Supporting Information

Air-stable Ni Catalysts Prepared by Liquid Phase Reduction Using Hydrosilanes for Reactions with Hydrogen

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1. Materials

The following materials were used as received: Ni(acac)$_2$ (Aldrich), phenylsilane (Aldrich), polymethylhydrosiloxane (Aldrich), triethoxysilane (TCI), tris(dimethylamino)silane, (Shin-Etsu) ethyltrimethoxysilane (TCI), phenyltrimethoxysilane (Kanto), N-benzylidene aniline (Aldrich), cis-stilbene (TCI), trans-stilbene (TCI), diphenylacetylene (TCI), nitrobenzene (Kanto), quinoline (Kanto), isoquinoline (TCI), benzofuran (TCI), tetrahydrofuran (Kanto), 1,4-dioxane (TCI), methanol, (Kanto), ethanol (Kanto), dichloroethane (Kanto), acetonitrile (Kanto), toluene (Kanto), cyclopentylmethyl ether (Kanto), N,N-dimethylacetamide (TCI), 1-butanol (Kanto), NaOH (Wako), hydrotalcite (Wako) and toluene-$d_8$ (Aldrich). Raney Ni (about 50%, Wako) was activated by NaOH according to the literature.$^{31}$ Nickel nanoparticles (<100 nm, Aldrich). SiO$_2$ (CaRiACT Q-10), TiO$_2$ (ST-01), Nb$_2$O$_5$·nH$_2$O, MgO (500A) were supplied from Fuji Silysia Chemical, Ishihara Sangyo Kaisha, Companhia Brasileira de Metalurgia e Mineração, and UBE Materials, respectively. Al$_2$O$_3$ (JRC-ALO-9), ZrO$_2$ (JRC-ZRO-6) and CeO$_2$ (JRC-CEO-1) was obtained from the Catalysis Society of Japan as reference catalysts.

2. Instruments

Brunauer–Emmett–Teller (BET) specific surface areas of the samples were measured by nitrogen adsorption–desorption at $-196$ °C (Quantachrome Nova-4200e). Prior to the adsorption measurements, the samples were degassed in situ under vacuum at 150 °C for 1 h. The BET surface area was determined using the multipoint BET algorithm in the P/P$_0$ range from 0.05 to 0.3. X-ray diffraction (XRD; Ultima IV, Rigaku) patterns of all samples were obtained using Cu Kα radiation (40 kV, 40 mA) in the 2θ range of 15−85°. X-ray photoelectron spectroscopy (XPS; ESCA-3200 Shimadzu) measurements were performed using Mg Kα radiation (1486.6 eV). Samples were pressed into pellets and fixed on double-sided carbon tape. The binding energies were calibrated using sputtered C (1s peak at 284.6 eV). The isolation of products was performed with a single channel automated flash chromatography system (Smart Flash EPCLC AI-580S, Yamazen). Transmission electron microscopy (TEM; JEM-2100F, JEOL)-energy dispersive X-ray spectroscopy (EDS, JED-2300T, JEOL) measurements were conducted at an acceleration voltage of 200kV. $^1$H NMR (400 MHz), $^{13}$C {$^1$H} NMR (100 MHz) and $^{29}$Si {$^1$H} NMR (79 MHz) spectra were measured on Bruker Avance III-400 spectrometers. All $^1$H NMR chemical shifts were recorded in ppm ($\delta$) relative to tetramethylsilane or referenced to the chemical shifts of residual solvent resonances (CHCl$_3$ was used as internal standard, $\delta$7.26). All $^{13}$C NMR chemical shifts were recorded in ppm ($\delta$) relative to carbon resonances in CDCl$_3$ at $\delta$77.16. All $^{29}$Si NMR chemical shifts were recorded in ppm ($\delta$) relative to silicon resonances in tetramethylsilane at $\delta$0. The net amounts of metals were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPS-8100, Shimazu). The contents of carbon and hydrogen were measured using CHN elemental analysis (JM10, J-Science). Fourier transform infrared (FT-IR) spectra
were obtained at a resolution of 4 cm\(^{-1}\) using spectrometer (FT/IR-6100, Jasco) equipped with an extended KBr beam-splitting device and mercury cadmium telluride (MCT) and a triglycerine sulfate (TGS) detectors. Gas chromatography (GC) analyses were conducted using a gas chromatography (GC-17A, Shimadzu) equipped with an InertCap 17 capillary column (internal diameter = 0.25 mm, length = 30 m) and a flame ionization detector (FID). The temperature was held at 60 °C for 5 min and then increased from 60 °C to 260 °C at a heating rate of 20 °C/min. Temperature programmed reduction (TPR) experiments and CO-pulse titrations were performed using an automatic measurement instrument (BELCAT-A, BEL Japan) with thermal conductivity (TCD) and mass (Belmass) detectors. For H\(_2\)-TPR measurement, the sample was pre-treated with He flow (30 ml/min) at 50 °C for 30 min. For CO-pulse titration, the sample was pre-reduced with H\(_2\)/Ar flow (5%, 30 mL/min) at 100 °C for 30 min. The stoichiometry of CO/Ni = 1 was assumed.\(^2\)

