



A facile method for the N-formylation of primary and secondary amines by liquid phase oxidation of methanol in the presence of hydrogen peroxide over basic copper hydroxyl salts

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ABSTRACT

N-formylation reactions by catalytic oxidation of methanol in the presence of primary or secondary amines and hydrogen peroxide has been investigated using a liquid phase reaction system over basic copper hydroxyl salts. A series of basic copper hydroxyl salts was prepared by the conventional precipitation method using aqueous ammonia and sodium hydroxide as precipitating agents. PXRD, SEM, FT-IR, BET were employed for physical characterization of the prepared basic copper hydroxyl salts. The composition of the catalytic material obtained was found dependent on the nature of the anion associated with the copper salt precursor. The copper hydroxyl chloride catalyst has shown the best catalytic performance in terms of the reaction rate and product selectivity whereas for the copper oxide catalyst the reaction rate was extremely slow. It is interesting to observe that 4-piperidone protected with acid-sensitive functional groups such as N-acetyl piperazine and ethylene glycol can also be formylated from moderate to good yields by these catalysts.

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1. Introduction

Formylation is a very important process in synthetic organic chemistry. Selective formylation of primary and secondary amine groups, in the presence of acid-sensitive functional groups has great practical utility. Formanilides are widely used in the synthesis of pharmaceutically active compounds [1–4]. Formamides are Lewis bases, which are known to catalyze reactions such as asymmetric allylation [5] and hydrosilylation [6] of carbonyl compounds. These formamides are useful reagents in Vilsmeier formylation reactions [7] and synthesis of formamidines [8] and isocyanides. A variety of methods are available [9–13] for N-formylation of amines and a number of formylating reagents were reviewed [14]. Many of these methods involved reagents, which are either moisture-sensitive, toxic or expensive. In this article we report a novel, less expensive, and selective catalysts for N-formylation of primary and secondary amines, including those with acid-sensitive functional groups.

2. Experimental

2.1. Catalyst preparation

Copper salts such as cupric acetate (Lobachemie, 98%), cupric chloride (Lobachemie, 98%), cupric nitrate (Lobachemie 99.5%), and cupric sulphate (Merck, 99%) were used without further purification. A 1.0 M solution of these salts was prepared by using double distilled water. Aqueous ammonia (Merck, 25–29%) was used as such and 3.0 M sodium hydroxide (Merck, 97%) solution was prepared by using double distilled water.

The basic copper hydroxyl salts were prepared under three different precipitation conditions by adjusting the pH of the solution and these conditions were referred to as method A, method B and method C.

Method A involves the use of aqueous ammonia to adjust the pH of the solution between 9 and 10. *Typical procedure:* 1.0 M cupric chloride solution (50.0 ml) was taken in a round bottom flask and was slowly added to it 7.8 ml of ammonia solution under stirring at 25–27 °C over a period of 45 min till the reaction mixture attained a pH of 9.5. The blue slurry mass thus obtained was continued to be stirred for 1.0 h at 27 °C. In the method B, aqueous ammonia was used to adjust the pH initially to the range of 6.5–7.5 and then 3.0 M sodium hydroxide to the pH 9–10. *Typical procedure:* 1.0 M cupric chloride solution (100.0 ml) was taken in a round

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Table 1
Copper-based catalysts prepared from different methods/sources and the abbreviations used.

S. No.	Copper salts used	Method A	Method B	Method C
1	Cupric acetate [Cu(OAc) ₂ ·H ₂ O]	CAA	CAB	CAC
2	Cupric chloride [CuCl ₂ ·2H ₂ O]	CCA	CCB	CCC
3	Cupric nitrate [Cu(NO ₃) ₂ ·3H ₂ O]	CNA	CNB	CNC
4	Cupric sulphate [CuSO ₄ ·5H ₂ O]	CSA	CSB	CSC

bottom flask and was slowly added ammonia solution (12.5 ml) over a period of 20 min until a pH of 7.2 was attained, followed by addition of 3.0 M sodium hydroxide solution (10.3 ml) over a period of 25 min under stirring at 27 °C to reach the pH of 9.6. The blue slurry mass thus obtained was stirred for another 1.0 h at 27 °C. In the method C, only 3.0 M sodium hydroxide solution was used to adjust the pH to 9–10. All the precipitation reactions were carried out at room temperature. *Typical procedure:* 1.0 M cupric chloride solution (100.0 ml) was taken in a round bottom flask and was slowly added 3.0 M sodium hydroxide solution (51.2 ml) under stirring at 25–27 °C over a period of 40 min to make the pH 9.5. The blue slurry mass was stirred for 1.0 h at 27 °C. The precipitates thus obtained were separated by filtration, washed thoroughly with water and dried at 120 °C for 18.0 h. The materials thus obtained were powdered and calcined at 300 °C for 2.0 h in a Therelek electric furnace (Type-K-1200).

Similar methods were followed to prepare basic copper hydroxyl salts from different cupric (II) salts, such as cupric acetate, cupric chloride, cupric nitrate and cupric sulphate. The type of catalysts prepared and the abbreviations used are shown in Table 1. For instance the code CAA represents the material obtained from copper acetate (CA) by method A.

