# Studies on the catalytic decomposition of $N_2O$ on $LnSrFeO_4$ (Ln = La, Pr, Nd, Sm and Gd)

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### Abstract

Oxides with the composition LnSrFeO<sub>4</sub> (Ln = La, Pr, Nd, Sm and Gd) were prepared by ceramic method and characterised by XRD, IR, conductivity and magnetic measurements. The surface of these oxides was characterised by XPS to estimate the valence state of each element and their relative concentrations. Decomposition of N<sub>2</sub>O was carried out on these oxides to establish the role of the rare earth on catalytic activity at 50 and 200 torr in the temperature range 420–480 °C. The catalytic activity was correlated to the bulk and surface properties of these oxides.

#### Introduction

Oxides with perovskite and related structures are emerging as important prototype models for catalytic studies. Reports on oxides having a  $K_2NiF_4$  structure have revealed that these oxides exhibited greater activity compared to the analogous perovskite oxides [1, 2]. The catalytic activity of Co-, Ni-, Cu-, and Zn-containing oxides with a  $K_2NiF_4$  structure has been examined for various reactions [1–6]. However, the catalytic activity of iron-containing oxides with a  $K_2NiF_4$  structure has been examined for various reactions [1–6]. However, the catalytic activity of iron-containing oxides with a  $K_2NiF_4$  structure has not received much attention in the literature, although corresponding perovskite oxides are known to be active for various reactions [7].

 $Ln_2FeO_4$  cannot be prepared due to the unfavourable tolerance factor and difficulty in stabilising iron in the divalent state. There are, however reports available wherein iron is stabilised in the trivalent and tetravalent states with  $K_2NiF_4$  structure, such as  $LnSrFeO_4$  [8],  $LaSrM_{0.5}Fe_{0.5}O_4$  [9] where M=Mg or Zn, and  $LaSrLi_{0.5}Fe_{0.5}O_4$  [10]. Although these compounds are known for their interesting solid state properties, no reports are available on their catalytic activity. In the present investigation, an attempt has been made to evaluate the catalytic activity of iron-containing oxides having a  $K_2NiF_4$  structure. The effect of substitution of rare-earth ions on the solid state and catalytic properties has been studied, choosing  $LnSrFeO_4$  compounds in which  $Fe^{3+}$  is stabilised in the presence of strontium. Decomposition of  $N_2O$  was used as a test reaction for the first time to evaluate the catalytic activity of these oxides.

# Experimental

The catalysts used in the present investigation were prepared by the ceramic method by heating  $Ln_2O_3$ ,  $SrCO_3$  and  $Fe_2O_3$  at 1300 °C for 48 h. The formation of a single phase was confirmed by XRD. IR spectra of these compounds were recorded on a Perkin-Elmer infrared spectrometer (Model 1310). Electrical conductivity measurements were carried out in a two-probe cell in the temperature range 30–500 °C. Magnetic measurements were performed in a vibrating sample magnetometer (Model PAR 155) at room temperature by applying a magnetic field of 0–12 kGauss. Surface area of these compounds was determined by BET method employing N<sub>2</sub> as adsorbate at liquid N<sub>2</sub> temperature. The surface of these oxides was examined by XPS using an Escalab Mark II (VG Scientific, U.K.) spectrometer. XP spectra were recorded at room temperature using Al K<sub>a</sub> radiation and a base pressure of  $5 \times 10^{-8}$  mbar.

Decomposition of  $N_2O$  was carried out in a static recirculatory reactor at two different pressures of  $N_2O$ , namely 50 and 200 torr, in the temperature range 400–480 °C. The catalysts were pretreated before each kinetic measurements: (i) evacuation of the catalyst to  $10^{-5}$  torr at 500 °C for 6 h; (ii) soaking the catalyst in oxygen (100 torr) for 12 h at reaction temperature; (iii) mild evacuation for 2 min using rotary pump for removing weakly adsorbed and gas phase oxygen. The pretreated catalysts are found to give reproducible results.

