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

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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 show excellent activity and selectivity for chemoselectivity 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 is improved by preparing bimetallic CoNi@C catalyst, leading to almost five-fold 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.

Keywords: Carbon coating, Co nanoparticles, CoNi bimetallic nanoparticles, Chemoselective hydrogenation, nitroarenes

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, 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 substitute 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 organometallic precursors with nitrogen-containing ligands yields

highly active catalysts for the above mentioned 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 to introduction metal-nitrogen interaction to achieve mono and bimetallic NNM catalysts with higher activities.

2. Experiments

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 h to 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.

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 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.

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 form 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 h to 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.

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 ($\text{Ni-Co}_3\text{O}_4$) NPs was used as the precursor. The other experimental procedures were the same.

Synthesis of Ni@C through carbon coating process.

5.0 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 h to 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, collect the solid and use 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.

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 was dissolved in a mixed solvent (20 mL DMF + 20 mL H₂O + 20 mL ethanol) under stirring at room temperature. When all the solid precursor was 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 N₂ at 600 °C.

Preparation of Co@C/C catalyst.

The supported Co@C/C catalyst was prepared according to literature. [10] Cobalt(II) acetate tetrahydrate (127 mg) and 1,10-phenanthroline (184 mg) (Co:phenanthroline=1:2 molar 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 hours. 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 hours. The oven was heated to 800 °C with a ramp rate of 25 °C/min, and held at 800 °C for 2 hours under Ar atmosphere. After that, the sample was cooled down to room temperature.

2.2 Characterizations

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

Samples for electron microscopy studies were prepared by dropping the suspension of solid sample using CH₂Cl₂ as the solvent directly onto holey-carbon coated copper grids. All the measurements were performed in a JEOL 2100F microscope operating at 200 kV both in transmission (TEM) and

scanning-transmission modes (STEM). STEM images were obtained using a High Angle Annular Dark Field detector (HAADF), which allows Z-contrast imaging.

Raman spectra were recorded at ambient temperature with a 785 nm HPNIR excitation laser on a Renishaw Raman Spectrometer (“Reflex”) equipped with an Olympus microscope and a CCD detector. The laser power on the sample was 15mW and a total of 20 acquisitions were taken for each spectra.

X-ray photoelectron spectra (XPS) of the catalysts were recorded with a SPECS spectrometer equipped with a Phoibos 150MCD-9 multichannel analyzer using non monochromatic MgK α (1253.6 eV) irradiation. Spectra were recorded using analyser pass energy of 30 eV, an X-ray power of 100W and under an operating pressure of 10^{-9} mbar. Peak intensities have been calculated after nonlinear Shirley-type background subtraction and corrected by the transmission function of the spectrometer. During data processing of the XPS spectra, binding energy (BE) values were referenced to C1s peak (284.5 eV). CasaXPS software has been used for spectra treatment. The H₂ pre-treatment on the NNM@C samples was performed in a reaction cell connected to XPS analysis chamber. After the H₂ reduction treatment, the samples were transferred into the XPS analysis chamber without contact with air.

H₂-D₂ exchange experiments were carried out in a flow reactor. The feed gas consisted of 4 mL/min H₂, 4 mL/min D₂ and 18 mL/min argon, and the total weight of catalyst was ca. 40 mg. Reaction products (H₂, HD and D₂) were analysed with a mass spectrometer (Omnistar, Balzers). For the samples that need to be reduced before the H₂-D₂ exchange experiments, they were *in situ* reduced at 120 °C for 2 h with a temperature-rising rate of 10 °C/min from room temperature to 120 °C. Then the temperature was decreased to 25 °C and, once stabilized, the H₂ feed was change to the reactant gas composition.

The redox properties of NNM@C NPs are evaluated by Temperature-programmed reduction (TPR). Micromeritics AutoChem 2910 catalyst characterization system with a thermal conductivity detector (TCD) was used. Prior to each experiment, about 40 mg of sample was pretreated at room temperature in flowing He (10 mL/min) for 20 min. The sample was treated by heating from 25 °C to 600 °C at a rate of 5 °C min⁻¹ in a flow of 10 vol.% H₂ in Ar. The total gas flow rate was 50 mL/min⁻¹.

