Shape-dependent catalytic activity of copper oxide-supported Pd(0) nanoparticles for Suzuki and cyanation reactions

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ABSTRACT

Palladium nanoparticles supported on different shapes of nanocrystalline CuO are prepared by the treatment of $Cu(NO_3)_2$ and $Pd(OAc)_2$ in polyethylene glycol (PEG-6000). The shapes of the CuO/Pd composite are dependent on the amount of PEG used. Suzuki coupling was catalyzed efficiently by the oval-shaped material, whereas the rod shape facilitates the cyanation reaction. The CuO/Pd catalyst is recovered and reused for subsequent Suzuki reactions; however, cyanation poisons the catalyst for further use. Both these reactions are very clean and high yielding.

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Nanoparticles are of considerable interest in catalysis, and this subject has undergone tremendous growth during the past few years.[1] It was revealed that supported nanophase metal and metal oxide catalysts with specific size and shape exhibit a high surface area and a high concentration of reactive sites resulting in improved catalytic performance over conventional catalysts.[2] This led to the development of a variety of novel-doped catalysts having useful applications.[3] We have been actively engaged in exploring the catalytic performance of metal nanoparticles,[4] and as a part of these activities we undertook an investigation to determine the influence of the shape of a catalyst on organic reactions. With this objective, we prepared palladium-doped CuO by stirring a solution of copper nitrate in aqueous ethanol and palladium acetate in polyethylene glycol-6000 followed by microwave irradiation at pH 10 and filtration. By varying the amount of PEG-6000, the shape of CuO containing Pd(0) nanoparticles was controlled. Primarily nanorods with an average diameter of 8 nm and length up to 55 nm (CuO/Pd-1) were obtained using 4 g of PEG for 2 g of $Cu(NO_3)_2$ (Fig. 1a), and the use of 8 g and 12 g of PEG furnished a mixture of rod- and oval-shaped (CuO/Pd-2) particles (Fig. 1b) and oval nanoparticles (associated with a small amount of rods) with an average diameter of 10 nm (CuO/Pd-3) (Fig. 1c), respectively. The supported CuO/Pd catalyst was characterized by Transmission Electron Microscopic (TEM) images and High Resolution TEM (Fig. 1a–c), Energy Dispersive X-ray spectra (Fig. 2), and X-

ray Diffraction studies (XRD) (Fig. 3). The effect of this catalyst having two different shapes on organic reaction was investigated.

We have observed that oval CuO/Pd-3 catalyzes Suzuki coupling very efficiently, while the cyanation of aryl halides proceeds well under the catalysis by rod-shaped CuO/Pd-1 (Scheme 1).

Suzuki coupling represents a widely accepted methodology in modern organic synthesis for carbon–carbon bond formation leading to biaryls.[5] The cyanation of aryl halides is a very useful reaction[6] as aryl cyanides constitute building blocks for the synthesis of fine chemicals[6a] and are integral parts of several dyes, natural products, herbicides, agrochemicals, and pharmaceuticals.[7]

For Suzuki coupling, a mixture of aryl halide and aryl boronic acid was heated at 110 °C in DMF in the presence of CuO/Pd-3 (oval) for a required period of time (TLC). Standard work-up and purification provided the product. Several substituted aryl bromides underwent coupling with a variety of boronic acids by this procedure to produce the corresponding biaryls. The results are summarized in Table 1. Both aryl iodides and bromides coupled readily by this procedure. The chloro- and fluoro-substituted aryl bromides underwent chemoselective coupling at the bromo-substituted position without any reaction at chloro- or fluoro-substituted carbon atoms (Table 1, entries 7–10). The presence of electron-withdrawing (Table 1, entries 11–16) or electron-donating (Table 1, entries 2, 4–6) groups in the aryl bromides did not influence the reaction rate and yields appreciably.

The reaction parameters for Suzuki coupling are optimized through a series of experiments as outlined in Table 2. The oval CuO/Pd-3 in DMF was found to give the best yield for a representative coupling reaction of 4-methylphenyl bromide and phenyl

