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# Poly(vinylpyridine)-Grafted Silica Containing Palladium or Nickel Nanoparticles as Heterogeneous Catalysts for the Sonogashira Coupling Reaction

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Efficient catalytic systems based on palladium and nickel nanoparticles supported on poly(4-vinylpyridine) (P4VPy)-grafted silica were prepared. After preparation of P4VPy-grafted silica, complexation with PdCl<sub>2</sub> and NiCl<sub>2</sub> was carried out to obtain the heterogeneous catalytic systems. Scanning and transmission electron microscopy (SEM and TEM) showed that palladium and nickel particles on the nanoscale were dispersed throughout the surface. Under copper-, amine-, and phos-

phine-free conditions, the palladium catalyst exhibited excellent activity in the Sonogashira cross-coupling reaction. An amine- and phosphine-free nickel-catalyzed Sonogashira reaction in the presence of CuI as a cocatalyst was also performed successfully. In both systems phenylacetylene reacted with aryl iodides, bromides, and chlorides in high yield and over short reaction times.

## Introduction

Palladium-catalyzed C–C coupling reactions are one of the most frequently employed organic transformations.<sup>[1–3]</sup> The Sonogashira reaction of terminal alkynes with aryl halides is one of the C–C coupling reactions that is employed for the synthesis of substituted arylated alkyne compounds, that is, C(sp<sup>2</sup>)–C(sp) bonds. These compounds are important intermediates for the synthesis of natural products, pharmaceutical compounds, organic materials for optical applications, and polymeric materials.<sup>[4,5]</sup>

The Sonogashira reaction is mostly catalyzed by homogeneous Pd complexes in the presence of phosphine ligands, a catalytic amount of CuI as a cocatalyst, and amine as a solvent or as a base on a large scale.<sup>[6,7]</sup> Phosphorous ligands are usually poisonous, air-sensitive, unrecoverable, and can degrade at elevated temperatures.<sup>[1–3]</sup> Copper salt is used to facilitate the oxidative addition of acetylene to palladium metal, but it results in dangerous waste materials that are difficult to separate.<sup>[8,9]</sup> An amine as a solvent or base is used to enhance the reaction rate and is not recovered. Furthermore, a problem that accompanies soluble Pd complexes is the loss of the expensive metals.<sup>[10,11]</sup> Consequently, most of the traditional

methods were economically and environmentally problematic, and modifications were carried out by introducing systems such as those that were phosphine-free,<sup>[12–14]</sup> copper- and amine-free,<sup>[15,16]</sup> copper-catalyzed Pd-free,<sup>[17–19]</sup> and the use of other transition metals such as Fe,<sup>[20]</sup> Co,<sup>[21]</sup> Ni,<sup>[22–28]</sup> Ru,<sup>[29]</sup> and In,<sup>[30]</sup> as well as the use of a solid supported catalyst.<sup>[15,31–33]</sup>

Nickel is a promising and cheaper alternative to the use of palladium as a transition-metal catalyst in coupling reactions. There are many reports in the literature on the use of nickel as an alternative to palladium in homocoupling<sup>[34–36]</sup> and cross-coupling reactions such as Heck, Suzuki, and Kumada,<sup>[37–43]</sup> but there are only a few reports on Ni-catalyzed Sonogashira reactions.<sup>[22–28]</sup> A nickel-catalyzed Sonogashira reaction was reported by Beletskaya et al. using homogeneous Ni<sup>II</sup> species.<sup>[22]</sup> Wang et al. reported the use of Ni<sup>0</sup> particles<sup>[21]</sup> and also nickel(0)-powder-doped KF/Al<sub>2</sub>O<sub>3</sub>.<sup>[22]</sup> In 2009, Hu et al. reported an Ni<sup>II</sup> pincer complex and its efficient use in the Sonogashira reaction of alkyl halides; following this study, they introduced nickamine as an efficient precatalyst for the same purpose.<sup>[25,26]</sup> In 2010, Bakherad et al. described Ni–Cu-catalyzed Sonogashira coupling of terminal acetylenes with aryl iodides in the presence of sodium lauryl sulfate as the surfactant,<sup>[27]</sup> and recently, an Ni/Cu catalytic system for the coupling of aryl iodides with various terminal alkynes in the presence of chiral amino alcohol was developed by Yang et al.<sup>[28]</sup> These Ni catalysts require the use of CuI as cocatalyst, and most of them are effective in the presence of phosphine ligands. The diversity of aryl halides used in these reactions is limited to iodides and bromides.

