JOURNAL OF MATERIALS SCIENCE 31 (1996) 3375–3385

# Temperature-programmed $CO_2$ hydrogenation 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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Product analysis with temperature increasing between 573 and 873 K has been studied for carbon dioxide hydrogenation. A non-stoichiometric mixed oxide, $Li_{0.9}Ni_{0.5}Co_{0.5}O_{2-\delta}$ was investigated. The exit gas stream was monitored by using the multiple-ion monitoring facility of a quadrupole mass spectrometer. The a.c. electrical characteristics of the catalyst pellet between 100 Hz and 1 MHz were simultaneously monitored *in situ*. A clear correlation between catalytic behaviour and electrical properties was obtained. Surface dipole effects during chemisorption, and reaction phases, were revealed. At the lower frequencies, desorption of the gases at 873 K resulted in a decrease in both conductance and capacitance until desorption was completed, as shown by the decay curves on the mass spectrometer. As a result of the chemical reaction, the catalyst becomes partially reduced, as shown by the changes in conductance–temperature–frequency characteristics. The reaction was compared between the freshly oxidized material and the catalyst in the reduced state. Its original oxidized state could be recovered by re-oxidation at 973 K for 1 h in air.

## 1. Introduction

Recently, the fixation of carbon dioxide has become more important due to the exhaustion of large amounts of $CO_2$ resulting from global warming. This gas is, furthermore, a significant resource of carbon for the production of commercially useful hydrocarbons. The main products from carbon dioxide hydrogenation are carbon monoxide, methanol, methane, hydrocarbons ($C_2$–$C_6$), higher alcohols (ethanol, propanol, etc.) and formic acid and its derivatives, depending on the catalyst chosen [1].

$CO_2$ hydrogenation has been shown to proceed via a similar mechanism to that of CO hydrogenation [2–4] with the initial step being $CO_2$ dissociation or the reverse water–gas shift prior to methane formation. $CO_2$ methanation is reported to proceed with a lower activation energy than CO methanation over the same catalyst [5]. The reverse water–gas shift, $CO_2 + H_2 \rightarrow CO + H_2O$, is known to be rapid between 473 and 700 K over a variety of catalysts, both metallic and oxidic [6]. The activation energies are low (ranging from about 50–95 $kJ\,mol^{-1}$ for different catalysts) and often coupled with high reaction rates. Two mechanisms have been proposed for this reaction; the associative mechanism involving a reaction intermediate such as a formate, or a redox mechanism in which the reactants separately oxidize or reduce the catalyst surface [6]. A study of both the forward and reverse WGS on model copper catalysts (representing high-area Cu/ZnO catalysts) showed, by comparison of kinetics, that a "surface redox" mechanism involving the formation and removal of oxygen adatoms is most consistent with the results [7]. Kinetic evidence for a hydrogen-induced surface reconstruction or phase-transition which strongly affects the reaction rate was also considered.

Nickel is commonly used as a selective hydrogenation catalyst, but more active catalysts with lower nickel levels are desirable. Cobalt is a possible substitute or more strongly bound nickel in an oxide form has been considered [8]. In this work, $CO_2$ hydrogenation was studied over a mixed oxide Li–Ni–Co–O catalyst. Previous research on the powdered catalyst has shown the main products of the reaction to be CO, $CH_4$ and steam, with no significant production of methanol [9].

The effect of stoichiometry on the stability and a.c. electrical properties of $Li_{0.9}Ni_{0.5}Co_{0.5}O_{2-\delta}$ and $Li_{0.9}Ni_{0.5}Co_{0.5}O_{2-\delta}$–$Al_2O_3$ composites at elevated temperatures has previously been examined [10]. These non-stoichiometric materials are mixed (i.e. electronic and ionic) conductors having a layered structure through which alkali ions can move with relative ease under an applied voltage. Using X-ray diffraction (XRD), thermogravimetry (TGA), differential thermal analysis (DTA) and a.c. electrical techniques, it was shown that maximum a.c. conductivity in argon was obtained for $Li_{0.9}Ni_{0.5}Co_{0.5}O_{2-\delta}$. The advantages of using mixed oxide catalysts possessing mixed ionic and electrical conductivity, and their

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potential use in a reactor powered by r.f. energy, were also outlined.

This current report concerns the catalytic properties of $Li_{0.9}Ni_{0.5}Co_{0.5}O_{2-\delta}$ using the multiple-ion monitoring facility of a VG Quadrupole mass spectrometer (QMS) to follow changes in the concentration of species over catalysts during temperature-programmed carbon dioxide hydrogenation. This technique gives an almost immediate response to changes in the distribution of product species. The techniques of temperature-programmed reaction and temperature-programmed desorption have recently been described and advocated elsewhere (e.g. [11–13]), whilst the identification of reaction products using mass spectrometry is described, for example, by Bao *et al.* [14].

When such analysis of products is coupled with a.c. electrical monitoring (100 Hz to 1 MHz) [15], unique insights into the mechanisms of catalysis at the surface via dipole effects may be observed. A.c. electrical monitoring of a catalyst *in situ* has been shown to be effective in identifying the temperature and conditions at which changes occur, e.g. onset of reaction, product spectrum, changes in catalyst morphology, desorption (e.g. [15–17]). This is particularly powerful when coupled to ion-monitoring of the effluent. Indeed, comparative studies of polymorphic phase transitions by DTA, high-temperature XRD and temperature-programmed d.c. electrical conductivity measurements (TPEC), have shown the latter to be effective at revealing surface changes at lower temperatures than those revealed by other techniques which measure bulk changes in the material [18].

