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Rhodium–nickel bimetallic nanocatalysts: high performance of room-temperature hydrogenation⁺

Haohong Duan,^a Dingsheng Wang,^a Yuan Kou^b and Yadong Li*^a

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Rhodium–nickel bimetallic nanocrystals were fabricated with high activity in hydrogenation of olefins, nitroarenes and arenes at room temperature, indicating that bimetallic nanocrystals of noble and non-noble metals represent a novel kind of nanocatalyst.

The selective hydrogenation of arenes is one of the most important organic reactions since it is used to prepare a wide variety of compounds which find applications as industrial feedstocks, such as cyclohexane, and in the production of low-aromatic diesel fuels.^{1–5} Hydrogenation of arenes is traditionally carried out using heterogeneous noble metal catalysts under forced reaction conditions (high temperature and/or high pressure)^{6–9} and developing effective catalysts that can catalyze hydrogenation of arenes under milder conditions remains a significant challenge.

Rhodium nanocrystals (Rh NCs) are commonly used as catalysts for the hydrogenation of arenes in the laboratory.^{10–13} However, their use on an industrial scale is restricted by the limited reserves and high price of Rh. Many efforts have been made by scientists worldwide to solve this problem. One approach has focused on increasing the efficiency of the utilization of Rh by preparing NCs with selective exposure of well-defined crystal facets that show high activity and high selectivity.^{14–16} Another potential solution is the partial replacement of Rh with a non-noble metal. In addition to the economic benefits of this substitution, the resulting bimetallic NCs do not always possess a simple combination of the properties of their individual constituents, and may also show new properties and capabilities due to a synergy between the two metals.^{17–23} Therefore, bimetallic NCs containing Rh and

tive catalysts that can reduce Rh usage while retaining or even enhancing the catalytic properties. In this work we focus on rhodium-nickel NCs because, in addition to its lower cost, nickel (Ni) offers an additional advantage of imparting ferromagnetic behavior to the NCs. Such magnetic catalysts can be reclaimed by magnetic separation after use, which allows the catalyst to be easily reused and minimizes loss of Rh during catalyst recycling. Since the nanoparticles can be easily separated in this way, it is not necessary to support them on materials such as Al₂O₃, silica, SBA-15, and carbon nanotubes (CNTs) to facilitate their recycling.8,10,24 The main drawback of such heterogeneous supported catalysts is the loss of activity and selectivity because the active sites are confined in twodimensional space which limits access of the reactants. Metal NCs can generally be well dispersed in non-polar solvents due to their hydrophobic surfaces, and so they should also be well dispersed in an arene hydrogenation reaction system. This type of catalyst, which combines the advantages of both homogeneous and heterogeneous catalysts, can be regarded as a "semi-homogeneous catalyst": the NCs are heterogeneous in nature but, similar to homogeneous catalysts, their high degree of dispersion in the solvent facilitates the access of reactant molecules.

non-noble metals may offer opportunities for developing effec-

Although many methods for preparation of monometallic Rh NCs have been developed in recent years,^{25–27} the controllable synthesis of bimetallic NCs of Rh and non-noble metals is much more difficult because non-noble metals are much less readily reduced than noble metals like Rh.28-30 Herein, we demonstrate the synthesis of Rh_xNi_{1-x} bimetallic NCs using a simple one-pot procedure. The composition of the bimetallic NCs can be tailored over a broad range of values of x. We have evaluated the catalytic performance of Rh-Ni NCs with different compositions in the room-temperature hydrogenation of arenes and found that they exhibit higher activity than pure Rh NCs. Furthermore, the bimetallic nanocatalysts exhibit high performance in hydrogenation of olefins and nitroarenes. These exciting preliminary results are an indication that bimetallic NCs of noble and non-noble metals represent a new kind of nanocatalysts that may replace noble metals.

^a Department of Chemistry and the State Key Laboratory of Low-Dimensional Quantum Physics, Tsinghua University, Beijing, China.

E-mail: ydli@mail.tsinghua.edu.cn; Tel: +86-10-62772350

^b PKU Green Chemistry Center, Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China. E-mail: yuankou@pku.edu.cn

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Fig. 1 (a) TEM image of Rh–Ni nanocrystals, (b) HRTEM image of an individual Rh–Ni nanocrystal (inset, up-right: enlarged HRTEM image, down-right: FFT pattern). (c–e) HAADF-STEM image together with the EDX mapping of an individual Rh–Ni nanocrystal (yellow = Rh–L, red = Ni–K).

