

Using the reduced $\text{La}(\text{Co,Cu})\text{O}_3$ nanoperovskites as catalyst precursors for CO hydrogenation

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Abstract. A series of ground $\text{La}(\text{Co,Cu})\text{O}_3$ perovskite-type mixed oxides prepared by reactive grinding has been characterized by X-Ray diffraction (XRD), BET, H_2 -TPR, O_2 -TPD, and CO disproportionation. All ground samples show a rather high specific surface area and nanometric particles. The solids were pretreated under H_2 atmosphere to provide a finely dispersed Co-Cu phase which is active for the hydrogenation of CO. The reduced perovskite precursors produced a mixture of higher alcohols and hydrocarbons from syngas following an ASF distribution.

Keywords: perovskite; Co-Cu metals; syngas; alcohol synthesis.

1. Introduction

Perovskites are mixed oxides with the general formula ABO_3 . In theory, the ideal perovskite structure is cubic with the space-group $\text{Pm}\bar{3}\text{m-Oh}$ [1]. The structure can be visualized by positioning the A cation at the body center of the cubic cell, the transition-metal cation (B) at the cube corners, and the oxygen at the midpoint of the cube edges. In this structure, the transition-metal cation is therefore 6-fold coordinated and the A-cation is 12-fold coordinated with the oxygen ions. Moreover, each of the A and B positions could be partially replaced by another element to prepare a variety of derivatives [1,2]. For example, a partial substitution of La in

lanthanum-cobaltate by either Sr or Th has remarkably affected the rate of carbon dioxide hydrogenation [3] and methane oxidation [4].

The substitution of the cation at A-position, however, is much less attractive than that at B-site due to the usual lack of activity of the A cation. Meanwhile, the introduction of another transition metal into perovskite lattice could therefore produce several supported bimetallic catalysts upon controlled reductions [5-8]. Bedel et al. [5], for instance, obtained a Fe-Co alloy after reduction of $\text{LaFe}_{0.75}\text{Co}_{0.25}\text{O}_3$ orthorhombic perovskite at 600°C . Lima and Assaf [8] found that the partial substitution of Ni by Fe in the perovskite lattice leads to a decreased reduction temperature of Fe^{3+} ions and the formation of Ni-Fe alloy. The presence of alloys can, moreover, modify the metal particles on the catalyst surface and the possible dilution of the active nickel sites. By this way,

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the reduction-oxidation cycles of perovskites under tailored conditions could produce active transition metals dispersed on an oxide (Ln_2O_3) matrix [5,7,8]. This characteristic may be used for a promising pathway of development of a finely dispersed metal catalyst from perovskite precursors.

In several previous contributions [7,9-11], we have reported some novel characteristics of lanthanum-cobaltates prepared by reactive grinding. This article is to further prepare well-homogenized supported Co-Cu metals for the conversion of syngas to higher alcohols and hydrocarbons.

2. Experimental

2.1. Materials

$\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$ perovskite-type mixed oxides were synthesized by the reactive grinding method also designated as mechano-synthesis in literature [9-11]. In brief, the stoichiometric proportions of commercial lanthanum, copper, and cobalt oxides (99%, Aldrich) were mixed together with three hardened steel balls (diameter = 11 mm) in a hardened steel crucible (50 ml). A SPEX high energy ball mill working at 1000 rpm was used for mechano-synthesis for 8 hours. Then, the resulting powder was mixed to 50% sodium chloride (99.9%) and further milled for 12 hours before washing the additives with distilled water. The slurry was dried in oven at 60-80°C before calcination at 250°C for 150 min.

A reference sample, $\text{LaCoO}_3 + 5.0 \text{ wt\% Cu}_2\text{O}$, was prepared by grinding a mixture of the ground perovskite LaCoO_3 having a specific surface area of 43 m^2/g with Cu_2O oxide (10:1 molar ratio) at ambient temperature without any

grinding additive before drying at 120°C overnight in oven.