The experiments reported here, using a single pellet, complement allied micro-reactor experiments over powdered catalyst also using the ion monitoring facility to study temperature-programmed reactions between 573 and 873 K [9]. In a reducing atmosphere at high temperatures, the catalyst will itself become increasingly reduced. The temperature-programmed reaction was performed on fresh material in its initial oxidized state and then repeated after partial reduction during experimental use. Thus a comparison between the catalytic behaviour of both oxidized and reduced catalyst could be made. The main aim of this report is not to discuss catalytic behaviour in any

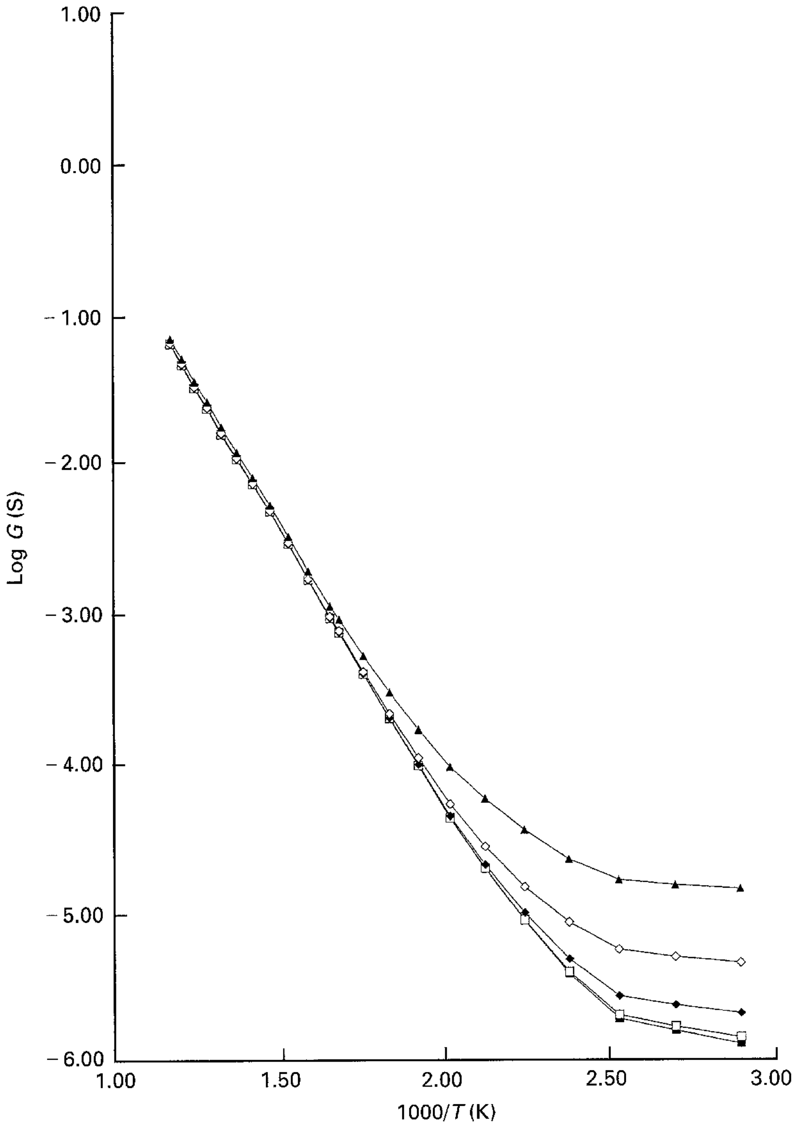

*Figure 1* Initial conductance in argon as a function of reciprocal temperature and frequency: (■) 100 Hz, (□) 1 kHz, (◆) 10 kHz, (◇) 100 kHz, (▲) 1 MHz.

detail, but to highlight the correlation between two different *in situ* techniques (i.e. a.c. electrical characterization and analysis of species on a mass spectrometer) used to monitor the temperature programmed reaction between $CO_2$ and $H_2$.

## 2. Experimental procedure

Polycrystalline $Li_{0.9}Ni_{0.5}Co_{0.5}O_{2-\delta}$ was prepared by fusion of $Li_2CO_3$, NiO and $Co_3O_4$ in stoichiometric proportions for 2 h at 773 K followed by reaction for 48 h at 1273 K under oxygen. Pellets 1.2 cm diameter and 6 mm thick were made using 10 kgm force applied for about 5 min. Platinum enamel contacts were fired on to the ends of the pellets for 1 h at 1073 K. A programmable horizontal Eurotherm split tube furnace and Hewlett Packard 4194A impedance analyser were used to monitor the a.c. properties of the pellet using methods described in detail elsewhere [15], taking care to compensate for the effects of the leads, which is particularly important at high temperatures when the material became highly conducting. A ramp rate of 2.5 K $min^{-1}$ was used in all the experiments. The sample was represented by a capacitance, $C_p$, in parallel with a resistance, $1/G$, and measurements between 100 Hz and 1 MHz were made every 10 min (equivalent to 25 K incremental intervals in temperature).

A total flow rate of 90 ml $min^{-1}$ was used. For the $CO_2$ hydrogenation experiments between 523 and 873 K, carbon dioxide and hydrogen were mixed with argon and regulated using Brookes mass flow meters with each gas having a flow rate of 30 ml $min^{-1}$. Any steam produced was condensed. Part of the remaining effluent was directed to a VG quadrupole mass spectrometer (QMS) for analysis and the residual gaseous products were burnt off. Argon, carbon dioxide, hydrogen, methane and carbon monoxide were monitored on the QMS, using the mass numbers 40, 44, 2, 15 and 28, respectively. At mass number 28, part of the signal is also associated with $CO_2$, hence in the current experiments the CO and $CO_2$ signals cannot be completely specified. No methanol was detected and hence this potential product was not monitored. After a temperature of 873 K had been reached, the reactant gases $CO_2$ and $H_2$ were turned

