APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 1239–1248
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.999

Heck and Suzuki–Miyaura couplings catalyzed by nanosized palladium in polyaniline

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Received 7 July 2005; Accepted 26 August 2005

A novel route to prepare polyaniline (PANI)-supported Pd(0) nanoparticles by a one-pot chemical route is presented. Nanosized Pd(0) particles were first prepared by reduction of $Pd(OAc)_2$ using *t*-BuONa activated sodium hydride in refluxing THF. A ligand exchange with aniline on *t*-BuONa-stabilized Pd(0) particles yielded aniline-stabilized particles. Pd(0)/PANI nanocomposites were finally obtained by polymerizing aniline-stabilized Pd(0) particles using ammonium persulfate. Nanocomposites were characterized by transmission electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy. Results show that this one-pot experimental route is successful in producing hybrid materials constituted of Pd(0) nanoparticles stabilized by PANI due to the strong binding of PANI amine groups to Pd(0) particles. TEM images of the nanohybrids show that metal particles with diameters of ca. 4.9 nm are homogeneously dispersed in PANI. The preliminary results indicate that the Pd(0) particles supported on PANI behave as efficient heterogeneous catalysts in the Heck and Suzuki–Miyaura reactions of aryl iodides. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: polyaniline; palladium; nanocomposite; Suzuki–Miyaura coupling; Heck coupling

INTRODUCTION

Heterogeneous catalysis is widely used in environmental catalysis, in the manufacture of chemicals and in the petrochemical industry. Ten years ago, the size-dependent reactivity of materials was established.[1] Today nanomaterials are widely employed as catalytic materials, not only as catalysts, but also in gas sensors, in electronic devices, in solar cells, etc.

In catalyst preparation, it is important to achieve a high degree of dispersion, as this maximizes the contact area of the catalyst with the reactants. At the same time, this minimizes the fraction of catalyst that is buried within large particles and is so unable to participate directly in the catalyzed reaction. The mass transport of reactants and reaction products is also increased when small particles are used.[2] The size of the particles can also have an influence on the selectivity of the catalyst.

Conducting polymers such as polyaniline (PANI) as the support for catalytic active metal particles fulfill several functions. They provide good electron and ion conductivity;[3] they also diminish the rate of agglomeration of the metal particles[4] and stabilize them mechanically.[5] The use of PANI as host media for the catalyst particles is particularly attractive since this medium provides an efficient route for the shuttling of electronic charges to the catalyst centers.[6]

Among transition metals commonly used in catalysis, palladium offers many advantages, e.g. no other transition metal is as versatile as palladium for C–C bond formation, palladium reagents show tolerance to many functional groups and its toxicity has posed no problem so far.[7] The Pd(0)/PANI composite materials have been prepared using a variety of chemical approaches. Incorporation of the anionic metal complex $PdCl_4^{2-}$ in polyaniline followed by the reduction of

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the Pd(II) complex using molecular hydrogen or NaH_2PO_2 is by far the most common method for the production of Pd(0)/PANI nanocomposites.[8–11] Spontaneous reduction of Pd(II) complexes by the electroactive polyemeraldine form of the PANI polymer,[12–19] γ-radiolysis of Pd(II) in the presence of aniline followed by polymerization,[17] electrodeposition[20] or electroless precipitation[21] methods have also been reported. In some cases, the materials produced by these methods have been assessed for their catalytic activity. Drelinkiewicz *et al*. used their Pd(0)/PANI nanocomposite in the liquid-phase hydrogenation of 2-ethylanthraquinone under hydrogen atmosphere.[8,9,11,13] Neoh *et al*. reported the use of palladium-containing polyaniline microparticles in the reduction of dissolved oxygen in water and in the reduction of nitrobenzene to aniline.[10] Although these procedures are effective for the preparation of Pd(0)/PANI nanocomposites, the control of the size and the shape of Pd(0) particles is generally poor.

Recently, we reported a method of synthesizing metal nanoparticles (Au, Bi, Sb, etc.) using alkoxide-activated sodium hydride in organic solvent (THF or 1,4-dioxane) as a mild reducing agent of the precursor metallic complexes.[22–27] Our technique to synthesize nanoparticles takes advantage of the weak coordinating properties of the alkoxide, which acts as a stabilizer and avoids aggregation of the metal nanoparticles generated in the course of the reduction. We report herein a simple and general procedure of the preparation of Pd(0)/PANI particle composites. Pd(0) particles were produced by reduction of $Pd(OAc)_2$ using *t*-BuONa-activated NaH. Ligand exchange with aniline on the surface of the *t*-BuONa-stabilized Pd(0) nanoparticles caused only slight aggregation and gave aniline-stabilized nanoparticles. Finally, polymerization of Pd(0)/aniline monomers in aqueous solution using ammonium persulfate allows the assembly of Pd(0) particles possessing an average diameter of 4.9 nm within the PANI framework (see Fig. 1). To the best of our knowledge, the synthesis of such small Pd(0) nanoparticles dispersed in PANI has not been reported to date. Various analytical techniques such as transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were employed to characterize the nanocomposites. Preliminary results on the catalytic activity of Pd(0)/PANI nanocomposites in Suzuki–Miyaura and Heck coupling reactions are also reported.

