

Short communication

## Direct methane oxidation over a $\text{Bi}_2\text{O}_3$ –GDC system

Ta-Jen Huang\*, Jia-Fu Li

*Department of Chemical Engineering, National Tsing Hua University, Hsinchu 300, Taiwan, ROC*

Received 2 July 2007; received in revised form 9 August 2007; accepted 9 August 2007

Available online 25 August 2007

### Abstract

A novel ceramic system was prepared by adding  $\text{Bi}_2\text{O}_3$  to gadolinia-doped ceria (GDC). This  $\text{Bi}_2\text{O}_3$ –GDC system was characterized by temperature-programmed and fixed-temperature reaction of methane in the absence of gas-phase oxygen. It was found that adding  $\text{Bi}_2\text{O}_3$  to GDC can promote the catalytic activity for direct methane oxidation. A  $\text{Bi}_2\text{O}_3$  loading of 25 wt% in the  $\text{Bi}_2\text{O}_3$ –GDC system maximized the activity of direct methane oxidation. Possible carbon deposition after the reaction can be negligible. In the temperature range of an intermediate-temperature solid oxide fuel cell (SOFC), pre-reduction promotes methane oxidation activity. At temperatures of about 600 °C or lower, only  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are produced. However,  $\text{CO}$  and  $\text{H}_2$  can be produced only at a temperature of about 700 °C or higher. This  $\text{Bi}_2\text{O}_3$ –GDC system can be applied to design SOFC anode materials for complete methane oxidation and thus full electricity generation, without syngas cogeneration, at low temperature.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Bismuth oxide; Gadolinia-doped ceria; Ceramic system; Methane; Oxidation

### 1. Introduction

Bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) has high oxygen-ion conductivity and has been considered as an electrolyte material for solid oxide fuel cells (SOFCs) [1]. Additionally, bismuth oxide has extensive applications as a catalyst for industrial oxidation reactions [2]. However, at low oxygen partial pressure, such as on the SOFC anode side, pure bismuth oxide is unstable. Although the high-temperature cubic phase,  $\delta$ - $\text{Bi}_2\text{O}_3$ , is among the most effective oxygen-ion conductors, it is stable only between about 730 °C and its melting point at 824 °C [3]. Therefore, various doped bismuth oxide have been proposed to stabilize its  $\delta$ -phase and also to enhance its oxidation activity [4,5]. Doped  $\text{Bi}_2\text{O}_3$  has been studied as the catalyst for the oxidative coupling of methane [6,7].

Gadolinia-doped ceria (GDC) has been employed as the electrolyte in intermediate-temperature SOFCs [8,9]. It has also been used as the anode cermet materials in direct-methane SOFCs (DM-SOFCs) [10]. In DM-SOFCs [11,12], the activity of methane oxidation to form  $\text{CO}_2$  and/or  $\text{CO}$  influences the fuel efficiency in electricity generation. This is because the electrochemical formation of  $\text{CO}_2$  involves four electrons while that

of  $\text{CO}$  involves only two electrons, and each oxygen-ion carries two electrons; consequently, the current density associated with  $\text{CO}_2$  formation is double that associated with  $\text{CO}$  formation. However, when DM-SOFCs are adopted in the cogeneration of syngas, the formation of only  $\text{CO}$  is preferred over that of  $\text{CO}_2$ . Notably, the activity of direct methane oxidation to form  $\text{H}_2\text{O}$  and/or  $\text{H}_2$  also influences the fuel efficiency in generating electricity; the formation of  $\text{H}_2\text{O}$  consumes one oxygen-ion, and thus generates two electrons, while that of  $\text{H}_2$  does not consume oxygen. Therefore, full electricity generation, without syngas cogeneration, is favored over an anode catalyst, which promotes  $\text{CO}_2$  and  $\text{H}_2\text{O}$  production. However, syngas cogeneration is favored over a catalyst which enhances  $\text{CO}$  and  $\text{H}_2$  productions.