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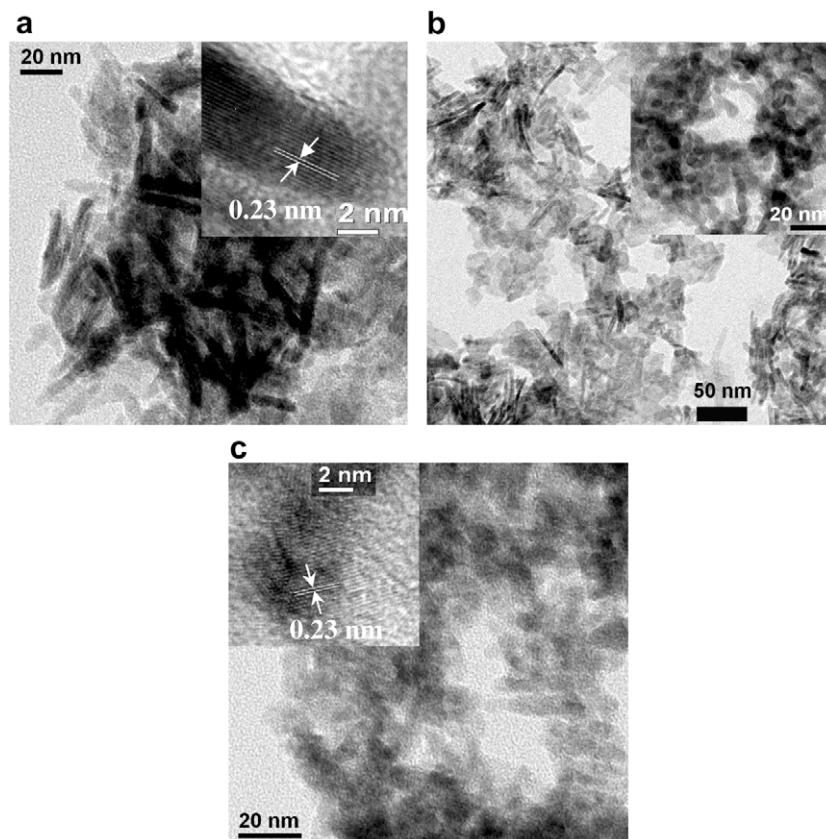 E-mail address: ocbcr@iacs.res.in (B.C. Ranu).

Figure 1. (a) TEM image of CuO/Pd-1; (b) TEM image of CuO/Pd-2; and (c) TEM image of CuO/Pd-3.
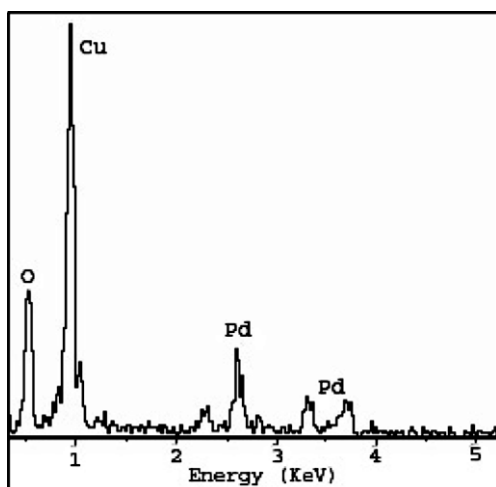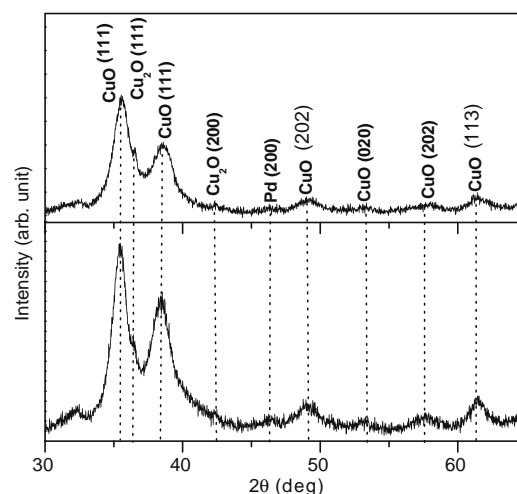

Figure 2. EDX spectra.

Figure 3. XRD pattern of CuO/Pd-1 and CuO/Pd-3.

boronic acid compared to CuO/Pd-2 (50%) and CuO/Pd-3 (32%). Potassium carbonate was chosen as it showed the best performance among other bases such as K_3PO_4 and CsF (Table 2, entries 4, 8 and 9).

In general, Suzuki couplings for all the substrates listed in Table 1 were very clean and high yielding. A variety of substituents such as OCH_3, $COCH_3$, CHO, NO_2, CN, Cl, and F were compatible with this procedure. The products were easily characterized by spectroscopic data (IR, ^1H NMR, and ^{13}C NMR). The catalyst was recovered easily and recycled for further reactions up to five runs without any loss of efficiency.
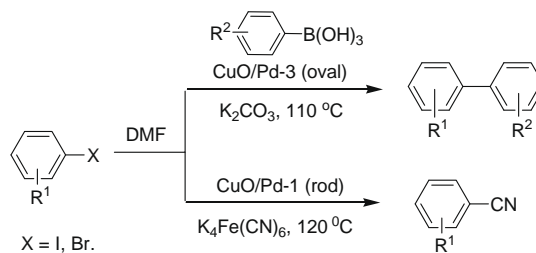
R^1 = H, Me, COMe, F, Cl etc.; R^2 = H, Me, CHO

Scheme 1.