2.2. Characterization

The chemical analysis (Co, Cu, Fe) of the perovskites and the residual impurities was performed by AAS using a Perkin-Elmer 1100B spectrometer. The specific surface area (S_{BET}) of all obtained samples was determined from nitrogen adsorption equilibrium isotherms at -196°C measured using an automated gas sorption system (NOVA 2000; Quantachrome). Phase analysis and particle size determination were performed by powder X-ray diffraction (XRD) using a SIEMENS D5000 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54059 \text{ nm}$).

Temperature programmed characterization (TPR, TPD, CO dissociation) was examined using a multifunctional catalyst testing (RXM-100 from Advanced Scientific Designs, Inc.). Prior to each test analysis, a 50 mg sample was calcined at 500°C for 90 min under flowing 20% O_2/He (20 ml/min, ramp 5°C/min). The sample was then cooled down to room temperature under flowing pure He (20 mL/min). TPR of the catalyst was then carried out by ramping under 4.65vol% of H_2/Ar (20 ml/min) from room temperature up 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. For TPD analysis, the O_2 -TPD conditions were 20 ml/min He, temperature from 25 to 900°C (5°C/min). The m/z signals of 18, 28, 32, 44 were collected using the mass spectrometer. For each CO disproportionation tests, a number of CO/He (0.586 vol%) pulses (0.25 mL) were then injected and passed through the reactor prior to reach to a quadrupole mass spectrometer (UTI

100). The m/z signals of 18, 28, 32, and 44 were collected.

2.3. Catalytic performance

The catalytic tests were carried out in a stainless-steel continuous flow fixed-bed micro-reactor (BTRS –Jr PC, Autoclave Engineers). Catalysts were pretreated *in situ* under flowing 5 vol% of H_2/Ar (20 ml/min) at 250°C (3h) and 500°C (3h) with a ramp of 2°C/min. Then, the reactor was cooled down to the reaction temperature while pressure was increased to 1000 psi by feeding the reaction mixture. The products were analyzed using a gas chromatograph equipped with two capillary columns and an automated online gas sampling valve maintained at 170°C. CO and CO_2 were separated using a capillary column (CarboxenTM 1006 PLOT, 30m x 0.53mm) connected to the TCD. Quantitative analysis of all organic products was carried out using the second

capillary column (Wcot fused silica, 60m x 0.53mm, Coating Cp-Sil 5CB, DF = 5.00 μ m) connected to a FID (Varian CP – 3800) and mass spectrometer (Varian Saturn 2200 GC/MS/MS). The selectivity to a given product is defined as its weight percent with respect to all products excluding CO_2 and water. Productivity is defined here as a weight (mg) product per gram of catalyst per hour.

3. Results and discussion

3.1. Physico-chemical properties

Table 1 collects the chemical composition and some physical properties of all the ground perovskites. The specific surface area is rather higher (16-60 m^2/g) because of the low synthesis temperature ($\sim 40^\circ C$), which allows to avoid the agglomeration of perovskite particles [7.11].

Table 1. Physical properties of ground $La(Cu,Cu)O_3$ perovskites

Samples	S_{BET} (m^2/g)	Crystal (nm) ^a	domain	Composition (wt.%)			
				Na ⁺	Co	Cu	Fe ^b
$LaCoO_3$	59.6	9.8		0.53	21.15	-	4.69
$LaCo_{0.9}Cu_{0.1}O_3$	19.5	9.7		0.31	19.31	1.89	1.12
$LaCo_{0.7}Cu_{0.3}O_3$	22.3	9.9		0.17	16.77	5.79	1.21
$LaCo_{0.5}Cu_{0.5}O_3$	10.6	9.2		0.44	10.60	9.96	0.64
$Cu_2O/LaCoO_3$	16.8	10.9		0.39	20.04	3.28	4.78

^a Estimated from the Scherrer equation from X-ray line broadening; ^b Iron impurity from mechano-synthesis.

