

Synthesis and activity tests of nano Perovskite catalysts for CO combustion

Bahman Seyfi¹, Morteza Baghalha²

Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran
baghalha@sharif.edu

ABSTRACT

Modified perovskite-type oxides were synthesized based on two different methods, namely co-precipitation and conventional citrate. The synthesized perovskite materials had the nominal compositions of LaCoO_3 , $\text{LaCo}_{0.8}\text{Cu}_{0.2}\text{O}_3$, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Cu}_{0.2}\text{O}_3$, $\text{La}_{0.8}\text{M}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (where $\text{M} = \text{Ce}$ and Sr). The catalytic activity of perovskite samples toward CO combustion were measured using a gas mixture containing $\text{N}_2/\text{O}_2/\text{CO}$ in the following proportions 97/1/2. The prepared perovskite samples were characterized by SEM, nitrogen adsorption (BET), XRF and XRD analyses. All the catalysts displayed good stability above 600°C and a high activity toward CO combustion. Our novel proposed perovskite composition, namely $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Cu}_{0.2}\text{O}_3$ showed the highest activity for achieving CO conversion above 80%. While homogeneous gas-phase combustion of CO requires temperatures in excess of 700°C to achieve fair kinetics, our novel catalyst sample achieved 100% CO combustion at 355°C .

Keywords: Combustion; Perovskite; catalyst; CO; lanthanum; cobalt; activity

1. Introduction

The removal of carbon monoxide from automotive exhaust gas is performed through catalytic converters. These devices consist of ceramic substrates impregnated with Pt, Pd and other platinum group metals (PGM), as active catalytic sites [1,2]. However, due to the rising cost of PGM, many researchers are searching for alternative materials as active catalytic phase. One of these materials is Perovskite crystal (ABO_3), where A and B are cations of different sizes (for example, LaMnO_3). To have high catalytic properties, at least one of the cations in perovskite crystal is selected from transition metals such as cobalt or nickel [3, 4]. A ions can also be a rare earth, alkaline earth, alkali or other large ions such as Pb^{+2} . Perovskite compounds can also tolerate significant partial non-stoichiometric substitution, while still maintaining the perovskite structure [5]. Perovskites have attracted much attention in recent years due to their potential commercial applications toward low temperature combustion of gaseous pollutants. Their high thermal stability can make them potential catalytic material even for high temperature applications, like combustion reactions. In 1970s, cobaltate and manganate type of perovskites were reported as potential substitutes for Noble metal-based auto exhaust catalysts [6]. Several synthesis methods for preparation of perovskite phases have been proposed and developed over the years [5,7]. These methods include pyrolysis, co-precipitation, citrate complexation, spray-drying, freeze-drying, micro emulsion sol-gel process, etc. [8-11]. Among those most popular seems to be co-precipitation and amorphous citrate methods [5,8]. In contrast to spray-freezing/freeze-drying methods, co-precipitation and citrate methods require addition of relatively large quantities of precipitating or complexing agents. These agents have to be removed during ensuing processing, typically by calcination. Calcination at high temperatures is necessary in almost all of these methods. Such treatments often result in a sharp decrease of the surface area of the catalyst, thus yielding a limited catalytic activity. For example, Co-based perovskite catalysts prepared by the conventional citrate complexation method, have a surface area of only $4\text{-}7\text{ m}^2/\text{gr}$ after calcination at 600°C for 6 h [8]. To overcome the shortage of surface areas, some of the researchers have synthesized the perovskite phase on alumina or other supports [7]. However, it has been shown that many supports, in fact, interact with the perovskite phase and reduce the perovskite activity toward hydrocarbon combustion [12]. It has also been found extremely difficult to properly characterize the presence and location of perovskite phase on various supports [2].

In this paper, two popular synthesis methods, namely, co-precipitation (Cop) and citrate (Cit) are implemented for preparation of perovskite catalyst samples. The catalyst activities are then compared. In addition, to study the effect of impurities on perovskite kinetics activity, five different formulations were also synthesized and tested for carbon monoxide combustion in stoichiometric oxygen.

