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Methane conversion over Nb-doped ceria

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Abstract

Methane steam reforming and dry methane conversion over ceria, and ceria doped with 1.4 and 5% Nb cation has been investigated at 900 °C (a typical solid oxide fuel cell temperature). The influence of the calcination atmosphere on the Nb-doped ceria has also been studied. Use of reducing conditions leads to significantly lower crystallite size, higher specific surface area and greater Nb solubility. Nb-doping lowers activity mainly as a consequence of strong segregation of Nb to the ceria surface. Kinetics of steam reforming are interpreted in terms of a redox mechanism.

Keywords: Catalysis; Nb; Ce; SOFC; Methane reforming

1. Introduction

Cerium oxide is used as a catalyst in a wide variety of reactions involving the oxidation, or partial oxidation, of hydrocarbons. It is well-known that ceria can act as a local source or sink for oxygen involved in reactions taking place on the ceria surface or on other catalytic materials supported on ceria. There is now increasing interest in using ceria in more reducing conditions [1], such as in methane reforming at the anodes (direct reforming) of solid oxide fuel cells (SOFCs) [2]. An interesting application of oxides in SOFCs could be as catalysts for indirect (or integrated) internal steam reforming of methane [3]. Conventional metal-based, reforming catalysts are too active [4] at typical SOFC operating temperatures of about 900 °C causing local cooling [5,6]. This local cooling can be alleviated by the use of catalysts with lower intrinsic activity for methane steam reforming [5,6], which would need to be highly resistant to deactivation.

The gas–solid reaction between CeO_2 and CH_4 produces [7] synthesis gas with a H_2/CO ratio of 2 and reduced ceria according to the following overall reaction:

$$CeO_2 + nCH_4 = CeO_{2-n} + nCO + 2nH_2 \tag{1}$$

Only a relatively low concentration of steam is required to regenerate the ceria [8–10]. Ceria is also noted for its ability to resist carbon deposition and to catalyse the combustion of carbon [11], making it an attractive oxide catalyst for indirect internal reforming SOFC applications although the activity for methane steam reforming is not known.

In this paper we report on the activity of CeO_2 for methane steam reforming at conditions appropriate to SOFC operation, and on the influence of Nb cation dopant. We also report on the effect of Nb-doping on direct conversion of methane to synthesis gas. Nb can be expected to increase the concentration of mobile electronic carriers, and/or decrease the concentration of oxygen vacancies with respect to undoped

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ceria, which can be expected to impact on the catalyst performance for methane conversion. Aspects of dry methane reforming have been reported previously [12].

2. Experimental

Undoped ceria was prepared by precipitation of cerium hydroxide from aqueous cerium nitrate (Aldrich) solution using ammonium hydroxide to a final pH in the range 7–8. The precipitate was washed, dried and then calcined for 1 h at 1000 °C in air to convert to CeO_2. The calcination temperature was chosen to be slightly higher than the maximum temperature in subsequent experiments and typical SOFC fuel inlet temperatures. Nb-doped ceria was also synthesised using hydroxide co-precipitation [13,14] from aqueous cerium nitrate and niobium chloride (Aldrich). Nb content was 1.4 and 5% (expressed as cation fraction). 1.4% Nb was estimated to be at the most likely value of the solubility limit. These doping levels are equivalent to 0.7 and 2.5% mole fraction of Nb_2O_5. One set of the Nb-doped samples was calcined at 1000 °C for 1 h in air. Another set of Nb-doped ceria, denoted “FG” was obtained by calcination at 1000 °C in reducing conditions using forming gas (10% H_2 in N_2) followed by furnace cooling in air.

Samples were characterised by XRD, electron microscopy (SEM and TEM), XPS, and by BET nitrogen adsorption using a Micromeritics ASAP2000. The XPS data were acquired on powder specimens using a VG ESCALAB MkII with Al Kα radiation and a pass energy of 50 eV. Binding energies were referenced to C 1s at 284.8 eV.

