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Catalytic oxidation over lanthanum-transition metal perovskite materials

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Abstract

The thrust of this work is to follow the defect chemistry of the simple $LaCoO_3$ system in an attempt to probe if there is a relationship between the defect chemistry and the activity of this perovskite-type material to catalytic methane combustion. A simple flow-through reactor has been used to study the combustion of methane between room temperature and 1100°C. Using a gel-type precipitation method it has been proved possible to synthesise a single phase perovskite material with a bulk La:Co metal atom ratio of 1:1.1. PXRD, Rietveld analysis and density measurements show that the perovskite phase is non-stoichiometric with a deficiency of lanthanum ions in the lattice. This material is rather ineffective as a catalytic material. A more active form can be prepared at a La:Co metal atom ratio of 1:1 when a mixed phase (perovskite/lanthana) is produced. This material exhibits both higher activity to methane combustion and the storage/evolution of oxygen (as measured using DSC and TPD techniques).

The results of activity tests have been rationalised using XPS where large amounts of O^- species are seen at the surface. It is proposed that these ions occupy anion vacancies created to compensate for the reduced cation charge in the lattice. This is not possible for the single phase material where vacancies are compensated for by the presence of valency changes of cobalt and/or oxygen.

Further work has been carried by doping of the perovskite with cations of valencies +2, +3 and +4 in an attempt to control the non-stoichiometry. In this way, it has been proved possible to provide simple synthetic routes to active methane combustion catalysts. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Perovskite; Catalytic combustion; Methane

1. Introduction

Perovskite materials have been used quite effectively for catalytic oxidation reactions [1] including hydrogenation and hydrogenolysis of hydrocarbons [2,3], CO oxidation [4], ammonia oxidation [5] and catalytic combustion [6]. Recently there have been attempts to use these materials in the catalytic combustion of methane for use in gas turbines [7].

There is considerable debate on the source of their catalytic activity. Amongst the most likely contributors to their high activity are unusual oxidation states of the transition metal ions, the amount of non-stoichiometric oxygen and the structure of lattice defects [5]. Literature suggests that non-stoichiometric oxy-

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gen is the most reasonable suggestion for understanding the catalytic oxidation activity of a series of transition metal lanthanum perovskites in both the pure and doped (Sr being the most active dopant) forms [1].

However, the structural chemistry of perovskite lattices is very complex, there are a whole series (with hundreds of individual members) of hexagonal, rhombohedral and tetragonal distortions possible [8]. These variations of the simple cubic system result from cation size mismatch and cation or anion non-stoichiometry. In catalysis, it is often not possible to study phase changes or non-stoichiometry of complex mixed oxides in the conditions used in reactors. However, in these highly oxidative systems (akin to simple ambient conditions) and if the phase diagram is well understood, it might be possible to relate bulk and surface defect chemistry to catalytic activity. The thrust of this work is to follow the defect chemistry of the simple $LaCoO_3$ system in an attempt to understand the activity of this material to methane catalytic combustion.

2. Experimental

Powder-XRD (PXRD) data were collected on a Philips MPD apparatus (Cu K_α irradiation). Profiles were analysed using the PC-Rietveld programme from Philips. DSC experiments were recorded on a Setaram DSC-92 instrument set-up for automatic flow control of nitrogen and reactive gas mixtures. XPS spectra were collected on a Surface Science Laboratories M-Probe instrument at a pass energy of 25 eV. Samples were mounted directly by pressing material into small holes drilled into a stainless steel mount. Binding energies are referenced to a C1s signal at 285.0 eV. Density measurements were made by a displacement method.

Catalyst activities were measured using a one atmosphere simple flow-through reactor at a linear gas velocity of $20\,cm\,s^{-1}$ or space velocity of $20\,000\,h^{-1}$. A 2.61% CH_4 in air mixture was used for testing. Data were recorded as TPR profiles between 25°C and 1100°C with a temperature sweep rate of $20°C\,min^{-1}$. A simple Lumidor combustion gas analyser was used to monitor exit and entry gas compositions. TPD data were collected in flowing He on a tube reactor system coupled to a mass spectrometer for ion detection.

La–Co perovskites were prepared by precipitation from mixed nitrate solutions using tetraethyl ammonium hydroxide. This route has provided a simple means for the preparation of pure phase perovskites [9]. Samples were dried, crushed, aged, ground and sieved prior to analysis and testing.