Immobilization of homogeneous catalysts on a solid support can provide advantages such as product separation, inhibition of metal loss, catalyst recovery, and recycling. Several methods, including supporting metal complexes on polymers,<sup>[44,45]</sup> silica, and modified silica,<sup>[46,47]</sup> have been reported in the literature. Silica- or modified-silica-supported catalysts are good alterna-

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tives to traditional homogeneous catalysts. They are environmentally friendly, have excellent (chemical and thermal) stability, good accessibility, and good dispersion of catalytic sites.

Grafting polymer chains onto the silica surface provides a system that can be completely compatible with solvents and substrates and has good dispersion. Polymer-grafted silica has found applications in practical and fundamental studies of interfacial phenomena.<sup>[48]</sup> There are also some reports on the applications of polymer-metal-complex-grafted silica as a catalyst in organic transformations. In 2008, Gao et al. reported grafting of a poly(4-vinylpyridine)-Cu complex to silica and its use as a heterogeneous catalyst in oxidation reactions.<sup>[49]</sup> And in 2009, Han et al. used a poly(vinylpyrrolidone)-Ru-complex-grafted silica as a catalyst for the hydrogenation of aromatics.<sup>[50]</sup>

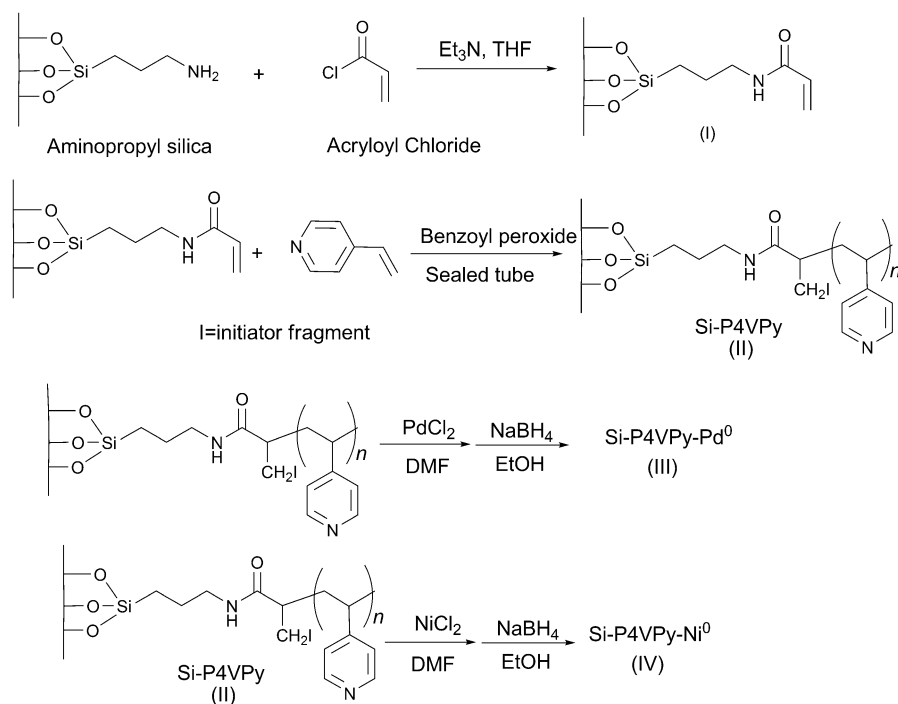
In continuation of our previous projects on heterogeneous Pd catalysts based on polymeric supports,<sup>[51–54]</sup> polymer-grafted silica,<sup>[55–57]</sup> and our related publication on the synthesis and application of poly(4-vinylpyridine)-Pd-grafted silica (Si-P4VPy-Pd) as a new heterogeneous catalyst in Heck and Suzuki cross-coupling reactions,<sup>[58]</sup> herein we report a Sonogashira cross-coupling reaction that uses Si-P4VPy-Pd as well as our newly synthesized and very promising comparatively cheap Si-P4VPy-Ni catalyst.

