



## Copper–cobalt oxide ceramic thin films from single source precursors: Preparation and characterization

Muhammad Shahid<sup>a</sup>, Muhammad Mazhar<sup>a,\*</sup>, Mazhar Hamid<sup>a</sup>, Paul O' Brien<sup>b,\*</sup>,  
Mohammad A. Malik<sup>b</sup>, James Raftery<sup>b</sup>

<sup>a</sup> Department of Chemistry, Quaid-I-Azam University, Islamabad 45320, Pakistan

<sup>b</sup> The School of Chemistry and School of Materials, The University of Manchester, Oxford Road, Manchester M13 9PL, UK

### ARTICLE INFO

#### Article history:

Received 17 September 2009

Accepted 4 November 2009

Available online 10 November 2009

#### Keywords:

Heterobimetallic complexes

X-ray structure

AACVD

XRD

Cu–CoO thin films

### ABSTRACT

Two heterobimetallic coordination complexes  $[\text{Co}(\text{acac})\text{Cu}_2(\text{bdmap})_2\text{Cl}_3]\cdot\text{C}_7\text{H}_8$  (**1**) and  $[\text{Co}(\text{acac})\text{Cu}_2(\text{bdmap})_2\text{Cl}_3]\cdot 3\text{CH}_2\text{Cl}_2$  (**2**) [bdmap = 1,3-Bis(dimethylamino)-2-propanol and acac = 2,4-pentanedionate], have been synthesized by simple chemical technique and characterized by their melting points, elemental composition, FT-IR spectroscopy, mass spectrometry and single crystal X-ray analysis. Thermograms of both the precursors indicated their facile decomposition at relatively low temperature of 454 °C to give stable residual mixture of Cu and CoO. Both the precursors are utilized for the deposition of Cu–CoO thin films by aerosol-assisted chemical vapor deposition (AACVD) equipment at 450 °C on glass substrates that were subsequently characterized for their morphology and composition of the ceramic material. The scanning electron microscopy of copper–cobalt oxide films grown from both the precursors describe highly compact and smooth morphology with homogeneously dispersed spherical particles with excellent adhesion properties to the substrates. The EDX analysis shows homogeneous distribution of metallic elements with Cu:Co ratio close to 2:1. Powder X-ray diffraction analysis of the films shows that they are composed of Cu/CoO composite and are crystalline in nature having particle size in the range of 0.3–0.8 μm.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

Mutual interactions of combination of transition metal oxides give rise to their superior electrical, magnetic and catalytic properties due to complex structure formation [1]. Oxides of copper and cobalt have been investigated as individuals, in the form of single phase and/or in the form of mixed phases for their catalytic properties [2,3]. Copper–cobalt oxide thin films have found applications in solid-state optical gas sensors [4], solar collectors [5,6] and catalysts in electrochemical devices [7]. The catalytic activity of copper and cobalt oxides supported on  $\gamma\text{-Al}_2\text{O}_3$  was studied and were found to have good  $\text{SO}_2$  antipoisoning activity [8]. In initial investigations, the Cu/Co atomic ratio of 0.5 was found to be suitable in the oxidation of CO and hydrocarbons in the presence of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{SO}_2$  at relatively low temperature [9–11]. Oxidation capabilities of transition metal oxides are improved by the introduction of another oxide, which demands establishment of stoichiometric composition. One of the synthetic strategies is to decompose the mixture of copper and cobalt nitrates to get the compound of required stoichiometric

composition or otherwise to decompose the single source bimetallic precursor [12].

In heterogeneous catalysis, finely and homogeneously dispersed nanoscale phases are found to have superior properties and the same can be achieved by the decomposition of single molecular precursor that provide interesting alternative approach for catalyst preparation [13].

Heterobimetallic single molecule precursors (SMPs) containing both the metals built-in a single molecule through multifunctional ligands can deliver the required components of the desired material [14]. These bimetallic precursors are also essential for the internal coatings of highly porous alumina or silica based catalyst supports through impregnation processes. This precursor method has the advantages of low temperature of decomposition, better compositional uniformity at molecular level and conformal coverage in the case of films [15].

Our concern is with the precursor synthesis and its ultimate transformation into a material of required stoichiometry. One of the main challenges to thin film science is the development of cheap, easy to synthesize, facile decomposable and soluble precursors [16–18].

