

# CHARACTERISTICS AND REACTIVITY OF La-Co-Cu BASED PEROVSKITES FOR THE LIQUID OXIDATION OF STYRENE

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## Abstract

LaCo<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub> (0.0 ≤ x ≤ 0.3) samples prepared by the conventional citrate method show a well perovskite structure although the solid products still have a small amount of constituent oxides. The mixed oxide powder possesses slit-like pores formed from the voids between by spherical nanoperovskite particles. An insertion of copper into La-Co perovskite lattice makes an observable decrease in perovskite particle size. All the synthesized perovskites were used as catalysts for the liquid oxidation of styrene. Under typically experimental conditions, styrene reagent was firmly converted into the benzaldehyde product over the synthesized perovskite catalysts at the moderate conversion in the range of 1-5 %.

**Keywords:** La-Co-Cu-O, Perovskite, nanoperovskite, styrene, oxidation.

## 1. INTRODUCTION

The oxidation reaction of unsaturated hydrocarbons to oxygenated compounds has become very important since its products are versatile intermediates for the synthesis of organic and pharmaceutical compounds [1-3]. The efficient oxidation of olefins is usually performed in the liquid phase with permanganate, perchromate, peracids and peroxides, but these oxidants always lead to unacceptable levels of waste (solvent, catalysts, e.g.) [4, 5]. In other context, the use of air or molecular oxygen as an oxidizing agent is a cheap and friendly environmental agent. So it is more interesting than other classical oxidants mentioned above [1, 5]. A number of attempts used molecular oxygen or air as oxidizing agents over heterogeneous catalysts such as TiO<sub>2</sub>/SiO<sub>2</sub> [2, 6], zeolite [7], CoO<sub>x</sub>/SiO<sub>2</sub> [8] or titania-silica mixed oxides [9] have been reported. More interesting, oxygen adsorbed on some mixed-oxides (perovskite, spinel...) plays an important role in the selective oxidation of olefins to desired intermediate products such as oxirane, aldehydes... [4, 6, 7, 9]. Among these oxides, perovskites are recently found to exhibit a good activity in the oxidation of aromatic alcohols and olefins [2, 11]. In general, perovskite type-oxides (general formula of ABO<sub>3</sub>) containing a rare earth element at the A-site position and a first

row transition metal at the B-site have a good ability to uptake a significant amount of oxygen species on the lattice vacancies [11-14]. In another point, these perovskite-type oxides are easy to synthesize at low cost and have a good thermal stability [11, 15]. Thus, the present publication reports the properties and the preliminary results on the catalytic activity of LaCo<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub> (0.0 ≤ x ≤ 0.3) in the oxidation of styrene.

## 2. EXPERIMENTAL

### 2.1 Perovskite preparation

A set of perovskite samples (LaCo<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub>, 0 ≤ x ≤ 0.3) was prepared by the conventional citrate method [12]. Typically, a stoichiometric amount of La(NO<sub>3</sub>)<sub>3</sub> was added into distilled water while slowly heating the mixture on a magnetic stirrer. After a clear transparent solution was obtained, stoichiometric amounts of cobalt and copper nitrates were added. Then one mole of citric acid per mole of metal atom was added to the dark pink/red translucent solution. The resulting solution was heated slowly to dryness and then dehydrated at 80°C overnight in an oven to yield an amorphous solid precursor. The sample was calcined at 550 °C for 6 h with a ramp of 5 °C/min under air.

## 2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a D8 Advance-Bruker instrument using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.540 \text{ nm}$ ). The scanning electron microscopy (SEM) microphotographs were obtained in a JEOS JSM-5410 LV. TEM image was collected on a Japan Jeol. Jem.1010 Microscope. The nitrogen physisorption was measured at 77 K on an Autochem II 2920 (USA).

## 2.3. Oxidation of styrene

The catalytic oxidation process of styrene was carried out in a 100 mL three-neck glass flask fitted with a reflux condenser. For a typical run, 10 mmol of styrene, 50 mL of solvent ( $\text{N,N}'$ -dimethylamide) and 0.2 grams of catalyst were loaded into the flask. After the reaction mixture was magnetically stirred and heated to the desired temperature, the flow of air (12-15 mL/min) was added at once, which initiated the reaction. After the reaction, the mixture was quenched to room temperature and then catalyst was filtered off. The filtrate was quantitatively analyzed by a GC-MS (HP-6890 Plus).

