

Effects of gold and platinum on the activity of catalysts for the complete oxidation reaction of hydrocarbons and carbon monoxide

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Abstract:

This study presents synthesis results of catalysts made of perovskite-like oxide $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0.0, 0.5, 1.0$) using the citrate method and crystallisation at 800°C . The structure of the catalysts was characterised by X-ray diffraction (XRD). The perovskite-like oxide catalyst activity was enhanced with gold (Au) and platinum (Pt). Au was mounted on the perovskite-like oxide catalysts by the sol-gel method. The activity of the perovskite-like oxide $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0.0, 0.5, 1.0$) and the perovskite catalyst $\text{LaMnO}_3/\text{LaCuO}_3$ was evaluated by complete oxidation of volatile hydrocarbons (HCs) in a mixture of toluene and methyl ethyl ketone (MEK) and carbon monoxide (CO) in a microflow analysis system combined with gas chromatography. The results showed that the light-off temperature (the 50% conversion temperature of the catalysts) of the Pt, Au/perovskite catalyst samples decreased significantly. The light-off temperature of the Au/ LaSrCuO_4 Au nanoparticle catalysts in the complete CO oxidation reaction reached a temperature of 150°C , lower than the Pt/ LaSrCuO_4 catalyst (170°C), allowing replacement of previous Pt catalysts with Au nanoparticle catalysts. The LaSrCuO_4 catalyst had better oxidising activities than the La_2CuO_4 catalyst, indicating that the addition of strontium (Sr) has increased the catalyst activity, and demonstrates the potential for application in catalytic converters in motorcycles.

Keywords: catalytic converter, gold catalyst, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, perovskite-like oxide, platinum catalyst.

Classification numbers: 2.2, 2.3

1. Introduction

Emissions emitted from industrial activities, motorcycle, and automobile engines affect the environment. Using a catalyst to completely oxidise the exhaust gases is a highly effective method. Inexpensive catalysts based on metal oxides are often used such as copper oxide, cobalt oxide, manganese oxide, chromium oxide, and nickel oxide. However, oxidation temperatures to achieve high conversion is quite high [1]. Metal-based catalysts such as Pt, Rh, and Pd are highly active, but expensive, and tend to be inactive in gas streams containing chlorine and sulfur compounds. This type of catalyst is now widely used in catalytic converters [1, 2].

Perovskite catalysts with the general formula ABO_3 have been studied. Perovskite catalysts can displace precious metals in the complete oxidation of HCs [2-6]. Elements A and B in ABO_3 are replaced by metals with different oxidation states and change the activity of the catalyst. For example, in the catalytic material $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, the authors partially replaced the La^{3+} ion with the Sr^{3+} ion, which increased defects in the structure and changed the catalytic properties [2, 3, 7].

Au metal has been used as a catalyst since 1906, but it was not until the 1980s that Au was intensively studied by M. Haruta (2004) [8]. Au catalysts are highly effective in the field of environmental

chemistry and exhaust gas treatment. Au catalysts are used very effectively for the oxidation reaction of not only CO but also many other compounds. Au catalysts can be carried on metal oxides such as Fe_2O_3 , MgO, ZrO_2 , Al_2O_3 , ZnO, and TiO_2 , and they have very strong activity and can be used for low-temperature CO oxidation reactions [8-10].

In one study [11], the authors made coatings with a perovskite $\text{Al-La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (LSCO) catalyst coating on a ceramic carrier. The results showed a significant reduction in HCs and CO when the LSCO coating was applied.

Pd catalysts on the perovskite LaAlO_3 have been studied to reduce NO at low temperatures. The catalyst $\text{Pd/La}_{0.9}\text{Ba}_{0.1}\text{AlO}_{3-\delta}$ has significantly higher activity than other Pd catalysts at temperatures lower than 300°C [12].

In another study [13], the author replaced 0.05 moles of La with Pd, which enhanced the activity of the LaMnO_3 catalyst during CO oxidation. The catalysts $\text{La}_{0.9}\text{Pd}_{0.1}\text{MnO}_3$ and $\text{La}_{0.85}\text{Pd}_{0.15}\text{MnO}_3$ exhibited extremely high activity.