2.3 Catalytic tests

2.3.1 Hydrogenation of nitroarenes

The chemoselective hydrogenation of nitroarenes was performed in batch reactors. The reactant, internal standard (dodecane), solvent (toluene or THF), powder catalyst as well as a magnetic bar were added into the batch reactor. After the reactor was sealed, air was purged by flushing two times with 10 bar of hydrogen. Then the autoclave was pressurized with H₂ to the corresponding pressure. The stirring speed is kept at 1100 rpm and the size of the catalyst powder is below 0.05 mm to avoid either external or internal diffusion limitation. Finally, the batch reactor was heated to the target temperature. For the kinetic studies, 50 µL of the mixture was taken out for GC analysis at different reaction time. For the scope studies, 100 µL of the mixture was taken out for GC analysis. The products were also analyzed by GC-MS.

2.3.2 Hydrogenation of levulinic acid to γ -valerolactone

The chemoselective hydrogenation of levulinic acid was performed in batch reactors. 1 mmol of levulinic acid, internal standard (dodecane), solvent (toluene), and powder catalyst as well as a magnetic bar were added into the batch reactor. After the reactor was sealed, air was purged by flushing two times with 10 bar of hydrogen. Then the autoclave was pressurized with H₂ to the corresponding pressure. The stirring speed is kept at 1100 rpm and the size of the catalyst powder is below 0.05 mm to avoid either external or internal diffusion limitation. Finally, the batch reactor was heated to the target temperature. The products were also analyzed by GC and GC-MS.

3. Results and discussions

3.1 Preparation of transition metal NPs

Fig. 1. Schematic illustration of the transformation of metal oxide NPs (MO_x) into metallic transition NPs covered by thin carbon layers (NNM@C) through a facile carbon-coating and graphitization process.

Metal oxide nanoparticles can easily be achieved by a precipitation-calcination procedure (see experimental section for details) and their transformation into non-noble metallic NPs covered by carbon layers (NNM@C) is described in **Fig. 1**. The carbon source was coated on the metal oxide NPs by a hydrothermal treatment with aqueous glucose. After graphitization treatment at 600 °C, the organic layers coated on the metal oxide NPs decomposed and condensed into thin carbon layers. Simultaneously, metal oxide NPs were reduced by the carbon, forming metallic NPs covered by thin carbon layers. More specifically, Co@C NPs were prepared starting from Co_3O_4 NPs with high surface areas (with a BET surface area of 110 m^2/g measured by N_2 isotherms). Preparation procedure of the Co_3O_4 NPs is given in the experimental section. The morphological characterization of Co_3O_4 nanoparticles is shown in **Fig. S1**. When Co_3O_4 nanoparticles were dispersed in a solution of glucose in water and treated under hydrothermal condition at 175 °C, they transformed into ultrathin Co(OH)_2 nanosheets (see **Fig. S2** and **Fig. S3**). During the hydrothermal process, glucose was coated on the Co(OH)_2 nanosheets, resulting in formation of $\text{Co(OH)}_2/\text{glucose}$ nanocomposites, as confirmed by elemental mapping (see **Fig. S4**). A subsequent thermal treatment in inert atmosphere at 600 °C led to the graphitization of carbon and the reduction of Co_3O_4 into metallic Co by carbon, resulting in the formation of Co@C NPs.

XRD pattern of Co@C NPs is shown in **Fig. S2**. Only the diffraction pattern of metallic Co including cubic Co (*fcc* type, PDF code 96-900-8467) and hexagonal Co (*hcp* type, PDF code 96-900-8493) can be observed. The morphology of Co@C NPs was characterized by TEM, and as

shown in **Fig. 2a**, Co NPs are dispersed on thin carbon films with good dispersion. The crystal lattice fringes corresponding to metallic Co can be observed in the high-resolution TEM images (see **Fig. 2b**). In addition, the Co NPs are partially covered by thin carbon layers. Those thin carbon layers can protect from over oxidation by air, avoiding the deep oxidation of Co NPs. Nevertheless, some CoOx patches can also be found in the Co@C NPs, which should come from re-oxidation of the surface of metallic Co NPs after preparation and exposure to air. The presence of CoOx and the disordered carbon layers coated on Co nanoparticles are also confirmed by Raman spectroscopy (see **Fig. S6**). For comparison, Co₃O₄ nanoparticles were directly reduced by H₂ at 450 °C to get metallic Co nanoparticles (the sample is denoted as Co₃O₄-R). As shown in **Fig. S7**, compared with Co@C sample, the Co₃O₄-R shows larger particle size and much higher percentage of CoOx species, suggesting that the introduction of carbon layers to Co nanoparticles can effectively protect the metallic Co nanoparticles from deep oxidation by air.

