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Temperature programmed oxidative coupling of methane over a Li-Ni-Co-O catalyst monitored *in-situ* by a.c. electrical parameters coupled to multiple-ion monitoring of the product species

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By using the multiple ion-monitoring facility of a quadrupole mass spectrometer, the on-line analysis of species has been studied for temperature programmed methane coupling over a non-stoichiometric mixed oxide $Li_{0.9}Ni_{0.5}Co_{0.5}O_{2-\delta}$ catalyst between 400–800 °C. The effects of water vapour, methane and oxygen were also separately studied. The a.c. electrical characteristics of the catalyst pellet between 100 Hz and 1 MHz were simultaneously monitored *in-situ*. Catalytic changes are immediately reflected in changes in the a.c. characteristics. Frequency dependent a.c. losses due to surface dipole effects dominate during phases of strong chemisorption and reaction, whilst reversion to thermally activated behaviour occurs during regions of reduced chemical activity. Lattice oxygen is able to act as a source of oxygen and react with methane. The oxidative coupling of methane showed stable behaviour for 3h at 750 °C.

1. Introduction

Due to the abundance of natural gas and liquified petroleum gas they could act as a cheaper alternative to petrochemical feed stock. Therefore extensive effort has been expended over the past decade on the investigation of direct and indirect conversion of methane to value-added products with minimum total oxidation to CO and CO_2 [1]. The direct conversion routes involve partial oxidation of methane to methanol, formaldehyde or olefins. Unfortunately, the desired products are more reactive than the more chemically stable methane. Indirect routes require methane oxidation to form syngas ($CO + H_2$) in a first stage, by steam reforming, direct partial oxidation or a combination of both. In a second stage, syngas is upgraded by Fischer–Tropsch technology or a methanol synthesis route.

Mixed oxide materials are often used in oxidation catalysis. Generally they are less costly than the noble metal catalysts, they are pre-sintered during preparation and are hence not subject to the severe sintering problems experienced during the use of metallic catalysts. The potential of the high temperature superconductor $YBa_2Cu_3O_{7-x}$ for use as an oxidation catalyst in which lattice oxygen (which may be regenerated) is used as a reactant has already been considered in this laboratory [2]. The facile movement of oxygen anions was monitored by following changes in electrical conductivity and the activation of surface dipoles (as opposed to those within the bulk of the material). This anion mobility was linked to the production of higher hydrocarbons observed in a reactor heated by radio frequency (RF) power [3]. This material, although an excellent candidate for use in an RF reactor, has potential disadvantages for long-term use due to its inherent instability under working conditions [4]. Consequently, alternative mixed oxide compounds of high electrical conductivity have been considered for reactions involving the selective oxidation of methane.

In an extensive review of the catalytic reactions of partial methane oxidation, Krylov notes that many oxides with a layered lattice structure have potential as oxidative coupling catalysts [5]. It is proposed that these systems contain oxygen anions which may be directly used in partial oxidation reactions whilst a small portion of this oxygen can be transferred to isolated centres, thus preventing complete oxidation. Selectivity can be substantially increased by the presence of Li within the layered structure. Li has been used in the presence of MgO in many studies of catalysts with effective activities and selectivities for the oxidative coupling of methane (OCM) [6]. Some complex oxides are more active and selective than simple oxides. In addition it is believed that for oxidation reactions involving hydrocarbons, catalysts having both a high electronic conductivity and a high ionic conductivity are beneficial [7]. The mixed conducting oxide $Li_{0.9}Ni_{0.5}Co_{0.5}O_{2-x}$ satisfies the above criteria [8] and is studied in the present work.

Previous research on a range of layered mixed oxides $Li_xNi_{1-y}Co_yO_{2-x}$ showed the particular

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stoichiometry $x = 0.9$, $y = 0.5$ to be stable up to 900 °C [9]. Furthermore, this material has a.c. loss properties which render it suitable for use in reactors powered by RF energy. Preliminary temperature programmed reaction spectrum (TPRS) tests for the oxidative coupling of methane in a small conventionally heated reactor, showed that significant ethane and ethylene are produced under certain conditions [10]. The products were monitored using the multiple ion-monitoring facility of a quadrupole mass spectrometer, which gives a powerful *in-situ* and immediate response to changes in the distribution of the effluent species. The techniques of temperature-programmed-reaction and temperature-programmed-desorption have been described and advocated elsewhere, [11–14] whilst the identification of reaction projects using mass spectrometry is described by Bao *et al.* for their research on the oxidative coupling of methane on silver catalysts [15].

In the present paper, experiments on pelleted samples, rather than powdered ones, are described in order that a.c. electrical changes in the catalyst can be observed as the reactions proceed. The effects of moisture, methane and oxygen (diluted in Ar) were investigated separately, in addition to the OCM reaction using a methane and oxygen co-fed system. The particular catalytic features of the chosen material will be discussed in greater detail elsewhere. Here, the effective combination of a.c. electrical characterization and ion-monitoring techniques in catalysis are illustrated. Single frequency or d.c. techniques are sometimes used to monitor catalytic behaviour; however, the additional dimension of frequency helps to differentiate between bulk and surface phenomena.

2. Experimental procedure

Polycrystalline $Li_{0.9}Ni_{0.5}Co_{0.5}O_2$ pellets (12 mm diameter and up to 4 mm thick) were prepared as previously described [16]. A single pellet was placed in a horizontal split-tube programmable furnace and a.c. electrical measurements between 100 Hz and 1 MHz were made (using a Hewlett Packard 4194A impedance analyser) every 10 min with the sample being electrically represented by a capacitance (C_p) in parallel with a resistance ($1/G$) as described elsewhere [16, 17].

A ramp rate of 2.5 °C min^{-1} was used in the experiments except where stated. For experiments purely in argon a flow rate of 90 ml per min was used. For the oxidative coupling experiments, CH_4 and O_2 were mixed and diluted with Ar and controlled using Brookes flow meters with each gas having flow rates as specified in the experiments. Care was taken to avoid the possibility of spontaneous detonation of the gaseous mixture [18]. Any steam produced was condensed, part of the remaining effluent was directed to a VG quadrupole mass spectrometer (QMS) for analysis and the remains of the gaseous products were burnt. Ar, O_2, CO_2, H_2, CH_4, CO, C_2H_4 and C_2H_6 were simultaneously monitored with time, using the mass numbers 40, 32, 44, 2, 15, 28, 30 and 27 respectively. Mass number 28 arises from an overlap of signals from CO, C_2H_4, C_2H_6 and a trace of CO_2, but for low selectivity to C_2 products it essentially represents CO. Mass number 27 represents a mixture of both C_2H_4 and C_2H_6. A software package was used to analyse the data.

