass processing and also accessible via variety of processes such as hydrolysis of methyl formate or $CO_2$ hydrogenation [5,6], has been intensely investigated in the chemical hydrogen storage due to its high energy density, stability and nontoxicity [7,8]. In general, FA can be decomposed *via* dehydrogenation (**1**) and dehydration (**2**) pathways depending on the catalyst, pH of the medium and the reaction temperature [7].

$$HCOOH \rightarrow H_2 + CO_2 \quad \Delta G_{298K} = -35.0\,\text{kJ/mol} \tag{1}$$

$$HCOOH \rightarrow H_2O + CO \quad \Delta G_{298K} = -14.9\,\text{kJ/mol} \tag{2}$$

The dehydration of FA (**2**) is the unwelcome reaction and should be avoided for following conversion of hydrogen into electrical energy in PEMFC, as it produces CO impurity, which is highly toxic to fuel cell catalysts [9]. Recently, selective dehydrogenation of FA at remarkable hydrogen generation rates has been achieved by different homogeneous catalysts [10]. However, the problems in the separation and reusability of these homogeneous catalysts hinder their use in practical applications. In this connection, owing to the advantages of nanocatalysis [11], the current research has been directed toward the development of metal nanocatalysts (NCs) that can provide high activity, selectivity and stability in the dehydrogenation of FA [7]. Up to date, most of the attention on NCs toward FA dehydrogenation has been focused on noble metals [12–17] and among these catalysts Pd based NCs exhibit excellent catalytic performances in terms of activity and selectivity. Unfortunately, these

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http://dx.doi.org/10.1016/j.apcatb.2014.06.004
0926-3373/

monometallic Pd NCs are easily deactivated throughout the catalytic decomposition of FA due to adsorption of poisonous carbon monoxide (CO) formed as intermediates. In this context, alloying with another metal that has better CO anti-poisoning ability over Pd, seems to be promising way to prevent CO-deactivation of Pd [18–23]. Alloying of Pd NPs with another metal especially first-row metals not only leads to the enhancement of the catalytic performance but also reduce the consumption of high-cost Pd. Therefore, it is highly fascinating to further increase CO resistance, catalytic performance of Pd NPs and lower the cost of nanocatalyst by integration of low-cost metals.

Herein, we report a facile synthesis of PdNiAg NPs supported on activated carbon, hereafter referred to as PdNiAg/C, and their excellent catalysis in the dehydrogenation of FA under mild conditions (<90 °C). PdNiAg/C were simply and reproducibly prepared through the conventional impregnation followed by simultaneous reduction method [24], and characterized by inductively coupled plasma-optical emission spectroscopy (ICP-OES), powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), conventional transmission electron microscopy (CTEM), high resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), scanning transmission electron microscope-energy dispersive X-ray spectroscopy (STEM-EDX) and high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM). The sum of their results revealed that the formation of well-dispersed 5.6 ± 2.2 nm PdNiAg NPs in the form of nanoalloy on the surface of activated carbon. The resulting PdNiAg NPs are acting as highly active (TOF = 85 $h^{-1}$) and selective (~100%) heterogeneous catalyst in the dehydrogenation of FA at 50 °C. Moreover, the exceptional durability of PdNiAg NPs even at high reaction temperature (70 °C) against to agglomeration, leaching and CO poisoning make PdNiAg/C isolable, bottleable and highly reusable catalyst in the dehydrogenation of FA.