Fig. 2. (a, b) TEM images of Co@C NPs, (c, d) TEM images of Ni@C NPs, (e, f) TEM images of CoNi@C NPs, (g) elemental mapping of Co, Ni and C in the CoNi@C sample and (h) linescan of the relative amount of Ni and Co in a single CoNi@C nanoparticle.

To show the effects of carbon-coating process on the catalytic properties of Co NPs, the chemoselective hydrogenation of 3-nitrostyrene was chosen as the model reaction. As it can be seen

in **Fig. S8**, both Co@C and Co₃O₄-R samples show hydrogenation activity. For Co@C sample, the hydrogenation of 3-nitrostyrene occurs very rapidly without obvious induction period (ca. 10 min), whereas, Co₃O₄-R sample shows an induction period of about 30 min, which is due to the in-situ reduction of CoOx patches in the sample. [15] Notably, Co@C NPs show higher selectivity to 3-aminostyrene than Co₃O₄-R sample. These results are consistent with our previous works, showing that the role of carbon layers is to protect the non-noble metal NPs from deep oxidation by air and promote the in situ reduction of CoOx patches in the Co@C NPs under reaction conditions. [15]

The kinetics for the hydrogenation of 3-nitrostyrene with Co@C sample was studied and results are presented in **Fig. S9**. It can be seen that the initial reaction rate for hydrogenation increases linearly with the partial pressure of H₂ while remains practically no affected when changing the concentration of 3-nitrostyrene. The direct conclusion from the above results would be that, with Co@C catalyst, the reaction is controlled by H₂ dissociation or hydrogen addition. It has been shown that in the case of Au/TiO₂, the reaction rate of hydrogenation of nitroarenes was significantly improved by introducing a small amount of Pt to Au/TiO₂ catalyst, which can dissociate H₂ much more rapidly than solely Au nanoparticles. [16] On those basis and aiming to prepare an active and selective NNM catalyst, we decide to prepare bimetallic CoNi@C NPs. It is expected that the presence of Ni should improve the rate of H₂ dissociation and still maintain the high chemoselectivity. For preparing such a bimetallic catalyst, we started from a sample of Ni-doped Co₃O₄ NPs as precursor. After the coating of glucose through hydrothermal reaction and annealing at 600 °C, CoNi@C bimetallic NPs (the molar ratio of Co/Ni in this sample is 77/23) covered by thin carbon layers can be prepared. As can be seen in **Fig. S9**, XRD pattern of the starting Ni-Co₃O₄ nanoparticles is similar to that of Co₃O₄ nanoparticles. The homogeneous dispersion of Ni species in Co₃O₄ nanoparticles is also confirmed by STEM elemental mapping (see **Fig. S10**). XRD pattern of CoNi@C NPs is shown in **Fig. S11**. Only diffraction peaks corresponding to *fcc*-type of CoNi alloys can be seen. The structures of CoNi@C NPs are investigated by TEM. As shown in **Fig. 2e**, the particle size of bimetallic CoNi@C NPs is ranging from 20 to 100 nm and lattice fringes with spacing of 0.21 nm corresponding to CoNi alloy can also be observed in high-resolution TEM image. Similarly, the CoNi NPs are also covered by thin carbon layers (see **Fig. 2f**). The distribution of Co and Ni in bimetallic CoNi@C NPs are studied by EDS elemental mapping. More mapping results are

presented in **Fig. S12**. As it can be seen in **Fig. 2g**, the spatial distribution of Co, Ni and C overlap very well, indicating that Co and Ni have formed fully alloyed structures. Nevertheless, the alloy structure of CoNi@C NPs is also confirmed by EDS line-scan profile of a single CoNi NP, as presented in **Fig. 2h**.

3.2 Characterizations of NNM@C NPs

Fig. 3 (a) Co 2p and (b) Ni 2p regions of the XPS spectra of fresh Co@C, Ni@C, CoNi@C and Ni-Co₃O₄ samples and the samples after reduction by H₂ at 400 °C.