## Results and Discussion

### Pd-catalyzed Sonogashira reaction

Solid supports that contain nitrogen as donor atoms are of special interest when designing heterogeneous catalysts. Pyridine-functionalized supports are nitrogen-containing compounds that can coordinate with various transition-metal ions.<sup>[45,59]</sup> They are used to replace phosphines, since they are air stable, less expensive, and nontoxic.<sup>[59]</sup>

In this study, P4VPy-grafted silica (II) was synthesized by copolymerization reaction between acrylamidopropylsilica (I) and 4-vinylpyridine according to our previous procedure<sup>[50]</sup> (Scheme 1). The amount of P4VPy grafted onto silica was calculated by thermogravimetric analysis (TGA) to be about 3.4 mmol P4VPy per gram. The complexation of P4VPy-grafted silica (II) with palladium chloride was carried out in dimethylformamide (DMF) and the subsequent reduction process in ethanol using NaBH<sub>4</sub> gave polymeric Pd<sup>0</sup> complex III. The Pd



**Scheme 1.** Synthesis of the poly(4-vinylpyridine)-grafted silica-Pd<sup>0</sup> and -Ni<sup>0</sup> complex.

content of the catalyst was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis to be 0.26 mmol Pd g<sup>-1</sup>.

The morphology of the catalyst was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Figures 1 and 2). The SEM image shows shiny Pd particles on the smooth surface of the cubiclelike grafted P4VPy. According to the TEM image, the Pd particles are well dispersed throughout the catalyst surface and are nanoparticle-sized between 30–50 nm.

The copper-amine- and phosphine-free Sonogashira reaction of phenylacetylene with aryl iodides, bromides, and chlorides were performed with this catalyst. In a model reaction, the coupling of iodobenzene with phenylacetylene was stud-



**Figure 1.** SEM image of III.

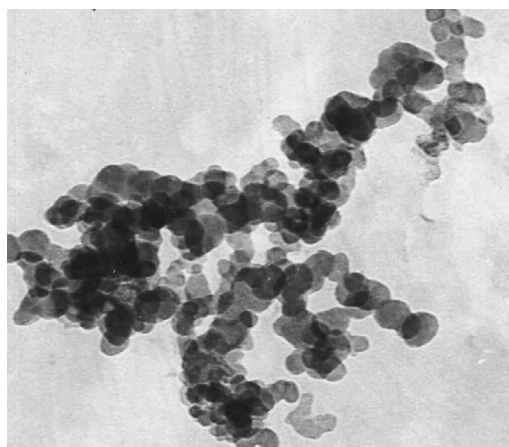


Figure 2. TEM image of III.

ied in the presence of different bases and solvents in the presence of the catalyst. The reaction parameters were optimized and the results are presented in Table 1.

**Table 1.** Optimization of base, solvent, CuI, and Ni catalyst for the Sonogashira reaction of iodobenzene with phenylacetylene.<sup>[a]</sup>

Entry	Base	Solvent	Pd [mmol %]	Time [h]	Conversion [%]
1	K <sub>2</sub> CO <sub>3</sub>	DMF	0.5	0.5	90
2	K <sub>2</sub> CO <sub>3</sub>	EtOH	0.5	1.25	65
3	K <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	0.5	2.0	70
4	K <sub>2</sub> CO <sub>3</sub>	THF	0.5	1.5	75
5	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	0.5	1.25	80
6	K <sub>2</sub> CO <sub>3</sub>	NMP	0.5	0.25	100
7	Et <sub>3</sub> N	NMP	0.5	0.75	70
8	NaOAc	NMP	0.5	0.5	90
9	NaOH	NMP	0.5	1.0	60
10	K <sub>2</sub> CO <sub>3</sub>	NMP	0.3	0.25	100
11	K <sub>2</sub> CO <sub>3</sub>	NMP	0.2	0.25	95
12	K <sub>2</sub> CO <sub>3</sub>	NMP	0.1	0.25	85

[a] Reaction conditions: iodobenzene (1 mmol), phenylacetylene (1.2 mmol), base (2 mmol) Pd catalyst (0.5–0.1 mmol %), and 3 mL of solvent at 120 °C.