3. Results

3.1. PXRD studies

Oxides derived from mixed metal nitrate solutions (metal atomic ratio of La:Co=1:1) following drying and ageing to 800°C for various times were prepared. Fig. 1 shows PXRD profiles after ageing at 12, 36 and 96 h. In all diffractograms, perovskite (as R-3C rhombohedrally distorted), Co_3O_4 (spinel) and La_2O_3 (hexagonal structure) are seen. As might be expected from our previous work some La_2O_3 is converted to the hydroxide. After 96 h of high-temperature treatment Rietveld quantification reveals 68.5 mol% as perovskite, 26% as La_2O_3, 2.5% as $La(OH)_3$ and the spinel at 3%. Since there is a large amount of lanthana visible, the data would suggest that the perovskite formed is cobalt-rich.

This conclusion was examined by making several formulations of varying La:Co ratio. An optimum preparation was found with a molar atomic ratio of 1:1.1 (Co excess). Fig. 2 shows PXRD profiles after ageing at 800°C for 12 and 60 h. Quantitative analysis of the long age material gives a composition of 99.6% perovskite and 0.4% Co_3O_4. Full Rietveld analysis of these data (perovskite phase, cation sites) is shown in Table 1 as appropriate fitting constants. The most crucial feature of the fits is that the La:Co ratio is greater than one strongly supporting the suggestion of a Co-rich perovskite lattice. Note that stoichiometric $LaCoO_3$ has been quoted as having a=5.42 Å and c=13.32 Å [10] compared to a=5.441 Å and c=13.101 Å (there is a small variation between pure perovskite and the mixed phase material) measured here. Again this would imply considerable defect chemistry in these materials.

Following this work it was decided to carry out extensive studies of the 1:1 (mixed phase) and 1:1.1

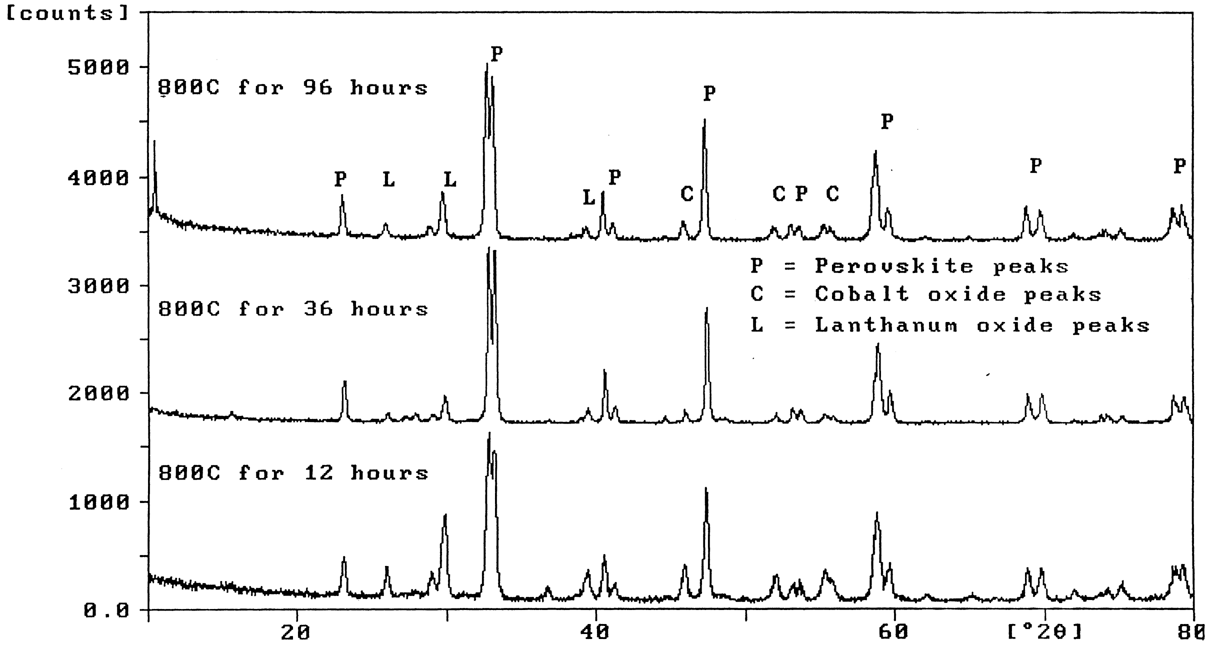

Fig. 1. Powder-XRD profiles of $LaCoO_3$ (molar atomic ratio of La:Co=1:1) after calcination at 800°C for 12, 36 and 96 h, respectively.

