Chemical Engineering Journal 148 (2009) 306–311

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Modified $LaCoO_3$ nano-perovskite catalysts for the environmental application of automotive CO oxidation

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ARTICLE INFO

Article history:
Received 22 January 2008
Received in revised form 27 August 2008
Accepted 29 August 2008

Keywords:
CO oxidation
Automotive catalytic converter
Citrate method
Co-precipitation method
Perovskite
Catalyst
Lanthanum
Cobalt
$LaCoO_3$

ABSTRACT

Modified perovskite-type oxides were synthesized through co-precipitation and conventional citrate methods. The synthesized perovskite materials had the nominal compositions of $LaCoO_3$, $LaCo_{0.8}Cu_{0.2}O_3$, $La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$, and $La_{0.8}M_{0.2}FeO_3$ (where M = Ce and Sr). The catalytic activity of the perovskite samples (for low-temperature CO oxidation) was measured using a quartz reactor with an inlet gas mixture containing 97% N_2, 1% O_2, and 2% CO. The prepared perovskite samples were characterized by SEM, nitrogen adsorption (BET), XRF, and XRD analyses. The perovskite catalysts showed good structural and chemical stability up to 600 °C and high activity for the catalytic CO oxidation reaction. The catalyst samples prepared by the citrate method achieved the same CO conversion at lower temperatures than those prepared by the co-precipitation method. This was attributed to a better-formed perovskite crystals by the citrate method. A new perovskite composition, $La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$, showed higher activity for CO conversions higher than 80%. This catalyst achieved 100% CO oxidation at 355 °C. Hence, for the environmental application of the automotive emission control, it can completely eliminate the poisonous CO gas. Among the other four synthesized perovskite formulations, the $LaCoO_3$ sample performed best in the whole range of CO conversions. SEM pictures of the perovskite samples produced by the citrate method showed that the particles sizes were close to 100 nm.

1. Introduction

The automotive exhaust gas that exits from the engine contains poisonous components, such as carbon monoxide. These harmful components convert to inert gases, such as carbon dioxide in catalytic converters, before the exhaust gas emitted to the atmosphere. The catalytic converters are, in fact, reactors that consist of monolithic honeycombs skeleton, made of ceramic or metallic materials [1]. This structure is then coated by a ceramic substrates impregnated with Pt, Pd, and other platinum group metals (PGM), as the active catalytic sites [2,3]. However, due to the rising cost of PGM, many researchers have been searching for alternative materials as the active catalytic phase. One of the promising active phases for the environmental applications is the perovskite group of materials (ABO_3), where A and B are cations of different sizes. The catalytic properties of perovskite-type oxides basically depend on the nature of A and B ions and on their valence state. The A site ions are catalytically inactive. The nature of these ions, however, also influences the stability of the perovskite phase. Replacement of part of A or B ions with other heterovalent ions can induce structural modifications that may generate oxygen vacancies and/or change the valence state of the original cations [4].

Perovskite compounds, in fact, can tolerate significant partial non-stoichiometric substitution, while still maintaining the perovskite structure [5–8]. In particular, partial substitution of La with divalent ions, e.g. Sr^{2+}, can increase the average oxidation state of the cation in position B. These effects are proposed to enhance the oxidation catalytic activity of this type of systems either by facilitating oxygen mobility or by enhancing the redox activity of the B^{n+} cation [4]. Their high thermal stability has made them potential catalytic material for high temperature combustion reactions.