As mentioned in experimental Section, the addition of a grinding additive (NaCl) during the last milling step leads to the partial separation of the crystal domains, making a significant change in surface-to-volume ratio and in the internal porosity of elementary nanometric particles [10,11]. Consequently, the surface area of such perovskites significantly increases [10]. It seems that the presence of copper in the perovskite lattice leads to a decreased surface area of $LaCoO_3$. Indeed, the

surface area (S_{BET}) of all Cu-based perovskites ($x < 0.3$) and the mixed oxides ($Cu_2O/LaCoO_3$) is much lower than that of the copper-free sample ($LaCoO_3$) [6,7,11,12]. The X-ray diffraction patterns are shown in Fig. 1. Their diffractograms indicate that all La-Co-Cu samples are essentially perovskite-type mixed oxides. The perovskite reflection lines are broadening, implying the formation of a nanophase. Indeed, the crystal domains of the ground perovskites calculated by the Scherrer

equation from X-ray line broadening are in the range of 9-10 nm (Table 1), in good agreement with the results reported previously [9,12,13]. Although all ground samples always contain a small amount of iron oxide impurities, no FeO_x species are detected by XRD (Table 1 and Fig. 1). For sample $\text{Cu}_2\text{O}/\text{LaCoO}_3$, it is clearly

observed that two strong reflection lines at 36.8° and 42.7° characterize the presence of Cu_2O (Fig. 1). This indicates that copper ions locate out of the perovskite lattice although a small amount of such oxides presented in the framework is not ruled out [13].

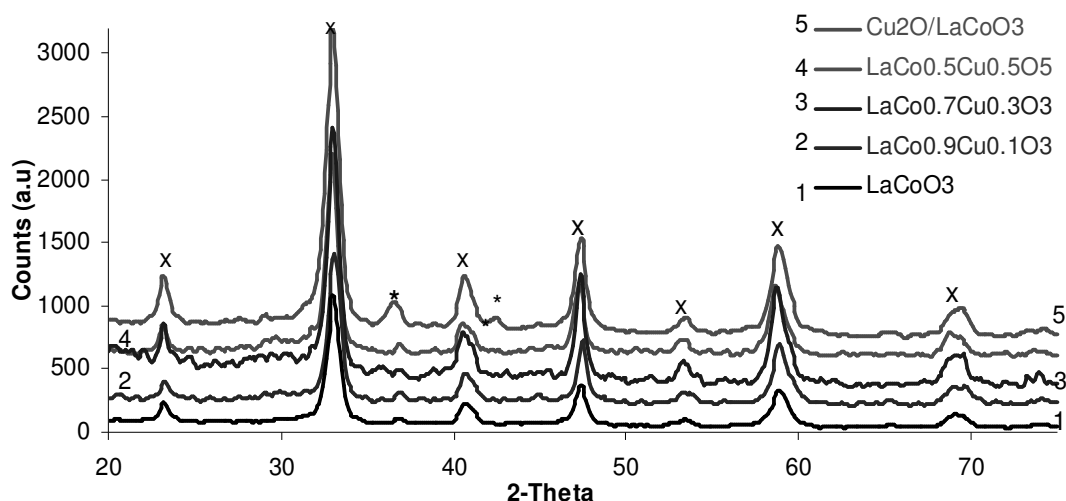


Fig. 1. XRD patterns (Perovskite: x; CuO : *).

3.2. Temperature-programmed reduction of hydrogen (H_2 -TPR)

The reducibility of La-Co-Cu perovskites was examined by performance of H_2 -TPR tests. Figure 2 shows H_2 -TPR profiles of all samples. For the free-copper sample, two main peaks were observed. According to the calculation of H_2 balance, the signal at around 390°C is attributed to the reduction of Co^{3+} to Co^{2+} . The other peak at a higher temperature (680°C) describes the complete reduction of Co^{2+} to Co^0 [7,13]. A similar curve of H_2 -TPR for La-Co-Cu perovskites is observed (Fig. 2). An increased content of copper in the perovskite lattice ($x = 0-0.3$) results in a substantially

decreased reduction temperature. A sharper peak at lower temperatures is ascribed to the simultaneous reduction of both Co^{3+} and Cu^{2+} to Co^{2+} and Cu^0 , respectively [6,7,12,13]. At this step, the perovskite framework is assumed to be still preserved, but the structure is strongly modified [7,13]. The reduced metallic copper and Co^{2+} species are suggested to be atomically dispersed in the perovskite at the end of the first reduction temperature peak. The presence of metallic copper has a promotion to the reducibility of cobalt ions, resulting in a decreased reduction temperature of $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Co}^{2+}/\text{Co}^0$.