Dry methane conversion was studied in a temperature-programmable quartz tube microflow reactor system operated at atmospheric pressure, which has been described in detail elsewhere [15]. The exhaust gases were analysed using a quadrupole mass spectrometer (QMS) or, for temperature-programmed reduction (TPR), by using a thermal conductivity detector (TCD). Samples were subjected to a consecutive chemical reaction sequence: TPR was first carried out (5% H_2/Ar, 10 °C/min) from ambient temperature to 1000 °C; the reactor was then cooled, purged with Ar and TPRx performed (5% CH_4/Ar, 25 °C/min); TPO was then used to check for deposited carbon (10% O_2/He, 10 °C/min). After TPO, the reactor was cooled rapidly to room temperature, purged with Ar, then heated to 900 °C at 25 °C/min in 5% CH_4/Ar and held at 900 °C for a period of 150 min. Steam reforming was carried out at atmospheric pressure in a similar quartz microflow reactor system fitted with a syringe pump to introduce steam via an evaporator-mixer. Feed gas composition ranges were 1–5% CH_4 and 1–6% H_2O in He. Analysis was done by GC.

3. Results

3.1. Characterisation

XRD patterns for the Nb-doped cerias after calcination for 1 h at 1000 °C in air are shown in Fig. 1. The data confirm ceria as the major crystalline phase. The samples calcined in forming gas gave similar results

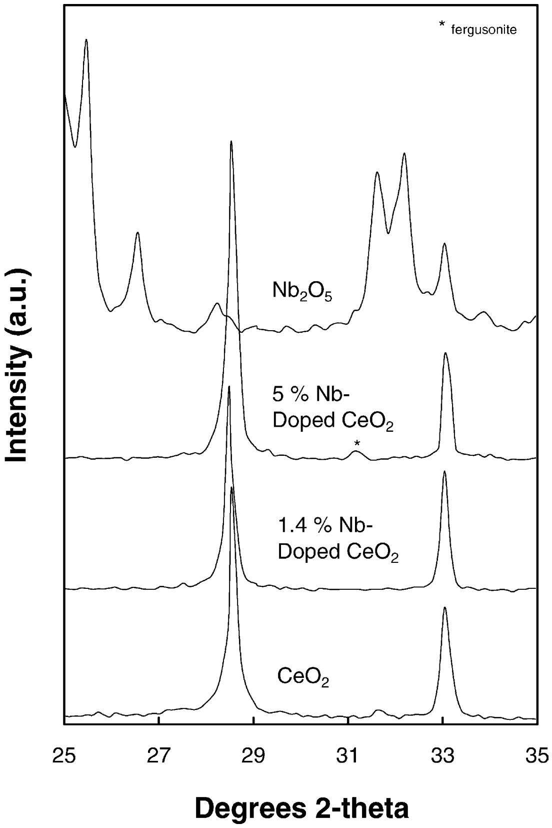

Fig. 1. XRD of Nb-doped cerias calcined in air at 1000 °C.

Table 1
BET surface areas and estimated relative activity with dry CH_4 at 900 °C

Material	Surface area ($m^2\ g^{-1}$)	Relative activity (weight basis)	Relative activity (area basis)
CeO_2	2.6	1.0	1.0
$Ce_{0.986}Nb_{0.014}O_{2.007}$	3.7	0.26	0.18
$Ce_{0.95}Nb_{0.05}O_{2.025}$	1.1	0.23	0.55
$Ce_{0.986}Nb_{0.014}O_{2.007}$ (FG)	25	2.6	0.27
$Ce_{0.95}Nb_{0.05}O_{2.025}$ (FG)	29	0.81	0.073
Nb_2O_5	1.4	0.12	0.2

[12], but with broader peaks indicating a smaller particle size, confirmed by TEM and consistent with the larger specific surface area (see below). There is evidence from XRD that fergusonite ($CeNbO_4$) was present as a minor second phase [9] in the 5% Nb-doped specimens. However, selected area diffraction of a 5% Nb-doped ceria FG specimen in TEM showed only ceria and no crystallites of fergusonite. Specific surface areas are given in Table 1. The materials prepared by calcination in forming gas were found to have much higher surface areas than for air calcination. The surface areas of the FG samples were found to decrease strongly for Nb cation concentrations greater than 5%.

