

RESEARCH PAPER

Preparation, Structure and Selected Catalytic Properties of La_2CuO_4 Nano Mixed Metal Oxides

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ARTICLE INFO

Article History:

Received 11 August 2016

Accepted 17 September 2016

Published 01 October 2016

Keywords:

Perovskite

Nanoparticles

La_2CuO_4

Ultrasonic

Oxidation

Aldehydes

ABSTRACT

The perovskite-structured La_2CuO_4 nanoparticles have been synthesized via an ultrasonic-assisted co-precipitation route using octanoic acid as organic surfactant, and the phase composition, morphology, lattice parameters and size of nanoparticles are characterized through Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy and Transmission electron microscopy. Magnetic measurements are carried out by a vibrating sample magnetometer on the resultant powders at room temperature. Vibrating sample magnetometer shows nanoparticles exhibit ferromagnetic behavior. The synthesized perovskite yields comparatively pure crystalline phase of La_2CuO_4 nanoparticles. These nanoparticles are used as an efficient and effective catalyst for the oxidation of aldehydes to corresponding carboxylic acids, and this oxidation protocol works well for various aldehydes. Also the La_2CuO_4 nanoparticles can be recycled for several times without obvious loss of activity. The results show the utilization of these nano catalysts have several advantages, viz. high yields, clean reaction, short reaction times and recyclability of the catalyst.

How to cite this article

Rahmani A, Saffari J. Preparation, Structure, and Selected Catalytic Properties of La_2CuO_4 Nano Mixed Metal Oxides. *J Nanostruct*, 2016; 6(4): 301-306. DOI: 10.22052/jns.2016.34270

INTRODUCTION

The developments of nanosized metal oxides have attracted a great deal of attention due to their unique properties such as high surface area, stability and effectively as catalyst in some organic transformations [1]. La_2CuO_4 (LCO) is an important, catalytically active perovskite [2]. So far, a large number of works have reported successful fabrication of perovskite with specific surface morphologies by the solid-state reaction or wet chemical routes (ca. Sol-Gel, co-precipitation), which show the dependence of the catalytic activity on the structure of the LCO [3,4]. For example, Gao and coworkers reported the preparation of LCO nanofibers prepared with hydrothermal process [5]. The parent materials of the first high-TC cuprate, LCO are known to be correlated with Mott insulators that become

metallic and superconducting upon doping with charge carriers [6]. A large number of researches have been performed on bulk samples in the LCO-based materials due to their simple chemical composition and crystal structures as well as the rich physical properties [7]. LCO is known to have three different structures, T-phase (K_2NiF_4 -type) containing edge-shared CuO_6 octahedra arranged in a planar array, T'-phase (Nd_2CuO_4 -type) in which the apical oxygen in the T-phase is shifted away from the Cu atoms, and S-phase (Sr_2CuO_3) which has isolated CuO_3 chains running along the a-axis of the orthorhombic structure. Transitions among T, T' and S phases were found in the annealing process of bulk LCO. These are quasi-two-dimensional materials which consist of layers of copper-oxide planes separated. It seems that most of the properties are determined by electrons

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moving within CuO_2 planes [8-10]. In recent years, various methods have been successfully used to synthesize different kinds of LCO nanostructured materials such as nanoparticles [11], nanorods [12], nanofibers [13], microspheres [14], and thin films [15]. LCO was a well catalyst, which can be used in reduction of NO by CO, and so on [16].

Recently, a great interest was paid to the development of more sustainable synthetic strategies, as greener alternatives to old traditional processes [17]. The oxidation of aldehydes [18] is a widely used reaction in organic chemistry, also for large scale applications. At present, some of these procedures require very expensive and the employment of solvents, so they are often characterized by production of toxic metal waste at the end of the reaction. All these aspects make many protocols environmentally polluting and so their application in the chemical industry is often difficult. Therefore, the possibility to realize alternative 'green' methodologies, also characterized by an easy separation and recycle of the catalyst seems to be desirable. In this context, the application of magnetic La_2CuO_4 nanoparticles (LCO NPs) is a very promising area in the catalysis field [19, 20]. The emerging interest for this kind of nanoparticles, is due to the possibility to modify their properties by simple protocols, involving the formation of covalent bonds with metal or organic ligands or, alternatively, simple coordination or adsorption of suitable activators [21]. Notably, different from other nanoparticles, LCO NPs can be easily recovered at the end of the reaction by an external magnet. We report herein, the synthesis of LCO NPs which obtained by new co-precipitation method by ultrasonic irradiation assisted with octanoic acid as an organic surfactant successfully. Then obtained CuFe_2O_4 nanoparticles have been used as a nano-heterogeneous catalysis in the oxidation of aldehydes to their corresponding carboxylic acids.

