

## Designed Synthesis of Atom-Economical Pd/Ni Bimetallic Nanoparticle-Based Catalysts for Sonogashira Coupling Reactions

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The search for more efficient catalytic systems that combine the advantages of both homogeneous and heterogeneous catalysts is one of the most exciting challenges of catalysis research. In this regard, the catalytic system based on well-dispersed colloidal nanoparticles, so-called semiheterogeneous systems, is one of the most promising candidates because this catalytic system shows homogeneous dispersion of catalyst particles in solution and the reuse of the catalyst.<sup>1</sup>

Palladium nanoparticles<sup>2</sup> have been tested as catalysts for various reactions.<sup>3</sup> Because catalytic reactions occur on the surface of the nanoparticles, a large fraction of metal in the core of the nanoparticle is wasted. This issue becomes very important for the nanoparticles of expensive noble metals such as palladium and platinum. In the view of "atom economy", the synthesis of core/shell nanoparticles having a cheap metal core and a noble metal shell is desirable.

Several palladium-containing bimetallic nanoparticles including core/shell structures have been synthesized.<sup>4</sup> In most of these core/shell nanoparticles, however, palladium is in the core and the other metal such as copper or nickel covers the surface of palladium (Figure 1b), which is not useful for the catalytic reactions involving palladium as an active catalytic species.<sup>5</sup> For example, Miyake and co-workers synthesized core/shell Pd/Ni nanoparticles from the consecutive reduction of H<sub>2</sub>PdCl<sub>4</sub> and nickel acetate through the polyol method. In this study, the authors claimed that palladium nanoparticles catalyzed the reduction of Ni(II) precursors and induced the deposition of Ni(0) atoms on the surface of Pd nanoparticles. Herein we report on the synthesis of Pd–Ni bimetallic nanoparticles with a Ni-rich core/Pd-rich shell structure (Figure 1c) from the thermal decomposition of palladium and nickel precursors.

The current synthetic procedure is a modified version of the method developed by our group for the synthesis of various nanoparticles of metals and metal oxides, which employs the thermal decomposition of metal–surfactant complexes.<sup>6</sup> The metal–trioctylphosphine (TOP) complex solution, prepared from the reaction of 1:1 mixture of Pd(acac)<sub>2</sub> (0.1 g, 0.328 mmol) and Ni(acac)<sub>2</sub> (0.082 g, 0.328 mmol) in 2 mL of trioctylphosphine, was injected to 7 mL of oleylamine at various temperatures (Table 1; see Supporting Information for additional TEM images). The resulting solution was aged at the indicated temperature for 30 min, producing colloidal nanoparticles. We varied experimental conditions to optimize the synthesis. The elemental analysis using energy-dispersive X-ray spectroscopy (EDX) in TEM and ICP-AES of the nanoparticles revealed that a large fraction of Pd–TOP complex was not decomposed below 235 °C. When the injection temperature

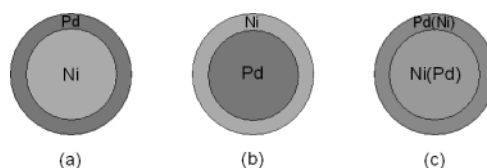


Figure 1. Model structures of Pd–Ni bimetallic nanoparticles.

Table 1. Synthesis of Pd–Ni Bimetallic Nanoparticles

entry	precursor molar ratios (Pd/Ni)		analyzed molar ratios (Pd/Ni) <sup>a</sup>		temp particles generation (°C)	aging time (h)	particles size (nm)
1	1.00	0.00			215	0.5	1.50
2	0.25	0.75	0.02 (0.05)	0.98 (0.95)	215	0.5	4.18
3	0.50	0.50	0.07 (0.08)	0.93 (0.92)	205	0.5	3.10
4	0.50	0.50	0.16 (0.14)	0.84 (0.86)	215	0.5	3.10 + 1.20
5	0.50	0.50	0.24 (0.28)	0.76 (0.72)	225	0.5	3.11 + 1.50
6	0.50	0.50	0.41 (0.49)	0.59 (0.51)	235	0.5	1.72
7	0.50	0.50	0.43 (0.47)	0.57 (0.53)	205–235	2, 0.5	3.85
8	0.75	0.25	0.46 (0.51)	0.54 (0.49)	215	0.5	4.34
9	0.00	1.00			215	0.5	3.12

<sup>a</sup> Analyzed by ICP AES, and values from EDX analysis are in parentheses.

