Rod-like Cu/La/O nanoparticles as a catalyst for phenol hydroxylation

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Rod-like La/Cu/O nanoparticles, synthesized by a simple coprecipitation reaction with a sonication process, are found to be highly active as a catalyst for the hydroxylation of phenol. Compared to the 4–6 h, 40% yield reported in the literature, our nanoparticle catalyst demonstrates a nearly 100% conversion within 4 h based on gas chromatography.

Metal oxide nanoparticles are receiving more and more attention due to their potential applications in structural materials, pigments and paint/ink materials.[1–4] They are also gaining tremendous importance in catalysis.[5] For example, CuO nanoparticles were found to be effective catalysts for CO and NO oxidation;[6–8] Cu_2O nanoparticles were reported to catalyze the decomposition of water under visible light,[9] and Cu-based binary or ternary nanocomposites were used to catalyze the fuel reforming process of short-chain hydrocarbons.[10–13]

A number of methods have been developed for the preparation of metal oxide nanoparticles with various size and shapes. Sol–gel and co-precipitation techniques are two traditional approaches to make metal oxide nanoparticles.[14–18] Feldmann and coworkers reported a polyol-mediated synthesis of a number of oxide nanoparticles;[19] Sugiyama *et al* demonstrated that microwave cold plasma heating could be used to prepare fine metal oxide powders;[20] the formation of MFe_2O_4 (M = Fe, Co, Mn) by an organic phase reaction was reported by Sun *et al.*[21]

We attempted to make La_2CuO_4 nanoparticles following Ghosh *et al.*'s co-precipitation and sonication approach for $ZnFe_2O_4$ and $MnFe_2O_4$ nanoparticles[22] as La_2CuO_4 is also known as a catalyst for many reactions.[23–26] However, instead of obtaining 4–5 nm particles as they did, we observed uniform rod-like particles with lengths of 50 ± 5 nm and widths of 12 ± 2 nm (Fig. 1).† These nanorods were amorphous and could not be identified as La_2CuO_4 by powder X-ray diffraction. Elemental analysis suggested that the dried powders contained 50.89% La and 5.69% Cu by weight, which is a ∼4 : 1 La : Cu mole ratio, although the initial reaction mixture consisted of a La : Cu 2 : 1 mole ratio. Powder X-ray diffraction data taken of powders after annealing at 650 °C were poor, and could be indexed as a mixture of La_2CuO_4, La_2O_3, and CuO. The magnetic behavior of the nanorod samples bore no resemblance to La_2CuO_4, and appeared as a simple paramagnet. We found that these particles had an overall 18.78% weight loss when they were heated to 650 °C during thermogravimetric analysis, due to the loss of H_2O and the organic surfactant that was also present in the initial reaction mixture.

Phenol hydroxylation, using hydrogen peroxide, is a widely used method of making biphenols and is a reaction of industrial importance, as the biphenols are widely used in chemical, pharmaceutical and food industries.[27–30] However, to date the best conversion reported in the literature for phenol to hydroxylated phenols is about 40%. As Cu(II) based complexes and oxides are well-known catalysts for phenol hydroxylation,[31,32] we studied the catalytic performance of our rodlike La/Cu/O nanoparticles with this reaction. (Scheme 1)

The catalysis of phenol hydroxylation has been studied by Maurya and Zhang *et al.*[27,28] and the conversion quantitated by gas chromatography. A detailed listing of reaction conditions and results is given in Table 1. We observed a high conversion, 65% at 3 h (based on a gas chromatographic decrease in phenol concentration and increases in dihydroxyphenol produce concentration) when La/Cu/O nanoparticles were used as catalysts. For comparison, Xiao *et al.* reported a 28% conversion at 4 h when $Cu_2(OH)PO_4$ was used as catalyst;[30] 33% phenol conversion was

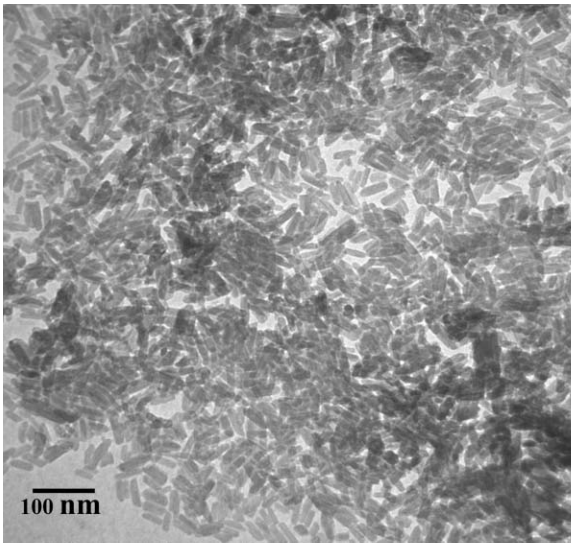
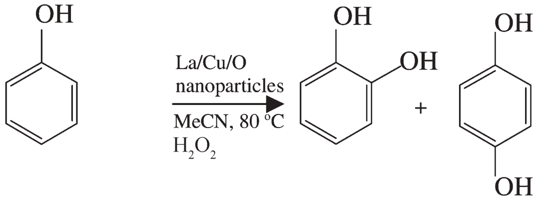


Fig. 1 TEM image of rod-like La/Cu/O nanoparticles.



Scheme 1 Catalytic phenol hydroxylation by H_2O_2.