Several synthesis methods for preparation of perovskite phases have been proposed and developed over the years [7,9]. These methods include pyrolysis, co-precipitation, citrate complexation, spray-drying, freeze-drying, microemulsion sol–gel process, etc. [10–13]. Among those, the benchmark methods are co-precipitation and citrate methods [7,10]. Calcination at high temperatures is necessary for almost all of these methods. Such treatments often result in a sharp decrease of the surface area of the catalyst, thus yielding low catalytic activity per unit mass. For example, Co-based perovskite catalysts prepared by the conventional citrate complexation method, have a surface area of only

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doi:10.1016/j.cej.2008.08.041

4–7 m^2/g after calcination at 600 °C for 6 h [10]. To overcome the shortage of surface areas, some of the researchers have synthesized the perovskite phase on alumina or other supports [9]. However, it has been shown that many supports react with the perovskite phase and reduce the perovskite activity for hydrocarbon oxidation [14]. It has also been found extremely difficult to properly characterize the perovskite phase on various supports [3]. Enhancement of the perovskite active catalytic surface area can also be achieved by the reduction of the grain size of the solid. Liu and his co-workers [15,16] have shown that if the particle size of the perovskite phase is controlled close to 15 nm during the perovskite synthesis process, an active surface area of 30 m^2/g can be achieved.

Garin and his co-worker [17] synthesized $LaCoO_3$, Co_3O_4, and a mix of them and studied the automotive exhaust reactions. Two preparation methods were used: simultaneous precipitation and sol–gel. The CO oxidation reaction was performed under dry or wet atmospheres for a binary $CO + O_2$ gas mixture. Under the complete wet gas mixture, the perovskite $LaCoO_3$ showed lower activation energy for the CO oxidation reaction than for Co_3O_4. Since, in many such studies on perovskites, $LaCoO_3$ has been compared to other perovskite phases, we also synthesized and studied this compound as our benchmark perovskite phase.

Fung and his co-workers [18] studied the electrocatalytic activity of Sr-substituted lanthanum metal perovskite, $La_{1-x}Sr_xMO_3$ (where M = Co or Cu), for direct methanol oxidation by cyclic voltammetry measurements. The strontium-substituted lanthanum cobaltite and cuprate were synthesized in homogeneous nano-size particles of about 25–30 nm. $La_{1-x}Sr_xCoO_3$ and $La_{1-x}Sr_xCuO_3$ showed excellent electrical conductivities (more than 1200 S/cm), where the strontium addition was more than 25%. The electrocatalytic activity for methanol oxidation of $La_{1-x}Sr_xCuO_3$ was much higher than that of $La_{1-x}Sr_xCoO_3$. The higher electrocatalytic activity of $La_{1-x}Sr_xCuO_3$ may be attributed to the capability of Cu ions for absorption of methanol. It may, also, enhance oxygen vacancies which facilitates oxygen ion (O^{2-}) transport into the proximity of adsorbed methanol oxidation intermediates at the reaction site.

Teraoka and his co-workers [19] have revealed that the incorporation of Cu (and Ru) into the inactive $La_{0.8}Sr_{0.2}AlO_3$ host produces a very active catalyst phase for CO–NO and CO–O_2 reactions. They inferred that Cu and Ru ions in the Al-based perovskite promote the reduction step of the catalyst by CO and the oxidation step of this reduced catalyst by NO, respectively. They found that partial substitution of Cu for Al in $La_{0.8}Sr_{0.2}AlO_3$ can make the perovskite phase as active as $La_{0.8}Sr_{0.2}CoO_3$ which is one of the most active perovskite catalysts [19]. In fact, considering the catalytic activity of Cu in CO oxidation [19], the presence of Cu, as partial substitution for Co may also enhance the catalytic activity of $La_{0.8}Sr_{0.2}CoO_3$ toward CO oxidations at low concentrations of CO and O_2. As a result, we prepared and tested two copper containing perovskites as follows: $LaCo_{0.8}Cu_{0.2}O_3$, $La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$ (a novel formulation).

