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## A kinetic study of CO oxidation over the perovskite-like oxide LaSrNiO<sub>4</sub>

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**Abstract:** The effect of reactant/product concentrations, reaction temperature and contact time on CO oxidation was investigated, using the perovskite-like oxide LaSrNiO<sub>4</sub> as the catalyst. It was found that the reaction order of CO (reactant), as well as that of CO<sub>2</sub> (product), is negative, the reaction orders for CO and CO<sub>2</sub> being –0.32 and –0.51, respectively. However, the reaction order for O<sub>2</sub> is positive, having a value of 0.62. The negative reaction order of CO and CO<sub>2</sub> might be due to their competitive adsorption with O<sub>2</sub>, preventing the proceeding of oxygen dissociation (the rate-determining step of the reaction). The activation energy ( $E_a$ ) of the reaction was calculated to be 49.3 kJ mol<sup>-1</sup>; this small activation energy suggests that LaSrNiO<sub>4</sub> is a potential candidate for the CO oxidation reaction. The optimum weight hourly space velocity (WHSV) of the reaction was found to be 0.6 g s cm<sup>-3</sup>. The reaction conditions in the present case were (0.5–1 % CO + 0.5–2 % O<sub>2</sub> + 0–2 % CO<sub>2</sub>), with He as the balance gas.

**Keywords:** CO oxidation; perovskite-like oxide; LaSrNiO<sub>4</sub>; kinetics; mechanism.

### INTRODUCTION

Carbon oxide is one of the gases that are toxic and unwanted in the environment. The oxidation of CO is not only of interest to eliminate this poisonous compound from exhaust, but also can act as a test reaction for surface structure–activity correlation studies.<sup>1</sup> Many catalysts<sup>2–10</sup> have been investigated and used for the CO oxidation reaction. Among them, noble metal catalysts (*e.g.*, Au) can show full CO conversion even at ambient reaction temperature, but they are susceptible to sintering and are expensive, and furthermore, their activity is lowered with increasing reaction time.<sup>7</sup> Comparatively, perovskite-type catalysts show full CO conversion at relatively high temperatures (> 300 °C), but they have a long catalyst life and their activity can be retained irrespective of the reaction time.<sup>1</sup>

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Perovskite-type oxides ( $\text{ABO}_3$ ) are one kind of excellent catalysts for oxidation reactions; they have attracted much attention in catalysis since the work of Libby<sup>11</sup> and Voorhoeve *et al.*<sup>2</sup> To date, many studies<sup>1–6,12–17</sup> have focused on the catalytic properties of perovskite-type oxides ( $\text{ABO}_3$ ) in CO oxidation reaction, but little on perovskite-like oxides ( $\text{A}_2\text{BO}_4$ ), consisting of alternating layers of perovskite ( $\text{ABO}_3$ ) and rock-salt (AO), which also show high activity in oxidation reactions.<sup>18–23</sup> In fact, the perovskite-like oxides ( $\text{A}_2\text{BO}_4$ ) possess better properties than perovskite-type oxides ( $\text{ABO}_3$ ) to some extent, such as: thermal stability,<sup>24</sup> ion exchangeability,<sup>25</sup> and so on. Thus, investigating the catalytic properties of perovskite-like oxides ( $\text{A}_2\text{BO}_4$ ) in CO oxidation is of interest.

In the present study, the effects of reactant/product concentration, reaction temperature and contact time ( $W/F$ ) on the activity of  $\text{LaSrNiO}_4$  for CO oxidation were investigated. By changing the concentration of CO,  $\text{O}_2$  and  $\text{CO}_2$  in the feed gas, the reaction order and the kinetics of CO oxidation are discussed and deduced. The activation energy of the reaction was also calculated, in order to illustrate the usability of this system in practice.

## EXPERIMENTAL

### Materials

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , A.R., Beijing Chemical Works,  $\text{Sr}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , C.P., Tianjin No.3 Chemical Reagent Factory,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , A.R., Beijing No. 57601 Chemical Works and  $\text{CO}/\text{H}_2/\text{He}$ , H.R., Dalian Guangming Special Type Gas Co., Ltd., were employed.

