CATALYTIC OXIDATION OF CO ON $La_{1-x}Sr_xCoO_3$ PEROVSKITE OXIDES

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Adsorbed oxygen species have been shown to participate in the catalytic oxidation of CO on $La_{1-x}Sr_xCoO_3$ oxides. Sr substitution appears to alter the strength of binding of these oxygen species and hence also the kinetics of oxidation.

Адсорбированные кислородные частицы принимают участие в каталитическом окислении CO на окисных $La_{1-x}Sr_xCoO_3$. Замещение Sr изменяет силу связи этих кислородных частиц, а тем самым и кинетику окисления.

In recent times perovskite type oxides have been explored to a great extent for their potential use in varying applications including as catalysts /1/. Among the various types of perovskite oxides, double oxides containing rare earth ions (La^{3+}) and cobalt ions have been examined extensively due to the interesting electrical and magnetic properties imparted to them by the presence of spin state equilibrium in these systems /2/. Among these cobaltites, $LaCoO_3$ with partial Sr substitution at the A site is known to exhibit high activity as oxygen electrode /3/ or as catalysts for complete combustion reactions /4/. The present communication deals with kinetic results obtained on the oxidation of CO on $La_{1-x}Sr_xCoO_3$ systems (x = 0, 0.1, or 0.3) in order to 1: find the relevance of the reduction-oxidation properties of these systems /5/ for the observed catalytic activity, 2: obtain information on the oxygen species /6/ responsible for catalytic oxidation.

EXPERIMENTAL

Three samples $LaCoO_3$, $La_{0.9}Sr_{0.1}CoO_3$ (x = 0.1) and $La_{0.7}Sr_{0.3}CoO_3$ (x = 0.3) were prepared by calcining the mixture of cobalt oxalate, lanthanum oxalate and $SrCO_3$ at 900 °C for 24 h. The products were analysed by X-ray diffraction (Table 1). Catalytic oxidation of CO was carried out in a recirculatory static reactor described elsewhere /7/. Between each run, the catalysts were activated by eva-

Table 1

X-ray diffraction data for $La_{1-x}Sr_xCoO_3$ systems
(d spacings)

	$LaCoO_3$	$La_{0.9}Sr_{0.1}CoO_3$	$La_{0.7}Sr_{0.3}CoO_3$
110	2.726 VS	2.739	
014	2.698 VS	2.730	2.693
022	2.224 M	2.224	2.217
204	1.921 S	1.927	1.914
212	1.723 VVW		
116	1.710 VVW		
124	1.570 S	1.573	1.569
108	1.555 M	1.562	1.540
220	1.363 M	1.368	1.362
028	1.347 M		1.354
306	1.276 VVW		
314	1.209 M		
218	1.206 M		
$a =$	5.3892	5.4267	5.3900
$\alpha =$	$60°35'$	$60°31'$	$60°46'$
$V =$	112.17	114.33	112.68

cuation at 400 °C for 6 h followed by treatment with 100 Torr of oxygen at the reaction temperature for 10 h. After pumping out the oxygen, stoichiometric mixtures of CO and oxygen were exposed to the catalyst at the desired reaction temperature and the reaction kinetics was followed by recording the changes in pressure at various time intervals.

RESULTS AND DISCUSSION

It was observed that the catalyst without oxygen pretreatment exhibited considerably lower catalytic activity as compared to the catalyst with oxygen pretreatment. The kinetic data after suitable regression for simultaneous adsorption /8/ obeyed a simple first order rate equation. The kinetic parameters calculated from the first order plots are given in Tables 2 and 3.

Nakamura et al. /5/ have reported that the rate in the steady state shows a maximum at a certain value of x (possibly between 0.2 and 0.4). Though this statement generally appears to be valid on the basis of the results obtained in the present investigation, it is seen that the rate of oxidation (as deduced from the values of the first order rate constants) depends also on the total initial pressure. In the case of

Table 2

Kinetic parameters (first order rate constants)
for the oxidation of CO on $La_{1-x}Sr_xCoO_3$ systems

$LaCoO_3$		$La_{0.9}Sr_{0.1}CoO_3$		$La_{0.7}Sr_{0.3}CoO_3$	
Temp. (°C)	$k \times 10^4$ (min^{-1})	Temp. (°C)	$k \times 10^4$ (min^{-1})	Temp. (°C)	$k \times 10^4$ (min^{-1})
140	5.9	140	13.1	130	8.4
150	8.0	160	14.6	160	10.9
190	11.5	180	14.7	180	14.3
220	8.9	200	14.5	200	12.4
240	13.4	220	19.4	230	10.6
280	16.4				

Table 3

Kinetic parameters (first order rate constants) for the oxidation
of CO on $La_{1-x}Sr_xCoO_3$ systems at different initial pressures

