

Highly Active and Selective Catalysis of Bimetallic Rh₃Ni₁ Nanoparticles in the Hydrogenation of Nitroarenes

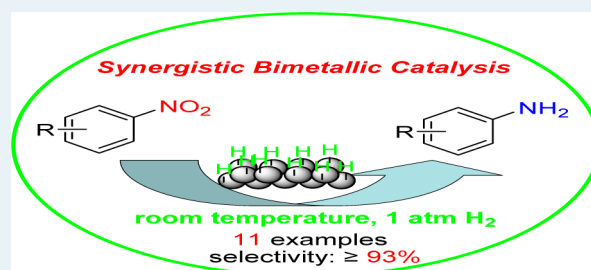
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S Supporting Information

ABSTRACT: Because of the requirements of sustainable development as well as the desirability of using molecular hydrogen as a chemical reagent, it is of paramount importance and great challenge to develop highly active and selective catalysts for the hydrogenation of organic molecules, including substituted nitroarenes. We approach this question by probing unsupported bimetallic nanoparticles. A series of novel bimetallic Rh_xNi_y ($x, y = 1, 2, 3$) nanoparticles were successfully prepared using our “noble metal-induced reduction” strategy. Unsupported Rh₃Ni₁ nanoparticles were subsequently identified to be a highly active and exceedingly selective catalyst for the hydrogenation of nitroarenes under ambient conditions, underscoring a remarkable synergistic effect of the two metals. Further experiments showed that the Rh₃Ni₁ catalyst could be a highly efficient, selective, and recyclable catalyst for a range of nitroarene substrates. This work showcased the value of bimetallic nanoparticles in catalysts development for sustainable chemistry.

KEYWORDS: bimetallic nanoparticle, synergistic effect, nitroarenes, hydrogenation, selectivity



1. INTRODUCTION

Functionalized anilines are ubiquitous intermediates for pharmaceuticals, polymers, dyes, and urethanes.¹ For their importance, a plethora of methods, including stoichiometric reducing agents,^{2–6} metal-catalyzed reduction featuring various reducing agents other than molecule hydrogen,^{7–14} and catalytic hydrogenation,^{15,16} to reduce nitroarenes have been developed. Among them, catalytic hydrogenation is of particular interest owing to its environmental friendliness, atomic efficiency, and compatibility with industrial processes. The sustainable development demands highly active and selective catalysts for the hydrogenation of organic molecules, including substituted nitroarenes. Unfortunately, existing catalysts have often failed to meet the dual requirements of activity and selectivity. On one hand, catalysts (e.g., Pd/C) with high intrinsic activity suffer from nonselective hydrogenation, leading to undesired byproducts and difficult purification. On the other hand, catalysts^{17–24} of higher selectivity require high reaction temperature and high H₂ pressure because of their lower intrinsic activity, leading to high energy input and difficulties in H₂ handling.

Bimetallic nanoparticle (BNP) catalysts represent an active frontier for heterogeneous catalyst development.^{25–32} They often show performance superior to their monometallic counterparts, a phenomenon collectively referred as “synergistic effects”.^{33,34} In addition, the cost of the catalyst could be significantly reduced by the incorporation of a nonprecious metal.³⁵ Despite these attractive features, few known BNPs

possess both high activity and high selectivity. Very recently, Yamamoto and co-workers reported an inspiring dendrimer-stabilized monodisperse bimetallic Rh/Fe NP catalyst for nitroarene hydrogenation. They showed that the introduction of Fe dramatically enhanced the catalytic performance.³⁴ Notably, the dendrimer matrices appear necessary to prevent NPs aggregation and to provide a desired chemical interface between the NPs and the reaction media.

Our research in this area^{33,36} has led us to explore unsupported NPs as highly active and selective catalysts.^{37–39} We have successfully synthesized a series of unsupported Rh_xNi_y ($x, y = 1, 2, \text{ and } 3$) BNPs of similar size and morphology on the basis of our “noble metal-induced reduction” strategy. Experimental data suggested that the composition of these Rh_xNi_y NPs plays an important role in dictating their catalytic performance in the hydrogenation of nitroarenes. We further demonstrate that the Rh₃Ni₁ BNPs could be a highly active and selective catalyst for the hydrogenation of an array of nitroarenes under ambient conditions.