3. Results

3.1. Effect of moisture

Preliminary TPRS experiments between 400–800 °C, using a pellet of 4 mm depth, involved a gas mixture of Ar, CH_4 and O_2 each flowing at 30 ml per min. Significant increases in CO and CO_2 were observed above 500 °C, coupled with a rapid increase in C_2H_6 and an increase in C_2H_4 which stabilized above about 700 °C. Thus the catalyst had resulted in some methane coupling in addition to oxidation to CO and CO_2 at high temperatures.

In an inert atmosphere of dry Ar, a.c. data shows that there is virtually no frequency dependence above 400 °C, the behaviour is thermally activated with an almost constant effective activation energy of about 1.1 eV up to 800 °C [16]. Since steam is one of the products of both full and partial oxidation of methane and could dominate the a.c. characteristics, it was necessary to ascertain its affect on the conductance at high temperatures. Conductance values were compared for a new freshly made pellet between 400–800 °C in dry Ar (10 ml per min) followed by moist Ar, by passing the gas over a water bath at room temperature (about 10% humidity). Little difference between the characteristics was found, as is shown in Fig. 1. However, when CH_4 and O_2 are introduced a change in slope appeared in an Arrhenius-type plot and above 727 °C, the conductance increased more rapidly than it would in an inert atmosphere. Thus, the presence of steam cannot be used to explain the rapid increase in conductance above 700 °C during the OCM reaction. These changes, are easier to discern when represented as a linear function of temperature as shown in Fig. 2. At the highest operating temperature of 800 °C, the effect of frequency starts to reappear. Frequency dependence of the a.c. conductance is due to surface dipolar effects as a result of dipole relaxation phenomena [17].

The value of the parallel capacitance as a linear function of temperature began to rise steeply as the temperature exceeded about 600 °C, with values at 100 Hz as high as 1 mF. The capacitance values were re-measured in Ar alone after the OCM experiment and they had returned to lower values of order of 1 μF at the highest temperatures, similar in magnitude to those initially measured in Ar prior to the reaction. Thus marked surface dipole effects, which increase the overall capacitance, appear during times of intense surface activity.

In Fig. 3, a.c. parameters at 100 Hz between 400–800 °C in dry Ar before and during the TPRS OCM experiment may be compared. In Ar alone, the conductance increases almost constantly with temperature but the capacitance increases more rapidly above 600 °C, causing the loss tangent, ($\tan\delta$) a geometry independent parameter, ($\tan\delta = G/(\omega C_p$,

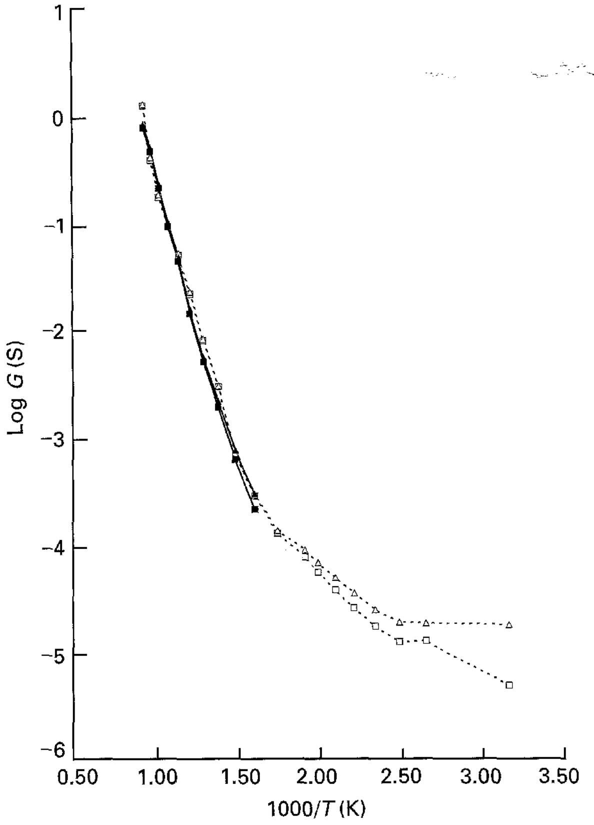

Figure 1 Conductance in dry Ar (10 ml per min) at (□) 100 Hz and (△) 1 MHz and humid (10 ml per min) at (■) 100 Hz and (▲) 1 MHz as a function of reciprocal temperature $dT/dt = 2.5$ °C per min.

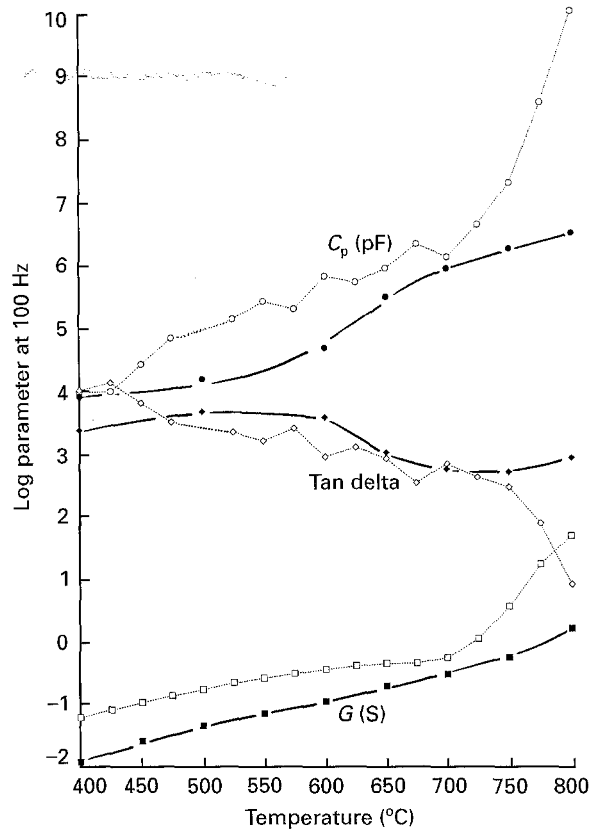

Figure 3 Conductance, parallel capacitance and loss tangent at 100 Hz between 400–800 °C, ($dT/dt = 2.5$ °C per min). Initial values in Ar (■), (●), and (◆) for G, C_p and tan δ respectively compared with values in Ar, methane and oxygen mixture (30, 40 20 ml per min) (□), (○) and (◇), respectively.

