

# Factors in forming CO and CO<sub>2</sub> over a cermet of Ni-gadolinia-doped ceria with relation to direct methane SOFCs

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Received 27 June 2006; received in revised form 21 July 2006; accepted 21 July 2006

Available online 19 October 2006

## Abstract

Temperature-programmed self de-coking tests were carried out to study the factors in forming CO and CO<sub>2</sub> over Ni-gadolinia-doped ceria (GDC), Fe-GDC, and Ni-Fe-GDC cermet catalysts with relation to direct methane SOFCs. It was found that the bulk lattice oxygen plays a very important role in forming CO and CO<sub>2</sub>. CO formation is generally associated with O species coming from the bulk lattice oxygen while CO<sub>2</sub> formation generally is associated with the surface OH species. With Ni:GDC = 3:5 in weight, a very large amount of CO is formed with relatively negligible CO<sub>2</sub> formation. With 1 wt% Ni, preferential CO<sub>2</sub> formation can be realized below 700 °C. The activity of CH<sub>4</sub> decomposition over Fe is much lower than that over Ni, but CO<sub>2</sub> formation is favored over Fe. A large promotion of the CO<sub>2</sub> formation activity appears with the addition of 0.1 wt% Fe into 1 wt% Ni and a synergistic effect is demonstrated. In general, CO<sub>2</sub> formation is favored below 700 °C while CO formation favored above 800 °C. However, with Fe addition, CO<sub>2</sub> formation can be favored over Ni-GDC at 1000 °C due to the high-temperature redox property of the Fe species. Thus, for preferential CO<sub>2</sub> formation, highly dispersive Ni distribution with Fe addition is recommended for the anode cermet of intermediate-temperature SOFCs.

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**Keywords:** Methane decomposition; Carbon monoxide; Carbon dioxide; Gadolinia-doped ceria; Nickel; Iron

## 1. Introduction

For direct methane solid oxide fuel cells (SOFC) [1,2], methane decomposition over the Ni cermet anode is a major reaction. Since methane decomposition over the Ni cermet anodes generally causes carbon deposition (coking) [3], self de-coking should also be an important reaction, which should occur simultaneously during SOFC operation or may be carried out intermittently. Note that, in this work, “self de-coking” means the removal of the deposited carbon-containing species by the oxygen species from under the surface, i.e. without the presence of oxygen in the gas phase. In the case of a direct methane SOFC, self de-coking can be done by the oxygen species transported from the cathode to the anode surface via the bulk of the oxygen-ion conducting materials. During self de-coking, the formation of only CO not CO<sub>2</sub> should lead to a large difference in SOFC performance. This is due to the electrochemical formation of

CO<sub>2</sub> which involves four electrons while that of CO involves only two electrons, with each oxygen ion carrying two electrons; thus, the current density with CO<sub>2</sub> formation is twice that with CO formation.

If the direct methane SOFC is used for the cogeneration of syngas, i.e. CO + H<sub>2</sub>, the formation of only CO not CO<sub>2</sub> should help the selectivity for syngas. As for the SOFC with the deposited carbon as a fuel [4], the formation of only CO not CO<sub>2</sub> would lead to a two-fold difference in the total current density.

In addition, for methane reactions, a nickel catalyst has been found to exhibit promising catalytic performance for steam reforming of methane [5,6] and carbon dioxide reforming of methane [7–9], both are reactions for direct internal reforming SOFCs and with methane decomposition as a step in the overall reaction. Methane decomposition over the nickel catalyst is well known to produce deposited carbon [10], which may lead to serious deactivation of the catalyst. However, it is also known that the deposited carbon can be removed via gasification by steam [11] or carbon dioxide [12]. Recently, Huang et al. [13,14] have shown that, with doped ceria as the support, a nickel catalyst

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may exhibit a self de-coking capability, i.e. the gasification of the deposited carbon by the O species supplemented from the lattice.

On the other hand, gadolinia-doped ceria (GDC) has been used for a direct methane SOFC as the anode cermet material [15]. It has also been used as the support material of the nickel catalyst for methane decomposition and carbon gasification [13], for steam reforming of methane [14,16], and for carbon dioxide reforming of methane [14].

In addition, methane decomposition has been studied over Fe catalysts for steam reforming of methane [17], and for the yield of carbon [18]. However, in methane decomposition for hydrogen production, nickel showed considerable deactivation, whereas the activity of iron decreased less [19]. Thus, it would be interesting to know the effect of Fe addition on CO and CO<sub>2</sub> formation during methane decomposition over Ni cermet catalysts.