¹ M.Sc. Student of Chemical Engineering

² Assistant Professor of Chemical Engineering

2. Experimental

2.1. Catalyst preparation

The following materials were used for perovskite synthesis: $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. The co-precipitation samples resulted from the precipitation of the nitrate precursors. A certain amount of nitrate salts containing the following cations La^{+3} , Ce^{+3} , Sr^{+2} , Co^{+2} and Fe^{+3} were dissolved in distilled water. NH_4OH (28%) was quickly added to the precursors under vigorous stirring until $\text{pH} = 10$. The obtained precipitate was filtered and washed with distilled water until a pH of around 7 is reached. The compound was then dried at 100°C for overnight and calcined at 700°C under air (5h, ramp = $3^\circ\text{C}/\text{min}$). The citrate compound was prepared by complexation of the nitrate salts with citric acid. Metal nitrate was first dissolved in water (50 ml). Citric acid (2 times the number of mole of metals) was dissolved in water (50ml) and added to the precursor solution under vigorous stirring. Excess water was evaporated under slow stirring at ambient temperature. The viscous gel was then dried at 100°C for 5 hours. The obtained sponge was finely ground and calcined under air (5h, ramp = $3^\circ\text{C}/\text{min}$). For perovskite phases, the temperature between 600°C and 700°C are suitable to produce nearly pure phase of nano perovskite particles [2-4]. A total of ten different perovskite samples were synthesized, as mentioned in Table 1, including five different chemical compositions with two different synthesis methods.

Table 1. Synthesized perovskite samples based on different methods and compositions.

Sample Name	composition	method
Cop1	LaCoO_3	co-precipitation
Cop2	$\text{LaCo}_{0.8}\text{Cu}_{0.2}\text{O}_3$	co-precipitation
Cop3	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Cu}_{0.2}\text{O}_3$	co-precipitation
Cop4	$\text{La}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$	co-precipitation
Cop5	$\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$	co-precipitation
Cit1	LaCoO_3	citrate
Cit2	$\text{LaCo}_{0.8}\text{Cu}_{0.2}\text{O}_3$	citrate
Cit3	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Cu}_{0.2}\text{O}_3$	citrate
Cit4	$\text{La}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$	citrate
Cit5	$\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$	citrate

2.2 catalyst characterization

To check the development of the crystal phases, the XRD patterns of the prepared materials were obtained after heating at 700°C for 4 h. The X-ray diffraction patterns were obtained with a URD diffractometer using $\text{Cu K}\alpha$ radiation. The specific surface area of the catalyst samples were obtained using N_2 adsorption-desorption at 77 K and based on the BET method. The instrument employed was a Belsorp Adsorption /Desorption Data Analysis Software (Bel Japan Inc). The microscopic texture of some of the synthesized catalyst samples was obtained by scanning electron microscopy, using a Vega Tescan MV 2300 instrument.

2.3. Catalytic activity

The catalytic combustion tests were carried out in a quartz tubular reactor, equipped with flow controllers and heating system. The picture of the set-up and its detailed components is shown in Fig. 1. 0.5 g of the synthesized catalyst was placed between two quartz wool pieces and inserted into the reactor. The feed gas with a total flow rate of $250 \text{ cm}^3/\text{min}$ and composition of 2 vol% CO , 1 vol% O_2 and the balance N_2 was used. The CO and O_2 concentrations represented a typical exhaust gas from a gasoline engine. Inlet and effluent gases to and from the reactor were analyzed using a portable gas analyzer. The effect of temperature on CO conversion was studied by increasing the reactor temperature from 150°C to 500°C .

