

## EFFECT OF THE INTRA-PEROVSKITE LATTICE COPPER ON THE REDUCIBILITY OF $\text{La}(\text{Co,Cu})\text{O}_3$

Received 29 January 2008

NGUYEN TIEN THAO<sup>c</sup>, NGO THI THUAN<sup>c</sup>, SERGE KALIAGUINE<sup>2</sup>

<sup>1</sup> Faculty of Chemistry, College of Sciences, Vietnam National University, Hanoi

<sup>2</sup> Department of Chemical Engineering, Laval University, Quebec, Canada. G1K 7P4.

### ABSTRACT

Nanocrystalline  $\text{La}(\text{Co,Cu})\text{O}_3$  perovskites have been characterized by several techniques including  $\text{N}_2$  absorption/desorption, X-ray diffraction, Temperature-Programmed Reduction ( $\text{H}_2$ -TPR), Temperature-Programmed Oxidation ( $\text{O}_2$ -TPO).  $\text{H}_2$ -TPR and  $\text{O}_2$ -TPO results indicate that the reducibility of  $\text{Co}^{3+}$  in the ground  $\text{La}(\text{Co,Cu})\text{O}_3$  perovskites was promoted by the presence of the intra-lattice copper. An increased copper content leads to a decreased reduction temperature of  $\text{Co}^{3+}$  to  $\text{Co}^0$  and an increased dispersion of metallic copper-cobalt phase. The XRD and  $\text{H}_2$ -TPR studies also revealed that the perovskite structure of  $\text{La}(\text{Co,Cu})\text{O}_3$  is somewhat less stable than the ones of  $\text{LaCoO}_3$ .

### I - INTRODUCTION

Perovskite-type mixed oxides  $\text{LnBO}_3$  (Ln = lanthanide; B = transition metals) have been known as oxidation catalysts or catalyst precursors with many potential applications [1-3]. They are, for example, used for total and partial oxidation of methane and carbon monoxide oxidation [2, 4]. Their modified forms are known as potential catalysts for reforming of  $\text{CO}_2$  [5], alkene hydrogenation [6], synthesis of alcohols and hydrocarbon from syngas [7 - 9]. For the latter attractive applications, perovskite —type mixed oxides have been reduced under controlled conditions, producing a solid containing the transition metal B atomically dispersed on an oxide matrix [1, 7, 8, 10]. Both the selectivity and activity in the latter mentioned reactions are strongly dependent on the extent of reduction of the transition metal B [6 - 8, 11, 12]. Therefore, understanding the nature of perovskite catalysts and the reducibility of such materials is

necessary to establish a new way preparing several “metal on oxide” catalysts.

The goal of this report is to study the reducibility of some ground lanthanum cobaltates partially substituted by copper [8,13]. This is one of steps of our industrial project to develop a proper catalyst for the synthesis of higher alcohols from syngas [14].

### II - EXPERIMENTAL

Perovskite-type mixed oxides containing Co-Cu were synthesized by reactive grinding as described in detail in Refs. [2, 8, 13]. The chemical analysis (Fe, Co, Cu) of the perovskites was performed by atomic absorption spectroscopy using a Perkin-Elmer 1100B spectrometer. The specific surface area of all obtained samples was determined by nitrogen adsorption equilibrium at  $-196^\circ\text{C}$  using an automated gas sorption system (NOVA 2000; Quantachrome). Phase analysis and crystal domain size determination were performed by

powder X-ray diffraction (XRD) using a SIEMENS D5000 diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.54059$  nm). Bragg's angles between 15 and 75° were collected at a rate of 1°/min. Temperature programmed characterization was carried out using a flow system (RXM-100, Advanced Scientific Designs, Inc.). The reactor was connected to a TCD. Prior to each TPR analysis, a 40-80 mg sample was calcined at 500°C for 90 min under flowing 20% O<sub>2</sub>/He (20 ml/min, ramp 5°C/min). Then, the sample was cooled down to room temperature under flowing pure He (20 mL/min). H<sub>2</sub>-TPR of the catalysts was then carried out by ramping under 4.65vol% of H<sub>2</sub>/Ar (20 ml/min) from room temperature up to 800°C (5°C/min). The hydrogen consumption was determined using a TCD with a reference gas of same composition as the reducing gas (H<sub>2</sub>/Ar). For each TPO test, the reduced sample was performed by ramping under 20 mL/min O<sub>2</sub>/He (5 vol.%) from room temperature to 800°C (5°C/min). The effluent gas was passed through a cold trap (dry ice/ethanol) in order to remove water prior to detection.

