Supporting Information

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

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Experimental Details

**Chemicals:** RhCl\(_3\)·3H\(_2\)O and Ni(acac)\(_2\) were purchased from Alfa Aesar. ODA, ethanol, cyclohexane, phenol, benzene, cyclohexanone, cyclohexanol, cyclohexene, cyclohexane, styrene, ethylenzene, Benzalacetone, benzylacetone, Nitrobenzene, Aniline, 4-Chloronitrobenzene, 4-Chloroaniline were of analytical grade from the Beijing Chemical Factory of China. All the reagents used in this work were used without further purification.

**Synthesis:** In a typical synthesis of Rh\(_{0.67}\)Ni\(_{0.33}\) NCs, 2 mL of RhCl\(_3\)·3H\(_2\)O aqueous solution (0.05 mmol/mL) and 0.0128 g Ni(acac)\(_2\) were mixed with 2 g of octadecylamine (ODA) and the resulting mixture was heated to 110 °C with strongly stirring to evaporate the water and form a transparent solution. The mixture was then injected into 6.6 g of ODA preheated at 250 °C with vigorous stirring. The solution turned black immediately with the formation of a precipitate. After reaction at 230 °C for 2 minutes, the precipitate was washed several times with ethanol, and then dispersed in a non-polar solvent such as cyclohexane. Rh\(_x\)Ni\(_{1-x}\) with 0<x<=1 were prepared using the same procedure of Rh\(_{0.67}\)Ni\(_{0.33}\) nanocrystals above except that the total molar amount of Rh and Ni was kept at 0.15 mmol.

In the synthesis of Ni NCs, 0.128 g Ni(acac)\(_2\) were mixed with 8.6 g of ODA and the resulting mixture was heated to 230 °C and kept at this temperature for 5 min. The precipitate was washed several times with ethanol, and then dispersed in a non-polar solvent such as cyclohexane.

**Characterization:** Powder XRD patterns were recorded with a Bruker D8 ADVANCE X-ray powder diffractometer with Cu K\(\alpha\) radiation (\(\lambda = 1.5406 \text{ Å}\)). The particle size and morphology of as-synthesized samples were determined by using Hitachi model H-800 transmission electron microscope and a JEOL-2010F high-resolution transmission electron microscope.

**Catalytic measurements:** The substrate and Rh\(_x\)Ni\(_{1-x}\) NCs solution (synthesized as described above) were placed in an autoclave. In a typical experiment, H\(_2\) (40 bar) was introduced into the autoclave after the reactor was purged 3 times with H\(_2\). The mixture was stirred at 800 rpm at room temperature (25 °C) for the required time.
Supplementary Figures

Fig. S1. The powder X-ray diffraction (XRD) patterns of the as-obtained Rh, RhxNi1-x, and Ni nanocrystals.
Fig. S2. TEM and HRTEM images as well as the particle size distributions of Rh–Ni NCs with different compositions: (a, b, c) Rh$_{0.45}$Ni$_{0.55}$; (d, e, f) Rh$_{0.33}$Ni$_{0.67}$; (g, h, i) Rh$_{0.2}$Ni$_{0.8}$; (j, k, l) Rh$_{0.12}$Ni$_{0.88}$; (m, n, o) Rh$_{0.1}$Ni$_{0.9}$. 
**Fig. S3.** The variation of lattice parameter of Rh$_x$Ni$_{1-x}$ with composition.

**Fig. S4.** (a) Representative TEM image of as-obtained Ni NCs. (b) HRTEM image of an individual Ni NC. (Inset, enlarged HRTEM image)
Fig. S5. Representative TEM and HRTEM images of (a, b) Rh, (c, d) Rh$_{0.67}$Ni$_{0.33}$ and (e, f) Rh$_{0.5}$Ni$_{0.5}$. (Inset, enlarged HRTEM images)

Fig. S6. Size distribution for Rh (black), Rh$_{0.67}$Ni$_{0.33}$ (red) and Rh$_{0.5}$Ni$_{0.5}$ (blue).
Table. S1 Hydrogenation of alkenes, nitroarenes and arenes in the presence of Rh$_{0.67}$Ni$_{0.33}$ NCs$^a$

\[
\begin{align*}
\text{Entry} & \quad \text{Substrate} & \quad \text{Product} & \quad \text{t[h]} & \quad \text{Conv}$^a$ [%] & \quad \text{Selectivity}$^b$ & \quad \text{TOF}$^c$ \\
1 & Cyclohexene & Cyclohexane & 1 & \text{>99} & \text{>99} & 3253 \\
2 & Styrene & Ethylenzene & 0.25 & \text{>99} & \text{>99} & 13012 \\
3 & Benzalacetone & Benzylacetone & 0.5 & \text{>99} & \text{>99} & 6506 \\
4 & Nitrobenzene & Aniline & 16 & \text{>99} & \text{>99} & 203 \\
5 & 4-Chloronitrobenzene & 4-Chloroaniline & 24 & \text{>99} & 96.6 & 136 \\
6 & Phenol & Cyclohexanone & 24 & 86.5 & 63.9 & 117 \\
7 & benzene & Cyclohexane & 24 & 21.7 & \text{>99} & 29.5 \\
\end{align*}
\]

$^a$Reaction conditions: 0.5 mmol of substrate and 0.03 mol% of Rh$_{0.67}$Ni$_{0.33}$ nanocatalyst (based on ICP analysis of Rh metal) in 3 mL ethyl acetate at room temperature (25 °C) under 1 atm of H$_2$. $^b$Determined by GC-MS. $^c$TOF measured in [mol product][mol metal]$^{-1}$[h$^{-1}$].
Table. S2 Hydrogenation performance using Rh0.67Ni0.33 NCs nanocatalyst under different hydrogen pressure

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Pressure (Mpa)</th>
<th>t [h]</th>
<th>Conv. [%]</th>
<th>Selectivity [%]</th>
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<td>&gt;99 N.D.</td>
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<tr>
<td>2</td>
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<td>&gt;99</td>
<td>&gt;99 N.D.</td>
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<tr>
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<tr>
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<td>&gt;99 N.D.</td>
</tr>
<tr>
<td>6</td>
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<td>4</td>
<td>24</td>
<td>&gt;99</td>
<td>96.2 3.8</td>
</tr>
</tbody>
</table>

*0.5 mmol substrates and 0.03 mol% catalyst (based on ICP analysis of Rh metal) in 3 mL ethyl acetate at room temperature (25 °C) under H₂ (1 atm). bDetermine by GC-MS.

Table. S3 Recycling of Rh0.67Ni0.33 nanocatalyst in the hydrogenation of styrene

<table>
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<th>Conv. [%]</th>
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<td>100</td>
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<tr>
<td>2</td>
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<td>97.4</td>
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</table>

*0.5 mmol styrene and 0.03 mol% catalyst (based on ICP analysis of Rh metal) in 3 mL ethyl acetate at room temperature (25 °C) under H₂ (1 atm). bDetermine by GC-MS.