In this work, temperature-programmed self de-coking tests were carried out to study the behavior of CO and CO<sub>2</sub> formation over Ni-GDC, Fe-GDC, and Ni-Fe-GDC cermet catalysts. The factors in forming CO and CO<sub>2</sub> with relation to direct methane SOFCs were investigated. It was found that the bulk lattice oxygen indeed plays a very important role in forming CO and CO<sub>2</sub>. The addition of Fe into Ni promotes the activity of CO<sub>2</sub> formation considerably. It is suggested that highly dispersed Ni species should be prepared for intermediate-temperature direct methane SOFCs with mixed-conducting materials for the anode cermet.

## 2. Experimental

### 2.1. Preparation of gadolinia-doped ceria

Gadolinia-doped ceria was prepared by a co-precipitation method. The details of the method have been reported elsewhere [13]. The calcinations of the GDC powders were carried out by heating in air at a rate of 10 °C min<sup>-1</sup> to 300 °C and held for 2 h, and then to 700 °C and held for 4 h, and then slowly cooled down to room temperature.

### 2.2. Preparation of cermet catalysts

The Ni-GDC cermet catalyst was prepared by mixing GDC powders with an appropriate amount of aqueous solution of nickel nitrate trihydrate, Ni(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (99.999% purity, SHOWA, Japan) for 7 h. After evaporating excess water at 80 °C, the catalysts were dried under vacuum at 110 °C for 10 h. The calcinations of the catalysts were carried out by the same procedure as for the GDC powders.

The Fe-GDC and Ni-Fe-GDC cermet catalysts were prepared with the same method as described above but with specifically required materials. In this work, the indicated metal loading is its weight percent with respect to the weight of the GDC powder.

### 2.3. Temperature-programmed reduction

Temperature-programmed reduction (TPR) was carried out under atmospheric pressure in a continuous flow reactor charged

with 100 mg of sample catalyst, which was fixed by quartz wool and quartz sand downstream of the bed. The reactor was made of an 8-mm-i.d. quartz U-tube imbedded in an insulated electric furnace. A K-type thermocouple was inserted into the catalyst bed to measure and control bed temperature. TPR tests were carried out with 30 ml min<sup>-1</sup> of 10% H<sub>2</sub> in Ar from room temperature to 880 °C at a rate of 10 °C min<sup>-1</sup> and then held at 880 °C. Some details of the TPR test have been reported elsewhere [14].

### 2.4. Temperature-programmed self de-coking

The temperature-programmed self de-coking test was conducted in the same reactor setup as in the TPR test and also charged with 100 mg of sample catalyst. The catalyst was reduced in 100 ml min<sup>-1</sup> of 30% H<sub>2</sub> for 1 h at 400 °C unless stated otherwise. The reactor was then purged with argon flow until no hydrogen will be detected in the reactor outflow. Afterwards, a mixture of 25% CH<sub>4</sub> in Ar was fed to the catalyst bed at a flow rate of 100 ml min<sup>-1</sup> to conduct carbon deposition at 400 °C for 40 min unless stated otherwise. Then, the catalyst was cooled down in Ar flow till room temperature and until no methane will be detected in the reactor outflow.

Temperature-programmed self de-coking test was carried out with 20 ml min<sup>-1</sup> of Ar flow and started from room temperature at a rate of 10 °C min<sup>-1</sup> to the designated temperature and then held at that temperature for 1 h before cooled down. The gas feed was passed through an oxygen filter to eliminate trace amounts of oxygen. The reactor outflow was analyzed on-line by gas chromatograph (China Chromatograph 8900, Taiwan), CO-NDIR (Beckman 880), and CO<sub>2</sub>-NDIR (Beckman 880).

## 3. Results and discussion

### 3.1. CO and CO<sub>2</sub> formations over Ni-GDC

Since self de-coking occurs simultaneously during SOFC operation or may be carried out intermittently, the self de-coking tests in this work can simulate the anode reactions in direct methane SOFCs. Note that the O species needed for oxidation over anode of direct methane SOFC is coming from the bulk lattice oxygen, while that for self de-coking is the same. However, the catalytic kinetics has a difference in that the concentration of the bulk lattice oxygen during self de-coking over conventional catalysts decreases since no refilling can be done but that during SOFC anode oxidation can be kept constant due to refilling of the oxygen species from the cathode.

