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Monodispersed Pd−Ni Nanoparticles: Composition Control Synthesis and Catalytic Properties in the Miyaura−Suzuki Reaction

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S *Supporting Information*

ABSTRACT: We have successfully prepared a series of magnetically separable "quasi-homogeneous" Pd−Ni nanoalloy catalysts with tunable composition in a one-pot wet chemical route. We have evaluated the catalytic activity of these Pd−Ni alloy catalysts with different compositions through the Miyaura−Suzuki coupling reaction. These palladium/non-noble metal alloy catalysts show better catalytic activity than an equal amount of palladium nanoparticles. Furthermore, these catalysts exhibited excellent performance in superparamagnetism owing to its great advantage for reducing the usage of noble metal.

Noble metal nanoparticles with high specific catalytic activity are ubiquitous in modern synthetic organic chemistry during the past decades. They have been widely applied to some important reactions such as Sonogashira-,[1] Heck-,[2] and Miyaura−Suzuki-type reactions.[3] However, how to reduce their dosage is one of the most exciting challenges because of the limited reserves of noble metals. In material science, mixing the other elements with the precious metal to generate intermetallic compounds and alloys has been proven to be an effective method in making better use of the precious metal.[4] In many cases, the hybrid structure alloyed by noble metal and non-noble metals such as iron, cobalt, and nickel not only combines the properties of the individual constituents but also shows an enhancement in specific properties because of the synergistic effects and the rich diversity of the compositions.[5] Furthermore, if magnetic heterometals are alloyed into noble metals, we can overcome the drawback of separation and reuse.[6] This magnetically separable nanocatalyst with a peculiar nature may have potential applications in catalysis.[7]

In this paper, we succeeded in the synthesis of a Pd−Ni nanoalloy with a defined size and shape through a one-pot wet chemical route. Pd−Ni exhibited much higher catalytic activity compared to an equal amount of palladium nanoparticles in the Miyaura−Suzuki coupling reaction. Because nickel owns a certain catalytic activity in the Miyaura−Suzuki reaction,[8] the better performance of these palladium/non-noble metal catalysts may be attributed to the nickel dopant and the interaction between these two metals. This facile research strategy also can be applied to the synthesis of other palladium-based hybrid nanoalloys such as Pd−Fe and Pd−Co.

As shown in Figure 1, uniform Pd−Ni alloy nanoparticles were successfully synthesized in octadecylamine (ODA). This synthetic procedure was developed by our group for the synthesis of various noble metal and noble metal−transition metal nanoalloys.[9,10] In the reaction, ODA was used as the solvent, surfactant, as well as reductant and tetra-*n*-octylammonium bromide was added as a phase-transfer agent and cosurfactant. We need to point out that the nickel nanoparticles could not form if the palladium precursor was not added. A previous study proposed that the noble metals perform as electron carriers.[11] The electron can transfer to a nickel ion from palladium much easier than from the solution, so the nickel ion can be reduced to nickel in such conditions. The effective electronegativity may play a major role in this reaction.[12]

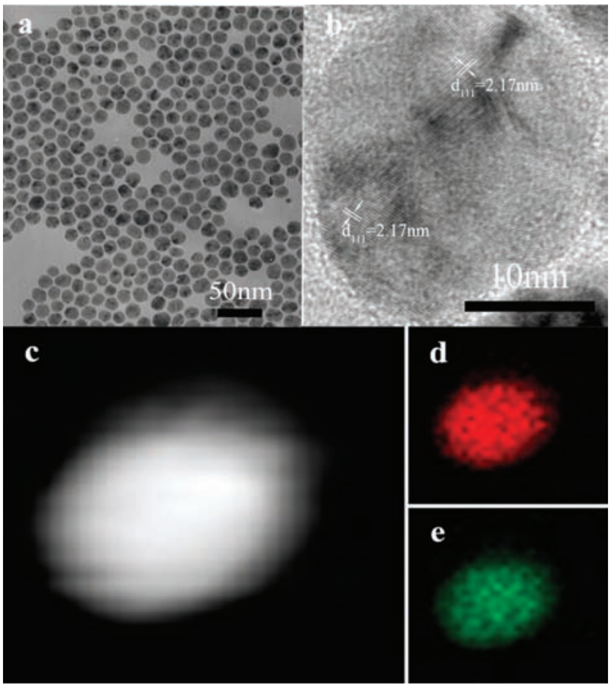

Figure 1. (a) TEM image of Pd−Ni nanoparticles, (b) HRTEM image of Pd−Ni nanoparticles, and EDS mapping of (c) one single Pd−Ni particle, (d) Ni−L, and (e) Pd−L.