Nb/Ce atomic ratios determined by XPS are given in Table 2. XPS spectra of the as prepared materials are given in Ref. [12]. In general, Nb is segregated to the surface of the ceria in the as prepared samples. The exception is the 1.4% Nb FG specimen, which shows no evidence of Nb segregation, and could indicate a higher solubility limit in reducing conditions. All the Nb-doped cerias show that the surface concentration of Nb decreases on exposure to methane at 900 °C (Table 2). The effect is dramatic for the 5% Nb FG sample, when the Nb surface concentration probably approaches the nominal bulk level. The 1.4% Nb FG sample has virtually no XPS visible Nb prior to methane exposure so that no change can be observed. Under steam reforming conditions at 900 °C, Nb again segregates to the surface so that even the 1.4% Nb sample has a significant enhancement of Nb surface concentration over the nominal bulk concentration (Table 2).

Table 2
XPS Nb/Ce atomic ratios

Material	As prepared	After dry CH_4, 900 °C	After steam reforming, 900 °C
$Ce_{0.986}Nb_{0.014}O_{2.007}$	0.41	0.21	–
$Ce_{0.95}Nb_{0.05}O_{2.025}$	0.54	0.24	–
$Ce_{0.986}Nb_{0.014}O_{2.007}$ (FG)	~0	~0	0.15
$Ce_{0.95}Nb_{0.05}O_{2.025}$ (FG)	0.48	~0	0.20

3.2. *Reaction with dry methane*

Methane oxidation and carbon formation were investigated during TPRx followed by isothermal reaction at 900 °C. CO production during isothermal reaction with methane at 900 °C tends to show two maxima, close together for ceria itself, but there are considerable differences between the Nb-doped cerias (Fig. 2). Niobia does oxidise methane, but at a lower intrinsic rate than does ceria. Reaction is significantly slower for the low surface area Nb-doped ceria containing 1.4 and 5% Nb, and oxygen is still being removed from these specimens even after 150 min of exposure at 900 °C. The high surface area, FG Nb-doped cerias reduce more readily. The estimated peak relative reaction rates based on methane conversion are given in Table 1. The intrinsic reaction rate decreases with Nb-doping, although 1.4% Nb FG shows a higher peak rate than ceria on a weight basis.

For ceria, the H_2/CO ratio was 2.13. The H_2/CO ratio also tends to be slightly greater than 2 for the Nb-doped cerias, although these are subject to greater error [12]. The products of reaction with methane mainly follow the stoichiometry of Eq. (1) until the ceria is exhausted of reducible oxygen. Carbon deposition by methane cracking on the reduced ceria occurs only very slowly since hydrogen production was not detected after oxygen exhaustion. The temperature at which deposited carbon is combusted during TPO for the Nb-doped specimens is lower than for ceria [12], although it is higher for Nb_2O_5. This probably reflects the greater electronic carrier concentration in the Nb-doped cerias under oxidising conditions, which are available for ionising adsorbed oxygen species that subsequently react with the carbon.

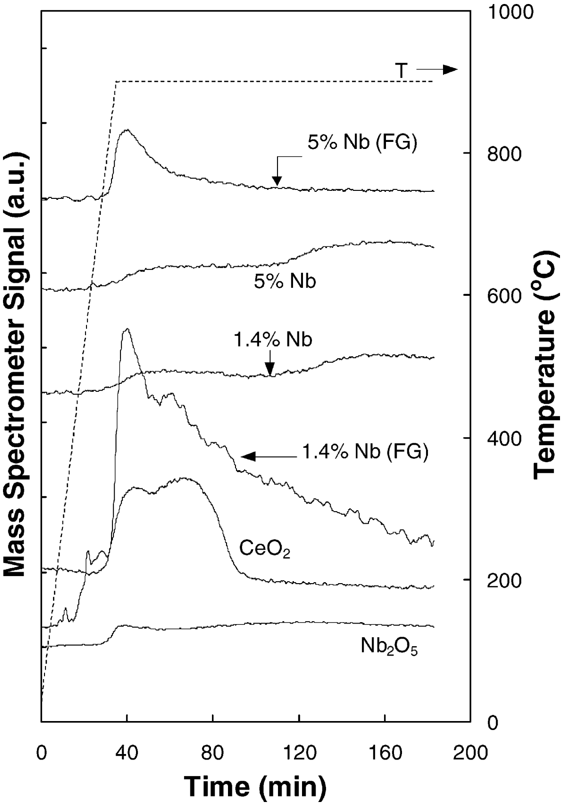

Fig. 2. CO production from reaction of dry methane with ceria and Nb-doped ceria.