In this work, the deposited carbon-containing species can be CH<sub>x</sub> with  $x=0-3$ . Bitter et al. [20] have reported that methane is decomposed on the metal to CH<sub>x</sub>, with average value of  $x$  equals 2. Over Ni(1 1 1), the CH species has been identified as the surface species from methane dissociation and it is more stable than the CH<sub>3</sub> species [21]. In this work, the process for carbon deposition over the catalysts is carried out at 400 °C, a temperature much lower than that for complete methane pyrolysis of 900 °C [4]. Thus, the deposited carbon-containing species in this work can represent all possible surface carbon-containing species from CH<sub>4</sub> decomposition.

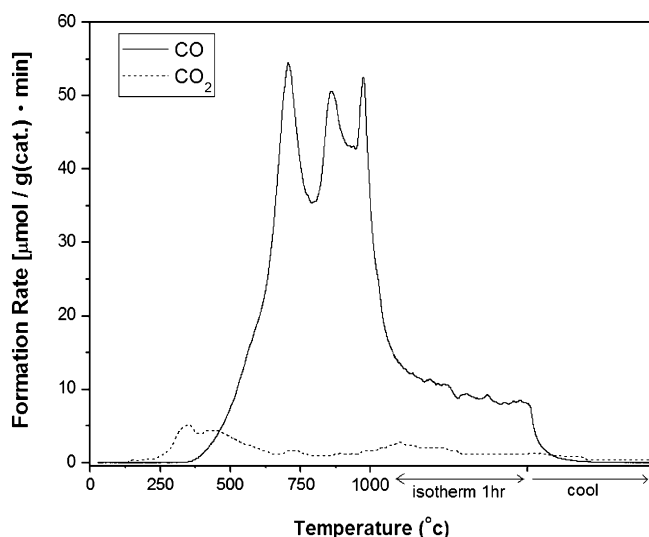


Fig. 1. Temperature-programmed self de-coking over 400 °C-reduced 60Ni-GDC after 10 min of methane decomposition.

In addition, CO and CO<sub>2</sub> are formed by the last step of the reaction sequence of methane decomposition or self de-coking, and then desorbed into the gas phase. This indicates that CO and CO<sub>2</sub> formation during methane decomposition and self de-coking should be the same [22]. Therefore, the self de-coking test can be employed to study the factors in forming CO and CO<sub>2</sub> over the cermet anode with relation to not only the SOFC with deposited carbon as fuel but also the direct methane SOFC.

### 3.1.1. Over 60Ni-GDC

The 60Ni-GDC cermet catalyst, with Ni:GDC=3:5 in weight, is the same material as the anode cermet with the optimum Ni:doped-ceria ratio [23]. Note that the indicated metal loading is its weight percent with respect to the weight of the GDC powder. It is seen that very large amount of CO is formed with relatively negligible CO<sub>2</sub> formation, as shown in Fig. 1. This large CO formation is attributed to a large amount of carbon deposition due to extensive methane decomposition over the catalyst with the very high Ni loading of 60 wt%. In addition, the extensive methane decomposition would also consume some surface of OH species and thus decrease CO<sub>2</sub> formation. Note

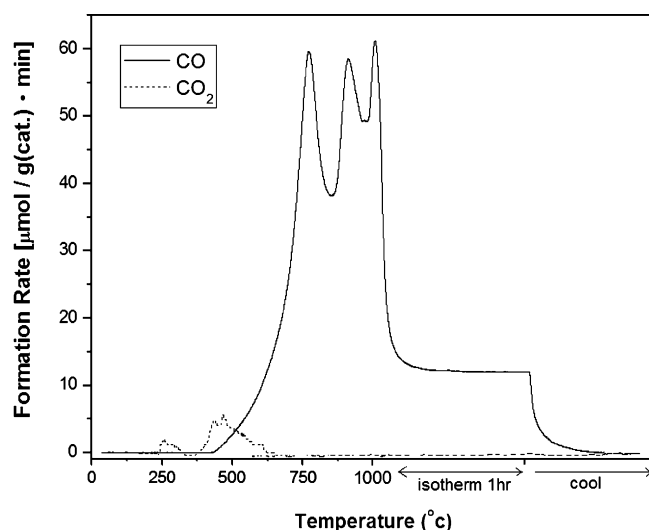


Fig. 2. Temperature-programmed self de-coking over 400 °C-reduced 60Ni-GDC after 12 h of methane decomposition.