### Instrumentation

X-Ray diffractometer: type D/MAX-IIIB, Rigaku; gas chromatograph: type 103, Shanghai Analyze Apparatus Company; temperature programmed desorption (TPD) and temperature programmed reduction (TPR): a self-made setup equipped with a thermal conductivity detector (TCD) were used.

### Preparation method

The sample of  $\text{LaSrNiO}_4$  was prepared by the citric acid combustion method as follows:<sup>25,26</sup> stoichiometric amounts of  $\text{La}^{3+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ni}^{2+}$  nitrates were first dissolved in deionized water, then a solution of citric acid 100 % in excess of the cations was added. The resulting solution was evaporated to dryness and subsequently, the precursors were thermal decomposed, calcined at 500 °C for 2 h, and finally pelletized and calcined in air at 900 °C for 5 h.

### Characterization

The characterization of the crystal structure and the physico-chemical properties of  $\text{LaSrNiO}_4$ , such as XRD,  $\text{O}_2$ -TPD and  $\text{H}_2$ -TPR, were previously described in detail<sup>25,26</sup> and will not be repeated herein.

### Activity test

The activities of CO oxidation over  $\text{LaSrNiO}_4$  were performed in a single-pass flow micro-reactor made of quartz with an internal diameter of 6 mm. The reactants (0.5–1 % CO + 0.5–2 %  $\text{O}_2$  + 0–2 %  $\text{CO}_2$ , balanced with helium) were passed through 0.2 g of catalyst at a rate of 10–30 mL/min in the temperature range of 250–325 °C. The gas compositions were analyzed before and after the reaction by an online gas chromatograph equipped with mole-

cular sieve 5A column and thermal conductivity detector (TCD). Here, the change of CO concentration was used as the means to evaluate the activity, *i.e.*,  $X_{[\text{CO}]} = ([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}) / [\text{CO}]_{\text{in}}$ , where  $[\text{CO}]_{\text{in}}$  and  $[\text{CO}]_{\text{out}}$  are the concentration of CO measured before and after the reaction, respectively. Before the data were obtained, reactions were maintained for a period of  $\approx 0.5$  h at each temperature to ensure steady-state conditions.

## RESULTS AND DISCUSSION

### *Effect of O<sub>2</sub> partial pressure*

The effect of the O<sub>2</sub> partial pressure on the activity of CO oxidation is shown in Fig. 1. The CO conversion increased almost linearly with the O<sub>2</sub> partial pressure, indicating that O<sub>2</sub> partial pressure has large and positive effect on the CO oxidation reaction. With increasing O<sub>2</sub> partial pressure, the dissociation rate of O<sub>2</sub> molecule increases, as reported elsewhere.<sup>27</sup> As a result, a greater number of oxygen atoms are incumbent on the catalyst surface, giving more opportunities for CO molecular contact and reaction, and thus improving the CO conversion.

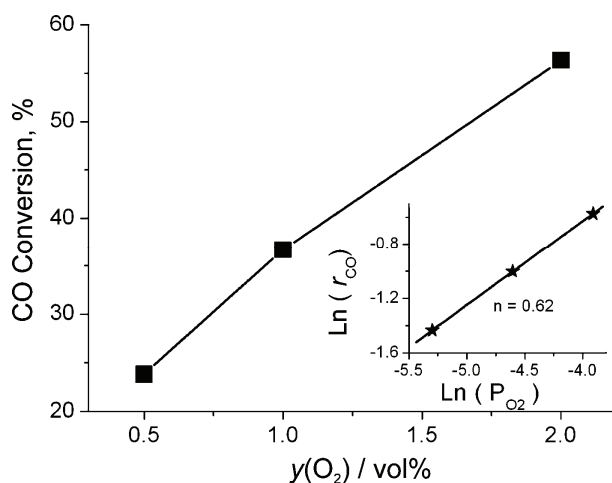


Fig. 1. Effect of oxygen partial pressure on CO conversion and the  $\ln(r_{\text{CO}}) - \ln(p_{\text{O}_2})$  plot (inset) over LaSrNiO<sub>4</sub>. Feed gas: 1% CO/He + 0.5–2 % O<sub>2</sub>/He;  $W/F = 0.6 \text{ g s cm}^{-3}$ ,  $t = 300 \text{ }^\circ\text{C}$ .

