

OXIDATION OF CARBON MONOXIDE ON RARE EARTH COBALTITES — ROLE OF SPIN STATE EQUILIBRIUM

B. Viswanathan and Susan George

Department of Chemistry,
Indian Institute of Technology, Madras 600 036, INDIA

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The catalytic oxidation of CO on a series of LnCoO_3 compounds (where $\text{Ln} = \text{La, Pr, Nd, Sm, Eu, Gd, Dy or Ho}$) has been studied. The Arrhenius plots show gradient changes around 180—200 °C which is the temperature range wherein ordering of low spin and high spin states starts. The activation energy for CO oxidation in the low temperature region varies linearly with oxygen deficiency. IR-Spectra of the adsorbed species in both the high and low temperature regions show the presence of carbonate species.

Каталитическое окисление CO было исследовано в серии LnCoO_3 (где $\text{Ln} = \text{La, Pr, Nd, Sm, Eu, Gd, Dy или Ho}$). Аррениусовские зависимости свидетельствуют о постепенном изменении при 180—200 °C, что представляет собой температурный интервал, где наступает упорядочение низкоспинового и высокоспиновых состояний. Энергия активации окисления CO в низкотемпературной области изменяется линейно с дефицитом кислорода. ИК-Спектры адсорбированных частиц в обеих высоко- и низкотемпературных областях указывают на присутствие карбонатных частиц.

The catalytic activity of mixed oxide perovskites for both oxidation and reduction [1, 2] reactions has been examined extensively recently especially because the valence band structures of these compounds are similar to those of transition metals. Rare earth orthocobaltites (LnCoO_3) are interesting perovskite compounds with varying magnetic and electrical properties [3] thus providing a scope for establishing interrelations useful for catalyst selection. It has been postulated [4] that the catalytic properties of these systems are related to the spin state equilibrium existing in these systems especially to the relative concentration of high spin Co^{3+} states. The experimental evidence (5) for this postulate is insufficient at the moment. The data obtained on the oxidation of CO on a series of LnCoO_3 compounds (where $\text{Ln} = \text{La, Pr, Nd, Sm, Eu, Gd, Dy and Ho}$) are presented in this communication from this point of view.

The samples were prepared by calcining the mixture of oxalates at 900 °C for 24 h. The products were analysed by X-ray diffraction. The oxygen deficiency in these samples was calculated from the analysis of the total and the cobalt(III) contents. Catalytic oxidation of CO was carried out in a recirculatory static reactor [6]. After activation, stoichiometric mixtures of CO and

oxygen were exposed to the catalyst at the desired reaction conditions and the reaction kinetics was followed by recording the changes in pressure as a function of time. Further details on experimental procedures are given elsewhere [7].

The kinetics of catalytic oxidation of CO from stoichiometric mixtures on LnCoO_3 compounds follows a first order rate law [7] and parameters deduced therefrom after due correction for concurrent adsorption are used in the construction of Arrhenius plots. The values of activation energy and frequency factor are given in Table 1. The observed non-stoichiometry for oxygen as deduced from the observed average oxidation state of cobalt together with the observed lattice parameters for each compound which agree with those reported in literature [8] are also included in this table. It is seen that each of these compounds shows gradient changes in the Arrhenius plots around 180–200 °C. This is the temperature range wherein the onset of ordering of low spin and high spin states occurs in these compounds [9]. In the low temperature range (< 200 °C) the values of activation energy show a correlation with the extent of non-stoichiometry in these compounds (Fig. 1). The catalytic oxidation of CO on these oxides has been shown to involve the adsorbed oxygen species at low temperature, while a redox mechanism has also to be invoked for oxidation at higher temperatures [10]. At higher temperatures in addition to spin state transitions, charge transfer resulting in the formation of Co^{2+} and Co^{4+} states also occurs and hence the e_g electrons are equally distributed over all cobalt ions, a situation probably favourable for the redox mechanism. IR Spectra of the adsorbed species showed the presence of unidentate type carbonate species (1540 cm^{-1}) at 180 °C, while both uni- and bi-dentate ($1540, 1650\text{ cm}^{-1}$) carbonate species were observed at 240 °C on LaCoO_3 in addition to weakly adsorbed CO_2 (2360 cm^{-1}) when the surface was exposed to a stoichiometric mixture of CO and oxygen. HoCoO_3 seems to be an exception in this series, as the relative concentration of spin states attains a constant value at higher temperatures [11].