Giannakas and his co-workers [12] prepared four different perovskite-type solids with nominal composition $LaFeO_3$, $La_{0.85}Sr_{0.15}FeO_3$, $La_{0.8}Sr_{0.1}Ce_{0.1}FeO_3$, and $La_{0.8}Ce_{0.2}FeO_3$ via a reverse micelles microemulsion route. The aim of their work was to investigate the effect of doping with Sr and Ce on the structural properties, surface area, and catalytic properties of final solids in comparison with un-doped reference solid $LaFeO_3$. Catalytic tests in NO + CO reaction were made with the use of gases He/NO/CO in the ratio 96/2/2. They found that the catalytic activities of the three doped perovskite solids were higher than the un-doped $LaFeO_3$ sample. Further, they observed that the relative sequence of their activities was in full agreement with the sequence of increment of specific surface area (ssa) of the solids. In this study, it was assumed that the same high activity of Sr- and Ce-doped $LaFeO_3$ may also hold valid in the case of CO oxidation. As a result, we synthesized and tested two more perovskite samples with the nominal formula $La_{0.8}M_{0.2}FeO_3$ (where M = Ce or Sr).

In this work, two synthesis methods, namely, co-precipitation (Cop) and citrate (Cit), were implemented for preparation of unsupported perovskite catalyst samples. To study the effect of Cu, Sr, and Ce substitution for A and B cations in the ABO_3 perovskite structure, five different formulations, as described above, were synthesized and tested for carbon monoxide oxidation in a stoichiometric oxygen gas stream.

Table 1
Synthesized perovskite samples based on different methods and compositions

Sample name	Composition	Method
Cop1	$LaCoO_3$	Co-precipitation
Cop2	$LaCo_{0.8}Cu_{0.2}O_3$	Co-precipitation
Cop3	$La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$	Co-precipitation
Cop4	$La_{0.8}Ce_{0.2}FeO_3$	Co-precipitation
Cop5	$La_{0.8}Sr_{0.2}FeO_3$	Co-precipitation
Cit1	$LaCoO_3$	Citrate
Cit2	$LaCo_{0.8}Cu_{0.2}O_3$	Citrate
Cit3	$La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$	Citrate
Cit4	$La_{0.8}Ce_{0.2}FeO_3$	Citrate
Cit5	$La_{0.8}Sr_{0.2}FeO_3$	Citrate

2. Experimental

2.1. Catalyst preparation

The following materials were used for perovskite synthesis: $La(NO_3)_3–6H_2O$, $Sr(NO_3)_2$, $Fe(NO_3)_3–9H_2O$, $Co(NO_3)_2–6H_2O$, $Ce(NO_3)_3–6H_2O$ $Cu(NO_3)_2–3H_2O$. The co-precipitation samples were produced by 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 pH 10. The obtained precipitate was filtered and washed with distilled water until a pH of 7 is reached. The compound was then dried at 100 °C overnight and calcined at 700 °C under air atmosphere (5 h, ramp = 3 °C/min). The citrate compound was prepared by complexation of the nitrate salts with citric acid. Metal nitrates were first dissolved in distilled water (50 ml). Citric acid (2 times the number of mole of metals) was separately dissolved in distilled water (50 ml) 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 h. The obtained spongy material was finely ground and calcined under air atmosphere at 700 °C (5 h, ramp = 3 °C/min). Other researchers have also used calcination temperatures between 600 °C and 700 °C [3–5]. They have reported that it is a suitable temperature range to produce nearly pure phase of nano-perovskite particles. A total of 10 different perovskite samples were synthesized, as mentioned in Table 1, including five different chemical compositions with two different synthesis methods.

2.2. Catalyst characterization

To check the development of the crystal phases, the XRD patterns of the prepared materials were obtained after calcination at 700 °C. The X-ray diffraction patterns were obtained with a URD diffractometer using Cu radiation. The specific surface areas of the catalyst samples were obtained using N_2 adsorption–desorption at 77 K, based on the BET method. The instrument employed was a Belsorp adsorption/desorption, using data analysis software (Bel

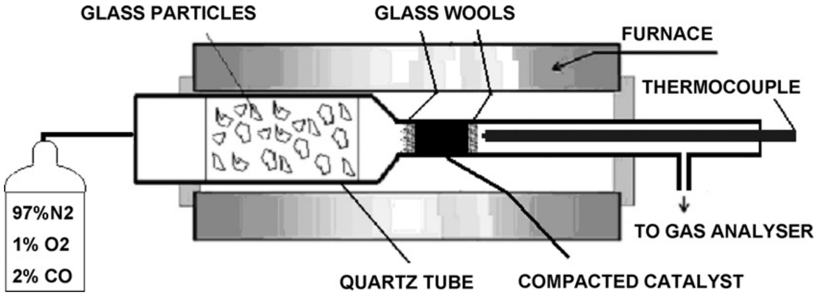

Fig. 1. CO catalytic oxidation quartz reactor, inside a heating mantle, with a thermocouple temperature probe, inserted into the reactor over the catalytic bed.