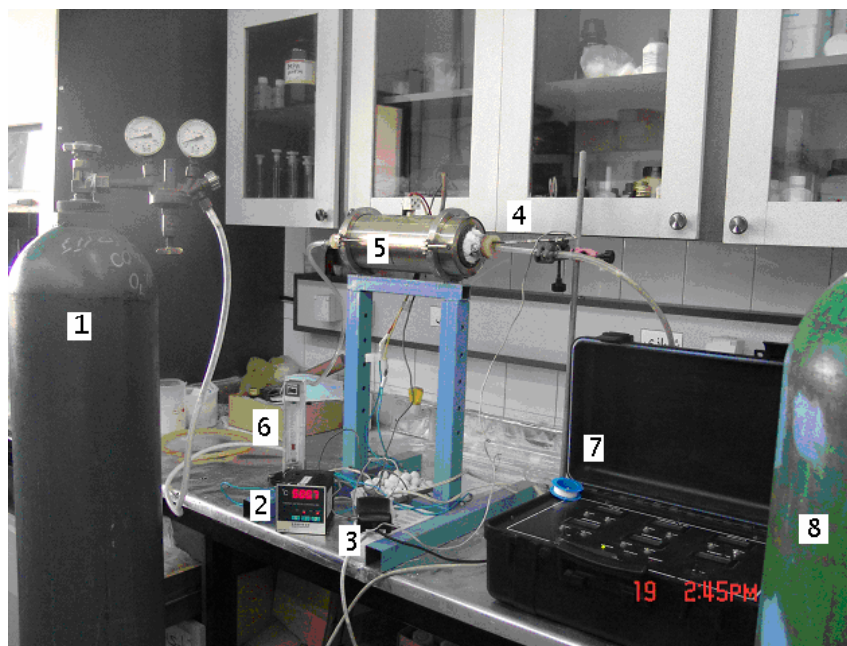
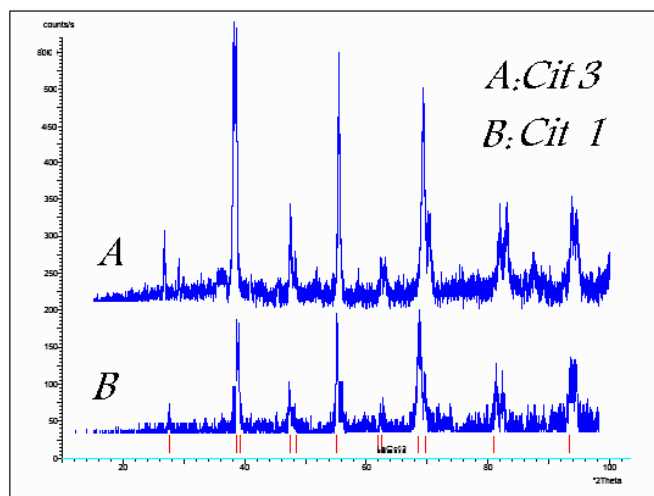


Fig.1. A picture of the catalytic combustion experimental set-up; consisting of 1.CO gas cylinder; 2.Temperature controller; 3.Dimmer; 4.Thermocouple, inserted into the reactor; 5.Horizontal reactor, including heating mantle; 6.Gas rotameter; 7.Gas analyzer; 8.Nitrogen cylinder far dilution.

3. Results

3.1 The catalysts characterization

The XRD spectra of LaCoO_3 (Cit1) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Cu}_{0.2}\text{O}_3$ (Cit3 and Cop3) samples after 5 h of carbon monoxide combustion, are compared in Figs. 2 and 3. Spectra B in Fig. 2 shows that calcination at 700°C for 4 h, completely transforms lanthanum and cobalt nitrates into LaCoO_3 perovskite phase. Spectra A in Fig. 2 shows $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Cu}_{0.2}\text{O}_3$ (Cit3) sample. As observed in Fig. 2, the presence of Sr and Cu impurities in the LaCoO_3 crystal has resulted in a small shift in its characteristics XRD peaks. No spinel phase La_2CoO_4 (that normally tends to form at higher temperatures) was observed in these samples. In Fig. 3, the XRD patterns of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Cu}_{0.2}\text{O}_3$ samples, prepared by co-precipitation and citrate methods, Cop3 and Cit3, respectively, are compared. They are mostly different at the intensity of the perovskite peaks at the same 2-theta angles. This, in fact, indicates that citrate method has been more successful in forming a perovskite phase with a higher degree of crystallinity.