The results of another study [14] demonstrated the synthesis of perovskite oxide LaCuO_3 and $\text{LaCu}_{0.53}\text{Ni}_{0.47}\text{O}_3$, prepared by the sol-gel citrate method, with 5% NiO/ LaCuO_3 was prepared by impregnation. Products were obtained after heat treatment in

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air at 800°C. The most successful results were achieved using the 5% NiO/LaCuO₃ precursor, where the amount of treated methane (CH₄) increased by 16.5% compared to LaCu_{0.53}Ni_{0.47}O₃.

In the present work, the authors study the effects of Au and Pt catalysts on the perovskite-like oxide La_{2-x}Sr_xCuO₄ (x=0.0, 0.5, 1.0) in a complete oxidation reaction of HCs and CO.

2. Experimental section and methods

2.1. Synthesis of the perovskite-like oxide La_{2-x}Sr_xCuO₄ (x=0.0, 0.5, 1.0), perovskite LaMnO₃ and LaCuO₃

A mixture consisting of 4.33 g La(NO₃)₃·6H₂O, m (g) Sr(NO₃)₂, and n (g) Cu(NO₃)₂, such that the molar ratio of La:Sr:Cu=(2-x):x:1 (x=0.0, 0.5, 1.0), was evenly dissolved in 20 ml H₂O, then added to another solution containing 3.82 g citric acid, 2.23 g ethylene glycol, and 20 ml H₂O. The mixture was stirred continuously at a temperature of 60°C until a highly viscous mixture (gel) was obtained. The gel was placed into a thermostat tank and dried at a temperature of 80°C over a period of 12 hours. This process produced the amorphous citrate precursors. The resulting porous solid was calcined at 800°C in an oxygen stream for 5 hours. The resulting black solid was the perovskite-like oxide La_{2-x}Sr_xCuO₄.

The synthesis of the perovskite LaMnO₃ and perovskite LaCuO₃ was similar to La_{2-x}Sr_xCuO₄, in which Sr(NO₃)₂ was replaced by Mn(NO₃)₂ and Cu(NO₃)₂ with the molar ratio of La:Mn=1:1 (La:Cu=1:1).

2.2. Preparation of perovskite-like oxide with Au and Pt catalysts

Preparation of platinum/perovskite-like oxide catalyst: The calculated PtCl₄ solution was added to a 250 ml beaker and water was added at a rate of 10 ml/g catalyst. The perovskite-like oxide material was ground very finely, and a mixture was created. The mixture was stirred for approximately 5 hours at 70°C. Then, it was placed in a beaker in a thermostat tank at 80°C for 12 hours. The catalyst was filtered to remove all the Cl⁻ ions. The catalyst was placed in the drying cabinet for 2 hours at 100°C to drain all the water. The catalyst was then calcined for 5 hours at 500°C to obtain the Pt/perovskite-like oxide catalyst.

Preparation of Au/perovskite-like oxide catalysts:

Chemicals: Au chloride solution HAuCl₄·3H₂O with 5.07 mM Au (Japan); NaBH₄ (Merck); sol stabiliser: polyvinyl alcohol (PVA) (C₂H₄O)_x (China).

The Au sol was stabilised by PVA. The required amount of HAuCl₄·3H₂O solution was placed into a 250 ml beaker. PVA solution was added and stirred at a rate of 1000 rpm at 60°C for 1 hour. Then, 0.1 M NaBH₄ solution was added dropwise while maintaining a stirring rate of 1000 rpm at 60°C for 2 hours. The pre-determined amount of perovskite was added to the mixture, and stirring was continued for 5 hours at 60°C. The mixture was filtered with distilled water and the resulting solids were dried at 140°C for 2 hours. The solids were calcined at 500°C for 5 hours to obtain the Au/perovskite-like oxide catalyst.

Research has shown that even small minor quantities of Au nanocatalysts can significantly enhance the low-temperature oxidation of CO and other compounds [8-10]. The Au sols are stabilised in PVA in proportions given by Table 1.

Table 1. Preparation of Au sols on the perovskite-like oxide.

