

Catalytic redox reaction of nitric oxide and carbon monoxide on perovskites

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Kinetics of oxidation-reduction reaction between CO and NO over perovskite catalysts LaMnO_3 and LaCoO_3 , prepared by ceramic and wet methods, has been studied in the temperature range of 473-1000 K. Results have been discussed in the light of X-ray powder diffraction, atomic absorption spectrometry, gas chromatography, electrical conductivity and surface area measurements. The rate-controlling step in the catalytic reduction of NO by CO is presumably the active site reduction process.

The present strategy for the removal of CO, NO and hydrocarbons (HC) from automotive exhaust, in order to reduce atmospheric pollution, depends heavily on the use of catalytic converters, such as the costly noble metals like platinum and platinum-palladium alloys. Substitute non-noble oxides suffer from relatively low catalytic activity, low thermal stability and chemical instability in the exhaust environment¹. The use of perovskite-type oxides² containing La, Mn, Fe, Co, etc. has been proposed as possible substitutes³.

Simultaneous oxidation-reduction reaction between CO and NO as a cost-effective strategy to reduce atmospheric pollution has been investigated on different catalysts^{2,4-8}. In the present paper are presented the results of simultaneous oxidation-reduction reaction between CO and NO over LaMnO_3 and LaCoO_3 catalysts synthesized by different preparative methods.

Materials and Methods

LaMnO_3 and LaCoO_3 were prepared by three different methods:

(i) The compositions LaMnO_3 and LaCoO_3 were prepared from their corresponding oxalates using the ceramic technique. Stoichiometric quantities of high purity (99.8%) oxalates were continuously mixed as a slurry using acetone in an agate mortar and pestle. The dried mixture was decomposed at 873 K and again mixed thoroughly. The resultant oxide mixture was pelletized and fired by placing over a platinum grid at 1373 K for 24 hr. The compounds thus prepared are denoted as $\text{LaMnO}_3(\text{a})$ and $\text{LaCoO}_3(\text{a})$ respectively.

(ii) Stoichiometric quantities of pure (99.9%) La_2O_3 and Mn or Co metal (purity 99.5%) were separately dissolved in conc. HNO_3 (AR), and the solutions were heated slowly with constant stirring to dryness. The residues were dried in an oven, mixed and finally fired at 873-973 K for 6-10 hr. The compounds prepared in this way are designated as $\text{LaMnO}_3(\text{b})$ and $\text{LaCoO}_3(\text{b})$ respectively.

(iii) Stoichiometric quantities of pure (99.9%) La_2O_3 and Mn or Co metal (purity 99.5%) were dissolved in conc. HCl (AR) to which NaOH (AR) solution was added with constant stirring till the pH reached 9.5. The resultant precipitate was heated for 4 hr on a water bath, oxidized by H_2O_2 (AR) with constant stirring and finally filtered, washed, dried

Table 1—X-ray powder diffraction data for LaMnO_3

Structure	a (\AA)	α (degrees)	V (\AA^3)
Rhombohedral	7.99	90.58	511
Target-Cu;			Filter-Ni
d (\AA)	I/I_0	hkl	
5.68	5	010	
3.90	28	110	
2.76	80	020	
2.74	100	200	
2.30	26	202	
1.95	50	220	
1.73	12	114	
1.59	45	024	
1.57	15	223	
1.40	15	040	
1.37	15	400	

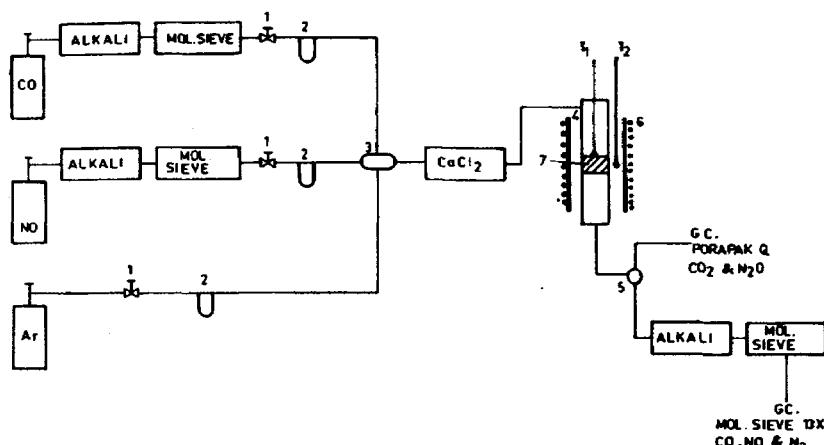


Fig. 1—Schematic diagram of the experimental set-up. [(1) fine control needle valve; (2) flow meter; (3) mixing bulb; (4) quartz reactor; T₁ and T₂ are thermocouples; (5) three-way valve; (6) electric furnace; and (7) catalyst]