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 oxidation tests were carried out in a quartz tubular reactor, equipped with flow controllers and heating system. A schematic picture of the reactor 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 cm^3/min and composition of 2 vol.% CO, 1 vol.% O_2, and the balance N_2 was used. CO and O_2 concentrations represented a typical exhaust gas from a gasoline engine system. Inlet and effluent gases to and from the reactor were analyzed using a portable CO gas analyzer. The effect of temperature on CO conversion was studied by increasing the reactor temperature from 150 °C to 500 °C.

3. Results

3.1. Catalysts characterization

The XRD spectra of $LaCoO_3$ (Cit1) and $La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$ (Cit3 and Cop3) samples after 5 h of carbon monoxide oxidation are compared in Figs. 2 and 3. Spectra Cit1 in Fig. 2 shows that calcination at 700 °C has completely transformed lanthanum and cobalt nitrates into $LaCoO_3$ perovskite phase. Spectra Cit3 in Fig. 2 shows the XRD pattern of $La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$ (Cit3) sample. As observed in this figure, 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 two $La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$ samples, prepared by the co-precipitation and the citrate methods, Cop3 and Cit3, respectively, are compared. They show some differences in the intensity of the perovskite peaks at the same angles. This, in fact, indicates that citrate method has been more successful in forming a perovskite phase with a higher degree of crystallinity.

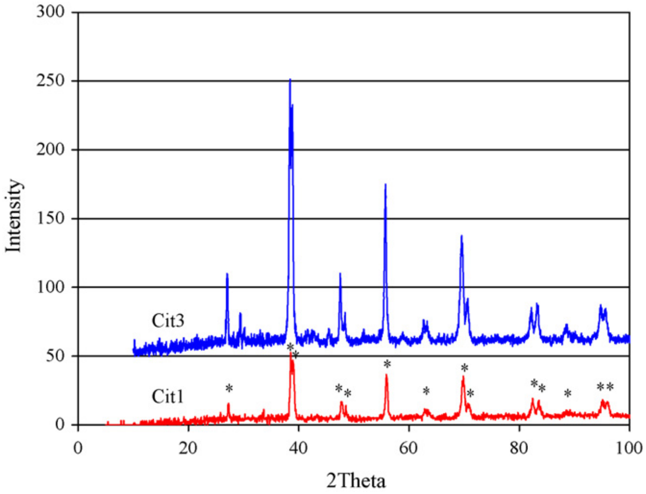

Fig. 2. XRD patterns of $LaCoO_3$ (Cit1) and $La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$ (Cit3) samples, prepared by citrate method. The asterisks (*) represent the standard peaks for pure $LaCoO_3$.

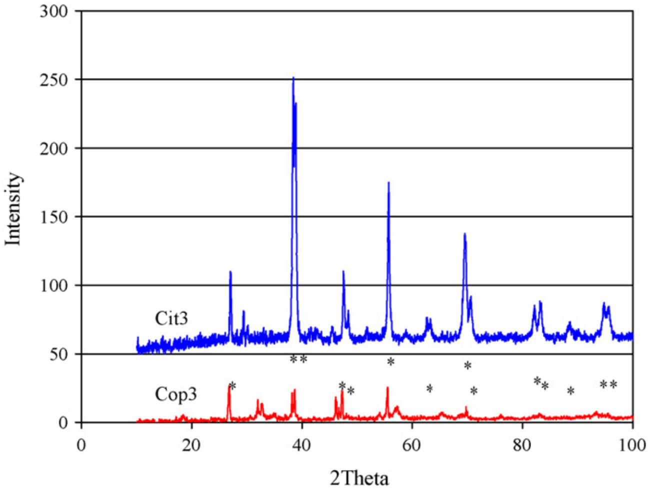

Fig. 3. XRD patterns of $La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$ samples Cop3 and Cit3, prepared by co-precipitation and citrate methods, respectively. The asterisks (*) represent the standard peaks for pure $LaCoO_3$.