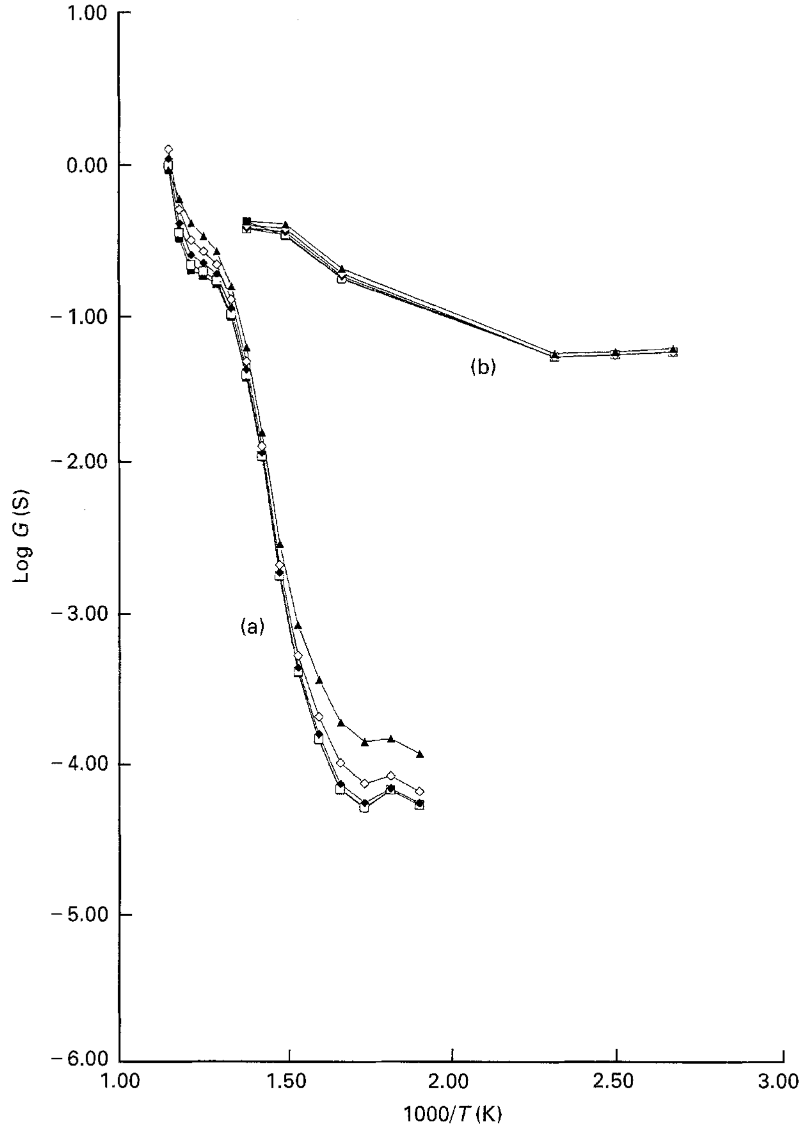

*Figure 2* Conductance as a function of reciprocal temperature and frequency: (■) 100 Hz, (□) 1 kHz, (◆) 10 kHz, (◇) 100 kHz, (▲) 1 MHz. (a) In Ar + $CO_2$ + $H_2$, (b) in argon after $CO_2$ hydrogenation.

off. The catalyst was then maintained at this temperature for 30 min in pure argon, allowing the desorption of all other gases to be monitored over this time period.

## 3. Results

### 3.1. Catalyst in the oxidized state

As shown in Fig. 1, the a.c. conductance in argon alone for the material in its initial oxidized state is thermally activated at high temperatures and becomes virtually independent of frequency above about 625 K, indicating that thermally activated charges govern the loss processes. Closer to ambient, temperature change has little effect but the a.c. conductance increases rapidly with increasing frequency, owing to dipole relaxation losses dominating the behaviour. Such dipoles arise from imperfections and impurities in the lattice [10, 15].

Once a mixture of hydrogen and carbon dioxide are introduced at 523 K, the shape of these characteristics is dramatically changed as shown in Fig. 2a. As the temperature is increased at the constant ramp rate of 2.5 K min$^{-1}$, dipole-type loss mechanisms prevail up to about 570 K owing to chemisorption of the $H_2$ and $CO_2$ molecules on the surface of the catalyst.

This process is followed by a rapid increase in conductance (with loss of the frequency dependence), typical of thermally activated charge mobility. Finally, a reversion to the dipole-like response takes place above about 770 K. These changes arise from the catalytic behaviour as $CO_2$ hydrogenation proceeds.

For conditions under which no carbon formation is expected, the following reactions occur

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

$$(\Delta H_{298} = 41 \text{ kJ mol}^{-1}) \qquad (1)$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$

$$(\Delta H_{298} = -206 \text{ kJ mol}^{-1}) \qquad (2)$$

The first reaction, (the reverse water-gas-shift), is mildly endothermic with equilibrium constants of 0.03 at 573 K and 0.21 at 773 K. The second reaction (the methanation reaction), is strongly exothermic with equilibrium constants $1.6 \times 10^7$ at 573 K and $1.1 \times 10^2$ at 773 K. Hence, as the temperature is increased from 573 to 873 K, some CO, $CH_4$ and steam can be produced at intermediate temperatures.

The changes in the QMS signal intensities with temperature showed the production of methane between 573 and 823 K coupled with a small decrease in $H_2$. These changes are shown as a function of temperature in Fig. 3. Changes in $CO_2$ and $H_2$ signals are difficult to detect in this differential reactor, but the product $CH_4$ reveals significant changes. Optimum $CH_4$ is produced between 673 and 750 K due to a balance of kinetic and thermodynamic parameters. This plateau region corresponds to the conductance behaviour shown in Fig. 4. In this temperature range, the conductance is thermally activated. The absorption/desorption processes are relatively rapid and

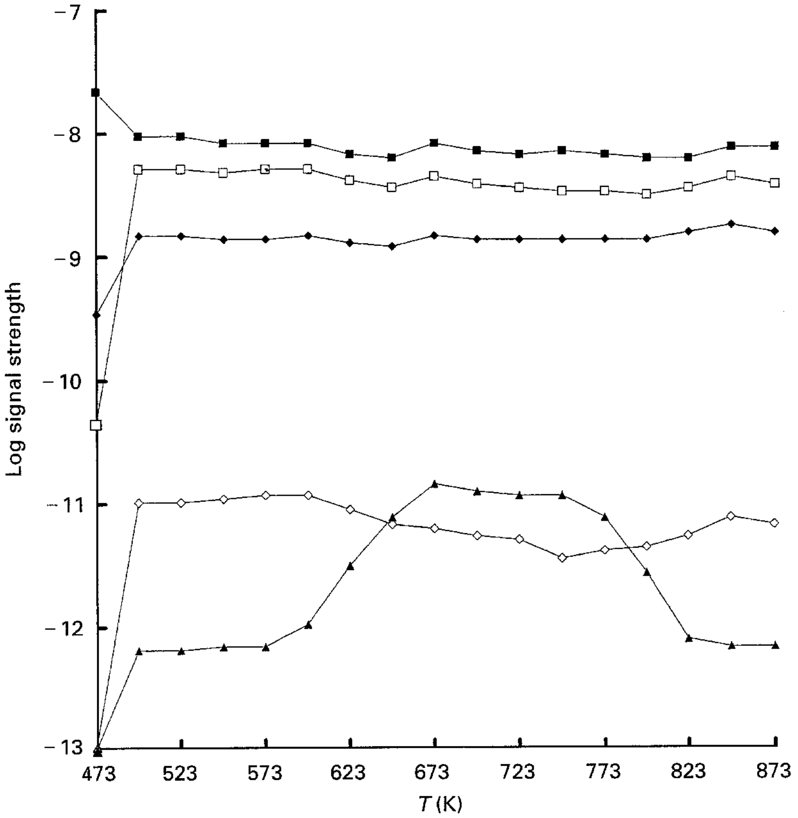

*Figure 3* Relative QMS ion signal strengths as a function of temperature during temperature-programmed $CO_2$ hydrogenation on oxidized catalyst. (■) Ar (40), (□) $CO_2$ (44), (◆) CO (28), (◇) $H_2$ (2), (▲) $CH_4$ (15).