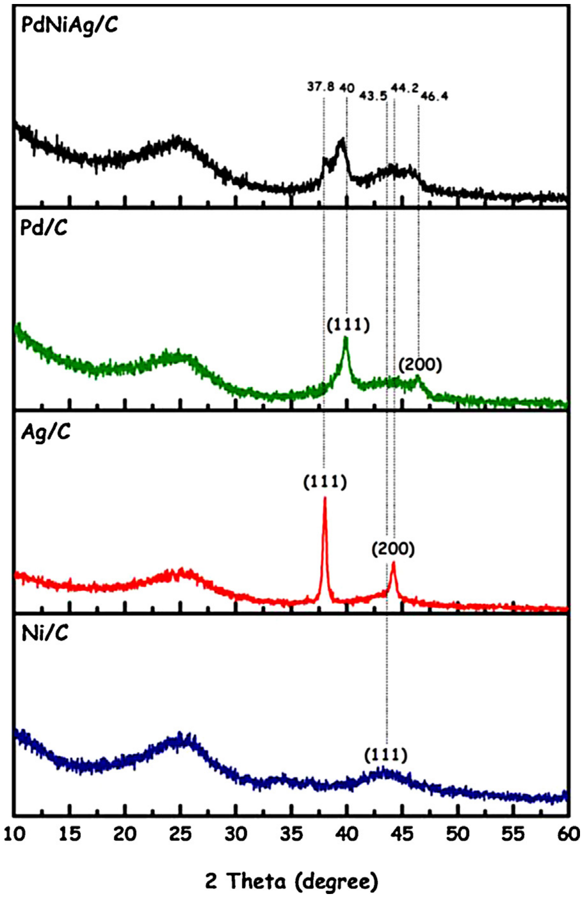

**Fig. 1.** P-XRD patterns of PdNiAg/C, Pd/C, Ag/C and Ni/C catalysts.

## 2. Experimental

### 2.1. Materials

Palladium(II) nitrate dihydrate ($Pd(NO_3)_2{\cdot}2H_2O$) (~40% Pd basis), nickel(II) chloride hexahydrate ($NiCl_2{\cdot}6H_2O$), sodium borohydride ($NaBH_4$), sodium formate ($CHO_2Na$; SF ~98%), silver nitrate ($AgNO_3$; ~99%) and activated carbon were purchased from Sigma-Aldrich®. Formic acid ($CH_2O_2$) was purchased from Merck® and all of them were used without further purification. Deionized water was distilled by water purification system (Milli-Q Water Purification System). All glassware and Teflon-coated magnetic stir bars were washed with acetone and copiously rinsed with distilled water before drying in an oven at 150 °C.

### 2.2. Characterization

Pd, Ni and Ag contents of the samples were determined by ICP-OES (Leeman, Direct Reading Echelle) after each sample was completely dissolved in a mixture of $HNO_3$/HCl (1/3 ratio). Powder X-ray diffraction (XRD) patterns were recorded with a MAC Science MXP 3TZ diffractometer using Cu-Kα radiation (wavelength 1.54 Å, 40 kV, 55 mA). CTEM, HRTEM, STEM, and HAADF-STEM samples were prepared by dropping one drop of dilute suspension on copper coated carbon TEM grid and the solvent was then dried. The conventional TEM was carried out on a JEOL JEM-200CX transmission electron microscopes operating at 120 kV. HRTEM, STEM and HAADF-STEM were run on a JEOL JEM-2010F transmission electron microscope operating at 200 kV. Oxford EDXS system and Inca software were used to collect and process STEM-EDX data. HAADF-STEM images were acquired with a convergence angle of 27 mrad and an inner collection angle of 100 mrad. EDX analysis was carried out with an electron beam size of 2 Å. The XPS analyses were performed on a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic Al-Kα radiation (1486.6 eV, the X-ray tube working at 15 kV and 350 W, and pass energy of 23.5 eV). The gas generated from the decomposition of formic acid was analyzed by Shimadzu-GC-2014 analyzer.

### 2.3. Preparation of Pd/C, Ni/C and Ag/C catalysts

In a three separate experiments, 5.0 mL of 65.2 μmol aqueous metal solution (Pd from $Pd(NO_3){\cdot}2H_2O$; Ni from $NiCl_2{\cdot}6H_2O$, and Ag from $AgNO_3$) is mixed with activated carbon (140 mg) at 400 rpm for 2 h. Then, 1.0 mL aqueous solution of $NaBH_4$ (45.4 mg, 1.1 mmol) was added to this mixture and the resulting solution was stirred for half an hour under air at room temperature. After centrifugation (6000 rpm, 5 min), copious washing with water (3 × 20 mL), filtration, and drying in oven at 100 °C, Pd/C, Ni/C and Ag/C catalysts were obtained as powder.

### 2.4. Preparation of PdAg/C, PdNi/C and NiAg/C catalysts

(a) PdAg/C: 5.0 mL aqueous solution containing $Pd(NO_3){\cdot}2H_2O$ (10.5 mg, 39.4 μmol Pd), $AgNO_3$ (4.5 mg, 26.1 μmol Ag) and activated carbon (140 mg) is mixed at 400 rpm for 2 h.

(b) PdNi/C: 5.0 mL aqueous solution containing $Pd(NO_3){\cdot}2H_2O$ (10.5 mg, 39.4 μmol Pd), $NiCl_2{\cdot}6H_2O$ (6.0 mg, 25.4 μmol Ni), and activated carbon (140 mg) is mixed at 400 rpm for 2 h.