## 3. RESULTS AND DISCUSSION

### 3.1. X-Ray diffraction

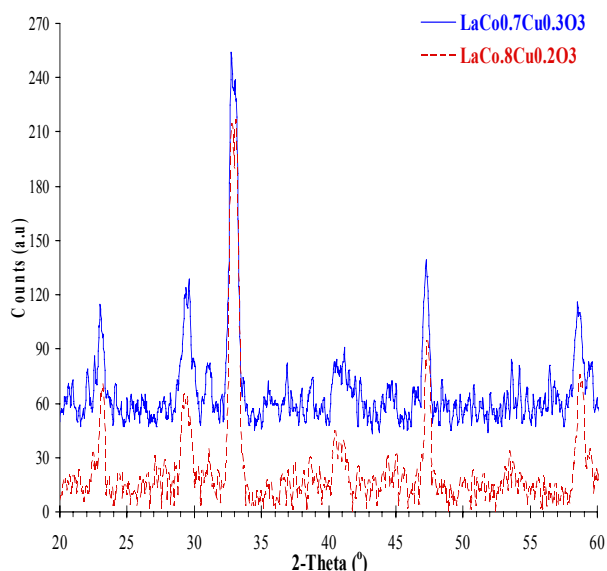


Figure 1: XRD patterns of representative samples

Phase analysis for the synthesized solids was investigated by X-ray diffraction. Figure 1 displays some XRD patterns for the representative Co-Cu based perovskites. In general, all observable peaks are essentially consistent with the X-ray reflection

signals of the perovskite structure [11-15]. Typically, a series of 2-theta values at 23.0; 29.6; 32.8; 33.1; 41.2; 47.3; 58.5° are well matched with the rhombohedral structure of perovskite [12, 14, 15]. A weak peak at 29.3° is attributed to the small amount of  $\text{La}_2\text{O}_3$  phase in the product and those at 31.3; 36.9° are attributed to  $\text{Co}_3\text{O}_4$  impurities. No reflections of  $\text{CuO}$  (35.6 and 38.8°) are detected, indicating that  $\text{Cu}^{2+}$  may be either in the perovskite lattice or in ultra small crystallites/amorphous phase [12, 15]. Microscopic analysis would bring more information about this statement.

### 3.2. Nitrogen adsorption/desorption

Figure 2A shows the BET surface area and the nitrogen adsorption/desorption isotherms of some selected samples. The BET specific surface area of the samples prepared by citrate-complex method is in the range of 1-14  $\text{m}^2/\text{g}$ . It is well known that the perovskites prepared by conventional citrate method usually have a low surface due to calcination stage at a high temperature [11, 12, 16]. Figure 2A also illustrates that the nitrogen adsorption curves of the perovskites fall in between type I and II [17]. Both adsorption and desorption lines are drawn as plots nearly parallel to the horizontal axis in the relative pressure range of 0-0.88. These plateau isotherms strongly reflect the nitrogen sorption on a material that has extremely fine pores (micropores) [17, 18]. Moreover, the appearance of hysteresis loops which are consistent with the type H4 hysteresis loop, but the hysteresis takes place at high relative pressure of 0.88 -1.0. This can be logically interpreted by the adsorption/desorption in the slit-shaped spaces formed by the aggregation of nanoparticles [14]. In other words, the catalyst porosity refers to an opening or cavity in the nanoperoovskite crystals [11, 12]. Taking into account the pore size distribution, one would elucidate the porosity of the solid materials. Figure 2B shows the pore with range in the examined samples. For  $\text{LaCo}_{0.9}\text{Cu}_{0.1}\text{O}_3$  perovskite-type oxide, a set of average micropore sizes are observed at 0.6, 1.2, 1.8 nm in addition to some macropores (not shown here) [17]. The intensity of incremental pore volume slightly decreases in order of  $\text{LaCo}_{0.9}\text{Cu}_{0.1}\text{O}_3 > \text{LaCo}_{0.7}\text{Cu}_{0.3}\text{O}_3 > \text{LaCoO}_3$ , which is in line with the variation of their BET surface areas.

Therefore, it is hypothesized that the specific surface area mainly estimated from microporous areas [14, 18, 19]. The existence of slit-shaped narrow spaces from the arrangement of uniform particles is supported by the analysis of SEM and TEM images.

