ORGANIC LETTERS

2008
Vol. 10, No. 22
5179−5181

Resin-Immobilized CuO and Cu Nanocomposites for Alcohol Oxidation

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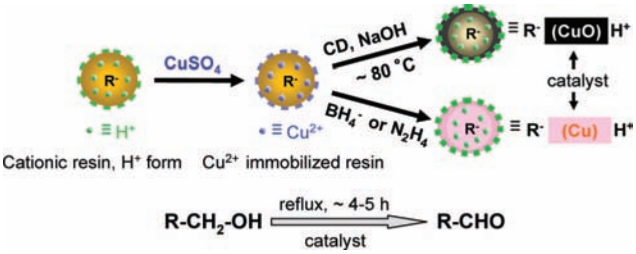
Received September 15, 2008

ABSTRACT



Resin immobilized stable, spherical CuO nanoparticles prepared in the presence of cyclodextrin (CD) act as catalysts for liquid phase alcohol oxidation in air. The catalytic activity of the CuO nanocomposites and its green chemistry approach make it superior to the related resin-bound Cu(0) nanocomposite. The effect of alcohol chain length and electron-donating or -withdrawing groups influence product yield. The nanocomposites exhibit good reusability, simple workup procedure, and a straightforward approach to aldehyde formation.

Metal, semiconductor, and oxide materials in the nanometer size range with their high surface-to-volume ratios have physical and chemical properties that are distinct from those of individual atoms and bulk materials. Among different metal oxides, cupric oxide (CuO) has been extensively studied for its potential as a high-critical-temperature superconductor,[1] heterogeneous catalyst,[2] complex magnetic phase,[3] p-type semiconductor, and its use in electrochemical cells.[4] Many methods are available to fabricate CuO nanostructures,[5a−d] although no reports of CuO on simple resin supports are available. The design of novel catalytic systems that facilitates the recovery of catalysts and isolation of a catalyst-free product is environmentally desirable.[6] Metallic copper and cupric compounds have a long tradition as promoters of alcohol oxidation, a major industrial process.[7a−e]

In this report, we present a method to synthesize nanocomposites of CuO and Cu(0) that consist of cation exchange resin-bound nanoparticles. The CuO-bound nanocomposite is used repetitively for alcohol oxidation and is found to be superior to its Cu(0) nanocomposite analogue. The report overcomes the challenges in this field in terms of reaction temperature and recovery of catalyst and product.

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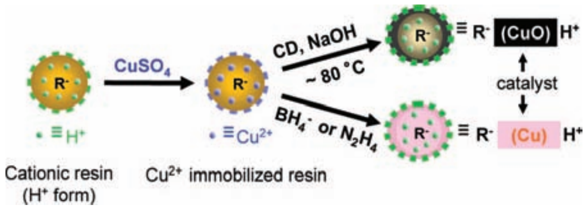
10.1021/ol802040x CCC: $40.75

SERALITE-SRC-120, a cation exchange resin in the H^+ form, exchanges Cu^{2+} ions from the precursor $CuSO_4$ solution (aqueous). Total loading of Cu^{2+} ion is authenticated from the absorbance of the supernatant solution. On reaction of the immobilized Cu^{2+} ions with strong reducing agents like aqueous borohydride or hydrazine, Cu(0) is produced. Interestingly, if the reducing agent is replaced with an alkaline solution of CD, a nanodeposite of CuO on the resin matrix is produced (see the Supporting Information) via the formation of $Cu(OH)_2$ on the resin surface due to NaOH treatment.[8a,b] A comparative XRD of a free and loaded resin matrix readily helps to know the formation and stabilization of nanoparticles onto the resin beads (Scheme 1).

Scheme 1. Formation of CuO and Cu(0) Nanocomposites on Solid Support



The XRD pattern of CuO on the solid resin support is shown in Figure 1a. The characteristic peak at a 2θ value of 32.4° indicates the (110) plane of CuO. Two intense peaks at 35.4° and 38.5° correspond to the (11−1) and (111 and 200) crystal planes of CuO. The other peaks are at 48.5°, 53.5°, 57.5°, 61.2°, 66°, and 68° and match well with the (20−2), (020), (202), (11−3), (31−1), and (220) crystal planes, respectively (JCPDS No. 80-1916). The XRD pattern of Cu(0) on the resin beads (Figure 1b) shows three major peaks observed at 2θ values of 43.38°, 50.57°, and 74.14° which correspond to (111), (200), and (220) of Cu(0) (JCPDS No. 85-1326) crystal planes, respectively.