The surface properties of Co@C, Ni@C and bimetallic CoNi@C NPs were studied by XPS (see **Fig. 3a and 3b**). For the fresh Co@C NPs, due to the re-oxidation by air after the synthesis, only CoOx without metallic Co⁰ can be detected by XPS. Metallic Co⁰ can only be detected by reducing the sample by H₂ in a high-pressure reactor connected to the XPS chamber. [17] However, in the CoNi@C sample, without any pre-treatments, metallic Co⁰ can be seen clearly in the Co 2p region, indicating that Ni can contribute to stabilize the active metallic Co⁰. In our previous work [15], it has been shown that metallic Co is the active phase for hydrogenation of nitroarenes. Therefore, the introduction of Ni into Co@C NPs can contribute to the stabilization of metallic Co, while increasing the role of H₂ dissociation.

As shown in the morphological characterizations, those carbon-coated transition metal nanoparticles (NNM@C NPs) will be re-oxidized by air, resulting in formation of oxide patches on the surface. Therefore, an in-situ reduction of those metal oxide patches on the surface on NNM@C

NPs will occur at the beginning stage of hydrogenation reaction. The redox property of NNM@C NPs can be studied by temperature-programmed reduction (TPR). As it can be seen in **Fig. S13**, the two metal oxide samples show high H₂ consumption, while three reduced sample show low H₂ consumption. Notably, the CoNi@C sample shows low reduction onset temperature and lowest H₂ consumption among all the samples, suggesting that the percentage of metal oxide patches in CoNi@C is lower than that in Co@C, and the introduction of Ni into Co@C NPs can promote the reducibility of CoO_x by H₂. [18]

3.3 Catalytic properties of NNM@C NPs

Fig. 4. H₂-D₂ exchange experiments on Co@C (a), CoNi@C (b) and Ni@C (c) NPs. All the three samples are pre-reduced by H₂ before the H₂-D₂ exchange experiments.

The activity of the as-prepared CoNi@C and Co@C NPs for H₂-D₂ exchange was measured and the results are presented in **Fig. 4**. It can be seen that with the bimetallic CoNi@C NPs show a more than two-fold improved rate for H₂ dissociation than Co@C NPs, and Ni@C NPs show the highest activity. Furthermore, the catalytic performance of three samples (Co@C, Ni@C and CoNi@C) have

also been tested for the hydrogenation of 3-nitrostyrene under mild conditions (120 °C and 7 bar of H₂). The initial reaction rates normalized to the mass of metal catalysts are shown in **Fig. 5**. Ni@C sample shows the highest activity and CoNi@C shows 4-fold higher activity than Co@C, which is in line with the H₂-D₂ exchange results. The selectivity to the desired 3-aminostyrene product at high conversion (> 95%) of three catalysts are presented in **Fig. 5b**. Co@C and CoNi@C NPs show excellent selectivity (> 97%) for the hydrogenation of 3-nitrostyrene while Ni@C shows lower chemoselectivity (~80%) towards 3-aminostyrene (see the distributions of products in **Fig. S14**), which is consistent with previous results from ours and other groups. [19-21] The synergistic effect between Co and Ni contributes the high activity and selectivity of CoNi@C NPs. [22] Moreover, Compared with Co@C NPs prepared by thermal decomposition of Co-EDTA complex, Co@C NPs generated by the carbon-coating method show much higher activity for hydrogenation of 3-nitrostyrene (see **Fig. S15**). H₂-chemisorption shows that, the percentage of exposed Co atoms in Co@C from carbon-coating method is much higher, which is probably responsible for the different catalytic activities observed.

Fig. 5. Catalytic performances of Co@C, CoNi@C and Ni@C NPs in selective hydrogenation of 3-nitrostyrene. (a) The initial reaction rates are calculated when the conversion of 3-nitrostyrene is below 20%. (b) The selectivity to 3-aminostyrene when the conversion reaches >90% on three catalysts under the same condition.

The structure of CoNi@C NPs after the hydrogenation of 3-nitrostyrene was also investigated by TEM. As shown in **Fig. S16**, the particle size distribution of CoNi NPs is similar to the fresh catalyst and they are still covered by the thin carbon layers, indicating the stability of CoNi NPs. As displayed in **Fig. S17** and **Fig. S18**, the alloyed structures of CoNi bimetallic NPs are preserved after the hydrogenation reaction. No obvious phase separation between Ni and Co can be observed, which further confirms that the carbon layers can effectively promote the chemical stability of bimetallic nanoparticles. The good stability of CoNi@C NPs is also reflected by its good recyclability for the selective hydrogenation of 3-nitrostyrene (see **Fig. S19**).