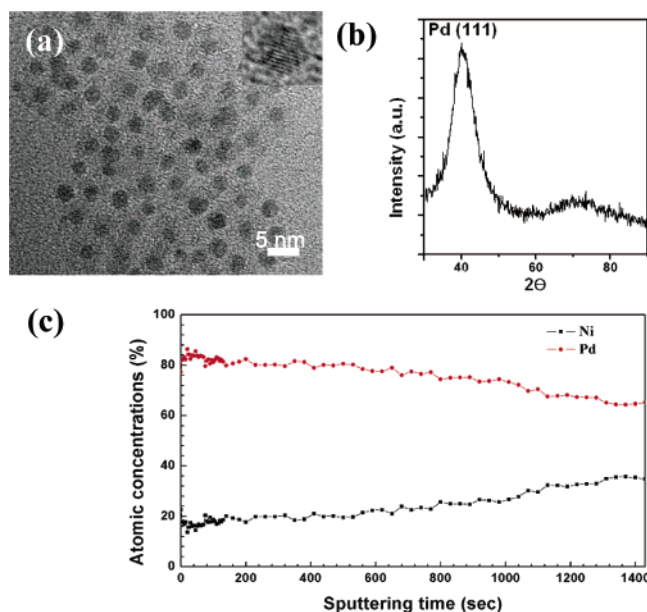
was increased gradually from 205 to 235 °C, the mole fraction of Pd increased from 7 to 41% (entries 3–6 of Table 1), demonstrating that Ni–TOP complex decomposes at a lower temperature than Pd–TOP complex. The particle size of pure nickel nanoparticles was larger than that of pure palladium nanoparticles synthesized under the same reaction conditions (entries 1 and 9 of Table 1). The reactions using various molar ratios of nickel and palladium precursors confirmed that nickel nanoparticles are more easily synthesized (entries 2, 4, and 8 of Table 1). Judging from these results, palladium metal is more difficult to form than nickel metal in our current synthesis. Even though palladium ions are more easily reduced than nickel ions in view of reduction potential, nickel nanoparticles are generated first, followed by palladium shell formation, because the Ni–TOP complex is more readily decomposed thermally compared to the Pd–TOP complex.

In the next step, we tried to synthesize Ni/Pd core/shell nanoparticles. Our strategy is as follows: Ni–TOP complex is decomposed at the relatively low temperature of 205 °C, where Pd–TOP complex is rarely decomposed. After aging at 205 °C for 30 min to decompose Ni–TOP complex completely, the temperature was slowly increased to 235 °C to decompose Pd–TOP complex, generating the Pd shell on the top of Ni core. To characterize the core/shell structure of the nanoparticles, we traced the particle size and elemental analysis of intermediate nanoparticles by taking aliquots of the reaction mixture and collecting TEM images and EDX data. The particle size and Pd mole fraction after

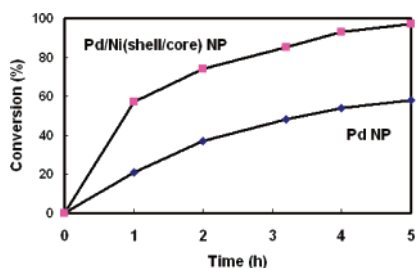
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**Figure 2.** (a) HRTEM image, (b) XRD pattern, and (c) depth profile of Ni/Pd (core/shell) bimetallic nanoparticles (entry 7 in Table 1).