The kinetic calculation in this study refer to the work reported by Teraoka *et al.*,<sup>28</sup> in which the subject was also a kinetic study of a catalytic reaction (*i.e.*, NO decomposition) over perovskite-type oxides. Thus, to determine the reaction order of O<sub>2</sub> in the CO oxidation reaction, it was assumed that the kinetics of CO oxidation ( $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ ) obeys the power rate law:

$$r_{\text{CO}} = k[\text{CO}]^m[\text{O}_2]^n[\text{CO}_2]^p$$

where  $k$  is the rate constant;  $[\text{CO}]$ ,  $[\text{O}_2]$  and  $[\text{CO}_2]$  are the concentrations of CO, O<sub>2</sub> and CO<sub>2</sub> in the feed gas, respectively;  $m$ ,  $n$  and  $p$  are the apparent reaction order for CO, O<sub>2</sub> and CO<sub>2</sub>, respectively. When determining the reaction order of the reactant (*i.e.*, O<sub>2</sub>), the  $\ln r - \ln [\text{O}_2]$  values were plotted. The O<sub>2</sub> concentra-

tion was varied in the feed while maintaining the total flow rate constant. In the same way, the reaction order for CO and CO<sub>2</sub> can also be determined.

The  $\ln r - \ln [\text{O}_2]$  plot is also shown in Fig. 1 (inset). The plot gave a straight line with a slope of 0.62, indicating the reaction order with respect to O<sub>2</sub> is positive with a value of 0.62. This is different from that reported by Zhang-Steenwinkel *et al.*, who observed that O<sub>2</sub> is near-zero order when the CO/O<sub>2</sub> ratio is stoichiometric.<sup>13</sup>

#### Effect of CO partial pressure

The effect of the CO partial pressure on the activity of CO oxidation is shown in Fig. 2. It was found that the CO conversion decreased with increasing CO partial pressure and the reaction order with respect to CO was calculated to be  $-0.32$ . This is also different from the results reported by Zhang-Steenwinkel *et al.*,<sup>13</sup> who found that the reaction rates were facilitated by the CO partial pressure with a first reaction order. The decrease of the CO conversion found in the present study could be explained by the fact that with increasing CO partial pressure, the CO/O<sub>2</sub> ratio increases, which means a decrease of the O<sub>2</sub> partial pressure; hence, the chance for O<sub>2</sub> adsorption and dissociation decreases, resulting in a decrease of the CO conversion. This is in accordance with the above result, *i.e.*, a decrease of the O<sub>2</sub> partial pressure (which means an increase of the CO/O<sub>2</sub> ratio) leads to a decrease in the CO conversion. However, it should be emphasized that the total amount of CO oxidized increases with increasing CO partial pressure. For example, at 0.5 vol. % CO partial pressure, the CO conversion was 69.86 vol. %; while at 1 vol. % CO partial pressure the CO conversion was 56.33 vol. %. Thus, the total amount of CO oxidized at 0.5 vol. % CO partial pressure was  $(0.5 \times 69.86)$  vol. %, which is lower than that at 1 vol. % CO partial pressure

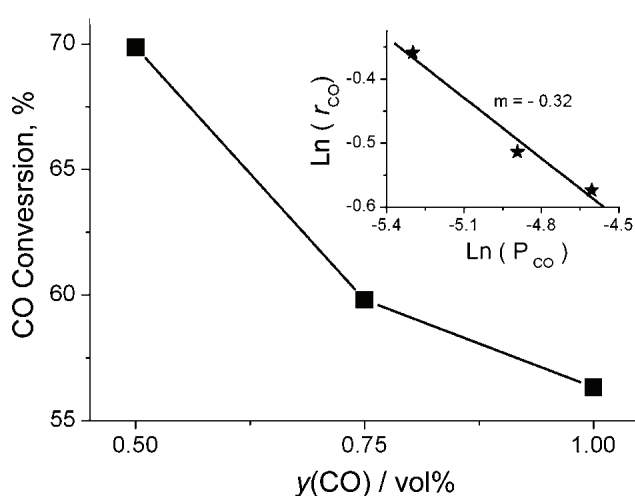


Fig. 2. Effect of CO partial pressure on CO conversion and the  $\ln(r_{\text{CO}}) - \ln(p_{\text{CO}})$  plot (inset) over LaSrNiO<sub>4</sub>. Feed gas: 0.5–1 % CO/He + 2 % O<sub>2</sub>/He;  $W/F = 0.6 \text{ g cm}^{-3}$ ,  $t = 300 \text{ }^\circ\text{C}$ .