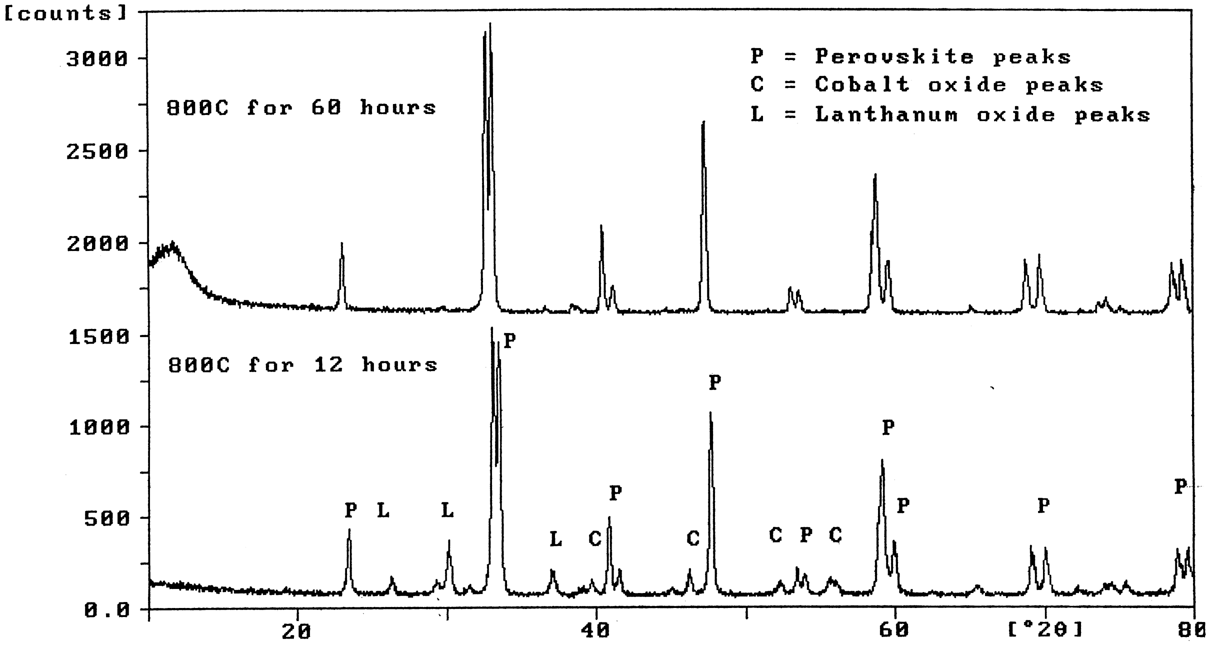

Fig. 2. Powder-XRD profiles of $LaCoO_3$ (molar atomic ratio of La:Co=1:1.1) after calcination at 800°C for 12 and 60 h, respectively.

Table 1
Rietveld best-fit parameters for the cation sites in a perovskite type phase of 1:1 and 1:1.1 La:Co atomic ratio materials

Name	Valency	*x*	*y*	*z*	*B*	SOF
(a) $LaCoO_3$ phase (1:1): mixed phase material[a]						
La	La^{+3}	0	0	0.25	1	5.63
Co	Co^{+3}	0	0	0	1	6.01
(b) $LaCoO_3$ phase (1:1.1): single phase material[b]						
La	La^{+3}	0	0	0.25	1	5.37
Co	Co^{+3}	0	0	0	1	5.97

a, *b*, *c*, α, β, and γ are crystallographic parameters. *x*, *y* and *z* are atom positions within the unit cell. The SOF indicates the occupancy of these sites. O^{2-} data are not shown because it is relatively weak scatterer and prone to error so in all cases has been set to its theoretical value.

[a] Space group: R-3C – *a*: 5.4412 Å, *b*: 5.4412 Å, *c*: 13.1014 Å, α: 90°, β: 90°, γ: 120°.

[b] Space group: R-3 C – *a*: 5.4412 Å, *b*: 5.4412 Å, *c*: 13.09 Å, α: 90°, β: 90°, γ: 120°.

(single phase) molar ratio materials aged at 800°C for 60 h in an effort to compare defect chemistry and catalytic activity. The data below refer to these substances.

3.2. *Density measurements*

The mixed phase and single phase materials had measured densities of 6.285 (corrected for lanthana presence) and 6.160 g cm^{-3} compared to a theoretical value of 6.5644 g cm^{-3}. Using the measured lattice parameters and La:Co ratios and adjusting the O^{2-} stoichiometry to give the measured density the stoichiometries of the mixed and single phase can be estimated as $La_{0.94}Co_{1.000}O_{2.92}$ and $La_{0.895}Co_{1.000}O_{3.10}$, respectively. Bearing in mind the errors involved, the simple calculations suggest the mixed phase has a defect chemistry where lanthanum ion vacancies are compensated for by anion vacancies. The single phase results imply that the defect mechanism where either an increase in cobalt valency or decrease in oxygen valency is seen.