2. RESULTS AND DISCUSSION

2.1. Catalyst Preparation. Although many successful methods have been developed for the syntheses of precious

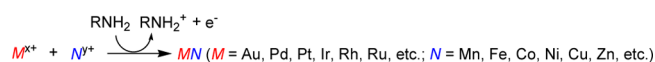
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monometallic nanoparticles (MNPs),^{40–42} controllable synthesis of monodisperse BNPs remains challenging.^{43,44} To this end, we recently developed a novel strategy termed “noble metal-induced reduction” (NMIR). This strategy features a process in which the noble metal induced reduction of the non-noble metal ions (Co^{2+} , Ni^{2+} , Cu^{2+}) by octadecylamine (ODA).^{45–47} By virtue of this process, a wide array of BNPs consisting of noble and non-noble metals could be synthesized using ODA as the surfactant, solvent, and reducing agent (Scheme 1). The size and morphology of the BNPs could be controlled by adjusting the reaction parameters (e.g., concentration of precursors and reaction temperature).

Scheme 1. The NMIR Strategy for the Synthesis of Various BNPs in ODA



Following this strategy, we prepared various Rh_xNi_y bimetallic nanoparticles with different compositions by the coreduction of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and Nickel(II) acetylacetonate in ODA (Table S1, Supporting Information).

2.2. Catalyst Characterization. The as-prepared Rh_3Ni_1 BNPs are composed of wormlike particles (Figure 1a). The

inductively coupled plasma mass spectrometry (ICP-MS) confirmed that the Rh/Ni ratios were in accordance with the designed compositions of the Rh_xNi_y BNPs (Table S2, Supporting Information). For example, Rh_3Ni_1 was composed of 75.4% of Rh and 24.6% of Ni. Further characterizations were carried out with Rh_3Ni_1 NPs. Figure 1b shows its XRD pattern. Vertical lines indicate the (111), (200), and (220) standard peak positions (left to right) for Rh and Ni. Three peaks corresponding to the planes (111), (200), and (220) reflections appeared between those of Rh (JCPDS 05-0685) and Ni (JCPDS 04-0850) standard peaks, which confirmed the formation of Rh_3Ni_1 BNPs. To further investigate the structure of Rh_3Ni_1 NPs, the elemental distributions of Rh and Ni were studied by a high-angle, annular dark-field scanning transmission electron microscope (HAADF-STEM). The representative STEM image and its corresponding Rh and Ni elemental maps are shown in Figure 1c–e. It could be seen that both Rh and Ni were evenly distributed in each individual nanoparticle.

The energy dispersive spectroscopy (EDS) line-scanning profile across a single particle of Rh_3Ni_1 shows a Rh/Ni ratio of 78.8%:21.2% (Figure 1f), which is in good agreement with the ICP-MS result.

Other Rh_xNi_y BNPs and Rh NPs were characterized by TEM, ICP-MS, and XRD (Figure S1 and Table S2 as well as