No.	Sol			Carrier
	[PVA] (µg/ml)	[Au] (µg/ml)	PVA/Au (wt/wt)	
1	64	100	64/100	Perovskite-like oxide
2	100	100	100/100	La _{2-x} Sr _x CuO ₄

2.3. Characteristics and activity of the catalysts

The structural characteristics of the catalyst were evaluated by XRD (Siemens, Germany). The scanning angle was varied from 0°<2θ<70° at a scanning speed of 1°/min and using Cu Kα radiation at a wavelength of 1.5406 Å.

The dispersion of the Au/perovskites was determined by field emission-scanning electron microscopy (FE-SEM) imaging on a Hitachi S-4800.

The activity of the catalysts was determined through the complete oxidation reactions of HCs such as toluene, MEK, and CO. The process was conducted by gas chromatography on a trace-flow system.

Toluene and MEK analysis conditions: The gas chromatography machine used was a Varian aerograph series 2800 with a flame ionization detector (FID). The separation column was di-n-decyl phthalate 15% Chromosorb 60-80 mesh. The N₂ carrier gas was set to 20 KPa. The H₂ flow rate was 2.7 l/hour, and the air flow rate was 13.8 l/hour. The column temperature was 83°C.

CO analysis conditions: The gas chromatography machine was a chromatron GCHF 18.3 with a thermal conductivity detector (TCD). The separation column was ZV95 zeolite, and the column temperature was room temperature.

Determine conversion degree: The conversion of HC to CO was determined by calculating the area of the input peaks and output peaks according to the following formula:

$$\theta = \left(1 - \frac{S_0}{S_1}\right) \times 100\%$$

where: θ is the conversion degree (%); S_1 is the maximum area of the starting material (unreacted); S_0 is the area of peak of the material remaining after the reaction.

3. Results and discussion

3.1. Structural characteristics of perovskite-like oxide

The perovskite-like oxide catalysts La_{2-x}Sr_xCuO₄ (x=0.0, 0.5, 1.0) were crystallized at 800°C. The XRD analysis results of the catalysts are presented in Fig. 1.

Lanthanum oxide crystals are diffracted at 2θ=26.2, 30.1, 39.9, 47.2, 47.2, 52.4, and 57.5°. Copper oxide crystals are diffracted at 2θ=35.55, 35.57, 38.41, and 38.73°. The strontium oxide crystals are diffracted at 2θ=26.46, 30.02, 32.36, 38.25, 44.14, 48.26, and 50.21°. Sr was added to the structure (x=0.5 and x=1.0), the XRD

spectra appeared to show diffraction characteristics of Sr oxide crystals. The XRD spectrum for LaSrCuO_4 ($x=1.0$) in Fig. 1 also showed that the clearest diffractions.

The XRD of perovskite samples LaMnO_3 and LaCuO_3 crystallized at 800°C similar to the results in studies [2, 14].

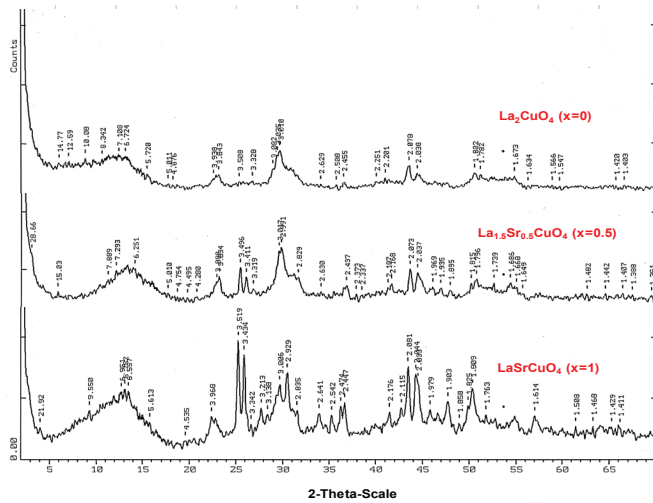


Fig. 1. XRD spectra of the perovskite-like oxide $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0.0, 0.5, 1.0$) at 800°C .

3.2. Activity of perovskite-like oxide catalysts in the complete oxidation of the mixture toluene and MEK

The activity of perovskite-like oxide LaSrCuO_4 and perovskite $\text{LaMnO}_3/\text{LaCuO}_3$ catalysts were evaluated in the complete oxidation reaction of the mixture toluene and MEK. The results are presented in Fig. 2 and Table 2.

