STUDY OF THE ACTIVITY AND DEACTIVATION OF \text{La}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.3} IN DRY \text{CH}_4 USING TEMPERATURE PROGRAMMED TECHNIQUES

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ABSTRACT

\text{La}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.3} was studied using temperature programmed (TP) techniques for application as a direct \text{CH}_4 oxidation anode in SOFCs. Activity for \text{CH}_4 oxidation, redox behaviour and extent of deactivation by carbon deposits were investigated. The oxide exhibited a much lower activity for the formation of carbon deposits and a higher onset temperature of deposition than the Ni-ZrO$_2$ cermet [1]. Over the oxide, two main \text{CH}_4 reaction regimes have been identified: complete oxidation at intermediate temperatures and \text{CH}_4 dissociation at high temperatures [2]. At approximately 400-600°C, where complete oxidation of \text{CH}_4 occurred over the oxide, no carbon deposition was detected. With Ni-ZrO$_2$, carbon deposition was observed over the entire active temperature range of the catalyst [1]. This suggested that such an oxide anode material may be operated at these temperatures with \text{CH}_4 without becoming deactivated by carbon deposits. The addition of H$_2$O to the \text{CH}_4 feed substantially reduced carbon deposition.

INTRODUCTION

There is presently much interest in using \text{CH}_4 feeds directly in SOFCs, thus avoiding the necessity for an (endothermic) steam reforming stage to provide fuel. Ni-YSZ cerments are used as the anode material almost exclusively in SOFC systems. However, when Ni catalysts are used with hydrocarbon feed stocks, they are prone to deactivation through the formation of carbonaceous deposits on the catalyst surface (this was recently investigated using TP techniques [1]). It has been proposed [3-6] that certain oxide materials may be more suitable for use as alternative \text{CH}_4 SOFC anode materials.

This paper contains the results of experiments performed to determine the suitability of the perovskite material \text{La(Ca)CrO}_3 for use as an anode material in a SOFC fuelled by \text{CH}_4. Many of the experiments were similar to those performed on the conventional anode material, Ni-YSZ [1], and direct comparisons of the results can be made. Further experimental work was aimed at elucidating the redox behaviour of the \text{La(Ca)CrO}_3 and the mechanisms of the interactions between \text{CH}_4 and \text{La(Ca)CrO}_3.
EXPERIMENTAL DETAILS

The oxide material were prepared by the modified Pechini method using nitrate precursors [7]. The resulting powder was calcined at 900°C for 5 h to remove the carbon residues and ball milled for 24 h before use in the experiments. The formula of the compound was confirmed as La_{0.8}Ca_{0.2}CrO_3 by XRD [7].

The experimental apparatus has been described previously [1].

Experimental Procedures

(i) Effect of Pre-treatment of La_{0.8}Ca_{0.2}CrO_3. Experiments to determine the effect of pre-oxidation (20% O_2/He; 60 min; 1000°C) and pre-reduction (5% H_2/He; 90 min; 1000°C) of the perovskite material, La(Ca)CrO_3, on its activity for CH_4 oxidation and dissociation were carried out. Approximately 75 mg samples were used. After pre-treatment, the microreactor was cooled, the system flushed with 100% He and TP reaction (TPRx) in 5% CH_4 in He performed.

(ii) Reduction Behaviour. The TP reduction (TPRd) of pre-oxidised La_{0.8}Ca_{0.2}CrO_3 was performed in a flow of approximately 60 ml/min of 5% H_2/He at a heating rate of 25°C/min.

(iii) Isothermal Exposure of Pre-oxidised La_{0.8}Ca_{0.2}CrO_3 to CH_4. Pre-oxidised samples of La_{0.8}Ca_{0.2}CrO_3 were exposed to CH_4/He for a period of 90 min. The microreactor was cooled rapidly to close to room temperature and a TP oxidation (TPO) performed to investigate the nature of any carbon deposits formed.

(iv) Isothermal Exposure of Pre-reduced La_{0.8}Ca_{0.2}CrO_3 to CH_4. Pre-reduced catalyst samples were exposed to 5% CH_4/He for 90 min at exposure temperatures, T_{(exp)} of 450°C, 600°C, 750°C and 900°C, after which a TPO was performed. The experimental procedure was as for the isothermal experiments on Ni-YSZ described previously [1]. The heating rate variation method [8] was used to obtain values of the activation energies, E_a, for the different reactions of CH_4 over pre-oxidised La_{0.8}Ca_{0.2}CrO_3. The standard TPRx experiment in 5% CH_4/He were repeated at different heating rates, β, of 5, 10, 20, 40 and 80°C/min.