In Figs. 4 and 5, SEM images of the Cit3 sample at different magnifications are shown. Fig. 5 shows that the citrate method has been capable of producing nano-size perovskite crystals close to 100 nm.

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

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) with the nominal 0.8 values.

Table 2
Measured BET surface areas of three samples

Sample	BET (m^2/g)	Calcination temperature (°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

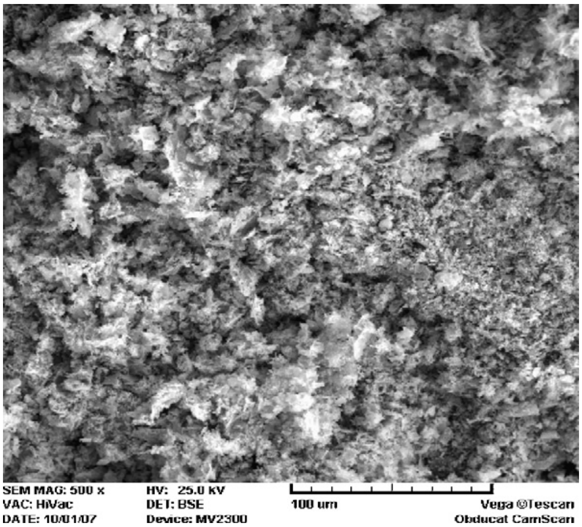

Fig. 4. SEM picture of sample Cit3 at low magnification.

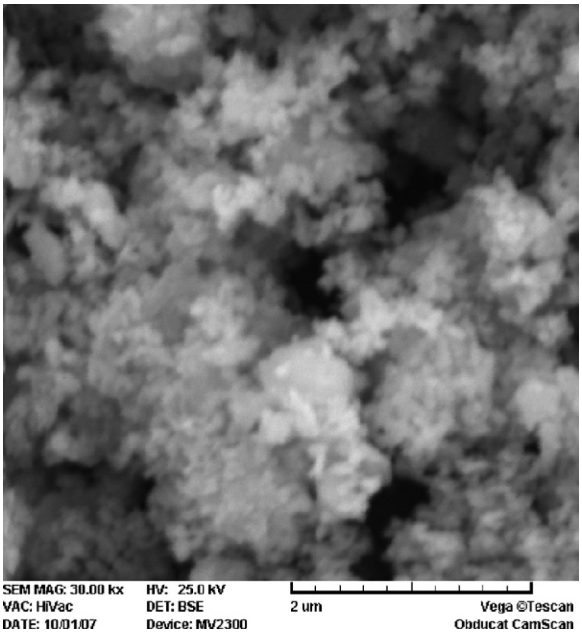

Fig. 5. SEM picture of sample Cit3 at high magnification.

3.2. Catalytic oxidation of CO

The catalytic combustion tests (W/F = 120 kg s/m^3) were performed with a gas mixture containing 2% CO, 1% O_2 and 97% N_2 over the catalyst samples prepared by the co-precipitation and the 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 illustrated in Fig. 6 for the Cit3 sample. A long-term activity test was also carried out, after reaching the temperature of T_{100} (100% CO combustion). The reaction was then continued at the constant temperature of T_{100} for at least 7 h. No change in the catalyst activity was ever observed.

