

THERMOGRAVIMETRIC REDUCTION OF LANTHANUM STRONTIUM IRON PEROVSKITE OXIDES WITH CARBON MONOXIDE

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(Received 24 April 1989)

ABSTRACT

The reduction behaviour from surface to bulk of lanthanum strontium iron perovskite oxide ($\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$; $0 \leq x \leq 1.0$) particles by CO gas was studied by means of TG, DSC, IR, XRD and X-ray micro-analysis. Interactions with CO and oxygen species that proceed exothermally gave a large weight loss and weight increase respectively. Both increased with the increase of x in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$. A weight loss was observed in the temperature range 525–725 K as a result of the desorption and reduction by CO of surface oxygen species. A weight increase was observed in the temperature range 775–1125 K as a result of the formation of carbon and/or carbonaceous species. It was concluded that the disproportionation of CO occurs at higher x and higher temperature.

INTRODUCTION

Some perovskite oxides have attracted considerable attention because of their use as functional materials in the catalysts [1], gas sensors [2] and electrode materials for fuel cells [3] or batteries [4]. It is known that the catalytic and/or electrochemical activities of perovskite oxides are strongly affected by substitution of the constituent elements. For example, Isaacs and Olmer [5] investigated the activity for the electrochemical reduction of oxygen and demonstrated that $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ is the most active perovskite oxide.

We have previously reported that substitution of Sr^{2+} for La in LaFeO_3 greatly changed the catalytic activity for the oxidative dehydrogenation of 1-butene [6] and the formation of acetaldehyde from ethanol [7]; it was also found that the product distributions were affected by the oxidation state of the oxide surface in these reactions.

The oxidation states at the surface or within the bulk of the perovskite oxides at higher temperature, in particular, the reduction behaviours in CO atmosphere, have been considered to be very important in connection with the behaviour of CO or CO_2 in the oxidative coupling of methane [8] or the

stability of lattice oxygen. However, there is little information on the reduction behaviours of surface or bulk perovskite oxides, with the exception of the low temperature reduction of LaNiO_3 [9] and LnCoO_3 ($\text{Ln} \equiv \text{La-Eu}$) [10] under H_2 atmosphere. In this paper, the effect of Sr^{2+} substitution on the reduction behaviour of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ oxide is discussed by investigating the thermal properties of surface or bulk oxygen in CO atmosphere.

EXPERIMENTAL

Preparation of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$

In the preparation of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0-1.0$), SrCO_3 , Fe_2O_3 and La(OH)_3 were used as starting materials. Well-ground mixtures of components were fired at 1373 K in air for 4 h. These compounds were analysed by XRD and confirmed as having the perovskite structure. Granules of 48–100 mesh were used as samples. Surface area was determined by Kr-adsorption at liquid nitrogen temperature.

Apparatus and procedure

TG and DSC experiments were performed in the flow (125 ml min^{-1}) of $\text{CO}(22.8 \text{ KPa})\text{-He}$ or $\text{H}_2(22.8 \text{ KPa})\text{-He}$ gas mixtures at atmospheric pressure using a Rigaku Thermoflex 8100 apparatus. The sample weight was 20 mg and the heating rate was 10 K min^{-1} . The oxides were also reduced by CO pulse (0.28 ml) in a quartz pulse reactor, in which 250 mg of oxide was held and heated up to 775 K in an He stream (32 ml min^{-1}) at the same heating rate prior to the reduction by CO pulse. The outlet gas was analysed by a gas chromatograph. Powder XRD patterns were recorded on a Rigaku Geiger-flex 2013 diffractometer using $\text{Cu } K\alpha$ radiation. IR spectra were obtained with a double-beam spectrophotometer (JASCO IRA-1) using the KBr method after pressing 30 mg of KBr and oxide mixture at a pressure of $8 \times 10^9 \text{ N m}^{-2}$. The carbon $K\alpha$ intensity was measured with an X-ray microanalyser (JXA-5A) after the thermal analysis.

RESULTS AND DISCUSSION

TG was measured in He and H_2 atmospheres. The weight loss in the He atmosphere was not detected up to 575 K, but then increased steadily. The amounts of oxygen desorbed up to 1025 K were, for example, 2.1 ml m^{-2} for $x = 0.7$ (surface area: $3.6 \text{ m}^2 \text{ g}^{-1}$) and 0.51 ml m^{-2} for $x = 0.2$ ($3.7 \text{ m}^2 \text{ g}^{-1}$). These represent much more than monolayer coverage (0.25 ml m^{-2}).