It should be remarked that the scope of the bimetallic CoNi@C NPs is very good as can be seen from results given in **Table S1**. At this point, it can be concluded that a facile method to synthesize stable, active and selective non-noble metal catalysts for chemoselective hydrogenation of nitroarenes has been developed.

Substituted anilines were obtained from the corresponding nitroarenes with high chemoselectivity using noble metal catalysts, such as Au/TiO₂, Au-Pt/TiO₂. [23] As shown in **Fig. S20**, CoNi@C sample shows much higher reaction rate than Au/TiO₂ when the same amount of solid catalyst is used for the reaction. Nevertheless, the turnover frequency (TOF) based on surface metal atoms were also calculated and compared. As it can be seen in **Fig. S20d and Fig. S20e**, regardless how the catalytic performance is compared (initial reaction rate with the same amount of solid catalyst or TOFs based on exposed surface metal atoms), CoNi@C sample is clearly more active than Au/TiO₂, indicating that non-noble bimetallic NPs can serve as promising substitute for noble metal catalysts.

3.4 Possible role of nitrogen for NNM hydrogenation catalysts

In some reported catalysts, it is claimed that the introduction of nitrogen into the carbon matrix plays a key role to give non-noble metal nanoparticles with high activity. [10,24] However, in our preparation method, though N-containing ligand was not used, we have still achieved high catalytic activity for the chemoselective hydrogenation of nitroarenes. Nevertheless, for the aforementioned samples, they were prepared by calcination in N₂, which may introduce tiny amount of N species into the sample at high temperature. In fact, we observed a nitrogen/metal ratio of ~0.3 in the CoNi@C sample by XPS, which is much lower than those samples prepared in the presence of N-containing

ligands in the literature (with a nitrogen/metal ratio around 4). [10,12,13] Nevertheless, to check the possible influences of nitrogen present in the sample, we have also prepared CoNi@C NPs by calcination in Ar instead of N₂. In that case, no nitrogen was detected in the final sample by XPS. Morphological characterizations (see **Fig. S21** and **Fig. S22**) show that the sample obtained by calcination in N₂ and Ar have very similar morphology and both samples contain alloyed CoNi bimetallic nanoparticles covered by thin carbon layers. Besides, we have also prepared a sample with nitrogen-doping in the carbon matrix by introducing urea in the synthesis as nitrogen source. As shown in **Fig. S23**, in that sample, bimetallic CoNi NPs are covered by N-doped carbon (named as CoNi@C-N doping). The catalytic performances of these three samples were tested for hydrogenation of 3-nitrostyrene. As can be seen in **Fig. S24**, CoNi@C-Ar and CoNi@C-N₂ sample show practically the same activity while the CoNi@C-N sample shows a slightly lower activity.

3.5 Comparison of non-noble metal catalysts prepared by different methods

Fig. 7. Comparison of the mass activity of non-noble metal NPs (NNM@C) prepared from different methods. The initial reaction rate is calculated at low conversion. The reaction condition is the same for all the samples: 0.5 mmol 3-nitrostyrene, 120 °C, 2 mL toluene as solvent and 7 bar of H₂.

Nevertheless, since it has recently been reported that a heterogeneous Co catalyst prepared from

decomposition of metal-organic complexes is active and selective for the hydrogenation of 3-nitrostyrene, [10,25] we have prepared those catalysts following the reported procedure. It is important to remark that, in the reported works, high pressure of H₂ (50 bar) and THF-H₂O as solvent were required, while our catalysts already work with 7 bar of H₂ in toluene. Moreover, we have also prepared Co nanoparticles supported on carbon (named as Co@C/C) according to the reported work and its activity and selectivity has been tested under the milder conditions required by our catalysts. Though the crystalline sizes of metal nanoparticles in the samples prepared according to literature are smaller than those prepared by our methodology, we have compared the activity on the basis of mass of metal weight introduced in the catalytic test, knowing that the TOFs of our catalysts will be underevaluated.