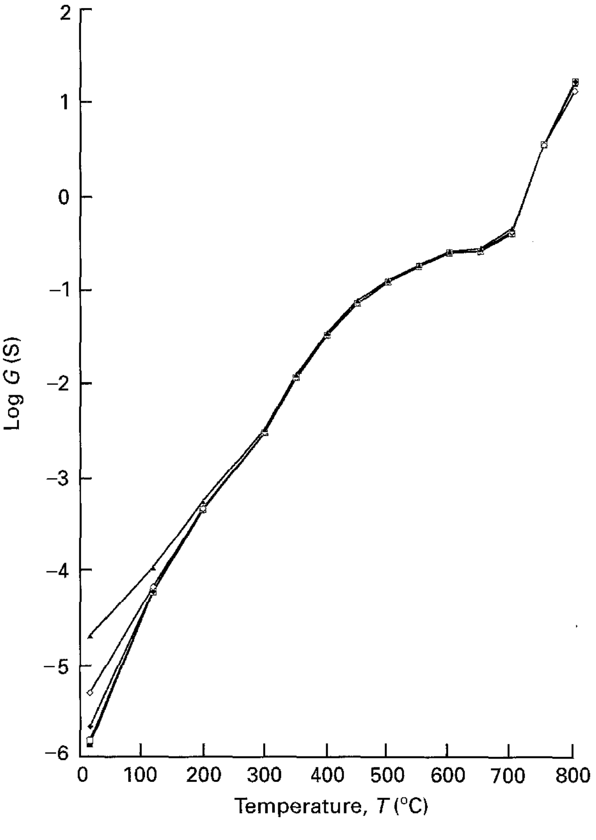

Figure 2 Conductance as a function of temperature and frequency (100 Hz (■), 1 kHz (□), 10 kHz (◆), 100 kHz (◇), 1 MHz (▲)) in Ar alone up to 300 °C, followed by Ar, methane and oxygen mixture (each at 30 ml per min) up to 800 °C, ($dT/dt = 2.5$ °C per min).

where ω is the angular frequency) to decrease accordingly. In comparison, during OCM, G and C_p both increase much more rapidly above 700 °C, accompanied by a more rapid fall in the loss tangent which means that the capacitance is reflecting changes in the material more strongly than is the conductance. The high capacitances are typical of those associated with chemical reactions, whilst those at the lower temperatures are typical of interfacial or intergrain surface dipole effects [19].

3.2. Effects of methane

Using a fresh pellet of 2 mm depth, the effects of single methane and oxygen atmospheres were investigated prior to more detailed experiments using the gas mixture. A temperature programmed reaction was carried out between 400–800 °C, using CH_4 diluted in Ar (20 and 100 ml per min respectively) followed by desorption of the gases in Ar alone at 800 °C for 30 min. Above 600 °C, Fig. 4 shows two significant features during the TPRS stage, (i) some production of CO_2, which increases from about 600 °C and reaches a maximum at about 700 °C, and (ii) the slight production of C_2 species at mass number 27 between 700–800 °C. Since no oxygen was present in the gaseous mixture, CO_2 and C_2s can only arise from a reaction of the methane with lattice oxygen, e.g., via the reactions:

$$CH_4 + 2O^{2-} \rightarrow CO_2 + 2H_2 \qquad (1)$$

$$2CH_4 + 2O^{2-} \rightarrow C_2H_4 + 2H_2O \qquad (2)$$

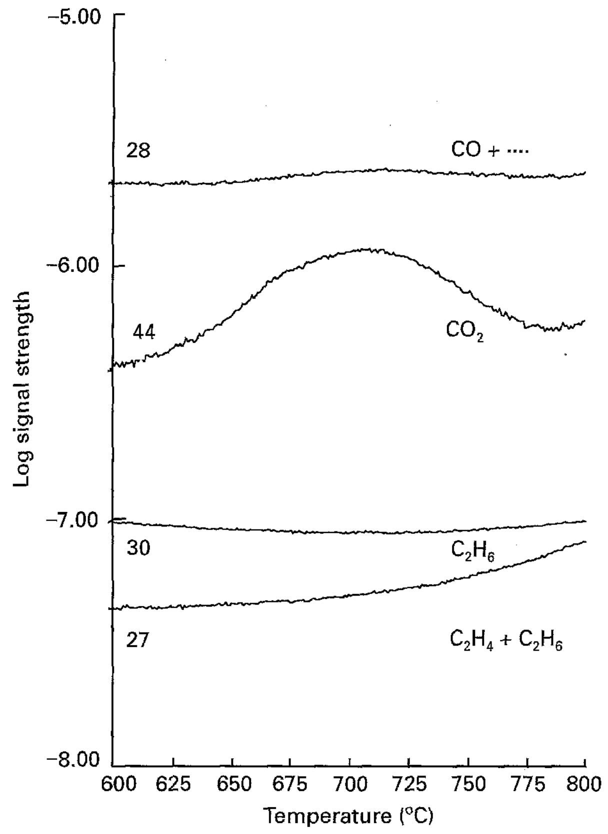

Figure 4 QMS ion signal strengths as a function of temperature ($dT/dt = 2.5\,^{\circ}C$ per min), for fresh pellet in CH_4/Ar (20:100 ml per min) at m/e values shown.

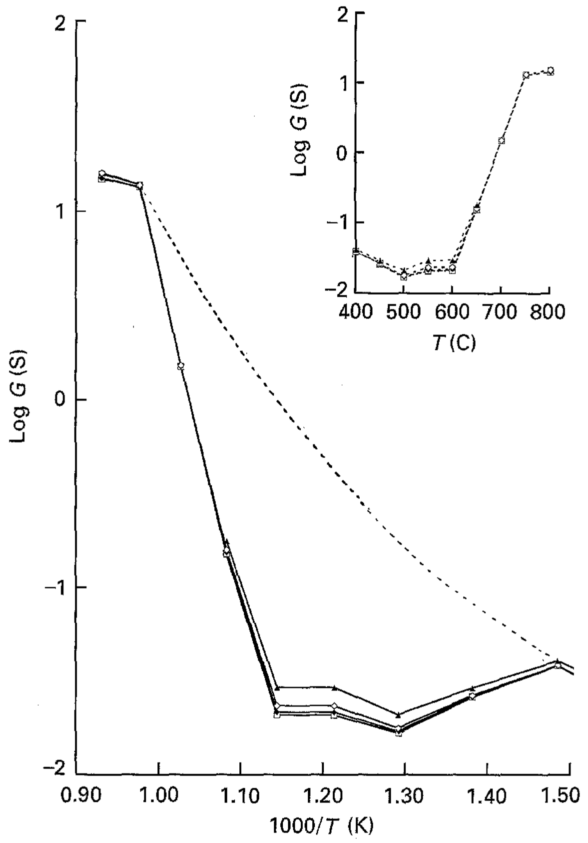

Figure 5 Conductance as a function of reciprocal temperature (insert as a function of T) and frequency (100 Hz (■), 1 kHz (□), 10 kHz (◆), 100 kHz (◇), 1 MHz (▲)), in CH_4/Ar, ($dT/dt = 2.5\,^{\circ}C$ per min). The dotted curve shows the frequency independent characteristic for Ar alone.

Above 700 °C, less CO_2 is produced (probably due to all available labile lattice oxygen having been consumed). Since the increase in mass number 27 (representing C_2s), was not accompanied by an increase for mass number 30 (C_2H_6), some slight production of C_2H_4 has occurred which increases slowly above 600 °C. During the desorption process at 800 °C after the temperature ramp and on further slow cooling to room temperature, CO_2 continued to be slowly released and the O_2 signal became more stable.