In the synthesis of Rh_xNi_{1-x} bimetallic NCs, RhCl₃·3H₂O and $Ni(acac)_2$ (acac = acetylacetonate) were used as the metal precursors while octadecylamine (ODA) was employed as simultaneously the solvent, stabilizing surfactant, and reducing agent. The reaction was performed at 230 °C and required only 2 min (the detailed procedure is described in the ESI[†]). Using the synthesis result of Rh_{0.67}Ni_{0.33} NCs as an example (Fig. 1a), Rh_{0.66}Ni_{0.33} NCs with an average size of 10 nm are successfully produced in high yield. Fig. 1b presents a representative enlarged HRTEM image of an individual Rh_{0.66}Ni_{0.33} NC. The well-resolved fringes and fast Fourier-transform (FFT) pattern shown in the insets of Fig. 1b reveal clear lattice fringes with a regular distance of 0.218 nm, indicating the {111} facets of bimetallic Rh-Ni NCs with face-centered cubic (fcc) structure. The powder X-ray diffraction (XRD) analysis also determines the structural nature of the NCs (Fig. S1, ESI⁺). In the XRD pattern of $Rh_{0.67}Ni_{0.33}$, the peaks corresponding to the (111), (200), and (220) reflections appeared between those of Rh (JCPDS 05-0685) and Ni (JCPDS-04-0850) standard peaks, demonstrating the bimetallic structure of obtained NCs. The (111) peak has a much higher intensity than the others due to the exposure of (111) planes. To further confirm the bimetallic structure, the elemental distributions of these two metals were studied by a high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM). Fig. 1c-e show a representative STEM image and its corresponding Rh and Ni elemental maps, clearly revealing that both Rh and Ni were distributed evenly in each individual NC. The compositions of the Rh_{0.66}Ni_{0.33} NCs - as determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) - were close to the expected stoichiometries, with the measured results for Rh_{0.66}Ni_{0.33} being Rh_{0.69}Ni_{0.31}.

It was also possible to prepare Rh_xNi_{1-x} NCs with other compositions in a broad range due to the high miscibility of Rh and Ni and the high versatility of the procedure. XRD patterns of the as-obtained products are also shown in Fig. S1 (ESI[†]). For all the Rh_xNi_{1-x} , the corresponding peaks appeared between those of Rh and Ni standard peaks. More importantly, with the increasing content of Ni, the peaks continuously shifted from the Rh standard peaks to Ni standard ones, demonstrating that the cubic unit cell parameter decreases when Rh atoms are progressively replaced by smaller nickel atoms. The HRTEM of Rh_xNi_{1-x} with different composition (Fig. S2, ESI[†]) and the

Table 1 Hydrogenation of phenol catalyzed by Rh_xNi_{1-x} NCs⁴

Catalyst	Conv. ^b (%)	Cyclohexanone ^b (%)	Cyclohexanol ^b (%)	${\mathop{\rm TOF}^c}{\left({{{{\rm{h}}^{ - 1}}}} ight)}$
Rh	42.5	38.8	61.2	283
Rh _{0.67} Ni _{0.33}	54.4	28.8	71.2	363
Rh _{0.5} Ni _{0.5}	22.3	38.5	61.5	149
Ni	N.D.	N.D.	N.D.	0

^{*a*} 64 mmol phenol substrate, 0.025 mol% catalyst (based on Rh), 6 mL cyclohexane under H₂ (40 atm) at room temperature (25 °C) for 6 hours. ^{*b*} Determined by GC-MS. ^{*c*} Turnover frequency (TOF) measured in [mol product][mol metal]⁻¹ h⁻¹.

corresponding variation of lattice parameters (Fig. S3[†]) also show the expected decrease in unit cell size with increasing values of *x*. It should be noted that monometallic Ni NCs (x = 0) could also be obtained but the process demands more harsh conditions and the methods changed a little (see ESI[†]).

As a probe reaction to evaluate the catalytic performance of Rh_xNi_{1-x} nanoparticles, phenol hydrogenation was carried out at room temperature (25 °C) and 40 bar hydrogen pressure for 6 h. We choose Rh, Rh_{0.67}Ni_{0.33}, Rh_{0.5}Ni_{0.5} and Ni nanoparticles (Fig. S4 and S5, ESI⁺) to preliminarily evaluate the catalysis for their obviously different Rh/Ni ratio and similar size distribution (Fig. S6[†]). The results are summarized in Table 1. The observed hydrogenation products of phenol were cyclohexanone and cyclohexanol. Compared with the monometallic Rh, the Rh_{0.66}Ni_{0.33} nanocatalyst showed both higher activity and higher selectivity for cyclohexanol. However, when the Ni content was further increased, the resulting Rh_{0.5}Ni_{0.5} NCs showed a much lower activity, and comparable selectivity, to the monometallic Rh nanocatalyst. Because the catalytic reactions using Rh_xNi_{1-x} NCs with similar size and morphology were performed under the same conditions, the very different performances of the three catalysts must arise from the different Ni content in the NCs as the influence of other parameters can be eliminated. The molar ratio of Rh to Ni can greatly influence the surface structure, electron density distribution, and the effective electronegativity of bimetallic NCs, all of which might play a key role in determining the catalytic activity and selectivity.