(vi) Affect of H_2O on Reaction of CH_4 over La_{0.8}Ca_{0.2}CrO_3. TPRx experiments were performed on pre-reduced or pre-oxidised samples of La_{0.8}Ca_{0.2}CrO_3. About 3 wt% of H_2O was added to the 5% CH_4/He reactant mixture by passing it through a H_2O saturator whose temperature was held constant at 27°C. The TPRx was started at 150°C to prevent the condensation of H_2O in the system. The TPRx runs were followed by TP oxidation (TPO) in 20% O_2/He to investigate the nature of any carbon deposits formed.
RESULTS AND DISCUSSION

(i) Effect of Pre-treatment of La₀.₈Ca₀.₂CrO₃

The TPRx spectra of the pre-oxidised (Figure 1) and the pre-reduced samples of La₀.₈Ca₀.₂CrO₃ were similar, the main difference being the absence of CO₂ and H₂O production at intermediate temperatures in the latter. The TPRx results are described in detail elsewhere [2]. In summary, CH₄ reaction was found to occur on this material in two separate ways:

(a) Complete oxidation to CO₂ and H₂O. As this reaction only occurred on the pre-oxidised sample at intermediate temperatures (500-850°C) where lattice oxygen was unlikely to be very mobile, it was ascribed to reaction with surface and near-surface oxygen. No H₂ or CO by-products were formed implying rapid and complete reaction of the oxygen with the products of CH₄ dissociation. CO₂ and H₂O had very closely matching traces indicating that they had a common precursor and rate determining step (r.d.s.). This r.d.s. is likely to be the initial scission of the first C-H bond of CH₄, provided that subsequent reaction steps are rapid.

(b) CH₄ dissociation. CH₄ formed atomic H and surface carbon species on the oxide surface. The H combined rapidly to form H₂ gas and some of the surface carbon was oxidised to CO. This reaction occurred at high temperatures (above 800°C) at which lattice oxygen was likely to be mobile, and in both pre-oxidised and pre-reduced samples, although less CO was produced in the latter. Therefore, mainly lattice oxygen was implicated in the formation of CO.

A TPRx experiment was performed on a pre-oxidised La₀.₈Ca₀.₂CrO₃ sample in which the temperature was programmed to a maximum of 600°C, where only the complete combustion reaction occurs. No COX was detected in a subsequent TPO experiment, indicating that the deposition of carbon species appeared only to have occurred in the CH₄ dissociation reaction.