### III - RESULTS AND DISCUSSION

#### 1. Chemical composition, surface area (BET) and X-ray diffraction (XRD)

Table 1 summarizes the main features of the perovskite samples in terms of crystal domains, surface area, and chemical composition. The presence of iron oxide contaminant is assumed to come from the mechano-synthesis (see Section 2) [8, 9]. It should be borne in mind that all ground perovskites usually have rather higher surface areas and are constituted of nanometric particles with diameters in the range of 9 - 12 nm [13]. Their particular morphology

would affect the physical properties and the catalytic activity [2, 8, 9, 13, 15].

As seen from table 1, the specific surface area is approximately 60 m<sup>2</sup>/g for the LaCoO<sub>3</sub> sample and gradually decreases upon Cu substitution, in good agreement with the previous results [8]. A declined surface area in the presence of copper species could be possibility that the ground La(Co,Cu)O<sub>3</sub> particles may be easily sintered by heating during calcination step because copper component is very sensitive to heating [9, 16].

The crystal phase analysis was performed by XRD. Figure 1 shows a main orthorhombic perovskite type structure for all LaCo<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub> samples. No clear diffraction lines corresponding to CuO was observed, suggesting that almost copper ions locate in the perovskite lattice or the formed particles of CuO were so tiny that they could not produce coherent X-ray diffraction (Fig. 1). Their small particles may cover the external surface and/or block some small slit-shaped spaces between nanoparticles, resulting in a decreased specific surface area (table 1) [9]. However, the presence of intra- and extra-perovskite lattice copper has different effects on the reducibility of Co<sup>3+</sup> [8, 16].

#### 2. Promotion of Cu<sup>2+</sup> on the reducibility of La(Co,Cu)O<sub>3</sub> perovskites

The introduction of copper into the perovskite lattice leads to the appearance some unusual physico-chemical properties of the solids. It is of interest to observe the influence of such ions at the B-position on the reducibility of Co<sup>3+</sup> in perovskite-type oxides and on the stability of the ground Co-Cu based samples under reducing conditions. Therefore, H<sub>2</sub>-TPR was run from room temperature to 800°C under hydrogen atmosphere.

Table 1: Properties of La(Co,Cu)O<sub>3</sub> mixed oxides

Samples	Surface area (m <sup>2</sup> /g)	Particle sizes (nm)	Calcination temperature (°C)	Chemical composition (wt.%)		
				Co	Cu	Fe
LaCoO <sub>3</sub>	59.6	9.8	250	21.15	-	4.69
LaCo <sub>0.85</sub> Cu <sub>0.15</sub> O <sub>3</sub>	43.7	9.3	120	19.84	3.97	-
LaCo <sub>0.70</sub> Cu <sub>0.30</sub> O <sub>3</sub>	22.3	9.9	250	16.77	5.79	1.21