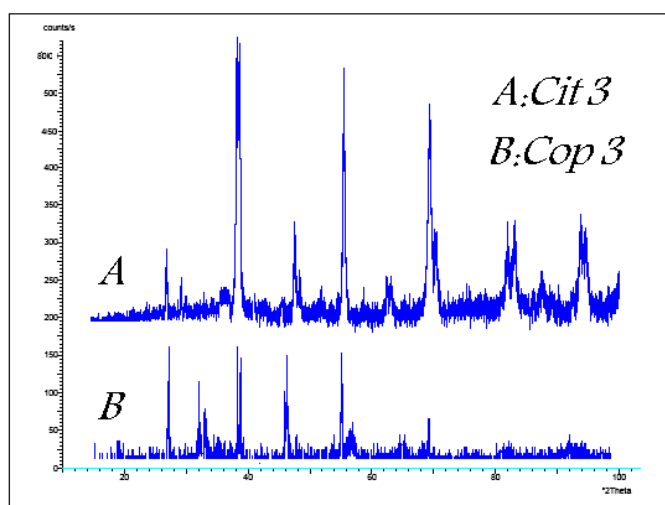


Fig. 3. XRD patterns of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Cu}_{0.2}\text{O}_3$ samples Cop3 and Cit3, prepared by co-precipitation and citrate methods, respectively.

In Figs. 4 and 5, SEM images of the Cit3 at different magnifications are shown. Fig. 5 shows that the citrate method is capable of producing nano-size perovskite crystals in the range of 70–120 nm.

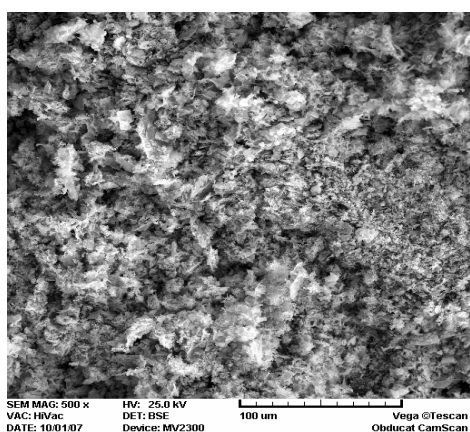


Fig. 4. SEM picture of sample Cit3 at low magnification

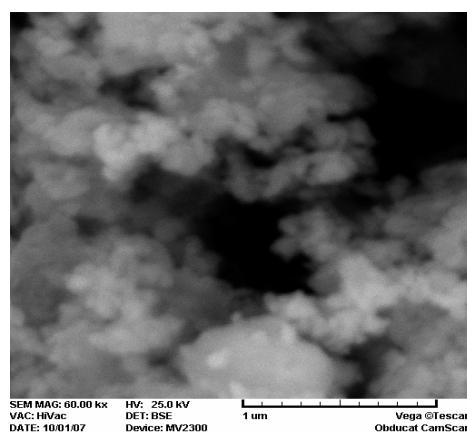


Fig. 5. SEM picture of sample Cit3 at high magnification

The specific surface areas of three synthesized perovskite samples are reported in Table 2. The perovskite samples prepared with citrate method show lower surface areas than the sample prepared with co-precipitation method (Cop3). The surface areas of the Cit1 and Cit3 samples are relatively close.

Table 2. Measured BET surface areas of three samples.

Sample	BET, m^2/g	calcination temp., $^{\circ}\text{C}$	phase	method
Cop3	20.3	700	LaCoO_3	co-precipitation
Cit1	5.3	700	La/Sr/Co/Cu/O_3	citrate
Cit3	7.1	700	La/Sr/Co/Cu/O_3	citrate

The XRF elemental analysis of the sample Cit3 is shown in Table 3. The experimentally measured lanthanum and cobalt contents (0.783 and 0.784, respectively) are in good agreement (~2% lower) than the nominal 0.8 values.

Table 3. Bulk composition of sample Cit3, as measured by XRF.