that CO formation involves the O species from the bulk lattice oxygen while CO<sub>2</sub> formation involves the surface hydroxyl (OH) species [5,22], as will be evidenced also in this work. Since the amount of the surface OH species is limited, the removal of the deposited carbon-containing species needs the O species from the bulk lattice oxygen, which is quite abundant as shown in Table 1. As a consequence, a large amount of CO is formed. These results indicate that the surface OH species favors CO<sub>2</sub> formation while the O species coming from the bulk lattice oxygen favors CO formation. Note that the O species of the metal oxides contribute the surface OH species if they are reducible. Note also that, with the TPR peak temperature of nickel oxide at about 390 °C [22], the nickel species over 400 °C-reduced Ni/GDC is in its metal form.

Fig. 2 shows that, with the methane decomposition time increases to 12 h, the CO<sub>2</sub> formation over 60Ni-GDC decreases very much to almost negligible and CO formation further increases, as also shown in Table 1. The formation of only CO after 740 °C indicates that CO is formed with the O species coming from the bulk lattice oxygen. Note that the high-temperature TPR peak of GDC is at about 740 °C [22], which designates

Table 1  
Total amounts of CO and CO<sub>2</sub> formations during self de-coking until cooled down

	Pre-reduction temperature (°C)	Methane time <sup>a</sup> (min)	Total amount in (μmol g <sup>-1</sup> ) catalyst <sup>b</sup>		
			CO <sub>2</sub> formation	CO formation	y <sup>c</sup>
60Ni/GDC	400	10	298	2526	0.118
60Ni/GDC	400	720	74	2880	0.026
1Ni/GDC	400	40	435	663	0.656
1Ni/GDC	600	40	338	223	1.52
1Fe/GDC	400	40	253	219	1.16
1Fe/GDC	400	10	238	150	1.59
1Ni-0.1Fe/GDC	400	40	421	173	2.43

<sup>a</sup> Methane time indicates the time of methane flowing over the catalyst.

<sup>b</sup> The total O content in NiO of the unreduced 1Ni-GDC catalyst is 168.7 μmol g<sup>-1</sup> catalyst, that in Fe<sub>2</sub>O<sub>3</sub> of the unreduced 1Fe-GDC catalyst is 265.9 μmol g<sup>-1</sup> catalyst, and that in GDC, i.e. (GdO<sub>1.5</sub>)<sub>0.1</sub>(CeO<sub>2</sub>)<sub>0.9</sub>, is 11270 μmol g<sup>-1</sup> GDC.

<sup>c</sup> y = amount of CO<sub>2</sub> formation/amount of CO formation (simply called CO<sub>2</sub>/CO ratio).

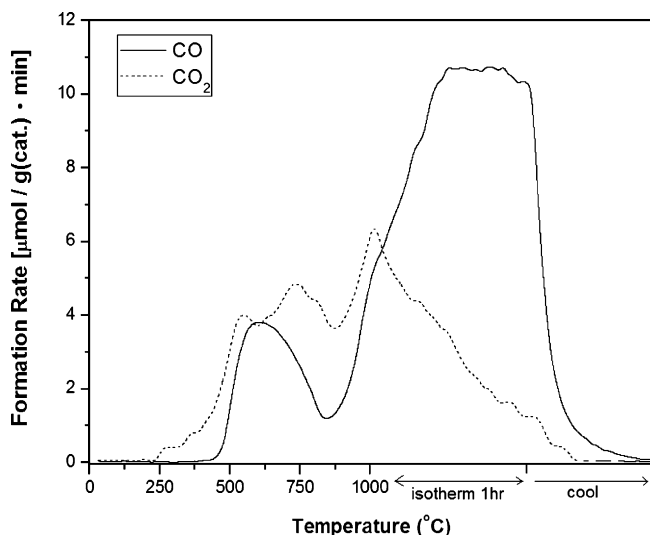


Fig. 3. Temperature-programmed self de-coking over 400 °C-reduced 1Ni-GDC after 40 min of methane decomposition.

the temperature for the bulk lattice oxygen becoming highly mobile.

The above results indicate that the optimum Ni:doped-ceria ratio of 3:5 in weight leads to preferential CO formation. This would be detrimental to the fuel utilization efficiency during electricity generation in comparison to CO<sub>2</sub> formation. Thus, the very high Ni loading to form a structure for electron conduction is not beneficial for CO<sub>2</sub> formation. This is possibly due to considerably fewer three-phase boundary (TPB), i.e. the Ni-GDC interface, can be formed in this Ni-connecting structure in comparison to a highly dispersive Ni distribution. Note that, with mixed-conducting materials such as GDC employed for the anode cermet, very low Ni loading to achieve highly dispersive Ni species is feasible.