3.3. *XPS measurements*

Data were collected from La_2O_3, Co_3O_4 and lanthanum–cobalt perovskites. Results from the 1:1 La:Co mixed phase material (after firing to 800°C for 8 h) are shown in Fig. 3. O1s spectra exhibit two strong fea-

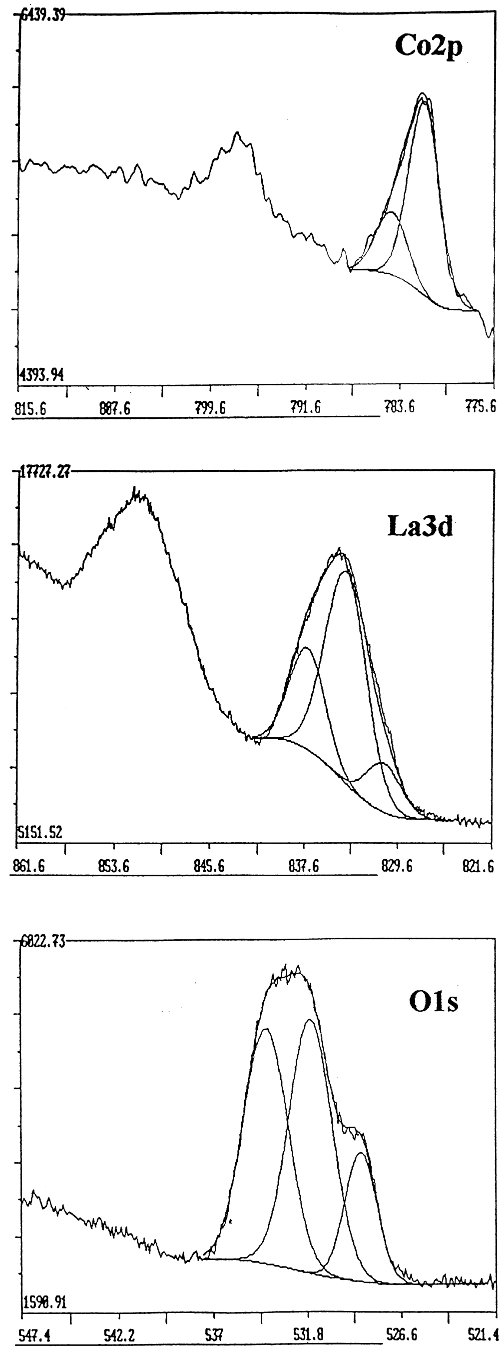

Fig. 3. Co2p, La3d and O1s XP spectra. Data has been curve-fitted. Co2p and La3d spectra are complicated by final state effects which cause line-broadening and asymmetry. The spectra shown have not been smoothed but have been charge-shifted to give a Cls signal at 25 eV.

tures at 532.2 and 528.9 eV. The peak at higher binding energy is very broad (half width=4.2 eV) but can be partly ascribed to oxygen in the form of –OH or as O^- [10]. The large width of this component in the perovskite material may reflect several O1s states existing in this energy range but has been curve-fitted with two components for convenience. The much narrower peak (at 528.9 eV and half-width=2.1 eV) is visible at the same O1s binding energy as data from pure lanthana and the cobalt oxide. La3d5/2 features (perovskite material) are recorded at 837.5 and 834.2 eV. These are close to values recorded from pure lanthana at 837.8 and 834.4 eV. As might be expected, the data indicate that lanthanum ions are present in the trivalent form. Small variations may be due to changes in crystal structure and/or electronic structure.

The Co2p3/2 signal gives a distorted peak typical of Co^{3+} and results from complex final state effects. There are no high binding energy satellites at 785–788 eV indicative of Co^{2+} [11]. Curve-fitting reveals a major component at 781.3 eV. Pure Co_3O_4 exhibits a very similar peak (in shape and position) centred at 780.1 eV. The increase in observed binding energy for the perovskite material is probably associated with the increase in Co valency from 2.66 to 3.00 (as in Co_2O_3). The data are strongly suggestive that all the cobalt is present as trivalent cations. These results are discussed in further detail elsewhere [12].

It is also useful to consider XPS derived stoichiometries. Quantification [13] reveals a La:Co ratio at the surface of 4.26. This would strongly suggest that the excess lanthana seen in the PXRD profiles of this material is at the surface. This is seen in the case of $NiLaO_3$ where surface lanthana has been identified using electron microscopy [9]. The oxygen-to-metal ion ratio is 3.35 instead of an expected value of 1.5. It would appear that at the surface of these material there is a large excess of oxygen species. Binding energy consideration (i.e. those features at binding energies greater than 530 eV) suggests that this oxygen is present as either –OH or $-O^-$ states [10].