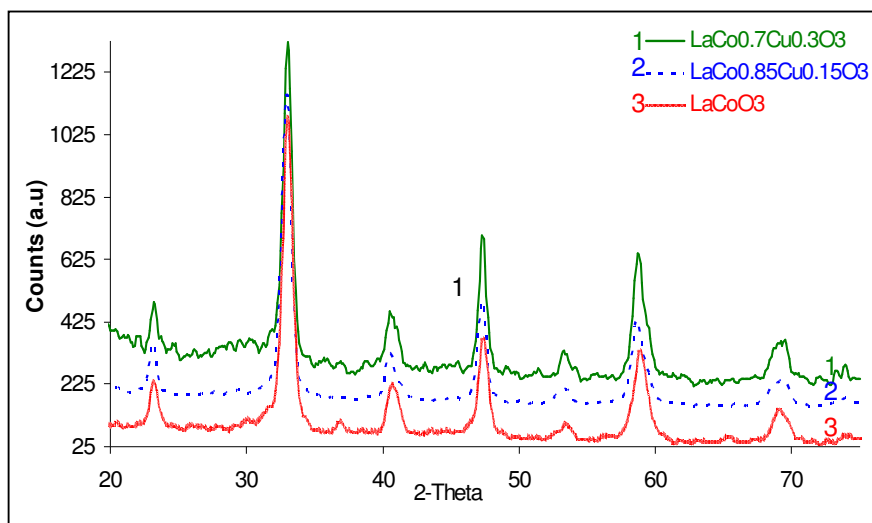


Figure 1: XRD patterns of  $\text{La}(\text{Co,Cu})\text{O}_3$

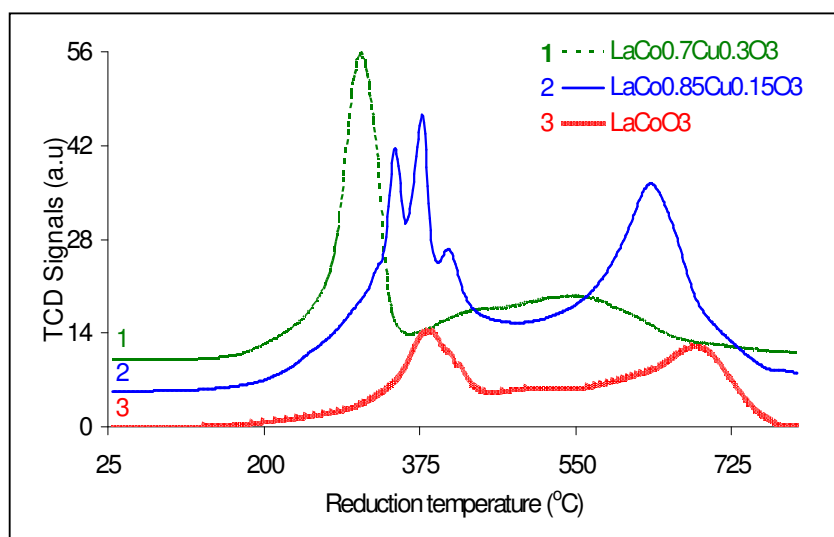


Figure 2: Temperature-programmed reduction profiles of  $\text{La}(\text{Co,Cu})\text{O}_3$

Figure 2 shows the comparative  $\text{H}_2$ -TPR spectra for all samples. In the absence of copper, the ground  $\text{LaCoO}_3$  perovskite shows two maximal temperatures around 390 and 690°C. According to the literature [1, 8 - 10], the lower temperature peak is ascribed to the reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  and the other is attributed to the further reduction of  $\text{Co}^{2+}$  to  $\text{Co}^0$ . Both these peaks display long tails in the lower temperature, implying that the catalyst surface

has many different surface  $\text{Co}^{3+}$  species. As reported in previous publications [8, 9, 13, 15], the  $\text{LaCoO}_3$  perovskites prepared by mechano-synthesis have higher surface area and a plentiful system of the grain boundaries. Cobalt ions in the grain boundaries or on the catalyst surface are reduced at a rather low temperature compared to those located in the bulk [9]. Indeed, calculation of  $\text{H}_2$ -consumption indicates a small amount of  $\text{Co}^0$  formed at the end of the

first reduction step (470°C). In order to identify the reduced species in the reduction steps,  $\text{LaCoO}_3$  sample was reduced at 550°C and then its XRD spectrum was collected. Figure 3 shows strong diffraction lines corresponding to the presence of  $\text{Co}^0$  (at  $2\theta = 44.2; 51.5^\circ$ ),  $\text{La}_2\text{O}_3$ , and perovskites. Under these reducing conditions, a part of  $\text{Co}^{3+}$  in  $\text{LaCoO}_3$  was presumably reduced to  $\text{Co}^0$  and finely dispersed on  $\text{LaCoO}_{3-x}$  without

destruction of the perovskite structure. This result suggests that the highly dispersed  $\text{Co}^0$  supported on  $\text{La}_2\text{O}_3$  or  $\text{LaCoO}_{3-x}$  matrix could be prepared by the isothermic reduction of  $\text{LaCoO}_3$  at a low temperature ( $< 500^\circ\text{C}$ ) [16]. The remaining cobalt ions in the  $\text{LaCoO}_{3-x}$  lattice are completely converted to metal at a higher temperature (690°C) following the collapse of the perovskite structure [15].