Thus here we report the simple synthetic route to the precursors  $[\text{Co}(\text{acac})\text{Cu}_2(\text{bdmap})_2\text{Cl}_3]\cdot\text{C}_7\text{H}_8$  (**1**) and  $[\text{Co}(\text{acac})\text{Cu}_2(\text{bdmap})_2\text{Cl}_3]\cdot$

\* Corresponding authors. Tel.: +92 3005193859 (M. Mazhar).

E-mail address: [mazhar42pk@yahoo.com](mailto:mazhar42pk@yahoo.com) (M. Mazhar).

$3\text{CH}_2\text{Cl}_2$  (**2**) that are subsequently decomposed to Cu–CoO composite thin films for technological applications.

## 2. Experimental

### 2.1. General considerations

All reagents were purchased from Sigma–Aldrich and synthetic work was carried out under an inert atmosphere of dry argon using Schlenk tube and glovebox techniques. Solvents were rigorously dried and distilled over sodium benzophenone. 1,3-Bis(dimethylamino)-2-propanol (bdmapH) was used without further purification, while  $[\text{Cu}(\text{OCH}_3)\text{Cl}]_4$  was prepared by literature procedure [19].

Elemental analyses were performed using CHN Analyzer LECO model CHNS-932. Melting points were determined in a capillary tube using an electrothermal melting point apparatus, model MP.D Mitamura Riken Kogyo (Japan) and are reported as recorded. FT-IR spectra were recorded on a specie single reflectance ATR instrument ( $4000\text{--}400\text{ cm}^{-1}$ , resolution  $4\text{ cm}^{-1}$ ). Mass spectra were recorded on a Micromass Platform II instrument.

The controlled thermal analyses of the complexes were investigated using a Seiko SSC/S200 thermal analyzer at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  under  $\text{N}_2$  flow of  $130\text{ ml}/\text{min}$ .

The phase analysis and crystallinity of deposited films were characterized by means of a Bruker AXS D8 diffractometer using monochromatic  $\text{Cu K}\alpha$  ( $\lambda = 0.154184\text{ nm}$ ) radiation on which a range of  $2\theta$  (from  $10.00$  to  $90.00$ ) was scanned, to cover the diffraction patterns of the oxide phases. Surface morphology of films was determined by a FEG-SEM Philips XL30. Samples were carbon coated before observation and EDAX-DX<sub>4</sub> was used to calculate the composition (metallic ratio) of the films.

### 2.2. Synthesis

#### 2.2.1. Synthesis of $[\text{Co}(\text{acac})\text{Cu}_2(\text{bdmap})_2\text{Cl}_3]\cdot\text{C}_7\text{H}_8$ (**1**)

