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Facile synthesis of palladium nanoclusters and their catalytic activity in Sonogashira coupling reactions

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ABSTRACT

This work reports a facile synthesis of palladium nanoclusters (PdNCs) in MeCN/MeOH mixture without any stabilizer. The PdNCs were found to be effective catalysts for copper-free, amine-free and ligand-free Songashira coupling reactions under ambient conditions.

The size and shape of materials at nanometer level modulates the related physical and chemical properties greatly. Thus, controlled synthesis of nanosized materials is of particular interest.[1] A plethora of metal nanoparticles have been prepared by several groups aiming at new and exciting properties.[2] Recently, palladium nanoparticles (PdNPs) have been shown to be effective catalysts for carbon–carbon coupling reactions.[3] Reduction of palladium ions by methanol[4] or methanol mixed with a co-solvent[5] is a known strategy for the preparation of PdNPs. However, the presence of a special stabilizer is very crucial in this technique. The size and stability of these nanoparticles are controlled by the stabilizer employed[4,5] (e.g., polymers, dendrimers, and bulky organic ligands). The drawback of the synthesis includes the efforts required for the preparation of stabilizers as well as possible contamination due to the same. Such problems can be solved by utilizing a co-solvent having weak coordination ability,[6] which could provide stability to the particles so that the use of stabilizers can be avoided.

Herein, we report a facile synthesis of stable palladium nanoclusters (PdNCs)[7] by dissolving Pd(II) in a mixed solvent system (MeCN/MeOH) in the absence of any stabilizer. We have also successfully tested the resulting nanoclusters as a catalyst for copper-free, amine-free and ligand-free Sonogashira coupling reactions at room temperature without employing an inert atmosphere.

The reduction of Pd(II) was performed at room temperature in five different mixed solvent systems viz. $CHCl_3$/MeOH, DMSO/MeOH, H_2O/MeOH, DMF/MeOH, and MeCN/MeOH in 1:1 ratios. Solutions of palladium acetate in the solvent systems were prepared and the concentration of the metal was maintained at 2 mM. Reduction of the palladium salt was facile in all the mixed solvents within a period of a few hours at room temperature, where MeOH acted as the reducing agent.[4,5] The PdNCs synthesized in the MeCN/MeOH mixture exhibited excellent stability, and no precipitation was detected for at least two weeks at room temperature and for months in a refrigerator. In all other cases, the clusters precipitated out within a day. MeCN favors the dissociation of trimeric palladium acetate[8] with time as reported in the literature. Further, MeCN also arguably prevented precipitation of the clusters, and thereby provided stabilization.

It is known from the literature[9] that disappearance of the peak above 400 nm (d–d band) and the appearance of a broad shoulder around 370–390 nm (surface plasmon peaks) in the UV–vis spectra correspond to the reduction of Pd(II) to Pd(0) and formation of nanoclusters, respectively. Since TEM, XRD, and EDX are ex situ methods, it is necessary to rely on UV–vis spectrometry to study the in situ behavior of the formation of palladium nanoclusters. We observed a comparable pattern in the UV–vis spectra, and hence infer the formation of nanoclusters (Fig. 1). Further, the ex situ methods stated above were also employed to characterize the material. The formation of Pd(0) was also confirmed from the powder X-ray diffraction pattern of the sample (Fig. 2). XRD pattern peaks were observed at 40°, 46°, 68°, and 82°. These peaks correspond to the {111}, {200}, {220}, and {311} planes of a fcc lattice, respectively, indicating that the material has a fcc structure. TEM images demonstrated that the sizes of the PdNCs ranged from ~20 to 50 nm (Fig. 3a). For freshly prepared samples as well as

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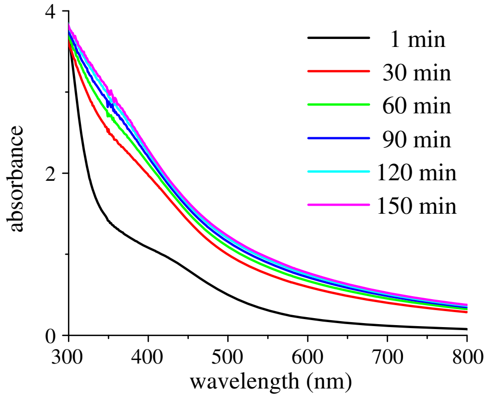


Figure 1. UV–vis spectra of the 2 mM solution obtained from a mixture of $Pd(OAc)_2$ in MeCN/MeOH (1:1) at 30 °C and monitored after 1, 30, 60, 90, 120, and 150 min following preparation of the solution.