3. **Procedure for IR measurements**

Ni-Si-90 (100 mg) and HNO\(_3\) (3 mL) were loaded to the flask. The suspension was sonicated for few minutes. The resulting white precipitate was collected by filtration and washing with water to give white powder (6.3 mg). The corrected sample was applied to IR measurement.

4. **Procedure for reuse experiments**

The catalytic reaction was conducted according to the general procedure. For reuse experiments, the catalyst was recovered by the filtration, washing with MeOH (20 mL) and drying at 90 °C. The corrected sample was applied for the next reaction. For Raney Ni, the catalyst recovery was performed in Ar-filled glovebox.

5. **Controlled NMR experiments**

Ni(acac)\(_2\) (0.05 mmol), phenylsilane (0.05 mmol), tetramethylsilane (TMS, 3 drops) and toluene-\(d_8\) (0.5 mL) were added to a NMR tube and flushed with Ar. The NMR tube was heated in oil bath (90 °C) for 1 min.

6. **Procedure for base treatment**

Ni-Si-90 (100 mg) was added to a MeOH solution of NaOH (3 mol/L, 25 mL). The suspension was stirred at room temperature for 5 h. The solid was corrected by filtration and washing with water/EtOH and was dried *in vacuo* to give black powder (98.6 mg). The corrected sample was applied to the catalytic reaction according to the general procedure.
### Table S1. Reaction conditions for the synthesis of hcc and hcp Ni nanoparticles