3.4. *Thermal analysis*

Mixed phase and single phase materials were subject to in situ DSC analysis. Samples were heated in oxygen at 250°C to remove adventitious carbon. Each was then heated to 550°C in N_2 and cooled in the same gas. A DSC–TPR experiment was then performed when oxygen was flowed over the sample subject to a heating cycle between 25°C and 550°C. The results are shown in Fig. 4. In the case of the mixed phase material only, a large exotherm due to the reaction of oxygen was observed between 225°C and 450°C.

These results were validated using TPD experiments in a microreactor. Samples (200 mg) were cleaned as above, treated in oxygen and then temperature-programmed in flowing helium between 25°C and 800°C. The results of the O_2-TPR are shown in Fig. 5. The mixed phase material exhibited a low-temperature peak at around 350°C and a large peak at 780°C. The single phase material exhibited only a small amount of desorption at 800°C.

3.5. *Catalyst testing*

The results above would indicate that the mixed phase material has a quite different defect chemistry and exhibits very different chemical activity than the single phase preparation. Using a simple flow-through microreactor, the samples were examined to test if these differences in behaviour were reflected in their catalytic activity to methane combustion. Typical results for the mixed and single phase materials are shown in Fig. 6. It can be seen immediately that the mixed phase material has a much lower light-off temperature and a 50% conversion temperature (T_{50}) of 580°C compared to 765°C. These results tend to support the suggestion that the mixed phase is much more chemically active. It should be noted that the average particle size as measured by XRD is very similar for all the perovskites discussed here and it is not believed that changes in these produce the greatly varying chemical properties observed here.

It is also of importance to note that these catalysts perform very well compared to traditional catalysts such as supported precious metals, ceria and doped cerias. These results are displayed in Table 2.

An attempt was made to improve the activity of these materials by doping with ions of similar and different valencies. Again the results are shown in Table 2. It can be seen that none of the catalysts prepared in this way reach the specific activity of the mixed phase lanthanum–cobalt material, as can also be seen in Table 2 that this is not because of