In direct-methane SOFCs, higher direct methane oxidation activity corresponds to a higher rate of methane decomposition, since methane decomposition is the main reaction step for the methane reaction in the absence of gas-phase oxygen [13]. Methane decomposition yields deposited carbon species, which may accumulate as coke and result in catalyst deactivation. However, the deposited carbon can be removed by gasification with steam [14] or carbon dioxide [15]. Recently, Huang et al. [13,16,17] demonstrated that doped ceria may exhibit self de-coking capability, meaning that the deposited carbon species are removed via gasification by the O species supplemented from the bulk lattice of doped ceria. Restated, “self de-coking” means carbon removal in the absence of gaseous oxygen. Notably, self

\* Corresponding author. Tel.: +886 3 5716260; fax: +886 3 5715408.

E-mail address: [tjhuang@che.nthu.edu.tw](mailto:tjhuang@che.nthu.edu.tw) (T.-J. Huang).

de-coking during SOFC operation is accompanied by electricity generation; that is, the deposited carbon serves as the fuel [18,19]. In fact, a carbon SOFC design has been proposed to store and use the deposited carbon [20]. It has been reported that a higher concentration of bulk lattice oxygen results in higher capability of self de-coking [13], which may solve the problem of coking in direct methane oxidation.

In this work, novel ceramic systems of  $\text{Bi}_2\text{O}_3$  and GDC were prepared in an attempt to take advantage of the high oxygen-ion conductivity of  $\text{Bi}_2\text{O}_3$ , which means a high concentration of oxygen vacancies in the bulk to take in the oxygen species [21]. Exploiting the high oxygen-ion conductivity should increase the methane oxidation activity and the self de-coking capability of the  $\text{Bi}_2\text{O}_3$ –GDC system. Under conditions associated with the intermediate-temperature DM-SOFCs, it was found that only  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were produced at temperatures of around  $600^\circ\text{C}$  or lower; on the other hand,  $\text{CO}$  and  $\text{H}_2$  can be produced only at a temperature of about  $700^\circ\text{C}$  or higher. This  $\text{Bi}_2\text{O}_3$ –GDC system can thus be adopted to design anode materials of direct-methane SOFCs for full electricity generation, without syngas cogeneration, at low temperature.

## 2. Experimental

### 2.1. Preparation of GDC and $\text{Bi}_2\text{O}_3$ –GDC system

Gadolinia-doped ceria was prepared by co-precipitation. The details of the method have been presented elsewhere [16]. Suitable amounts of gadolinium nitrate and cerium nitrate were used to make a nominal atomic ratio of  $\text{Gd}:\text{Ce} = 1:9$ . The GDC powders were calcined by heating in air at a rate of  $10^\circ\text{C min}^{-1}$  to  $800^\circ\text{C}$  and held for 4 h before cooling. GDC prepared in this work is  $(\text{GdO}_{1.5})_{0.1}(\text{CeO}_2)_{0.9}$ . The  $\text{Bi}_2\text{O}_3$ –GDC system was prepared by mixing GDC and  $\text{Bi}_2\text{O}_3$  powders in the designated weight ratio. Then, the mixture was calcined at  $800^\circ\text{C}$  for 4 h to yield a  $\text{Bi}_2\text{O}_3$ –GDC system. The indicated weight percentage is the weight of  $\text{Bi}_2\text{O}_3$  in terms of GDC.

### 2.2. Temperature-programmed reaction of methane

A temperature-programmed reaction of methane ( $\text{CH}_4$ -TPR<sub>x</sub>) was performed at atmospheric pressure in a continuous flow reactor that was 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 that was embedded in an insulated electric furnace. A K-type thermocouple was inserted into the catalyst bed to measure and control the bed temperature. The gas feed was passed through an oxygen filter to eliminate trace oxygen. A blank test was performed and the results indicated that no oxygen leak occurred in this reactor system.

The calcined  $\text{Bi}_2\text{O}_3$ –GDC system was pre-reduced with  $30\text{ ml min}^{-1}$  of 10%  $\text{H}_2$  in argon from room temperature at a rate of  $10^\circ\text{C min}^{-1}$  to  $800^\circ\text{C}$  and then cooled. Notably, pure  $\text{Bi}_2\text{O}_3$  was not pre-reduced because it is completely reducible. A mixture of 1%  $\text{CH}_4$  in argon was fed to the catalyst bed at a flow rate of  $20\text{ ml min}^{-1}$ , which is a molar feed rate of methane of

$81.3\text{ }\mu\text{mol g}^{-1}\text{ min}^{-1}$ ), calculated using the ideal gas law. The  $\text{CH}_4$ -TPR<sub>x</sub> test was conducted from at room temperature at a rate of  $10^\circ\text{C min}^{-1}$  to  $850^\circ\text{C}$ , which temperature was held for 1 h before cooling. The reactor outflow was analyzed on-line by gas chromatography (GC, China Chromatograph 8900, Taiwan), CO-NDIR (non-dispersive infrared, Beckman 880) and  $\text{CO}_2$ -NDIR (Beckman 880).