(ii) Reduction Behaviour

Figure 2 shows the TPRd spectrum for pre-oxidised La₀.₈Ca₀.₂CrO₃. The main reduction peak occurred at 560°C with a low temperature shoulder at 483°C. After the TPRd experiment, the temperature of the sample was maintained at the maximum value for a period of 2 h. The total amount of H₂O produced represented reduction of the sample by the equivalent of 0.098 O/molec (oxygen atoms per molecule of bulk La₀.₈Ca₀.₂CrO₃). The effect of the partial substitution of Ca²⁺ ions for La³⁺ ions is considerable, since Fierro and Gonzalez [9] observed a reduction of unsubstituted LaCrO₃ equivalent to only 6.5 × 10⁻³ O/molec at 1000°C. In their work on La₁₋ₓSrₓCrO₃-δ (where x = 0.1 to 0.3), Mizusaki et al [10] state that it is generally believed that δ is equal to zero (i.e. the material is stoichiometric) when La₁₋ₓSrₓCrO₃-δ is exposed to air and that δ tends to a value of x/2 in extremely low O₂ partial pressures. The partial substitution of La³⁺ by Sr²⁺ is believed to stabilise an equivalent number of Cr⁴+ ions at the Cr³+ site in the fully oxidised, stoichiometric form of the material. On
chemical reduction or exposure to extremely low partial pressures of O\(_2\), the Cr\(^{4+}\) ions are reduced to Cr\(^{3+}\) ions and an equivalent amount of oxygen, \(\frac{x}{2}\) O atoms per molecule of the perovskite, is lost from the material. This oxygen is denoted as absorbed or \(\alpha\)-oxygen. Substitution of La\(^{3+}\) by Ca\(^{2+}\) rather than Sr\(^{2+}\) can be expected to have an analogous effect on La\(_{0.8}\)Ca\(_{0.2}\)CrO\(_3\) pre-oxidised in 20% O\(_2\)/He. Therefore, a reduction of \(\frac{x}{2} = 0.1\) O/molec would be expected. This agrees well with the value obtained from the TPRd experiment. Therefore, it is reasonable to attribute the main reduction peak at 560°C and its high temperature tail to the removal of the available lattice oxygen, that is, absorbed or \(\alpha\)-oxygen. This tail is likely to correspond to bulk \(\alpha\)-oxygen and the peak itself to the more accessible \(\alpha\)-oxygen at (or near) the surface of the La\(_{0.8}\)Ca\(_{0.2}\)CrO\(_3\) particles. The lower temperature peak must then be either more weakly bound surface lattice oxygen, for example, lattice oxygen of low co-ordination, or adsorbed oxygen. From the XPS work of Fierro and Tejuca [11] and others [12-14] it seems quite likely that this is O\(^2\)-. Other possible assignments of the low temperature peak are as coordinatively unsaturated lattice O\(^2\)- ions at the surface. Fierro and Tejuca also showed that LaCrO\(_3\) exhibited considerable oxidative non-stoichiometry at the surface, attaining the surface composition LaCrO\(_{4.06}\) after pre-oxidation. This 'excess' surface lattice oxygen might be less strongly held and therefore more reactive.

The total amount of equivalent atomic O removed from La\(_{0.8}\)Ca\(_{0.2}\)CrO\(_3\) during several TPRx experiments was calculated and was found to vary from 0.15 to 0.19 O/molec for pre-oxidised samples. This is more than could be accounted for by reduction of the Cr\(^{4+}\) ions to Cr\(^{3+}\) and indicates that the Cr\(^{3+}\) ions were partly reduced. Carbon is a stronger reducing agent than H\(_2\) and is in fact used in the preparation of metallic Cr from the ore FeCr\(_2\)O\(_4\) [15]. Therefore, this further reduction could be attributed to reduction of Cr\(^{3+}\) by surface carbon deposits at high temperature.

(iii) Isothermal Exposure of Pre-oxidised La\(_{0.8}\)Ca\(_{0.2}\)CrO\(_3\) to CH\(_4\)

90 min exposure experiments were performed at \(T_{\text{exp}} = 432°C, 614°C, 637°C, 685°C, 698°C, 707°C, 767°C, 783°C\) and \(829°C\).

The overall product distributions in mmoles of product per g of catalyst were calculated for each experiment. The CO\(_2\) level was seen to remain approximately constant above \(T_{\text{exp}} = 600°C\). The H\(_2\)O level followed a broadly similar trend. A strong increase in CO and H\(_2\) showed how the CH\(_4\) dissociation reaction became dominant at elevated temperatures. This is very clearly shown in Figure 3. Here, the ratios of moles of products to the total number of moles of CH\(_4\) converted to carbon-containing products were plotted. A clear switch between the two reaction regimes occurred between 600°C and 700°C. At low temperatures, the product ratio of CO\(_2\) was just below 1 and that of H\(_2\)O was at about 2 or above (the accuracy of H\(_2\)O determination was limited at low temperatures due to high background levels in the vacuum system). Thus they were close to their stoichiometric values, indicating that the complete oxidation was the dominant reaction. H\(_2\) and CO ratios were very low in this temperature range, but rose at intermediate temperatures as the ratios of the complete oxidation products fell. CO and H\(_2\) reached approximately constant levels, at the higher temperatures, of just below 1 and about 1.5, respectively. The final level of H\(_2\) was
slightly below the value expected from the stoichiometry, whilst the level of H₂O at these temperatures seems slightly high. Therefore, it appears that a small fraction of the atomic surface H formed on CH₄ dissociation was converted to H₂O. The level of the CO₂ ratio at these temperatures was almost zero, implying that the complete oxidation reaction had declined to almost insignificant levels with respect to the dissociation reaction.