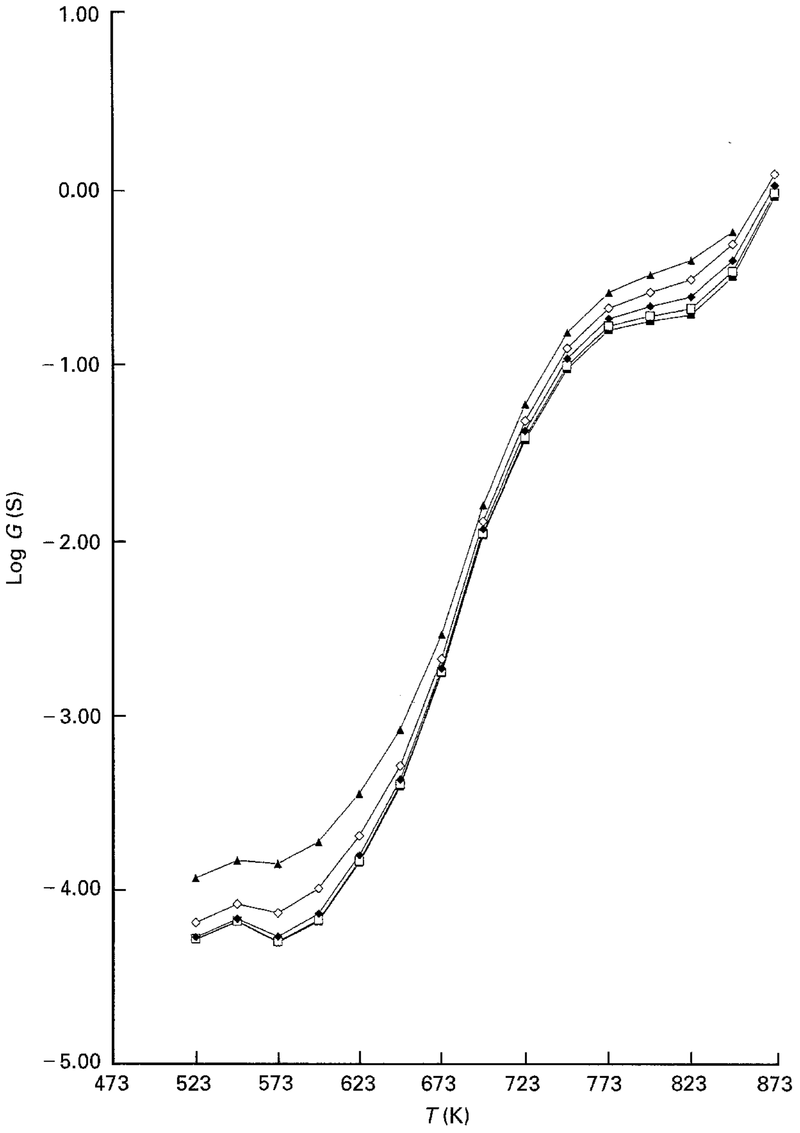

*Figure 4* Conductance as a function of temperature and frequency during temperature-programmed $CO_2$ hydrogenation. (■) 100 Hz, (□) 1 kHz, (◆) 10 kHz, (◇) 100 kHz, (▲) 1 MHz.

there are insufficient stable strongly adsorbed species to give rise to surface dipole losses. The effect of frequency becomes apparent at temperature regions below 673 K and above 750 K. Dipole effects become dominant due to strongly chemisorbed molecules at the lower temperatures and reduced catalytic activity at the higher temperatures.

In a reducing atmosphere, some reduction of the catalytic material itself will occur. Hence as the mixed oxide approaches a more "metallic" state the conductance increases rapidly as temperature increases. After 30 min stabilization at 873 K in argon alone, this "reduced" state of the catalyst is clearly shown by the new a.c. data measured at pre-set temperatures (Fig. 2b).

The magnitude of the capacitance of the pellet gives additional information about the nature of the dielectric processes under given conditions [19]. Values of order of picofarads are generally associated with bulk behaviour, values of order of nanofarads with intergrain or surface effects, whilst values of order of microfarads and above indicate strong chemisorption or electrocatalytic reactions. The capacitance–temperature–frequency characteristics for the material in its initial state in argon are shown in Fig. 5 to be below 1 nF as expected. However, during temperature-programmed reaction, values rise much more rapidly as temperature increases (Fig. 6) with values of order of 10 μF above 800 K at the lowest frequency. This behaviour is clear indication of strong interactions taking place at the surface of the material. The changes in capacitance correlate well with the above observations linking conductance and the temporal analysis of species.

The changes in QMS signal strengths with time during the desorption process for 30 min at 873 K showed a return to base line values after about 20 min. Similarly the conductance and capacitance values reduced to constant values in the same time period. After the desorption at 873 K, the capacitance values (remeasured in argon), were significantly higher at 673 K, giving further evidence of a change in the oxidation state of the catalyst (Fig. 7).