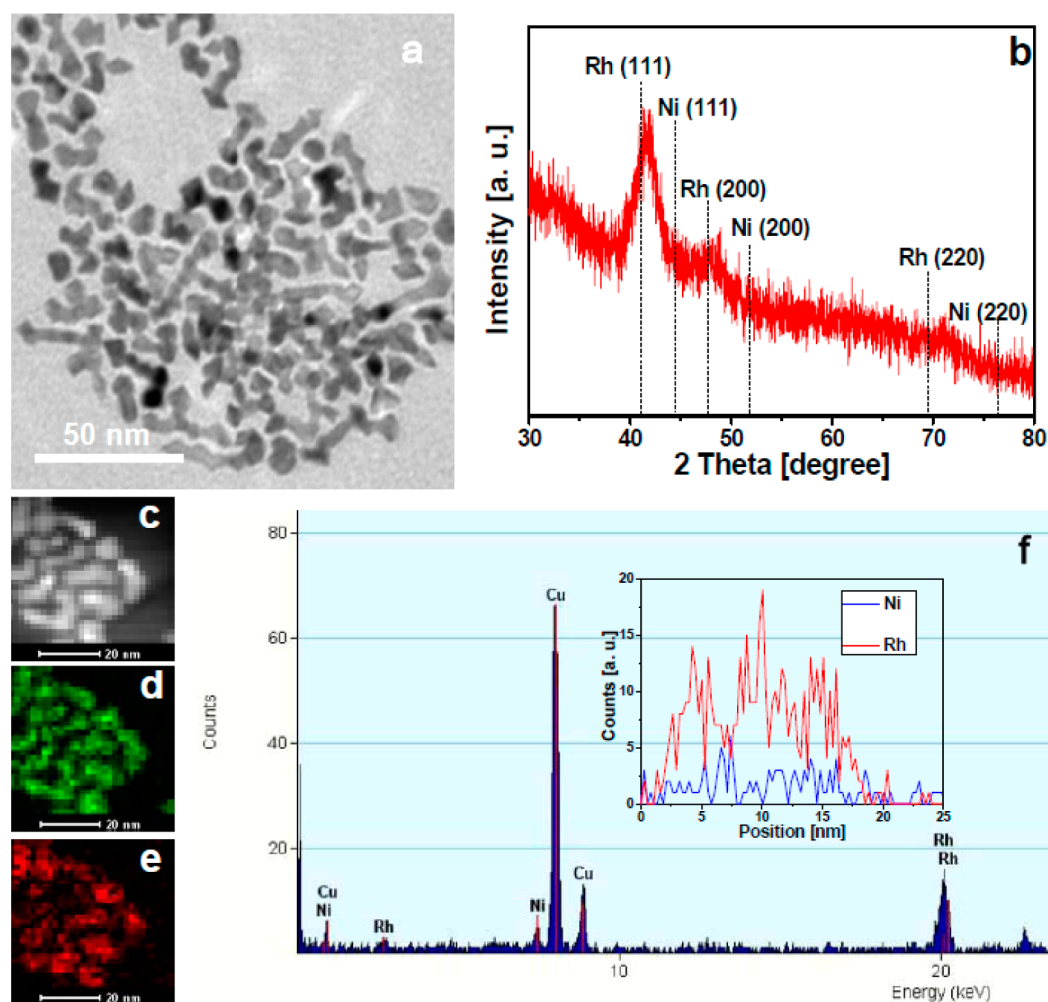
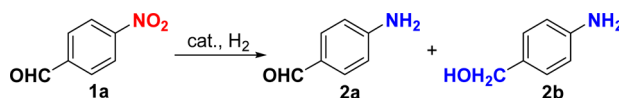


Figure 1. Characterization of the as-prepared Rh_3Ni_1 BNPs: (a) TEM image, (b) XRD pattern, (c–e) HAADF-STEM image together with the EDS mapping of an individual Rh–Ni nanoparticle (green = Rh–K, red = Ni–K), and (f) EDS spectrum.

Figure S2, Supporting Information). Overall, the size, morphology, and composition of the Rh_xNi_y BNPs were effectively controlled, which allowed meaningful comparison of their catalytic performance.

2.3. Catalytic Activity. Using 4-nitrobenzaldehyde **1a** as the model substrate for selective hydrogenation, we started our initial evaluation of the NPs (Table 1). To detect potential

Table 1. Hydrogenation of 4-Nitrobenzaldehyde Using Different NP Catalysts^a



entry	catalyst	conv [%] ^b	sel of 2a [%] ^b
1	Rh	84	55
2	Rh_1Ni_3	<1	
3	Rh_1Ni_2	41	31
4	Rh_1Ni_1	60	43
5	Rh_2Ni_1	82	62
6	Rh_3Ni_1	> 99	> 99
7 ^c	Rh_3Ni_1	>99	>99

^aStandard reaction conditions: 0.5 mmol substrate, 0.3 mol % catalyst (based on metal), 3 mL of AcOEt under room temperature/ H_2 atmosphere for 12 h. ^bSelectivity = yield/conversion, where conversion and yield were determined by GC. The rest of the product was mainly the 4-aminobenzyl alcohol **2b**. ^cThe 5th run.