The product ratio of surface carbon was back-calculated from the TPO data and is also plotted in Figure 3. It can be seen that carbon deposition occurred only in the high temperature reaction regime, above about 700°C. The majority of the surface carbon was oxidised completely to release CO₂. The average surface area occupied by a carbon atom was assumed to be 0.026 nm² [1]. On this basis, the total amount of carbon removed in the TPO experiment after exposure to CH₄ at 829°C for 1.5 h was calculated to be approximately 0.41 monolayers. Using the analogous plot for the Ni-YSZ material [1] to obtain the equivalent number of monolayers for the same temperature and exposure time gave a value of 112 monolayers of carbon. This difference was due mainly to the much higher activity of Ni-YSZ for CH₄ dissociation, but also to the higher selectivity to surface carbon deposits exhibited by the Ni-YSZ. The CO₂ production traces from the TPO spectra performed on the samples after their exposure to CH₄ showed the existence of a maximum of five CO₂ production peaks representing five types of surface carbon species.

(iv) Isothermal Exposure of Pre-reduced La₀.₈Ca₀.₂CrO₃ to CH₄

The variation of product distribution with exposure temperature for these experiments showed increases in the products of the CH₄ dissociation reaction, carbon deposits (subsequently removed in the TPO runs), CO and H₂. The rates of the dissociation reaction were comparable to those for the pre-oxidised samples at the same exposure temperatures. The mole ratios of all carbon containing products, CO, CO₂ and surface carbon species, with respect to the total carbon conversion are plotted in Figure 4. This shows that there was a small amount of complete oxidation occurring at the lower T(exp), but that this fell further in importance as the rate of the CH₄ dissociation reaction increased strongly. Carbon deposition was seen to have begun essentially at the exposure temperature of 600°C (It must be remembered that Figure 4 shows selectivities and not rates of production, so, although there is an appreciable selectivity to surface carbon below 600°C, the rate is very low.) The mole ratio of surface carbon species remained approximately constant, at a level of about 0.4. This compares with a maximum selectivity for the pre-oxidised material of about 0.1.

Three main CO₂ peaks were seen in the TPO spectra taken after exposure to CH₄. The positions of the three peaks appeared to match reasonably well with the first, second and third peaks, respectively, of the TPO spectra of the pre-oxidised material. The amount of carbon deposition at a temperature of 829°C was estimated to be equivalent to 1.0 monolayers. This compares directly with the figure of 0.41 equivalent monolayers for the pre-oxidised material under the same conditions. Therefore, appreciably more carbon deposits built up on the pre-reduced material. As T(exp) was increased, the amount deposited increased also.
Determination of Kinetic Variables

Ea values of 120, 147, 202 and 442 kJ/mole were obtained by the temperature variation method for the four peaks seen in the TPRx spectrum of the pre-oxidised material [2]. These correspond to the two intermediate temperature complete oxidation processes and two high temperature CH4 dissociation processes, in order of ascending temperature. The Ea values obtained for the two complete oxidation peaks agree well with those found by McCarty et al (142 kJ/mole)[16], and by Arai et al (120 kJ/mole) [17], for unsubstituted LaCrO3.

It is believed [16, 17] that the complete combustion of CH4 over perovskite oxides proceeds by two reaction routes. At low temperatures, reaction takes place predominantly with oxygen species adsorbed from the gas-phase. At higher temperatures, lattice O2- ions become reactive with CH4 and this reaction becomes dominant as the coverage of adsorbed oxygen decreases with increasing temperature.

The existence of two complete oxidation peaks (and two Ea values) for the substituted material, La0.8Ca0.2CrO3, implies two different reaction sites and these are highly likely to involve reaction with the two different forms of catalyst oxygen detected in the TPRd experiment described earlier i.e. weakly bound or adsorbed oxygen and α-oxygen. The Ea values were relatively low and imply that these processes were catalysed. The relatively low Ea value of the lower temperature CH4 dissociation also suggests a catalysed reaction. The Ea of 442 kJ/mole obtained for the higher temperature CH4 dissociation, which is evident as a high temperature shoulder on the main dissociation peak at 860°C (see Figure 1), suggests non-catalysed H3C-H bond scission, as it is very similar to the first C-H bond dissociation energy for CH4, 438 kJ/mole.