### 3.1.2. Over 1Ni-GDC

Fig. 3 shows the results of temperature-programmed self de-coking after 40 min of CH<sub>4</sub> decomposition over the 400 °C-reduced 1Ni-GDC. It is seen that there are two CO peaks, with the lower-temperature peak at about 610 °C, and roughly three CO<sub>2</sub> peaks, with the lowest-temperature peak at about 540 °C. It is also seen that, at 800 °C or lower, the amount of CO<sub>2</sub> formed is higher than that of CO. A comparison with 60Ni-GDC indicates that not only the CO<sub>2</sub>/CO ratio, i.e.  $y$  in Table 1, increases considerably but also the amount of CO<sub>2</sub> formed increases very much.

The occurrence of the lowest-temperature CO<sub>2</sub> peak and lower-temperature CO peak has been reported to be due to the formation and reaction of the intermediate CHO species. CHO formation is by the reaction of the deposited carbon-containing species with the surface OH species, and then CHO reacts with surface OH species to form CO<sub>2</sub> or decomposes to form CO [22]. Since the rate of CHO decomposition is lower than its rate of reaction with the surface OH species, CO<sub>2</sub> formation would be preferred if there is surface OH species. This is evidenced by the formation of the lowest-temperature CO<sub>2</sub> peak at a temperature lower than that of the lower-temperature CO peak.

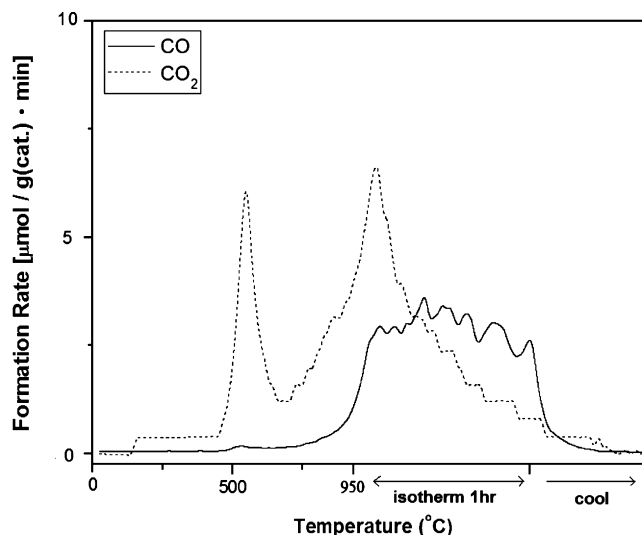


Fig. 4. Temperature-programmed self de-coking over 600 °C-reduced 1Ni-GDC after 40 min of methane decomposition.

Fig. 4 shows the temperature-programmed profiles of self de-coking over the 600 °C-reduced Ni-GDC catalyst after 40 min of CH<sub>4</sub> decomposition. It is seen that the total amount of CO<sub>2</sub> formation becomes higher than that of CO, as also shown in Table 1. In addition, there is almost only CO<sub>2</sub> formation before 740 °C. This is attributed to, in comparison to the 400 °C pre-reduction, higher mobility of the lattice oxygen during the 600 °C pre-reduction, which leads to higher supply rate of the bulk lattice oxygen to the surface and thus higher amount of the surface O species left over from pre-reduction. Note that the OH species is formed by the reaction of the O species with the H species dissociated from CH<sub>4</sub> during CH<sub>4</sub> decomposition. Also note that the O species can migrate over Ni surface [24]. As a consequence, enough CHO species can be formed, and the concentration of the surface OH species remained after CH<sub>4</sub> decomposition can be high enough for CO<sub>2</sub>-only formation before 740 °C. Nevertheless, after 740 °C, CO formation occurs and increases with temperature. This clearly indicates that CO formation can be associated with the O species coming from the bulk lattice oxygen. Note that the OH species dissociates considerably at high temperature [25].

Fig. 4 also shows that the lowest-temperature CO<sub>2</sub> peak appears at about 540 °C, the same as that in Fig. 3. However, the temperature of the lowest-temperature CO<sub>2</sub> peak over the 600 °C-reduced Ni-GDC is higher than that over the 400 °C-reduced one. This can be attributed to the above-described higher concentration of the surface OH species, which leads to both higher CHO formation and followed higher CO<sub>2</sub> formation. This further indicates that CO<sub>2</sub> formation is associated with the surface OH species.