Table 2—Kinetic parameters for reduction of NO by CO on LaMnO₃ and LaCoO₃ catalysts*

Catalyst	Temp. range (K)	Surface area (m ² /g)	Rate (molecules m ² s)	E _a (kJ/mol)	Frequency factor (molecules m ² s)
LaMnO ₃ (a)	473-673	1.3	1.4 × 10 ¹⁷	35.4	1.1 × 10 ¹⁶
	473-673	6.3	3.4 × 10 ¹⁶	30.6	2.4 × 10 ¹⁶
	543-643	45.5	9.2 × 10 ¹⁵	16.9	2.1 × 10 ¹⁷
LaCoO ₃ (a)	473-673	1.0	4.6 × 10 ¹⁷	38.3	2.7 × 10 ¹⁶
	643-783	5.9	1.8 × 10 ¹⁶	26.1	2.3 × 10 ¹⁸
	473-673	5.5	5.1 × 10 ¹⁶	23.4	2.1 × 10 ¹⁶

*T = 643 K; P_{NO} = 38 torr; P_{CO} = 38 torr

and fired at 773-873 K for 5-7 hr. The compounds prepared in this way are designated as LaMnO₃(c) and LaCoO₃(c) respectively.

Simultaneous oxidation-reduction reaction

This reaction was studied in a continuous flow, fixed-bed quartz reactor, in which the catalyst powder was supported between quartz wool plugs (see Fig. 1). The catalytic activity was determined using a feed gas composition of 5% NO, 5% CO in 90% Ar. The individual gas flow rates were controlled using flow meters and precision needle valves. The feed gases and the products were analyzed employing an on-line gas chromatograph with molecular sieve 13X and porapak columns and H₂ as the carrier gas. The H₂, N₂ and Ar were obtained from Indian Oxygen Ltd, Bombay. The NO and CO were prepared by standard procedures and further purified by passing through appropriate traps. The catalysts

were preactivated by passing H₂ gas over them at 673 K for 20-30 min.

Results and Discussion

The synthesized compounds were characterized by X-ray powder diffractograms. The calculated d_{hkl} values and lattice parameters of LaMnO₃ and LaCoO₃ prepared by wet methods agreed with the samples prepared by the ceramic technique⁹. Table 1 gives the X-ray powder data for LaMnO₃, which has not been reported in the ASTM data file. Thus, the gross crystal structure appears to remain unaffected when either acidic (HNO₃) or basic (NaOH) medium is employed during preparation.

The extent of sodium contamination in the samples, prepared by the coprecipitation method using NaOH, was estimated by atomic absorption spectrometry; it was found that LaMnO₃(c) and

Table 3—Product distribution of NO with CO over different catalysts^a

Catalyst	Surface area (m ² /g)	Reaction temp (K)	NO conversion (%)	Mole (%)		
				CO ₂	N ₂	N ₂ O
LaMnO ₃ (a)	1.30	833	38	67.3	32.7	—
	6.33	683	34	64.3	31.5	4.2
	45.50	683	86	67.7	30.7	4.6
LaCoO ₃ (a)	1.00	808	80	65.5	34.5	—
	5.90	683	57	65.5	29.1	5.4
	5.5	683	60	67.3	30.1	2.6

^aInlet composition 5% NO, 5% CO in Argon, 1 atm., 3×10^3 GHSV.