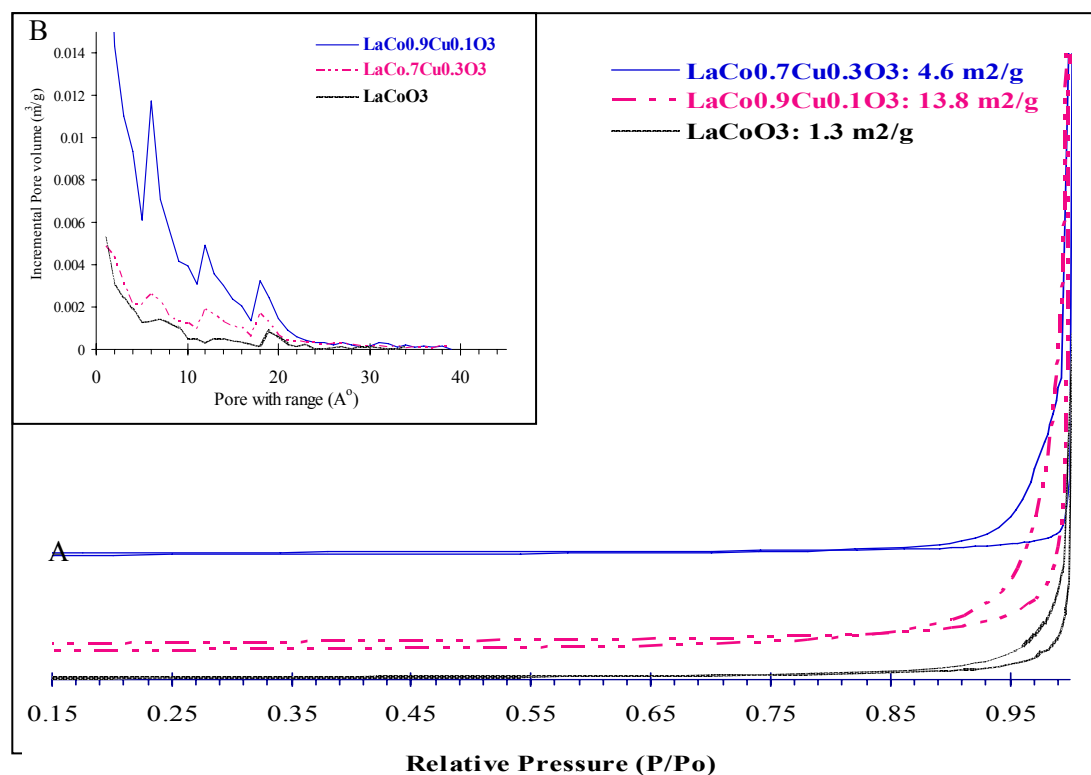


Figure 2: Nitrogen adsorption/desorption isotherms (A) and pores with range (B) of perovskites

### 3.3 Microscopic investigation

Surface morphology of the catalysts was observed by SEM technique. Figure 3 illustrates the perovskite morphology of the copper-free perovskite and Co-Cu based sample. SEM images in general indicate that the conventional citrate method is capable of producing nano-size perovskite crystals. Under a similar magnification level (10.0k), SEM micrograph of  $\text{LaCoO}_3$  perovskite shows the presence of spherical platelets, but these primary

grains aggregate to form various agglomerate chains as clearly indicated by TEM image in Fig 4A. The aggregation is possibly caused by a stepwise calcination at high temperature (Section 2), which also makes a dramatic decrease of specific surface area (Fig. 2A). Meanwhile, transmission electron micrograph of ultrafine  $\text{La}(\text{Co,Cu})\text{O}_3$  perovskite is observed (Fig. 4B), in good agreement with the observation on SEM image (Fig. 3B). The overall average particle sizes of  $\text{La}(\text{Co,Cu})\text{O}_3$  are about 20-30 nm.