EXPERIMENTAL

Characterization of the samples

Powder (XRD) analyses were obtained using automated powder diffractometer with Mo Kα radiation (Rotaflex RU-200B, RIGAKU generator and CPS 120 INEL detector, transmission assembly). Powder was introduced under argon into Lindemann tubes, which were further sealed to avoid any pollution. The particle size was calculated using Scherrer's formula: $d = 0.9\lambda/2\beta\cos\theta$, where d is the mean of particles, λ is wavelength and β is full-width at half maximum. Transmission electron microscopy (TEM) images were taken by placing a drop of the particles in THF onto a carbon film-supported copper grid. Samples were studied using a Philips CM20 instrument with LaB_6 cathode operating at 200 kV. The standard deviation of the size distribution was calculated from the equation $\sigma = [\sum n_i\,(D_i - D)^2/(N-1)]^{0.5}$, where n_i is the number of particles having diameter D_i, D is the average diameter $[= (\sum n_i D_i)/N]$, and N is the total number of particles. The relative standard deviation of the size distribution was calculated from the equation $\sigma_r = 100\sigma/D$, where σ is the standard deviation and D is the average diameter of particles. XPS measurements were performed

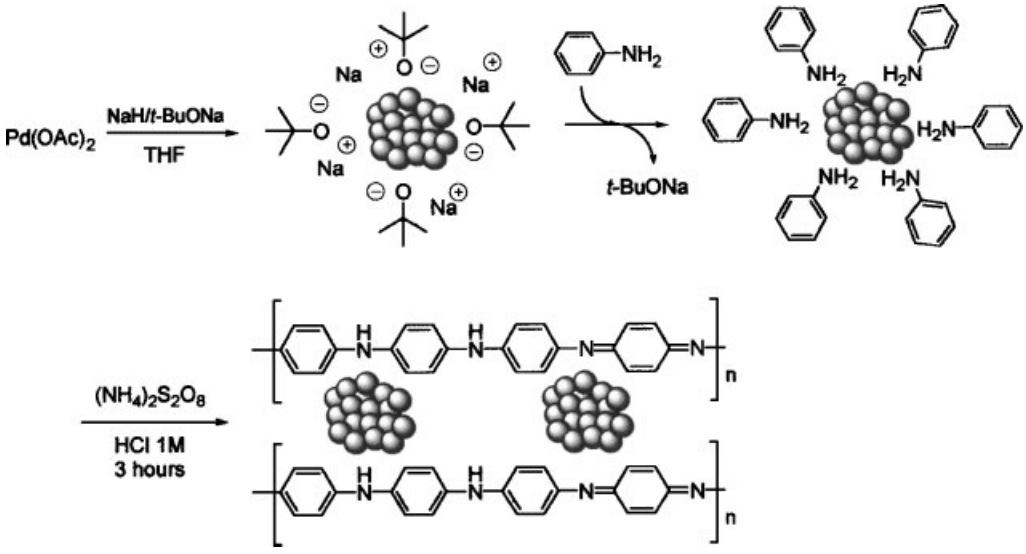


Figure 1. Synthesis of Pd(0)/PANI nanocomposites.

at a residual pressure of 10^{-9} mbar, using a KRATOS Axis Ultra electron energy analyzer operating with an Al Kα monochromatic source.

Synthesis of Pd(0)/PANI nanocomposites

In our synthesis procedure, there are three steps: (i) synthesis of *t*-BuONa-stabilized Pd(0) particles; (ii) functionalization of the Pd(0) particle surface by aniline; and (iii) polymerization of aniline-stabilized Pd(0) particles with ammonium persulfate to generate PANI-stabilized Pd(0) particles.

Synthesis of t-BuONa-stabilized Pd(0) nanoparticles

A Schlenk tube was loaded with degreased sodium hydride (40 mmol) and 20 ml of anhydrous THF, and the mixture was heated to 65 °C. A solution of freshly distilled *t*-butanol (20 mmol) in 5 ml THF was then injected into the tube and the mixture was held at 65 °C for 5 min. After cooling to room temperature, anhydrous Pd(II) acetate (10 mmol) were added in one portion. The Schlenk contents were further stirred at 65 °C for 1 h.

Reduction of $Pd(OAc)_2$ into *t*-BuONa-stabilized Pd(0) nanoparticles takes place through the following reaction:

$$Pd(OAc)_2 + 2\ NaH/2\ t\text{-}BuONa \xrightarrow[65\,^\circ C]{THF} Pd(0)/2\ t\text{-}BuONa + H_2 + 2\ NaOAc$$

TEM analysis indicated that the sample was composed of Pd(0) particles having an average diameter of 2.3 ± 1.3 nm.

Synthesis of aniline-stabilized Pd(0) nanoparticles

Aniline was rapidly passed through a short plug of alumina before use. Under a nitrogen atmosphere, aniline (0.73 ml, 7.95 mmol) was added at room temperature to the above-described solution of *t*-BuONa-stabilized Pd(0) particles. The mixture was stirred for 10 min before polymerization.

TEM analysis indicated that the sample was composed of Pd(0) particles having an average diameter of 3.2 ± 1.8 nm.

Synthesis of PANI-stabilized Pd(0) nanoparticles

Ammonium persulfate $(NH_4)_2S_2O_8$ (1.55 g, 6.8 mmol) was dissolved into 50 ml of 1 M aqueous HCl solution to prepare a stock solution of the oxidant. A solution of the oxidant (30 ml) was added dropwise to the above-described aniline-stabilized Pd(0) particles in THF and the mixture was vigorously stirred at room temperature. Polymerization was carried out for 3 h at 25 °C. The black solid of PANI-stabilized Pd(0) particles was allowed to settle and filtered. Distilled water (50 ml) was added in small portions to the filtrate to precipitate PANI-stabilized Pd(0) particles remaining in the organic phase. Combined solids were washed repeatedly with distilled water (3×10 ml) and centrifugated. PANI-stabilized Pd(0) particles were finally dried in vacuum at room temperature and used without further purification for characterization and catalytic applications.