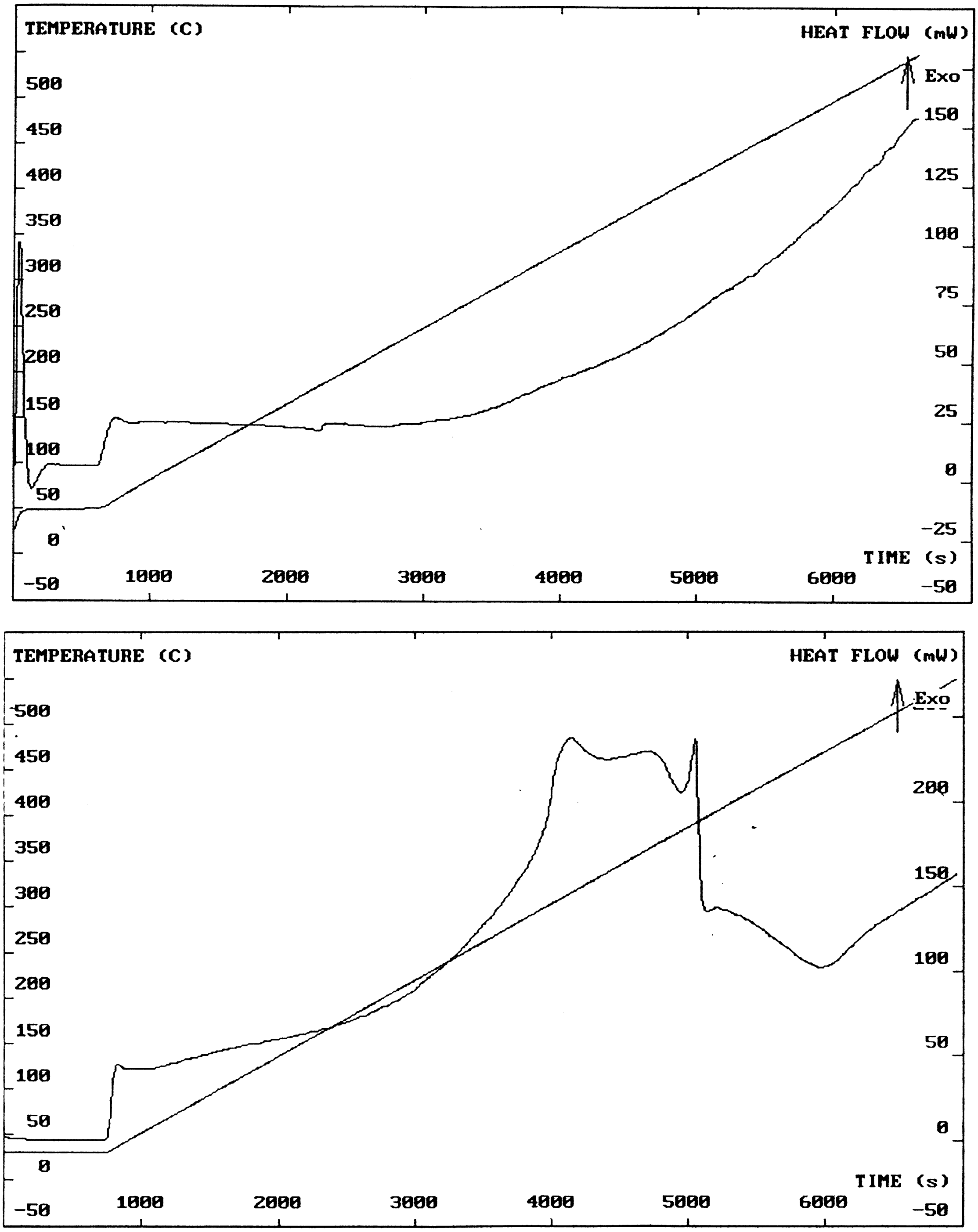

Fig. 4. DSC profiles of (a) $LaCoO_3$ (lower panel mixed phase) and (b) $LaCoO_3$ (upper panel single phase) in O_2.