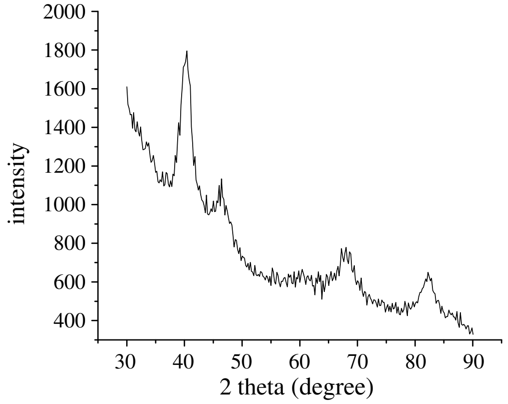


Figure 2. Powder XRD pattern of palladium nanoclusters obtained from the reduction of Pd(II) by standing a 2 mM solution of $Pd(OAc)_2$ dissolved in a 1:1 mixture of MeCN/MeOH.

those aged for a few days, the TEM pattern remained unchanged, indicating the stability of the clusters. The lattice fringes are clearly exposed in the high resolution TEM (Fig. 3b), suggesting a highly crystalline nature of the material. The elemental composition of the material was confirmed by energy dispersive spectroscopy.

Palladium compounds are well-known for catalyzing a variety of organic reactions. Cross-coupling reactions of aryl halides with terminal alkyne (Sonogashira coupling reactions) are important in organic synthesis. Sonogashira reactions are generally co-catalyzed by Cu(I) and a phosphine-based ligand for palladium.[10] The presence of the copper co-catalyst favors oxidative homocoupling (Glaser coupling) of the terminal alkyne to the corresponding diyne by-product, which is difficult to separate from the desired product.[11] Moreover, Sonogashira reactions are carried out in high boiling solvents such as amines, toluene, THF, DMF, or dioxane and at high temperature.[12,13] The reactions also need a base, which is usually an amine such as triethylamine or piperidine.[14] However, the elimination of amines (generally used in large excess) from these reactions is of importance because of environmental concern.

Recently, instead of the palladium complexes, PdNPs have been exploited for Sonogashira coupling reactions.[15,16] We have used the PdNCs prepared in this work for Sonogashira reactions under modified reaction conditions which address all the concerns noted above.

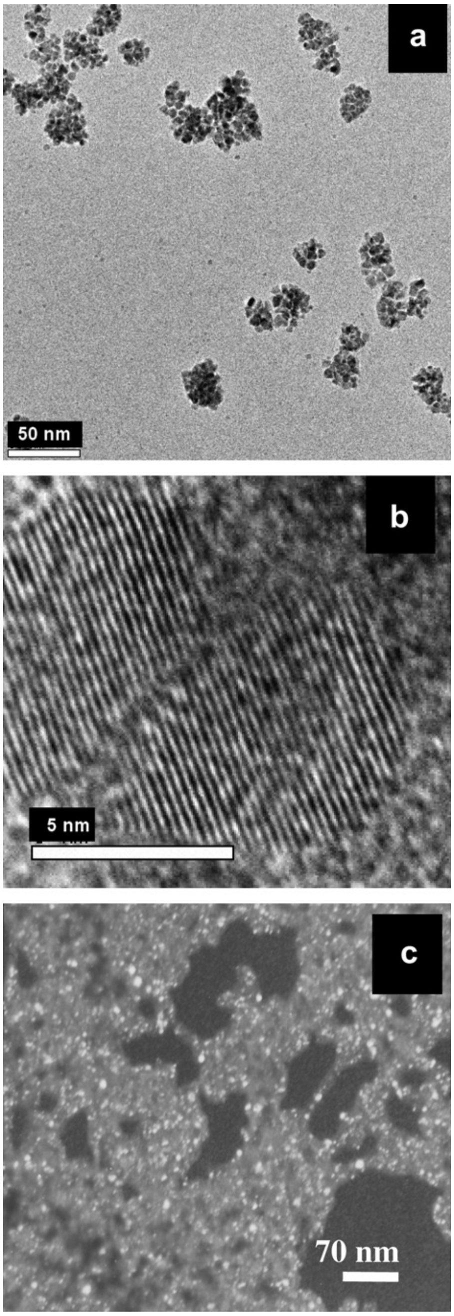
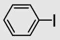
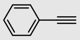
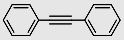
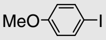
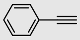
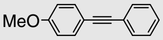
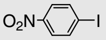
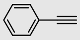
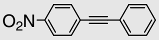
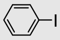
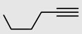
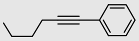
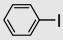
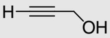
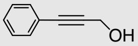