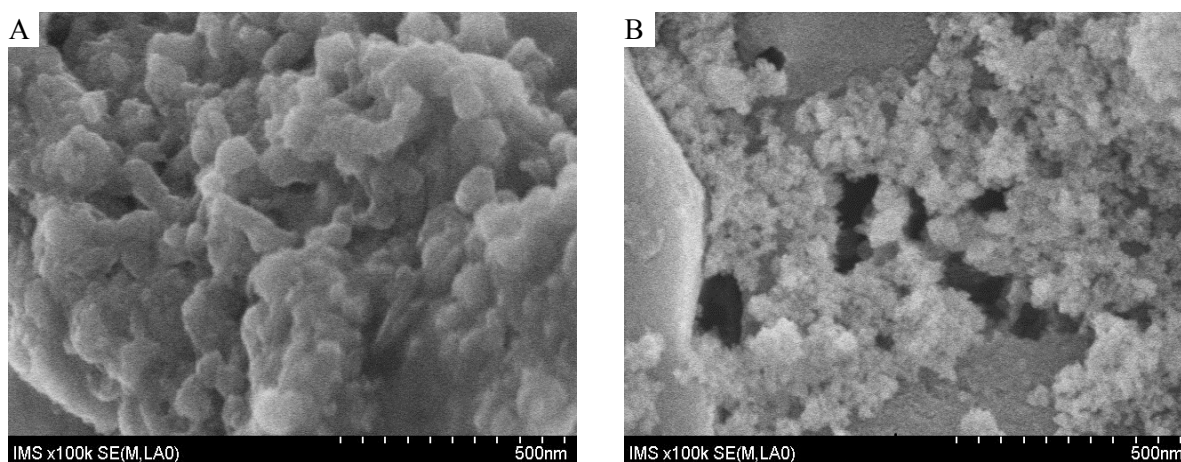


Figure 3: SEM micrographs of two selected perovskites:  $\text{LaCoO}_3$  (A) and  $\text{LaCo}_{0.7}\text{Cu}_{0.3}\text{O}_3$  (B)

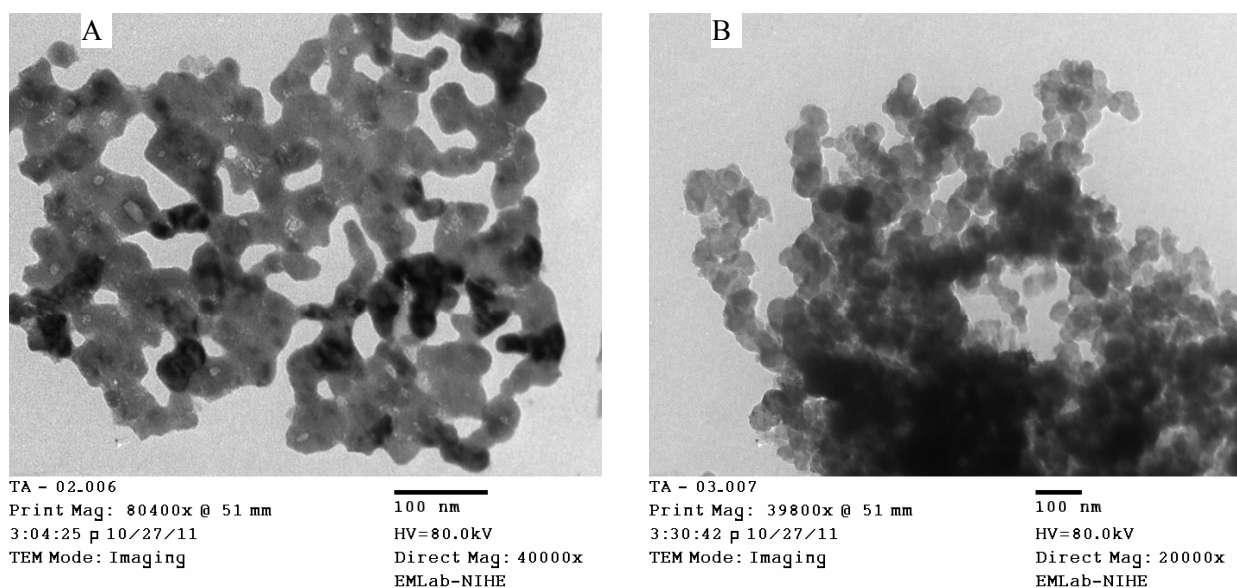


Figure 4: TEM images of two selected perovskites: LaCoO<sub>3</sub> (A) and LaCo<sub>0.7</sub>Cu<sub>0.3</sub>O<sub>3</sub> (B)

With smaller particle sizes, it is explained a better surface area for the Cu-Co based perovskites, as evidenced by nitrogen adsorption analysis (Fig. 2). Thus, addition of copper into perovskite sample may prevent the ultrafine perovskite particles from aggregation process [18, 20]. Furthermore, the ultrafine Co-Cu based perovskite particles are expected to retain a high amount of adsorbed oxygen that participates in the selective oxidation process of styrene.