Table 1
Suzuki cross-coupling catalyzed by CuO/Pd-3

Entry	R^1	R^2	Time (h)	Yield[b] (%)	Ref.
1	H	H	8	90	4d
2	4-OMe	H	12	90	4d
3	H	H	10	80	4d
4	3-OMe	H	12	70	4d
5	4-NO_2	H	8	80	5a
6	4-Me	H	12	80	4d
7	4-COMe	H	10	90	4d
8	4-CN	H	10	90	8
9	4-Cl	H	9	90	4d
10	4-F	H	8	88	4d
11	H	4-CHO	10	80	4d
12	3-CHO		10	80	5c
13	4-F		10	88	8
14	4-COMe	4-Me	12	90	13
15	4-COMe	3-Me	10	90	5a

[a] Entries 1 and 2, X = I; entries 3–15, X = Br.
[b] Yields of purified products characterized by IR,^{1}H, ^{13}C NMR spectroscopic data.

Table 2
Optimization of reaction conditions for Suzuki cross-coupling

Entry	Solvent	Temp. (°C)	Base	Catalyst	Time (h)	Yield (%)
1	Ethanol	75	K_2CO_3	CuO/Pd-3	8	15
2	H_2O	90	K_2CO_3	CuO/Pd-3	8	10
3	Xylene	120	K_2CO_3	CuO/Pd-3	8	20
4	DMF	110	K_2CO_3	CuO/Pd-3	12	80
5	DMF	110	K_2CO_3	CuO/Pd-2	12	50
6	DMF	110	K_2CO_3	CuO/Pd-1	12	32
7	DMF	110	K_2CO_3	CuO	12	—
8	DMF	110	K_3PO_4	CuO/Pd-3	12	78
9	DMF	110	CsF	CuO/Pd-3	12	30

For the cyanation of aryl iodides by $K_4Fe(CN)_6$, the rod-shaped CuO/Pd-1 showed the best catalytic activity in DMF at 120 °C, as summarized in Table 3. No base was required for this reaction in

Table 3
Optimization of reaction conditions for the cyanation of aryl iodide catalyzed by CuO/Pd catalyst

Entry	Solvent	Catalyst	Cyanide source	Yield (%)
1	DMF	CuO/Pd-3	$K_4Fe(CN)_6$	30
2	DMF	CuO/Pd-2	$K_4Fe(CN)_6$	38
3	DMF	CuO/Pd-1	$K_4Fe(CN)_6$	75
4	DMF	CuO/Pd-1	$K_4Fe(CN)_6$[a]	50
5	H_2O	CuO/Pd-1	$K_4Fe(CN)_6$	10
6	NMP	CuO/Pd-1	$K_4Fe(CN)_6$	20
7	Toluene	CuO/Pd-1	$K_4Fe(CN)_6$	10
8	DMF	CuO/Pd-1	$K_3Fe(CN)_6$	55

[a] 0.5 mmol has been used in place of 0.17 mmol.

Table 4
Cyanation of aryl iodides catalyzed by CuO/ Pd-1

Entry	R^1	Time (h)	Yield[a] (%)	Ref.
1	H	12	60	6d
2	2-Me	10	80	6a
3	2-CO_2Me	12	75	12
4	3-Me, 4-Cl	12	82	10
5	3-NO_2	13	60	6d
6	3-F	13	75	9
7	4-Me	15	75	6d
8	4-OMe	14	72	6a
9	4-O CF_3	12	75	11
10	4-Br	12	80	3c
11		12	80	6a

[a] Yields refer to those of purified products characterized by IR,^{1}H, ^{13}C NMR spectroscopic data.

contrast to other conventional procedures. All six CN groups of $K_4Fe(CN)_6$ is utilized in the cyanation process and thus, $K_4Fe(CN)_6$ is, nevertheless, the most efficient and green cyanating agent.[6a]

Several substituted aryl iodides underwent cyanation by $K_4Fe(CN)_6$ in DMF at 120 °C in the presence of CuO/Pd-1 (rod) to produce the corresponding nitriles in good yields. The results are presented in Table 4. Only aryl iodides are reactive under the present procedure, and other halides remained inert (Table 4, entries 4, 6, and 10).

