



## 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  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Pd}(\text{OAc})_2$  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.<sup>1</sup> 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.<sup>2</sup> This led to the development of a variety of novel-doped catalysts having useful applications.<sup>3</sup> We have been actively engaged in exploring the catalytic performance of metal nanoparticles,<sup>4</sup> 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  $\text{Cu}(\text{NO}_3)_2$  (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.<sup>5</sup> The cyanation of aryl halides is a very useful reaction<sup>6</sup> as aryl cyanides constitute building blocks for the synthesis of fine chemicals<sup>6a</sup> and are integral parts of several dyes, natural products, herbicides, agrochemicals, and pharmaceuticals.<sup>7</sup>

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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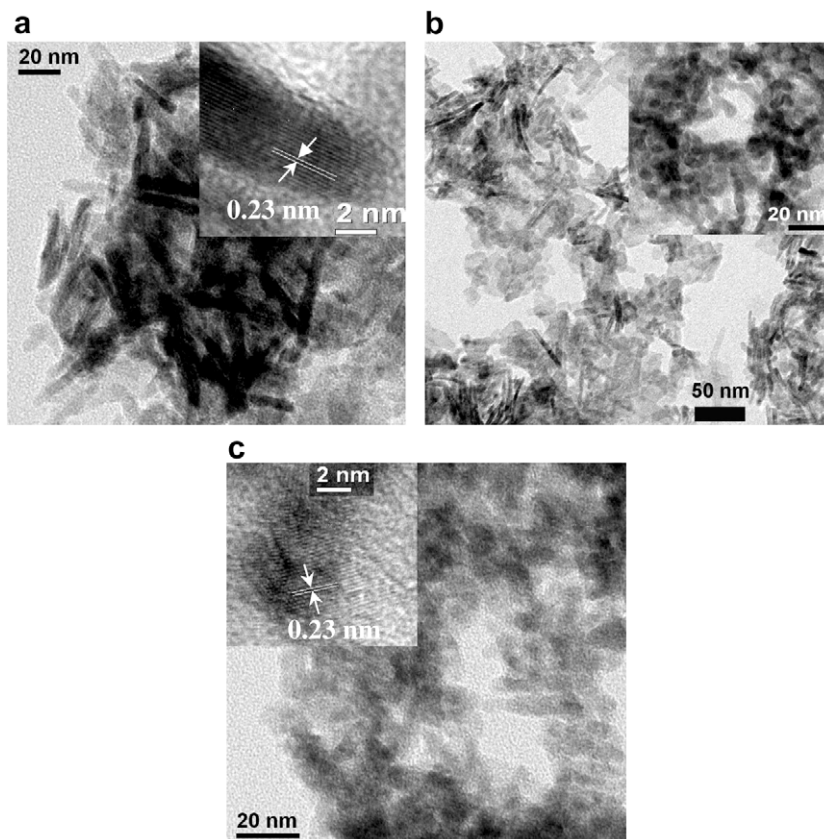


Figure 1. (a) TEM image of CuO/Pd-1; (b) TEM image of CuO/Pd-2; and (c) TEM image of CuO/Pd-3.

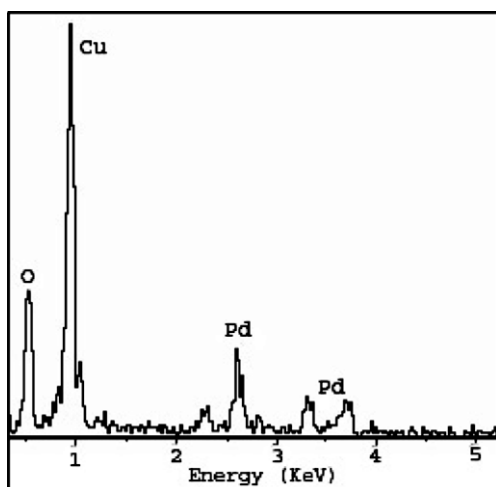


Figure 2. EDX spectra.

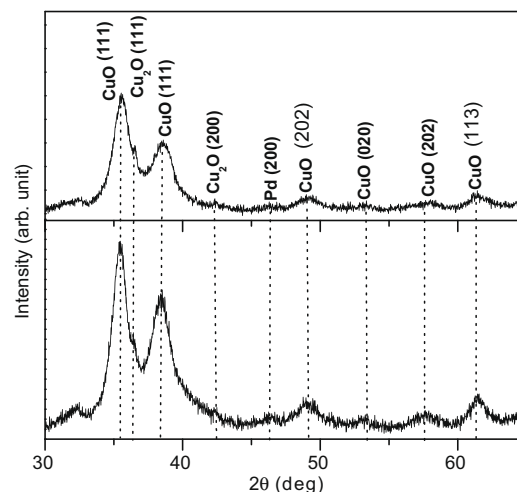
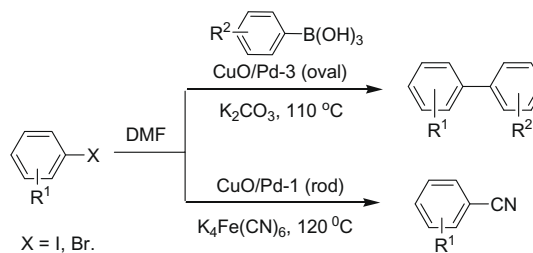


Figure 3. XRD pattern of CuO/Pd-1 and CuO/Pd-3.

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.

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