Thus this experiment showed that gaseous methane had reacted with lattice oxygen to essentially give complete oxidation to CO_2. This observation may be correlated with the changes in conductance/frequency characteristics. Initially, at room temperature in Ar, the complex impedance plot was a single semicircle, inclined at an angle of about 11° to the real axis [17]. This shape confirmed that the material was principally a good ionic conductor, through the presence of Li^+ ions in this case, with some electronic conduction also present [17]. Upon the initial chemisorption of CH_4 the originally smooth Arrhenius curve in dry Ar becomes immediately distorted (Fig. 5). At 400 °C, the conductance fell, reaching a minimum at about 500 °C. Between 500–600 °C the increased effect of frequency is evidence of increased surface dipole activity, which at this stage dominates the electrical behaviour. This region is associated with the slow evolution of CO_2.

Between 600–750 °C, the frequency effects are reduced with the conductance becoming thermally activated with an apparent activation energy of about 3 eV. In this region some lattice oxygen reacts with the methane to produce CO_2. None of the species are strongly bound to the surface sites, but are readily desorbed, hence the bulk behaviour of the catalyst again becomes dominant. The high activation energy is typical for ionic conduction and could arise from both Li^+ or O^{2-}ions. Oxygen ion conduction may in fact increase as more vacancies become available and ions are attracted from the interior towards the surface of the catalyst in order to fill these vacancies as the reaction proceeds.

A reversion to dipole dominated behaviour occurs above 750 °C. With the formation of CH_3 radicals and ionization of the H atoms to protons, ($H \rightarrow H^+ + e^-$) some loss in G may be caused by the release of electrons and a net decrease in conductance since it is a p-type material. In this region, a small but increasing production of C_2H_4 with reduced production of CO_2 will be linked to the relative change in bond strengths of the species, which is immediately reflected in the observed changes in a.c. behaviour.

The parallel capacitance at 100 Hz increased slowly from 10 nF to about 1 μF between 400–650 °C and thereafter increased much more rapidly, reaching high values of 1 mF at 800 °C, as surface chemical activity becomes more dominant. The characteristic was similar to that shown in Fig. 3 for the OCM conditions for the first pellet investigated. At the highest temperatures, the capacitances became erratic and difficult to measure as the impedance of the sample became almost as low as that of the measuring leads. The sample would probably be better represented by a pure resistance.

During desorption in Ar at 800 °C, the conductance fell by about a factor of 5.5 at all frequencies during the first 10 min, after which time a slight increase in the frequency dependence was observed. The capacitances simultaneously decreased by a factor of 10 during the first 10 min.

After slow cooling in Ar to room temperature, both conductance and capacitance data (after 20 min stabilization at pre-set temperatures) were close to values for the material in its pristine state. Thus no fouling of the catalyst had occurred since this would have resulted in a significant increase in G. The ambient complex impedance semicircle was remeasured and found to be similar to the original one, with an associated capacitance of about 20 pF, corresponding to bulk behaviour for this type of ceramic (in the absence of the dielectric, the capacitance *in vacuo* would be ~1 pF).

3.3. Effect of oxygen

Following the experiment with methane, the procedure was repeated using oxygen diluted in Ar (20 and 100 ml per min respectively). The oxygen signal increased slowly reaching a plateau after about 12 rather than the 2 min expected in the absence of the catalyst. This is due to a significant amount of oxygen being absorbed and filling the oxygen vacancies left over from the previous experiment. The most significant change in the effluent occurred between 650–800 °C for the CO_2 species as shown in Fig. 6. Since there was no indication of carbon fouling on the catalyst the carbon could only have come from residual strongly absorbed hydrocarbon species from the previous methane reaction. Two peaks in CO_2 at about 720 and 750 °C indicate that reaction may have occurred with oxygen from two different types of site. The production of CO_2 is finite due to the limited supply of carbon. Above 770 °C, all the signals become erratic which is coupled with a fall in hydrocarbons.

The effect of oxygen, from uptake at 400 °C up to 550 °C, was to flatten the Arrhenius type G-T^{-1} characteristic (Fig. 7). As oxygen is readsorbed into the lattice, the conductance becomes dominated by temperature-independent dipole relaxation losses. Between 550–600 °C there is a rapid fall in G with a greatly increased frequency dependence as more oxygen is taken up. This could arise from a decrease in the proportion of the lattice imperfections in the bulk of the material as the deeper oxygen vacancies become refilled. However, as CO_2 production starts, there is a reduced effect of frequency as species break away from the surface and a more regular lattice is restored. At 100 Hz, capacitances of the order of 100 nF to 1 μF were recorded during the TPRS stage, with somewhat erratic behaviour shown above 650 °C linked to the erratic mass spectrometer (MS) signals over the same period. Up to 650 °C, the capacitance characteristics between 100 Hz and 1 MHz were similar to those measured for fresh material in an argon atmosphere. However, above this temperature, the values slowly fall (to about 100 nF at 100 Hz and 800 °C) instead of

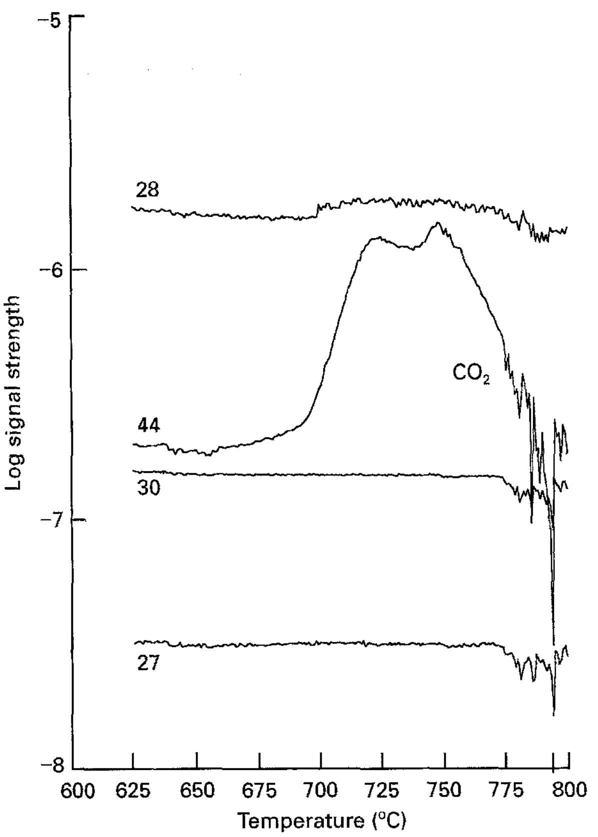

Figure 6 Relative QMS ion signal strengths as a function of temperature ($dT/dt = 2.5$ °C per min), in O_2/Ar (20 : 100 ml per min) at m/e values shown.