MATERIALS AND METHODS

All chemicals were obtained from Merck or Fluka and were used without further purifications. XRD patterns were recorded by a Philips, X-ray diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation. For SEM images the samples were coated by a very thin layer of Au to make the sample surface conductor and prevent charge accumulation, and obtaining a better contrast. Room temperature magnetic properties were investigated using a vibrating sample magnetometer (VSM, made by Meghnatis Daghigh Kavir Company, Iran) in an applied magnetic field sweeping between ± 10000 Oe, Infrared (IR) spectroscopy was taken on Rayleigh (WQF-510A).

Synthesis of LCO NPs

The appropriate amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (with a La:Cu molar ratio of 2:1) were dissolved in distilled water, separately. Then, two solutions were added together. 2 mL of octanoic acid was added to the solution as a surfactant. Then, NaOH solution (1.5 M) was slowly added into the solution until the pH of the mixture was 8-9. After complete precipitation, the solution was irradiated with ultrasonic waves. The sonication time was found effective in the formation of the crystalline phase of nanoparticle. In our experimental condition, 30 min/30 °C (250 W, 40 kHz) sonication resulted in the most pure nanoparticles. After this process, the resulting products were centrifuged for 10 min at 2,000 rpm, washed with distilled water and ethanol several times to remove the excess surfactant from the solution. Then, precipitation was dried in an oven at 100 °C for 5 h. The resulting blue-white powder was calcinated at 800 °C for 3 h to remove any organic residue.

General Procedure for Oxidation of Aldehydes to Carboxylic Acids by LCO as Catalyst

To a vial with the catalyst (10 mol %) under air, aldehyde (0.0625 mmol) and ethyl acetoacetate

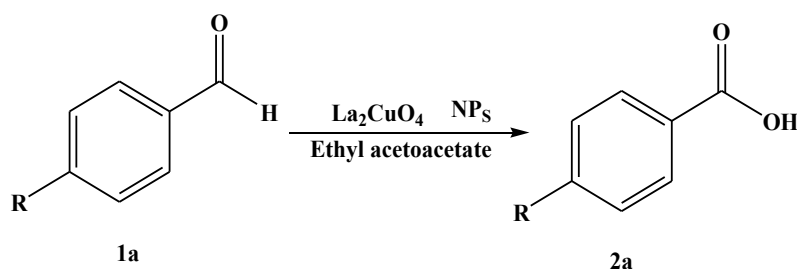


Fig. 1. Model reaction.

Table 1. Synthesis of carboxylic acid derivatives using LCO NPs as catalyst

Entry	1a	2a	Time/min	Yield % ^a	Mp/°C
1	Benzaldehyde	Benzoic acid	10	90	120
2	4-Nitrobenzaldehyde	4-Nitro Benzoic acid	22	80	238
3	4-folourobenzaldehyde	4-folouro Benzoic acid	19	88	253
4	4-Chlorobenzaldehyde	4-Chloro Benzoic acid	15	79	240
5	2-Chlorobenzaldehyde	2-Chloro Benzoic acid	18	81	140
6	4-Bromobenzaldehyde	4-Bromo Benzoic acid	13	79	251
7	3-Bromobenzaldehyde	2-Bromo Benzoic acid	14	75	157
8	4-Methoxybenzaldehyde	4-Methoxy Benzoic acid	14	88	180
9	4-Methylbenzaldehyde	4-Methyl Benzoic acid	15	70	178

^aIsolated yields after purification; The pure isolated product(s) was characterized by comparison of their physical data with those of known compounds [22-29].

(1 equiv) were added. The mixture was heated at 75–80°C and the resulting reaction mixture was stirred at room temperature for a specified period (Fig. 1, Table 1). After complete conversion as indicated by thin layer chromatography (TLC), and cooling at rt, ethyl acetate (1.0 ml) was added and the catalyst was separated by simple magnetic decantation. Then, the combined solvent was removed in vacuo and the mixture was purified via flash column. Spectroscopic data of products 2 were consistent with those reported in the literature [22-29].

RESULTS AND DISCUSSION

Characterization of LCO NPs

Fig. 2 shows the FT-IR spectra of organic surfactant (Fig. 2 (a)), the product before (Fig. 2 (b)) and after (Fig. 2 (c)) calcination in the frequency range from 4200 to 400 cm^{-1} . In FT-IR spectrum of pure organic surfactant, octanoic acid (Fig. 2a), the very broad feature from 3500 to 2500 cm^{-1} is due to a very broad O–H stretch of the carboxylic acid.

