



A new strategy to transform mono and bimetallic non-noble metal nanoparticles into highly active and chemoselective hydrogenation catalysts



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ARTICLE INFO

Article history:

Received 9 February 2017

Revised 14 March 2017

Accepted 15 March 2017

Keywords:

Carbon coating

Co nanoparticles

CoNi bimetallic nanoparticles

Chemoselective hydrogenation

Nitroarenes

ABSTRACT

A new strategy to transform non-noble metal oxide nanoparticles (NPs) into highly active and selective metallic NPs as hydrogenation catalysts by a simple carbon coating process based on hydrothermal treatment with glucose is presented. During the carbon coating process, metal oxide NPs will be reduced to metallic NPs and covered by thin carbon layers, resulting in formation of Metal@C NPs. Through this method, monometallic Co@C has been prepared, which shows excellent activity and selectivity for chemoselective hydrogenation of substituted nitroarenes to corresponding anilines under mild conditions. Kinetic, isotopic and spectroscopic studies indicate that hydrogen dissociation-addition is the controlling step in chemoselective hydrogenation reaction with Co@C NPs. Stabilization and the reaction rate of metallic Co are improved by preparing bimetallic CoNi@C catalyst, leading to almost fivefold improved activity. Our preparation method enables to synthesize non-noble bimetallic CoNi@C nanoparticles with nearly one-order magnitude higher activity than any Co-based non-noble metal catalysts prepared by other methods, without necessity to involve the promoting role of metal-N interactions. At last, we also show the application of Co@C NPs for hydrogenation of levulinic acid to γ -valerolactone.

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1. Introduction

Substituting noble metal (NM) catalyst by non-noble metal (NNM) catalyst not only presents economic advantages but also represents a promising approach for a more sustainable chemistry [1]. Non-noble metal nanoparticles (NPs) have been utilized as efficient catalyst for electrocatalysis, photocatalysis and heterogeneous catalysis [2–4]. Nevertheless, in most of the results presented up to now, the catalytic performances achieved by the alternative NNM are still lower than those of NM catalysts.

With the aim to improve activity and selectivity of NNM, several catalyst synthesis methodologies have been presented and for preparing and stabilizing the transition metal NPs, and they have to be protected by some capping ligands or solid support. In the last decade, the preparation of transition metal NPs by wet-chemistry method has been well established, and it has been shown that organic ligands can stabilize transition metal NPs [5,6]. However, the productivity of this method is usually low and these metal NPs are not stable enough in air. In addition, expensive organic ligands are required in some cases. Bimetallic

NPs can also be prepared by wet-chemistry method through the thermal decomposition of metal precursors in solvent [7], though in some cases, it is difficult to obtain alloyed bimetallic nanoparticles due to their different nucleation dynamics in solution [8,9]. Thermal decomposition of metal complex or metal-organic framework (MOF) materials is another preparation procedure leading to metal NPs covered by carbon layers [10,11]. Unfortunately, it will be difficult to prepare bimetallic or multi-metallic NPs by the thermal decomposition procedure.

In this work, we will present a general strategy to transform easily transition metal oxide NPs into mono and bimetallic NPs with well-defined nanostructures. The synthesis methodology presented here uses glucose as a green carbon source and employs a hydrothermal treatment to obtain mono and bimetallic catalysts coated by thin carbon layers. The resultant materials are protected by the carbon layers from deep oxidation by air. The catalyst preparation strategy is illustrated here by Co@C and CoNi@C samples. The obtained materials show much higher catalytic activity for chemoselective hydrogenation of substituted nitroarenes into corresponding substituted anilines than previously reported non-noble metal catalysts.

It has to be pointed out that in previous works, it has been proposed that preparation of NNM catalysts by decomposition of

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organometallic precursors with nitrogen-containing ligands yields highly active catalysts for the abovementioned reaction. It was claimed that a metal-nitrogen interaction was established in the final catalyst and metal-nitrogen interaction was thought to be a key factor to explain the high catalytic activity [12,13]. In this work, we will present that our preparation strategy does not require organometallic compound as metal source, neither requires for introduction metal-nitrogen interaction to achieve mono and bimetallic NNM catalysts with higher activities.

2. Experiments

2.1. Synthesis of Co_3O_4 NPs as precursor for Co@C NPs

Co_3O_4 NPs were prepared by following a reported procedure [14]. 4.94 g of $\text{Co}(\text{Ac})_2$ was dissolved in 100 mL of glycol under stirring at 160 °C. 4.24 g of Na_2CO_3 was dissolved in 160 mL of distilled water. When $\text{Co}(\text{Ac})_2$ was totally dissolved in glycol and a purple solution was formed, Na_2CO_3 aqueous was added into the $\text{Co}(\text{Ac})_2$ glycol solution drop by drop. It took about 1.5–2 h to finish the process. After adding Na_2CO_3 aqueous, the suspension was aged for one additional hour before cooling down. Purple solid product would be obtained after filtration of the suspension and washed with water and acetone. After drying in oven at 60 °C for 16 h, the solid product was sent to calcination in static air at 450 °C for 3 h with a ramp rate of 1 °C/min from room temperature to 450 °C.

