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Calculation of the metal–carbon bond strength of surface carbon deposited on solid oxide fuel cell nickel/zirconia fuel reforming anodes

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The activation energy for the removal of surface carbon formed by methane decomposition following high-temperature reforming, from a nickel/zirconia solid oxide fuel cell (SOFC) anode has been calculated using two methods based on temperature-programmed oxidation. It is found that there is a fairly good agreement between the two methods. In addition, it was observed that the addition of small quantities of lithium to the anode resulted in a significant lowering of the activation energy for surface carbon removal by about 50 kJ mol^{-1}.

Keywords: solid oxide fuel cells, fuel reforming anodes, steam reforming, methane, nickel, yttria-stabilised zirconia, temperature-programmed oxidation, adsorption, surface carbon

1. Introduction

Fuel cells have tremendous potential as a more efficient and cleaner alternative method of electricity generation than heat engines, steam and gas turbines and combined cycles, since they operate electrochemically, so are not limited by the Carnot cycle, and they are catalytic. Consequently fuel cells are currently attracting a great deal of interest [1]. The solid oxide fuel cell (SOFC) is the ideal device for small-scale application, offering the potential of cheap, clean production of electrical power from natural gas and other hydrocarbons, because it operates at temperatures where methane (and other hydrocarbons) react readily with oxygen and steam. The possibility of internal reforming of methane and other hydrocarbon fuels directly on the anode is one of the main advantages of the SOFC compared to other fuel cell systems [2,3]. However, several major problems of internal reforming remain to be solved before such cells can ever be routinely operated on hydrocarbon fuel, in particular the problem of carbon deposition on the anode at the high operating temperatures involved and the subsequent deactivation of the anode which leads to a loss of cell performance and poor durability [4]. For this reason many SOFC studies are carried out using hydrogen as the fuel, and there are a relative lack of studies using hydrocarbons as fuels. The deposition of carbon on the fuel reforming anode in SOFCs running on methane, natural gas and higher hydrocarbons is an important area requiring further study.

Steam reforming of natural gas itself is an important industrial process for the conversion of natural gas into value-added products, including hydrogen for ammonia synthesis and syngas for methanol synthesis [5–7]. The problems associated with carbon deposition on nickel steam reforming catalysts are largely overcome by using an appropriate catalyst support, which both gives good dispersion of the nickel without affecting its activity and does not catalyse side reactions, particularly those which produce carbon deposits; typically α-alumina is used, and also by ensuring that the steam/hydrocarbon ratio exceeds a certain minimum value. This value varies with temperature and pressure [5]. Alkali additives, generally potassium in the form of potash, are also added which serve both to accelerate the reaction of carbon with steam and to neutralise the acidity of the catalyst support, and hence reduce carbon deposition [8–10].

In recent publications we have discussed the formation of surface carbon on nickel/yttria-stabilised zirconia (YSZ) cermet anodes both coated on a tubular zirconia electrolyte and in powder form [11,12]. We have demonstrated that during high-temperature dry methane adsorption or steam reforming of methane, several types of carbon species are formed on the anode which can be characterised using temperature-programmed methods [11]. The level of carbon deposition on the anode is found to depend on both the operating temperature and the methane/steam ratio [11,12]. The addition of small quantities of molybdenum has been found to lead to a very significant reduction in the amount of carbon deposited on the anode during

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reforming, whilst having little effect on the reforming activity of the anode or the cell performance [11,12].

Temperature-programmed methods have been shown to be very powerful for the characterisation of catalysts and studying reaction pathways in catalysis [13–16]. The basic principles of temperature-programmed methods have been described in a number of publications [13,17,18]. In this letter the strength of adsorption of the surface carbon, formed from methane decomposition, following high-temperature reaction, on the nickel/zirconia fuel reforming anode and on a lithium-doped nickel/zirconia anode, have been calculated by two methods, both of which involve temperature-programmed oxidation (TPO).

2. Experimental

All the experiments described here were carried out on a custom-built catalytic and electrochemical reactor, which has been described in more detail in a recent publication [19]. The essential components of the apparatus are a ceramic furnace which is operated by a Eurotherm temperature controller which allows the heating rate to be linearly controlled between room temperature and 1373 K; heating rates of between 1 and 20 K min^{-1} are possible. The reactor temperature is measured using a K-type thermocouple. The reactor inlet is linked to a stainless-steel gas manifold which allows complete flexibility in gas handling. The feed can be instantly switched between hydrogen, oxygen, inert gas and fuel, and gas mixtures of any combination and ratio can be achieved. Flow rates can be precisely controlled. Water can be introduced into the reactant gas stream via a water saturator. The gas manifold has been designed in such a way that any fuel/steam ratio can be achieved. The apparatus allows either a conventional stainless-steel or quartz reactor or tubular yttria-stabilised zirconia electrolyte to be used in the furnace. The exit from the reactor is connected to the gas analysis system. The entire gas sampling system is heated to 383 K to avoid the problem of water or product condensation. Gas analysis is carried out by a computer-interfaced on-line mass spectrometer (Leda-Mass Satellite).