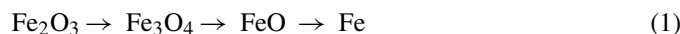
For direct methane SOFC, the O species is supplied continuously from the cathode to the anode via the bulk lattice of the oxygen-ion conducting materials such as GDC, the concentration of the surface OH species can be kept high during methane reaction if the operating temperature is not too high for too fast OH dissociation. Thus, preferential CO<sub>2</sub> formation to increase its current density can be realized if the operation

temperature is kept below 700 °C and the Ni species is highly dispersive. These requirements for preferential CO<sub>2</sub> formation can be fulfilled by intermediate-temperature SOFC operating at low temperature such as 500–700 °C. However, if syngas cogeneration is required, SOFC operating at higher temperature such as 1000 °C is preferred.

### 3.2. CO and CO<sub>2</sub> formations over Fe-GDC

Fig. 5 presents the temperature-programmed profiles of self de-coking over the 400 °C-reduced 1Fe-GDC catalyst after 40 min of CH<sub>4</sub> decomposition. It is seen that there is only a continuously formed but temperature-varied CO peak, a behavior different from that of 1Ni-GDC as shown in Fig. 3. In addition, the amounts of CO and CO<sub>2</sub> formations over 1Fe-GDC are much less than those over 1Ni/GDC, as shown in Table 1. However, the CO<sub>2</sub>/CO ratio over 1Fe/GDC is much higher than that over 1Ni-GDC. These indicate that the activity of CH<sub>4</sub> decomposition over Fe is much lower than that over Ni, but CO<sub>2</sub> formation is favored over Fe. The latter behavior is considered to be due to the high-temperature redox properties of the Fe species.

The role of Fe in Pd-Rh/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> three-way catalyst has been reported as an oxygen storage component under oxidizing conditions through the process Fe → FeO → Fe<sub>3</sub>O<sub>4</sub> (FeO·Fe<sub>2</sub>O<sub>3</sub>) → Fe<sub>2</sub>O<sub>3</sub> [26]. Thus, it is reasonable to propose that, under reducing conditions, the reverse of the above process, i.e.



can occur. As shown in the temperature-programmed reduction profile of Fig. 6, there are three TPR peaks appear during the reduction of iron oxide. These three peaks at 587, 880, and 970 °C should thus represent the reduction processes of Fe<sub>2</sub>O<sub>3</sub> → Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub> → FeO, and FeO → Fe, respectively. Note that the reduction of nickel oxide occurs via NiO → Ni with the TPR peak temperature at about 390 °C [22]. Thus, dur-

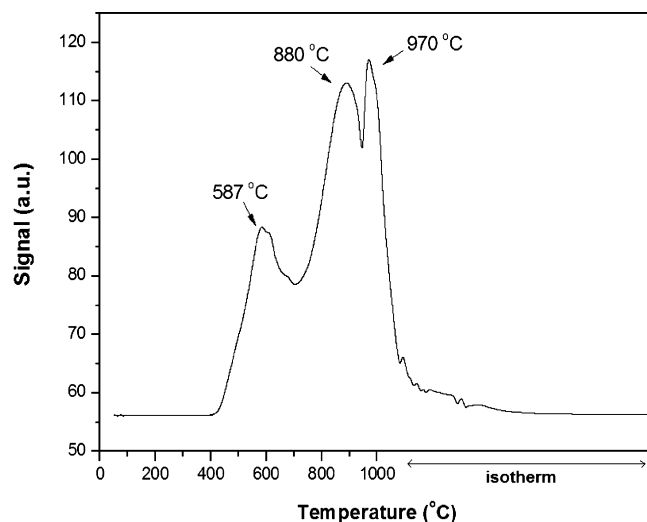


Fig. 6. Temperature-programmed reduction profile of iron oxide.

ing self de-coking, the Ni species in 400 °C-reduced Ni-GDC is only in its metal form, but the iron species in 400 °C-reduced Fe-GDC is in its oxide forms of Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, or FeO depending on the temperature until 970 °C. Thus, with the temperature-programmed self de-coking tests over Fe-GDC carried out until 1000 °C, the O species of the iron oxides can be fully utilized, in the form as the surface OH species. In other words, iron can supply enough surface OH species to help the CO<sub>2</sub> formation.