The X-ray diffraction (XRD) pattern of an as-prepared series of Pd−Ni alloys is shown in Figure 2. With an increase in the addition content of nickel, the peaks continuously shift from the palladium standard peaks (JCPD-65-6174) to Pd−Ni intermetallic standard ones (JCPD-65-9444). The accurate composition of the

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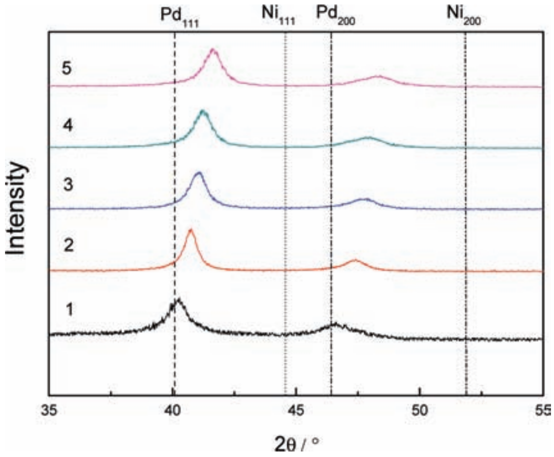

Figure 2. XRD patterns of as-prepared (1) Pd95Ni5, (2) Pd80Ni20, (3) Pd67Ni33, (4) Pd55Ni45, and (5) Pd50Ni50.

Pd—Ni catalyst further measured by inductively coupled plasma atomic emission spectrometry was Pd $_{51}$Ni$_{49}$, which was very close to the precursor (1:1; Table S1 in the Supporting Information, SI). In summary, the choice of a different ratio of the precursor can control the composition of the product obtained.

Figure 1a exhibits the transmission electron microscopy (TEM) image of the as-prepared palladium-based catalyst with a uniform spherical shape, which mainly results from the minimized surface energy. With an increase in the composition of nickel, the particle morphology and size remain the same (Figure S1 in the SI). The high-resolution TEM (HRTEM) image (Figure 1b) shows that Pd—Ni alloy nanoparticles have morphological features of polycrystalline structure, and the study of a series of single nanoparticles identified the (111) planes of the face-centered-cubic (fcc) Pd—Ni intermetallics with a 0.217 nm spacing between two adjacent lattice planes. To further confirm this Pd—Ni alloy structure, we take the text of energy-dispersive spectrometry (EDS) mapping of a single $Pd_{50}Ni_{50}$ nanoparticle. Figure 1c shows that the distribution of palladium and nickel is very uniform throughout the whole particle. Meanwhile, these experimental results coconfirmed the formation of Pd—Ni alloy compounds.

Semihomogeneous catalysts that bridge the traditional homogeneous and heterogeneous catalysts are attracting increasing interest. The homogeneous catalysts have high catalytic efficiency because they are well-defined on a molecular level and readily dissolved in the reaction medium. However, the expensive and tedious purification for removal of the catalysts from the reaction system results in their deficiencies in separation and recycling. The heterogeneous catalysis has won out in the performance of separation and recycling, but there are still many limitations in its application because of the lower catalytic activity and complexity of the catalytic process. So, how to find an efficient catalyst that combines the merits of these two kinds of catalytic species is an important issue in current research focus.[13,14] The as-prepared Pd—Ni alloy catalysts can be well dispersed in an oil phase; therefore, they can be widely used in nonpolar solvents. Additionally, these nanoparticles can be easily recoverd by a magnet from the system because of its superparamagnetic nature. Consequently, owing to its semihomogeneous property, the Pd—Ni catalyst with a nanoalloy structure can greatly save usage of the precious metal and shows a better potential industrial application than equivalent palladium. According to the advantages listed above, this so-call semihomogeneous Pd—Ni catalyst has the potential to be used as a highly efficient semihomogeneous catalyst in an oil-phase reaction.

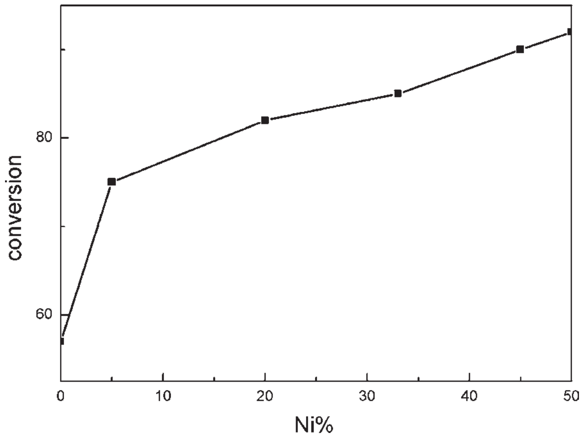

Figure 3. Corresponding conversion — nickel molar percentage curve. The reaction conditions are listed in Table S2 in the SI.