Interestingly, the yields of products decreased when the amount of $K_4Fe(CN)_6$ was increased beyond the required stoichiometric amount (Table 3, entries 3 and 4). This might be due to the poisoning of the catalyst by excess CN ions. Thus, the catalyst lost its activity after one reaction possibly by the presence of trace of unreacted CN ions. A number of substituents including F, Cl, Br, NO_2, OCH_3, and OCF_3 were compatible with this procedure.

The precise role of the rod and oval particles for catalyzing Suzuki and cyanation reactions, respectively, is not clearly understood at this moment. However, we tried to understand this phenomenon based on their defect sizes. The HRTEM micrographs of both nano rod (Fig. 1a, inset) and oval particles (Fig. 1c, inset) exhibited lattice fringes of CuO (1 1 1) planes with some defects (Fig. 4a and b) due to trace amounts of incorporated Pd. The crystalline nature of CuO are well ordered in some zones, while in other zones, rather disordered arrangements are observed. However, in ordered zones some pore walls disappeared as marked by white arrows, showing structural defects. The defect sizes vary with the shape of the nanocrystals. The defects in nanorods are larger than those in oval shapes, although the amount of Pd is the same in both as observed in Atomic Absorption Spectroscopy (AAS) (Table 5). Usually, the catalytic activity increases with decreases in particle size.[1e] Thus, Suzuki coupling proceeds better under catalysis by oval CuO/Pd-3 containing smaller defects (Pd nanoparticles) than rods having larger defects (Table 2). However, cyanation catalyzed by metals such as Pd or Pt is not very straightforward, since it is controlled by two competing reactions—complexation with metal and the cyanation of aryl iodide.[6a] The oval CuO/Pd-3 containing smaller sizes of Pd nanoparticles is likely to be more reactive than the rod-shaped one. Thus, we assume that the formation of the cyano-Pd complex is the primary reaction with more reactive oval CuO/Pd-3 providing only 30% cyanation of aryl iodide, while, on the other hand, rod-shaped CuO/Pd-1 being comparatively less
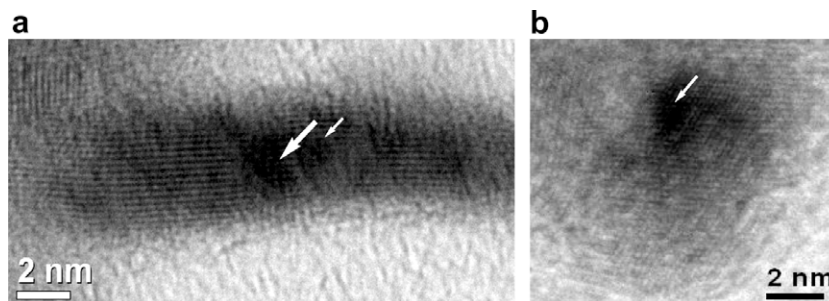
Figure 4. (a) HRTEM of CuO/Pd-1; (b) HRTEM of CuO/Pd-3.

Table 5
Physical data of CuO supported palladium

Sample	Shape[a]	% of Pd (wt/wt)[b]
CuO/Pd-1	Rod	7.1
CuO/Pd-2	Mixture of rod and oval	7.4
CuO/Pd-3	Oval	7.0

[a] From TEM image.
[b] From atomic absorption spectroscopy.

reactive is more selective leading to cyanation as the major path. We believe that these Suzuki coupling and cyanation reactions proceed through the usual mechanism as depicted in earlier reports.[5,6]

In conclusion, we report for the first time the preparation of rod- and oval-shaped copper oxide-supported palladium(0) nanoparticles (CuO/Pd) by the reaction of copper nitrate and palladium acetate controlled by the amount of polyethylene glycol (PEG-6000) used, and their application for selective organic transformation. Very significantly, oval CuO/Pd catalyzes Suzuki coupling better, and rod shapes catalyze the cyanation of aryl halides efficiently. The compartmental accomplishment of Suzuki coupling and the cyanation reaction by the shape of the catalyst is novel, and is of much potential for further applications. The other significant advantages of these procedures are simple operation, relatively low Pd-loading (1 mol %), easy recovery of products from the catalyst, high yields of products, and reusability of the catalyst in the case of Suzuki coupling.

Acknowledgments

Supplementary data

Experimental procedures for the preparation of the catalyst, CuO/Pd, Suzuki coupling and cyanation reactions and the recyclability chart of the catalyst in the Suzuki reaction are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.01.027.

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