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	7.80	3.90	0.217
La	44.41	14.03	0.783

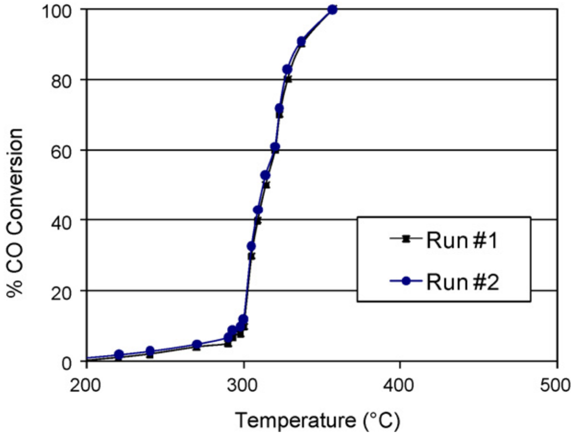

Fig. 6. Reproducibility tests for the catalytic combustion of 2% CO/1% O_2 over Cit3 sample as a function of temperature. Conditions: 0.5 g sample, 250 ml/min gas volume flow rate.

Figs. 7 and 8 show the effect of temperature on %CO combustion for the catalysts prepared by the co-precipitation and the citrate methods, respectively. These figures show that those samples exhibit large differences in terms of the catalytic activity, with the sample Cit3 (our novel composition) displays the highest activity for CO conversions higher than 80%. As Fig. 8A shows, 100% CO combustion for this catalyst sample was achieved only at 355 °C. In general, the Cop samples show lower CO conversions than the citrate samples at the same temperature. In fact, for the 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 T_{50} and T_{100}, the temperatures of 50% and 100% conversion of CO, respectively, for all 10 samples are reported. For the 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 $LaCoO_3$ has a very high catalytic activity per unit surface area.

4. Discussion

The effect of partial substitution of Cu for Al in the inactive $La_{0.8}Sr_{0.2}AlO_3$ perovskite structure was tested by Teraoka and his co-workers [19] to produce a very active catalyst sample. This hinted us to propose partial substitution of Cu for Co in the $La_{0.8}Sr_{0.2}CoO_3$ perovskite structure (named Cop3 and Cit3 in this paper). It was observed that the Cit3 sample performed better than

Table 4
The values of T_{50} and T_{100} (°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

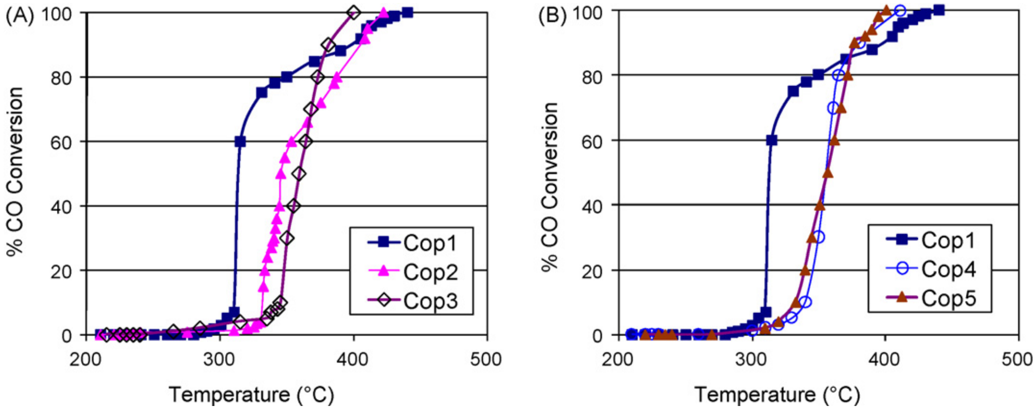

Fig. 7. Catalytic combustion of 2% CO/1% O_2 over La/Sr/Co/Cu/O samples prepared by co-precipitation method as a function of temperature. Conditions: 0.5 g sample, 250 ml/min gas volume flow rate. (A) Comparison of benchmark $LaCoO_3$ with Cu-doped Co perovskite samples. (B) Comparison of benchmark $LaCoO_3$ with Ce- or Sr-doped La perovskite sample $LaFeO_3$.