TEM analysis indicated that the sample was composed of Pd(0) particles having an average diameter of 4.9 ± 2.3 nm.

Elemental analysis showed the following composition for the Pd/PANI sample: C 34.71%, H 2.24%, N 6.54%, Pd 54.59%, O 1.47%, S 0.38%.

Synthesis

All reactions were carried out using standard Schlenk techniques under an atmosphere of nitrogen. Gas chromatographic analyses were performed on a capillary gas chromatograph fitted with an 'Optima 5' column ($22\ m \times 0.25$ mm i.d. $\times\ 0.25\ \mu m$). All quantifications of reaction constituents were achieved by gas chromatography using a known quantity of decane as reference standard. Melting points were taken on a Tottoli apparatus and were uncorrected. The ^1H and ^{13}C NMR spectra were recorded at 400.13 and 100.40 MHz using $CDCl_3$ as solvent. Compounds previously described were characterized by ^1H and ^{13}C NMR and their purity was confirmed by GC analysis.

THF was distilled under nitrogen from sodium benzophenone ketyl. *t*-Butanol was distilled from sodium before use. Sodium hydride (65% in mineral oil) was purchased from Fluka and used after two washings with THF under nitrogen. Aryl halides, aryl boronic acids and alkenes were purchased from commercial sources and were used without further purification. Pd(II) acetate was purchased from Acros and used as received.

Representative procedure for Pd(0)/PANI-catalyzed Suzuki–Miyaura couplings (Table 1)

The Pd(0)/PANI composite (1 mol% Pd) was placed in a Schlenk flask under nitrogen. A mixture of the aryl iodide (5 mmol) and of the arylboronic acid (7.5 mmol) in 1,4-dioxane (10 ml) was then added to the flask, followed by K_3PO_4 (10 mmol). The resulting mixture was stirred at 100 °C and the progress of the reaction was monitored by GC/MS. After 15 h, the mixture was cooled to room temperature and concentrated under reduced pressure. Purification by column chromatography on silica gel gave the coupling product.

All the biaryls prepared are known compounds: 1-methyl-4-phenylbenzene;[28] 1-(4-methylphenyl)naphthalene;[29] 4-phenylbenzonitrile;[30] and 1-methoxy-4-phenylbenzene.[31]

Representative procedure for Pd(0)/PANI-catalyzed Heck couplings (Table 2)

Iodobenzene (5 mmol), the acrylate ester or styrene (25 mmol) and *N*,*N*-dimethylformamide (10 ml) were added to the Pd(0)/PANI composite (5 mol% Pd) in a Schlenk flask equipped with a heating arrangement and a stirrer. *n*-Pr_3N (10 mmol) was added, and the resulting mixture was stirred at 130 °C. The reaction progress was monitored by GC/MS and TLC. After completion of the reaction, the Schlenk contents were poured into 10% aqueous HCl (20 ml) and extracted with ethyl acetate (2×30 ml). The combined extracts were washed with brine (20 ml) and water (20 ml), and concentrated. Usual

chromatographic purification on silica gel gave the Heck arylation products.

All the Heck coupling products prepared are known compounds: methyl (*E*)- and (*Z*)-3-phenyl-2-propenoate;[32] butyl (*E*)- and (*Z*)-3-phenyl-2-propenoate;[33] (*E*)- and (*Z*)-1,2-diphenyl-1-ethene.[32]

RESULTS AND DISCUSSION

To examine the immobilization of palladium(0) nanoparticles on PANI, transmission electron microscopy (TEM) measurements of the sample were carried out at the three stages of the synthesis. Representative TEM micrographs of the *t*-BuONa-stabilized Pd(0) nanoparticles (Fig. 2), after ligand exchange with aniline (Fig. 3), after immobilization of Pd(0) nanoparticles on PANI (Fig. 4), are shown.

A statistical analysis of the TEM image shows that, before ligand exchange, *t*-BuONa-stabilized Pd(0) particles are spherical and have an average diameter of 2.3 nm, with a size distribution standard deviation of 1.3 nm (Fig. 2). The (111), (200), (220) and (311) reflections observed in the electron diffraction pattern are clearly due to a face-centered cubic (fcc) Pd(0) structure. In the EDX spectrum, the signals of C, O and Na are present as well as the Pd(0) signal, indicating either the adsorption of the *t*-butylalkoxide on the particle core surface or their presence in the vicinity of the particle.

Aniline-stabilized nanoparticles were prepared through ligand exchange by adding aniline at room temperature to *t*-BuONa-stabilized Pd(0) nanoparticles. Owing to the strong affinity of palladium for nitrogen, we suppose that exchange of *t*-BuONa with aniline was effective and yielded aniline-stabilized Pd(0) nanoparticles. The EDX spectrum (Fig. 3) shows, however, that sodium *t*-butoxide is still present around the particle. The formation of a mixed shell constituting *t*-BuONa and aniline around Pd(0) particles can therefore not be excluded. There was no precipitation observed by the eye before and after ligand exchange,