## **Results and discussion**

All the compounds were found to crystallise in tetragonal symmetry. Table 1 presents the structural parameters such as crystal symmetry, lattice parameters, volume of unit cell and tolerance factors. The unit cell parameters calculated in this investigation are in fairly good agreement with those reported for the same systems. As can be seen, the unit cell decreases from  $La \rightarrow Gd$ , indicating lanthanide contraction across the series. The tolerance factors given in Table 1 were calculated using the high spin ionic radius of

Compound	Symmetry*	Lattice pa	rameters (A°)	t	c/a
		a	c		
LaSrFeO4	т	3.854	12.667	0.9209	3.287
PrSrFeO <sub>4</sub>	Т	3.840	12.588	0.9145	3.279
NdSrFeO <sub>4</sub>	Т	3.832	12.503	0.9131	3.263
SmSrFeO <sub>4</sub>	Т	3.825	12.487	0.9064	3.265
GdSrFeO₄	Т	3.821	12.434	0.9024	3.254

TABLE 1

Structural parameters of LnSrFeO<sub>4</sub>

T = tetragonal.

Fe<sup>3+</sup> (0.645 Å) which falls in the range reported for the  $K_2NiF_4$  structure [11]. Table 1 also shows a decrease in c/a values from La  $\rightarrow$  Gd. It is known [12] that if the transition metal ion present in oxides having  $K_2NiF_4$  is a Jahn–Teller ion such as Ni<sup>2+</sup> or Cu<sup>2+</sup>, then the c/a value will be greater than 3.35. In the present case Fe<sup>3+</sup> is not a Jahn–Teller ion and hence c/a values are less than 3.35.

Figure 1 shows the IR spectra of LnSrFeO<sub>4</sub> recorded at room temperature. All the compounds showed 3 bands in the Fe–O stretching region, suggesting a low symmetry of FeO<sub>6</sub> octahedra [13]. The higher band (665–670 cm<sup>-1</sup>) was assigned to the Fe–O stretching frequency while the peak at lower frequency (330–365 cm<sup>-1</sup>) is due to the deformation mode. The additional band at 525–570 cm<sup>-1</sup> was assigned to the Ln–O stretching frequency. Singh and Ganguly [14] compared the IR spectra of oxides having K<sub>2</sub>NiF<sub>4</sub> structure with pervoskite oxides. The highest frequency band, corresponding to the B–O bridge stretching frequency of LnSrFeO<sub>4</sub>, was found to be higher than the B–O stretching frequency which appears at 540–560 cm<sup>-1</sup> in LnFeO<sub>3</sub> oxides [12]. This was attributed to the difference in lattice parameters.



Fig. 1. IR spectra of LnSrFeO<sub>4</sub>.

Compound	Sign of $\alpha$	Electrical behaviour at 30 °C $(\Omega^{-1} \text{ cm}^{-1})$	Moment $\mu_{eff}$ (B. M.)	Surface area $(m^2 g^{-1})$
LaSrFeO <sub>4</sub>	+	p-type semiconductor $(1.4 \times 10^{-4})$	3.49	0.7
PrSrFeO₄	+	$1.6 \times 10^{-4}$	4.31	1.0
NdSrFeO	+	$3.5 \times 10^{-5}$	4.63	1.2
SmSrFeO₄	+	$1.0 \times 10^{-4}$	3.55	1.0
GdSrFeO₄	+	$2.8 \times 10^{-5}$	8.25	0.8

TABLE 2 Solid state properties of LnSrFeO<sub>4</sub>

All the compounds in the series exhibit semiconducting behaviour. The positive Seebeck values (Table 2) indicate that holes are the majority charge carriers which are responsible for conduction. This confirms the fact that native defects play a major role in the conduction process. The conduction may be due to the hopping of positive holes from one site to the other among the localised levels. The high resistivity at room temperature observed in LnSrFcO<sub>4</sub> compared to LnFeO<sub>3</sub> [16] may be due to the presence of SrO layers between ABO<sub>3</sub> layers.