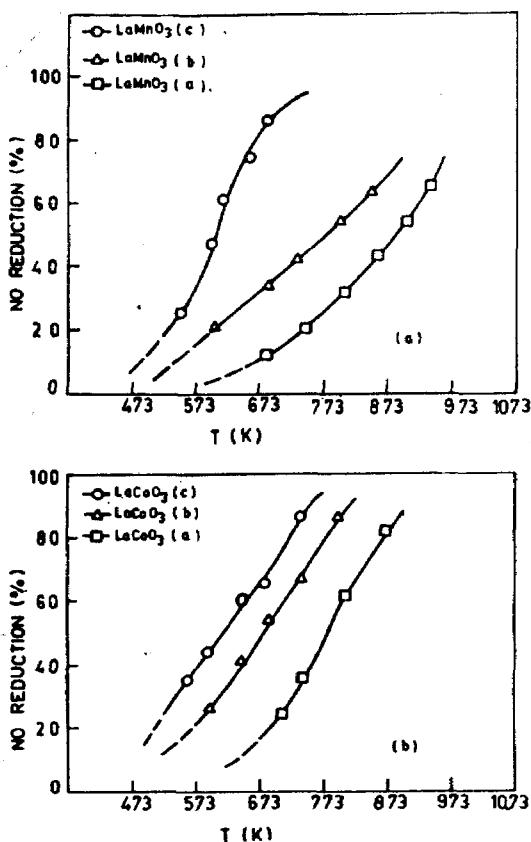


Fig. 2—Relation between NO reduction and catalyst temperature (T)

LaCoO₃(c) contained 0.4% and 0.3% of sodium (by wt) respectively.

The temperature-dependence of NO conversion efficiency of LaMnO₃ and LaCoO₃ prepared by different methods is shown in Fig. 2. The fractional conversion of NO (X_{NO}) versus W/F_{NO} plot, where W

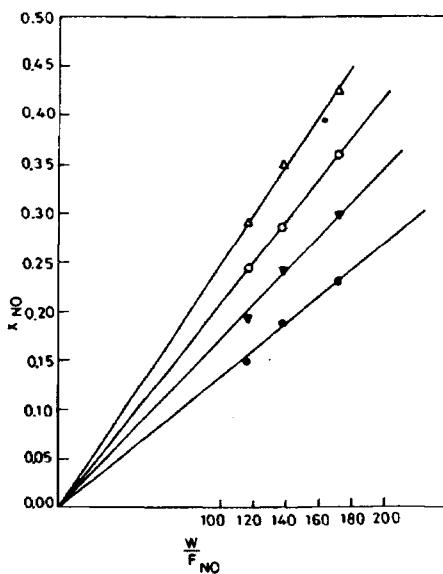


Fig. 3—Resident time plot for the representative sample of LaMnO₃(c)

and F_{NO} are the mass of the catalyst taken and the number of moles of NO flowing per hour, respectively, is shown in Fig. 3 for a representative sample. The kinetic parameters are listed in Table 2. Table 3 gives the product distribution for the reduction of NO by CO.

Inspection of Fig. 2 reveals that the catalysts prepared by the wet methods showed higher activities than those prepared by the ceramic method and the efficiencies of the various catalysts are in the order: (a) ceramic < (b) HNO₃ < (c) NaOH. Voorhoeve¹⁰ classified the reaction of NO with CO and H₂ over perovskite-type catalysts as an intrafacial process, i.e., via the removal of oxygen from the lattice of the catalyst.