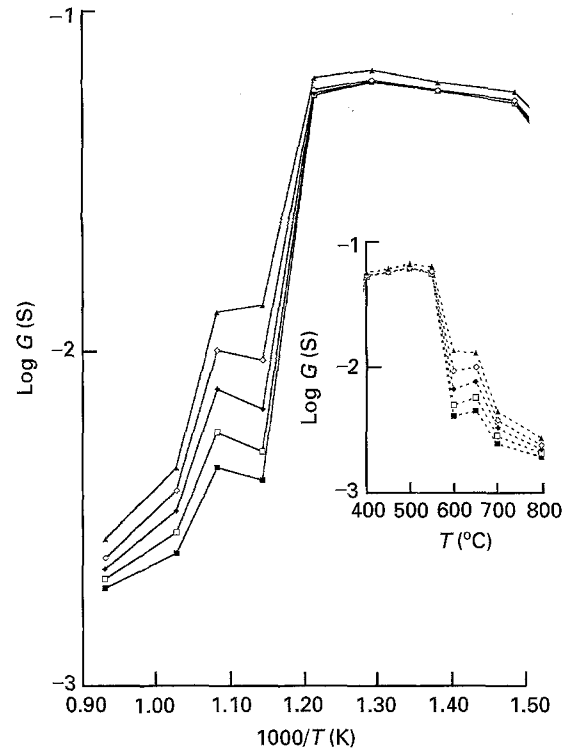

Figure 7 Conductance as a function of reciprocal temperature (insert as a function of T) and frequency (100 Hz (■), 1 kHz (□), 10 kHz (◆), 100 kHz (◇), 1 MHz (▲)), in O_2/Ar, ($dT/dt = 2.5$ °C per min).

continuing to increase; this is due to the lattice becoming more regular as the oxygen vacancies become re-filled.

Over the holding period of 30 min at 800 °C in Ar, G increased steadily by a factor of about 10 at 100 Hz and about 20 at 1 MHz as shown in Fig. 8, possibly due to desorption of some excess surface oxygen anions with consumption of electrons

$$O^{2-} + 2e^{-} \rightarrow O \qquad (3)$$

$$O + O \rightarrow O_2 \qquad (4)$$

The increased conductance was coupled with a steady increase in capacitance with time (Fig 8a), the magnitudes being typical of predominantly bulk effects at the lowest frequencies and of surface of grain boundary effects at the higher frequencies [17].

On cooling slowly in Ar and re-measuring the conductance at pre-set temperatures, the conductance was found to have been greatly reduced, particularly at the lower temperatures as shown in Fig. 9. After the refilling of deep oxygen vacancies, the mobility of oxygen anions will be reduced (due to fewer vacancies for them to move into); thus only Li^+ ionic and electronic conduction will appear, both of which will be thermally activated. At the lowest frequencies, due to the more perfect lattice, dipole effects will also have become greatly reduced, hence the net a.c. conductance is substantially reduced at lower temperatures. Thus after oxygen treatment alone, in contrast to the effect of methane, the electrical characteristics of the material have significantly changed. The 100 Hz conductance at 400 °C is reduced by over three orders of magnitude.

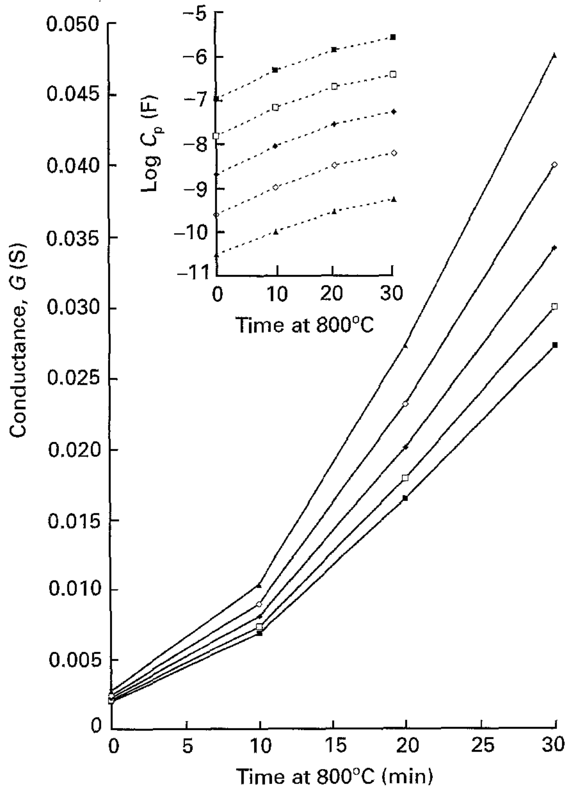

Figure 8 Conductance (insert, parallel capacitance) in Ar alone, (following O_2 treatment), as a function of time at 800 °C and frequency (100 Hz (■), 1 kHz (□), 10 kHz (◆), 100 kHz (◇), 1 MHz (▲)), (dT/dt = 2.5 °C per min).

3.4. Methane oxidation

The previous experiment was immediately followed by temperature programmed methane oxidation between 400–800 °C. In contrast to the initial experiments, a higher CH_4:O_2 ratio of 2 was chosen for both safety reasons and reputed enhanced selectivity towards C_2 products [10, 20], with the gases CH_4, O_2 and Ar having flowrates of 40, 20 and 30 ml per min respectively. At 800 °C, O_2 and CH_4 were turned off, the Ar flow rate was increased to 90 ml per min, and the temperature was maintained for 30 min, followed by slow cooling in Ar.

MS signals between 400–800 °C show CO_2 to steadily increase with temperature up to 700 °C (Fig. 10). From about 650 °C the amount of oxygen in the effluent rapidly decreases as it becomes consumed in increasing amounts. Below 600 °C, total oxidation to CO_2 occurs, but at higher temperatures C_2s are also produced with C_2H_4 increasing at a faster rate than C_2H_6 and with the latter reaching a peak at 700 °C. Above 770 °C, there is an increase in the partial pressures for all species, due to a change in the total number of molecules during reaction. Above 700 °C, the amount of CH_4 begins to fall, showing a high conversion of the input gases at high temperatures despite the small amount of catalyst placed in the tubular furnace over which the gases are passed.

