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Copper aluminate spinel by soft chemical routes

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Abstract

Copper aluminate spinel ($CuAl_2O_4$) was obtained by two different chemical routes: the precursor method and the solution combustion method involving glycine-nitrates. The polynuclear complex compounds: $(NH_4)_2[CuAl_2(C_4O_6H_4)_3(OH)_4]\cdot 2H_2O$ (**I**), $(NH_4)[CuAl_2(C_6O_7H_{11})_3(OH)_6]\cdot 2H_2O$ (**II**) and $[CuAl_2(NH_2CH_2COOH)_{4.5}]\cdot(NO_3)_8\cdot 4H_2O$ (**III**) were characterized by elemental chemical analysis, infrared spectroscopy (IR), ultraviolet–visible spectroscopy (UV–vis) and thermal analysis. The final oxide powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), IR, Raman spectroscopy (RS), UV–vis and photoluminescence (PL) spectroscopy. X-ray diffraction patterns indicated the formation of the cubic phase $CuAl_2O_4$ with good crystallinity. The crystallite size ranged from 18.70 to 19.50 nm. Electron microscopy revealed the morphology corresponding to the complete crystallization into $CuAl_2O_4$. The band gap values ranged between 1.97 and 2.03 eV. The photocatalytic degradation of methyl orange (MO) was investigated using copper aluminate as catalyst.

Keywords: A. Powders chemical preparation; B. Spectroscopy; D. Spinels; Scanning electron microscopy

1. Introduction

Nanocrystalline aluminum based spinels are a class of metal oxides with high thermal stability, high mechanical resistance, hydrophobicity and low surface acidity [1–3]. Due to these properties, they have been used as catalysts in the decomposition of methane and the dehydration of saturated alcohols to olefins, as supports for the active metals, as pigments and as refractory or magnetic materials [4–6].

Among the aluminate spinels, the nanocrystalline copper aluminate ($CuAl_2O_4$) is known to be active in the degradation of some organic compounds [7,8] and in the reduction of NO with CO [6]. The nanocrystalline copper aluminate has also been used as sensor material [9] and as ceramic pigment for the production of ceramic coatings [10]. In all these applications, the copper aluminate has to have high purity, small average diameter particle and narrow distribution or high surface area. These properties are achieved when the copper aluminate is synthesized by wet chemical methods such as: coprecipitation [11], hydrothermal synthesis [12], sol–gel [4,7,9,13,14], microemulsion [15], sonochemical [1,5] and Pechini route [16]. Ragupathi et al. described the preparation of $CuAl_2O_4$ by a microwave combustion method (MWCM) using the plant extract (*aloe vera*) as a fuel without using any other template or surfactant [17].

Considerable efforts have been made to develop such methods in which precursors were "*single-source*" polynuclear complex compounds [3,8,18–20]. The multimetallic complex compounds are preferred as "*single molecular precursors*" because they ensure a good control of the stoichiometry of nanostructured oxides and a narrow distribution at low temperature [21].

The goal of this research is to obtain $CuAl_2O_4$ spinel powders through two different soft chemical methods: i) the precursor method involving the thermal decomposition of

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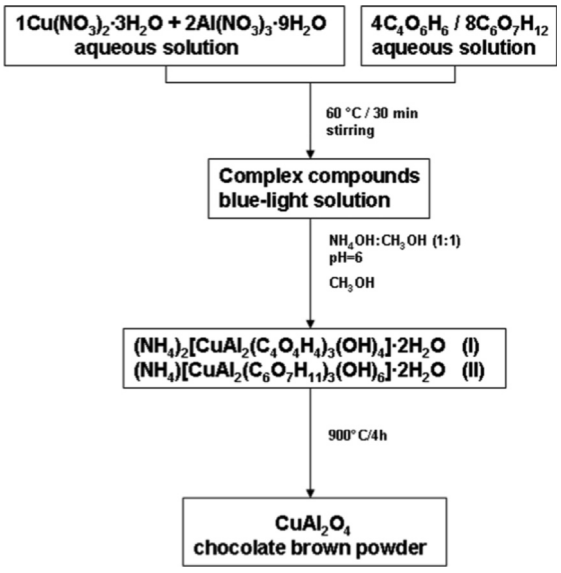
Table 1
Chemical analysis data of $(NH_4)_2[CuAl_2(C_4O_6H_4)_3(OH)_4]\cdot 2H_2O$ (**I**), $(NH_4)[CuAl_2(C_6O_7H_{11})_3(OH)_6]\cdot 2H_2O$ (**II**) and $[CuAl_2(NH_2CH_2COOH)_{4.5}]\cdot(NO_3)_8\cdot 4H_2O$ (**III**) compounds.