The higher peak is essentially responsible for the reduction of the remaining Co^{2+} to Co^0 .

XRD spectra of the reduced Co-Cu based perovskites (not shown here) show the appearance of signals of Cu and Co metals after reduction at 375 and 450°C [7]. A similar profile in H_2 -TPR between sample $LaCo_{0.5}Cu_{0.5}O_3$ and $Cu_2O/LaCoO_3$ is observed,

indicating that at a higher copper content ($x = 0.5$), a remarkable amount of copper oxides exists out of the perovskite lattice. Their oxides are so highly dispersed in the grinding $La(Co,Cu)O_3$ that they could not be detected by XRD techniques.

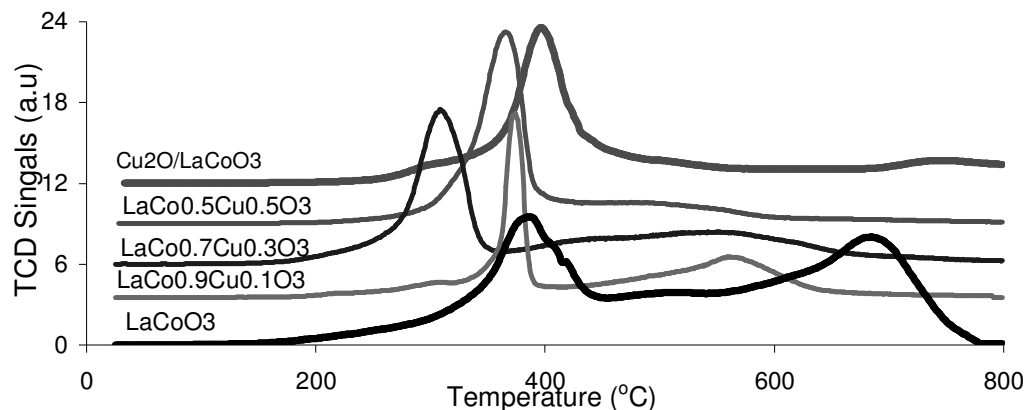


Fig. 2. H_2 -TPR profiles of the ground perovskites.

3.3. Temperature-programmed desorption of oxygen (O_2 -TPD)

TPD of O_2 over all samples was investigated in order to shed light on the reduction-oxidation properties of Co-Cu based samples. O_2 -TPD spectra show two typical peaks with a strong shoulder at a high temperature for Co-Cu based perovskites. In the case of the free-copper catalysts, a large peak with a long tail at a lower temperature of oxygen desorption is observed in the broad temperature range of 400-650°C as depicted in Fig. 3. The lower temperature peak, namely preferred to as α -oxygen, is attributed to oxygen species weakly bound to the surface of the perovskite-type rare-earth cobaltate. This peak is very broad, indicating that the oxygen released at low temperatures is adsorbed on several different sites of the catalyst surface [9]. For Cu-based perovskites, this peak slightly

shifts to a lower temperature and becomes sharper with increasing copper content. The oxygen desorption signal (β -oxygen) appeared at a higher temperature (650-820°C) is ascribed to the liberation of oxygen in the lattice. It is noted that this peak of the non-substituted $LaCoO_3$ has the maximum at 785°C while that of the Co-Cu based perovskites shows the maximum at a lower temperature with a shoulder approximately at 670-680°C (Fig. 3). The shoulder of the second peak is believed to the reduction of Cu^{2+} to Cu^+ in harmony with increasing its intensities with the amount of the intra-lattice copper [6,14]. In addition, the other peak is firmly designated as to the difficult reduction of Co^{3+} to Co^{2+} in lattice. An increased amount of α -oxygen desorbing from $LaCo_{1-x}Cu_xO_3$ suggests that Cu substitution leads to the production of more oxygen vacancies and the therefore facilitation of the reducibility of Co^{3+} .