2.2. Catalyst characterisation

The textural properties of the catalysts were analysed by powder X-ray diffraction (PXRD, Philips, X'perts) at 293 K using Cu K α ($\lambda = 0.15418$ nm) radiation in the range of 2θ 10–70°, at a scanning speed of 2°/min and scanning electron microscopy (SEM) images were recorded on gold-coated samples using a Philips apparatus equipped with a hemispherical energy analyser. The Fourier transform infrared (FT-IR) spectra of copper-based catalysts were recorded using KBr pellets by a Shimadzu (Model 8101 M) FT-IR spectrometer, in the range of 4000–400 cm⁻¹. The surface areas of all the catalysts were assessed by the Brunauer, Emmett, and Teller (BET) technique via N₂ adsorption at liquid nitrogen temperature—using a Nova-1000, ver. 3.7 instrument. Prior to adsorption–desorption experiments, the samples were degassed at 120 °C at 10⁻⁴ Torr for 2.0 h.

2.3. Catalytic activity of basic copper hydroxyl salts

The catalytic activity of the materials prepared have been investigated by adding hydrogen peroxide very slowly to a mixture of primary or secondary amine and methanol. The reaction was carried out in a round bottom flask and the contents were stirred using a magnetic stirrer. TLC technique was used to observe the reaction progress.

The evaluation of catalytic activity of all the prepared materials has been performed initially using p-chloroaniline as a substrate. A typical procedure is as follows: To a solution of p-chloroaniline (100.0 mg) in methanol (5.0 ml) containing 100.0 mg of the catalyst, 2.0 ml, 6% (w/w) of hydrogen peroxide was added slowly. The resulting mixture was continued to be stirred at room temperature. Samples were periodically taken and the reaction progress was monitored by thin layer chromatography (TLC) (hexane:ethyl

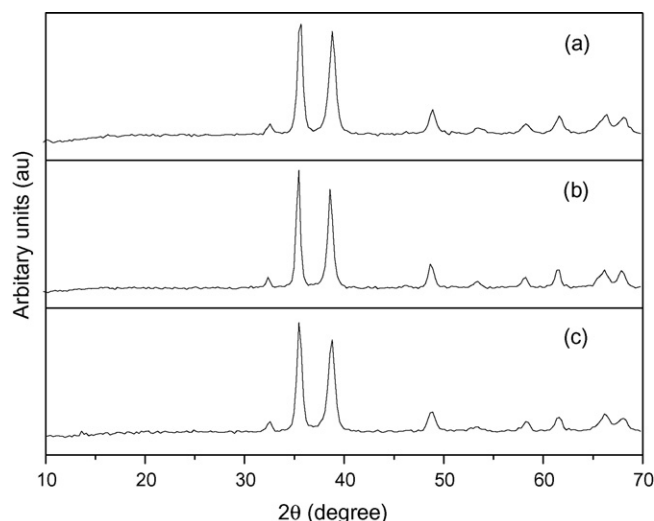


Fig. 1. PXRD patterns of: (a) sample CAA, (b) sample CAB, and (c) sample CAC from cupric acetate salt as precursor.

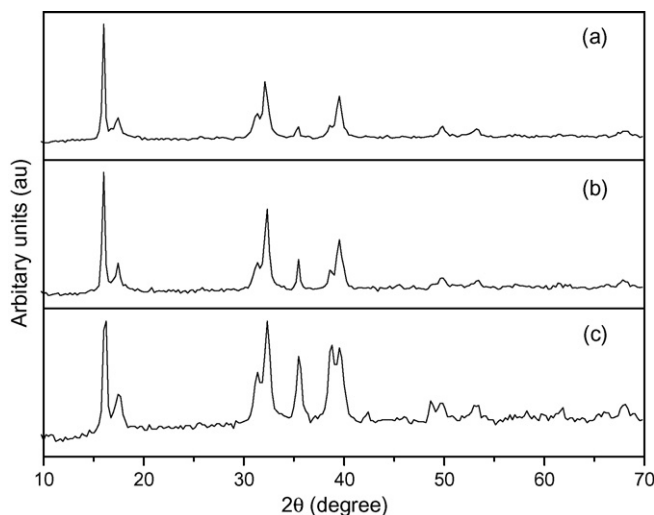


Fig. 2. PXRD patterns of: (a) sample CCA, (b) sample CCB, and (c) sample CCC from cupric chloride salt as precursor.

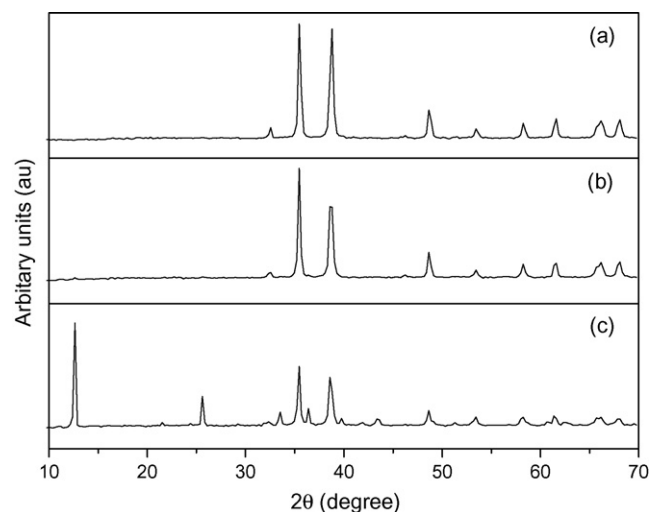


Fig. 3. PXRD patterns of: (a) sample CNA, (b) sample CNB, and (c) sample CNC from cupric nitrate salt as precursor.

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