The magnetic moments calculated for LnSrFeO<sub>4</sub> are presented in Table 2. All the compounds are paramagnetic at room temperature. The magnitude of the magnetic moment ( $\mu_{eff}$ ) increases from La  $\rightarrow$  Gd, indicating the participation of the rare earth in determining magnetic properties.

### Surface characterisation

Characterisation of the surface of the catalyst is important because reactions take place on the catalyst surface. In the present investigation, the surface of  $LnSrFeO_4$  was analysed by XPS to estimate the valence state of various elements and their relative surface concentrations. The C 1s peak at 285.0 eV was taken as the reference peak.

The salient features of XP spectra of  $LnSrFeO_4$  are summarised in Table 3 and the spectra of Ln 3d, Fe 2p and O 1s regions are shown in Figs. 2-4. Figure 2 show the 3d level of Ln in  $LnSrFeO_4$ . In all the compounds, the rare earth is found to be in the trivalent state, as evidenced from binding energy values reported for corresponding rare earth oxides [17-19]. Rare earth oxides generally show satellite features (indicated by an arrow) which was considered to be due to charge transfer from  $O(2p) \rightarrow metal$  (4f). In the case of La, the satellite is attributed to an energy loss process [20] and hence the satellite appears at a higher binding energy. In the case of other LnSrFeO<sub>4</sub> where Ln  $\neq$  La, the satellite peaks appear at lower binding energies, which was attributed to the shake-down process [19].

XP spectra of the Ln 4d region, however, showed broad bands. The peculiar broad spectra of the 4d regions of the lanthanide ions were attributed

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TABLE 3 XP spectral results<sup>a</sup> of LnSrFeO<sub>4</sub>

Region	LaSrFeO,	:	PrSrFeO4		NdSrFeO4		SmSrFeO,		GdSrFeO4	
	Core level	Satellite	Core level	Satellite	Core level	Satellite	Core level	Satellite	Core level	Satellite
0 1s	529.65 531.50		529.00 531.25		529.25 531.85		529.00 531.50		529.75 531.50	
Fe 2p <sub>3/2</sub> 2p <sub>1/2</sub> 3p	710.75 724.25 55.25	718.00	710.75 725.25 55.75	717.75	710.50 724.75 56.00	718.25	710.50 724.75 55.75	718.25	711.00 724.00 55.50	717.0 719.5
Ln 3d <sub>62</sub> 3d <sub>322</sub> 4d	835.05 852.50 103.00 105.50	838.00 855.10	933.50 953.25 broad	929.50 950.50	983.25 1005.75 broad	981.00 1003.00	1084.50 1107.50 broad	1082.00 1105.00	1187.00 1218.00 broad	1185.5 1215.5
Sr 3d 2p	133.50 135.25 268.75		134.00 135.75 269.00		133.75 136.00 268.50		134.25 136.25 269.75		134.25 135.75 269.75	
*Binding en	lergy in eV.									



Fig. 2. XP (Ln 3d) spectra of LnSrFeO<sub>4</sub>.

to electrostatic coupling between 4d and 4f, with concomitant production of many final states with different energies. The broad peaks may also be due to the fact that the 4d hole state has a very short lifetime [21]. However, La 4d showed sharp peaks due to the absence of electrons in the f-shell.

Figure 3 shows the Fe(2p) spectra of LnSrFeO<sub>4</sub> compounds. The binding energy values for Fe  $2p_{3/2}$  for these compounds are found to be in the range 710–711 eV (Table 3), which clearly indicates the presence of iron in the trivalent state. This is in accordance with reports in the literature for Fe<sup>3+</sup>containing oxides [22–24]. However, GdSrFeO<sub>4</sub> showed a broad peak which might be due to the presence of iron in mixed valence states, namely Fe<sup>3+</sup> and Fe<sup>2+</sup>. The broad satellite peak centered between 717–719 eV (7–8 eV away from the Fe  $2p_{3/2}$  peak) is characteristic of Fe<sup>3+</sup> species, independent