In the H_2 atmosphere, a large steady weight loss, 2.6 and 1.0 wt.% oxide for $x = 0.7$ and 0.2, respectively, was observed in the temperature range 505–1025 K.

Weight loss of $La_{1-x}Sr_xFeO_3$ ($x = 0-1.0$) in a CO atmosphere

In a CO atmosphere, the weight loss and increase which proceed exothermally were observed in the temperature ranges 525–725 and 775–1125 K respectively. The TG results and the maximum DSC temperature measured in the CO atmosphere in the temperature range 525–725 K are shown in Fig. 1 against various values of x in $La_{1-x}Sr_xFeO_3$.

It is obvious from this figure that the weight loss occurs at the lowest temperature for $x = 0.2$ and increases linearly with x . Nitadori and Misono [11] reported that the increase of oxygen desorption in TPD with increasing x resulted in the reduction of Fe^{4+} to Fe^{3+} . The amount of weight loss was about twice that of the TPD desorption.

The sample was also reduced by CO pulse injection in the same temperature range as the weight loss in the thermal analysis. When the sample was heated in flowing He up to 775 K, prior to the reduction by CO pulse, the amounts of desorbed oxygen estimated from weight losses were 0.93 and 0.09 ml m^{-2} for $x = 0.7$ and 0.2 respectively. The adsorption of CO and CO_2 was confirmed from the difference of mass balance of CO at the reactor inlet and outlet and the CO_2 pulse (0.28 ml) injection. These results demonstrated that the adsorption of CO and CO_2 is involved in the CO oxidation mechanisms as reported by Tascon et al. [12], who showed that the surface reaction between adsorbed CO and dissociatively adsorbed oxygen, which proceeds through the formation of intermediate carbonate species, is the controlling step in the CO oxidation of $LaCoO_3$. As the exothermal DSC reflects the difference in reactivities between the surface and CO or H_2 , the enthalpy change per unit weight loss was measured using 20 mg of oxide and

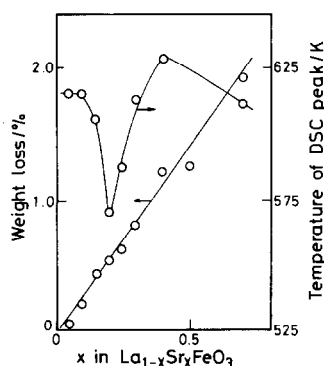


Fig. 1. Effect of Sr^{2+} substitution on weight loss (500–725 K) and DSC peak temperature.

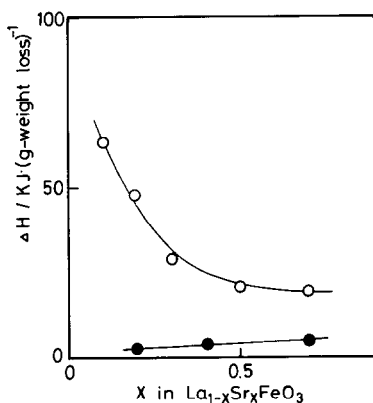


Fig. 2. Effect of Sr^{2+} substitution on enthalpy change in CO (○) (525–725 K) and H_2 (●) atmospheres (375–600 K).

plotted in Fig. 2 against x in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$.

It is obvious from this figure that the enthalpy change per unit weight loss for the reduction by CO sharply decreases with x and suggests that the reduction behaviours are more complex, as compared with the enthalpy change by H_2 , which slightly increases with x and is based on the decrease in the reactive oxygen. This result, at least, indicates that at higher x values a part of the oxygen species absorbs very weakly on the surface and easily desorbs without the possibility of reaction with CO.

TG and DSC were measured in a CO atmosphere after heating to 1025 K in a He atmosphere. The effect of He treatment on weight loss and enthalpy change is shown in Table 1.

As shown in Table 1, the weight loss after He treatment decreases over the entire range of x , except for $x = 0.3$ and 0.5, but the enthalpy change increased except for $x = 0.15$, 0.2 and 0.7. The decrease in weight loss and

TABLE 1

Effect of He treatment on weight loss and enthalpy change

x	Before He treatment		After He treatment	
	Weight loss (%)	Enthalpy change (J)	Weight loss (%)	Enthalpy change (J)
0.10	0.22	2.97	0.14	3.45
0.15	0.44	3.45	0.33	3.13
0.20	0.55	4.74	0.50	3.90
0.25	0.62	4.65	0.57	5.69
0.30	0.80	4.82	0.81	5.16
0.40	1.22	5.49	0.60	6.11
0.50	1.25	6.37	1.35	7.07
0.70	1.91	7.05	1.19	5.32

the increase in enthalpy change may be because of the increase of adsorbed CO or CO₂ as described above.