### 2.3. Fixed-temperature reaction of methane

The fixed-temperature test was performed in the same reactor setup as the  $\text{CH}_4$ -TPR<sub>x</sub> test, with 100 mg of calcined  $\text{Bi}_2\text{O}_3$ –GDC system. Some catalyst samples were un-reduced as designated in the text. Other catalyst samples were pre-reduced with  $100\text{ ml min}^{-1}$  of 10%  $\text{H}_2$  in argon from room temperature at a rate of  $10^\circ\text{C min}^{-1}$  to the designated temperature, which was held for 1 h. Then, the reactor setup was purged with argon flow until no hydrogen was detected in the outflow. Then, a mixture of 25%  $\text{CH}_4$  in argon was fed to the catalyst bed at a flow rate of  $100\text{ ml min}^{-1}$  to conduct the activity test of the methane reaction at the designated temperature. The reactor outflow was analyzed using the same detectors as the  $\text{CH}_4$ -TPR<sub>x</sub> test. In this work, when unspecified, the catalyst was pre-reduced and the reaction temperature was the same as the pre-reduction temperature, with the pre-reduction procedure described above. The highest reaction temperature was set to  $780^\circ\text{C}$  in consideration of the melting point of  $\text{Bi}_2\text{O}_3$ , which is  $824^\circ\text{C}$ .

## 3. Results and discussion

### 3.1. Effect of $\text{Bi}_2\text{O}_3$ loading

In this work, the  $\text{Bi}_2\text{O}_3$ –GDC samples, consisting of 10–40 wt%  $\text{Bi}_2\text{O}_3$  in GDC, are considered to be two-phase mixtures according to the report of Gil et al. [22] that the solubility limit of  $\text{Bi}_2\text{O}_3$  in the GDC structure is about 0.8 wt%. Thus, the 10–40 wt%  $\text{Bi}_2\text{O}_3$  in GDC of this work can be considered to be two-phase mixtures. In accordance with literature ceramic terminology, these two-phase mixtures are termed  $\text{Bi}_2\text{O}_3$ –GDC systems.

The characteristics of  $\text{Bi}_2\text{O}_3$ –GDC systems with various  $\text{Bi}_2\text{O}_3$  loadings were analyzed by  $\text{CH}_4$ -TPR<sub>x</sub>, which is direct methane oxidation in the absence of gas-phase oxygen, yielding the results presented in Fig. 1. The catalyst was pre-reduced to  $800^\circ\text{C}$ , to simulate the conditions in an intermediate-temperature SOFC. A  $\text{Bi}_2\text{O}_3$  loading of 25 wt% in the  $\text{Bi}_2\text{O}_3$ –GDC systems maximizes the rate of formation of not only  $\text{CO}_2$  but also  $\text{CO}$ . Since  $\text{CH}_4$  oxidation produces  $\text{CO}_2$  and/or  $\text{CO}$ , the total amounts of formed carbon oxides,  $\text{CO}$  and  $\text{CO}_2$ , are related to the conversion of methane,  $\Delta\text{CH}_4 = \Delta\text{CO} + \Delta\text{CO}_2$ , based on carbon balance. Notably, possible carbon deposition over the catalyst was analyzed after the  $\text{CH}_4$ -TPR<sub>x</sub> tests and found to be negligible. Table 1 reveals that the 25 wt%  $\text{Bi}_2\text{O}_3$ –GDC system has maximum methane activity. Therefore, the 25 wt%  $\text{Bi}_2\text{O}_3$ –GDC system was used in tests of the fixed-temperature reaction of methane.