The best conversion was obtained in the presence of *N*-methyl-2-pyrrolidone (NMP) as solvent, K<sub>2</sub>CO<sub>3</sub> as a base, and using 0.3 mol% of the catalyst at 120 °C. The amount of the catalyst could be even reduced to 0.1 mol%. The turnover number (TON = mmol of product/mmol of Pd catalyst) of the catalyst was defined for the lowest mass of catalyst to be 850, which was regarded as a factor to show the high efficiency.

A study of the generality of this coupling reaction was carried out by using phenylacetylene with different aryl halides (Table 2). The electron-neutral, electron-rich, and electron-poor aryl halides were treated with phenylacetylene to generate the corresponding cross-coupling products in good to high yields.

**Table 2.** Pd-catalyzed Sonogashira reaction of phenylacetylene with aryl halides.<sup>[a]</sup>

Entry	Aryl halide	Time [h]	Yield <sup>[b]</sup> [%]
1		0.25	90
2		1.75	85
3		1.5	50
4		1.5	50
5		0.75	75
6		0.5	90
7		0.25	93
8		1.5	60
9		1.0	70
10		2.0	70
11		7.0	40
12		6.0	75
13		4.5	80
14		2.0	65 <sup>[c]</sup>
15		1.5	85 <sup>[c]</sup>
16		3.0	70 <sup>[c]</sup>

[a] Phenylacetylene/K<sub>2</sub>CO<sub>3</sub>/Pd catalyst = 1.0:2.0:0.003. Reaction conditions: NMP, 120 °C. [b] Isolated yield. [c] With additional TBAB (0.1 mmol). The characterization of the product was performed by comparison of its FTIR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra and physical data with those of the authentic sample.

Although aryl chlorides are not so reactive and are employed less in palladium-catalyzed coupling reactions,<sup>[60–62]</sup> Sonogashira reactions were performed with this catalyst using phenylacetylene and aryl chlorides in the presence of a catalytic amount of tetra-*n*-butylammonium bromide (TBAB; Table 2, entries 14–16).

To check the recyclability of the catalyst, the Sonogashira cross-coupling of iodobenzene with phenylacetylene was examined under optimized conditions. After completion of the reaction, the Pd catalyst was separated by filtration and was reused for a subsequent reaction under similar reaction conditions. The catalyst could be recycled efficiently up to six times and the results are presented in Table 3. ICP-AES analysis re-

**Table 3.** Recycling of the Si-PVPy-Pd catalyst for the Sonogashira reaction of iodobenzene with phenylacetylene.<sup>[a]</sup>

Entry	Cycle	Time [h]	Isolated yield [%]
1	1st	0.25	90
2	2nd	0.5	90
3	3rd	1.0	90
4	4th	1.0	90
5	5th	1.5	87
6	6th	1.5	87

[a] Reaction conditions: iodobenzene (1 mmol), phenylacetylene (1.2 mmol), base (2 mmol) Pd catalyst (0.5–0.1 mmol%), and 3 mL of solvent at 120 °C.

vealed negligible leaching after each step (1.5 ppm in the first cycle to 3 ppm in the last).

### Ni-catalyzed Sonogashira reaction

The formation of the Ni catalyst was achieved by the reaction of P4VPy-grafted silica (II) and nickel chloride and subsequent reduction in the presence of NaBH<sub>4</sub> (Scheme 1). The nickel content of IV was determined by ICP-AES to be 0.23 mmol Ni g<sup>-1</sup>. The morphology of IV was studied by using SEM and TEM images (Figures 3 and 4). The SEM image shows Ni particles on the smooth surface of the cubiclike grafted P4VPy and this was so similar to its Pd analogue. According to the TEM image, Ni particles are well dispersed through the catalyst surface in fiberlike nanoparticles of 10–30 nm width and 100–1100 nm in length.