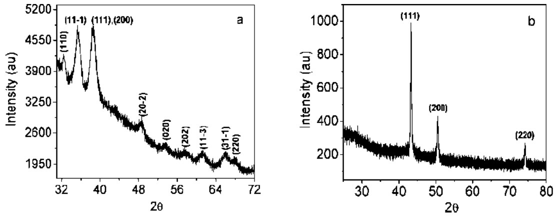


Figure 1. XRD pattern of CuO (a) and Cu(0) (b) nanocomposites on solid support.

XPS results confirm the presence of CuO in the black nanocomposite, as shown by the Cu $2p_{3/2}$ peaks. Cu^{2+} has one main peak at 935.5 eV.[5b,c,7d] The O_{1s} core-level spectrum is broad; the peak is found around 533.5 eV indicating the presence of O^{2-}. The XPS spectrum of Cu(0) nanocomposite indicates the presence of a single peak at 935 eV due to the Cu^0 $2p_{3/2}$ binding energy (see the Supporting Information).

FESEM images of CuO and Cu(0) on the solid resin supports show the nanoparticles to have spherical morphology with diameters in the range 30 ± 5 nm. EDAX spectra of the CuO (stoichiometry 1:1) and Cu(0) nanocomposites show the presence of the respective elements (see the Supporting Information).

TEM images of the CuO and Cu(0) nanocomposites on the resin beads confirm the spherical morphology and 30 ± 5 nm size. The interfringe distance for the CuO nanocomposite is measured to be 2.8 Å, which corresponds to the (110) plane of monoclinic CuO and agrees well with the XRD analysis, whereas for the Cu(0) nanocomposite the value is 2 Å, corresponding to the (111) plane of Cu(0) (Figure 2a,b). The SAED pattern from the CuO nanocomposite shows the bright single crystalline spots corresponding to the diffraction of (110), (202), (31−1), and (311) planes. The SAED pattern from the Cu(0) nanocomposites exhibits many diffused rings, which could be assigned to the (111), (200), and (311) reflections (see the Supporting Information).

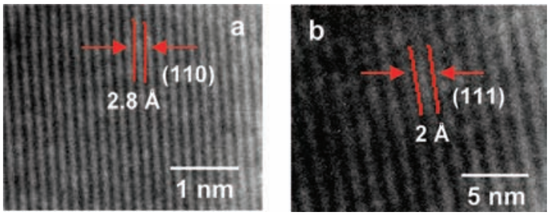


Figure 2. Interfringe distance of CuO (a) and Cu(0) (b) nanocomposites on solid support.

The resin beads have a porous, multichannel structure. CuO and Cu(0) nanoparticles remain occupied in the porous channels of the resin structure presumably due to their nanosize and spherical morphology. Water or common organic solvents cannot leach out the nanoparticles (even after sonication) from the resin beads. The mechanism of compact attachment of the nanoparticles onto the resin matrix is not clear yet and needs further investigation. It is observed that the CuO nanocomposite formation takes place in the presence of an alkaline solution of CD but at a low (~80 °C) temperature. Here CD has two roles to play. First, it lowers the activation energy making the reaction facile for the quantitative conversion of $Cu(OH)_2$ to CuO. Otherwise, a higher temperature and longer reaction time would be necessary for CuO formation, which is leached out easily from the resin in the absence of CD.[8a,b] Second, CD offers a distinct control for the growth of CuO nanoparticles with its capping property[9] as a result of which the composite material does not grow beyond nanoregime.

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Table 1. Result of Conversion of Alcohol to Aldehyde with CuO Nanocomposite

reactant	product	time (ca. h)	yield (%)
CH_3-OH	H-CHO	4	95
CH_3-CH_2-OH	CH_3-CHO	4	90
CH_3-$(CH_2)_2$-OH	CH_3-CH_2-CHO	4.5	85
CH_3-$(CH_2)_3$-OH	CH_3-$(CH_2)_2$-CHO	4.5	74
CH_3-$(CH_2)_4$-OH	CH_3-$(CH_2)_3$-CHO	4.5	65
CH_3-$(CH_2)_5$-OH	CH_3-$(CH_2)_4$-CHO	5	20
CH_3-$(CH_2)_7$-OH		5	0
CH_3-$(CH_2)_9$-OH		5	0
C_6H_5-CH_2-OH	C_6H_5-CHO	5	90
p-CH_3O-C_6H_4-CH_2-OH	*p*-CH_3O-C_6H_4-CHO	4.5	74
p-NO_2-C_6H_4-CH_2-OH	*p*-NO_2-C_6H_4-CHO	4.5	80

A major interest of this process lies with the preparation of this catalytic material under mild conditions, reusability of the catalyst, and the green chemistry approach for liquid phase alcohol oxidation in air. Catalytic oxidations of various alcohols by air are carried out in the following way.