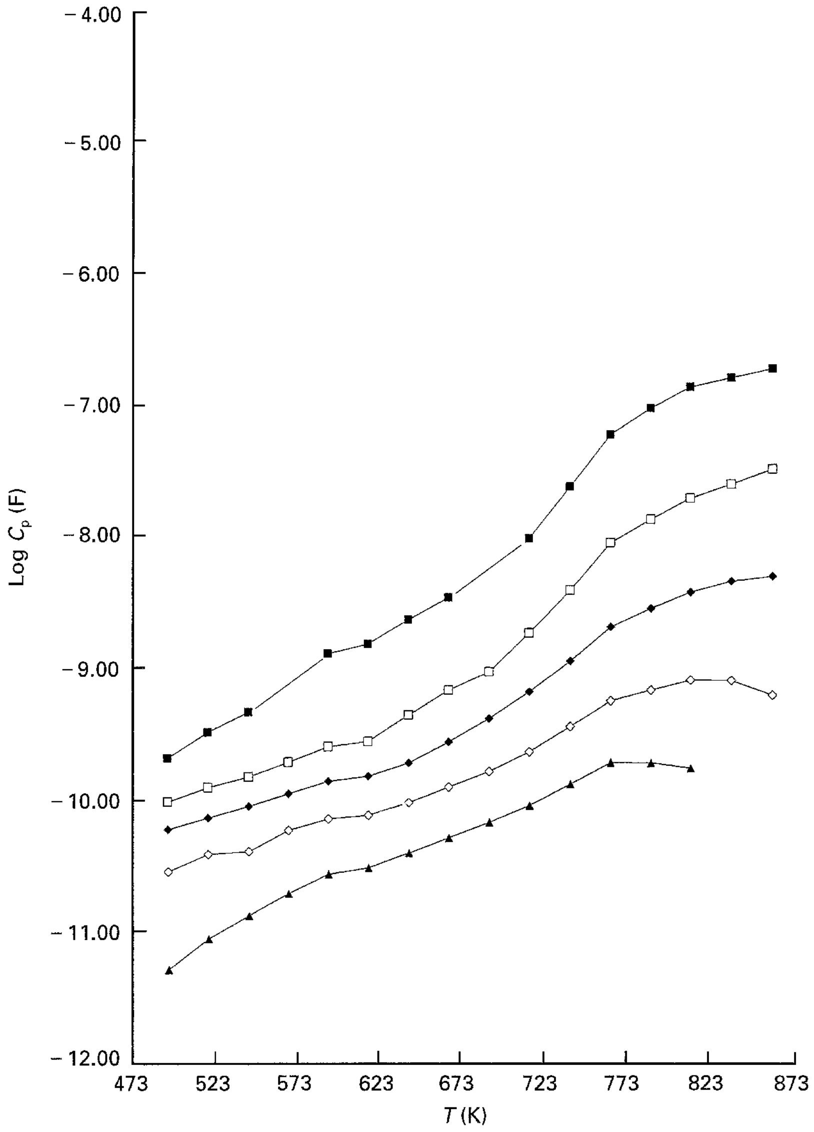

*Figure 5* Initial values of capacitance as a function of temperature and frequency in argon: (■) 100 Hz, (□) 1 kHz, (◆) 10 kHz, (◇) 100 kHz, (▲) 1 MHz.

## 3.2. Catalyst in the reduced state

Measurements on the catalyst in the partially reduced state were repeated in the same sequence as in the previous experiments as shown in Fig. 8. The pattern of the catalytic behaviour given by the QMS signals during temperature-programmed reaction was similar as before (Fig. 3). However (after taking account of the day-to-day variation in base-line values), the hydrogen remains at an almost constant level whilst the methane starts to decrease at about 700 K in contrast to the oxidized catalyst at about 750 K.

After the temperature-programmed reaction, the catalyst was maintained at 873 K for 30 min in argon alone in order for the chemisorbed species to desorb from the catalyst surface. During this desorption process, the QMS signals for the desorbing species decreased to constant levels after about 20 min. The conductance at 100 Hz simultaneously decreased by a factor of ten over this period and then remained constant. The capacitances below 1 kHz also decreased and then remained constant whilst those at higher frequencies were unaffected by the desorption processes. This behaviour is further evidence that the lower frequencies are reflecting changes in surface dipole activity whilst the higher frequencies reflect changes in the bulk of the material which are relatively independent of short-term surface processes.

The Arrhenius conductivity–temperature characteristics for the catalyst in the initial partially reduced state in argon (Fig. 9a) may be compared with the temperature-programmed reaction experiment in Fig. 9b. The initial decrease and broadening of the frequency effect during heightened surface activity is again apparent (compare with Fig. 2a). Above about 710 K, the conductance became so high ( $> 1$ S) that only values at the lowest frequency could be considered to be reasonably accurate. The large increase in $G$ with increasing temperature indicate further reduction of the catalyst to a more metallic state. If, at 873 K, the measured value is considered to be a bulk effect the conductivity of the pellet is of order $10^4$ S m$^{-1}$, a value typical of a low band-gap semiconductor.