**Figure 3.** Comparison of the catalytic activity of 3.9 nm Pd/Ni bimetallic nanoparticles and 3.5 nm Pd nanoparticles (synthesized from ref 2f). Reaction conditions: 0.5 mol % catalyst based on Pd atoms, 15 mg of PPh<sub>3</sub>, 7.5 mg of CuI, 4 mL of diisopropylamine (DIA) as a solvent, 80 °C, 7.6 mmol of phenylacetylene, and 3.8 mmol of 4-bromoacetophenone as the substrate.

aging at 205 °C for 30 min were 3 nm and 9 mol %, respectively. After aging at 235 °C for 30 min, the particle size was increased to 4 nm and the Pd content was simultaneously increased to 47 mol % (entry 7 of Table 1; see Supporting Information for detailed results). In addition, we conducted a depth profile of a nanoparticle using field-emission Auger electron spectroscopy (FE-AES) (Figure 2c). These data clearly demonstrated that bimetallic Pd–Ni nanoparticles having a Ni-rich core and a Pd-rich shell, similar to the structure shown in Figure 1c, were synthesized. A high-resolution TEM (HRTEM) image of the nanoparticles revealed the highly crystalline nature of the nanoparticles (Figure 2a). The X-ray diffraction pattern of the nanoparticles, shown in Figure 2b, revealed an *fcc* Pd crystal structure.

We tested the catalytic activity of the Pd/Ni nanoparticles and similarly sized Pd nanoparticles for Sonogashira coupling reactions (Figure 3) using an equal amount of palladium in the reaction mixtures.<sup>7</sup> As clearly shown in Figure 3, the Pd/Ni nanoparticles showed much better catalytic activity than Pd nanoparticles, which resulted from the larger number of nanoparticles derived from the core/shell structure (remember that an equal amount of Pd was used). The nanoparticle catalyst can be recycled and reused at least five times without losing the catalytic activity (entries 1–5 in Table 2), demonstrating the semiheterogeneous characteristics (see Supporting Information for the details). The nanoparticle catalyst was active for bromo-aryl substrates and inactive for chloro-aryl substrates (entries 6 and 7 in Table 2). In addition, the nanoparticle

**Table 2.** Test of Catalytic Activity of Pd–Ni Nanoparticles for Sonogashira Reaction<sup>a</sup>

		$\text{Ar-X} + \text{C}\equiv\text{C-Ph} \xrightarrow[\text{cat. DIA}]{\text{Ph}_3\text{P, CuI}} \text{Ar-C}\equiv\text{C-Ph} \quad \mathbf{A}$			
		$\text{Ar-X} + \text{C}\equiv\text{C-TMS} \xrightarrow[\text{cat. Toluene}]{\text{Ph}_3\text{P, DBU, H}_2\text{O}} \text{Ar-C}\equiv\text{C-Ar} \quad \mathbf{B}$			
entry	X	substrate (Ar)	reaction type	catalyst	yield (%) <sup>b</sup>
1	Br	4-acetylbenzene	A	Pd–Ni NP	92
2	Br	4-acetylbenzene	A	recovered from entry 1	95
3	Br	4-acetylbenzene	A	recovered from entry 2	91
4	Br	4-acetylbenzene	A	recovered from entry 3	92
5	Br	4-acetylbenzene	A	recovered from entry 4	90
6	Br	2-thienyl	A	Pd–Ni NP	95
7	Cl	4-acetylbenzene	A	Pd–Ni NP	nr
8	Br	4-acetylbenzene	B	Pd–Ni NP	86
9	Br	2-thienyl	B	Pd–Ni NP	86

<sup>a</sup> Reaction conditions: 2 mol % catalysis based on Pd atoms, 80 °C, for 2 h (type A) or 18 h (type B). <sup>b</sup> Isolated yield.

catalyst was active for sila-Sonogashira reactions (Scheme B in Table 2), which were recently developed and consist of two consecutive coupling reactions (entries 8 and 9 in Table 2).<sup>8</sup>

In conclusion, we synthesized Ni/Pd core/shell nanoparticles from the consecutive thermal decomposition of metal–surfactant complexes. The nanoparticle catalyst was atom-economically applied for various Sonogashira coupling reactions.

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**Supporting Information Available:** TEM images of Pd–Ni bimetallic nanoparticles in Table 1, TEM images and the corresponding EDX results of nanoparticles during various stages of the synthesis, photographs showing semiheterogeneous catalytic processes, TEM images of synthesized Pd/Ni nanoparticles using various precursor ratios, and XPS results of Pd/Ni nanoparticles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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