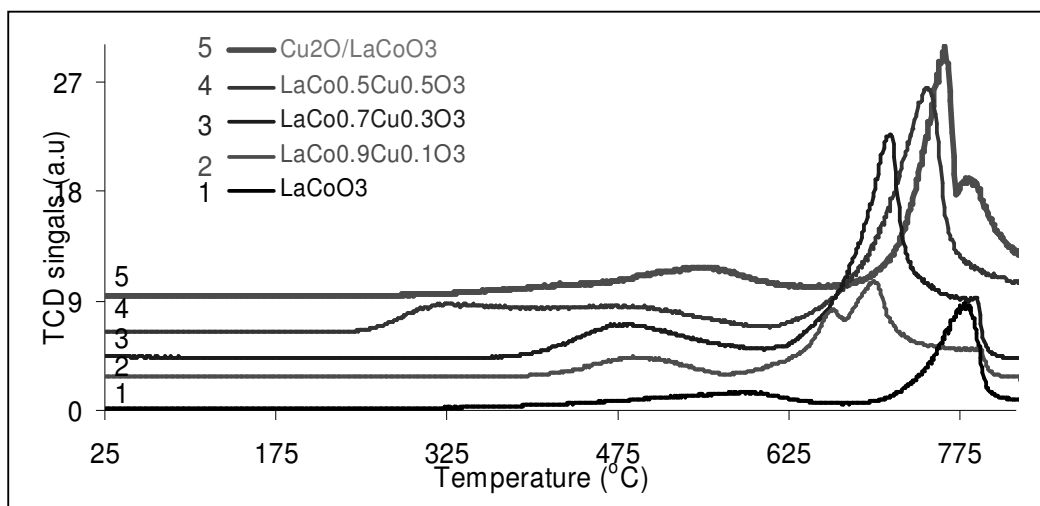
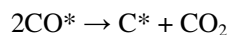


Fig. 3. O₂-TPD profiles of the ground perovskites.

3.4. CO Disproportionation

CO dissociation was investigated in order to foresee the reactivity of the partially reduced perovskite precursors in the synthesis of higher alcohols from syngas [7,13,14]. The ability to dissociation of carbon monoxide has been proposed according to the Boudouard reaction [5,13].



Here the asterisk (*) implies the chemisorbed species on the reduced catalyst surface. Figure 4 displays a relationship between CO conversion and the number of pulses at 275°C for a series of the reduced samples. It is clearly observed that the presence of the intra-lattice copper results in a significant decline in CO conversion.

The conversion of CO disproportionation on Cu₂O/LaCoO₃ sample is higher than that on

La-Co-Cu based samples, but still slightly lower than the one on the free-copper perovskite (LaCoO₃). This indicates the significant different effects between extra- and intra- perovskite lattice copper on the ability of cobalt sites to dissociate the CO molecule. When copper incorporates into the perovskite structure, it has a strong interaction with the intra-lattice cobalts, giving rise to a remarkable decrease of CO chemisorbed on Co atoms at 275°C. This is consistent with the results of H₂-TPR and O₂-TPD (Figs. 2-3). In contrast, the presence of extra-lattice copper has an insignificant effect on the activity of cobalt in the dissociation of CO because of both copper and cobalt in such case assumed to exist as two individual sites after reduction. Therefore, a close distance between cobalt and copper site affects the ability of the metals to the disproportionation of CO. This is a prerequisite for higher alcohol synthesis catalyst [15].