The activity of the Ni catalyst was examined in the Sonogashira reaction between phenylacetylene and iodobenzene as a model in the presence of different bases and solvents at 120 °C (Table 4). The reaction yields were not high, even in Et<sub>3</sub>N, which is known to be highly favorable media for the Pd-catalyzed Sonogashira reaction.<sup>[6–7,11]</sup> The probable reason might be inactivation of the Ni catalyst due to coordination with the triple bond of phenylacetylene.<sup>[63]</sup> To solve this problem we added a catalytic amount of CuI as an activator of the

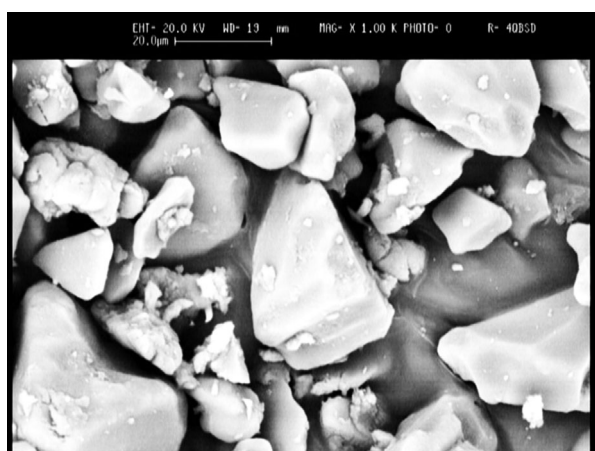


Figure 3. SEM image of (Si-PVPy-Ni).

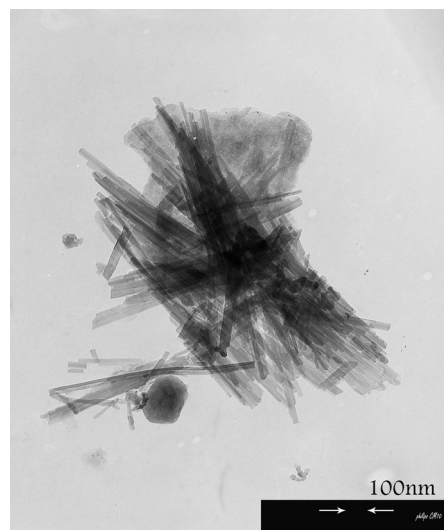


Figure 4. TEM image of (Si-PVPy-Ni).

**Table 4.** Optimization of base, solvent, CuI, and Ni catalyst for the Sonogashira reaction of iodobenzene with phenylacetylene.<sup>[a]</sup>

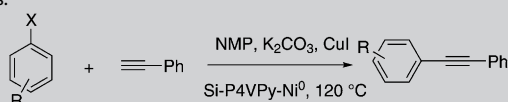
Entry	Base	Solvent	Ni [mmol%]	CuI [mmol%]	Time [h]	Conversion [%]
1	K <sub>2</sub> CO <sub>3</sub>	THF	0.5	–	24	no reaction
2	K <sub>2</sub> CO <sub>3</sub>	DMF	0.5	–	24	10
3	K <sub>2</sub> CO <sub>3</sub>	NMP	0.5	–	24	20
4	Et <sub>3</sub> N	NMP	0.5	–	24	20
5	Et <sub>3</sub> N	NMP	1.0	–	24	20
6	Et <sub>3</sub> N	NMP	0.5	10	7	90
7	NaOAc	NMP	0.5	10	2.5	95
8	K <sub>2</sub> CO <sub>3</sub>	NMP	0.5	10	1.75	100
9	K <sub>2</sub> CO <sub>3</sub>	NMP	0.3	10	1.75	100
10	K <sub>2</sub> CO <sub>3</sub>	NMP	0.1	10	2	80
11	K <sub>2</sub> CO <sub>3</sub>	NMP	0.3	5	2	100

[a] Reaction conditions: iodobenzene (1 mmol), phenylacetylene (1.2 mmol), base (2 mmol) Ni catalyst (10–5 mmol%), CuI (0.1–0.05 mmol%) and 3 mL of solvent at 120 °C.

triple bond. The coupled product was then obtained in high yield (Table 4, entry 6). The optimized conditions for the reaction were NMP as solvent, K<sub>2</sub>CO<sub>3</sub> as a base, 0.3 mol% of catalyst, and 5 mmol% of CuI as a cocatalyst at 120 °C. When the catalyst amount was reduced to 0.1 mmol% the TON was found to be 800.