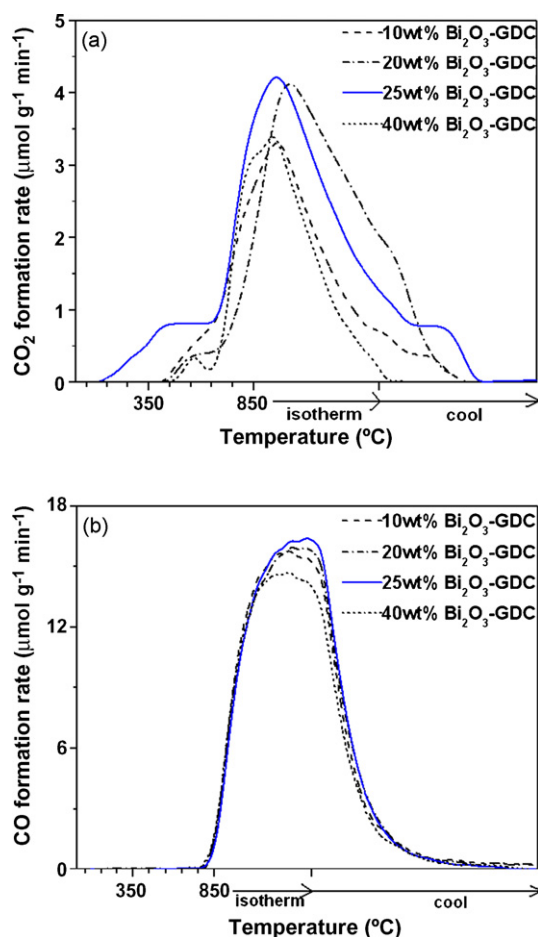


Fig. 1. Effect of  $\text{Bi}_2\text{O}_3$  loading on carbon oxides formation profiles during  $\text{CH}_4\text{-TPR}_x$  over  $\text{Bi}_2\text{O}_3\text{-GDC}$  systems (a)  $\text{CO}_2$  (b)  $\text{CO}$ .

Table 1 also indicates that the methane activity of the  $\text{Bi}_2\text{O}_3\text{-GDC}$  system may exceed that of GDC and markedly exceed that of  $\text{Bi}_2\text{O}_3$ . Notably, the ratio of the BET surface areas of GDC, 25 wt%  $\text{Bi}_2\text{O}_3\text{-GDC}$  and  $\text{Bi}_2\text{O}_3$  has been determined as 1:0.81:0.66. This means that the much higher methane oxidation activity over 25 wt%  $\text{Bi}_2\text{O}_3\text{-GDC}$  is not due to a higher surface area. Thus, a synergistic effect exists for the  $\text{Bi}_2\text{O}_3\text{-GDC}$  system. This effect is considered to be caused by a combination of the methane adsorption activity of GDC and the high mobile oxygen content in  $\text{Bi}_2\text{O}_3$  [1]. The lower methane activity of 40 wt%  $\text{Bi}_2\text{O}_3\text{-GDC}$  than GDC is considered to follow

Table 1  
Effect of  $\text{Bi}_2\text{O}_3$  loading on total amount of carbon oxides<sup>a</sup> formation during  $\text{CH}_4\text{-TPR}_x$  tests over  $\text{Bi}_2\text{O}_3\text{-GDC}$  systems

	Total amount of carbon oxides formation ( $\times 10^3 \mu\text{mol g}^{-1}$ )
GDC	1.27
10 wt% $\text{Bi}_2\text{O}_3\text{-GDC}$	1.40
20 wt% $\text{Bi}_2\text{O}_3\text{-GDC}$	1.42
25 wt% $\text{Bi}_2\text{O}_3\text{-GDC}$	1.50
40 wt% $\text{Bi}_2\text{O}_3\text{-GDC}$	1.18
$\text{Bi}_2\text{O}_3$	0.132

<sup>a</sup> Carbon oxides consists of  $\text{CO}$  and  $\text{CO}_2$ .

from the fact that the methane activity of  $\text{Bi}_2\text{O}_3$  is much lower than that of GDC, as also shown in Table 1. Separate analysis of energy dispersive X-rays over a  $600^\circ\text{C}$ -reduced 40 wt%  $\text{Bi}_2\text{O}_3\text{-GDC}$  sample indicated the existence of surface particles which are composed of a large amount of elemental Bi and relatively little elemental O; this suggests the distribution of the Bi species at the catalyst surface and its being reduced. Consequently, the amount of GDC over the surface decreases and the methane activity drops. When the effect of  $\text{Bi}_2\text{O}_3$  in enhancing methane oxidation activity is weaker than its detrimental effect on methane adsorption activity, the total amount of carbon oxides formed should drop to a level lower than that of GDC.