In the FT-IR of product before calcination (Fig. 2b), the characteristic bands of surfactant are shown to be shifted to a lower frequency region relative to free surfactant. As can be seen from Fig. 2c, all bands of a and b spectra were disappeared when the product was calcinated and we can see two strong absorption bands at about 684 and 511 cm^{-1} which correspond to M–O stretching vibration and O–M–O bending vibration of LCO, respectively.

Fig. 3 shows the X-ray powder diffraction pattern of La_2CuO_4 nanoparticles calcined at 800 °C. All the reflections can be readily indexed to orthorhombic phase La_2CuO_4 (space group Fmmm, JCPDS No. 38-0709) with cell constants $a=5.2988$ Å, $b=5.3811$ Å, and $c=13.1500$ Å. In Fig. 3, no characteristic peaks were observed as the other impurities such as La_2O_3 and CuO. Additionally, the sharp diffraction peaks show that the obtained LCO NPs have high crystallinity.

The morphology of the LCO NPs is examined by SEM (Fig. 4(a, b)). From the micrographs, it was observed that the nanoparticles were spherical

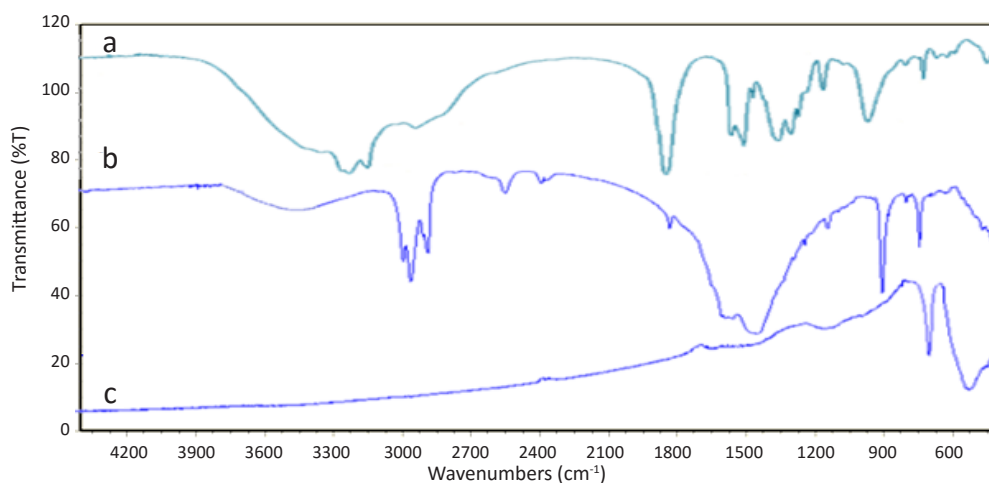


Fig. 2. FT-IR spectrum of (a) octanoic acid, (b) product before, (c) after calcination.

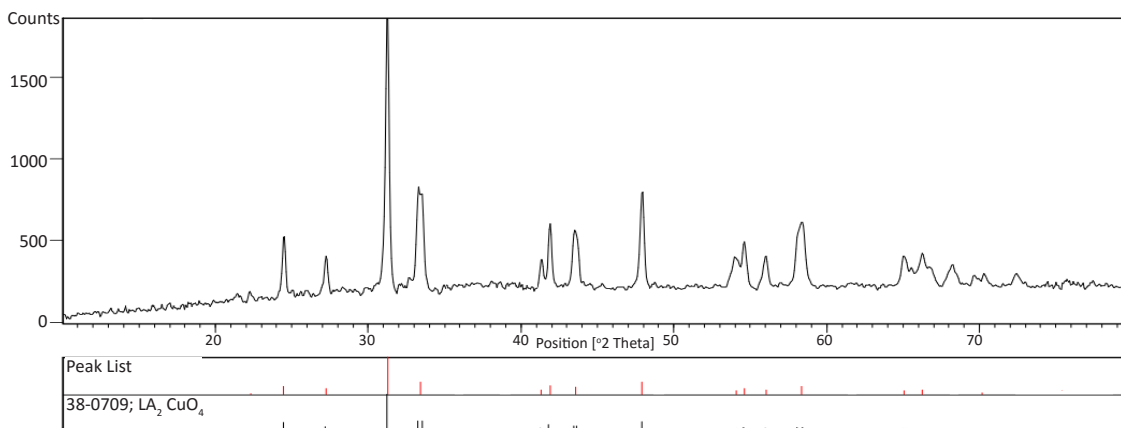


Fig. 3. XRD pattern of the LCO NPs.

and the surface of the spheres is not smooth. It was built up of many small nanoparticles. Also, these micrographs show porous structures and highly specific area on the surface of the particles. This type of morphology may provide more possibility to give an ideal host material for the insertion and extraction of guest ions, to realize region-dependent surface reactivity, and to act as molecular sieves [30].