Generally, a portion of the Fe³⁺ is oxidised to unstable Fe⁴⁺ with Sr²⁺ substitution, as reported by Takano et al. [13] and Mizusaki et al. [14]. As a result, the covalence of the Fe–O bond may be lowered and become more ionic and, furthermore, oxygen desorption and dissociation on the surface may be appreciably facilitated as previously reported [6].

The existence of CO in the gas phase probably accelerates these phenomena as well as the structural or valence changes of the surface as previously reported [5] with the easy reduction of Fe⁴⁺ to Fe³⁺.

Weight increase of La_{1-x}Sr_xFeO₃ (x = 0–1.0) in a CO atmosphere

The weight increase, which proceeds exothermally, was observed in a CO atmosphere in the temperature range 775–1125 K and is shown in Fig. 3 as a function of x in La_{1-x}Sr_xFeO₃. This weight increase occurred in two temperature ranges of 775–1000 and 1000–1125 K for $x \leq 0.3$ and proceeded in one step for $x \geq 0.4$. Its amount increased with increasing x , as shown in Fig. 3, and was about five times the weight loss. The peak temperature in weight increase was observed to shift to a higher temperature for $x \geq 0.4$.

After the oxide was heated in a CO atmosphere up to 773, 873, 973 and 1075 K at a heating rate of 10 K min⁻¹, the oxide was cooled to room temperature in an He atmosphere and reheated in air at the same heating rate to 1075 K.

The XRD patterns of La_{1-x}Sr_xFeO₃ ($x = 0.7$) heated in a CO atmosphere up to each above temperature showed that the peak (22.3°) of the perovskite phase shifted to a lower angle and the maximum peak of the SrCO₃ phase (25.2–25.8°), whose intensity tends to increase with temperature, was detected in the major perovskite phase. However, the shift of the 22.3° peak was not observed at $x \leq 0.3$. Furthermore, XRD patterns of

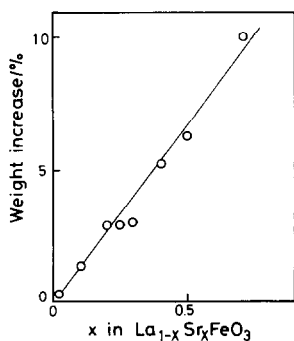


Fig. 3. Effect of Sr²⁺ substitution on weight increase (775–1125 K) in a CO atmosphere.

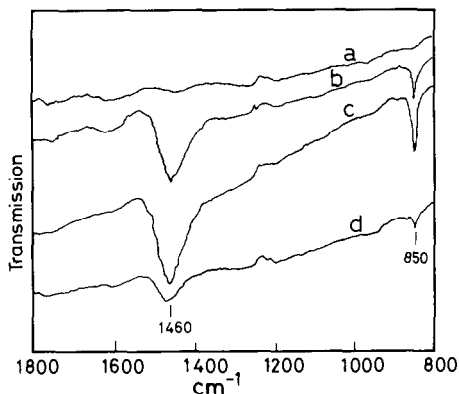


Fig. 4. IR spectra after various gas treatments, $x = 0.7$ in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$.

$x = 0.7$ heated in air up to 1075 K after the CO treatment showed almost the same patterns as fresh oxide. Therefore, it was concluded that the perovskite structure is completely restored with easy decomposition of the unstable SrCO_3 in an air atmosphere at high temperature.

Figure 4 shows the IR spectra of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.7$) treated at various conditions. In this figure, spectra a and b are those for fresh oxide and for a sample heated in a CO atmosphere up to 1075 K respectively. There are two major bands which increase with x and temperature of the CO treatment: a sharp band (850 cm^{-1}) attributed to the vibration of the carbon atom [15] and a wide band (1460 cm^{-1}) due to the monodentate carbonate species according to the result reported by Fierro and Tejuca [16]. As shown in spectra c and d, these bands remain almost unchanged by He

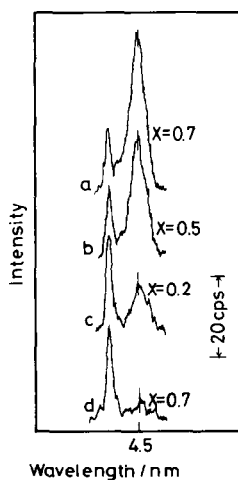


Fig. 5. Intensity of carbon $K\alpha$ for various x in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$. d is a sample treated in air up to 1075 K after CO treatment.