Different aryl halides were treated with phenylacetylene under optimized conditions and the results are presented in Table 5. The electron-neutral, electron-rich, and electron-poor aryl iodide and bromides were treated with phenyl acetylene and the coupled products were obtained in reasonable yields. The reaction of aryl chlorides was performed in the presence of TBAB (0.1 mmol) as an additive (Table 5, entries 10–12). Comparison of the presented catalytic system with other Ni-

**Table 5.** Ni-catalyzed Sonogashira reaction of phenylacetylene with aryl halides.<sup>[a]</sup>



Entry	Aryl halide	Time [h]	Yield <sup>[b]</sup> [%]
1		1.75	87
2		5	75
3		5	65
4		3	75
5		10	75
6		10	80
7		5	90
8		10	80
9		5	60
10		5	50 <sup>[c]</sup>
11		4	65 <sup>[c]</sup>
12		10	40 <sup>[c]</sup>

[a] Molar ratios of ArX/phenylacetylene/K<sub>2</sub>CO<sub>3</sub>/nickel catalyst/CuI = 1.0:1.2:2.0:0.003:0.1. Reaction conditions: NMP, 120 °C. [b] Isolated yield. [c] With additional TBAB (0.1 mmol). The characterization of product was performed by comparison of its FTIR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra and physical data with those of the authentic sample.

catalyzed systems showed<sup>[22–28]</sup> improvements in reaction times and yields without the addition of the phosphine ligand.

To check the recyclability of the Ni catalyst the cross-coupling of iodobenzene with phenylacetylene was examined as a model under optimized conditions. It could be recycled up to eight times without lengthening the reaction time. The results are presented in Table 6. ICP-AES analysis revealed negligible leaching after each step (0.8 ppm in the first cycle to 2 ppm in the last). The Ni catalyst showed better efficiency in recycling experiments than the Pd analogue.

## Conclusion

Poly(4-vinylpyridine)-grafted silica (Si-P4VPy) was prepared. The complexation of Si-P4VPy with Pd and Ni was performed followed by subsequent reduction with NaBH<sub>4</sub> to obtain Si-P4VPy-Pd<sup>0</sup> and Si-P4VPy-Ni<sup>0</sup>. TEM images showed that Pd or Ni particles of nanoparticle-size were dispersed throughout the polymer surface. The Sonogashira reactions were performed with both catalysts. The Pd catalyst showed good reactivity to generate the corresponding cross-coupling products in good

**Table 6.** Recycling of the Si-PVPy-Ni catalyst for the Sonogashira reaction of iodobenzene with phenylacetylene.<sup>[a]</sup>

Entry	Cycle	Time [h]	Isolated yield [%]
1	1st	1.75	87
2	2nd	1.75	87
3	3rd	1.75	87
4	4th	1.75	87
5	5th	2.0	87
6	6th	2.0	85
7	7th	2.0	85
8	8th	2.0	85

[a] Molar ratios of iodobenzene/phenylacetylene/K<sub>2</sub>CO<sub>3</sub>/nickel catalyst/CuI = 1.0:1.2:2.0:0.003:0.1. Reaction conditions: NMP, 120 °C.

to excellent yields. The Ni catalyst as a cheaper alternative to its Pd counterpart showed good reactivity in the Sonogashira reaction. The presence of CuI as a cocatalyst was needed for the Ni analogue and the corresponding cross-coupling products were obtained in good to high yields. Both catalysts worked efficiently without the presence of any phosphine ligands. The electron-neutral, electron-rich, and electron-poor aryl iodides, bromides, and also chlorides showed excellent reactivity with both systems. The use of aryl chlorides in cross-coupling reactions is usually hardly successful, but comparatively reasonable yields were gained in the presence of tetra-*n*-butylammonium bromide (TBAB) as an additive for both catalysts. Simple filtration, excellent dispersity, recycling, high product yields, and large-scale synthesis are among the advantages of these heterogeneous Pd and Ni catalysts.