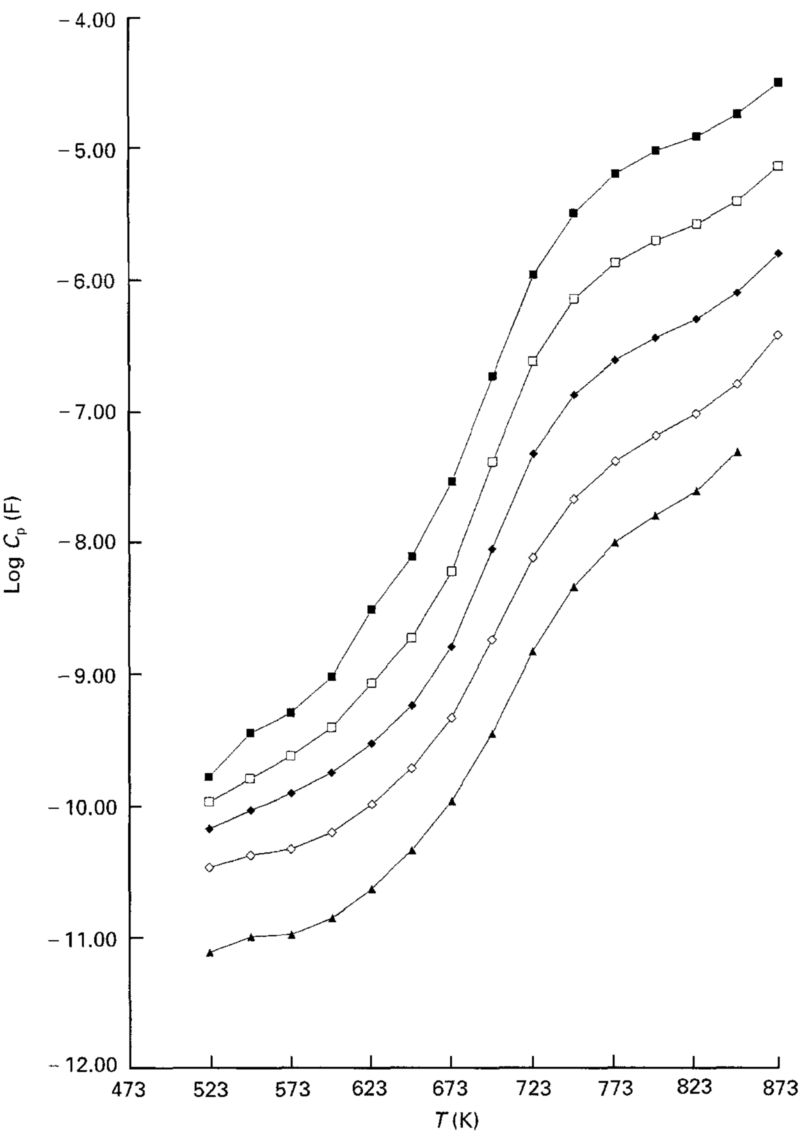

*Figure 6* Capacitance as a function of temperature and frequency during temperature-programmed $CO_2$ hydrogenation. (■) 100 Hz, (□) 1 kHz, (◆) 10 kHz, (◇) 100 kHz, (▲) 1 MHz.

The corresponding capacitance–frequency characteristics as a function of temperature during temperature-programmed reaction are shown in Fig. 10; the high values at low frequencies were difficult to measure being close to the limits of experimental accuracy. In contrast to the "oxidized" material, the high-frequency capacitances tend to become independent of temperature as temperature increases; this is probably related to the more rapid decrease in catalytic behaviour observed at higher temperatures for the "reduced" catalyst.

The catalyst was finally re-oxidized for 1 h at 973 K. The pellet became slightly swollen after this procedure, (a feature commonly observed with intercalation compounds) with some loss of the platinum contact; however, its a.c. parameters re-measured in argon at pre-set temperatures between ambient and 873 K were similar in magnitude to those of the initial oxidized state prior to reaction (Fig. 1). Hence despite the considerable reduction of the catalyst which had taken place during the $CO_2$ hydrogenation reactions, the material could be essentially re-oxidized to its original state of conduction.

It is possible that some of the increase in conductance at high temperatures during reaction could have been due to carbon deposition. However, allied experiments on a micro-reactor using powdered catalyst and the same experimental conditions and reaction mixture have shown that $CO_2$ evolution did not occur on reoxidation of the catalyst [9].

## 4. Discussion

The analysis of effluent species with respect to temperature for the pellets with a platinum contact showed similar behaviour to those obtained for the micro-reactor. Consequently, the addition of platinum of low surface area on the ends of the pellets is considered to have no significant effect. In the absence of the catalyst, experiments had shown that no reaction occurred over the temperature range 573–873 K in the empty reactor.

For the same material mixed with alumina, it was previously found that at 650 K the conductivity reversibly increased in $CO_2$ but rapidly decreased in $H_2$.

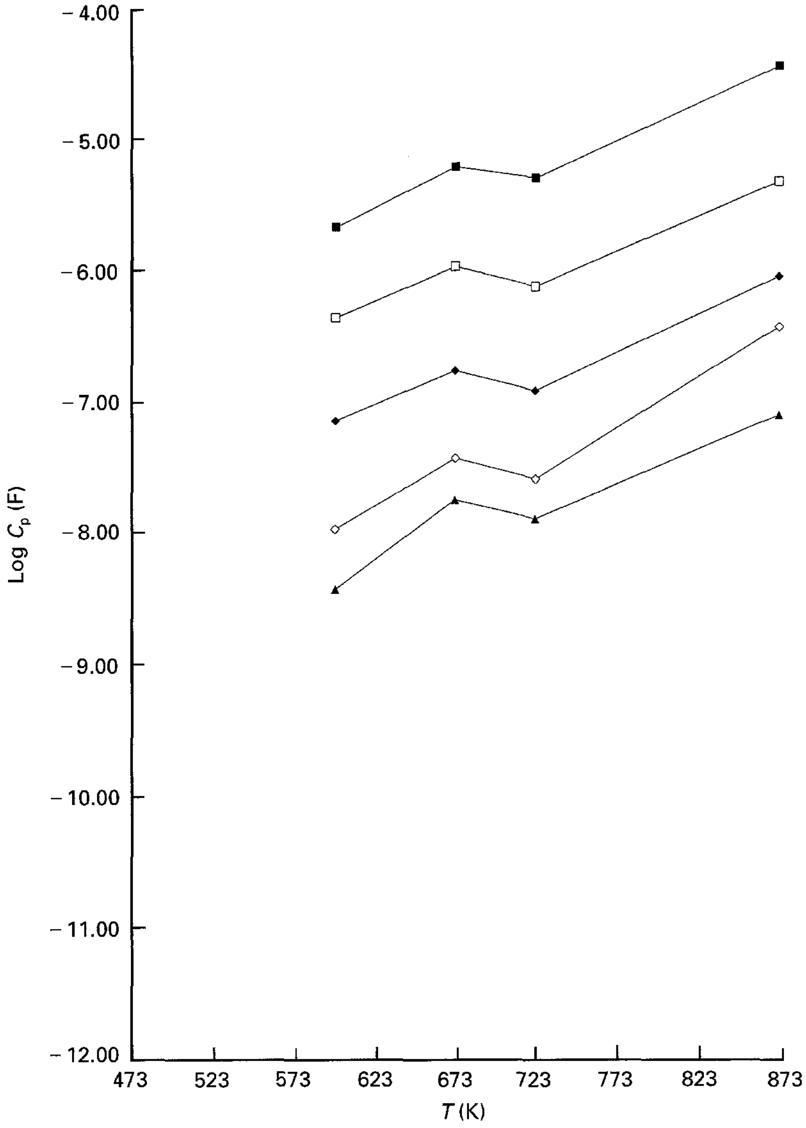

*Figure 7* Capacitance in argon as a function of temperature and frequency after temperature-programmed $CO_2$ hydrogenation. (■) 100 Hz, (□) 1 kHz, (◆) 10 kHz, (◇) 100 kHz, (▲) 1 MHz.