About  $0.44\text{ g}$  ( $3.01\text{ mmol}$ ) of bdmapH was added to a stirred mixture of  $0.50\text{ g}$  ( $4.38\text{ mmol}$ )  $[\text{Cu}(\text{OCH}_3)\text{Cl}]_4$  and  $0.38\text{ g}$  ( $1.46\text{ mmol}$ )  $\text{Co}(\text{acac})_2\cdot x\text{H}_2\text{O}$  in  $30\text{ ml}$  toluene in  $100\text{ ml}$  Schlenk tube to give violet precipitates. The reaction mixture was further stirred for  $2\text{ h}$  for completion of reaction. The precipitates were filtered off, washed three times with toluene and dissolved in  $10\text{ ml}$  of dichloromethane with  $2\text{ ml}$  of toluene as non solvent. The solution was cannula filtered to remove insoluble  $\text{Cu}(\text{OCH}_3)_2$  and kept for five days with  $2\text{ ml}$  addition of toluene to give rod-like violet crystals of (**1**) (yield  $65\%$ ), m.p.  $160\text{ }^\circ\text{C}$ . *Anal. Calc.* for  $\text{C}_{26}\text{H}_{49}\text{Cl}_3\text{CoCu}_2\cdot\text{N}_4\text{O}_4$ : C,  $40.34$ ; H,  $6.38$ ; N,  $7.24$ . *Found:* C,  $40.01$ ; H,  $6.53$ ; N,  $7.16\%$ . FT-IR (KBr,  $\text{cm}^{-1}$ ):  $2954\text{w}$ ,  $2867\text{m}$ ,  $1591\text{vs}$ ,  $1523\text{s}$ ,  $1461\text{m}$ ,  $1390\text{s}$ ,  $1331\text{w}$ ,  $1277\text{m}$ ,  $1249\text{w}$ ,  $1205\text{w}$ ,  $1106\text{m}$ ,  $1019\text{m}$ ,  $996\text{m}$ ,  $900\text{m}$ ,  $857\text{m}$ ,  $776\text{w}$ ,  $740\text{m}$ ,  $700\text{m}$ ,  $536\text{ m}$ ,  $453\text{w}$ . Electrospray-MS (positive scan) *m/z*:  $683.5$   $[\text{Cu}_2(\text{bdmap})_2\text{Co}(\text{acac})\text{Cl}_3]^+$ ,  $626.1$   $[\text{M}-(\text{bdmap})]^+$ ,  $540.3$   $[\text{M}-\text{Cu}(\text{acac})\text{Cl}_2]^+$ ,  $469.8$   $[\text{M}-\text{Cu}(\text{bdmap})\text{CoCl}]^+$ ,  $412.6$   $[\text{Cu}(\text{bdmap})(\text{acac})\text{Cl}_3]^+$ ,  $356.1$   $[\text{Cu}(\text{bdmap})_2]^+$ ,  $351.6$   $[\text{Co}(\text{bdmap})_2]^+$ ,  $314.6$   $[\text{M}/2-\text{Cl}_2]^+$ ,  $308.6$   $[\text{Cu}(\text{bdmap})(\text{acac})]^+$ ,  $286.6$   $[\text{M}/2-(\text{acac})]^+$ ,  $251.4$   $[\text{M}/2-(\text{acac})\text{Cl}]^+$ ,  $246.7$   $[\text{Cu}(\text{bdmap})\text{Cl}]^+$ ,  $208.4$   $[\text{Cu}(\text{bdmap})]^+$ ,  $182.2$   $[\text{M}/2-\text{Co}(\text{bdmap})]^+$ ,  $177.6$   $[\text{M}/2-\text{Cu}(\text{bdmap})]^+$ ,  $146.7$   $[(\text{bdmap})]^+$ . TGA:  $125\text{--}165\text{ }^\circ\text{C}$  ( $11.1\text{ wt}\%$  loss),  $165\text{--}345\text{ }^\circ\text{C}$  ( $53.0\text{ wt}\%$  loss),  $345\text{--}454\text{ }^\circ\text{C}$  (residue  $26.31\%$ ).

#### 2.2.2. Synthesis of $[\text{Co}(\text{acac})\text{Cu}_2(\text{bdmap})_2\text{Cl}_3]\cdot 3\text{CH}_2\text{Cl}_2$ (**2**)

About  $0.66\text{ g}$  ( $4.52\text{ mmol}$ ) of bdmapH was added drop-wise by a syringe to a stirring mixture of  $0.75\text{ g}$  ( $6.57\text{ mmol}$ )  $[\text{Cu}(\text{OCH}_3)\text{Cl}]_4$  and  $0.57\text{ g}$  ( $2.19\text{ mmol}$ )  $\text{Co}(\text{acac})_2\cdot x\text{H}_2\text{O}$  in toluene ( $25\text{ ml}$ ). The reaction mixture was stirred for  $2\text{ h}$  to give violet precipitates. After filtration, the solid was washed three times with  $7\text{ ml}$  toluene