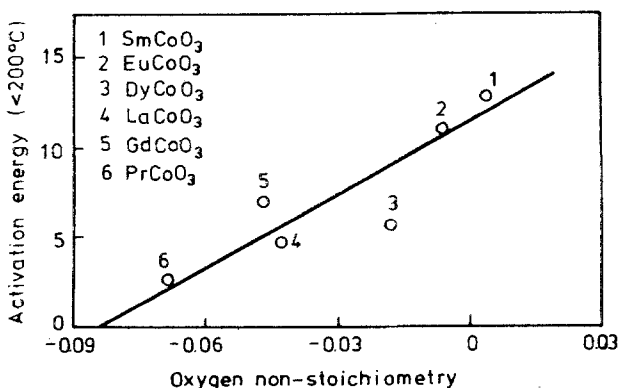


Fig. 1. Variation of the activation energy for CO oxidation (<200 °C) with the extent of non-stoichiometry in LnCoO_3 type oxides

Table 1
 Physico-chemical characteristics and kinetic parameters for CO oxidation on LnCoO_3 compounds

Compound	Extent of oxygen non-stoichiometry	Lattice parameters			Temperature range (°C)	E° (kcal/mol)	Kinetic parameters*					
		a (Å)	b (Å)	c (Å)			A (min ⁻¹)	Temperature range (°C)	E° (kcal/mol)	A (min ⁻¹)		
LaCoO_3	-0.0425	5.389	—	—	140—200	4.7	—	—	1.8 × 10 ¹	220—260	8.1	2.7 × 10
PrCoO_3	-0.0685	5.357	5.381	7.61	80—210	2.5	—	—	4.6 × 10 ²	320—370	12.6	5.5 × 10 ¹
NdCoO_3	-0.025	5.332	5.350	7.54	—	—	—	—	—	220—280	6.6	5.8 × 10 ⁻¹
SmCoO_3	+0.0635	5.289	5.356	7.51	150—190	12.9	—	—	—	300—360	11.9	2.2 × 10 ¹
EuCoO_3	-0.0065	5.256	5.371	7.47	160—180	10.7	—	—	1.6 × 10 ³	210—250	4.3	9.6 × 10 ⁻²
GdCoO_3	-0.047	5.184	5.404	7.47	180—200	7.0	—	—	9.5 × 10 ²	280—310	8.2	4.1 × 10 ¹
DyCoO_3	-0.018	5.180	5.432	7.37	170—220	5.6	—	—	8.4 × 10 ⁻¹	220—260	3.5	4.0 × 10 ⁻²
HoCoO_3	—	5.155	5.458	7.30	140—170	18.3	—	—	8.5 × 10 ⁻¹	230—250	13.7	1.6 × 10 ³
									3.4 × 10 ⁶	220—240	15.3	1.6 × 10 ⁴

* Calculated using least square analysis — Correlation factors are ≥ 0.90 .

Yamazoe and coworkers [12] have characterized the oxygen sorptive properties of perovskite oxide catalysts by TPD and TG experiments and have shown that the α -oxygen state is associated with oxygen vacancies or the presence of considerable amount of Co^{4+} or positive holes, while the high temperature β -state desorption is ascribed to the conversion of Co^{3+} into Co^{2+} . The communication from a Chinese research group [13] shows that the defect structure of perovskite oxides is responsible for the observed ammonia oxidation activity and the adsorbed oxygen species O_2^- or O^- might be the possible active centers for the catalytic reaction. The observation of the present investigation that at low temperatures the activity is linearly related to the oxygen deficiency is in accord with these reports, thus showing that adsorbed oxygen species together with Co^{4+} species function as active centers for the oxidation reaction. The onset temperatures of activity of these systems are probably connected with the charge transfer process which sets in only when the high spin state concentration of Co^{3+} exceeds 65%. It is therefore interesting to reexamine all the catalytic activity results on rare earth orthocobaltites in terms of the spin state equilibrium and charge transfer processes existing in these systems and will be taken up subsequently.

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