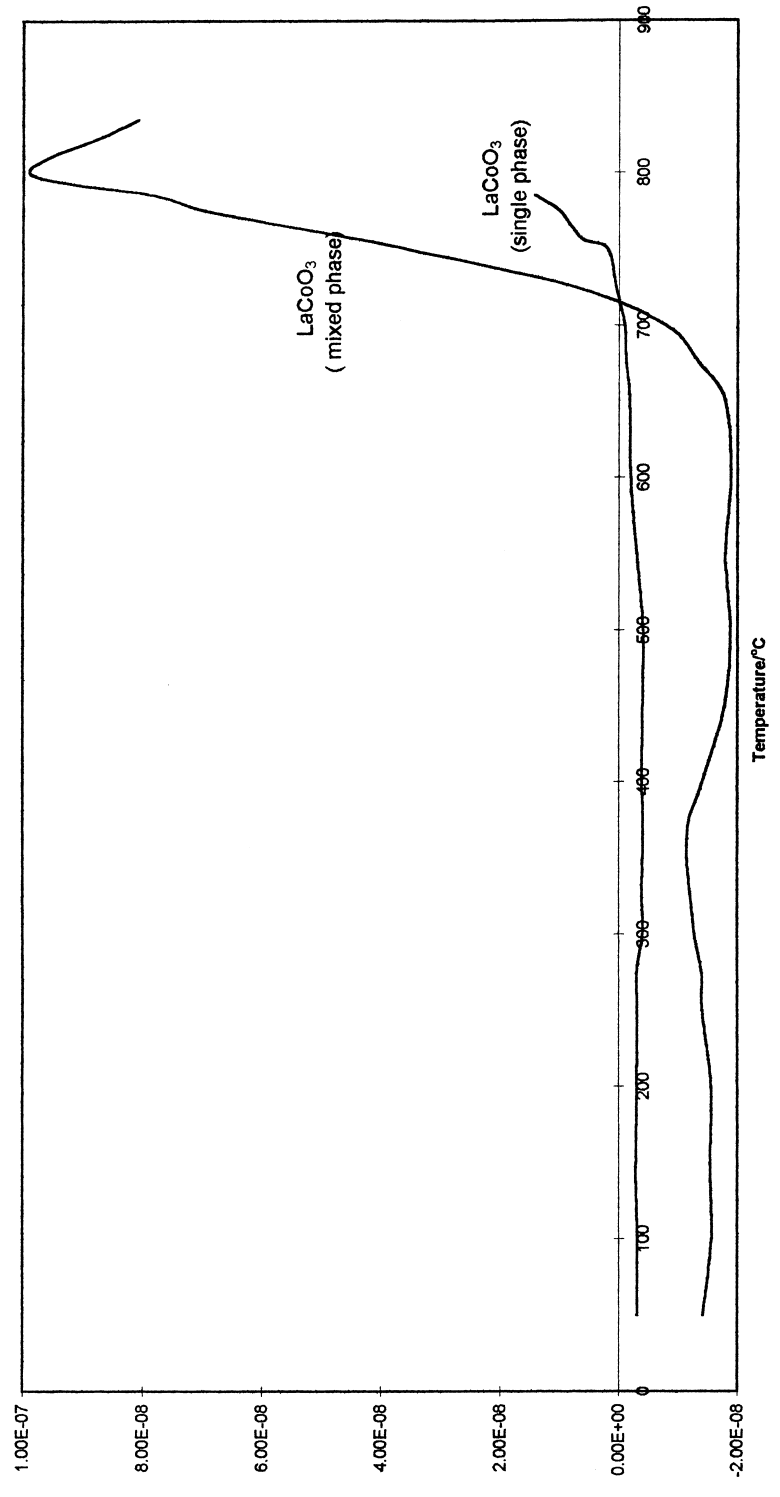

Fig. 5. TPD profiles of (a) $LaCoO_3$ (mixed phase) and (b) $LaCoO_3$ (single phase) in He.

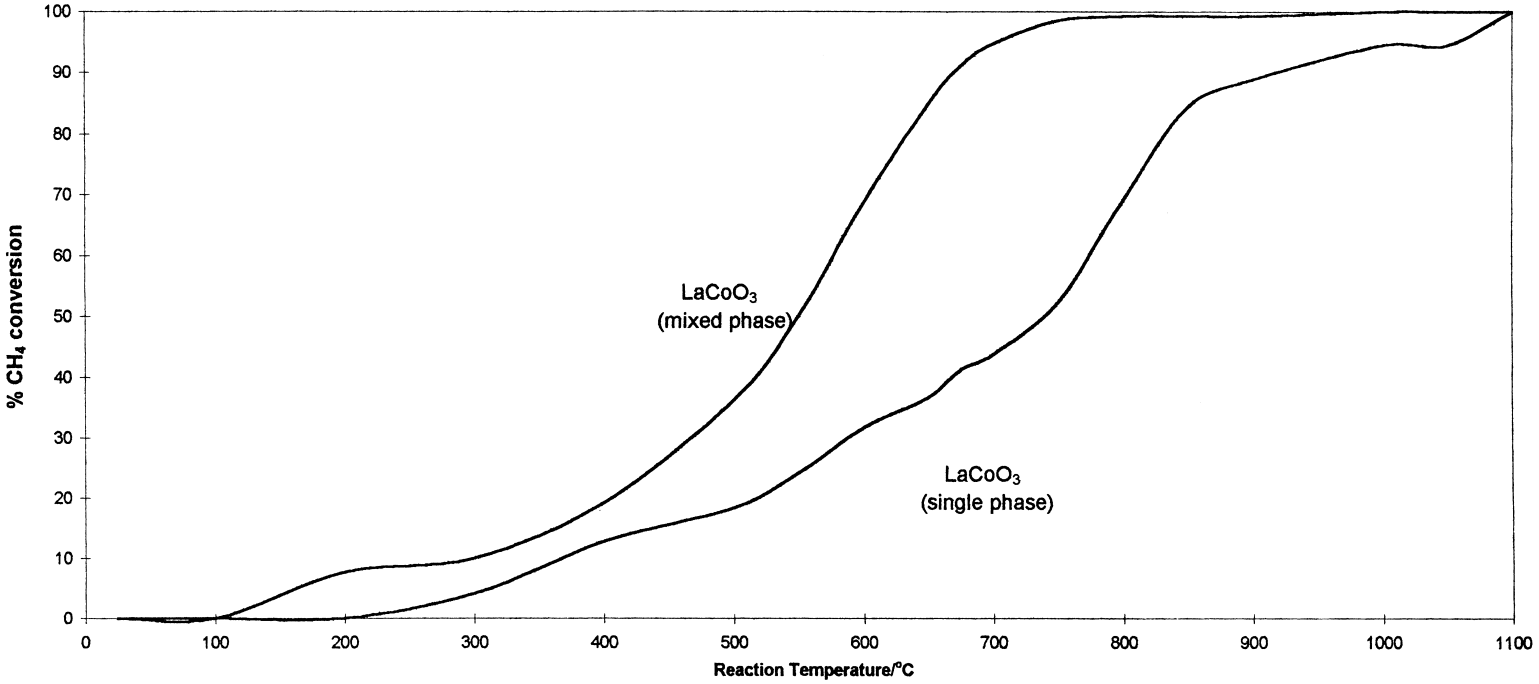

Fig. 6. Combustion profiles of CH_4: (a) $LaCoO_3$ (mixed phase) and (b) $LaCoO_3$ (single phase).