To further investigate the details of morphology, TEM images of the LCO NPs were taken and shown in (Fig. 5). The agglomerated LCO NPs with particle size of about 15–25 nm were observed.

Hysteresis loop for LCO magnetite nanoparticles is shown in Fig. 6. Coercivity and saturation magnetization of this sample are about 25 Oe and 6.7 emu/g respectively, which also show para-magnetic behavior.

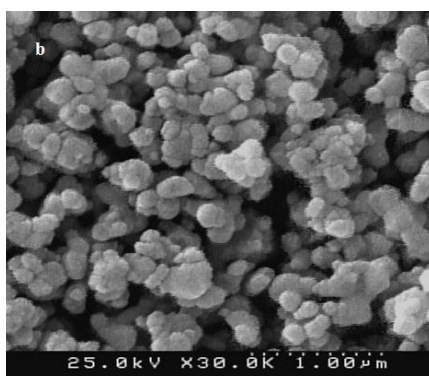


Fig. 4. SEM images of LCO NPs.

Catalytic Activity of LCO NPs

The catalytic activity of LCO nanoparticles has been studied in the oxidation of aromatic aldehydes to the respective carboxylic acids under the optimized reaction conditions in sec. (2.3). Aldehydes can be oxidized to the corresponding carboxylic acids in excellent yields (Fig. 1). The results are summarized in Table 1.

As shown in Table 1, the reaction was compatible successfully with a variety of aryl aldehydes having electron-donating and electron-withdrawing

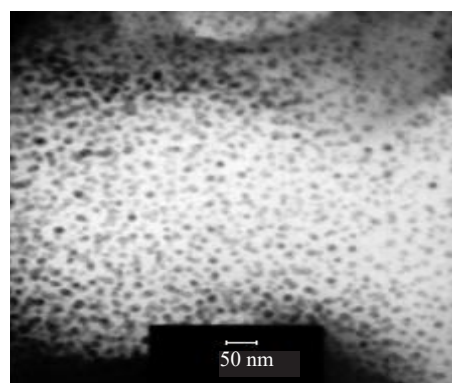


Fig. 5. TEM images of LCO NPs.

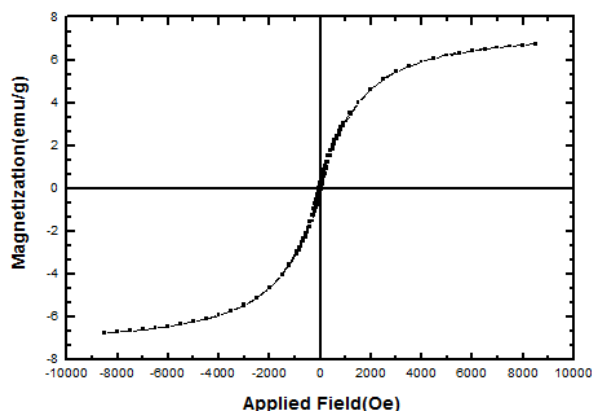


Fig. 6. Hysteresis curve of LCO NPs.

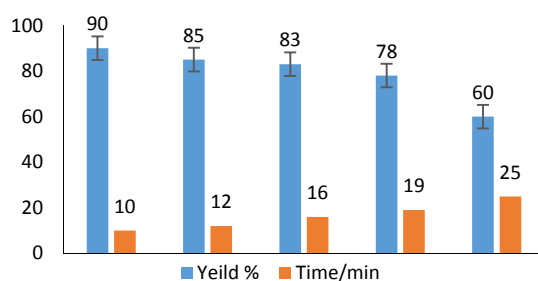


Fig. 7. Reusability of LCO NPs (yield for product).

substituent. Aromatic aldehydes substituted with electron-withdrawing groups react slowly.

The reusability of the catalyst was tested in the oxidation of benzaldehyde to benzoic acid, as shown in Fig. 7. The catalyst was recovered after each run, washed three times with CH_2Cl_2 , dried prior to use and tested for its activity in the subsequent run and fresh catalyst was not added. The catalyst was tested for 5 runs. It was seen that the catalyst displayed very good reusability.

CONCLUSION

In conclusion, LCO NPs have been successfully prepared via sonochemical assisted co-precipitation products in high temperature condition, and characterized on the basis of XRD, TEM, SEM, VSM, and FT-IR analysis.

The catalytic activity of these nanoparticles has been studied in the oxidation of various aromatic aldehydes.

We have also demonstrated that these nanoparticles are efficient and environmentally friendly catalysts for the oxidation of aldehydes. The advantages of this method are shorter reaction times, simple work-up, environmentally benign, high yield, and reusability of catalyst in comparison with the other reported methods.

ACKNOWLEDGMENTS

Authors are grateful to the council of Islamic Azad University, Zahedan branch, for supporting this work.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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