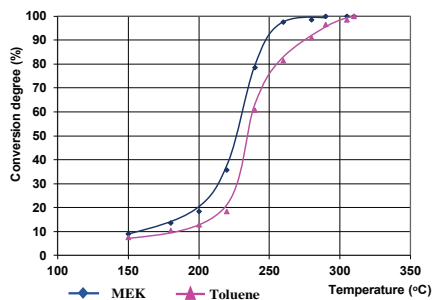


Fig. 2. The conversion degree of the toluene and MEK mixture on the LaSrCuO_4 catalyst at 800°C .

Table 2. The light-off temperature of perovskite catalysts in the complete oxidation of the toluene and MEK mixture.

Catalysts	The light-off temperature ($^\circ\text{C}$)	
	Toluene	MEK
LaMnO_3	230	190
LaCuO_3	235	205
LaSrCuO_4	235	220

The results from Fig. 2 show that the light-off temperature of MEK on LaSrCuO_4 is lower than that of toluene (temperatures at 220°C and 235°C).

The results of Table 2 show that the perovskite catalysts $\text{LaMnO}_3/\text{LaCuO}_3$ and the perovskite-like oxide LaSrCuO_4 catalyst are fully applicable to the treatment of motorcycle exhaust gases. These catalysts are capable of completely oxidising VOCs such as toluene and MEK present in motorcycle exhaust gases, and the catalyst can work at lower temperatures if toluene and MEK are present. The light-off temperature ranges from $230\text{--}260^\circ\text{C}$, which is suitable for the highest working temperature of motorcycle exhaust gases.

The results from Table 2, the perovskite catalyst LaMnO_3 has the light-off temperature of MEK is lower than that of toluene. This is also consistent with the theory. Because MEK has an intramolecular oxygen element, its oxidation capacity occurs more easily than that of toluene. Besides, the presence of MEK makes toluene more susceptible to oxidation in the absence of MEK. The light-off temperature of toluene in the presence of MEK was 230°C compared to 245°C without MEK [5, 6].

The light-off temperature of the catalyst is the temperature at which the catalyst converts 50% of the substance to be processed. This can be considered as the priming temperature, which is the lowest temperature at which the catalyst begins to have the activity required for industrial application. This temperature partly reflects the true value of the catalyst [1, 2].

According to a study [2], thermal decomposition of toluene in perovskite catalysts releases energy (39,500 to 74,000 kJ), whereas MEK gives off a much higher energy (137,000 to 230,000 kJ). MEK emits a large amount of heat, which speeds up the reaction process, resulting in MEK being better oxidised. Thus, the conversion degree is higher than that of toluene, the jump interval is shorter, and the light-off temperature is lower.

According to a previous study, Pt carried in large specific surface carriers such as Al_2O_3 is considered a traditional catalyst for the deep oxidation of HCs [2]. With perovskite catalysts, they also have strong oxidizing activity. However, when carrying out Pt impregnation on perovskite, the activity of the catalysts increases further, and the light-off temperature decreases significantly.

The catalytic mechanism is explained as follows: The perovskite catalysts are applied in the catalytic converter to treat the exhaust gases of motorcycles. The catalytic converter converts toxic substances into CO_2 and H_2O [2-6, 11-14]. The activity of the catalytic converter is shown in Fig. 3.

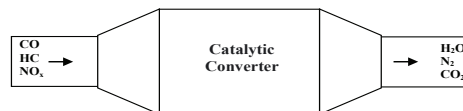
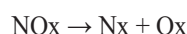


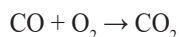
Fig. 3. The activity of a catalytic converter.

The catalytic converter has three simultaneous functions:

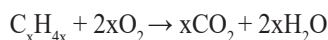
Reduction of nitrogen oxides (NO_x) into nitrogen and oxygen elements:



Oxidation of CO to carbon dioxide:



Oxidation of HCs into carbon dioxide and water:



Reactions require high activation energies for the reaction to begin and the reaction lasts a long time if there are no catalysts. In the presence of catalysts, the activation energy for the reaction and reaction time are significantly reduced.

These reactions are varied, HCs include not only toluene and MEK but also many compounds contained in gasoline or diesel.

