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Short Communication

Copper incorporated nanorod like mesoporous silica for one pot aerobic oxidative synthesis of pyridines

Suman Ray [a], Biplab Banerjee [b], Asim Bhaumik [b,*], Chhanda Mukhopadhyay [a,**]

[a] Department of Chemistry, University of Calcutta, 92 APC Road, Kolkata 700009, India
[b] Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

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ABSTRACT

Copper incorporated nano-rod like mesoporous silica catalyst was synthesized, characterized by N_2 adsorption, HRTEM–EDX, XRD, AAS, XPS and TPD-NH_3 analyses and applied in the one-pot aerobic oxidative synthesis of highly substituted pyridines. Both the enhanced surface acidity of copper incorporated silica and the redox property were essential for pyridine synthesis. Standard leaching experiment proved that the reaction was heterogeneous.

1. Introduction

Oxidation of organic compounds represents an important approach towards the expansion of complex molecular structures. However, it remains a tremendous challenge to develop a quasi-nature catalyst for green and sustainable oxidation [1]. Oxidation by molecular oxygen as stoichiometric oxidant offers one of the most environmentally benign and ideal oxidation processes [2]. However, oxygen from air cannot be readily utilized for oxidation purposes. This is because organic molecules are in spin paired singlet state ($S = 0$) whereas oxygen molecule is in spin free triplet state ($S = 1$) and the reaction between singlet and triplet state is forbidden. All reactions of O_2 require initial activation from triplet to singlet state and thus the use of a catalyst becomes inevitable. The traditional catalysts for catalytic oxidation can be classified into the following categories: (a) supported precious metals [3,4]; (b) supported metal oxides and non-precious metals [5]; and (c) mixtures of metal oxides and precious metals [6]. Compared to precious metal/metal oxides, transition metal oxides are more abundant and less expensive [7]. However, the catalytic efficiency of bulk metal oxide is seriously restricted because of its low surface area. One way to circumvent this problem is to disperse the metal oxide particles onto supports with high surface area. If the metal oxide nanoparticles can be confined within a nanoporous host material, this may restrict the size to which the metal oxide nanoparticles can grow [7,8]. Mesoporous silicas have been considered as the most suitable hosts for the stabilization of metal/metal oxide nanoparticles [9–11]. The nanoscale porosity of such supports may prevent the formation of large and catalytically inactive particles [12].

It has been noticed that silica and some of the support materials like alumina and zirconia exhibit a significant amount of surface acidity in the copper based catalysts [13]. Previously, silica supported copper has been utilized as an acid catalyst in the Biginelli, Mannich, different multicomponent reactions and catalytic transformation of benzyl alcohol [13–16]. Besides the modification of acidity, the presence of multivalent transition metal cations in the framework also creates isolated redox centers, which are suitable for their application as heterogeneous oxidation catalysts. Magnificent results have been achieved in transition metal incorporated silica catalyzed oxidation of benzyl alcohol, selective oxidation of cycloalkanes, oxidation of phenol and cyclohexanol, etc. [17,18].

In the present context, we have synthesized the copper incorporated nanorod like mesoporous silica catalyst and exploited both its surface acidity and the redox property in the one pot aerobic oxidative synthesis of pyridines using molecular O_2 as the stoichiometric oxidant (Scheme 1).

2. Experimental

2.1. Materials and instrumentation (see supporting information)

2.1.1. Preparation of copper incorporated silica nanorod

390 mL water and 400 mL MeOH were taken together in a 1 L open beaker fitted with a magnetic stirrer. Then 3.52 g CTAB was added at room temperature (30–35 °C) and stirred for 30 min. After a clear solution was obtained, tetraethylorthosilicate (TEOS) was added drop

* Corresponding author.
** Corresponding author. Tel.: +91 33 23371104.
E-mail addresses: msab@iacs.res.in (A. Bhaumik), cmukhop@yahoo.co.in (C. Mukhopadhyay).

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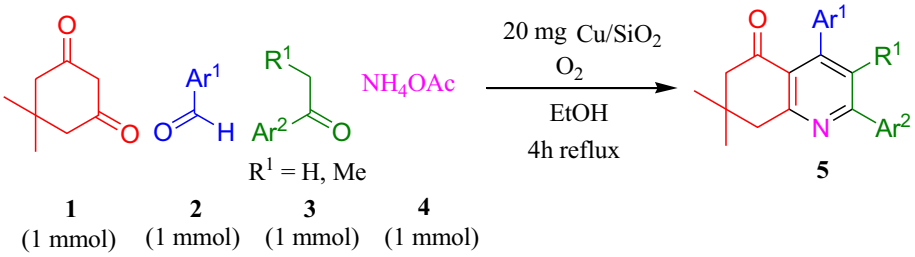

Scheme 1. Oxidative synthesis of pyridines.