<table>
<thead>
<tr>
<th>Entry</th>
<th>Hydrosilane</th>
<th>Atmosphere (MPa)</th>
<th>Temp. (°C)</th>
<th>solvent</th>
<th>Crystallite diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phenylsilane</td>
<td>H₂ (0.5)</td>
<td>90</td>
<td>toluene</td>
<td>9 (fcc)</td>
</tr>
<tr>
<td>2</td>
<td>Phenylsilane</td>
<td>H₂ (0.5)</td>
<td>60</td>
<td>toluene</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>Phenylsilane</td>
<td>H₂ (0.5)</td>
<td>300</td>
<td>toluene</td>
<td>59 (fcc), 71 (hcp)</td>
</tr>
<tr>
<td>4</td>
<td>Phenylsilane (5 equiv.)</td>
<td>H₂ (0.5)</td>
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<td>toluene</td>
<td>Amorphous</td>
</tr>
<tr>
<td>5</td>
<td>Phenylsilane (2 equiv.)</td>
<td>H₂ (0.5)</td>
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<td>toluene</td>
<td>Amorphous</td>
</tr>
<tr>
<td>6</td>
<td>Phenylsilane (0.5 equiv.)</td>
<td>H₂ (0.5)</td>
<td>150</td>
<td>toluene</td>
<td>38 (fcc)</td>
</tr>
<tr>
<td>7</td>
<td>Phenylsilane (0.33 equiv.)</td>
<td>H₂ (0.5)</td>
<td>150</td>
<td>toluene</td>
<td>45 (fcc)</td>
</tr>
<tr>
<td>8</td>
<td>Phenylsilane</td>
<td>H₂ (0.5)</td>
<td>90</td>
<td>CH₃CN</td>
<td>17 (fcc)</td>
</tr>
<tr>
<td>9</td>
<td>Phenylsilane</td>
<td>H₂ (0.5)</td>
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<td>(CH₂Cl)₂</td>
<td>18 (fcc)</td>
</tr>
<tr>
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<td>90</td>
<td>THF</td>
<td>19 (fcc)</td>
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<td>ethanol</td>
<td>10 (fcc)</td>
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<td>12</td>
<td>Phenylsilane</td>
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<td>toluene</td>
<td>–</td>
</tr>
<tr>
<td>13</td>
<td>Phenylsilane</td>
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<td>toluene</td>
<td>5 (fcc)</td>
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<td>14</td>
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<td>Ar (0.5)</td>
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<td>toluene</td>
<td>11 (fcc)</td>
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<tr>
<td>15</td>
<td>PMHS</td>
<td>H₂ (0.5)</td>
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<td>toluene</td>
<td>–</td>
</tr>
<tr>
<td>16</td>
<td>PMHS</td>
<td>H₂ (0.5)</td>
<td>150</td>
<td>toluene</td>
<td>61 (fcc)</td>
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<td>17</td>
<td>triethoxysilane</td>
<td>H₂ (0.5)</td>
<td>90</td>
<td>toluene</td>
<td>–</td>
</tr>
<tr>
<td>18</td>
<td>triethoxysilane</td>
<td>H₂ (0.5)</td>
<td>150</td>
<td>toluene</td>
<td>74 (fcc)</td>
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<tr>
<td>19</td>
<td>ethyltrimethoxysilane</td>
<td>H₂ (0.5)</td>
<td>90</td>
<td>toluene</td>
<td>–</td>
</tr>
<tr>
<td>20</td>
<td>ethyltrimethoxysilane</td>
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<td>150</td>
<td>toluene</td>
<td>–</td>
</tr>
<tr>
<td>21</td>
<td>phenyltrimethoxysilane</td>
<td>H₂ (0.5)</td>
<td>150</td>
<td>toluene</td>
<td>–</td>
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</tbody>
</table>

*Preparation conditions: Ni(acac)₂ (0.5 mmol), hydrosilane (0.5 mmol), toluene (5 mL) for 2 h.*

The difference between H₂ and Ar on the preparation can be rationalized by the structure of organosilicon species. There is not so big difference in the contents of organosilicon compounds between Ni-Si-90 and Ni-Si-Ar (30.5 and 40.1 wt%) by the ICP-AES analysis, whereas Ni-Si-Ar contains larger amounts of Si (Ni:Si = 67:33) than Ni-Si-90 (Ni:Si = 92:8) from the TEM-EDS analyses (Fig. S8 and S9). Thus, H₂ may induce the incorporation of other organic compounds such as pentane-2,4-diol observed in GC-MS analysis of the filtrate during the catalyst separation.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal Loading (mol%)</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>$p$H₂ (MPa)</th>
<th>Yield (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Si-90</td>
<td>5</td>
<td>60</td>
<td>5</td>
<td>0.5</td>
<td>90</td>
<td>This work</td>
</tr>
<tr>
<td>Cu/Al₂O₃</td>
<td>5</td>
<td>120</td>
<td>24</td>
<td>5.0</td>
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<td>Co/C</td>
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<td>100</td>
<td>18</td>
<td>0.5</td>
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<td>S4</td>
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<tr>
<td>Co</td>
<td>5</td>
<td>60</td>
<td>24</td>
<td>1.0</td>
<td>91</td>
<td>S5</td>
</tr>
<tr>
<td>FeNP@PS-PEG-NH₂</td>
<td>31</td>
<td>100</td>
<td>53 s</td>
<td>4.0</td>
<td>100</td>
<td>S6</td>
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<tr>
<td>Au$_{99}$Ag$_1$NP</td>
<td>5</td>
<td>90</td>
<td>24</td>
<td>0.8</td>
<td>99</td>
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</table>
Table S3. Effects of crystal phase of Ni-Si-x on hydrogenation of imine\(^a\)