((1×56.33) vol. %). In all, this result indicates that the CO reaction order calculated is negative in the present case ( $m = -0.32$ , see inset in Fig. 2).

#### Effect of CO<sub>2</sub> partial pressure

It was reported that CO<sub>2</sub> desorption is the rate-determining step in CO oxidation,<sup>13</sup> which certifies the importance of the CO<sub>2</sub> partial pressure to the reaction rate. Hence, it was considered worthwhile to investigate the influence of CO<sub>2</sub> on the reaction. The change of CO conversion with CO<sub>2</sub> partial pressure is shown in Fig. 3 (here, the CO<sub>2</sub> partial pressure includes the CO<sub>2</sub> added in the feed gas and that produced by CO oxidation. For example, when adding 1 % CO<sub>2</sub> to the feed gas, the CO conversion was 60.76 % ( $\approx 0.61$ ), then, the CO<sub>2</sub> partial pressure was considered to be 1.61 %). It can be seen that the CO conversion decreased progressively with increasing CO<sub>2</sub> partial pressure, showing the inhibitory action of CO<sub>2</sub> due to the difficulty of CO<sub>2</sub> desorption from the active sites, which decreases the chance for O<sub>2</sub> dissociation and hence for CO oxidation. Based on the activity data, the CO<sub>2</sub> reaction order in the reaction,  $p$ , was calculated to be  $-0.51$  (see inset in Fig. 3). This certifies that the CO<sub>2</sub> partial pressure has indeed a large negative effect on the CO oxidation reaction.

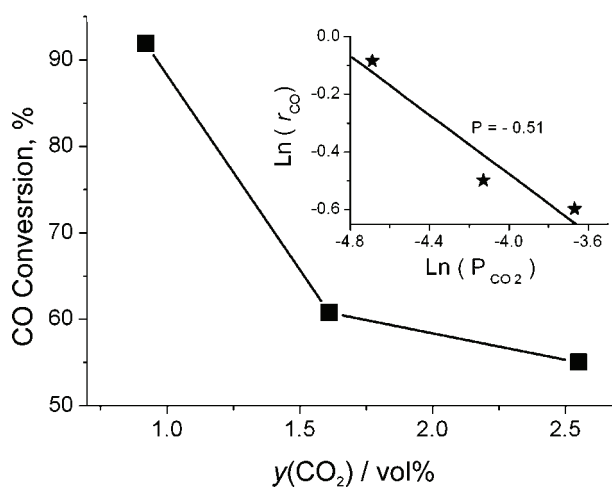


Fig. 3. Effect of CO<sub>2</sub> partial pressure on CO conversion and the  $\ln(r_{\text{CO}}) - \ln(p_{\text{CO}_2})$  plots (inset) over LaSrNiO<sub>4</sub>. Feed gas: 1% CO/He + 2 % O<sub>2</sub>/He + 0–2 % CO<sub>2</sub>/He; W/F = 0.6 g s cm<sup>-3</sup>  $t = 300$  °C.

#### Effect of reaction temperature

The plot of CO conversion vs. reaction temperature is shown in Fig. 4. The CO conversion increase slightly at low temperatures ( $t < 275$  °C), then a substantial increase was observed at  $t > 275$  °C, indicating that CO oxidation over perovskite type oxides mainly occurred at high temperatures ( $t > 275$  °C). This is similar to the results reported by Ciambelli *et al.*<sup>1</sup> The reason might be that above this temperature (275 °C), the oxygen that was chemically adsorbed on the catalyst surface was activated,<sup>29</sup> leading to the creation of oxygen vacancies and,

hence, improving the activity, since oxygen vacancies are a crucial parameter of the oxidation reaction.