An aliquot of 5 mL of neat alcohol is taken in a two-necked round-bottomed flask and ~2.9 mol % catalyst is employed. The flask is then fitted with a water condenser and heated at refluxing temperature for ~4−5 h. After that, the solid black catalyst is separated simply by decantation/filtration and the product is analyzed. Then the beads are thoroughly washed ten times with distilled water to remove any adhering alcohol or aldehyde that might remain on the catalyst surface. The washings are discarded, and the catalyst is dried and recycled to carry out the next set of oxidation reaction. For oxidation of methanol to decanol and benzyl alcohol no other solvent is used, but in the case of *p*-methoxybenzyl alcohol and *p*-nitrobenzyl alcohol, tetrahydrofuran (THF) is used as solvent. Characterization of the sole product, aldehyde, is done by co-TLC, UV−vis, FTIR, ^{1}H NMR, ^{13}C NMR, and HPLC studies (see the Supporting Information).

The percent yields are calculated for all the compounds by using calibration graphs obtained from UV−visible spectroscopy at the respective λ_{max} (~230−300 nm) positions. The results (Table 1) are also authenticated from HPLC studies. A representative chromatogram and the calibration graph for benzyl alcohol oxidation are included as Supporting Information.

In the present alcohol oxidation reactions, CuO nanocomposite has proven to be an efficient heterogeneous catalyst with more remarkable efficiency than the corresponding Cu(0) (yield is always <10% and detachment of Cu from the resin takes place) supported resin matrix and commercial CuO. The employed 2.9 mol % CuO nanocomposite remains active over ten cycles of operation indicating its catalytic action. Transition metal oxides often become nonstoichiometric and might accommodate a higher proportion of oxygen in their lattice position.[10] This helps the oxidation of alcohol to aldehyde in air under mild conditions presumably due to the nonstoichiometry, tenacious oxygen retention, and oxygen-activating property of CuO. Longer reaction time (>5 h) marginally increases the yield of the sole product, aldehyde. The presence of surface oxygen makes the oxidation entropically favorable and the most probable mechanism is via the abstraction of α-hydrogen[7a−e] by the surface oxygen. We observed that product yield is lowered drastically from methanol to decanol (Table 1). Reports on oxidation of higher aliphatic alcohol[7a−e] under harsh conditions with extended reaction time also corroborated our observation. On the other hand, results of the oxidation of aromatic alcohol account for the electronic factor with different substition in the phenyl ring (Table 1). Again, the yield becomes significantly low with CD capped CuO/Cu nanoparticles (without resin support) and during the course of the reaction nanoparticles become aggregated. Commercically available bulk CuO could not produce even traces of aldehyde under the experimental time scale.

The recovered catalyst upon re-examination by XRD, FESEM, and EDAX revealed unaltered morphology. Hence the used catalyst is successfully re-employed for a series of consecutive runs (see the Supporting Information). Apart from the abovementioned advantages, the ease of separation of the product and the mild conditions employed may be advantageous for different applications in the future.

In conclusion, we have reported a green chemistry protocol for the generation of stable nanocomposites of CuO and Cu(0) at the gram level. Additionally, we have applied our synthesized nanocomposites straightforwardly for the oxidation of alcohol in air at a milder condition prompting simple recovery of the catalyst and product.

Acknowledgment. Financial assistance from UGC, DST, NST, CSIR, and IIT Kharagpur is acknowledged. We are thankful to Prof. C. J. Murphy (USC), Prof. L. Romsted (RU), Prof. J. A. Creighton (UKC), and Prof. T. Tsukuda (HU) for their suggestions.

Supporting Information Available: Experimental section, photographs of nanocomposites, XRD of free resin beads, XPS, FESEM, EDAX, TEM, SAED, UV, FTIR, ^{1}H NMR, ^{13}C NMR, HPLC, calibration curve, and conditions for catalytic oxidation, and again XRD, FESEM, and EDAX of the catalyst CuO after reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

OL802040X

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