Table 2
The catalytic activity of various materials as indicated by temperatures for 50% combustion (T_{50})

Material tested	Particle size prior to combustion (Å)	T_{50} (°C)
$La_1Co_1O_3$ (mixed phase)	1103.85	550
$La_1Co_{1.1}O_3$ (single phase)	1013.41	765
$La_1Co_{1.1}Pr_{0.1}O_3$	656.6	637
$La_1Co_1Pr_{0.1}O_3$	621.08	634
$La_{0.9}Co_1Eu_{0.1}O_3$	646.07	631
$La_{0.8}Co_1Eu_{0.2}O_3$	376.07	700
$La_{0.8}Co_1Eu_{0.1}\ O_3$	801.93	579
$La_1Co_{1.1}Eu_{0.1}O_3$	787.8	642
$La_{0.9}Co_1Ce_{0.1}O_3$	735.37	782
$La_1Co_{0.9}Mn_{0.1}O_3$	438.66	601
$La_1Co_{0.9}Zn_{0.1}O_3$	409.28	572
$La_1Co_{0.9}Cu_{0.1}O_3$	511.29	745
$La_1Co_{0.9}Fe_{0.1}O_3$	339.38	615
CeO_2	255.8	850
15% La_2O_3 in CeO_2	467.66	787
Pt–Rh on CeO_2/Al_2O_3	37.5	865
Rh on CeO_2	271.5	725

All samples were pre-aged to 800°C for at least 12 h prior to testing; average particle sizes from XRD are given to indicate the effect of the ageing.

changes in the surface area. XRD analysis suggests that all these materials form well-ordered perovskite phases.

4. Discussion

Generally speaking, many authors consider the $LaCoO_3$ system to be stoichiometric. As pointed out by Wu et al. [14] the system is essentially non-stoichiometric. In the studies presented here (PXRD, Rietveld and density measurements) it appears that the perovskite can be prepared in two forms both with a strong lanthanum deficiency in the lattice. A pure single (perovskite) phase material can be formed if excess cobalt oxide is used (10 at%) and the cation vacancies are compensated for by the presence of either higher valent cobalt or oxygen.

The same analysis methods reveal that at a 1:1 stoichiometry a mixed phase (perovskite and lanthana) is produced. The perovskite is again lanthanum ion deficient but here the vacancies are compensated for by the presence of anion vacancies. It is this mixed phase material that is more interesting catalytically as it exhibits much greater reactivity. DSC methods show that it is much more active to oxygen adsorption and TPD indicates that it has a low-temperature desorption peak (absent for the single phase material) and a rapid desorption of oxygen at elevated temperatures (very much reduced for the single phase). The low-temperature desorption is often referred to as α-oxygen and is associated with the presence of cobalt. The higher temperature desorption (β) is associated with the release of oxygen and decrease in Co valency from 3 to 2 [15].

Clues to the source of the increased catalytic activity and oxygen sorption properties can be seen in XPS. As predicted by PXRD, there is 'free' lanthana present and XPS suggests that this is at the surface of the perovskite particles. It is believed that this surface lanthana is very strongly modified compared to pure lanthana. On the basis of previous work [9] it would be expected that any pure lanthana would react rapidly in air to yield complete conversion to bulk hydroxide, $La(OH)_3$. This was never observed (witness the low levels of the hydroxide seen in the Rietveld analysis). It is also apparent that this surface phase lanthana is explicitly related to the nature and activity of the surface of the perovskite.

The intimate link between surface lanthana and activity can be directly observed. The-low temperature α oxygen desorption observed here, has been seen from many perovskite materials [16] and has been related to high catalytic activity. Further, it is not observed in TPD experiments from either lanthana or the single phase material. It is quite clear from other results given in this work that the bulk of this material has a high concentration of anion vacancies. Roberts [10] has shown that weakly held oxygen species of approximate formal charge -1 are seen in XPS at binding energies around 531–532 eV and it would seem that these are observed in this work. The XPS O1s results presented here would suggest that at the surface, these vacancies might be occupied by weakly held (i.e. compared to lattice O^{2-} ions) oxygen species, and thus, the high oxygen-to-metal ion ratio that is observed. By inference, it can be concluded that it is these oxygen species responsible for low-temperature catalytic activity and the oxygen sorption properties observed here.

The activity of the doped catalysts is difficult to rationalise without further work. Addition of dopant levels of 2, 3 and 4 valent cations does not have a beneficial effect on the activity of these materials. However, it can be concluded that the most active site in this system is the one formed on the surface of the mixed phase perovskite.

5. Conclusions

Lanthanum–cobalt perovskites can be prepared, but all prepared materials exhibit lanthanum ion deficiency in the lattice. The most catalytically active materials to methane combustion exhibit a mixture of lanthana and perovskite phases. The activity appears to be associated with the availability of relatively weakly held oxygen ions at the surface and it is tentatively suggested that this is associated with anion vacancies created by the lattice non-stoichiometry. It is not possible to further improve the activity by doping with other metal cations.

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