and dried in a vacuum. The solid was dissolved in  $10\text{ ml}$  dichloromethane and filtered through a cannula to remove insoluble by-product. Violet cube-like crystals of (**2**) suitable for X-ray analysis formed after about  $15$  days with  $73\%$  yield, m.p.  $155\text{ }^\circ\text{C}$ . *Anal. Calc.* for  $\text{C}_{21}\text{H}_{45}\text{Cl}_7\text{CoCu}_2\text{N}_4\text{O}_4$ : C,  $29.61$ ; H,  $5.32$ ; N,  $6.58$ . *Found:* C,  $30.26$ ; H,  $5.86$ ; N,  $6.99\%$ . FT-IR (KBr,  $\text{cm}^{-1}$ ):  $2977\text{w}$ ,  $2869\text{m}$ ,  $1591\text{vs}$ ,  $1520\text{s}$ ,  $1463\text{m}$ ,  $1388\text{s}$ ,  $1330\text{w}$ ,  $1273\text{m}$ ,  $1202\text{w}$ ,  $1104\text{s}$ ,  $1021\text{m}$ ,  $989\text{m}$ ,  $898\text{s}$ ,  $858\text{m}$ ,  $785\text{w}$ ,  $736\text{m}$ ,  $702\text{m}$ ,  $536\text{m}$ ,  $450\text{w}$ . APCI-MS (negative scan) *m/z*:  $718.2$   $[\text{M}-(\text{acac})\text{Cl}]^-$ ,  $684.8$   $[\text{Cu}_2(\text{bdmap})_2\text{Co}(\text{acac})\text{Cl}_3]^-$ ,  $585.8$   $[\text{M}-\text{CoCl}_3]^-$ ,  $546.3$   $[\text{Cu}(\text{bdmap})_2\text{Co}(\text{acac})\text{Cl}]^-$ ,  $424.4$   $[\text{Cu}(\text{bdmap})_2\text{Cl}_2]^-$ ,  $410$   $[\text{Co}(\text{bdmap})(\text{acac})\text{Cl}_3]^-$ ,  $350.9$   $[\text{Co}(\text{bdmap})_2]^-$ ,  $288.5$   $[\text{M}/2-(\text{acac})\text{Cl}]^-$ ,  $227.5$   $[\text{M}/2-\text{Cu}(\text{acac})\text{Cl}]^-$ ,  $197$   $[\text{Cu}(\text{acac})\text{Cl}]^-$ ,  $128.5$   $[\text{CuCl}_2]^-$ . TGA:  $125\text{--}159\text{ }^\circ\text{C}$  ( $11.3\text{ wt}\%$  loss),  $159\text{--}348\text{ }^\circ\text{C}$  ( $57.1\text{ wt}\%$  loss),  $348\text{--}454\text{ }^\circ\text{C}$  (residue of  $24.18\%$ ).

### 2.3. X-ray crystallography

Single crystal X-ray data measurements were made using graphite monochromated  $\text{Mo K}\alpha$  radiation on a Bruker APEX diffractometer. The structures were solved by direct methods [20] and refined by full-matrix least-squares on  $F^2$  [21]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters and allowed to ride on their parent carbon atoms. Table 1 summarizes the crystal data and refinement details for both the complexes.

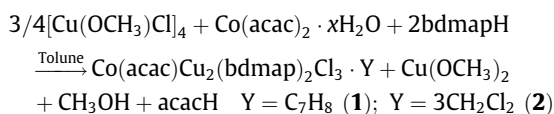
### 2.4. Thin film deposition

Cu–CoO composite thin films were grown on bare glass substrates in a hot-walled reactor containing a quartz ( $1.5\text{ cm}$  diameter) tube, by gas phase reactions of the precursors in an argon environment using a self-designed aerosol-assisted chemical vapor deposition assembly described elsewhere [22]. In a typical experiment,  $0.1\text{ g}$  of precursor dissolved in  $10\text{ ml}$  toluene and  $5\text{ ml}$  dichloromethane in a two neck round bottomed flask was connected via rubber tubing to a quartz reactor into which  $2.5 \times 1\text{ cm}$  substrate slides were placed inside a carbolite tube furnace and a flow of argon gas was regulated using a Platon flow gauge on the other neck. The flask was mounted on piezoelectric modulator of an ultrasonic humidifier for atomization of the precursor solution to tiny droplets of aerosol that were ultimately transferred by the carrier gas into the reactor chamber. Glass substrates were treated with concentrated nitric acid, followed by washings with deionized water several times and then oven dried at  $100\text{ }^\circ\text{C}$  before deposition. Deposition was carried out at  $450\text{ }^\circ\text{C}$  for complexes (**1**) and (**2**) at a constant argon flow rate of  $130\text{ ml}/\text{min}$  on substrates for  $2.5\text{ h}$ .

## 3. Results and discussion

### 3.1. Synthesis and characterization

The synthetic procedure used for both heterobimetallic complexes is simple and involve the mixing of  $[\text{Cu}(\text{OCH}_3)\text{Cl}]_4$ ,  $\text{Co}(\text{acac})_2\cdot x\text{H}_2\text{O}$  and bdmaeH in appropriate stoichiometric ratios in toluene as given in the chemical equation below.



$\text{Co}(\text{acac})\text{Cu}_2(\text{bdmap})_2\text{Cl}_3\cdot\text{C}_7\text{H}_8$  (**1**) was crystallized in a mixture of dichloromethane and toluene in  $5:1$  ratio to give rod like crystals after five days, while the cubic crystals of the complex  $\text{Co}(\text{acac})-$

Download English Version:

<https://daneshyari.com/en/article/1311271>

Download Persian Version:

<https://daneshyari.com/article/1311271>

[Daneshyari.com](https://daneshyari.com)