$LaCoO_3$		$La_{0.9}Sr_{0.1}CoO_3$		$La_{0.7}Sr_{0.3}CoO_3$	
p_0 (Torr)	$k \times 10^4$ (min^{-1})	p_0 (Torr)	$k \times 10^4$ (min^{-1})	p_0 (Torr)	$k \times 10^4$ (min^{-1})
37.6	13.9	48.0	7.9	45.0	11.9
52.2	7.9	61.7	14.7	59.4	14.3
81.5	5.8	109.3	4.6	67.7	10.9
123.6	4.2	127.3	4.6	998.6	8.2
153.7	3.5	145.8	4.7	116.9	8.0
				131.0	8.2

$LaCoO_3$, the rate constants decrease with increasing the initial total pressure, while for Sr-substituted systems they show a maximum around 60 Torr. However, the rate of oxidation of CO on Sr-substituted systems is always higher than that observed on $LaCoO_3$ above this total initial pressure. The implications of the dependence of the rate on initial total pressures have been considered in a separate communication /9/.

The temperature coefficient of the reaction shows abrupt gradient changes around 200–210 °C for all the three systems studied. This result indicates the operation of two different surface process in these two temperature ranges. From results /6/ of TPD studies of oxygen from Sr-substituted $LaCoO_3$ it is inferred that the rate of desorption of the adsorbed oxygen (α state) is considerable even around 200 °C,

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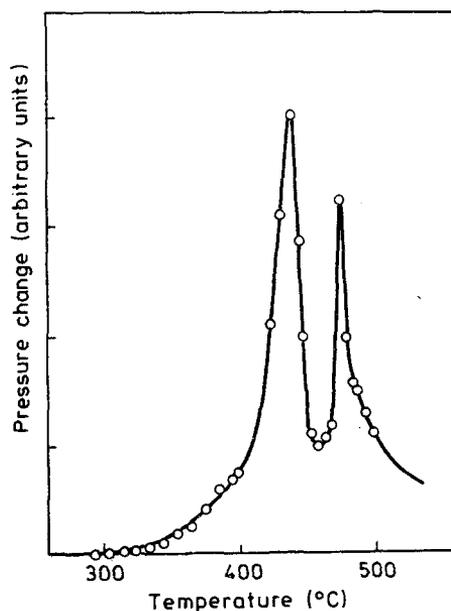
Fig. 1. TPD of oxygen adsorbed on $La_{0.9}Sr_{0.1}CoO_3$ adsorption at 100 °C

while that of the lattice oxygen can be effected only around 800 °C. Seiyama et al. /6/ have further shown that the adsorbed oxygen is not uniform but it is in a broadly dispersed state concerning its desorption, what is associated with a heterogeneity also borne out in their XPS results. The binding energy of the 1s electron in the adsorbed oxygen (α state) is higher than that of lattice oxygen (β state). The intensity of the XPS signal corresponding to the α state of adsorbed oxygen increased with the increase in x and decreased with increase in the temperature of evacuation. In an attempt to clarify these aspects, the TPD of oxygen adsorbed at 100 °C on $La_{0.9}Sr_{0.1}CoO_3$ was carried out and the desorptogram obtained is shown in Fig. 1. It is seen that two desorption peaks appear which correspond probably to the α state of adsorbed oxygen according to the observations of Seiyama et al. The splitting of the desorption peak into two components shows that the adsorbed oxygen species is heterogeneous in nature with varying binding energies. The total amount desorbed corresponding to these two peaks accounts for about 40% of the adsorbed oxygen. The amount of oxygen required for the total oxidation observed up to 90 minutes corresponds to the amount desorbed at 430 °C. Therefore, it may be postulated that at temperatures above 200 °C the participation of adsorbed oxygen in catalytic oxidation becomes less and less, while at temperatures below

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200 °C the reaction can possibly be promoted predominantly by this adsorbed oxygen species, whose concentration should be the saturation one or an optimum level because of the activation procedure employed. At low temperatures, i.e., below 200 °C the reaction proceeds predominantly by the participation of adsorbed oxygen, while at higher temperatures the contribution of the redox component to the observed rate of the reaction can also be considerable. Yoneda et al. /5/ have recognized the need to invoke both mechanistic pathways to explain the observed oxidation rates at low values of x at 150 °C, which is in agreement with this conclusion.

The variation of the rate constants with the initial total pressure shows a maximum for Sr substituted systems, while it decreases continuously with the increase in the total initial pressure for $LaCoO_3$ (Table 3). This trend of variation in the case of Sr substituted systems indicates that the surface characteristics of Sr-substituted systems are different from those of the parent compound.

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