Room-temperature hydrogenation of benzene catalyzed by Rh, $Rh_{0.67}Ni_{0.33}$, and $Rh_{0.5}Ni_{0.5}$ NCs was also studied, and the results are given in Table 2. Hydrogenation of benzene catalyzed by Rh_xNi_{1-x} nanocatalysts afforded the completely saturated product cyclohexane. In this case, the activity of the catalysts increased with increasing nickel content, with the TOF

Table 2 Hydrogenation of benzene catalyzed by $Rh_xNi_{1-x} NCs^a$					
Catalyst	Conv. ^{b} (%)	$\mathrm{TOF}^{c}\left(\mathrm{h}^{-1} ight)$			
Rh	28.6	164			
Rh _{0.67} Ni _{0.33}	45.7	261			
Rh _{0.5} Ni _{0.5}	50.8	290			
Ni	N.D.	0			

^{*a*} 64 mmol benzene substrate, 0.025 mol% catalyst (based on Rh), 6 mL cyclohexane under H₂ (40 atm) at room temperature (25 °C) for 7 hours. ^{*b*} Determined by GC-MS. ^{*c*} TOF measured in [mol product][mol metal]⁻¹ h⁻¹. for Rh_{0.67}Ni_{0.33} and Rh_{0.5}Ni_{0.5} nanocatalysts being, respectively, 1.6 and 1.8 times higher than that of the pure Rh catalyst. It is interesting that for hydrogenation of phenol the catalytic activity increases in the order Rh_{0.5}Ni_{0.5} < Rh < Rh_{0.67}Ni_{0.33}; while for hydrogenation of benzene the catalytic activity increases in the order Ni < Rh < Rh_{0.67}Ni_{0.33} < Rh_{0.5}Ni_{0.5}. By virtue of the differences in steric effects and electron density distributions between benzene and arene derivatives, hydrogenation catalysts often show different performance. Clarification of the influence of the composition of Rh_xNi_{1-x} NCs on their catalytic properties in different reactions requires further detailed investigation which is currently underway in our laboratory.

The above two hydrogenation reactions confirm that partial replacement of the noble metal Rh with the non-noble metal Ni in nanocatalysts is an effective means not only to reduce Rh usage and the overall cost of the catalyst, but can also endow the new catalysts with higher activity resulting from a synergistic effect between Rh and Ni. From the preliminary results, it is obvious that the composition of the Rh_xNi_{1-x} nanoparticles has marked influence on their catalytic performance. It must be stated that, here, we have just provided proof of concept without any attempt to optimize the composition of the catalysts or the reaction conditions. It should therefore be possible to develop other Rh–Ni bimetallic nanocatalysts with lower Rh content, as well as higher activity and selectivity, for room-temperature hydrogenation of arenes.

Furthermore, we choose the Rh_{0.67}Ni_{0.33} nanocatalyst to expand the hydrogenation reactions to a wide range of substrates, from olefins, nitroarenes, to arenes. The catalytic results are shown in Table S1. As expected, the Rh_{0.67}Ni_{0.33} nanocatalyst showed excellent activity under mild conditions. The hydrogenation of olefins, for example, is complete within one hour (entry 1-3 in Table 2). Nitrobenzene and 4-chloronitrobenzene were hydrogenated cleanly after 16 and 24 hours, respectively. The catalytic reactions under different hydrogen pressures (1 and 40 atm) were also investigated (Table S2, ESI⁺). Under a hydrogen atmosphere, the hydrogenation reaction exclusively proceeds on the branch and the selectivity is higher than 99%, mainly because the steric resistance of benzene ring hinders the hydrogenation occurring on it. However, when the applied hydrogen pressure was as high as 40 atm, part of the benzene ring was completely hydrogenated. Although the selectivity is low, changing the hydrogen pressure is still an effective and promising approach to control the selectivity. To test the stability of the Rh_{0.67}Ni_{0.33} nanocatalyst during catalytic reaction, the system of hydrogenation of styrene was recycled further five times (Table S3, ESI⁺). As a result, high product yields of 97.4% were still obtained after five batches, demonstrating the high stability of the ODA-protected Rh_{0.67}Ni_{0.33} nanocatalyst in ethyl acetate.

In summary, this work presents a successful synthesis of Rh–Ni bimetallic NCs with advantages in room-temperature hydrogenation of olefins, nitroarenes and arenes, showing that incorporation of Ni into Rh NCs can endow them with superior catalytic properties compared to pure Rh. Therefore these novel Rh–Ni bimetallic nanocatalysts have potential applications in industrial hydrogenation reactions.

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