A comparison of Fig. 5 with Fig. 3 shows that, during the isothermal period at 1000 °C, CO<sub>2</sub> formation relative to that of CO over 1Fe-GDC is much higher than over 1Ni-GDC. This is considered to be due to the high-temperature redox properties of the Fe species. At 1000 °C, the FeO → Fe process is still going on, as Fig. 6 shows, and thus the Fe → FeO process can also take place.

When the duration of carbon deposition via CH<sub>4</sub> decomposition is shortened from 40 to 10 min, CO<sub>2</sub> formation is started at a lower temperature, as shown in Fig. 7 in comparison to Fig. 5.

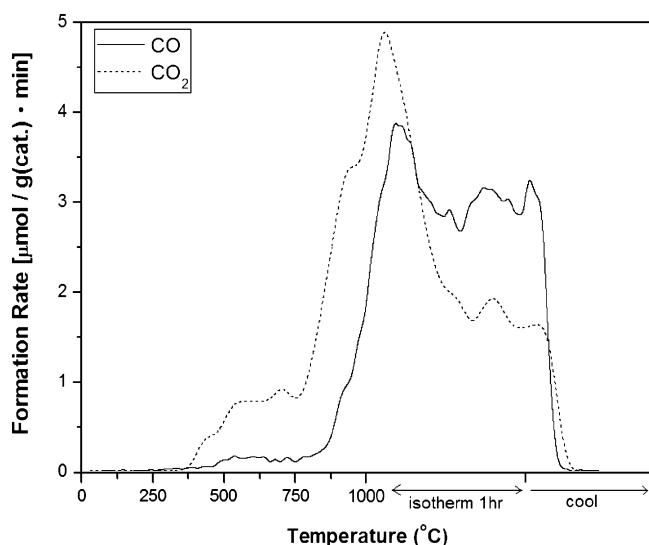


Fig. 5. Temperature-programmed self de-coking over 400 °C-reduced 1Fe-GDC after 40 min of methane decomposition.

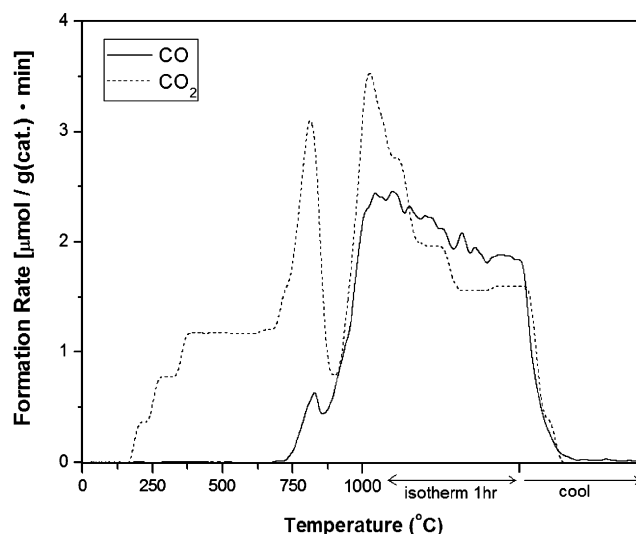


Fig. 7. Temperature-programmed self de-coking over 400 °C-reduced 1Fe-GDC after 10 min of methane decomposition.

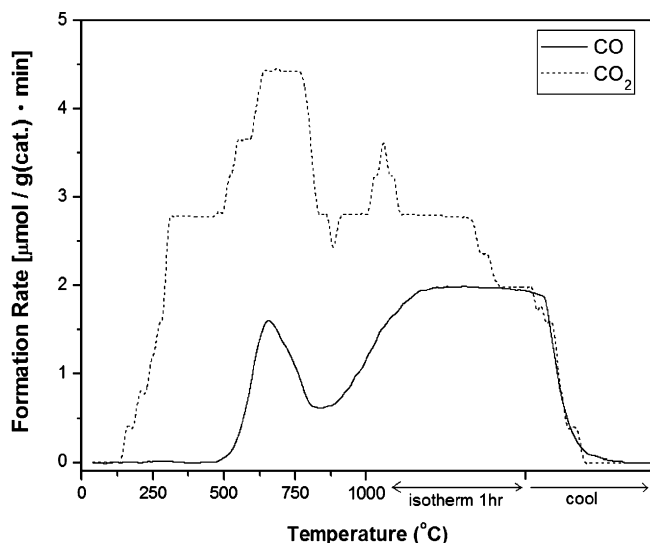


Fig. 8. Temperature-programmed self de-coking over 400 °C-reduced 1Ni-0.1Fe-GDC after 40 min of methane decomposition.