Figure 3. (a) TEM and (b) HRTEM image of palladium nanoclusters obtained from a 2 mM solution of palladium acetate in a 1:1 ratio MeCN/MeOH mixture. (c) Representative dark field TEM image of Pd nanoparticles obtained from 2 mM palladium acetate in a 1:1 ratio of MeCN/MeOH during the catalytic reaction.

Sonogashira reactions were carried between iodobenzenes and terminal alkynes in the presence of PdNCs (5 mol % in Pd) prepared in 1:1 MeCN/MeOH mixture as catalyst and K_2CO_3 as base under ambient conditions. To our knowledge, this is the first report of Sonogashira coupling reactions using palladium nanoclusters[17] in a mixed solvent system of MeCN/MeOH without using any other stabilizing agent. It is worth noting that the reactions were successful under an open atmosphere. Various reactions for the coupling of representative substrates are listed in Table 1. Alkyl and aryl alkynes were coupled with iodobenzene as well as with iodobenzenes containing electron releasing and withdrawing substituents. The desired products were isolated in high yields. The catalyst obtained at the end of the reaction was washed with hexane and

Table 1

Palladium nanocluster-catalyzed coupling of terminal alkynes and aryl iodides[a]

Entry	Aryl iodide	Alkyne	Product	Time (h)	Yield (%)
1				3	90
2				6	80
3				3	95
4				9	90
5				4	80

[a] Reaction conditions: Terminal alkyne (1 mmol), aryl iodide (1 mmol), K_2CO_3 (2 mmol), PdNCs (5 mol % in Pd), 25 mL of 1:1 MeCN/MeOH mixture, air, room temperature (see Ref. 17).

methanol, and re-dispersed in the solvent mixture and could be re-used for Sonogashira coupling without loss of the activity. The products obtained were purified via column chromatography and characterized by spectroscopic methods such as ^{1}H NMR and ^{13}C NMR. The analytical data were in good agreement with reported data.[16,18]

It is already demonstrated[13,19] that leached Pd(0) species from the catalyst surface are true catalytic species in various cross coupling reactions catalyzed by PdNCs. It is also claimed that leaching processes are favored by the aryl halide and the coordinating base used in the reactions.[19a] We wanted to check the occurrence of leaching during the Sonogashira coupling reactions in our system. A dark field TEM image recorded during the catalysis is shown in Figure 3c, which indicates leaching of the PdNCs. This shows that the material existed as leached PdNPs during the reactions, which could be the true catalytic species.

In conclusion, we have synthesized palladium nanoclusters by a simple method in a 1:1 mixed solvent system of MeCN/MeOH without any stabilizer. The PdNCs were found to catalyze the copper-free, amine-free and ligand-free Sonogashira coupling reactions and ambient conditions and an air atmosphere.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.06.089.

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7. *Procedure for the synthesis of palladium nanoclusters*: Palladium(II) acetate (0.0112 g, 0.05 mmol) was added to a 1:1 MeCN/MeOH mixture (25 mL) to prepare a 2 mM solution. This solution was stirred at room temperature (~30 °C) for about 3 h until the yellow color of the solution was changed to brownish-black due to reduction of Pd(II) to Pd(0). It is also possible to perform the reaction by stirring the solution at 60 °C for only 10 min.
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17. *Procedure for the representative Sonogashira reaction*: K_2CO_3 (0.276 g, 2 mmol) was added to 25 mL of a freshly prepared solution of palladium nanoclusters (as described in Ref. 7), followed by phenyl acetylene (0.102 g, 1 mmol) and 1-iodo-4-nitrobenzene (0.249 g, 1 mmol). The solution so obtained contains 5 mol % of Pd(0). The solution was allowed to stir at room temperature (~30 °C) for 3 h under ambient condition. The reaction was monitored by TLC. After completion, the solvent was evaporated and the crude mixture was extracted with 1:9 ethyl acetate/hexane mixture. The organic layer was evaporated, and the residue was purified by column chromatography on silica gel using hexane as an eluent to obtain (4-nitrophenyl)phenylacetylene as a yellow solid (0.212 g, 95%).
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