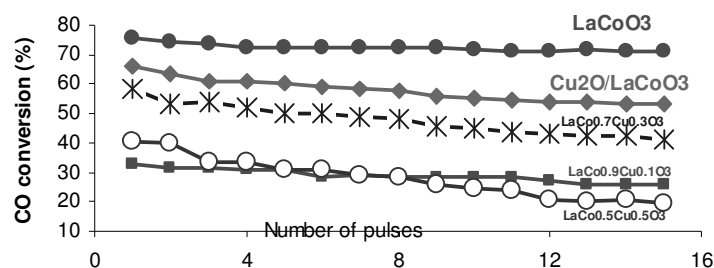


Fig. 4. CO disproportionation on the reduced La(Co,Cu)O₃ samples at 275°C.

3.5. Synthesis of higher alcohols from syngas

Synthesis of higher alcohols from syngas has been performed at 250-375°C under 1000 psi and velocity = 5000 h⁻¹ (H₂/CO/He = 8/4/3) over the reduced La(Co,Cu)O₃ perovskites. A mixture of products is composed of linear primary monoalcohols (C₁OH -C₇OH) and paraffins (C₁-C₁₁). The activity is defined as a micromole of CO per gram of catalyst per hour is presented in Figure 5. From this Figure, it is observed that the activity in CO hydrogenation increases with increasing copper content to x = 0.3. The conversion on sample LaCo_{0.5}Cu_{0.5}O₃ is very close to that on the blend of Cu₂O and LaCoO₃, indicating a similar catalytic behavior of the two samples. Therefore, both the selectivity and productivity of alcohols over sample LaCo_{0.5}Cu_{0.5}O₃ are much lower than those of the LaCo_{0.7}Cu_{0.3}O₃ perovskite although

copper content of the former is much higher (Table 1 and Figs 6-7). The general consensus in literature is that a mixed Co-Cu based catalyst is active for the synthesis of higher alcohols from syngas as a distance of a metallic copper atom from a cobalt site is within atomic. Consequently, the requirement for the perovskite precursor is therefore that Cu²⁺ should be in the La(Co,Cu)O₃ framework and a homogeneous distribution of the two Co-Cu active sites is reached after pretreatment under hydrogen atmosphere [11,15]. Metallic cobalt is widely known as a good Fischer-Tropsch catalyst because it shows very high activity in the appropriately dissociative adsorption of CO molecules, the propagation of carbon chain, and the production of methane when exposed to synthesis gas [7,15].

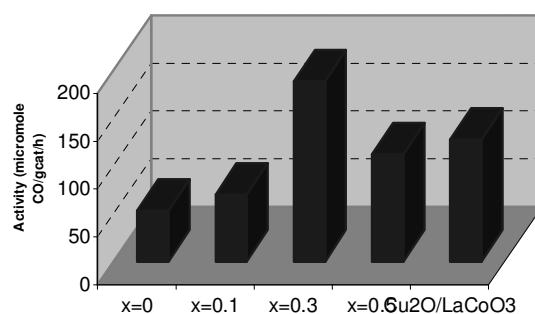


Fig. 5. The correlation between copper content (x = 0 - 0.5) and the activity in alcohol synthesis at 275°C, 1000 psi, 5000 h⁻¹, H₂/CO/He = 8/4/3.

The appearance of a neighboring copper leads to a substantial decrease in cobalt reactivity in CO hydrogenation. The coexistence of such dual sites results in the

formation of a mixture of alcohols and hydrocarbons instead of paraffins only. Indeed, Figure 6 shows a variation in the selectivity to products with copper content at 275°C.