Element	Weight%	Atomic%	In Formula
Co	18.79	13.99	0.784
Cu	5.59	3.86	0.216
Sr	7.8	3.9	0.217
La	44.41	14.03	0.783

3.2. Catalytic combustion of CO

The catalytic combustion tests ($W/F=120 \text{ kg.s.m}^{-3}$) were performed with a gas mixture containing 2% CO, 1% O₂ and 97% N₂ over La/Sr/Co/Cu/O catalysts samples prepared by co-precipitation and citrate methods as a function of temperature. The reproducibility of the experimental data was confirmed by repeating some of the tests for a few times, as exemplified in Fig. 6 for Cit3 sample. A long-term activity test was also carried out, after reaching the temperature of T₁₀₀ (100% CO combustion). The reaction was then continued at constant temperature of T₁₀₀ for at least 7 h. No change in catalyst activity was observed.

Fig. 7 and 8 show the effect of temperature on %CO combustion for a variety of catalysts compositions for the co-precipitation and citrate methods of preparation, respectively. These figures show that the tested samples exhibit large differences in activity, with the sample Cit3 (our novel composition) displays the highest activity. As Fig.8 shows, 100% CO combustion for this catalyst sample was achieved only at 355°C. In general, the Cop samples show lower conversions than the citrate method at the same temperature. In fact, for Cop samples, a higher temperature of 30-40°C is required to reach the same conversions as the Cit samples.

In Table 4, the values of T₅₀ and T₁₀₀, the temperature of 50% and 100% conversion of CO, respectively, for all 10 samples are reported. In sample Cit1, 50% CO combustion was achieved at 280°C, even though the specific surface area of this material is very low. Hence, this indicates that LaCoO₃ has a high activity per unit surface area.

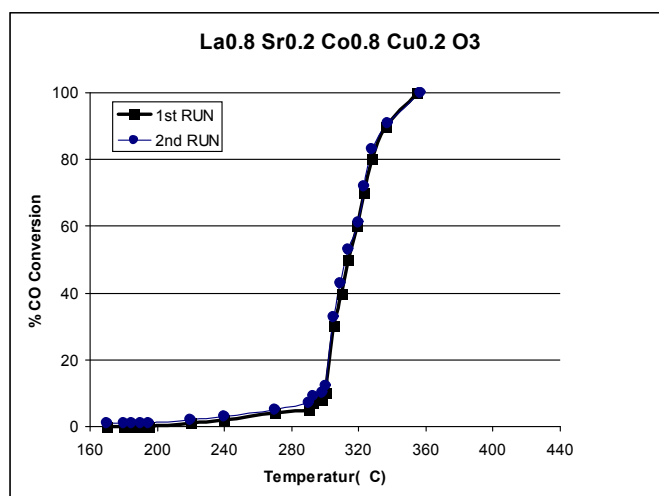


Fig.6. Reproducibility tests for the catalytic combustion of 2% CO in 1% O₂ over Cit3 sample as a function of temperature. 0.5 g sample, 250 ml/ min gas volume flow rate.

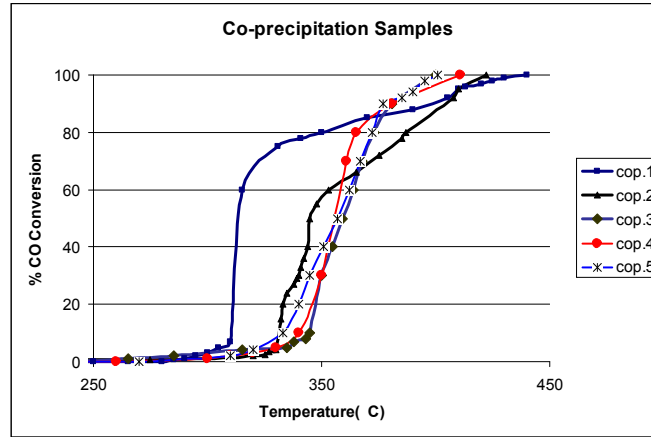


Fig.7. Catalytic combustion of 2% CO in 1% O₂ over La/Sr/Co/Cu/O samples prepared by co-precipitation method as a function of temperature. 0.5 g sample, 250 ml/ min gas volume flow rate.