This is due to that, with the duration of CH<sub>4</sub> decomposition shortened, the consumption of the O species of the iron oxides also decreases. These O species will be reacted to form the OH species during CH<sub>4</sub> decomposition and these OH species over Fe, being the nearest neighbor with Fe, should be more active than those over GDC. Thus, a higher concentration of the OH species over Fe leads to higher activity of CO<sub>2</sub> formation, as evidenced by the lower starting temperature.

Fig. 7 also shows that CO<sub>2</sub>-only formation occurs before about 740 °C, i.e. before the lattice O species becoming highly mobile. This behavior is similar to that over the 600 °C-reduced 1Ni-GDC catalyst as shown in Fig. 4, and that over the 400 °C-reduced 1Fe-GDC as shown in Fig. 5. Thus, it may be concluded that high enough surface OH species can lead to CO<sub>2</sub>-only operation and CO is mostly formed with the O species coming from the bulk lattice oxygen.

### 3.3. CO and CO<sub>2</sub> formations over Ni-Fe-GDC

With an addition of 0.1 wt% Fe into 1Ni-GDC, a profound effect on CO<sub>2</sub> formation relative to CO formation appears, as shown in Fig. 8 and Table 1. It is seen that, with the same pre-reduction temperature of 400 °C, the amount of CO<sub>2</sub> formed over 1Ni-0.1Fe-GDC is roughly the same as that of 1Ni-GDC, but that of CO formed is very much lower, resulting in about four times higher CO<sub>2</sub>/CO ratio. In addition, the CO<sub>2</sub>/CO ratio over 1Ni-0.1Fe-GDC is much higher than that over 1Fe-GDC, as also shown in Table 1. This large promotion of the CO<sub>2</sub> formation activity with the addition of Fe into Ni clearly demonstrates a synergistic effect. That is, the high CH<sub>4</sub> reactivity of the Ni species couples with the high-temperature redox property of the Fe species, which supplies the critically needed surface OH species in nearest neighbor. However, the redox process seems to be faster than CH<sub>4</sub> decomposition and thus 0.1 wt% Fe addition seems to be enough to promote the 1 wt% Ni catalyst largely in CO<sub>2</sub> formation. Since the methane decomposition activity over

Fe is much lower than that over Ni, too high Fe addition can decrease the overall activity for CO<sub>2</sub> formation.

Fig. 8 also shows that the lower-temperature CO peak is at about 655 °C, which is higher than that over 1Ni-GDC; the starting temperature to form this peak is also higher, as a comparison of Fig. 8 with Fig. 3 shows. This is considered to be due to that Fe addition into Ni decreases the CHO decomposition activity. Note that the formation of the lower-temperature CO peak over 1Ni-GDC has been considered to be due to the decomposition of the intermediate CHO species.

In addition, Fig. 8 also shows that the CO<sub>2</sub> formation rate is always higher than that of CO during self de-coking, even during the isothermal period at 1000 °C. A comparison with Fig. 3 may lead to a conclusion that preferential CO<sub>2</sub> formation can be achieved during direct methane SOFC operation, for operating temperature of 1000 °C and below, by adding Fe into Ni in the anode cermet.

## 4. Conclusions

Based on the above results and discussion, it can be concluded that the bulk lattice oxygen plays a very important role in forming CO and CO<sub>2</sub>. CO formation is generally associated with O species coming from the bulk lattice oxygen while CO<sub>2</sub> formation generally is associated with the surface OH species. With Ni:GDC = 3:5 in weight, a very large amount of CO is formed with relatively negligible CO<sub>2</sub> formation. With 1 wt% Ni, preferential CO<sub>2</sub> formation can occur below 700 °C. The activity of CH<sub>4</sub> decomposition over Fe is much lower than that over Ni, but CO<sub>2</sub> formation is favored over Fe. A large promotion of the CO<sub>2</sub> formation activity appears with the addition of 0.1 wt% Fe into 1 wt% Ni and a synergistic effect was demonstrated. In general, CO<sub>2</sub> formation was favored below 700 °C while CO formation was favored above 800 °C. With Fe addition, CO<sub>2</sub> formation is favored at 1000 °C due to the high-temperature redox property of the Fe species.

## Acknowledgment

The authors acknowledge that Fig. 6 has been provided by Mr. Meng-Chin Huang.

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