Fig. 3. XP (Fe 2p) spectra of LnSrFeO<sub>4</sub>.

of the nature of the oxide and the coordination number [24]. The combination of the main  $2p_{3/2}$  line and its satellite provides a reliable identification of the valence state of iron in these compounds. The presence of a satellite at ~717 eV in GdSrFeO<sub>4</sub> shows the possibility of a small amount of Fe<sup>2+</sup> in the system along with Fe<sup>3+</sup>. This is also evidenced from the broad peak for  $2p_{3/2}$ .

The XP(O 1s) spectra of LnSrFeO<sub>4</sub> are shown in Fig. 4. The spectra show two peaks, with binding energy values ~529 and ~531 eV respectively. These two peaks can be assigned to  $O^{2-}$  and  $O^{-}$ ,  $OH^{-}$  or  $CO_{3}^{2-}$  species, as reported in literature [25, 26]. The XP(Sr 3d) spectra of LnSrFeO<sub>4</sub> show two peaks with binding energies ~133.5 and ~135.5 eV (Table 3), corresponding to  $3d_{5/2}$  and  $3d_{3/2}$ , indicating the presence of strontium in the divalent state [27, 28].

#### **Catalytic** studies

The kinetic examination of  $N_2O$  decomposition was carried out on the series  $LnSrFeO_4$  at two initial pressures of  $N_2O$ , namely 50 and 200 torr,



Fig. 4. XP (O 1s) spectra of LnSrFeO<sub>4</sub>.

in the temperature range 400-480<sup>1</sup>°C. The kinetic results were analysed using the rate equations corresponding to no inhibition or strong inhibition [29].

$$dP_{N_2O}/dt = k_1 P_{N_2O} \tag{I}$$

$$dP_{\rm N_{2O}}/dt = k_2 P_{\rm N_{2O}}/P_{\rm O_2}^{1/2}$$

Typical kinetic plots are shown in Fig. 5 and the corresponding kinetic parameters are presented in Tables 4 and 5. Using these rate constants, Arrhenius plots were drawn (Fig. 6) and the Arrhenius parameters are given in Tables 4 and 5.

At 50 torr, on all the catalysts, the kinetics obeyed the inhibition equation (I), indicating the adsorption of  $N_2O$  is rate controlling as shown below:

$$N_{2}O_{+}e^{-} \longrightarrow N_{2}O_{ads}^{-}$$
(1)  
$$N_{2}O_{ads}^{-} \longrightarrow N_{2} + O_{ads}^{-}$$
(2)

$$\overline{}_{ds} \longrightarrow N_2 + O_{ads}^-$$
 (2)

)

(II)



Fig. 5. Kinetic plots for the decomposition of N<sub>2</sub>O on LaSrFeO<sub>4</sub>.

TABLE 4

Kinetic and Arrhenius parameters for the decomposition of N<sub>2</sub>O on LnSrFeO<sub>4</sub> at 50 torr<sup>a</sup>

Compound	Temp. (°C)	$k \times 10^3$ (min <sup>-3</sup> )	$E_{a}$ (kcal mol <sup>-1</sup> )	ln A
LaSrFeO	440	0.91	32.8	16.0
•	460	1.50		
	480	3.05		
PrSrFeO₄	420	2.72	24.0	11.4
•	440	4.75		
	460	6.73		
	480	9.04		
NdSrFeO₄	420	0.96	23.8	10.0
•	440	1.93		
	460	3.18		
	480	5.50		
SmSrFeO₄	440	1.23	28.6	13.4
•	460	2.24		
	480	3.70		
GdSrFeO₄	420	2.18	1.71	6.6
-	440	4.03		
	460	5.54		
	480	8.60		

\*Kinetic equation obeyed: eqn. 1.10 (no inhibition).

$$O_{ads}^{-} + O_{ads}^{-} \longrightarrow O_2 + 2e^{-}$$
(3)

$$O_{ads}^{-} + N_2 O \longrightarrow N_2 + O_2 + e^{-}$$
(4)

Generally at low pressure,  $N_2O$  adsorption occurs preferentially by the interaction of the  $\pi^*$  orbital of  $N_2O$  with the surface valence states of the oxide lattice. Because of the limited surface states, adsorption of  $N_2O$  becomes rate controlling. This is the case at 50 torr.