In Ar at 800 °C, apart from CH_4, most gases desorbed within about 8 min. However, further oxygen is released after about 10 min accompanied by

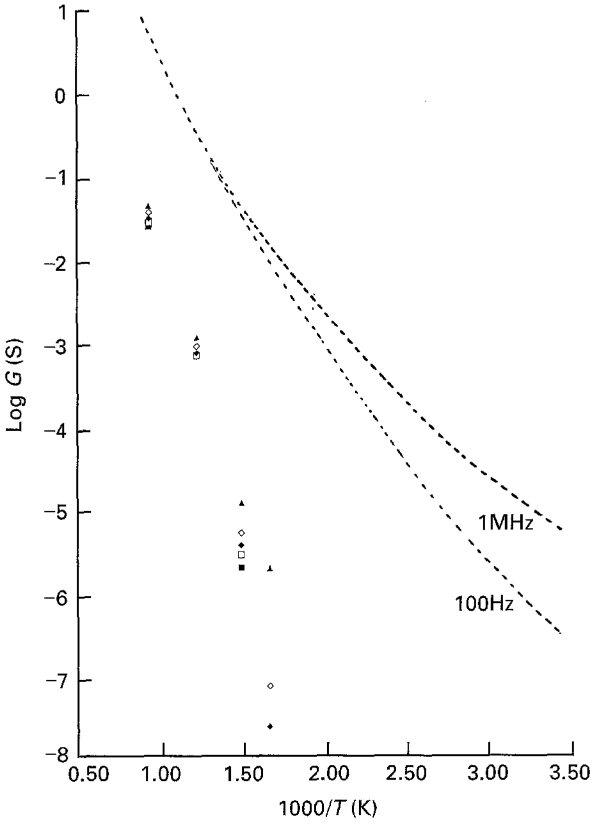

Figure 9 Conductance as a function of reciprocal temperature and frequency (100 Hz (■), 1 kHz (□), 10 kHz (◆), 100 kHz (◇), 1 MHz (▲)) in Ar at pre-set temperatures (following O_2 treatment and 30 min desorption at 800 °C in Ar). Initial curves in Ar before treatment shown for comparison (dotted curves).

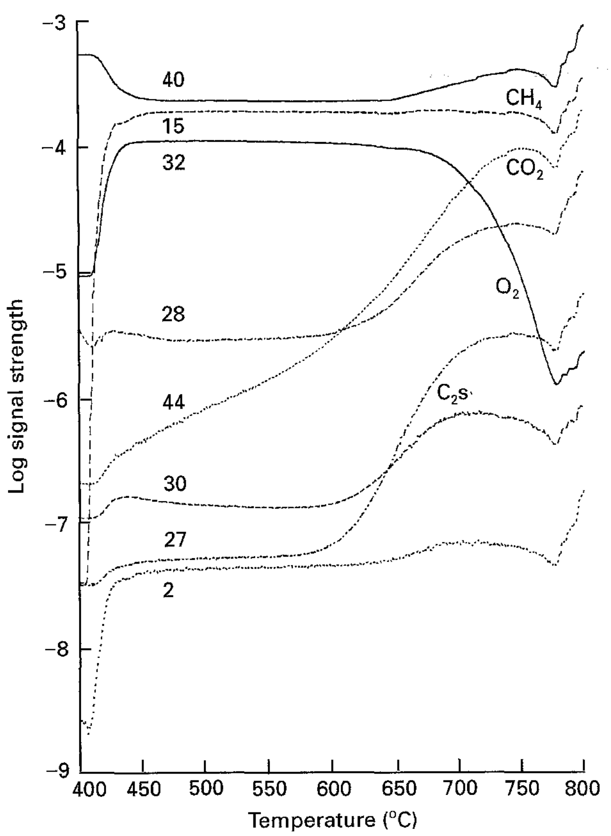

Figure 10 QMS ion signal strengths as a function of temperature ($dT/dt = 2.5\,°C$ per min), in $CH_4/O_2/Ar$ (40:20:30 ml per min) at m/e values shown.

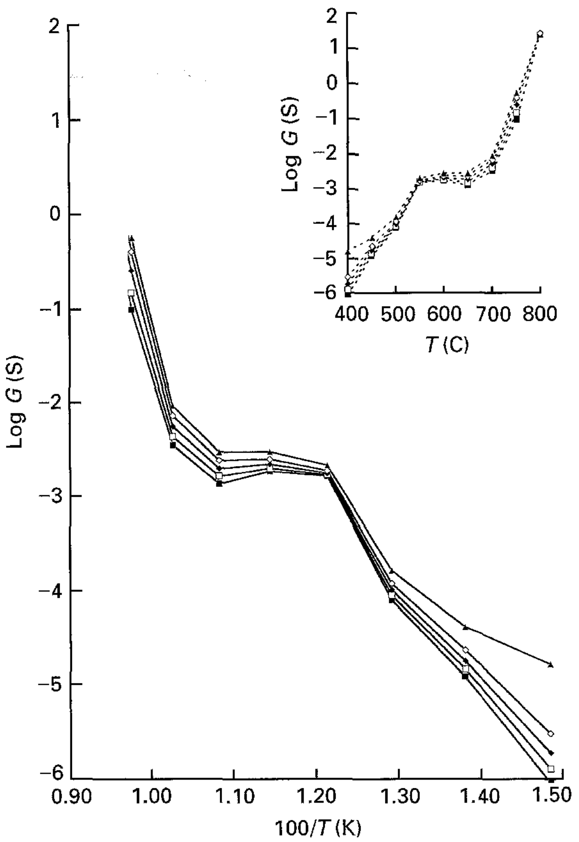

Figure 11 Conductance as a function of reciprocal temperature and frequency (100 Hz (■), 1 kHz (□), 10 kHz (◆), 100 kHz (◇), 1 MHz (▲)) in $CH_4/O_2/Ar$ (40:20:30 ml per min), ($dT/dt = 2.5\,°C$ per min), (Insert as a function of T).

some subsequent production of CO_2. This must be due to some reaction between oxygen and methane strongly held on the surface of the catalyst. On further cooling in Ar, the CO_2 signal fell rapidly.

The conductance–frequency–temperature data show that the conductance rises rapidly upon the introduction of CH_4 and O_2 at 400 °C (Fig. 11) and up to 550 °C the behaviour is the same thermally activated type shown in Ar prior to this experiment. Significant changes occur between 550–650 °C, with a loss of thermal effects and gain of frequency dependence. This indicates the dominance of strong surface chemisorption of species resulting in a dominant dipole behaviour. Above 650 °C, as some coupling of methane begins, there is a reduction in the proportion of surface dipoles and thermally activated behaviour of the conductance is re-established between 700–800 °C.

Above 700 °C the apparent electrical activation energy is extremely high, (about 5.7 eV between 700–750 °C at 100 Hz). This effect may be partly associated with the strong exothermicity of the methane coupling reactions causing the temperature of the catalyst itself to be significantly higher than the programmed furnace temperature. Care must be taken to avoid decomposition of the mixed oxide above 850 °C. No evidence for this was observed in this experiment. At 800 °C, the conductance is difficult to measure accurately, but is several orders of magnitude higher than after the previous experiment in oxygen.

During TPRS up to 700 °C, the capacitance rises to 1 μF at 100 Hz, but above 700 °C much higher values up to 10 mF were recorded as is shown in Fig. 12. These apparently high values indicate strong surface activity on the catalyst during the increased selectivity to C_2s.