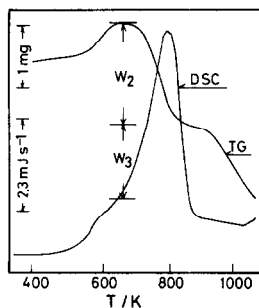


Fig. 6. TG and DSC for $x = 0.7$ reheated in air after being heated up to 1075 K in a CO atmosphere.

treatment up to 1075 K after the CO treatment (c), however, with air treatment, decreased for $x = 0.7$ or vanished for $x = 0.3$ (d).

Figure 5 shows the intensity of the carbon $K\alpha$ obtained from EPMA for various x values in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ heated up to 1075 K in a CO atmosphere. The intensities increased with x , but, remarkably, decreased following air treatment because of the combustion of carbon.

We conclude from these results that the weight increase at temperatures higher than 775 K is related to the production of carbon and/or carbonaceous species by the decomposition of CO over reduced $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$.

The weight loss (W_2) and the large exothermal enthalpy change (H_1) caused by reheating in air after heating in a CO atmosphere up to 1075 K were observed in the temperature range 500–1075 K and are shown in Fig. 6 against $x = 0.7$ in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$. As shown in this figure, weight loss (W_3) with no enthalpy change, which seems to represent the decomposition of carbonaceous species, was observed for $x \geq 0.4$ at temperatures in the 875–1075 K range.

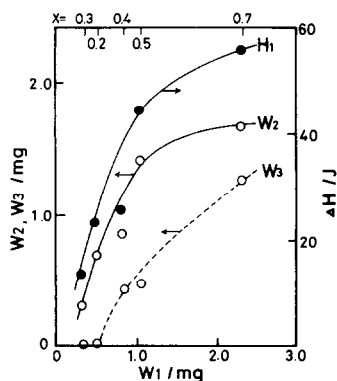
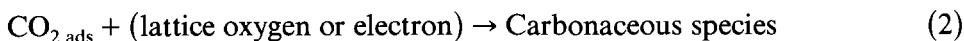
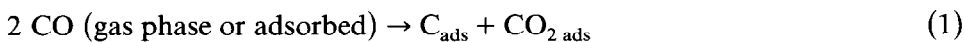


Fig. 7. W_2 , W_3 and H_1 as a function of the weight increase (W_1) of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ heated up to 1075 K in a CO atmosphere.

W_2 , W_3 and H_1 are plotted in Fig. 7 against the weight increase (W_1) (or x in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$) caused by CO treatment up to 1075 K. It is obvious from this figure that the behaviour of W_2 is very similar to that of H_1 . The amounts of carbon calculated from H_1 by assuming the combustion agreed well with the values of W_2 . ($W_2 + W_3$) increased linearly with increase of W_1 .

Because the weight increase for values of $x \leq 0.3$ in a CO atmosphere proceeded in the two temperature ranges of 775–1000 and 1000–125 K, it was concluded that the weight increase in the first step (775–1000 K) is related to the production of carbon and that in second step to the production of the carbonaceous species which easily decompose in air. Furthermore, these two steps proceed simultaneously at $x \geq 0.4$.

Consequently, the following disproportionation reaction of adsorbed CO or gas phase CO will occur more easily at higher values of x and temperature.



The weight increase is the result of reactions (1) and (2). It is expected that the participation of adsorbed CO in reaction (1) exceeds that of gas phase CO for $x \geq 0.2$ and that the adsorption of produced CO_2 tends to occur more easily with increase in x . Furthermore, as the capability of diffusion of lattice oxygen remarkably increases with increasing x in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ at elevated temperatures, it is expected that the lattice oxygen should contribute to reaction (2), as is supported by the presence of SrCO_3 in XRD patterns. Carbonaceous species may exist in the ionic state as reported by Arakawa et al. [17] and are advantageous for the formation of SrCO_3 .

ACKNOWLEDGMENTS

The authors wish to thank K. Shimada for experimental assistance in the X-ray microanalyser measurements.

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