## Experimental Section

### General

The substrates and solvents were obtained from Fluka AG and Merck. Aminopropylsilica with an average particle size of 0.015–0.035 mm and a loading of 0.95 mmol g<sup>-1</sup> was supplied by Fluka AG. All products were characterized by comparison of their IR and NMR spectra and physical data with those reported in the literature. Thin-layer chromatography was performed on silica-gel Polygram SIL/UV 254 plates. Gas chromatographic analysis was performed on a Shimadzu GC 14A with a hydrogen flame ionization detector. IR data were collected on a Shimadzu FT-IR-8300 spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance DPX instrument (250 MHz). TGA was performed using a PerkinElmer instrument under N<sub>2</sub> gas and a heating rate of 20 °C min<sup>-1</sup>. TEM analysis was performed on a Philips model CM 10 instrument. Scanning electron micrographs were obtained by using a XL-30 FEG scanning electron microscope (Philips) at 20 kV. Metal-loading tests were carried out with an ICP-AES analyzer (Varian, Vista-Pro).

### Preparation of poly(4-vinylpyridine)-grafted silica (Si-P4VPy)

Si-P4VPy was prepared according to our reported procedure.<sup>[58]</sup> To a suspension of acrylamidopropylsilica, distilled 4-vinylpyridine and recrystallized benzoyl peroxide were added in a 10 mL sealed tube. The mixture was heated at 100 °C in an oven for 24 h. The grafted

silica polymer was Soxhlet-extracted with  $\text{CHCl}_3$ , followed by washing and drying. The amount of poly(4-vinylpyridine) grafted was determined by TGA. It was approximately 3.4 mmol P4VPy per gram. IR (KBr):  $\tilde{\nu}$  = 2900–2985 (C–H str., weak), pyridine ring 1423, 1550 (C–C), 1596 (C–N), 1037 (Si–O), 3420  $\text{cm}^{-1}$  (OH).

### Preparation of Si-P4VPy-Pd and Si-P4VPy-Ni catalysts

Si-P4VPy (1.0 g) was added to a solution of  $\text{PdCl}_2$  or  $\text{NiCl}_2$  (5.0 mmol) in DMF and stirred at 80 °C for 10 h. The solid (yellowish  $\text{PdCl}_2$  and greenish  $\text{NiCl}_2$ ) was treated with  $\text{NaBH}_4$  (5 mmol) in ethanol for 15 min under reflux conditions. The mixture was then filtered and washed thoroughly with DMF and acetone. The black solid of  $\text{Pd}^0$  and the grayish solid of  $\text{Ni}^0$  catalysts were dried under vacuum at 60 °C for 10 h.

### General procedure for the Pd-catalyzed Sonogashira reaction

The Pd catalyst (0.3 mmol%, 9 mg) was added to a suspension of aryl halide (1 mmol) and  $\text{K}_2\text{CO}_3$  (2.0 mmol) in NMP (5 mL). The reaction mixture was stirred at 120 °C. Phenyl acetylene (1.2 mmol) was added dropwise to the reaction mixture over an hour. The progress of the reaction was followed by TLC on silica gel using a 90:10 petroleum ether/chloroform mixture until no trace of starting aryl halide was observed. The mixture was then filtered and the filtrate was poured into water (50 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  (3 × 15 mL). The combined organic phases were dried over  $\text{Mg}_2\text{SO}_4$ , filtered, and the solvent was evaporated under vacuum. The product was isolated by flash chromatography using petroleum ether/chloroform (95:5) as eluent.

### General procedure for the Ni-catalyzed Sonogashira reaction

A mixture of aryl halide (1 mmol),  $\text{K}_2\text{CO}_3$  (2.0 mmol), Ni catalyst (0.3 mmol%, 9 mg), and  $\text{CuI}$  (0.05 mmol) in NMP (5 mL) was stirred at 120 °C. Phenyl acetylene (1.2 mmol) was added dropwise to the reaction mixture over an hour. Progress of the reaction was followed by TLC on silica gel until no trace of starting aryl halide was observed. After completion of the reaction, the procedure outlined above was followed.

### General procedure for recycling reactions

Recycling of Si-P4VPy-Pd or Si-P4VPy-Ni was performed for the reaction between iodobenzene and phenylacetylene according to the procedure described above. After completion of the reaction, the suspension was cooled to room temperature and filtered. The catalyst was washed with DMF, water, and acetone. It was dried under vacuum and reused for repeating cycles.

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**Keywords:** C–C coupling • nanoparticles • nickel • palladium • supported catalysts

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