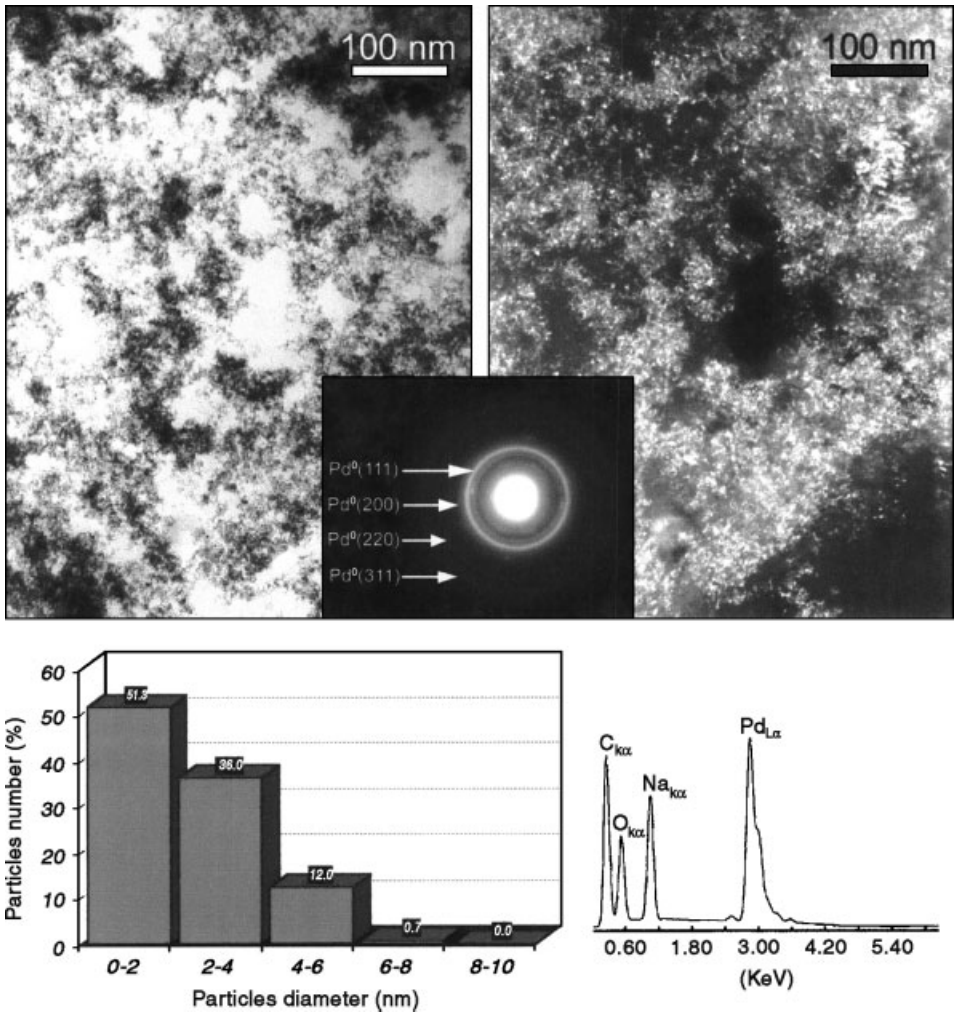


Figure 2. Bright field, dark field TEM micrographs, ED pattern, the corresponding particle size distributions and EDX spectrum of *t*-BuONa-stabilized Pd(0) particles.

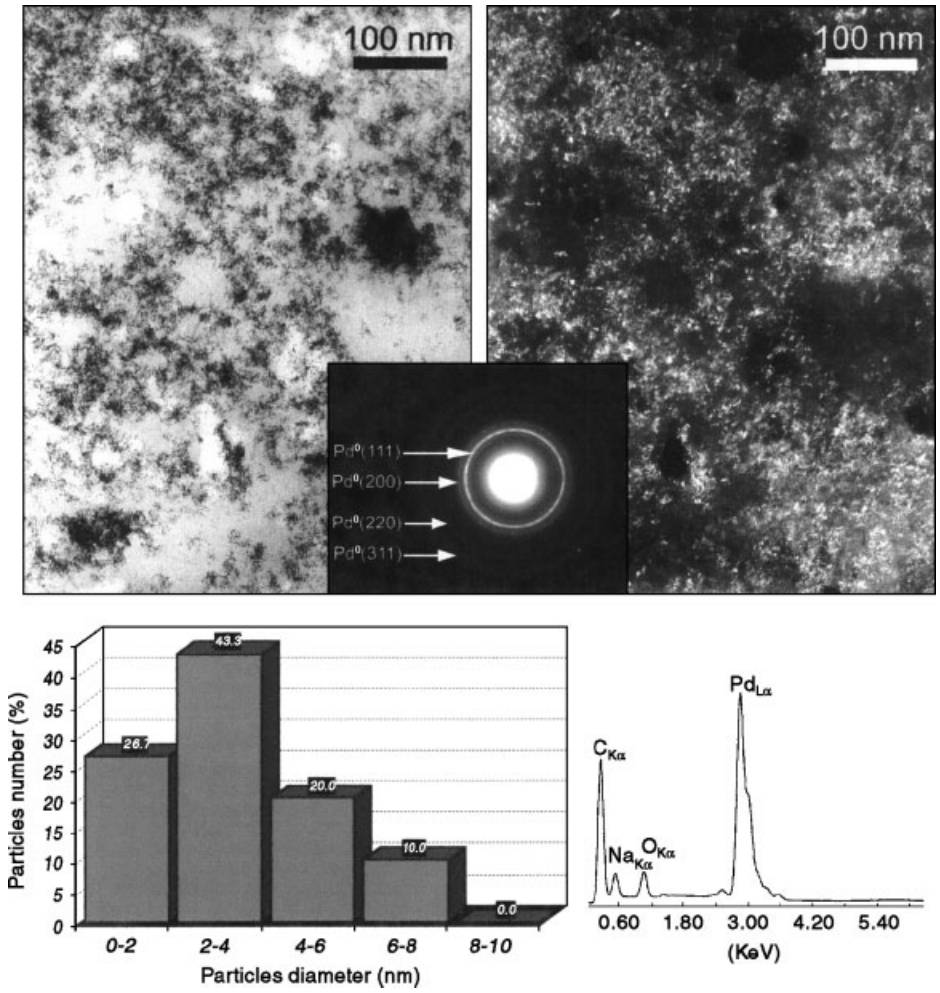


Figure 3. Bright-field, dark-field TEM micrographs, ED pattern, the corresponding particle size distributions and EDX spectrum of aniline-stabilized Pd(0) particles.