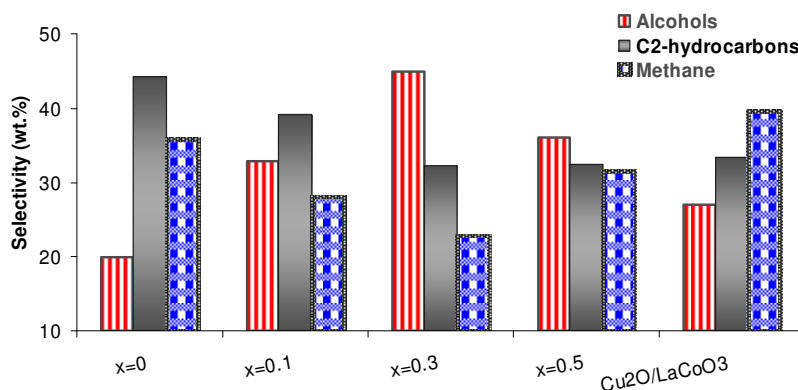


Fig. 6. The correlation between copper content ($x = 0-0.5$) and alcohol selectivity.

This Figure shows an increased alcohol selectivity with increasing amount of intra-lattice copper perovskite from $x = 0$ to $x = 0.3$. Meanwhile, total hydrocarbon selectivity displays an opposite trend. Therefore, the presence of intra-lattice copper promotes the yield of alcohols and suppresses the formation of methane, leading to an increased productivity of alcohols as illustrated in Fig. 7. Indeed, copper is a typical methanol catalyst [16]. Its

ability is to dissociate hydrogen molecule and to adsorb CO molecule without dissociation. Under alcohol synthesis conditions, the adsorbed CO species are inserted in the alkyl chain group bound to a neighboring cobalt site in order to yield an alcohol precursor. This process is indeed facilitated if both cobalt and copper sites are very proximate. In other words, these two ions should be present in the perovskite lattice.

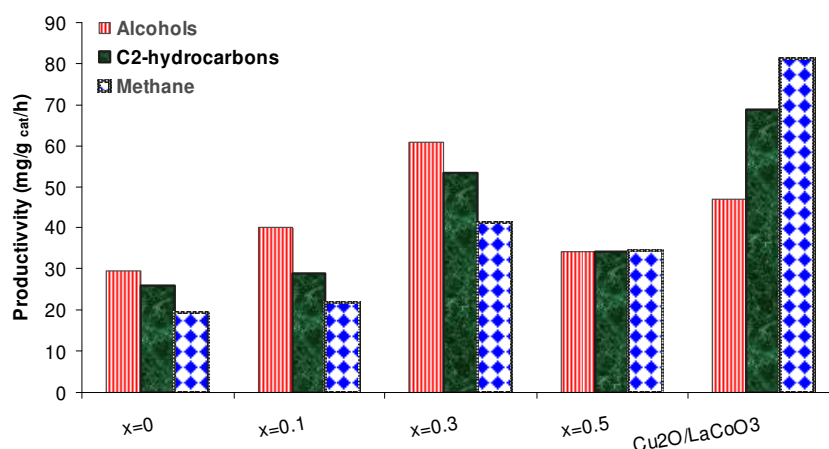


Fig. 7. The correlation between copper content ($x = 0-0.5$) and alcohol productivity.

This suggestion is substantiated as we estimate the distribution of products. Figure 8 shows Anderson-Chulz-Flory (ASF) carbon number distributions at 275°C of products obtained on the representative sample $\text{LaCo}_{0.7}\text{Cu}_{0.3}\text{O}_3$. As seen from this Figure, all products are in good agreement with an ASF distribution. The alpha values of all samples calculated from ASF plots are about 0.35-0.45. In essence, the carbon chain growth probability factor of higher alcohols (α_1) should be very close to that of hydrocarbons (α_3), owing to the assumption that the carbon skeleton of these two homolog series is formed on the same active site [15]. However, Figure 8 presents a small difference in the propagation constants between higher alcohols ($\alpha_1 = 0.38$) and hydrocarbons ($\alpha_3 = 0.43$). To compare with the

alpha value of hydrocarbons, the second carbon chain growth probability factor (α_2) of higher alcohols was calculated without methanol point because methanol is usually overproduced during the synthesis of higher alcohols from syngas [7,15-17]. This may be also associated with the role of extra- perovskite lattice copper which can form methanol in the absence of a neighboring cobalt site [7,17]. As seen from Fig. 8, when the point of methanol ($n = 1$) is excluded in the alcohol molecular distribution, a close resemblance between the two slopes of alcohol and hydrocarbon plots is clearly observed, indicating that the reaction pathway likely occurs through sequential addition of CH_x intermediate species in to the carbon chain for the propagation [14].