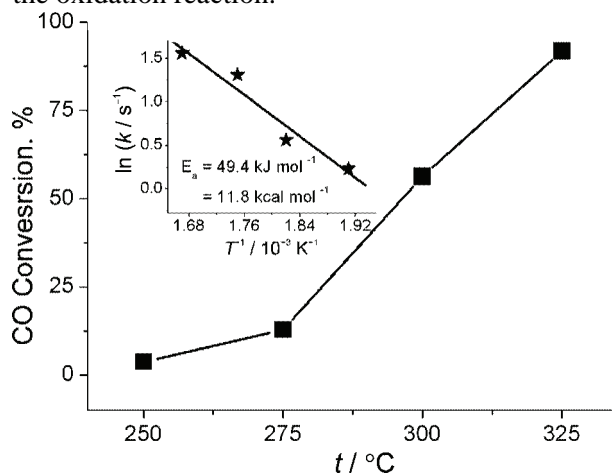


Fig. 4. Effect of reaction temperature on CO conversion and the  $\ln k - 1/T$  plot over  $\text{LaSrNiO}_4$ . Feed gas: 1 %  $\text{CO}/\text{He} + 2$  %  $\text{O}_2/\text{He}$ ;  $W/F = 0.6 \text{ g s cm}^{-3}$ .

On the other hand, according to the reaction order of  $\text{CO}$ ,  $\text{O}_2$  and  $\text{CO}_2$  calculated above, the kinetics of  $\text{CO}$  oxidation could be written as:

$$-r_{\text{CO}} = k [\text{CO}]^{-0.32} [\text{O}_2]^{0.62} [\text{CO}_2]^{-0.51}$$

Therefore, the  $k$  value at different temperatures could be deduced. By plotting the function of  $\ln k$  vs.  $1/T$  (see inset in Fig. 4), the activation energy ( $E_a$ ) is deduced. The calculated  $E_a$  value is  $11.8 \text{ kcal mol}^{-1}$ , which is far lower than that of  $\text{LaAl}_{0.985}\text{Fe}_{0.015}\text{O}_3$  ( $18.1 \text{ kcal mol}^{-1}$ ) – the lowest activation energy for  $\text{CO}$  oxidation in the  $\text{LaAl}_{1-x}\text{Fe}_x\text{O}_3$  system, as reported by Ciambelli *et al.*,<sup>1</sup> indicating that  $\text{LaSrNiO}_4$  is a more suitable catalyst for  $\text{CO}$  oxidation.

#### Effect of contact time ( $W/F$ )

The effect of contact time ( $W/F$ ,  $W$  = catalyst weight (g);  $F$  = flow rate of the reactant (mL/min)) on the  $\text{CO}$  oxidation reaction is shown in Fig. 5. An abrupt increase in  $\text{CO}$  conversion was observed from  $W/F = 0.4$  to  $0.6 \text{ g s cm}^{-3}$  and then remained almost constant from  $W/F = 0.6$  to  $1.2 \text{ g s cm}^{-3}$ . At a low contact time ( $W/F = 0.4 \text{ g s cm}^{-3}$ ), the  $\text{CO}$  cannot be oxidized sufficiently before elution due to the high flow rate. In other words, the catalyst is overloaded and the active sites cannot be regenerated in time for  $\text{CO}$  oxidation under this condition. As a result, only a low conversion of  $\text{CO}$  was observed. With increasing contact time or decreasing flow rate ( $W/F = 0.6 \text{ g s cm}^{-3}$ ), the amount of active sites used for  $\text{CO}$  oxidation could be regenerated in time, which thus leads to the abrupt increase in the  $\text{CO}$  conversion. However, only a minor increase in the  $\text{CO}$  conversion was observed when the contact time was increased further (from  $0.6$  to  $1.2 \text{ g s cm}^{-3}$ ), which might mean that the catalyst had reached its maximal capa-

bility for CO oxidation at  $W/F = 0.6 \text{ g s cm}^{-3}$ . That is to say, the optimum contact time for CO oxidation is  $0.6 \text{ g s cm}^{-3}$  under the present conditions.