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Table 1 Percent yield of phenol hydroxylation under different reaction conditions

Catalyst	Amount of phenol/g	Amount of H_2O_2 (30%)	Solvent/mL	Temp./°C	Highest phenol conv. (%)	[1,2]/[1,4]/[1,3] (%)
La/Cu/O NPs[a]	2.0	5.0 mL	MeCN (8)	80	~100	67/33/0
[Cu(hybe)]-Y[b]	4.7	5.4 g	MeCN (2)	80	40	63/18/16
$CuCl_2 + SiW_{12}$[c]	2.0	4.5 mL	H_2O (12)	70	39	~90/10/0

[a] This work. [b] From reference 27. [c] From reference 28. [1,2], [1,4] and [1,3] represent the relative amounts of the isomers of dihydroxyphenol formed.

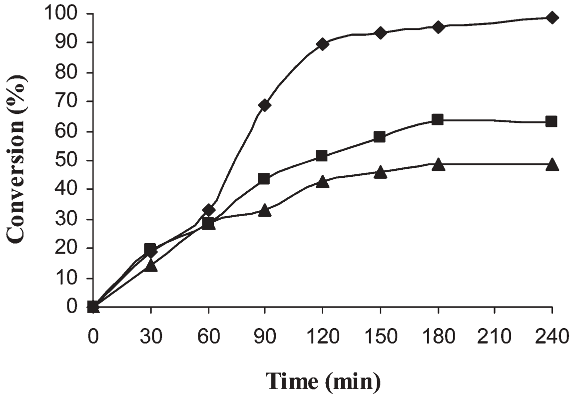

Fig. 2 Catalytic phenol hydroxylation by H_2O_2. Diamonds: H_2O_2 was injected in a pattern of 2.0 mL at 0 min, 1.0 mL at 30 min, and 2.0 mL at 60 min, solvent: MeCN; squares: H_2O_2 was injected all at once at 0 min, solvent: MeCN; triangles: H_2O_2 was injected in a pattern of 2.0 mL at 0 min, 1.0 mL at 30 min, and 2.0 mL at 60 min, solvent was DI water. Conversion was based on gas chromatography, which included all isomers.

achieved by Villa *et al*;[29] and 40% conversion was achieved in 4–6 h as reported in ref. 27 and 28. Furthermore, we found the yield of hydroxylated phenols could be further improved by altering the way of adding H_2O_2. A nearly 100% conversion was achieved when we injected 2.0 mL H_2O_2 at the beginning of the reaction, 1.0 mL at 30 min and 2.0 mL at 60 min instead of adding the H_2O_2 solution into the reaction mixture all at once (Fig. 2). We did this because both lanthanum and copper oxides are also able to catalyze the decomposition of H_2O_2.[31–36] Our results on how the amount of catalyst, amount of H_2O_2 and temperature affect the reaction were similar to what was described in Maurya's work,[27] although our process has much higher yield and produces none of the 1,3 dihydroxyphenol isomer. Peroxide added without the nanorod catalyst produced less than 1% of the product.

We also examined the role of solvent in the catalytic process, since in Maurya's work, acetonitrile was used as solvent[27] whereas deionized (DI) water was used in Zhang's report.[28] We found the conversion efficiency in acetonitrile was nearly 100% for the hydroxylation reaction, compared to only 48% when water was used as the solvent (Fig. 2).

In summary, we found uniform rodlike La/Cu/O nanoparticles can be prepared by a co-precipitation of La and Cu salts followed by a sonication process. These rodlike particles were highly active in catalyzing phenol hydroxylation with H_2O_2.

Notes and references

† *Experimental details*: The rod-like La/Cu/O nanoparticles were prepared as follows: 2.971 g $LaCl_3{\cdot}7H_2O$ and 0.5378 g $CuCl_2{\cdot}2H_2O$ were dissolved in 40 mL DI water and mixed with 60 mL 0.1 M cetyltrimethylammonium bromide (CTAB) solution. CTAB is a surfactant that we have previously found useful to control the particle size of Cu_2O nanoparticles.[37] The entire solution was heated to 70 °C, and an aqueous 3.0 M NaOH solution was added dropwise to adjust the pH to ~12. The temperature was maintained at 70 °C for one hour, while the blue precipitate turned dark. The precipitate was collected by centrifugation at 5500 rpm for 10 min, washed with DI water to remove salts and excess surfactant, and were re-centrifuged in the same manner, then dried in an oven at 60 °C overnight. A 0.2 g sample of the dried powder was then transferred to a solution which contained 9.5 mL toluene and 0.5 mL *n*-octylamine and was sonicated in a bath sonicator for 4 h. The precipitate was collected by the same centrifugation, washing and drying process described above. For the catalyst reaction, 25 mg of the dried powder was redispersed in 1.0 mL DI water and injected to the reaction solution.

The catalyst reaction was carried out in a 50 mL flask fitted with a water-cooled condenser and magnetic stirrer. In a typical reaction, 2.0 g phenol was dissolved in 8 mL acetonitrile, and 25 mg of solid was then added while the reaction mixture was heated at 80 °C with continuous stirring. Subsequently, 5 mL of a 30% H_2O_2 solution was added into the reaction mixture in a pattern of 2.0 mL at 0 min, 1.0 mL at 30 min, and 2.0 mL at 60 min. At certain time intervals during the reaction, 0.3 mL of the reaction mixture was withdrawn and mixed with 0.2 mL 1.0 M HCl solution and 2.0 mL methylene chloride. After phase separation, 0.6 mL of the organic phase was diluted with 3.0 mL methylene chloride, and the products were then separated and analyzed by gas chromatography (Shimadzu GC-17A, with helium as the carrier gas). The products were also characterized by a ^1H NMR (Varian Mercury 400 MHz) to determine the different isomers with deuterated methylene chloride as the solvent at 25 °C.

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