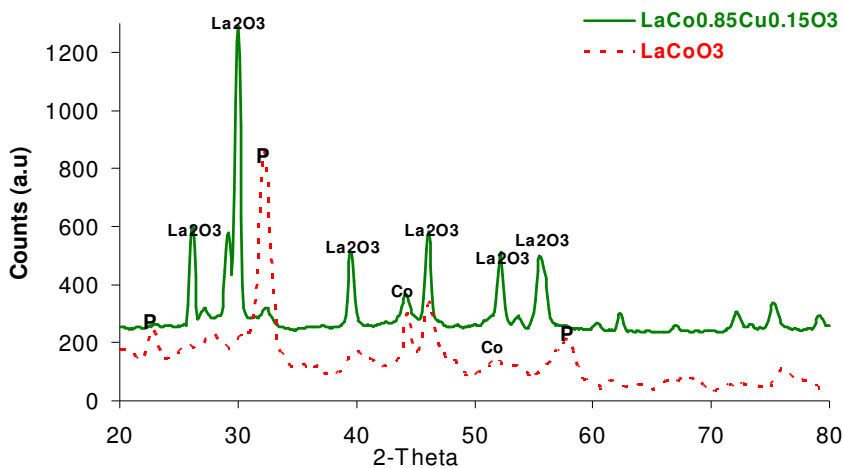


Figure 3: Power X-ray diffraction patterns of  $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$  after reduction at 550°C

For  $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$  samples,  $\text{H}_2$ -TPR curves reported in Fig. 2 displays several peaks, demonstrating the occurrence of a multiple-step reduction. The lower temperature peak at 340°C ascribed to the reduction of  $\text{Cu}^{2+}/\text{Cu}^0$  in the perovskite lattice is somewhat different from that in the extra-lattice copper ions ( $\text{CuO}/\text{LaCoO}_3$ ) which are previously reported in Refs. [8, 16]. Another peak at 380°C is assigned to the conversion of  $\text{Co}^{3+}$  in the lattice to  $\text{Co}^{2+}$ . In addition, the shoulder present at 410°C is attributed to the reduction of a small amount of  $\text{Co}_3\text{O}_4$  impurities.  $\text{H}_2$ -TPR profiles clearly indicate that the reduction temperature of the ground perovskites depends markedly on the catalyst composition. Indeed, as content of the intra lattice copper increases from  $x = 0.15$  to  $x = 0.3$ , the twin peaks at the lower temperature tends to incorporate, showing a main peak at 311°C. Meanwhile, the higher temperature peak becomes larger, ranging from 420 to 670°C (Fig.

2). Simultaneously, an increased copper content also leads to a significantly decreased reduction temperature. All the observed reduction peaks uniformly shift to lower temperatures with increasing amount of copper in the perovskite lattice [8]. These demonstrate that the cobalt species in the  $\text{La}(\text{Co,Cu})\text{O}_3$  framework are more reducible than those in the free-copper sample. It is well known that the addition of a noble metal to a mixed cobalt oxide leads to the enhancement of the reducibility of cobalt ions via “hydrogen spillover” effect [8, 11, 17]. In the present study, the reduced copper has a promotion to the reduction of cobalt ions, apparently by providing hydrogen dissociation sites [8, 11]. Indeed, a metallic copper site can adsorb and dissociate from hydrogen molecule to atom. Because of a close distance between cobalt and copper atom in the perovskite framework, the dissociated hydrogen on a copper site can easily react with cobalt ions,