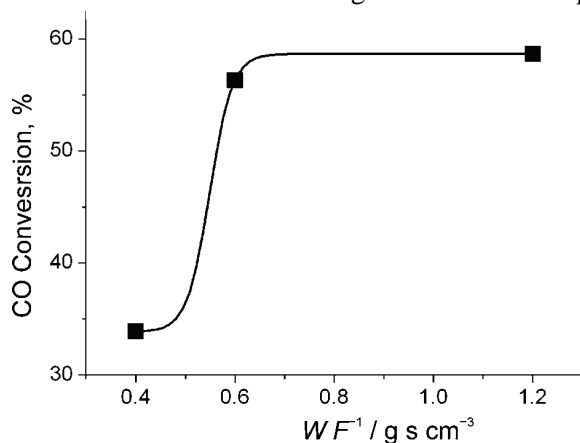
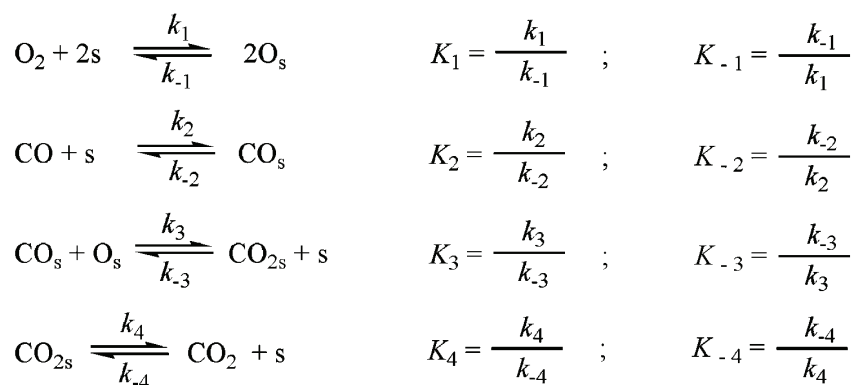


Fig. 5. Effect of contact time ( $W/F$ ) on CO conversion over  $\text{LaSrNiO}_4$ . Feed gas: 1 % CO/He + 2 %  $\text{O}_2$ /He,  $t = 300 \text{ }^\circ\text{C}$ .

#### Reaction mechanisms based on the kinetic analysis

The reaction steps for CO oxidation from the literatures<sup>13</sup> could be described as follows:



Here, "s" is a surface active site. To determine the kinetics of CO oxidation, each step has been assumed to be the rate-determining step; accordingly, the following four equations could be deduced:

*Case 1.* The dissociation of oxygen is the rate-determining step:

$$-r = \frac{Nk_1p_{\text{O}_2}}{\left(1 + \frac{k_{-3}k_{-4}}{k_2} \frac{p_{\text{CO}_2}}{p_{\text{CO}}} + k_2p_{\text{CO}} + k_{-4}p_{\text{CO}_2}\right)^2} \quad (\text{R1})$$

*Case 2.* The adsorption of CO is the rate-determining step:

$$-r = \frac{Nk_2 p_{\text{CO}}}{1 + k_1^{1/2} p_{\text{O}_2}^{1/2} \frac{k_{-3}k_{-4}}{k_1^{1/2}} \frac{p_{\text{CO}_2}}{p_{\text{O}_2}^{1/2}} + k_{-4} p_{\text{CO}_2}} \quad (\text{R2})$$

Case 3. The formation of  $\text{CO}_{2\text{s}}$  is the rate-determining step:

$$-r = \frac{Nk_3 k_1^{1/2} k_2 p_{\text{CO}} p_{\text{O}_2}^{1/2}}{1 + k_1^{1/2} p_{\text{O}_2}^{1/2} + k_2 p_{\text{CO}} + k_{-4} p_{\text{CO}_2}} \quad (\text{R3})$$

Case 4. The desorption of  $\text{CO}_2$  is the rate-determining step:

$$-r = \frac{Nk_4 k_1^{1/2} k_2 k_3 p_{\text{CO}} p_{\text{O}_2}^{1/2}}{1 + k_1^{1/2} p_{\text{O}_2}^{1/2} + k_2 p_{\text{CO}} + k_1^{1/2} k_2 k_3 p_{\text{CO}} p_{\text{O}_2}^{1/2}} \quad (\text{R4})$$