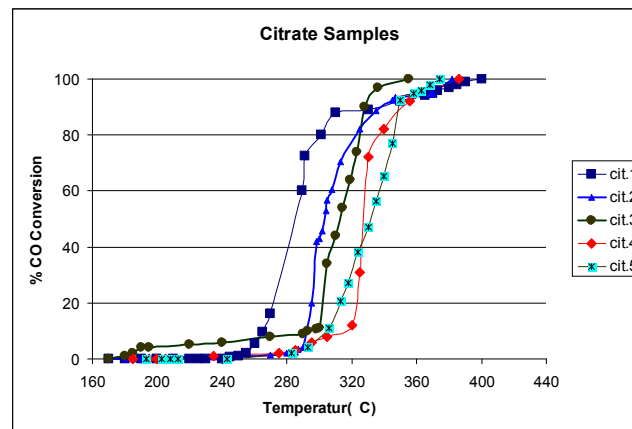


Fig.8. Catalytic combustion of 2% CO in 1% O₂ over La/Sr/Co/Cu/O samples prepared by citrate method as a function of temperature. 0.5 g sample, 250 ml/ min gas volume flow rate.

Table 4. The values of T₅₀ and T₁₀₀ (°C)

No	T ₅₀ %	T ₁₀₀ %
Cop1	312	440
Cop2	345	422
Cop3	359	400
Cop4	355	411
Cop5	357	401
Cit1	280	400
Cit2	303	382
Cit3	314	355
Cit4	327	386
Cit5	332	374

4. Discussion

The catalytic activity of perovskite samples chiefly depends on three factors; chemical composition, degree of crystallinity, and crystals morphology (including particle sizes, pore size distribution and specific surface area of the perovskite catalyst). All these factors are affected by the synthesis method and conditions. Adding impurities, in general, to the basic LaCoO₃ perovskite sample may increase the combustion kinetics, due to an increase in oxygen mobility in the bulk of the solid [12]. This is probably the reason that our novel proposed perovskite composition of La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O₃ has resulted in best CO combustion performance. Comparing the XRD patterns for the two implemented synthesis methods revealed that citrate method normally produces solids with a higher degree of crystallinity. However, the specific surface areas of Cit samples were lower than

that of Cop samples. Activity tests showed that Cit samples have, generally, faster overall combustion kinetics. As a result, it can be concluded that the degree of crystallinity plays a more important role than the internal surface area of these catalysts.

As Table 5 shows, previous researchers have also reported relatively low surface areas (in the range of 3 – 11 m²/g) for perovskite phases obtained by either co-precipitation or citrate methods. Our obtained results are well within this range, except for the Cop3 sample which is rather higher. Considering the relatively lower intensity peaks for XRD pattern of Cop3 than the peaks for Cit3 (Fig. 2), it is understood that as the perovskite phase becomes more crystalline, the pore areas collapse and hence, the surface area decreases. The smaller particles may also agglomerate and form bigger solids. SEM images have also shown nano-sized perovskite particles that have formed bigger agglomerates.

Table 5. Some of the earlier works and their obtained specific surface area

Reference	Area, m ² /g	Calcination Temp.	Perovskite phase	Method of synthesis
[5]	3.5	700	LaCoO ₃	Co-precipitation
[5]	6.6	600	LaCoO ₃	citrate
[11]	4.2	800-950	LaRuO ₃	Co-precipitation
[13]	11	800	LaFeO ₃	Co-precipitation
[14]	6	1000	LaFeO ₃	citrate

5. Conclusion

Modified perovskite samples were synthesized by co-precipitation and citrate methods. Five different compositions, including our novel proposed composition La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O₃, were synthesized by the two mentioned preparation methods and then tested toward CO combustion, using a gas mixture containing 2% CO and 1% O₂. All the catalysts displayed good stability above 600°C and a high activity toward CO combustion. Our novel perovskite composition showed the highest activity for achieving CO conversion above 80%. It achieved 100% CO combustion at 355°C. Various characterization techniques showed that co-precipitation produces lower crystallinity and higher surface area than the citrate method. The combustion catalytic activity of samples produced by citrate method was, in general, higher than the samples produced by co-precipitation.

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