and this suggests that *t*-BuONa and aniline act as effective protective agents for formation and control of the size of palladium nanoparticles. The average diameter of Pd(0) nanoparticles is only slightly affected by the ligand exchange and nanoparticles, with an average diameter of 3.2 ± 1.8 nm observed on the TEM micrograph (Fig. 3). As shown on the electron diffraction pattern, the cristallinity of the material is not modified by the ligand exchange.

Addition of an aqueous solution of ammonium persulfate to the black mixture of aniline-stabilized Pd(0) nanoparticles resulted in the immediate formation of microscopic particulates, and subsequent stirring at room temperature for 3 h yielded black dispersions of PANI-stabilized Pd(0) nanoparticles. The complete uptake of Pd(0) nanoparticles into the PANI framework was observed by TEM analysis. No free Pd(0) nanoparticle was observed on the TEM grid, and polymerization of Pd(0)/aniline monomers results in a well-defined Pd(0)/PANI nanocomposite. The diameter of the Pd(0) nanoparticles was modified by the aniline polymerization, and a weak aggregation of particles was observed (Fig. 4). Palladium particles appeared as uniformly dispersed spots in the PANI matrix with an average diameter of 4.9 nm (size distribution standard deviation ~2.3 nm). In addition, the TEM image showed regions were no Pd/PANI composite was present. The elemental analysis of the nanocomposite carried out using EDX confirmed that the deposited particles were palladium(0) (signal at 2.84 keV).[34]

Figure 5 is a typical electron diffraction pattern of the same sample. From the diffraction pattern, two conclusions can be drawn: (i) the PANI matrix is amorphous (see also X-ray diffraction of PANI in Fig. 6); (ii) Pd(0) particles are crystallized. The diffraction rings have been indexed in the figure. The (111), (200), (220), (311) and (331) reflections observed are clearly due to a fcc palladium structure. From these data, it is clear that the composite consists of crystallized Pd(0) particles dispersed in an amorphous PANI matrix.

X-ray diffraction was also used to provide additional information on the purity and on the crystallinity of the Pd(0) nanoparticles. The materials obtained after each

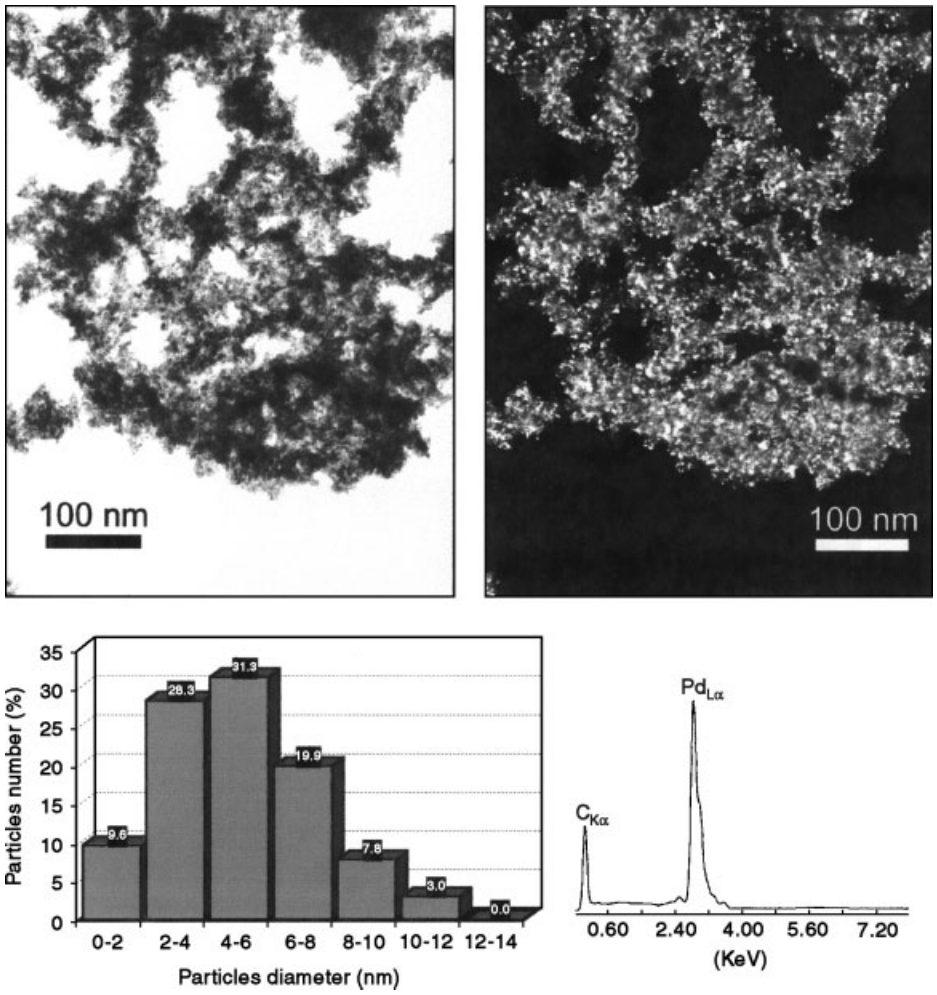


Figure 4. Bright field, dark field TEM micrographs, the corresponding particle size distributions and EDX spectrum of PANI-stabilized Pd(0) particles.