3.3. Steam reforming of methane

The high surface area, Nb-doped cerias and ceria were studied in the steam reforming of methane at 900 °C. Catalysts were brought slowly to the reaction temperature in $H_2O/CH_4/He$ and the product gas composition followed as a function of time at isothermal conditions. The main products of the initial reaction from methane steam reforming over the cerias were H_2, CO with a small amount of CO_2 indicating a small contribution from the shift reaction. The conversion of methane in steam reforming at 900 °C over ceria and the FG, high surface area, Nb-doped cerias is shown in Fig. 3. The activities for the Nb-doped cerias decline with time reaching significantly lower steady-state rates. The effect is most dramatic for the 1.4% Nb–CeO_2, which has an initial activity greater than ceria itself, as expected based on the performance in dry methane reforming, but has a steady-state rate lower than ceria. The measured rates for 900 °C $H_2O/CH_4 = 1.2$ (4% CH_4, 5% H_2O in He) are given in Table 3 where it is seen that Nb-doping lowers the steady-state rate. Similar results were obtained for other steam/methane ratios up to 2.5. No significant carbon deposition is detected by TPO following steam reforming on any of the catalysts.

It is tempting to assign the lower steady-state steam reforming activity of the Nb-cerias to the influence

Table 3
CH_4 steam reforming at 900 °C with 4% CH_4, 5% H_2O

Material	Initial rate (mol kg^{-1} h^{-1})	Steady-state rate (mol kg^{-1} h^{-1})
CeO_2	30	22
$Ce_{0.986}Nb_{0.014}O_{2.007}$ (FG)	39	16
$Ce_{0.95}Nb_{0.05}O_{2.025}$ (FG)	22	14

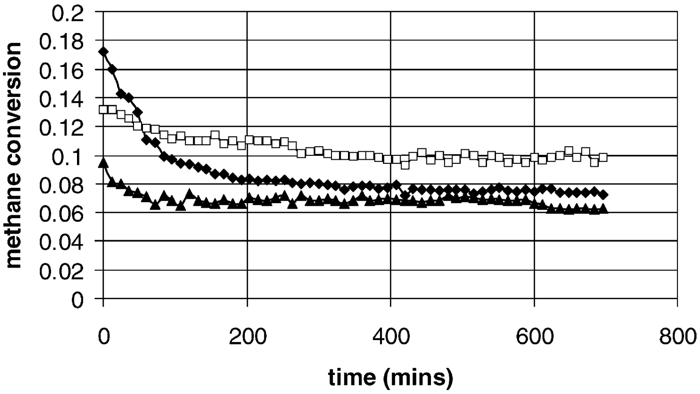

Fig. 3. Steam reforming of methane at 900 °C with 4% CH_4, 5% H_2O in He over: (□) CeO_2; (◆) 1.4% Nb–CeO_2 FG; (▲) 5% Nb–CeO_2 FG.

Table 4
Kinetics of CH_4 steam reforming at 900 °C

Material	Order related to CH_4	Order related to H_2O	Order related to H_2
CeO_2	0.53	∼0	−0.46
$Ce_{0.986}Nb_{0.014}O_{2.007}$ (FG)	0.49	∼0	−0.35
$Ce_{0.95}Nb_{0.05}O_{2.025}$ (FG)	0.59	∼0	−0.34

of bulk doping. However, post-reaction XPS analysis (Table 2) shows strong surface segregation of Nb. Sintering of these high surface area materials may also take place under steam reforming conditions, whereas no sintering was observed (by TEM) following exposure to dry methane at the same temperature. However, the extent of CO_2 production via the shift reaction increases with time for the Nb-cerias but not for ceria itself. These results suggest that Nb segregation is likely to be the main cause of the observed decline in steam reforming activity.