Upon desorption at 800 °C, G decreased rapidly in the first 10 min, then more slowly over the next 10 min. At 1 kHz, a peak was observed after about 15 min which could be associated with the observed increase in CO_2 production at this time. After cooling in Ar, the final state of the material was close to that of the original state with a much reduced activation energy and values of G at 100 Hz of about 1 μS at room temperature and about 50 mS at 400 °C, with little effect of frequency. The capacitances simultaneously decreased by an order of magnitude within the first 10 min and then started to rise again without the original values being retrieved. Thus indicating that some strongly absorbed species were still present on the catalyst surface. However, after cooling slowly in Ar and reheating, lower values were restored, as shown in Fig. 12.

In order to perform a preliminary test for the stability of the catalyst, the oxidative coupling experiment was conducted continuously using CH_4, O_2 and Ar (at 40, 20 and 30 ml per min respectively) for 3h at 750 °C. There was no significant change in the product gas mixture observed, and the effective methane conversion and selectivity values remained constant at about

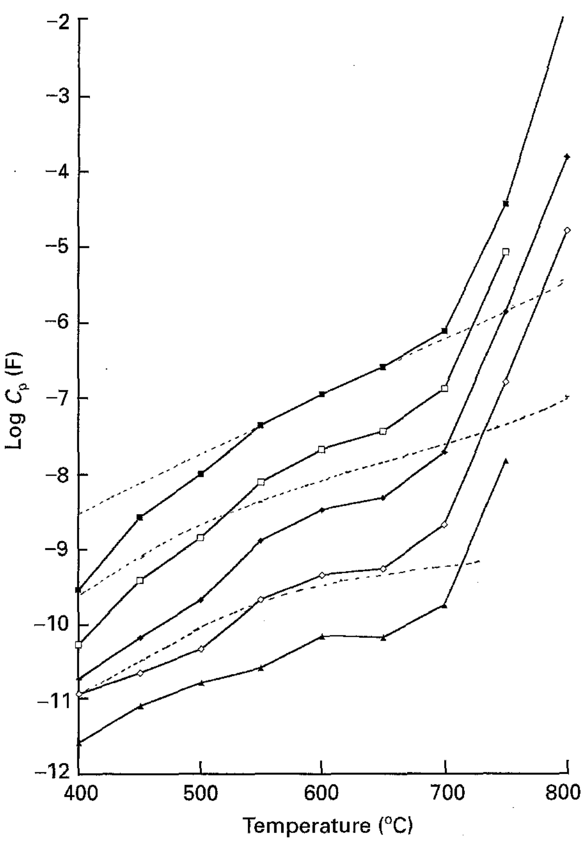

Figure 12 Capacitance as a function of temperature and frequency (100 Hz (■), 1 kHz (□), 10 kHz (◆), 100 kHz (◇), 1 MHz (▲)) in $CH_4/O_2/Ar$ (40 : 20 : 30 ml per min), ($dT/dt = 2.5$ °C per min). Dotted curves at 100 Hz, 1 kHz and 1 MHz in Ar after desorption shown for comparison.

46% and 7% respectively. Although the selectivity is low in this experiment, it has been found to be significantly increased to about 27% by using higher CH_4:O_2 ratios. The conversion is relatively low due to the use of a single pellet in a large tube; much higher values up to about 90% are achieved using powdered catalyst in a micro-reactor under the same conditions.

4. Discussion

It is generally believed that most OCM catalysts are *p*-type semiconductors under high-temperature working conditions and normal operating oxygen partial pressures [21]. The oxygen vacancies favour the accommodation of O_2 and the generated h^+, as an electron acceptor, promotes the transformation of lattice oxygen to not fully reduced species such as O^-, O_2^{2-} or O_2^-. Yu *et al.* [22] have demonstrated that for acceptor doped $SrTiO_3$ perovskite, the C_2 selectivity improved as the *p*-type semiconductivity was enhanced. Their results suggested that active oxygen on the catalyst surface is changed by doping, which then alters the selectivity, but not conversion; also that oxygen from the bulk of the solid can diffuse to the catalyst surface and react with methane. This mechanism assumes but does not prove that the surface electrical properties vary in a similar way to those of the bulk. *P*-type materials will enable significant chemisorption of oxygen, and oxygen ion mobility is also important for increased activity [21].

A similar mechanism may occur for OCM on $Li_{0.9}Ni_{0.5}Co_{0.5}O_{2-\delta}$, also considered to be *p*-type at high temperatures when in a fully oxidised state, as shown by the rapid decrease in conductance upon the chemisorption of methane (Fig. 7), (or decrease with the introduction of H_2 or increase in CO_2 shown in previous experiments [16]). The present results also indicate a significant mobility of oxygen ions towards the surface of the material which become available to react with methane above about 600 °C. If this mobility did not exist, such reactions would die out much more rapidly than observed. Once this available lattice oxygen has been consumed, the electronic character will change as shown by the subsequent behaviour in an oxygen-rich atmosphere (Figs 9 and 11), with no increase in conductance as would be expected for a *p*-type material. It is important to appreciate that at high temperatures, ionic conductivity also contributes to the total effective a.c. conductance, unlike d.c. conductivity which is used to determine the semiconducting nature of a solid. The a.c. results presented show that significant dipole relaxation also occurs during conditions of chemisorption and surface activity. Dipole effects are essentially frequency but not temperature dependent and may be sufficiently strong to mask any other thermally activated phenomena. In earlier work on a high temperature superconductor it was shown that on initial chemisorption of a gas, dipole relaxation losses increase and the effective total conductance is increased. Eventually some charges may break away so reducing the concentration of surface dipoles and resulting in a decreased net conductance [3].

The mechanisms for OCM, as originally proposed by Lunsford [6] and more recently reviewed for example by Dubois and Cameron [21] are considered to be a coupling between heterogeneous and homogeneous reactions, with heterogeneous surface reactions providing methyl radicals, which then couple in the gas phase to form C_2H_6 with some subsequent dehydrogenation to C_2H_4. Further work is needed in order to test the various reaction pathways for our material and to identify which oxygen species are most prevalent.

The results show that methane is able to react with lattice oxygen, confirming the significant role of this source of oxygen in partial methane oxidations. Many others have shown the effective use of this oxygen in oxidic catalysts, e.g., appreciable conversion of methane over Li, Mn, Cd and Zn promoted MgO has been demonstrated in the absence of free oxygen, with pulsed experiments showing the diffusion of bulk lattice oxygen to the surface in order to help replenish the catalyst surface oxygen [23]. Nibbelke *et al.* [24] found both surface and bulk lattice oxygen to participate for MgO based catalysts. Promotion using Li and particularly using Li/Sn increased the oxygen mobility. The coupling of methyl radicals in the gas phase was confirmed using temporal analysis of products. Henrich and Cox [25] discuss the fundamentals of gas-surface interactions on metal oxides and show that point defects, largely consisting of oxygen vacancies often significantly change the surface electronic structure and are the active sites for many types of chemisorption. A general feature is the rather facile breaking of C–H bonds but not of C–C bonds, an important feature for selective oxidation catalysis.