### 3.2. Effect of pre-reduction on direct methane oxidation activities

The intermediate-temperature SOFCs operate in a temperature range  $500\text{--}800^\circ\text{C}$ . The SOFC anode may be activated via reduction by the methane feed, which is denoted as a case without pre-reduction, or by a hydrogen flow before operation, which is denoted as a case with pre-reduction. Fig. 2 shows that, for catalysts without pre-reduction, an induction period, during which no  $\text{CO}_2$  or  $\text{CO}$  is formed, of about 3 min applies. The existence of the induction period is considered to be caused by the initial activation of the catalyst by the methane feed. Additionally, the formation rate jumps to a high level in a subsequent period. Notably, the activity can exceed the roughly constant pseudo-steady-state level, because of the existence of the surface oxygen species of the catalyst without pre-reduction. These oxygen species increase the oxidation rate of methane to produce carbon oxides. The extent of the increase with the reaction temperature, associated not only with a higher peak but also with a much faster jump, is also shown in Fig. 2. Notably, also,  $\text{CO}$  forms only at a temperature that exceeds or markedly exceeds  $600^\circ\text{C}$ . Otsuka et al. [23] reported that, for direct methane oxidation over cerium oxide,  $\text{CO}$  must be produced by the reaction of carbon with the lattice oxygen of  $\text{CeO}_2$ . Notably, also, methane decomposition yields surface carbon species [16] and the bulk lattice oxygen of GDC becomes mobile at a temperature of over

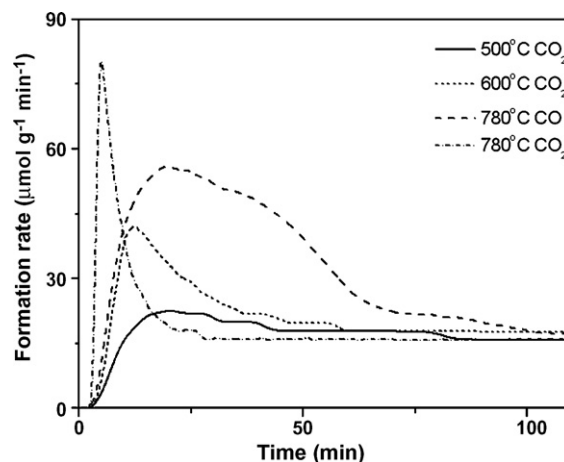


Fig. 2.  $\text{CO}_2$  and  $\text{CO}$  formation profiles during fixed-temperature methane reaction over 25 wt%  $\text{Bi}_2\text{O}_3\text{-GDC}$  without pre-reduction.

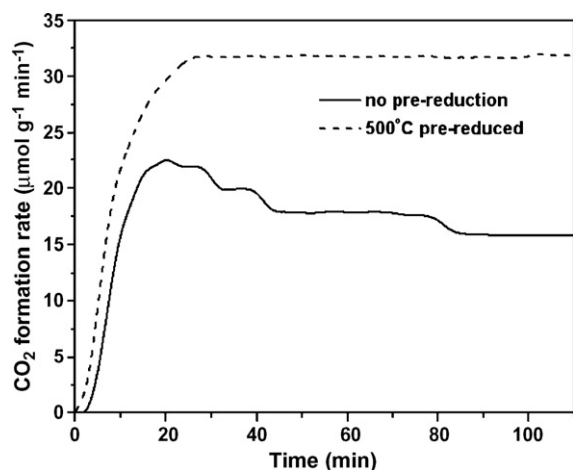


Fig. 3. CO<sub>2</sub> formation profiles during methane reaction over 25 wt% Bi<sub>2</sub>O<sub>3</sub>-GDC at 500 °C.

700 °C [24]. This may explain the observation that CO forms only at high temperatures.