2.2. Synthesis of Co@C NPs through carbon coating process

360 mg of glucose was dissolved in 20 mL distilled water. Then 0.5 g of Co_3O_4 NPs was dispersed in the glucose aqueous under ultrasonic treatment. The black suspension was transferred into autoclave and kept at 175 °C for 18 h. After cooling down to room temperature, the solid product was washed by water and acetone and dried in oven at 60 °C, resulting in the formation of two-dimensional $\text{Co}(\text{OH})_2/\text{C}$ composites. Co@C NPs could be obtained by annealing the $\text{Co}(\text{OH})_2/\text{C}$ composites in N_2 at 600 °C for 2 h with a ramp rate of 10 °C/min from room temperature to 600 °C. After keeping at 600 °C for 2 h, the sample was cooled down in N_2 flow to room temperature and stored in glass vial in the ambient environment.

2.3. Synthesis of Ni- Co_3O_4 NPs as precursor for bimetallic NPs

The preparation of Ni- Co_3O_4 NPs was similar to Co_3O_4 NPs with some modifications of the amount of inorganic metal salts. 4.94 g of $\text{Co}(\text{Ac})_2$ and 2.5 g of $\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 100 mL of glycol under stirring at 160 °C. 5.0 g of Na_2CO_3 was dissolved in 160 mL of distilled water. When $\text{Co}(\text{Ac})_2$ and $\text{Ni}(\text{Ac})_2$ were totally dissolved in glycol and formed a red solution, Na_2CO_3 aqueous was added into the $\text{Co}(\text{Ac})_2$ glycol solution drop by drop. It took about 1.5–2 h to finish the process. After adding Na_2CO_3 aqueous, the suspension was aged for one additional hour before cooling down. Solid product would be obtained after filtration of the suspension and washed with water and acetone. After drying in oven at 60 °C for 16 h, the solid product was sent to calcination in static air at 450 °C for 3 h with a ramp rate of 1 °C/min from room temperature to 450 °C.

2.4. Synthesis of bimetallic CoNi@C NPs through carbon coating process

For the preparation of bimetallic CoNi@C NPs, we followed a similar procedure to the one described for monometallic Co@C

NPs. 0.5 g of Ni-doped Co_3O_4 (Ni- Co_3O_4) NPs was used as the precursor. The other experimental procedures were the same.

2.4.1. Synthesis of Ni@C through carbon coating process

7.0 g of $\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 100 mL glycol under stirring at 160 °C. 5.0 g of Na_2CO_3 was dissolved in 160 mL of distilled water. When $\text{Ni}(\text{Ac})_2$ was totally dissolved in glycol and a green solution was formed, Na_2CO_3 aqueous was added into the $\text{Ni}(\text{Ac})_2$ glycol solution drop by drop. It took about 1.5–2 h to finish the process. After adding Na_2CO_3 aqueous, the suspension was aged for one additional hour before cooling down. Green solid product would be obtained after filtration of the suspension and washed with water and acetone. After drying in oven at 60 °C for 16 h, the solid is collected and used as the precursor for Ni@C NPs.

The preparation of Ni@C NPs was similar to monometallic Co@C NPs using 0.5 g green solid from the precipitation of $\text{Ni}(\text{Ac})_2$ as the precursor. The other experimental procedures were the same.

2.4.2. Preparation of Co@C nanoparticles from the thermal decomposition of metal-organic framework (MOF) precursor

Herein, two types of Co-containing MOF materials were prepared using different linkers. One linker is trimesic acid with nitrogen and the other is 2-methylimidazole with nitrogen.

Co-BTC MOF was prepared using trimesic acid as linker. In a typical synthesis, 1.05 g of trimesic acid and 2.91 g of cobalt nitrate hexahydrate were dissolved in a mixed solvent (20 mL DMF + 20 mL H_2O + 20 mL ethanol) under stirring at room temperature. When all the solid precursors were dissolved, the mixture was transferred to an autoclave and kept at 100 °C for 18 h. After the hydrothermal reaction, the solid purple product was washed and dried at 60 °C. The Co@C-BTC sample was obtained by thermal decomposition of Co-BTC-MOF in Ar at 600 °C.

In a typical synthesis of ZIF-67, cobalt nitrate hexahydrate (0.9 g) was dissolved in 6 mL of deionized water, and 2-methylimidazole (11.0 g) was dissolved in 40 mL of deionized water. The two solutions were mixed and kept stirring for 24 h at room temperature. The resulting purple precipitates were collected by centrifugation and filtration, washed with water and methanol subsequently for 3 times, and finally dried under vacuum at 60 °C for 24 h. The Co@C-ZIF sample was obtained by thermal decomposition of ZIF-67 in N_2 at 600 °C.

2.4.3. Preparation of Co@C/C catalyst

The supported Co@C/C catalyst was prepared according to the literature [10]. Cobalt(II) acetate tetrahydrate (127 mg) and 1,10-phenanthroline (184 mg) (Co:phenanthroline = 1:2 M ratio) were dissolved in ethanol (50 mL) at room temperature. Then, carbon powder (690 mg) (VULCAN® XC72R, Cabot Corporation) was added and the whole mixture was refluxed for 4 h. The mixed suspension was cooled to room temperature and the solvent was removed by evaporation. The solid sample obtained was dried at 60 °C for 12 h. The oven was heated to 800 °C with a ramp rate of 25 °C/min, and held at 800 °C for 2 h under Ar atmosphere. After that, the sample was cooled down to room temperature.

2.5. Characterizations

Powder X-ray diffraction (XRD) was performed with a HTPhilips X'Pert MPD diffractometer equipped with a PW3050 goniometer using $\text{Cu K}\alpha$ radiation and a multisampling handler.

Samples for electron microscopy studies were prepared by dropping the suspension of solid sample using CH_2Cl_2 as the solvent directly onto holey-carbon coated copper grids. All the measurements were performed in a JEOL 2100F microscope operating at 200 kV in both transmission (TEM) and scanning-transmission

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