resulting in a declined reduction temperature of cobalt species and preventing the sintering of metallic cobalt in the reduced phase. Moreover, the substitution of  $\text{Co}^{3+}$  ( $r_{\text{Co}} = 0.75 \text{ \AA}$ ) by  $\text{Cu}^{2+}$  ( $r_{\text{Cu}} = 0.73 \text{ \AA}$ ) gives rise to a distorted orthorhombic structure of perovskite and yields more oxygen vacancies [8, 19]. Subsequently, the ground  $\text{La}(\text{Co,Cu})\text{O}_3$  perovskites are less stable than the free-copper sample under reduction conditions. Figure 3 shows the XRD spectrum of the representative Co-Cu based sample  $\text{LaCo}_{0.85}\text{Cu}_{0.15}\text{O}_5$  reduced at  $550^\circ\text{C}$ . No diffraction lines characterizing to the  $\text{La}(\text{Co,Cu})\text{O}_3$  perovskite structure are observed instead of those corresponding to the  $\text{La}_2\text{O}_3$  and Co phases. Although 15% of cobalt is replaced by copper, no reflections of  $\text{Cu}^0$  are detected after reduction pretreatment. This can be explained by the possibility that the reduced metallic copper was so highly dispersed in the resulting matrix of  $\text{La}_2\text{O}_3$  that it was not detectable by using X-Ray technique [8 - 10]. Therefore, both Cu and Co metals in the position B could remain in a high degree of dispersion on a matrix of the  $\text{La}_2\text{O}_3$  oxide after reduction pretreatment. This may be a promising methodology for preparation of highly active bimetallic catalysts by the reduction of La-Co-

Cu perovskites under tailored conditions [8 - 10, 15].

### 3. Temperature-Programmed Oxidation ( $\text{O}_2$ -TPO) of the reduced $\text{La}(\text{Co,Cu})\text{O}_3$

$\text{H}_2$ -TPR results show that all Co-Cu based perovskites are less thermal stability in reducing conditions in comparison with the copper free-sample. In order to investigate the stability of such systems towards gas phase oxygen, the reduced catalysts were re-oxidized under flowrate of 5 vol%  $\text{O}_2/\text{Ar}$  heating from 25 to  $500^\circ\text{C}$  at a rate of 5 K/min. As illustrated in Fig. 4,  $\text{O}_2$ -TPO spectra display a broad peak below  $300^\circ\text{C}$  for  $\text{La}(\text{Co,Cu})\text{O}_3$  samples. A higher oxidation temperature peak for the copper free-sample is observed. Clearly, the presence of copper in perovskite lattice facilitates the oxidation of the reduced cobalt species. The co-existence of a dual site of Cu-Co leads to the prevention of the growth of larger individual metal particles and an increased dispersion of the reduced cobalt species. Figure 4 also shows that the oxidation process of all samples starts at rather low temperatures ( $85^\circ\text{C}$ ), demonstrating that the high metal surface area of the reduced (Co,Cu) species.

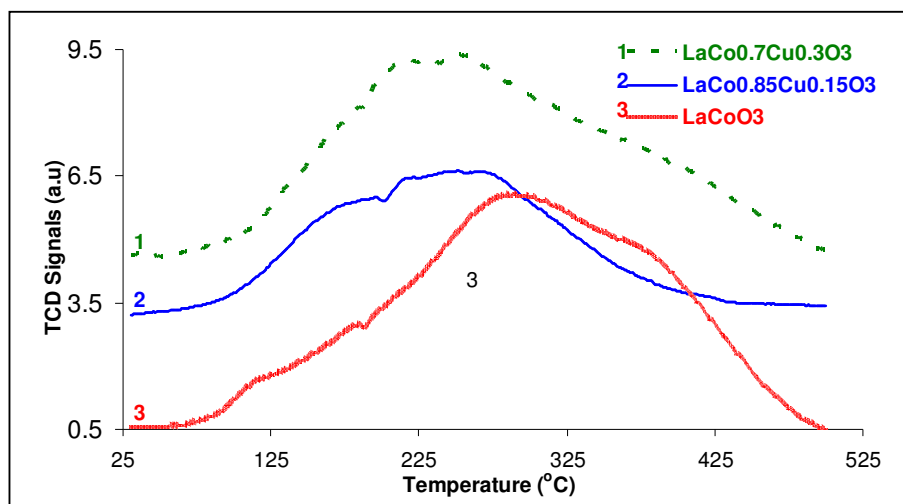


Figure 4: Temperature-programmed oxidation profiles of the ground  $\text{La}(\text{Co,Cu})\text{O}_3$  reduced at  $800^\circ\text{C}$

In the temperature range of 125 - 425°C, both Co and Cu are only oxidized to CuO and Co<sub>3</sub>O<sub>4</sub> [1, 18]. The further oxidation step forming perovskites La(Co,Cu)O<sub>3</sub> are required at a higher temperature [9, 15, 19].