Compound	Temp. (°C)	$k \times 10^3$ (mm <sup>1/2</sup> min <sup>-1</sup> )	$E_{a}$ (kcal mol <sup>-1</sup> )	ln A
LaSrFeO <sub>4</sub>	420	0.21	37.5	20.5
	440	0.30		
	460	0.61		
	480	1.20		
PrSrFeO <sub>4</sub>	400	2.47	30.0	14.9
-	420	3.70		
	440	6.10		
	460	10.53		
NdSrFeO <sub>4</sub>	400	1.15	35.2	11.9
·	420	2.43		
	440	3.03		
	460	5.80		
SmSrFeO <sub>4</sub>	420	1.10	31.3	16.8
	440	2.48		
	460	4.52		
	480	7.83		
GdSrFeO₄	400	3.51	18.7	8.2
	420	5.25		
	440	7.83		
	460	11.05		

TABLE 5

Kinetic and Arrhenius parameters for the decomposition of  $N_2O$  on LnSrFeO<sub>4</sub> at 200 torr<sup>a</sup>

\*Kinetic equation obeyed: eqn. 1.11 (strong inhibition).

At high N<sub>2</sub>O pressure, multipoint adsorption leads to population of the  $\sigma^*$  orbital of N<sub>2</sub>O and hence causes facile N-O fission, resulting in a situation in which desorption of oxygen controls the overall rate due to the saturation with N<sub>2</sub>O molecules. This is the case at 200 torr. The presence of a large density of filled localised electronic states of d-symmetry at the surface is essential for the adsorption of N<sub>2</sub>O, while the localised empty d-orbitals are essential for oxygen desorption. In perovskite-related oxides, the d<sub>z<sup>2</sup></sub> orbitals of B ions have the proper energy and symmetry to interact with N<sub>2</sub>O molecules [30]. Thus the effect of pressure on the kinetics of decomposition is well portrayed in the present series. A similar effect of pressure on kinetics has been reported for perovskite oxides [31].

A linear correlation between the frequency factor and energy of activation at both pressures is shown in Fig. 7. These linear plots demonstrate that although the B site ions are responsible for their activity, the energetics of the B sites are modified significantly by the presence of different rare earth ions at the A sites and hence a compensation effect [32] was observed.



Fig. 6. Arrhenius plot for the decomposition of  $N_2O$ .



Fig. 7. Compensation plots.

# **Physicochemical correlations**

Adsorption of  $N_2O$  in the multipoint mode has been well recognised on the mixed metal oxide catalysts [2, 4]. A similar model has been proposed for the adsorption of  $N_2O$  on LnSrFeO<sub>4</sub> catalysts. According to this model, a molecular orbital scheme has been visualised for N<sub>2</sub>O adsorption on clusters of the type M-O-M' where M and M' are different metal ions. In the present case, clusters of the type Ln-O-Fe, Ln-O-Sr, Sr-O-Fe, Ln-O-Ln and Fe-O-Fe are possible. In perovskite-related oxides, it is the B ion that plays the active role in deciding the solid state and catalytic properties, whereas the A ion plays only a modifying role. Therefore, when the A site ion is changed from La  $\rightarrow$  Gd, the electron density around Fe is affected. In order to establish the role of the A ion in the catalytic decomposition of N<sub>2</sub>O, which is the scope of the present investigation, the cluster of the type Ln-O- Fe is considered. Moreover, Sr<sup>2+</sup> compounds are reported to be active only at very high temperature [33, 34].