The kinetics of steam reforming over the cerias has been investigated by varying the methane and steam partial pressures, and by adding hydrogen to the feed gas (Table 4). The reaction order in methane was observed to be less than one for all the cerias, while the rate was found to be essentially independent of the steam partial pressure for the range of conditions studied. The reaction order in hydrogen was observed to be negative.

4. Discussion

The results for the kinetics of steam reforming are in sharp contrast to metal-based catalysts such as Ni zirconia cermet SOFC anodes [16], where steam inhibits the reaction and hydrogen promotes the steam reforming of methane. Reaction order in methane is usually close to 1 for metals, and the kinetics are explained by a Langmuir–Hinshelwood type, multi-step mechanism [17,18]. The present results suggest that methane steam reforming over the cerias occurs by a redox mechanism. The estimated value of the activation energy for methane steam reforming over the cerias is about 155 $kJ\,mol^{-1}$, which is similar to the 160 $kJ\,mol^{-1}$ determined by Otsuka et al. [10] for the conversion of methane to synthesis gas over ceria.

The measured value of the oxygen ion diffusion coefficient in ceria [19] is sufficiently high that in the powder catalysts used here, the overall reaction rate will be controlled by the surface reaction and not by diffusion of oxygen from the bulk of the solid particles to their surfaces. The measured values of isotopic surface exchange rate constant k at 900 °C are [20] $3 \times 10^{-5}\,cm\,s^{-1}$ for reduced ceria in CO/CO_2 and $1 \times 10^{-5}\,cm\,s^{-1}$ for $Ce_{0.8}Y_{0.2}O_{1.9}$ in oxygen. The corresponding turnover frequencies are 840 and 280 atoms of oxygen $site^{-1}\,s^{-1}$. These are several orders of magnitude greater than the activities for direct methane conversion [12] or the steam reforming rates given in Table 3, which indicates that reaction with methane is much slower than with oxygen, CO or CO_2. We assume that the reaction with methane proceeds by successive loss of hydrogen followed by oxidation of surface carbon, or a carbon containing intermediate, with lattice oxygen, thus giving rise to the independence of steam pressure and inhibition by hydrogen.

The slower reaction rate on the surfaces of the Nb-doped catalysts is therefore due to their different composition. Based on the XPS evidence, it is concluded that the segregation of Nb to the ceria surface is inhibiting reaction with methane for the dry conversion to synthesis gas and for steam reforming. For dry methane conversion over the Nb-doped FG materials, which show no detectable Nb segregation, the lower rate would appear at first sight to be mainly due to the effect of bulk doping (e.g. by reducing the concentration of oxygen vacancies). Unfortunately, this simple picture is complicated by the apparent surface segregation of Cl, which takes place when Nb is fully dissolved in the ceria. Work is in progress to resolve the influence of the Cl, but it should be stressed that it is not detected under steam reforming conditions. The initial activities for steam reforming and the conversion of dry methane show that the effect of 1.4% Nb FG on the surface area compensates for the decrease in intrinsic activity.

The cerias show a useful activity in relation to application as steam reforming catalysts in indirect internal reforming SOFCs. The rates given in Table 3 would correspond to an estimated relative activity of about 0.01% of a conventional Ni catalyst at 900 °C [6].

5. Conclusions

The rate of methane steam reforming over the ceria and Nb-doped ceria is essentially independent of the steam partial pressure at SOFC temperatures; hydrogen was found to have a significant inhibitory effect. The results suggest a redox mechanism in which the rate is controlled by the slow reaction of a surface carbon species with oxygen in ceria, and a more facile reaction between steam and the cerias to replenish the oxygen. Nb-doping slows down the rate of steam reforming or the direct reaction with dry methane, mainly as a consequence of strong segregation of Nb to the ceria surface. Calcination of Nb-doped ceria under reducing conditions leads to significantly lower crystallite size, higher specific surface area and greater Nb solubility. As a consequence of the increased surface area, initial activities on a weight basis are higher than ceria for 1.4% Nb. Nb-doped ceria is extremely resistant to carbon deposition in steam reforming conditions (even for steam/methane ratio less than unity).

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