The Miyaura—Suzuki reaction between the aryl halides and arylboronic acid is a significant C—C coupling reaction; at the same time, it has became a somewhat important example of the semihomogeneous reaction mechanism.[15] Because palladium-based catalysts exhibit excellent performance in C—C coupling reactions such as Miyaura—Suzuki,[16] Sonogashira,[17] and Heck,[18] it has drawn more and more attention. Up to now, not only many types of homogeneous catalysts including palladium acetate,[19] palladium chloride,[20] and palladium complexes stabilized by phosphorus ligands[21] but also some kinds of heterogeneous catalysts such as ligand-protected palladium nanoparticles,[22] polymer-coated palladium,[23] palladium on active carbon (Pd/C),[24] and palladium-based with structures of core—shell[25] and porous[26] have been applied to this reaction.

As mentioned above, the Miyaura—Suzuki coupling reactions between benzeneboronic acid and aryl halides were used to evaluate the activity of nanoalloys with an equal molar amount of palladium nanoparticles of similar size and morphology (Figure S1 in the SI). As shown in Table S2 in the SI, the Pd—Ni alloys show better catalytic performance than palladium nanoparticles. Meanwhile, these palladium-based catalysts have high selectivity to diphenyl coupling (100%). The self-coupling product obtained from 4-bromoanisole and iodobenzene was not observed. Furthermore, the reaction yield between benzeneboronic acid and 4-bromoanisole continuously improved with an increase in the proportion of nickel (Figure 3). The Pd—Ni catalysts can be recycled at least five times without losing the catalytic activity in the coupling reaction between iodozene and benzeneboronic acid (entries 2—6 in Table S3 in the SI), which demonstrated that the Pd—Ni catalysts have the characteristic of semihomogeneousness. The catalyst kinetic parameter ln(1 − conversion) obtained from Figure S3 in the SI revealed that the coupling reaction catalyzed by the as-prepared palladium-based catalyst was a first-order one. The results of the catalytic reactions at different temperatures revealed that the Pd—Ni alloy had such good reactivity that even the reaction conducted using iodobenzene at 80 °C proceeded in 92% yield. However, when we continued to drop the reaction temperature to 25 °C, the yield decreased significantly to 40%. Additionally, a similar decreasing trend was also observed when the reaction was carried out using 4-bromoanisole as a raw material.

Previous studies revealed that nickel(0) can catalyze such a Miyaura−Suzuki-type aromatic coupling reaction because Nickel is a good nucleophile.[27] The transition metal has better electronegativity than the precious metal, which leads to more efficient conversion. The proposed mechanism is shown in Scheme S1 in the SI. The reaction starts from the oxidative addition of aryl halide to the Pd−Ni nanoparticle surface, followed by leaching of palladium(II) and nickel(II) molecular species that enter the catalytic cycle, and ends at the re-formation of the nanoparticles. Reetz and co-workers indicated that leaching is likely to occur from the nanoparticle surfaces[28] because the surface atom of a metal is the highly active catalytic site.[29,30] Lai and co-workers assumed that the nanoparticles were subjected to a chemical dealloying process;[31] however, the clarified mechanism of the catalytic process has not been confirmed. There was no significant change in the size of the recovered Pd−Ni alloys, and the multiple-twinned structures remained after the reaction (Figure S1f in the SI).

The as-obtained Pd−Ni alloys exhibit superparamagnetic properties, as demonstrated in Figure S4 in the SI. Therefore, the alloys are nonmagnetic without a magnetic field and can be well-dispersed in a nonpolar solvent. During the reaction, the good dispersity of alloys ensures sufficient contact between the catalysts and reactants. After the finish of the reaction, the catalysts could be easily separated from the reaction mixture in the presence of an additional external magnetic field (Figure S4, inset, in the SI). Furthermore, low-field magnets are enough to recover these particles quantitatively from solution because of their superparamagnetism.

As shown in Figure S5 in the SI, the Fourier transform IR (FT-IR) spectral broad band around 3400 cm^{-1} is assigned to the O−H stretch. The peaks of 2924 and 2853 cm^{-1} are attributed to the antisymmetric methyl stretch and the symmetric methylene stretches, which means that the catalyst has been capped by a hydrophobic long chain. The N−H modes at 1631, 1465, and 1386 cm^{-1} indicate anchoring of ODA. The weakening of the peaks shows removal of the long-chain molecules from the catalyst after the fifth reaction cycle.

In summary, we have successfully synthesized a series of Pd−Ni alloys with different compositions through a facile procedure. Thanks to the effect of nickel substitution and the alloy structure, the as-prepared Pd−Ni catalysts showed much better performances for the Miyaura−Suzuki-type coupling reaction in an oil phase with outstanding stability and reusability. The combination of the efficiency of the homogeneous catalyst and the durability of the heterogeneous catalyst as presented in this work will draw more attention in the foreseeable future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. TEM image of Pd−Ni alloys with different compositions and Pd−Ni nanoparticles after recycle, dependency of iodobenzene conversion on the reaction time, corresponding time−ln(1 − conversion) curve, hysteresis loop of Pd50Ni50, FT-IR spectra, composition of the catalyst, comparison of the catalytic activity, and an Experimental Section. This material is available free of charge via the Internet at http://pubs.acs.org.

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