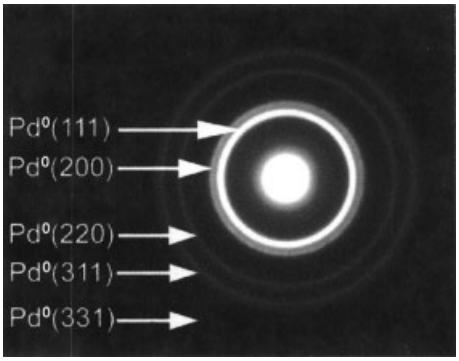


Figure 5. Diffraction pattern showing (111), (200), (220), (311) and (331) reflections from fcc Pd(0).

step of the synthesis were dried *in vacuo*, sealed in glass capillaries and the products were examined using a Rotaflex RU-200B X-ray diffractometer with Mo Kα radiation (Fig. 6). Figure 6(a) shows the XRD patterns of polyaniline prepared by polymerization of aniline in THF using ammonium persulfate. The X-ray diffraction patterns exhibit only a broad 'halo' centered around $2\theta = 10°$, characteristic of PANI.[35] The position of this halo does not interfere with the palladium diffraction pattern, as shown in Fig. 6(b–d). For *t*-BuONa- [Fig. 6(b)], aniline- [Fig. 6(c)] and PANI-stabilized [Fig. 6(d)] palladium particles, Pd(0) appears in the crystalline form, observed in the XRD patterns at $2\theta = 17.7, 20.4, 29.4$ and $34.7°$. These data match well the ASTM data for fcc palladium. As Fig. 6 shows, the intensity of Pd(0) peaks increased at each step of the synthesis. This effect indicates that the size and/or the crystallinity of Pd(0) particles increases both during the ligand exchange and the polymerization of PANI. Estimation of the approximate average particle diameters from the XRD line broadening of the (220) peak using the Scherrer equation leads to calculated values of 2.8, 3.2 and 4.5 nm, respectively, for *t*-BuONa-, aniline- and PANI-stabilized Pd(0) particles. These diameters of Pd(0) particles are in good harmony with the crystallite size obtained from the TEM experiments. It is also worth noting that the patterns of the Pd(0)/PANI

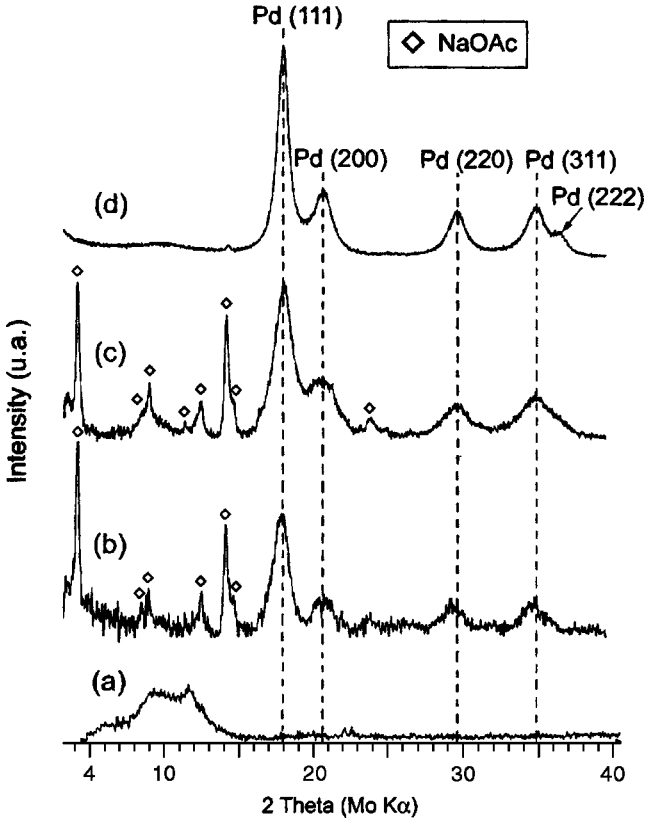


Figure 6. XRD pattern of (a) PANI, (b) *t*-BuONa-, (c) aniline- and (d) PANI-stabilized Pd(0) particles.

hybrid present the same profile as observed in the *t*-BuONa-stabilized Pd(0) particles, indicating that the structure of the Pd(0) nanoparticles was not modified by the polyaniline. Reflections of NaOAc produced during the reduction of $Pd(OAc)_2$ can also be observed in Fig. 6(b, c). Elimination of NaOAc is effected by washing the nanocomposite with water, as indicated in Fig. 6(d). This treatment caused neither alteration of the metal particles nor change in the cristallinity of the material.

The Pd/PANI nanocomposite collected after reaction, washing and drying was subjected to XPS analysis. The results are shown in Fig. 7. From the XPS spectra [Fig. 7(a)], we derived the XPS survey spectrum of N and palladium atoms. The N 1*s* spectra [Fig. 7(b)] can be separated into two major component peaks at 398.0 and 399.0 eV, attributed to the –N═ and –NH– groups of polyaniline, respectively.[36,37] A higher binding energy (>401 eV) tail corresponding to oxidation species or positively charged nitrogen was not observed. This result shows that an undoping, resulting in the conversion of some the N^+ units to –NH– and –N═ units, occurs during the washing of the Pd/PANI nanocomposite with deionized water after reaction.