catalysts of high activity, we employed the reactions with a very low catalyst loading (0.3 mol %) under mild reaction conditions (atmospheric H_2 pressure and room temperature). As the benchmark, pure Rh NPs showed good activity but low selectivity (entry 1). Rh_1Ni_3 was found to be inactive (entry 2). Interestingly, a steady improvement in both activity and selectivity was observed when the Rh ratios increased (entries 3–5). To our great delight, the best results were obtained with Rh_3Ni_1 NPs (entry 6). We further identified that several solvents, including EtOAc, THF, and MeOH, were compatible with this catalyst (Table S3, Supporting Information), underscoring the intrinsic catalytic property of the Rh_3Ni_1 catalyst.

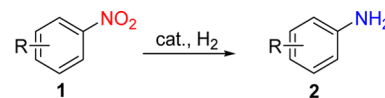
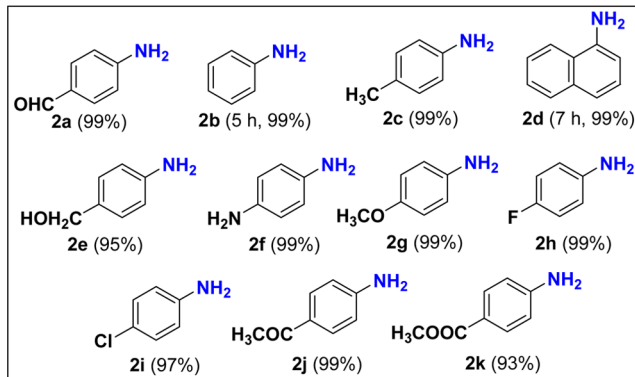
The Rh_3Ni_1 catalyst could be easily recycled by centrifugation or sedimentation, without decay in activity and selectivity for at least 5 cycles (entry 7). After the fifth cycle, various experiments were carried out to examine the recycled catalyst. The TEM image showed that the catalyst did not have obvious changes in the shape and size (Figure S5, Supporting Information) relative to the fresh catalyst. ICP-MS results showed that it was composed of 74.7% of Rh and 25.3% of Ni, in accordance with the composition of the fresh catalyst. In addition, in the filtrate, no Rh_3Ni_1 BNPs were observed to the detectable limits. These results show that leaching did not occur and the reaction was catalyzed exclusively by the heterogeneous Rh_3Ni_1 BNPs. It is possible that the mild reaction conditions contributed to the stability and recyclability of the catalyst.

We then turned our attention to the reaction mechanism. To this end, we carried out kinetic studies using the optimized conditions (Table 1, entry 6). The concentrations of nitroarene **1a** and aniline **2a** did not increase linearly with increased reaction time (Figure S4, Supporting Information), suggesting that the reaction did not have dynamically pseudo-zero-order dependence on neither reactant. This observation revealed the multistep nature of nitro group reduction.^{48,49} It is likely that

the nitro group was absorbed more strongly on the surface of Rh_3Ni_1 BNPs than the aldehyde carbonyl group, leading to the quick reduction of the nitro group to produce the nitroso intermediate. Subsequent fast reduction to hydroxylamine, followed by final reduction in the rate-determining step, gave rise to product aniline **2a**. Importantly, using crude NMR or GC, we did not detect any known side products (e.g., imine and secondary amine) during the reaction course (Scheme S1, Supporting Information).

2.4. Reaction Scope. We extended the Rh_3Ni_1 catalyst to various nitroarenes to examine the generality of the reaction (Table 2). Satisfyingly, in all cases, the desired products were

Table 2. Selective Hydrogenation of Various Nitroarenes^a

^aStandard reaction conditions: **1** (0.5 mmol) and Rh_3Ni_1 (0.3 mol %) in 3 mL of AcOEt under hydrogen atmosphere at room temperature for 12 h. Isolated yields.

obtained in excellent isolated yields with high selectivity. The electronic features of the nitroarenes did not affect the reaction rate or selectivity. Importantly, several reducible groups, including aryl-chloride (**2i**), ketone (**2j**), and ester (**2k**), were compatible with the catalyst. These results indicate that the Rh_3Ni_1 represents the first catalyst that has both high activity and high selectivity in nitroarene hydrogenation.