Compound	Al (wt%)		Cu (wt%)		C (wt%)		N (wt%)		H (wt%)	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
I	7.70	7.73	9.05	9.34	20.53	20.84	3.99	3.99	3.99	4.34
II	6.29	6.29	7.40	7.61	25.16	24.84	1.63	1.44	5.47	5.29
III	5.28	5.32	6.21	6.26	10.58	10.64	17.11	17.25	2.98	3.01



Scheme 1. The flow chart for the preparation of $CuAl_2O_4$ from tartarate/gluconate precursors.

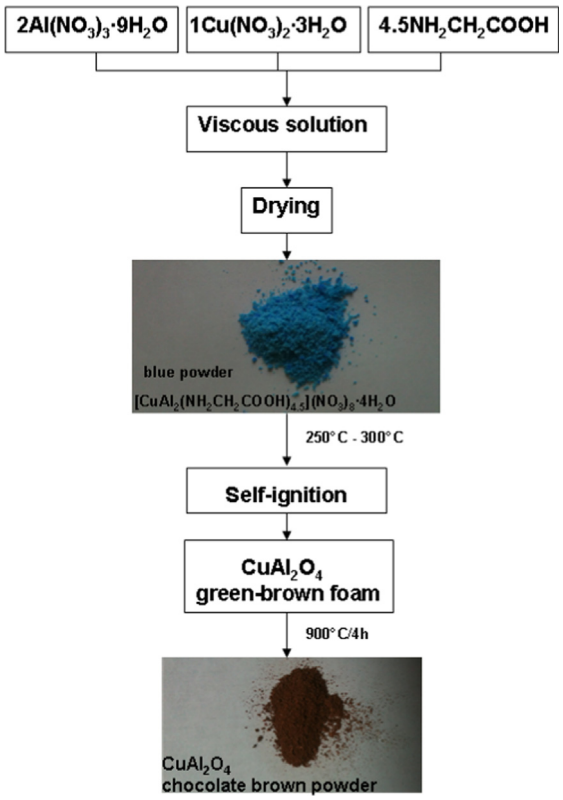
polynuclear multimetallic compounds containing as ligands the anions of tartaric/gluconic acids; ii) the solution combustion method, namely glycine-nitrate process (**GNP**).

2. Experimental

The aluminum(III) nitrate ($Al(NO_3)_3\cdot 9H_2O$), copper(II) nitrate ($Cu(NO_3)_2\cdot 3H_2O$), tartaric acid ($C_4O_6H_6$), δ-gluconolactone ($C_6H_{10}O_6$) and glycine (NH_2CH_2COOH) were of reagent quality (Merck) and were used without any further purification.

2.1. Precursor method

The polynuclear multimetallic precursors were prepared as follows: the aluminum and copper nitrates were dissolved in minimum amount of water and mixed with an aqueous solution of carboxylic acid, in a $2Al(NO_3)_3$: $1Cu(NO_3)_2$: $4C_4O_6H_6$ ratio and $2Al(NO_3)_3$: $1Cu(NO_3)_2$: $8C_6O_7H_{12}$ ratio, respectively. The gluconic acid ($C_6O_7H_{12}$) was obtained from the δ-gluconolactone ($C_6H_{10}O_6$) by hydrolysis at 80 °C. The pH was raised to 6 by adding NH_4OH:methanol (1:1). Methanol was added until a light blue precipitate was formed. After 24 h at 4 °C, the precipitate was filtered and dried over P_4O_{10}. Table 1 shows the elemental chemical analysis for the tartarate/gluconate precursors (compounds **I, II).**



Scheme 2. The flow chart for the preparation of $CuAl_2O_4$ by the solution combustion.

2.2. Solution combustion method

The following system was investigated:

$Al(NO_3)_3\cdot 9H_2O$: $1Cu(NO_3)_2\cdot 3H_2O$: $4.5NH_2CH_2COOH$

The ratio of the aluminum and copper nitrates to glycine in the initial mixture was derived from the total oxidation number of the oxidizer and fuel, using the concepts of propellant chemistry [22,23].

The reactants were mixed in an agate mortar until a concentrated homogeneous solution was formed. The hydration