In catalytic partial methane oxidation, a heterogeneous-homogeneous mechanism is considered to be common to a large number of oxide catalysts [5]. Krylov discusses the significant role of lattice oxygen. Regular O^{2-} lattice oxygen does not participate in the reaction, the probable methane activation sites are likely to be O^- and O_2^{2-}. The best catalysts are thought to be systems containing transition metal oxides and reducible rare-earth metal oxides. Their oxygen capacity seems to be sufficiently high, but in addition the absence of weakly bound oxygen at the surface prevents deep oxidation.

Thus, OCM on even relatively simple oxides is a complex process involving both lattice oxygen as a reactant and oxygen vacancies for chemisorption sites. Control of the proportion of such vacancies both in the surface and bulk of the material needs further investigation and understanding. Step sites, unlike adsorption on metals, are considered relatively unimportant for oxides [25], and indeed most OCM experiments on many materials have effective low surface areas of order 1–5 $m^2 g^{-1}$.

Although steam, in the presence of Ar, was found to have no significant effect on the a.c. data at reaction temperatures, it may have an effect on the subsequent catalytic behaviour of the material. Recent allied experiments at lower temperatures up to 400 °C for the same catalyst indicated that moisture can compete with other molecules such as hydrocarbons or oxygen for chemisorption sites and so may assist in deterring deep oxidation and promote partial oxidation [26]. Others have found that the presence of water vapour in the reactant gases can favourably influence the selectivity towards coupling [14, 27]

During OCM, the rapid rise in the conductance with temperature may partly arise from some reduction of the catalyst itself as has already been found for this material during CO_2 hydrogenation [16]. Protons are likely to be present under reaction conditions and significantly contribute to the total a.c. conductivity. They may also replace some of the Li ions in the structure resulting in increased cationic conduction and assist in reducing part of the catalyst to a lower oxidative state.

The use of a.c. monitoring has clearly illustrated the need for taking careful account of the past history of the catalyst when attempting to interpret data for new conditions. Using single frequency data at lower temperatures, Caldararu *et al.* [26] have previously illustrated this to be the case for a variety of mixed oxide catalysts including Li–Ni–Co–O.

For micro-reactor experiments using powdered catalyst, with the use of a calibration gas mixture, the QMS signals may be analysed to yield approximate quantitive partial pressures of the product gases and hence conversion and selectivity data may be compared with other materials. The product distribution for pellets was found to be similar to that of powdered catalyst. The main purpose of the present report was to illustrate the correlations between real-time a.c. electrical and catalytic behaviour for a pellet. The results presented clearly illustrate that any changes in surface activity of the catalyst are immediately coupled with significant changes in the electrical behaviour. In particular, strong chemisorption results in surface dipoles which are manifested in dipole relaxation, a phenomenon which is strongly frequency dependent in regions of high reactivity. Surface dipoles will be destroyed as charged species break away from the surface. Here, a more normal thermally activated (frequency-independent) a.c. behaviour is observed at high temperatures. In turn, a.c. monitoring may be a useful technique for illustrating conditions under which changes in catalyst behaviour occur. A.c. is more useful than d.c. in that with the added dimension of frequency, more information is acquired relating to surface dipole effects.

The effects of alteration of the $CH_4:O_2$ ratio are featured elsewhere [10]. On the grounds of both safety and efficiency, the choice of fuel: O_2 ratio and temperature are all important [20]. Further research concerns the manufacture of such material on a larger scale with experiments to determine the long term stability of this catalyst. Its use may be limited to relatively low temperatures for OCM since it starts to become unstable above 850 °C. Potential use of an oxygen-ion-conducting membrane to separate the oxygen from the methane reactant before reaction on the catalyst surface (to avoid complete combustion in the gas phase) is also currently being investigated. The use of a novel fluidized bed reactor to help control the exothermicity of the methane coupling reaction will be tested.

5. Conclusions

Using the multiple ion-monitoring facility of a Quadrupole Mass Spectrometer, the *in-situ* on-line analysis of product species has shown that the layered mixed oxide $Li_{0.9}Ni_{0.5}Co_{0.5}O_{2-\delta}$ is catalytic for the oxidation of methane between 600–800 °C, with substantial selectivity for the formation of ethane and ethylene as the temperature increases. The product distribution for a pellet is similar to that for powdered catalyst in a micro-reactor. No carbon fouling was observed and the product distribution at 750 °C remained stable over a period of 3 h.

At high temperatures the material is a *p*-type semiconductor with some additional ionic conductivity. The a.c. electrical characteristics of the catalyst pellet between 100 Hz and 1 MHz were simultaneously monitored *in-situ* during temperature programmed adsorption, reaction and desorption experiments. A clear correlation between catalytic behaviour and electrical properties was obtained. Frequency dependent a.c. losses due to surface dipole effects were dominant during phases of strong chemisorption and reaction, whilst reversion to thermally activated behaviour occurred during regions of reduced chemical activity.

Water vapour was found to have no significant effect on the electrical properties between 400–800 °C. By studying the effect of methane in dry argon, mobile lattice oxygen is shown to participate in an oxidative reaction. In a subsequent O_2 atmosphere, the conductance remains constant as oxygen is restored but then decreases rapidly at higher temperatures as oxygen is used to oxidize any remaining absorbed hydrocarbons to CO_2. The final state is less conducting after this treatment, but readily restored by further oxidation. The temporary changes in the state of oxidation of the catalyst can be correlated with changes in the electrical characteristics of the material. In a CH_4/O_2 (2:1) atmosphere the conductance increases rapidly up to 550 °C with behaviour similar to that shown for CH_4 alone.

Since lattice oxygen is readily removed and is able to participate as an oxidizing agent, the catalyst acts as an oxygen reservoir, with a significant proportion of oxygen ions being able to move freely in and out of the lattice. This facility enables the amount of oxygen to be limited and selectivity to higher hydrocarbons to occur without all the methane being totally converted to CO and CO_2. Since the $Li_{0.9}Ni_{0.5}Co_{0.5}O_{2-\delta}$ may be readily restored to its original state after pre-treatment in various gases, this particular mixed oxide mixed conducting ceramic is a good catalyst for partial oxidation reactions. Further tests are underway to determine the long term stability and also to assess its potential use in a fluidized bed reactor in which the catalyst alone is heated by using RF power. Due to the conductance increasing rapidly with rising temperature, thermal runaway is a potential problem for exothermic reactions in electromagnetic reactors [28]. The inclusion of a ceramic insulator such as alumina (known not to chemically react with the catalyst at high temperatures [9]) can help reduce the net conductivity to acceptable levels.

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