3. CONCLUSIONS

We have achieved the controllable syntheses of Rh_xNi_y ($x, y = 1, 2, \text{ and } 3$) BNPs with similar morphology and size using our NMIR strategy. Screening of these NPs in the nitroarene hydrogenation led to the identification of the optimal Rh_3Ni_1 BNPs catalyst that significantly out-performed the corresponding monometallic Rh NPs, underscoring a remarkable “synergistic effect”. In-depth characterization revealed the stability of the catalyst under the reaction conditions, which accounts well for its high recyclability. We further demonstrated that this catalyst is highly active and selective for the hydrogenation of a scope of nitroarenes bearing various reducible groups. This work should spur much interest in searching novel BNPs as inexpensive and selective catalysts for other important hydrogenation reactions. Ongoing efforts are dedicated to understand the origin of the enhanced activity and selectivity so as to guide future design of the optimal catalysts.

4. EXPERIMENTAL SECTION

4.1. Preparation of Catalysts. We employed the NMIR strategy in the synthesis of various Rh_xNi_y BNPs. Take the synthesis of Rh_3Ni_1 for example. An aqueous solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (2.25 mL, 0.05 mmol/mL) and nickel(II) acetylacetonate (9.6 mg) was mixed with a solution containing 2 g of ODA, and the resulting mixture was slowly heated to 120 °C to form a transparent solution, then injected into 8 g of ODA at 250 °C with vigorous stirring and aged at 230 °C for 1.5 min. Finally, the resulting precipitate was washed several times with ethanol and dried. The as-obtained Rh_3Ni_1 BNPs were dispersed in *n*-hexane for future use. By adjusting the amount of metal precursors, other Rh_xNi_y BNPs and Rh NPs were prepared by the similar procedure mentioned above (for more details, see Table S1, Supporting Information).

4.2. Analysis. TEM observation was performed on a Hitachi model H-800 transmission electron microscope (JEM 2010F, JEOL) operated at 200 kV. TEM specimens were prepared via the following procedure: the samples were dispersed in cyclohexane with the aid of 10 min of ultrasonic vibration. Then a drop of the solution was transferred onto a standard holey carbon-covered-copper TEM microgrid. Powder X-ray diffraction (XRD) patterns of all the products obtained in this work were recorded with a Bruker D8 Advance X-ray powder diffractometer with monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Energy dispersive spectroscopy (EDS) was recorded to determine the composition of the obtained products. The content of NPs was determined by inductively coupled plasma mass spectrometry (ICP-MS). ^1H NMR was conducted on a JEOL JNM-ECX400 400 MHz instrument. GC chromatography was performed on a SP-6890 with a FID detector equipped with a capillary column (SE-54, 30 m \times 0.50 μm \times 0.53 mm). Parameters were as follows: initial oven temperature, 60 °C, 3 min; ramp, 15 °C/min; final temperature, 260 °C; final time, 10 min; injector temperature, 260 °C; detector temperature, 250 °C; injection volume, 1 μL .

4.3. Typical Procedure for the Hydrogenation of Nitroarenes. To a solution of substrate (0.5 mmol) in 3 mL of solvent in a 25 mL round flask, catalyst (containing 0.3 mol % metal with respect to the substrate) was added, and the reaction mixture was degassed two times, each time replacing the vacuum with hydrogen, then stirred at room temperature under H_2 . When the reaction was over, the catalyst was recovered by centrifugation. The supernatant obtained was analyzed by GC and purified by silica gel chromatography using an appropriate eluent for ^1H NMR test.

■ ASSOCIATED CONTENT

Supporting Information

Preparation and characterization of Rh NPs and Rh_xNi_y ($x, y = 1, 2, 3$) BNPs, reaction mechanism studies, and the spectral data for all the products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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