The anodes used in this work were studied in the powder form and were prepared by physically mixing nickel oxide (Alfa Chemicals) and 8 mol% yttria-stabilised zirconia (YSZ) (Unitec-FYT11). To this a mixture of methanol, 1,1,1-trichloroethane and glycerol trioleate was added as a solvent and the resultant slurry was milled for 3 h. A small quantity of poly-vinyl butyrol was added at the end of the milling period as a binding agent. The anode ink was then dried in air at 423 K, before firing to 1573 K to form the anode powder. Lithium was added in the form of $LiNO_3$ (BDH), to produce a nominal final lithium loading of 1 mol%. Nickel oxide and zirconia were present in equal volume % (denoted as 50/50 Ni/YSZ). Following firing the anode was reduced in the reactor at 1173 K for 30 min in a 29.2% H_2/He stream (total flow = 31.6 $\text{cm}^3\ \text{min}^{-1}$) to convert the NiO to metallic nickel. We have shown previously that this results in complete reduction of NiO [20].

In any temperature-programmed experiment where parameters such as heating rate, β, or reactant gas concentration, C_0, are altered, it is important to keep the sample size constant to obtain meaningful results. As we were interested in measuring surface carbon a coking regime was developed in order to deposit a fixed quantity of carbon on the anode. 10.2 mg of anode powder was loaded into the reactor and pre-reduced at 1173 K. Carbon was then deposited on the anode by passing 10.4% CH_4/He (total flow = 18.6 $\text{cm}^3\ \text{min}^{-1}$) over the sample for 30 min at 1173 K. Temperature-programmed oxidation (TPO) was used to characterise the surface carbon and measure its strength of adsorption on the anode. All TPO experiments were carried out using an 11.4% O_2/He mixture (total flow = 26.1 $\text{cm}^3\ \text{min}^{-1}$).

The first method which was used to calculate the activation energy for C–Ni bond breaking was based on that developed by Gentry et al. for calculating activation energies for metal-oxide reduction [17]. From TPR theory, assuming first-order kinetics with respect to hydrogen, the activation energy for reduction, E, is related to the heating rate, b, and the concentration of hydrogen at the maximum rate of reduction, C_m, by the following expression:

$$2\ln T_m + \ln C_m - \ln\beta = (E/RT_m) - \ln C\,, \qquad (1)$$

where T_m is the temperature of the peak maximum, R is the gas constant, and C is a constant relating to the pre-exponential factor for the reduction and the peak maximum. A plot of $2\ln T_m + \ln C_m - \ln\beta$ as a function of $1/T_m$ affords a straight line with slope equal to E/R.

The second method for calculating E was by leading-edge calculation. For this method the following can be assumed. As the TPO progresses there is an associated uptake of O_2 as the carbon is removed from the anode surface. The measured O_2 signal intensity at any given temperature is therefore proportional to the rate of reaction at that temperature. An Arrhenius-type plot can therefore be obtained by plotting the O_2 consumption as a function of reciprocal temperature for each of the TPO traces. When calculating the activation energies using this method it is important to work in the low-temperature region of the TPO peak, as at low temperatures one would also expect low conversions.

3. Results and discussion

TPO experiments were carried out on both the nickel/zirconia and lithium-doped nickel/zirconia anodes using four different heating rates, from 5 to 20 K

Table 1
Values of T_m and $[O]_m$ for TPO experiments to remove surface carbon from a 50/50 Ni/ZrO_2 SOFC anode using different heating rates

Heating rate, β ($K\ min^{-1}$)	T_m (K)	$[O]_m$ (%)
5	879	6.9
10	905	5.8
15	935	5.9
20	926	4.6

Table 2
Activation energies calculated for the removal of surface carbon from a 50/50 Ni/ZrO_2 SOFC anode from the leading edge of the TPO peaks

Heating rate, β ($K\ min^{-1}$)	E^a ($kJ\ mol^{-1}$)
5	189 ± 1
10	174 ± 10
15	164 ± 8
20	175 ± 4

[a] Errors calculated from the standard error of the best-fit line.

min^{-1}. These, together with the corresponding values of T_m are given in table 1 for the 50/50 Ni/YSZ anode.

From equation (1) the activation energy for surface carbon removal from the SOFC anode following high-temperature reforming was calculated as 153±9 kJ mol^{-1}. Activation energies were also calculated from the leading edge of the TPO peaks, the results of these calculations are presented in table 2. The Arrhenius plots used in the calculation of the activation energy by the leading-edge method are presented in figure 1. From the results given in table 2 an average value for the activation energy for surface carbon removal with the leading-edge method can be calculated as 176±13 kJ mol^{-1}. The errors were calculated from the standard error on the best fit line, and do not take into account possible errors in temperature measurement. For this reason some of the errors quoted in table 2 can appear quite small.