#### IV - CONCLUSION

A set of nanocrystalline perovskites prepared by the reactive grinding method has a rather high specific surface area. The reducibility of such materials is investigated under hydrogen atmosphere. H<sub>2</sub>-TPR results indicate that various Co<sup>3+</sup> ions present in the crystalline structure and in the grain boundaries of LaCoO<sub>3</sub> are reduced at different reduction temperatures. The reduction of the ground LaCoO<sub>3</sub> occurs in two consecutive steps (Co<sup>3+</sup>/Co<sup>2+</sup> and Co<sup>2+</sup>/Co<sup>0</sup>). An introduction of copper into the LaCoO<sub>3</sub> perovskite lattice has a promotional effect on the reducibility of cobalt and the thermal stability of perovskites. In the presence of neighboring copper, cobalt species in the perovskite lattice are reduced at a lower temperature and its dispersion significantly increases after reduction pretreatment. These findings may lead to a new way to prepare several active catalysts containing homogeneously dispersed transition metals over the rare earth sesquioxide supports.

**Acknowledgements:** *Financial support of NSERC and Nanox Inc. (Québec, Canada) through its industrial chair program is gratefully acknowledged.*

#### REFERENCES

1. M. A. Pena and J. L. G. Fierro. Chem. Rev., 101, 1981-2017 (2001).
2. V. Szabo, M. Bassir, A. Van Neste, S. Kaliaguine. Appl. Catal. B, 43, 81 - 92 (2003).
3. T. Hirano, H. Purwanto, T. Watanabe and T. Akiyama. J. Alloys Compd., 441, 263 - 266 (2007).
4. T. Vaz and A.V. Salker, Mater. Sci. Eng. B, 143, 81 - 84 (2007).
5. V. R. Choudhary, K. C. Mondal, A. S. Mamman, and U. A. Joshi. Catal. Letters, 100, 271 - 276 (2005).
6. J. O. Petunchi, M. A. Ulla, J. A. Marcos, and E. A. Lombardo. J. Catal., 70, 356 - 363 (1981).
7. L. Bedel, A.C. Roger, C. Estournes, A. Kiennemann, Catal. Today, 85, 207 - 218 (2003).
8. N. Tien-Thao, H. Alamdari, M. H. Zahedi-Niaki, S. Kaliaguine. Appl. Catal. A 311, 204-212 (2006).
9. N. Tien-Thao, M. H. Zahedi-Niaki, H. Alamdari, S. Kaliaguine. J. Catal., 245, 348 - 357 (2007).
10. J. L. G. Fierro, M. A. Pena, L. G. Tejuca. J. Mater. Sci. 23 (1988) 1018-1023.
11. X. Xiaoding, E. B. M. Doesburg and J. J. F. Scholten, Catal. Today 2, 125 - 170 (1987).
12. J. O. Petunchi, J. L. Nicastro and E. A. Lombardo, J. C. S. Chem. Comm., 467 - 468 (1980).
13. S. Kaliaguine, A. V. Neste, V. Szabo, J. E. Gallot, M. Bassir and R. Muzychuk. Appl. Catal. A 209, 345 - 358 (2001).
14. S. Kaliaguine, G. Xu, Literature Search for Higher Alcohol Synthesis, Centre des Technologies du Gaz Naturel, Boucherville (2000).
15. N. Tien-Thao, M.H. Zahedi-Niaki, H. Alamdari, S. Kaliaguine, Appl. Catal. A, 326, 152 - 163 (2007).
16. N. Tien-Thao, M. H. Zahedi-Niaki, H. Alamdari, S. Kaliaguine. Int. J. React. Chem. Eng., 5, A82 (2007).
17. N. W. Hurst, S. J. Gentry, A. Jones, B. D. McNicol. Catal. Rev. Sci. Eng., 24, 233 - 309 (1982).
18. V. Ramaswamy, P. Awati, A. K. Tyagi. J. Alloy Comp., 364, 180 - 185 (2004).
19. R. Lago, G. Bini, M. A. Pena and J. L. G. Fierro, J. Catal., 167, 198 - 209 (1997).