The  $\pi^*$  orbital of N<sub>2</sub>O has an orbital throw in a direction similar to the  $d_{z^2}$  orbitals of Fe<sup>3+</sup>. The  $\pi$  orbital of middle nitrogen can interact with the  $p_z$  orbital of an oxide ion while  $\pi$  orbitals of a rare earth ion, having a maximum throw in the axial direction, lead to the multicentre adsorption of N<sub>2</sub>O molecules, forming an adsorbed cluster over the Ln-O-Fe system.\*\*

Recently Larsson [35] proposed another model for the adsorption of  $N_2O$  on clusters of the type M-O-M' which is more appropriate than the former model. This model (Fig. 8) shows a schematic representation of the adsorption of  $N_2O$  on Ln-O-Fe clusters. During adsorption, the throw of orbitals in space is distorted due to the change in electron density around each atom. At a sufficient degree of activation, the N-O bond elongation is such that an  $Fe^{3+}-O^-$  bond is formed. Further elongation leads to splitting of the N-O bond, giving rise to  $N_2(g)$  and  $O^-$  on the surface.

The interaction between the axial f-orbitals of rare earth ions and the  $d_{z^2}$  orbital of iron with the  $p_z$  orbital of oxide ions depends on the electron density of the f-orbital of the rare earth ion. As the rare earth is changed from La  $\rightarrow$  Gd, the f-electrons are filled successively, and the f- $p_z$  interaction between the rare earth ion and the oxide ion of the lattice increases. Consequently the electron density around Fe<sup>3+</sup> increases. As a result, the residual time of O<sup>-</sup> on the iron site can be expected to decrease and desorption becomes facilitated. This is reflected in the decrease in  $E_z$  at 200



Fig. 8. Adsorption of N<sub>2</sub>O on Ln-O-Fe cluster.

<sup>\*\*</sup>The authors are thankful to the referee who pointed out that multipoint adsorption of N-N-O on Ln-O-Fe cluster is not possible based on bond length considerations.



Fig. 9. Plot of  $E_a$  vs. lattice parameters.

torr from La  $\rightarrow$  Gd, except Sm, on which at this pressure desorption of oxygen is rate controlling.

The plot of  $E_a$  vs. a or c presented in Fig. 9 shows a linear correlation between catalytic activity and lattice parameters. When the lattice parameter increases, the distance between two Fe<sup>3+</sup> ions increases and makes the desorption process comparatively difficult, as it involves union of two O<sup>-</sup> ions for the desorption of oxygen. This is reflected in the increase in  $E_a$  at 200 torr going from Gd  $\rightarrow$  La.

As discussed above, desorption of oxygen involves union of two O<sup>-</sup> to give an O<sub>2</sub> molecule. This involves decoupling of spins of the  $p\pi$  orbital electron of an oxygen atom to form O<sub>2</sub>. This kind of decoupling will be facile on catalysts having a high magnetic moment, as evidenced from the plot of  $E_a vs. \mu_{eff}$  shown in Fig. 10. As  $\mu_{eff}$  increases, the desorption of O<sup>-</sup> as O<sub>2</sub> becomes facile and hence  $E_a$  decreases.

Figure 11 shows a plot of  $E_a$  vs. concentration of iron on the surface of the series LnSrFeO<sub>4</sub>, calculated by the method of Powell and Larson [36]. A parallelism observed between  $E_a$  and surface concentration of iron indicates that Fe is the active site for the decomposition of N<sub>2</sub>O. This is in accord with the compensation effect (Fig. 7) observed for the series. Figure 11 indicates that Fe is the active site for these oxides, while Fig. 7 indicates that the energetics of the active site are modified by the presence of a rare earth at A site.



Fig. 10. Plot of  $E_a$  (200 torr) vs.  $\mu_{eff}$ .



Fig. 11. Plot of  $E_a$  (200 torr) vs. concentration of Fe on the surface of LnSrFeO<sub>4</sub>.

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