The palladium 3*d* spectra is shown in Fig. 7(c). The spectra was deconvoluted to determine the differences in the shares of individual peak components in the Pd(0)/PANI composite. The presence of Pd(0) was confirmed by the palladium $3d_{5/2}$ peak at 334.2, while the component peak with binding energy at 335.6 eV was attributed to the Pd–O bond of palladium oxide.[38] According to the literature,[37] the third peak at 337.0 can be assigned to the Pd–O bond of $Pd(OAc)_2$ or to Pd–N bonds. Chemical analysis of the particle surfaces shows that the atomic ratio of Pd(+2)/Pd(0) is 1.9. The presence of Pd(II) at the surface of the particles deserves further comment. Palladium oxide and palladium acetate have been detected neither by XRD nor by TEM. We therefore cannot exclude that some oxidation occurred at the surface of Pd(0) particles during the transfer of the sample in the XPS machine.

With the goal of examining the catalytic performance of Pd/PANI nanocomposites, we report finally their use in Suzuki–Miyaura and Heck coupling reactions.

The palladium-mediated cross-coupling of arylboronic acids with aryl halides, the Suzuki–Miyaura reaction, is a versatile and useful method for the synthesis of biaryl-containing molecules.[39,40]

Preliminary studies with 4-iodotoluene and phenylboronic acid as the coupling partners revealed that the Pd(0)/PANI nanocomposite (1 mol% Pd) was an efficient catalyst in the Suzuki–Miyaura coupling (Table 1). Investigations into the optimal base showed that the rate of reaction and the activity of the catalyst were significantly influenced by the base used. A number of inorganic bases such as K_3PO_4, Cs_2CO_3 and KF could provide cross-coupling products in high yields (respectively 85, 84 and 79%). However, when organic bases such as triethylamine or diisopropylethylamine were used, the reactions ceased within minutes and the precipitation of palladium black was observed. Considering its high activity, K_3PO_4 was ultimately chosen as the base for the system.

Various solvents were also tested in the coupling reaction with K_3PO_4 as the base. Dioxane proved to be the best solvent, giving the fastest reaction. An attempt to conduct the reaction at a lower temperature led to a decrease in the conversion of 4-iodotoluene (50 °C/24 h, 37% conversion). Under the optimized reaction conditions, activated- or non-activated aryl iodides can react with phenylboronic or 4-methylphenylboronic acid, providing cross-coupling products in high yields (Table 1). The reactions were routinely performed under nitrogen; however, it was an adventitious finding that the process was tolerant to the atmosphere. It is also worth noting that the symmetrical biaryls, formed by homocoupling of the starting arylboronic acid, are only minor side-products (less than 2%).

Aryl iodides are better reaction partners than bromides in Suzuki–Miyaura couplings catalyzed by the Pd/PANI nanocomposite. Modest conversions were observed when bromobenzene or 3-bromoanisole was reacted with phenylboronic acid (respectively 39 and 48%), even after extended reaction times (>24 h).

The catalytic activity of Pd/PANI nanocomposites was also tested in the Heck coupling of aryl iodides with alkenes.[41,42] The vinylation of aryl and vinyl halides in the presence of