The corresponding values obtained for the lithium-doped anodes are 101±1 kJ mol^{-1} from the T_m method and 123±7 kJ mol^{-1} from the leading-edge method. The activation energies for surface carbon removal from both lithium-doped and undoped anode samples, obtained using the two methods of calculation are summarised in table 3. It can be seen that for both anode formulations the activation energy calculated from the leading-edge method is about 22 kJ mol^{-1} higher than that obtained from using the method of T_m. This phenomenon could arise from the difficulty in deciding which section of the leading edge of the peak to use in the Arrhenius calculations. In each case it is found that doping the nickel anode with small quantities of lithium results in a lowering of the activation energy for surface carbon removal by about 50 kJ mol^{-1} (52 kJ mol^{-1} using the method of T_m and 53 kJ mol^{-1} using the leading-edge method).

It has been shown in other studies, where the effect of potassium promotion on Ni/SiO_2 catalysts was studied, that the addition of an alkali metal to the supported Ni catalyst did alter the activation energies of the reactions studied and affect the strength of the Ni–C bond for various surface species [8,9]. It has been concluded that potassium addition to Ni catalysts blocks a certain number of Ni atoms and acts as an electronic modifier of the remaining free Ni atoms [9]. In these studies it was observed that potassium generally increased the bond strength between Ni and C of surface adsorbed CO and raised the measured activation energy for hydrocarbon reactions. However, in those studies it was the strength

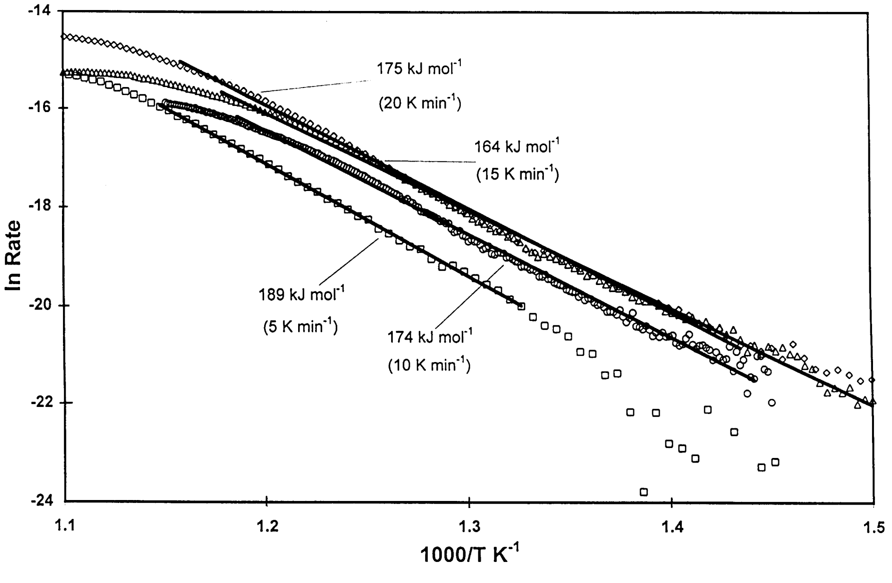

Figure 1. Determination of the activation energies for surface carbon removal from a 50/50 Ni/ZrO_2 anode using the leading-edge method.

Table 3
Calculated activation energies (kJ mol^{-1}) for removal of surface carbon from a 50/50 Ni/ZrO_2 SOFC anode and a 1 mol% Li-doped 50/50 Ni/ZrO_2 SOFC anode

50/50 Ni/YSZ		1 mol% Li-doped 50/50 Ni/YSZ	
from T_m	leading edge	from T_m	leading edge
153 ± 9	176 ± 13	101 ± 1	123 ± 7

of the Ni–C bond for adsorbed CO which was measured and not that for surface adsorbed carbon species which we are considering.

It has been suggested in a more recent publication that surface carbon formed during methane steam reforming originates from both CH_4 and CO_2 molecules [21], implying that the Boudouard reaction is a significant route in the formation of surface carbon species:

$$2CO \rightleftharpoons CO_2 + C_{ads} \qquad (2)$$

An increase in the basicity of the catalyst surface, caused by the addition of an alkali metal such as Li or K would lead to an attraction of CO_2 to the surface [22]. This in turn would push the equilibrium in reaction (2) towards the left and could minimise the formation of adsorbed carbon or influence the Ni–C bond strength.

4. Conclusions

In this letter we have shown that the activation energy required for the removal of surface carbon adsorbed on a Ni/YSZ anode in a solid oxide fuel cell running on methane can be measured using temperature-programmed oxidation. This can be done by one of two methods: by varying the heating rate and observing the change in T_m, or from Arrhenius parameters calculated directly from the leading edge of the CO_2 evolution peak. The second method results in an activation energy which is 22 kJ mol^{-1} higher than that obtained from method 1, and it is thought that this is caused by inaccuracies in determining the correct temperature range over which the reaction should be measured.

The addition of small quantities of lithium to the nickel/zirconia cermet anode results in a very significant lowering of the activation energy for removal of surface carbon, deposited during high-temperature methane reforming on the SOFC anode at 1173 K, by about 50 kJ mol^{-1}. This is attributed to an electronic effect.

Our results suggest that the addition of small amounts of lithium to conventional nickel/zirconia fuel reforming anodes could have an important promotional role in helping to reduce deleterious carbon formation on the anode of solid oxide fuel cells operating on natural gas.

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