Affect of H2O on Reaction of CH4 over La0.8Ca0.2CrO3

The TPRx experiment with the pre-reduced sample gave rise to a relatively simple. The main reaction involved the consumption of CH4 and H2O and the production of a large amount of H2, some CO and some CO2. The molar ratio of these products was calculated over the temperature range from 750°C to the end of the experiment at 1020°C. The overall reaction can be attributed to a combination of the steam reforming of CH4 and the further oxidation of some of the CO to CO2,

\[ CH_4 + (1+x)H_2O \rightarrow (1-x)CO + xCO_2 + (3+x)H_2 \]  \[1\]

where x was about 0.55, in this case. The rate of H2 and CO production increased with temperature as did that of CO2, initially. This showed that the rate was not limited by catalyst deactivation by carbon deposition, as it was in the TPRx spectra in which no H2O was added. In the corresponding TPRx spectrum the pre-oxidised sample exhibited intermediate temperature complete oxidation of CH4 (similar to that seen for TPRx of the pre-oxidised sample with dry CH4) and high temperature CH4 steam reforming, similar to that described for the pre-reduced sample. Again, there was no
evidence for catalyst deactivation by carbon deposition. The pre-reduced sample did not exhibit the complete oxidation reaction with H₂O/CH₄ or with dry CH₄. Therefore, the reactive oxygen species must be formed in the pre-oxidation process, must be destroyed during pre-reduction and cannot be formed simply by exposing the pre-reduced material to H₂O.

Neither of the spectra for the TPO experiments performed after the H₂O/CH₄ TPRx experiments on the pre-reduced oxide or the pre-oxidised sample showed any production of CO₂. Therefore, this level of H₂O addition, which is relatively low compared to the amounts used in internal reforming SOFCs, was sufficient to completely prevent carbon deposition on pre-oxidised or pre-reduced samples of La₀.₈Ca₀.₂CrO₃ under these experimental conditions. Addition of the same amount of H₂O in a TPRx experiment performed with the Ni-YSZ cermet material was seen [1] to significantly reduce, but not to eliminate carbon deposits, under the same conditions.

CONCLUSIONS

The perovskite material, La₀.₈Ca₀.₂CrO₃, was studied using TP techniques with a view to its application as a direct CH₄ oxidation anode material in SOFCs. Activity for CH₄ oxidation, redox behaviour and extent of deactivation by carbon deposits were investigated and compared with the behaviour of the Ni-YSZ cermet conventional anode material studied previously [1]. The Ni-YSZ exhibited a much higher activity for the formation of carbon deposits than the oxide. In addition, the temperature of onset of carbon deposition was much lower on the cermet than on the oxide.

Over the oxide, two main CH₄ reaction regimes were identified. Complete oxidation occurred at intermediate temperatures and CH₄ dissociation, forming carbon deposits, took place at high temperatures. Each of these reactions was found to take place via two mechanisms. Complete oxidation involved reaction with either surface or absorbed oxygen species. CH₄ dissociation appeared to occur via a catalysed (probably at oxygen ion vacancies) and an uncatalysed mechanism. Activation energy values were obtained for these four mechanisms using the heating rate variation method. Over a particular temperature range (approximately 400-600°C) at which complete oxidation of CH₄ occurred over the oxide, no carbon deposition was detected on prolonged exposure of the oxide to CH₄. This suggested that a CH₄ direct oxidation SOFC with such an oxide anode material may be operated at these temperatures without becoming deactivated by carbon deposits. This is not the case with Ni-YSZ with which carbon deposition was observed over the entire active temperature range of the catalyst [1].

The effect of the addition of a small amount of H₂O to the CH₄ feed caused no detectable carbon to be deposited on the oxide.

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Figure 1. TPRx of pre-oxidised La_{0.8}Ca_{0.2}CrO_3 in 5% CH_4/He. Mass spectrometer signals (arbitrary units) versus temperature (m/q = mass to charge ratio).

Figure 2. Temperature programmed reduction of La_{0.8}Ca_{0.2}CrO_3 in 5% H_2/N_2. H_2O production (arbitrary units) versus temperature.
Figure 3. Product distribution for isothermal reaction of pre-oxidised $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ in 5% CH$_4$/He in moles per mole CH$_4$ converted.

Figure 4. Product distribution for isothermal reaction of pre-reduced $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ in 5% CH$_4$/He in moles per mole CH$_4$ converted.