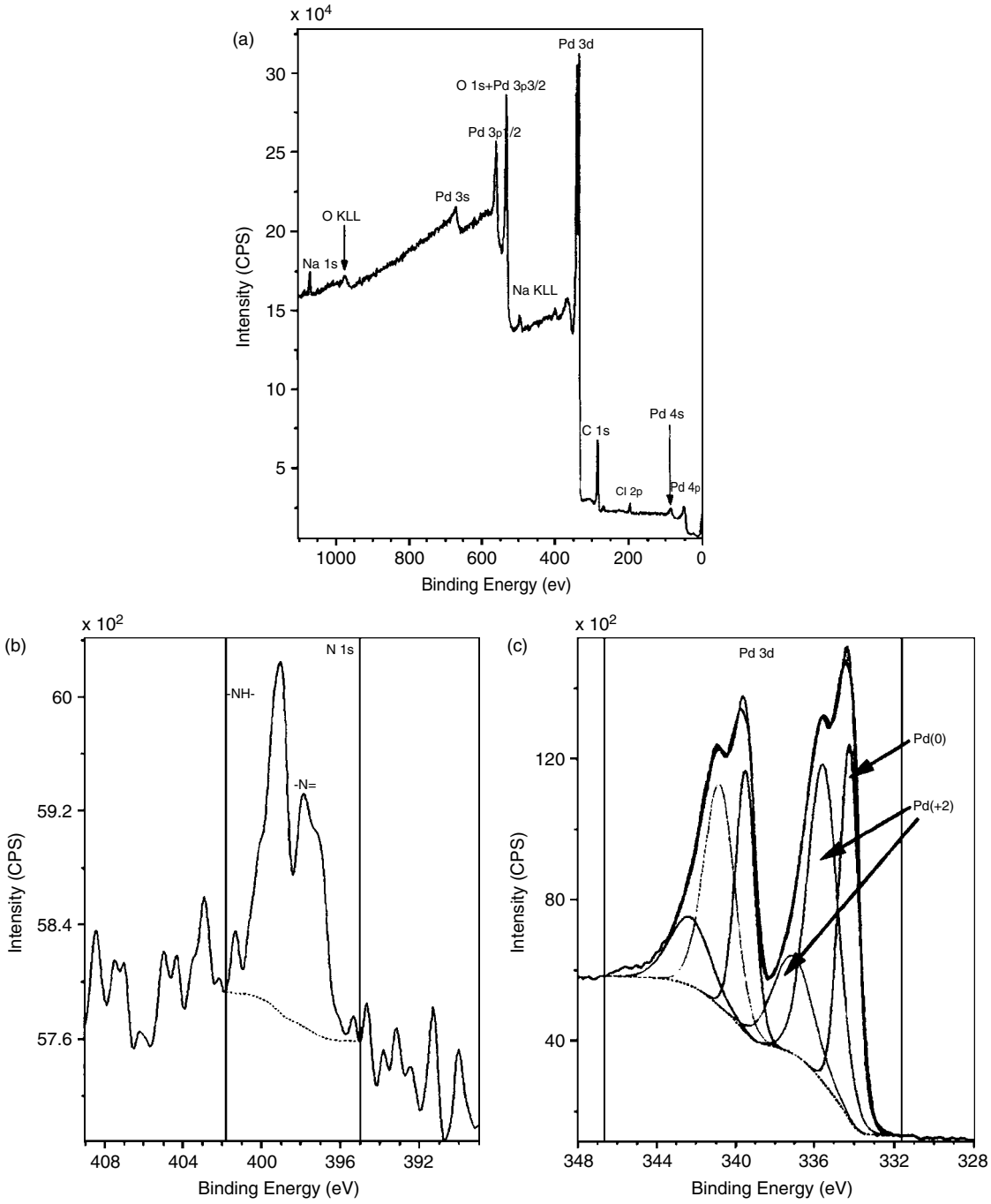


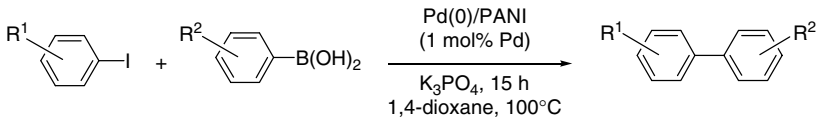
Figure 7. XPS analysis of PANI-stabilized Pd(0) nanoparticles. (a) The XPS survey spectrum; (b) Pd/PANI in the N *1s* region (c) Pd/PANI in the Pd *3d* region.

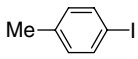
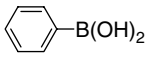
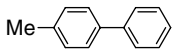
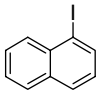
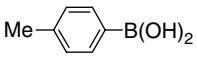
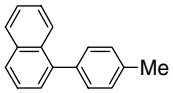
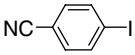
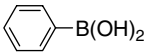
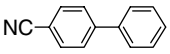
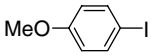
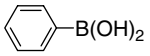
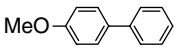
palladium catalysts is a well-studied reaction and is one of the most versatile tools in modern synthetic chemistry.[43–46]

The catalytic activity of the Pd/PANI nanocomposite was initially investigated in the Heck coupling reaction of iodobenzene with methyl acrylate (Table 2, entry a). The precipitation of palladium black was observed in toluene or 1,4-dioxane. A low conversion of iodobenzene (<30%) was observed with inorganic bases such as K_3PO_4 or AcONa. The best results were obtained in DMF using *n*-Pr_3N as base.

Using these optimized conditions, methyl acrylate was reacted with iodobenzene in DMF in the presence of the Pd/PANI catalyst (5 mol% palladium). After 24 h, a conversion of 78% was observed and the primary product formed was (*E*)-methylcinnamate (*E*/*Z* = 90/10). The catalyst was also tested with *n*-butyl acrylate and styrene (Table 2,

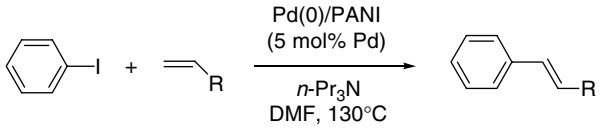
Table 1. Suzuki–Miyaura couplings catalyzed by the Pd/PANI nanocomposite

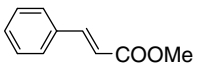
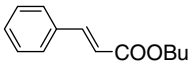
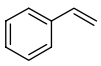
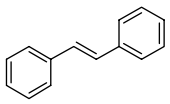


Entry	Aryl iodide	Boronic acid	Conversion (%)[a]	Product	Yield (%)[b]
a			87		85
b			84		82
c			89		87
d			78		74

[a] Determined by GC.
[b] Isolated yields.

Table 2. Heck couplings catalyzed by the Pd/PANI nanocomposite



Entry	Aryl iodide	Alkene	Time (h)	Conversion (%)[a]	Product	E/Z[b]	Yield (%)[c]
a			24	83		90/10	78
b			36	74		75/25	69
c			30	72		97/3	65

[a] Determined by GC.
[b] Determined by ^{1}H NMR and GC.
[c] Isolated yields.

entries b and c). In both cases, good conversions of iodobenzene were obtained.

CONCLUSIONS

We have demonstrated the ability to prepare palladium nanoparticles dispersed in polyaniline by a one-pot chemical process. The methods employed involved reduction of $Pd(OAc)_2$ by *t*-BuONa-activated sodium hydride, surface functionalization of *t*-BuONa-stabilized Pd(0) particles followed by polymerization of aniline-stabilized Pd(0) particles using ammonium persulfate. The existence of palladium particles in the elemental state was confirmed by XPS analysis. TEM analysis shows a uniform distribution of Pd(0) particles having an average diameter of 4.9 ± 2.3 nm homogeneously dispersed in PANI. To the best of our knowledge, such small Pd(0) particles dispersed in PANI have not been reported to date.

Further to this, we have shown that the Pd(0)/PANI material shows good activity as catalyst in both Suzuki–Miyaura and Heck couplings.

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