The oxidation mechanism of the catalyst is as follows: In the catalytic process, there is oxidation and reduction. For oxidation, oxygen is needed, and for reduction, CO is needed. Toxic substances such as CO, HCs, NO_x , and the components involved in the reaction such as O_2 and CO must exist in a specific proportion to ensure the best conversion degree is achieved.

For a chemical reaction to occur, the catalyst requires a minimum temperature, called the light-off temperature. For the conversion to reach 50%, the temperature of the catalysts must immediately reach 250-280°C. Therefore, the catalytic converter is located directly above the exhaust pipe. The old catalytic converters have a high light-off temperature. The best temperature range is between 400-800°C [2-6, 11-14].

The catalytic converter of the motorcycles must have a light-off temperature as low as possible to meet the above requirements.

3.3. Activity of Au and Pt on perovskite-like oxide catalyst $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ in the CO oxidation reaction

The perovskite-like oxide catalysts $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0.0, 0.5, 1.0$) prepared with $x=1.0$ had the best crystallinity at 800°C. Therefore, that LaSrCuO_4 sample was chosen as the carrier for the preparation of the Au/LaSrCuO_4 catalyst.

The FE-SEM image of the catalyst sample 1% $\text{Au/LaSrCuO}_4/100$ PVA/100 Au is shown in Fig. 4.

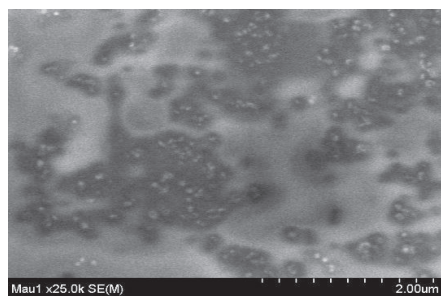


Fig. 4. FE-SEM image of 1% $\text{Au/LaSrCuO}_4/100$ PVA/100 Au catalyst.

Figure 4 shows Au particles dispersed in the catalyst, with an average particle size estimate of 34.64 nm.

The FE-SEM image of the 1% $\text{Au/LaSrCuO}_4/64$ PVA/100 Au catalyst sample is shown in Fig. 5.

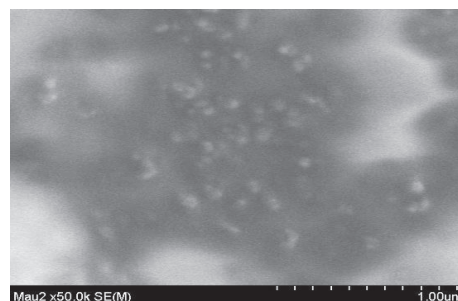


Fig. 5. FE-SEM image of a catalyst 1% $\text{Au/LaSrCuO}_4/64$ PVA/100 Au.

The FE-SEM image from Fig. 5 shows the dispersion of the Au nanoparticles in the 1% $\text{Au/LaSrCuO}_4/64$ PVA/100 Au sample with an average particle size of 36.12 nm.

FE-SEM images showed Au nanoparticles formed on the sample. When the ratio was reduced from 100 PVA/100 Au to 64 PVA/100 Au, the Au nanoparticle size increased. This is also consistent with the study of F. Forta, et al. (2000) [9].

The catalytic activity in the CO oxidation reaction was carried out on perovskite-like oxide catalysts $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0.0, 0.5, 1.0$) with 1% Pt and 1% Au. The results are shown in Figs. 6, 7 and Table 3.

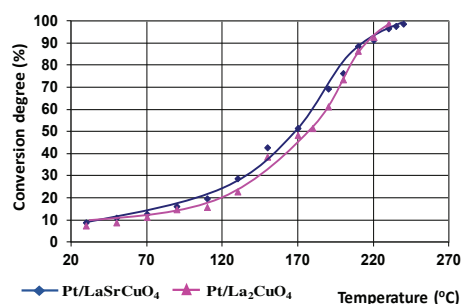


Fig. 6. The CO conversion on 1% $\text{Pt/La}_2\text{CuO}_4$ 800°C and 1% Pt/LaSrCuO_4 800°C catalysts.

The results from Fig. 6, the light-off temperature of the Pt/LaSrCuO_4 and $\text{Pt/La}_2\text{CuO}_4$ samples was 170 and 180°C. The Pt/LaSrCuO_4 catalyst had a lower light-off temperature due to the addition of the Sr element into the structure. Thus, the Pt/LaSrCuO_4 catalyst is suitable for industrial production, especially for very high heat and mechanical resistance applications.