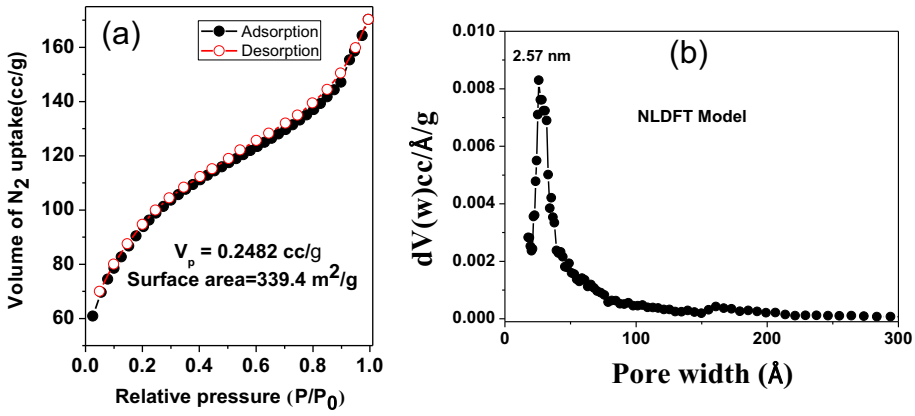

Fig. 1. N_2 adsorption isotherm and pore size distribution of Cu/SiO_2.

wise from a dropping funnel under stirring condition. Next, 142.6 mg $Cu(OAc)_2$ was added and the stirring was continued for another 5 min. Then 10 mL 0.4 N NaOH solution was added drop wise taking the time period of 1 h. The stirring was continued for the next 8 h at room temperature and then aged overnight (12–14 h) at room temperature. It was filtered, washed thoroughly with deionized

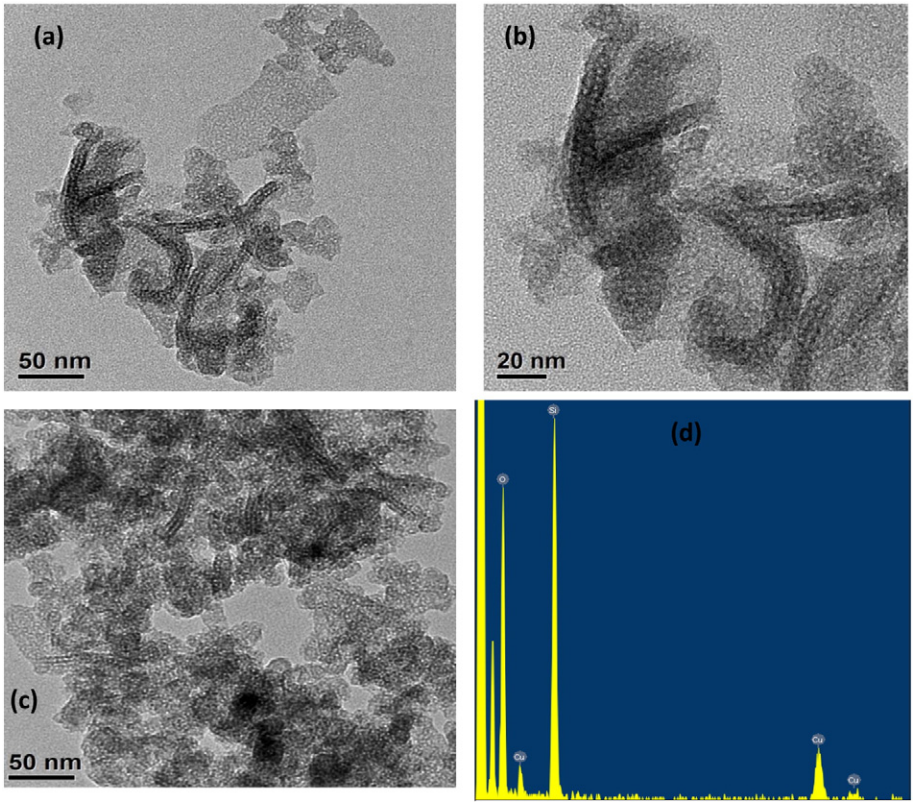

Fig. 2. (a–c) HRTEM images and (d) EDX spectrum Cu/SiO_2.