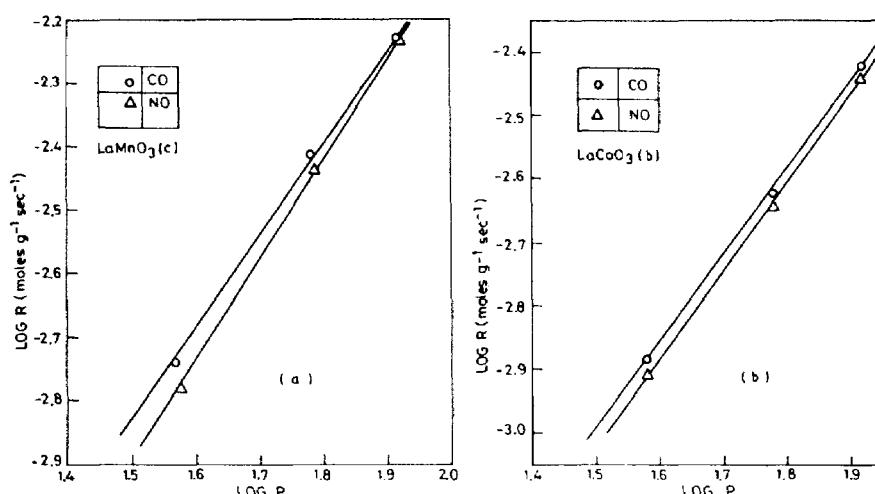


Fig. 4—Effect of reactant partial pressures on the rate of reduction of NO by CO

For $\text{LaMnO}_{3+\lambda}$, the structure is orthorhombic for $\lambda=0$ and trigonal for $\lambda>0.15$ (ref. 2). Since the structure observed from X-ray analysis of all the samples is rhombohedral, the extent of non-stoichiometry in the rhombohedral phases may not be appreciably different. This is an ideal situation for testing the intrafacial mechanism of Voorhoeve, since the surface oxide site is presumed to be actively involved in the simultaneous oxidation-reduction process. As the surface area of $\text{LaMnO}_3(\text{c})$ is the largest, it shows the highest conversion efficiency per unit mass of the catalyst. It is possible that in $\text{LaMnO}_3(\text{c})$ and λ values may be higher than when prepared by the other methods, albeit without changing the rhombohedral symmetry. The resultant non-stoichiometry may involve the presence of Mn^{4+} ions and/or A-site vacancies. The relative proportion of Mn^{4+} ions was qualitatively determined by measuring the electrical resistivity (ρ) at ambient temperature by the two-probe method. It was found that $\text{LaMnO}_3(\text{c})$ and $\text{LaCoO}_3(\text{c})$ have $\rho \approx 10^7 \text{ ohm m}$ and 10^4 ohm m respectively, indicating a higher proportion of Mn^{4+} ions and a lower proportion of A-site vacancies than those in $\text{LaMnO}_3(\text{b})$. The sodium content of $\text{LaMnO}_3(\text{c})$ is 0.4%. Since the electrical resistivity of $\text{LaMnO}_3(\text{c})$ is the highest, as compared to $\text{LaMnO}_3(\text{a})$ and (b) , the Na^+ ions in $\text{LaMnO}_3(\text{c})$ might have entered the lattice interstitially. Hence, some Mn^{4+} ions would be converted into mn^{3+} , which is likely to favour the release of lattice oxygen by weakening the $\text{Mn}-\text{O}$ bond; this conclusion, coupled with the high surface area, accounts for the high activity.

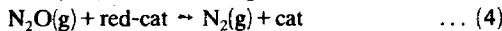
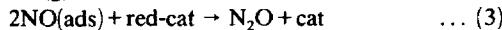
For LaCoO_3 , a trend similar to that for LaMnO_3 is seen. It may be noted from Fig. 2 that the NO conversion efficiencies are in the order: $\text{LaCoO}_3(\text{a}) < (\text{b}) < (\text{c})$ (Fig. 2) but the notable difference is that the surface areas of $\text{LaCoO}_3(\text{b})$ and (c) are almost the same. It is known that $\text{LaCoO}_{3-\delta}$ is oxygen-deficient², giving rise to Co^{2+} ions for charge neutrality. The ρ -value of $\text{LaCoO}_3(\text{c})$ is $\approx 10^3 \text{ ohm m}$, corresponding to a sizeable proportion of Co^{2+} ions. The sodium content in $\text{LaCoO}_3(\text{c})$ is 0.3%, indicating conversion of some Co^{3+} to Co^{2+} ions, thus destabilising the $\text{Co}-\text{O}-\text{Co}$ bond. This is likely to favour release of lattice oxygen, giving rise to enhanced activity.

The kinetic data (cf. Table 2) indicate that $\text{LaCoO}_3(\text{b})$ shows higher activation energy and rate than those shown by $\text{LaMnO}_3(\text{c})$. The frequency factor (A) for $\text{LaCoO}_3(\text{b})$ is also higher. However, on the basis of per unit mass of the catalyst, $\text{LaMnO}_3(\text{c})$ shows higher activity than $\text{LaCoO}_3(\text{b})$ and this may be due to the higher surface area of the former. If we consider the activity per unit surface area, $\text{LaCoO}_3(\text{b})$ has activity higher than that exhibited by $\text{LaMnO}_3(\text{c})$.

The effect of partial pressure of the reactants (NO, CO) on the kinetics was studied on $\text{LaMnO}_3(\text{c})$ and $\text{LaCoO}_3(\text{b})$. At fixed partial pressure of CO, and varying partial pressure of NO, the slope of $\log R$ versus $\log P$ plot was unity. An exactly similar dependence was found when partial pressure of CO was fixed and that of NO varying.

The catalytic reaction between NO and CO is considered to follow the sequence $\text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$,

as seen from the observed product. For this reaction, several models have been proposed^{11,12}. The mechanism, shown in Scheme 1, accounts for the results obtained. The scheme is exactly analogous to that proposed by Yoneda *et al.*¹²



Scheme 1

Here, 'cat' is the catalyst and 'red-cat' is the reduced catalyst site. At lower temperatures, CO₂, N₂O and N₂ are the products, while above 673 K, only CO₂ and N₂ are formed, indicating the dominance of step (4) at high temperatures (cf Table 3). Thus the catalytic reduction of NO by CO is rate-controlled by the active site reduction process.

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