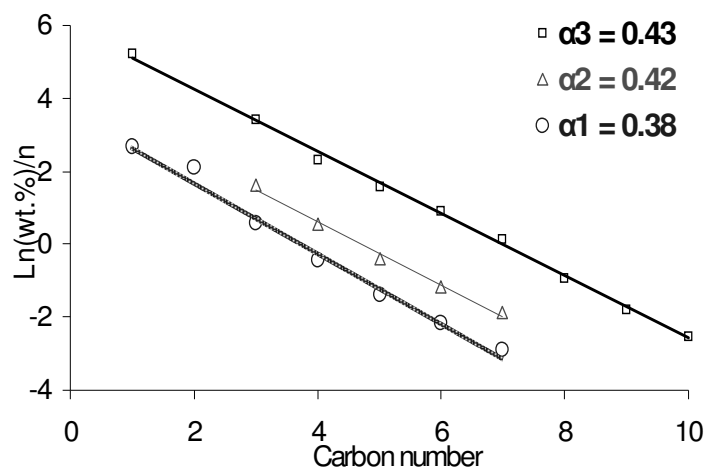


Fig. 8. ASF distribution of products over sample $\text{LaCo}_{0.7}\text{Cu}_{0.3}\text{O}_3$ ($\alpha_1 = \text{C}_1\text{OH}-\text{C}_7\text{OH}$; $\alpha_2 = \text{C}_2\text{OH}-\text{C}_7\text{OH}$; $\alpha_3 = \text{C}_1-\text{C}_{10}$ hydrocarbons)

4. Conclusion

A set of nanocrystalline $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$ perovskites has been prepared using reactive grinding method. All samples have a rather high surface area and comprise elementary

nanoparticles. At $x > 0.3$, a blend of oxides is obtained instead of a perovskites phase only. The presence of copper has a strong effect on the reducibility of perovskite and on the reactivity of cobalt in CO hydrogenation. A highly dispersed bimetallic phase is obtained

after reduction of the Co-Cu based perovskites under hydrogen atmosphere. The reduced perovskite precursors are rather active for the conversion of syngas to oxygenated products. The selectivity to alcohols is about 20-45 wt% and the productivity ranges from 30 to 60.9 mg/g_{cat}/h under these experimental conditions. The distribution of both alcohols (C₁OH-C₇OH) and hydrocarbons (C₁-C₁₀) is good consistent with an ASF distribution with the carbon chain growth probability factors of 0.35-0.45. Copper in the perovskite structure plays an important role in the synthesis of higher alcohols. The intra-lattice copper is found to promote the formation of alcohols and to suppress the production of methane.

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Tính chất xúc tác của các perovskit $\text{La}(\text{Co,Cu})\text{O}_3$ ở trạng thái khử trong phản ứng hidro hóa CO

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Các đặc trưng của họ xúc tác perovskite $\text{La}(\text{Co,Cu})\text{O}_3$ được tổng hợp bằng phương pháp nghiền hoạt hóa được xác định bằng các phương pháp như: X-ray, BET, khử bằng H_2 theo chương trình nhiệt độ (TPR- H_2), deoxy bằng chương trình nhiệt độ (TPD- O_2), phân bố bất đối xứng CO. Các mẫu xúc tác có cấu hình từ các hạt nano và có diện tích bề mặt riêng khá lớn. Khử hóa học bằng hidro thu được Co, Cu kim loại phân tán tốt trên chất mang La_2O_3 . Pha Co-Cu kim loại được sử dụng làm xúc tác cho phản ứng hydro hóa CO, tạo ra 1 hỗn hợp các alcol và hydrocacbon tuân theo quy luật phân bố ASF.