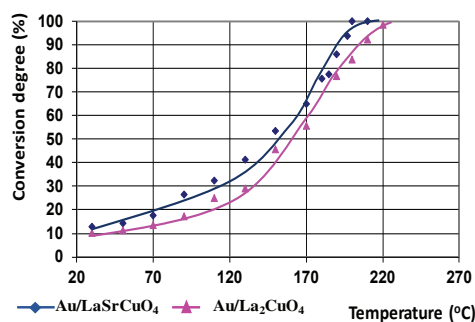


Fig. 7. The CO conversion on 1% $\text{Au/La}_2\text{CuO}_4$ 800°C and 1% Au/LaSrCuO_4 800°C (100 PVA/100 Au) catalysts.

The results from Fig. 7, the light-off temperatures of the Au/LaSrCuO₄ and Au/La₂CuO₄ catalysts were 150 and 160°C. Au catalysts are particularly effective for CO complete oxidation reactions. The results are similar to that of toluene oxidation [5], where Au/LaSrCuO₄ catalyst outperformed the Au/La₂CuO₄ catalyst.

Table 3. The light-off temperature of the catalysts in the CO complete oxidation reaction.

Catalysts	Light-off temperature (°C)
Pt/LaSrCuO ₄	170
Pt/La ₂ CuO ₄	180
Au/LaSrCuO ₄	150
Au/La ₂ CuO ₄	160
0.64 Au/LaSrCuO ₄	160
0.64 Au/La ₂ CuO ₄	170

The CO conversion results from Tables 2 and 3 show that the light-off temperature is lower than that of the toluene and MEK mixture. The light-off temperature of the Au/LaSrCuO₄ catalyst was the lowest at 150°C.

The results show that Au/LaSrCuO₄ 800°C is a catalyst with good activity. The light-off temperature of Au/LaSrCuO₄ for a complete oxidation reaction of CO was 150°C, while the light-off temperature of Pt/LaSrCuO₄ was 170°C. The working temperature of the Au/LaSrCuO₄ catalyst is very favourable for applications in the treatment of motorcycle exhaust gases.

The results from Tables 2 and 3, the light-off temperatures of all catalysts did not exceed 270°C, which is the highest temperature that a motorcycle engine can reach during work [2-6, 11-14]. Therefore, it can be confirmed that all catalysts in this study are capable of treating motorcycle exhaust gases, of which the perovskite-like oxide Au/LaSrCuO₄ catalyst was the most active.

Perovskites can be dual-acting catalysts that have many prospects for practical application, for example, they can simultaneously process HCs and CO. This shows that CO and HCs do not have the opposite chemical effect when the two substances are present in the system at the same time. The CO conversion temperature is lower than that of toluene, therefore, if a product of toluene oxidation has CO, then this gas will also be completely converted to CO₂. In addition, CO is an easily oxidised gas; therefore, under the conditions of the toluene oxidation reaction, if there is unconverted CO gas, the content in exhaust gases will be small.

4. Conclusions

The synthesis of perovskite-like oxide catalysts La_{2-x}Sr_xCuO₄ (x=0.0, 0.5, 1.0) by the citrate method and crystallization at 800°C produced good catalytic activity for the complete oxidation of the mixture of toluene and MEK, in which the LaSrCuO₄ catalyst (x=1.0) was the best performing. The light-off temperature of the Au/LaSrCuO₄ Au nanoparticle catalyst in the complete oxidation reaction of CO reached 150°C, lower than that of the Pt/LaSrCuO₄ catalyst (170°C). This would allow the replacement of previous Pt catalysts with a better performing, Au nanoparticle catalyst.

Additionally, the LaSrCuO₄ catalyst (x=1.0) had better oxidising activity than the La₂CuO₄ catalyst (x=0.0), showing that a partial replacement of La³⁺ ions with Sr³⁺ ions increased catalyst activity. Thus, there is potential for application of these catalysts in the catalytic converter of motorcycles.

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COMPETING INTERESTS

The author declares that there is no conflict of interest regarding the publication of this article.

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