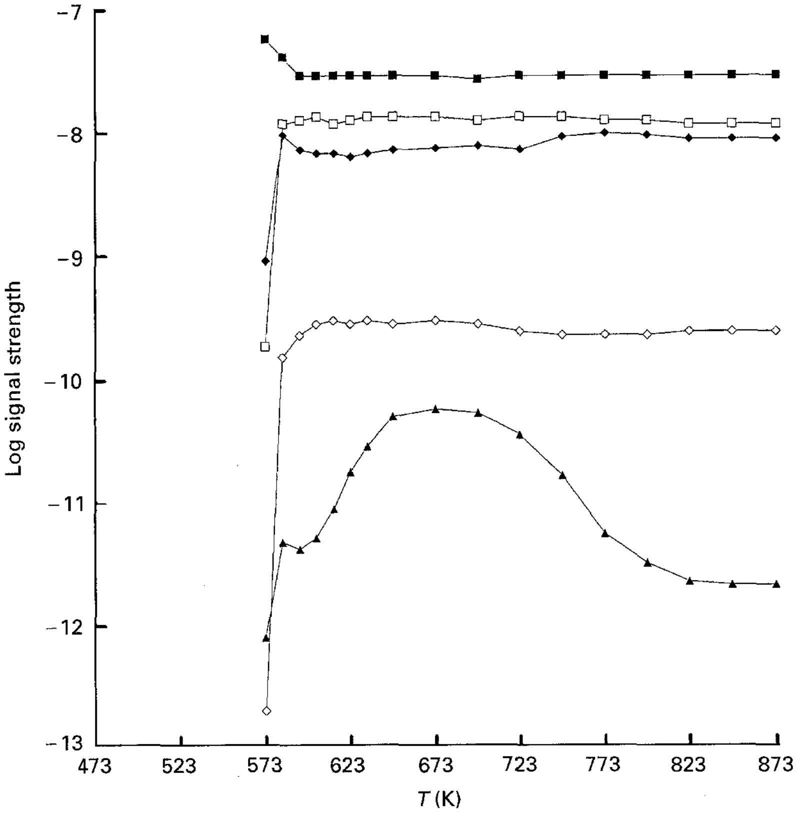

*Figure 8* Relative QMS ion signal strengths as a function of temperature during temperature-programmed $CO_2$ hydrogenation on partially reduced catalyst. (■) Ar (40), (□) $CO_2$ (44), (◆) (28), (◇) $H_2$ (2), (▲) $CH_4$ (15).

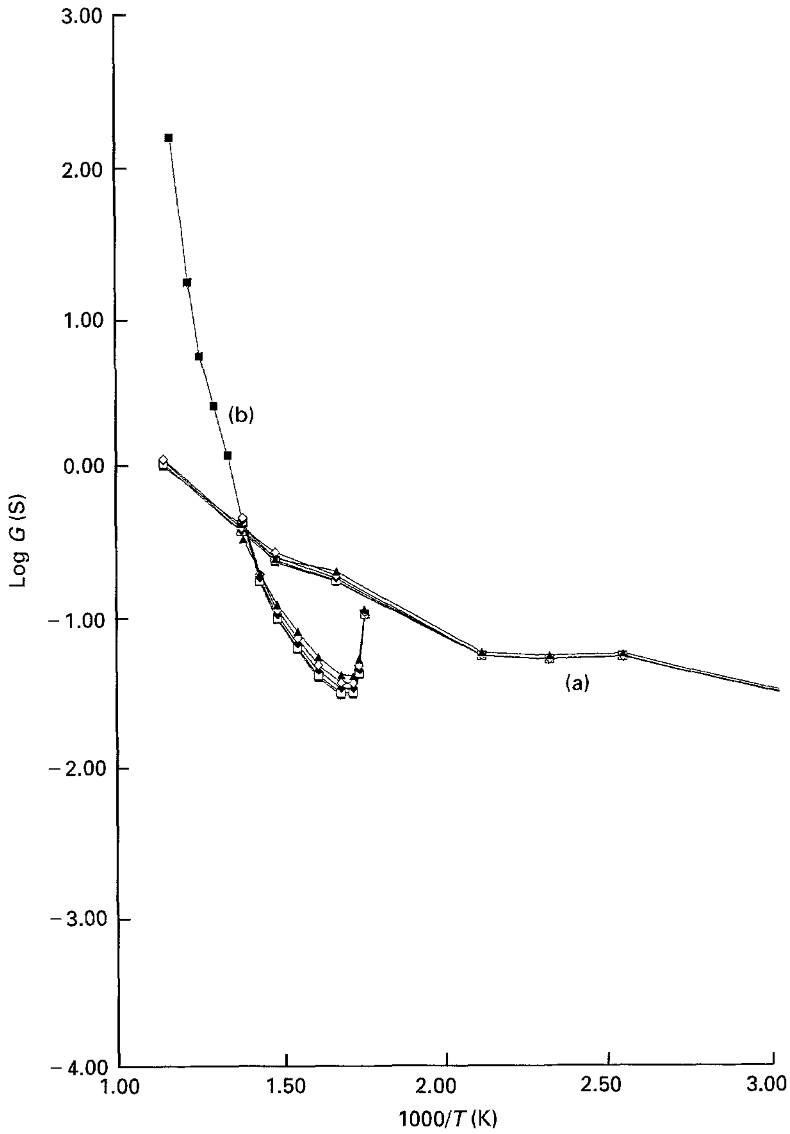

*Figure 9* Conductance as a function of reciprocal temperature and frequency: (■) 100 Hz, (□) 1 kHz, (◆) 10 kHz, (◇) 100 kHz, (▲) 1 MHz. (a) In argon (catalyst partially reduced after first $CO_2$ hydrogenation experiment) and (b) in Ar + $CO_2$ + $H_2$ on the partially reduced catalyst.

This behaviour is typical of a p-type semiconductor for which holes are the principal charge carriers [10]. However, at 870 K the conductivity increased in $H_2$ due to slow reduction of the oxides. For a gaseous mixture of $H_2 + CO_2$ (diluted by argon at 738 K), there was an initial decrease followed by a less rapid increase in conductance.

In the present work, using the unsupported catalyst, the initial decrease in conductance when the $H_2 + CO_2$ mixture is introduced at 573 K, is similar. Hydrogen is likely to be more strongly adsorbed than $CO_2$ hence the initial decrease is typical of $H_2$ alone. Once reaction between the gases occurs, various adsorption, reaction and desorption mechanisms will interact and may affect the overall a.c. conductance in different ways.