As it is shown in **Fig. 7a**, Co@C and CoNi@C NPs prepared by our carbon-coating method give higher activity than other previously reported Co@C/C catalyst (also see **Fig. S25**). For further comparison, we have also prepared here two Co@C catalysts by decomposition of a metal-organic framework (MOF) precursor (i.e. Co@C-BTC without N-containing organic linkers in the MOF precursor and Co@C-ZIF with N-containing organic linkers in the MOF precursor). [23,26] From TEM and HRTEM images (see **Fig. S26** and **Fig. S27**), it can be seen that, those Co NPs are encapsulated in the carbon matrix. As shown in **Fig. S28**, both Co@C-BTC and Co@C-ZIF show low activity for hydrogenation of 3-nitrostyrene under the same conditions as Co@C NPs prepared in this work by carbon-coating method. And the similar performance of Co@C-BTC and Co@C-ZIF samples indicates that the introduction of N in the carbon matrix doesn't show obvious advantage for improving the activity of Co@C NPs.

After presenting that the CoNi@C was more active under our reaction conditions, we also tested CoNi@C NPs with a high substrate/catalyst ratio for hydrogenation of 3-nitrostyrene using similar conditions to the previously reported works. As shown in **Fig. S29**, CoNi@C sample still gives ca. 6 times higher activity than the reported Co@C/C catalyst under the same reaction conditions (110 °C, 10 bar of H₂ in THF-H₂O solvent) with the same loading amount of metal catalyst (molar ratio substrate/metal is 40). In summary, the bimetallic catalyst prepared with the present carbon-coating methodology shows a significant advantage for performing the chemoselective hydrogenation under milder conditions (much lower pressure and shorter reaction time) than any of the catalysts reported

before (see **Table S2**), without requiring the so-claimed metal-N interaction to achieve high activity and selectivity.

3.6 Application of Co@C NPs for hydrogenation of levulinic acid

Fig. 8. Hydrogenation of levulinic acid to γ -valerolactone by Co@C NPs and the stability tests. Reaction conditions: 1.0 mmol γ -valerolactone, 200 °C, 2 mL toluene as solvent and 10 bar of H_2 .

The catalytic behavior of NNM@C NPs was also studied for hydrogenation of levulinic acid to γ -valerolactone, which is an important model reaction in the field of biomass to chemicals. As can be seen in **Fig. 8**, the Co@C NPs can work at 200 °C with 10 bar of H_2 , which are milder than those reports using Au-, Ru- and Cu-based catalysts. [27-29] Over 98% yield of γ -valerolactone was obtained within 45 min in the first run. The stability of non-noble metal catalysts is an important issue for the hydrogenation of levulinic acid. A significant leaching of Cu into the solution can be observed on supported Cu catalysts. [30] Besides, Shimizu et al. reported the application of Ni-MoOx/C catalyst for the hydrogenation levulinic acid under mild conditions. [31] However, the reported Ni-MoOx/C catalyst deactivated after the first use. In the case of Co@C NPs, after the first use, the solid catalyst can be easily recycled and used again after simply washing with acetone and toluene. Although the reaction rate decrease, 98% yield can still be obtained when prolonging reaction time to 1 h. Further recycle tests show that the activity can be further maintained for at least

5 cycles without obvious deactivation. The morphology of Co@C NPs after the hydrogenation of levulinic acid reaction is also checked by TEM. As one can see in **Fig. S30**, monodispersed Co NPs are preserved after the reaction, indicating the chemical stability of Co@C NPs during the hydrogenation of levulinic acid. Future works on developing more efficient and stable mono and bimetallic NNM NPs for hydrogenation of levulinic acid and other reactions are undergoing in our laboratory.

4 Conclusions

In this work, we demonstrate a facile method to prepare monometallic and bimetallic NPs via a simple carbon coating process. Bimetallic CoNi NPs show significantly higher activity than monometallic Co and maintain high selectivity in chemoselective hydrogenation of nitroarenes. In addition, we also show that these materials can be promising catalyst for other reactions like hydrogenation of levulinic acid to γ -valerolactone. Our new method can also be a general method to prepare non-noble metal nanoparticles for heterogeneous catalytic applications and the results presented here also provide new insights for rational design of non-noble metal nanoparticulate catalysts as substitute of noble metal catalysts.

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