Of all these cases, only the rate equation (R1) shows a negative reaction order for CO, which was the case in the present study. Hence, oxygen dissociation is considered to be the rate-determining step and Eq. (R1) is the expression of rate equation. The apparent reaction order for CO in Eq. (R1) is between  $-2$  and  $2$ , which contains the value ( $-0.32$ ) found in this study. The apparent reaction order for  $\text{O}_2$  is  $1$ , which is higher than that found in this work ( $0.62$ ). The reason might be ascribed to the competitive adsorption of CO (reactant) and  $\text{CO}_2$  (product) with  $\text{O}_2$  for the active sites, thus decreasing the opportunity for oxygen adsorption and hence the reaction order. The apparent reaction order for  $\text{CO}_2$  is  $-0.51$ , which is within the range appearing in Eq. (R1) ( $-2$ – $0$ ). In addition, the low value of  $\text{CO}_2$  reaction order,  $-2$ , in Eq. (R1) suggests that, in some cases,  $\text{CO}_2$  desorption could predominate in the reaction and become the rate-determining step.

Altogether, the present study suggests that the dissociation of oxygen is the rate-determining step of CO oxidation. Therefore, it is possible that  $\text{LaSrNiO}_4$  shows an efficient activity for CO oxidation since it contains large numbers of oxygen vacancies,<sup>26</sup> which were reported to be very active sites for oxygen dissociation.<sup>27</sup> This might also be part of the reasons why noble metals can show high activity for CO oxidation even at low temperatures, since they are efficient materials for promoting oxygen dissociation at low temperatures.

#### CONCLUSIONS

CO oxidation on the compound oxide  $\text{LaSrNiO}_4$  was investigated. Based on the CO conversion found under different conditions, the reaction order of CO,  $\text{O}_2$  and  $\text{CO}_2$  were determined. It was found that the reaction orders of CO and  $\text{CO}_2$  are negative, while that of  $\text{O}_2$  is positive with the value of  $0.62$ , suggesting that oxygen dissociation is the rate-determining step of the reaction. The kinetics of



CO oxidation was discussed assuming each elementary step to be the rate-determining step. The activation energy of the reaction is very small ( $11.8 \text{ kcal mol}^{-1}$ ), which suggests that  $\text{LaSrNiO}_4$  maybe a potential candidate for CO oxidation. The optimum contact time of the reaction found in the present case is  $0.6 \text{ g s cm}^{-3}$ .

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## ИЗВОД

КИНЕТИКА ОКСИДАЦИЈЕ УГЉЕНИК(II)-ОКИДА НА ОКСИДИМА  
СЛИЧНИМ ПЕРОВСКИТУ  $\text{LaSrNiO}_4$ 

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Испитан је утицај концентрације реактанта/производа реакције, реакционе температуре и времена контакта ( $W/F$ ) на кинетику каталитичке оксидације CO на оксидима сличним перовскиту  $\text{LaSrNiO}_4$ . Утврђен је негативан парцијални ред реакције како у односу на реактант CO ( $-0,32$ ) тако и у односу на производ реакције  $\text{CO}_2$  ( $-0,51$ ), док је ред реакције у односу на  $\text{O}_2$  позитиван,  $0,62$ . Негативни ред реакције у односу на CO и  $\text{CO}_2$  потиче вероватно од њихове компетитивне адсорпције са  $\text{O}_2$ , која је спори ступањ реакције. Вредност израчуната за енергију активације ( $E_a$ ) је  $49,3 \text{ kJ mol}^{-1}$  и указује на то да  $\text{LaSrNiO}_4$  може бити потенцијални катализатор за оксидацију CO. Оптимално време контакта за реакцију је  $0,6 \text{ g s cm}^{-3}$ . Састав реакционе смеше у хелијуму као носећем гасу је био:  $0.5\text{--}1 \text{ vol } \% \text{ CO} + 0.5\text{--}2 \text{ vol } \% \text{ O}_2 + 0\text{--}2 \text{ vol } \% \text{ CO}_2$ .

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