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>(pH_2) (MPa)</th>
<th>Temp. (°C)</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni-Si-200</td>
<td>0.3</td>
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<td>&lt;1</td>
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<td>2</td>
<td>Ni-Si-200</td>
<td>0.5</td>
<td>80</td>
<td>73</td>
<td>62</td>
</tr>
<tr>
<td>3</td>
<td>Ni-Si-hcp</td>
<td>0.3</td>
<td>60</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>4</td>
<td>Ni-Si-hcp</td>
<td>0.5</td>
<td>80</td>
<td>41</td>
<td>5</td>
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\(^a\) Reaction conditions: catalyst (0.02 g of Ni), 1 (1 mmol), toluene (2 mL), \(pH_2\) (0.3 MPa), 5 h. Conversion and yield were determined by GC analysis.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Crystallite size (nm)</th>
<th>Specific Surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni-Si/SiO₂</td>
<td>9.9</td>
<td>305</td>
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<td>2</td>
<td>Ni-Si/TiO₂</td>
<td>6.1</td>
<td>152</td>
</tr>
<tr>
<td>3</td>
<td>Ni-Si/Nb₂O₅</td>
<td>4.8</td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td>Ni-Si/Al₂O₃</td>
<td>10.7</td>
<td>207</td>
</tr>
<tr>
<td>5</td>
<td>Ni-Si/CeO₂</td>
<td>-</td>
<td>24</td>
</tr>
<tr>
<td>6</td>
<td>Ni-Si/ZrO₂</td>
<td>-</td>
<td>247</td>
</tr>
<tr>
<td>7</td>
<td>Ni-Si/MgO</td>
<td>-</td>
<td>68</td>
</tr>
<tr>
<td>8</td>
<td>Ni-Si/HT</td>
<td>-</td>
<td>38</td>
</tr>
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</table>

* The peaks due to metallic Ni were not observed.
Table S5. Reported Ni Catalysts Direct Amination of Alcohols with Ammonia.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>substrate</th>
<th>product</th>
<th>temp. (°C)</th>
<th>pNH₃ (MPa)</th>
<th>yield (%)</th>
<th>ref</th>
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</thead>
<tbody>
<tr>
<td>Ni-Si/HT</td>
<td>Ph-&lt;OH&gt;</td>
<td>Ph-&lt;NH₂&gt;</td>
<td>160</td>
<td>0.5</td>
<td>93</td>
<td>This work</td>
</tr>
<tr>
<td>Ni/Al₂O₃</td>
<td>Ph-&lt;OH&gt;</td>
<td>Ph-&lt;NH₂&gt;</td>
<td>160</td>
<td>0.4</td>
<td>78</td>
<td>S8</td>
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<tr>
<td>Ni/CaSiO₃</td>
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<td>0.4</td>
<td>70</td>
<td>S9</td>
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<tr>
<td>Raney Ni</td>
<td>4-&lt;OH&gt;</td>
<td>4-&lt;NH₂&gt;</td>
<td>180</td>
<td>0.35</td>
<td>76.5</td>
<td>S10</td>
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<td>Ni-&lt;OH&gt;</td>
<td>H₂N-&lt;OH&gt;</td>
<td>H₂N-&lt;NH₂&gt;</td>
<td>180</td>
<td>17.5</td>
<td>41.3</td>
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<td>Ni-Re/Al₂O₃</td>
<td>H₂N-&lt;OH&gt;</td>
<td>H₂N-&lt;NH₂&gt;</td>
<td>175</td>
<td>17.5</td>
<td>41.3</td>
<td>S11</td>
</tr>
<tr>
<td>Ni/Ce-Al</td>
<td>C₈H₁₇-&lt;OH&gt;</td>
<td>C₈H₁₇-&lt;NH₂&gt;</td>
<td>180</td>
<td>0.7</td>
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<td>Ni-Al₂O₃/SiO₂</td>
<td>Ph-&lt;OH&gt;</td>
<td>Ph-&lt;NH₂&gt;</td>
<td>160</td>
<td>flow</td>
<td>96</td>
<td>S13</td>
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<td>Ni-Pd/Al₂O₃-CD</td>
<td>C₈H₁₇-&lt;OH&gt;</td>
<td>C₈H₁₇-&lt;NH₂&gt;</td>
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<td>0.7</td>
<td>66</td>
<td>S14</td>
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<tr>
<td>Raney Ni</td>
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<td>Ni/HAP</td>
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<td>C₃H₇-&lt;NH₂&gt;</td>
<td>150</td>
<td>flow</td>
<td>9.9</td>
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This work
Table S6. Optimization studies on direct amination of benzyl alcohol with ammonia over Ni-Si/support\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>solvent</th>
<th>Pre-reduction Temp. (°C)</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
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<td>15</td>
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\textsuperscript{a} Reaction conditions: Ni-Si/support (0.05 g, 17 mol%), 5 (0.5 mmol), solvent (2 mL), $p\text{NH}_3$ (0.5 MPa). Conversion and yield were determined by GC analysis.
Figure S1. XRD patterns for (a) Ni-Si-60 prepared through the heating for 2 and 4 h, and (b) Ni-Si-90 prepared at 0.5 and 1 MPa of H$_2$ pressure.