### 3.4. Preliminary results of styrene oxidation

In the oxidation of styrene, benzaldehyde, phenyl-acetaldehyde, styrene oxide, and polystyrene are identified in the liquid product [1, 3, 5, 9, 23]. Nevertheless, a trace of benzaldehyde and large amount of polystyrene were obtained in the absence of catalyst, whereas benzaldehyde is a major product in addition to a negligible quantity of phenyl-acetaldehyde, styrene oxide in the presence of catalyst [1, 3]. In detail, all perovskite-type oxides are screened catalytic activity and their reaction results are displayed in figure 5 [2, 23].

As seen in figure 5, the styrene conversion, in general, is only in the scale of 0-5%. The selectivity to benzaldehyde obtained in these cases is about 98-99%, indicating the selective oxidation of styrene to benzoic aldehyde over perovskite catalysts [6, 9, 23]. The conversion slightly varies with the copper content and specific area. With  $x = 0.2$ , the conversion of styrene reaches about 4.6 % and decreases at a higher copper content ( $x = 0.3$ ). The low conversion of styrene is explained by the low specific surface areas of perovskites which lead to a limited amount of

oxygen absorbed on the perovskite surface. However, these catalysts are highly selective for benzaldehyde product, indicating a crucial role of absorbed oxygen as a mild oxidant in the oxidation reaction and the behavior of catalyst. Indeed, a high selectivity to benzaldehyde may be related to the “shape-selectivity” effect [3, 8, 10, 21]. As indicated by N<sub>2</sub> sorption analysis, the synthesized perovskites have some types of micropores with the diameters in the range of 0.6-1.8 nm that is capable of admitting transition complexes and product [7, 9, 10]. Indeed, these pore sizes well coincide with the diameter of benzaldehyde molecule (a diameter of 0.68 nm) [21, 22].

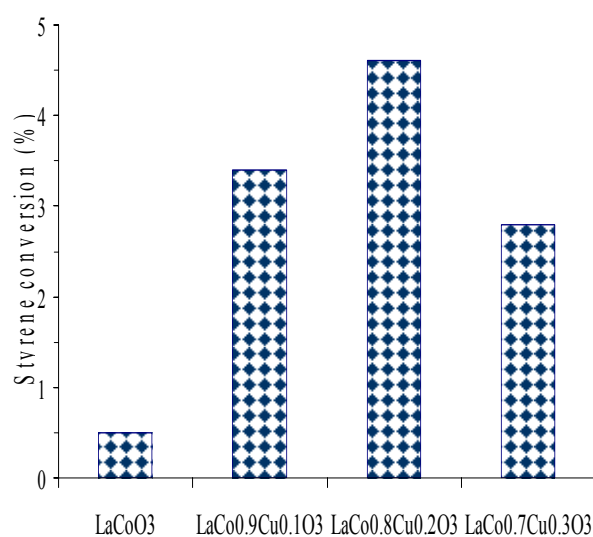


Figure 5: Styrene conversion at 60°C, 4-hours-on-time

## 4. CONCLUSIONS

Co-Cu containing perovskite samples were prepared by the conventional citrate method. The solid product is consisted of mainly rhombohedrally structured perovskite powder along with a small amount of constituent oxides. The perovskite morphology showed the formation of nanoparticles. The synthesized perovskites present some slit-shaped spaces between uniform perovskite nanoparticles. An introduction of copper into La-Co perovskite resulted in a decrease in perovskite crystal domains. All the synthesized perovskites were tested for the oxidation of styrene with air at 60°C. The conversion of styrene depends on the copper-inserting content and perovskite texture. A highest conversion of styrene is about 4.6 % over  $\text{LaCo}_{0.8}\text{Cu}_{0.2}\text{O}_3$  perovskite-type oxide catalyst. For all catalysts, benzaldehyde was produced as a main product with the selectivity of 98 %. The preliminary reaction results indicate the perovskites prepared by citrate complex method acting as selective catalysts for conversion of styrene to benzaldehyde.

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