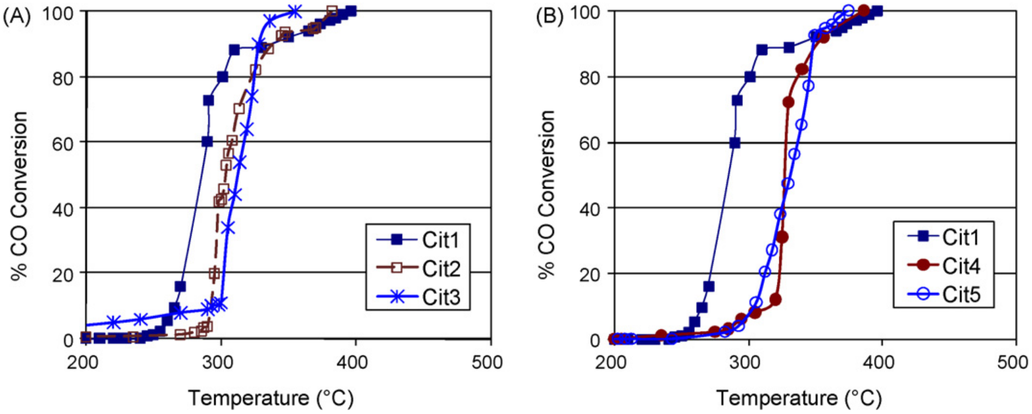

Fig. 8. Catalytic combustion of 2% CO/1% O_2 over La/Sr/Co/Cu/O samples prepared by citrate method as a function of temperature. Conditions: 0.5 g sample, 250 ml/min gas volume flow rate. (A) Comparison of benchmark $LaCoO_3$ with Cu-doped Co perovskite samples. (B) Comparison of benchmark $LaCoO_3$ with Ce or Sr-doped La perovskite sample $LaFeO_3$.

the benchmark $LaCoO_3$ (Cit1) perovskite phase at low concentrations of CO and O_2.

The catalytic activity of the perovskite samples chiefly depends on three factors: chemical composition, degree of crystallinity, and the 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 the specific synthesis operating conditions. Adding impurities to the benchmark $LaCoO_3$ perovskite sample, in general, may enhance the rate of combustion, due to an increase in the oxygen mobility in the bulk of the solid [14]. This is probably the reason that our novel proposed perovskite composition of $La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$ has resulted in the best CO oxidation 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 the Cit samples were lower than that of the Cop samples. The catalytic activity tests showed that the Cit samples have, generally, faster overall combustion rate. 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 [7,13,20,21] have also reported relatively low surface areas (in the range of 3–11 m^2/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 somewhat higher. Considering the relatively lower intensity peaks for the XRD pattern of the Cop3 sample than the peaks of the Cit3 sample (Fig. 2), it is understood that as the perovskite phase becomes more crystalline, the pore volumes shrink and hence, the surface area decreases. The smaller particles may also agglomerate and form bigger solids. The SEM images of samples have also shown that nano-sized perovskite particles tend to form bigger agglomerates.

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

Reference	Area (m^2/g)	Calcination temperature (°C)	Perovskite phase	Method of synthesis
[7]	3.5	700	$LaCoO_3$	Co-precipitation
[7]	6.6	600	$LaCoO_3$	Citrate
[13]	4.2	800–950	$LaRuO_3$	Co-precipitation
[20]	11	800	$LaFeO_3$	Co-precipitation
[21]	6	1000	$LaFeO_3$	Citrate

5. Conclusion

Modified perovskite samples were synthesized by the co-precipitation and the citrate methods. Five different compositions, including a new composition $La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$, were synthesized by the two preparation methods and then tested toward CO oxidation reaction, using a gas mixture containing 2% CO and 1%

O_2. The prepared catalysts showed good stability up to 600 °C and high activity for CO combustion. The new perovskite composition showed the highest activity for CO conversion higher than 80%. It achieved 100% CO combustion at 355 °C. Various characterization techniques confirmed that the co-precipitation method produces lower crystallinity and higher surface area than the citrate method. The oxidation catalytic activity of the samples produced by the citrate method was, in general, higher than the samples produced by co-precipitation.

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