With additional characterization of the catalyst using TGA and DTA and XRD, it should be possible to elucidate mechanisms for the observed behaviour, not just at a macroscopic level but at a more microscopic level. To complement and extend the understanding of the a.c. data. DTA/TGA measurements between room temperature and 673 K have shown good correlations with conductivity data obtained at a single frequency of 1592 Hz [20]. These allied experiments have highlighted

(a) the importance of the pre-history of the specimen in determining its future behaviour,

(b) the role of moisture and its potential capability of co-operating/competing with oxygen for adsorption on the surface and hence influencing the selectivity for partial hydrocarbon oxidation reactions,

(c) the possible strong adsorption of hydrocarbons on $Li_{0.9}Ni_{0.5}Co_{0.5}O_{2-\delta}$. At the higher temperature range of 573–873 K it is likely that protonic conduction will play a significant role; it is also possible that protons could displace some of the lithium ions in the catalyst structure.

With regular calibration of the QMS using a standard gas mixture, a good assessment of the catalytic activity and selectivity should be possible. The use of temperature-programmed partial oxidation of methane reactions have also been studied for this catalyst

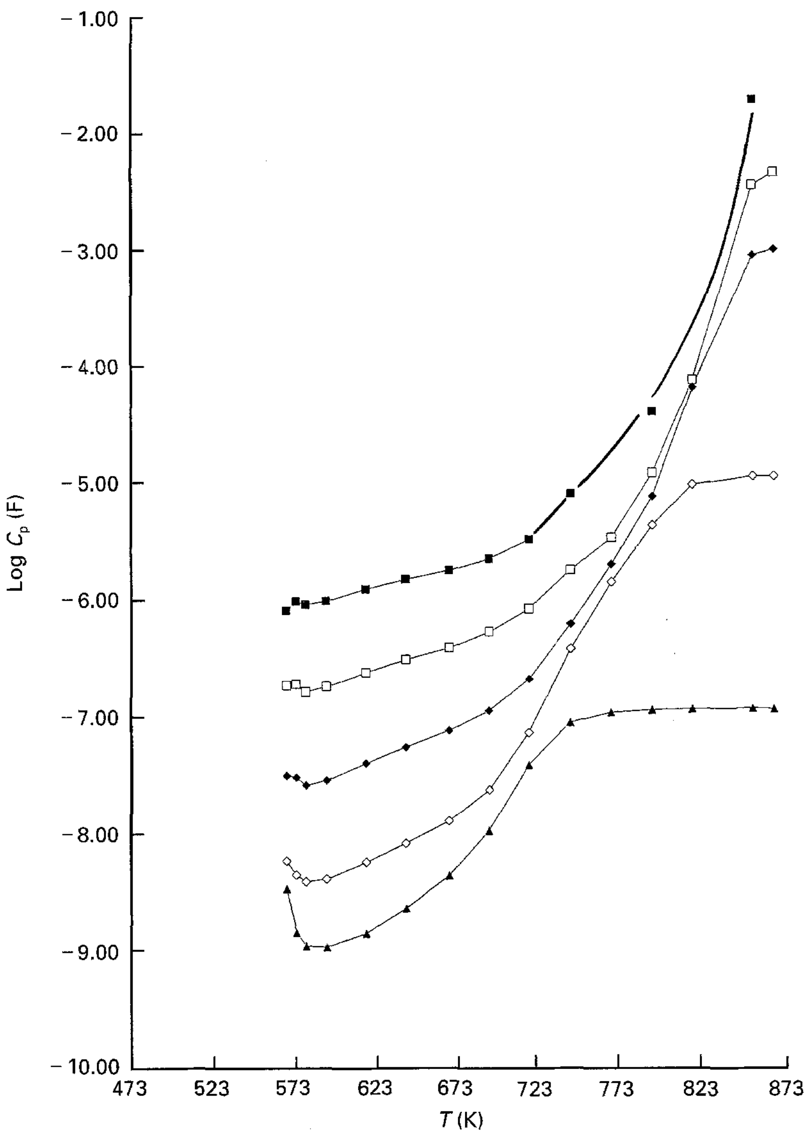

*Figure 10* Capacitance as a function of temperature and frequency during temperature programmed $CO_2$ hydrogenation on partially reduced catalyst. (■) 100 Hz, (□) 1 kHz, (◆) 10 kHz, (◇) 100 kHz, (▲) 1 MHz.

and will be the subject of a separate publication. Future research is concerned with the manufacture of this mixed oxide on a larger scale for the purpose of more extensive long-term catalytic tests, both in a conventionally heated reactor and in a dielectric heater in which this catalyst of high a.c. loss is heated by the absorption of electromagnetic r.f. energy.

Intercalation mixed oxide compounds have generally unusual and potentially useful properties. Apart from applications for battery materials and sensors [21], they may be useful catalysts which may be cheaper and as effective as the commonly used supported noble metal catalysts. The need for the conduction properties for such oxide catalysts to be better understood has already been highlighted [22]; the combination of *in situ* a.c. techniques and ion-monitoring during temperature-programmed reaction is a small step to fulfil these aims.

## 5. Conclusion

In an oxidizing atmosphere, $Li_{0.9}Ni_{0.5}Co_{0.5}O_{2-\delta}$ is stable up to about 1473 K; however, in a reducing environment some reduction may occur at high temperatures. Temperature-programmed reaction experiments showed that $Li_{0.9}Ni_{0.5}Co_{0.5}O_{2-\delta}$ exhibited good catalytic activity for carbon dioxide hydrogenation between about 610 and 810 K for material in both fully oxidized and in partially reduced states. Reduction of the catalyst occurs at higher temperatures, but the oxidized state may be retrieved by re-oxidation in air at 973 K. The temporal analysis of the product species using the multiple ion-monitoring facilities of a mass spectrometer showed the changes in catalytic behaviour with increasing temperature by using a constant ramp rate of 2.5 K min$^{-1}$. The use of simultaneous *in situ* a.c. monitoring of the catalyst pellet revealed enhanced surface dipole activity over the ranges of temperature at which the methane product was increasing and decreasing. A.c. conductance and parallel capacitance values decreased during desorption of the gases at 873 K, becoming constant after desorption was complete after about 15 min in accordance with the MS data.

The changes in signal strengths for the product species were similar to those found in allied experiments on the powdered catalyst. For the pelleted material, the activity was marginally higher for the catalyst in a partially reduced state but further tests are needed to confirm this observation. The change in the oxidation state was clearly revealed by studying the a.c. parameters in argon using a constant ramp rate of 2.5 K $\text{min}^{-1}$.

## Acknowledgements

The authors are grateful to the EPSRC for the provision of equipment and post-doctoral support for D. Qin.

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*Received 31 October*
*and accepted 15 December 1995*