Figure S2. XRD patterns for Ni-Si-150 prepared using different amount of phenylsilane.
Figure S3. XPS spectra of (a) O 1s and (b) Si 2p regions for Ni-Si-90.
Figure S4. IR spectrum of Ni-Si-90 (A) after acid treatment and (B) without any treatment.

Si-O-Si structure can be generated during acid treatment.
Figure S5. $^1$H NMR spectra of the mixture of Ni(acac)$_2$ with phenylsilane in toluene-$d_8$ at 90 °C. ○: Hacac, ▼: phenanthrene
Figure S6. $^2$Si NMR spectra of the mixture of Ni(acac)$_2$ with phenylsilane in toluene-$d_8$ at (a) room temperature and (b) 90 °C
**Figure S7.** Reuse experiments of Ni-Si-90 at lower conversion level. Reaction conditions: Ni-Si-90 (0.02 g), 1 (1 mmol), toluene (2 mL), \( \rho \text{H}_2 \) (0.5 MPa), 80 °C, 1 h.

**Figure S8.** \( \text{H}_2 \)-TPR profiles for fresh Ni-Si-90, recovered Ni-Si-90 and commercial Ni NPs.

The observation of \( \text{CO}_2 \) signal during the \( \text{H}_2 \)-TPR measurements indicates that the hydrogenated products could interact tightly with the catalyst surface.
Figure S9. Reuse experiments of Ni-Si-90 and Raney Ni on hydrogenation of benzylidene aniline. Reaction conditions: Ni-Si-90 (0.02 g), 1 (4 mmol), toluene (2 mL), $p$H$_2$ (0.3 MPa), 60 °C, 5 h.

Catalyst recovery was operated under air.

Catalyst recovery was operated in Ar-filled glovebox.
Figure S10. Reuse experiments of Ni-Si-90 and Ni/NiO on one-pot reductive amination of benzaldehyde with nitrobenzene. Reaction conditions for Ni-Si-90: Ni-Si-90 (0.02 g), nitrobenzene (1 mmol), benzaldehyde (1.2 mmol), toluene (5 mL), $pH_2$ (0.5 MPa), 60 °C, 20 h. Reaction conditions for Ni/NiO: Ni/NiO (0.05 g), nitrobenzene (1 mmol), benzaldehyde (1.2 mmol), toluene (5 mL), $pH_2$ (1 MPa), 80 °C, 20 h.
Figure S11. XRD patterns of the supported Ni catalysts prepared using hydrosilane-assisted method. *: fcc Ni (JCPDS 00-004-0850)
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**Figure S12.** TEM-EDS analysis of Ni-Si-90
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<td>Si K</td>
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**Figure S13.** TEM-EDS analyses of Ni-Si-Ar
Figure S14. H$_2$-TPR profiles of Ni-Si-90 and NiNPs with TCD detector and mass detector.
8. References