The aforementioned induction period is eliminated over the pre-reduced catalyst, shown in Figs. 3 and 4 for reactions at 500 °C and 600 °C, respectively. Additionally, the jump in activity over the pseudo-steady-state value, presented in Figs. 2 and 4, can be eliminated by pre-reducing the catalyst, verifying that this phenomenon is caused by the presence of the surface oxygen species over the catalyst without pre-reduction. Notably, the formation of carbon oxides, CO and CO<sub>2</sub>, depends on surface oxygen species. Over the pre-reduced catalyst, where surface oxygen does not exist initially, oxygen must be extracted from the bulk to the surface. Since this oxygen extraction process provides surface oxygen species for oxidation more slowly than the initially present ones become available, the carbon oxides formation rates do not exceed the pseudo-steady-state value.

Fig. 3 also indicates that, with pre-reduction at 500 °C and reaction at the same temperature, the catalyst yields a higher CO<sub>2</sub> formation rate than obtained without pre-reduction. Notably, pre-reduction is considered to create some oxygen vacancies, a characteristic of doped ceria, noting that the methane oxi-

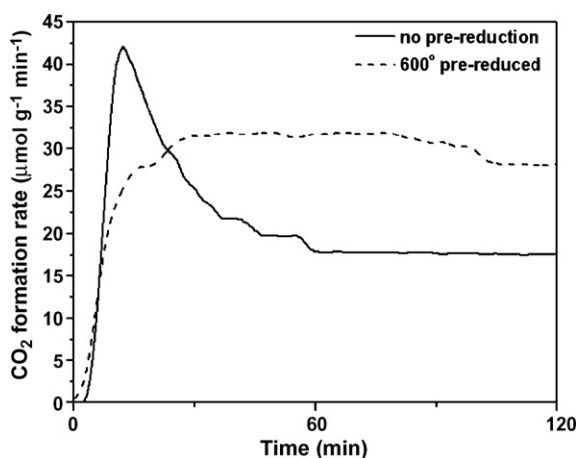


Fig. 4. CO<sub>2</sub> formation profiles during methane reaction over 25 wt% Bi<sub>2</sub>O<sub>3</sub>-GDC at 600 °C.

dation to produce CO and CO<sub>2</sub> occurs mostly over GDC as shown in Table 1. The oxygen vacancy can enhance the reaction activity, such as for CO oxidation [25,26]. Thus, it may be proposed that the oxygen vacancy created by pre-reduction enhances the methane oxidation. Fig. 4 reveals that, with the reaction at 600 °C, although the CO<sub>2</sub> formation rate of the non pre-reduced catalyst exceeds the pseudo-steady-state CO<sub>2</sub> rate of the catalyst that was pre-reduced at 600 °C, the former finally declines to a pseudo-steady-state level that is much lower than the latter. This trend is the same as that of the reaction at 500 °C. Notably, the jump in the CO<sub>2</sub> formation rate of the un-reduced catalyst over that of the pre-reduced catalyst at 600 °C, which does not occur at 500 °C, is considered to be associated with a higher activity of the reaction with the surface oxygen species of the un-reduced catalyst at higher temperature. Therefore, pre-reduction increases the pseudo-steady-state CO<sub>2</sub> formation rate. Notably, also, no CO is formed at 600 °C and lower temperatures over catalysts with or without pre-reduction, as shown in Figs. 2 and 5, indicating that pre-reduction promotes methane oxidation activity, noting that the total amount of carbon oxides formed can be related to methane conversion as discussed above.

Over GDC, Huang and Wang [24] reported that pre-reduction at 700 °C can make some lattice oxygen species to migrate from the bulk to near the surface without being consumed, and the CO<sub>2</sub> formation rate after an extensive pre-reduction can thus be increased. Nevertheless, the CO formation rate is decreased. In conclusion, CO<sub>2</sub> formation is associated with the surface lattice oxygen while CO formation depends on the O species coming directly from the bulk lattice [24]. This is in agreement with the observation as shown in Fig. 4 that CO<sub>2</sub> formation rate can be higher with 600 °C pre-reduction.

The appearance of a roughly constant CO<sub>2</sub> formation rate is regarded as being caused by the presence of surface Bi<sub>2</sub>O<sub>3</sub>, which acts as an oxygen reservoir, similar to an oxygen storage component used in an automobile catalytic converter but with dramatically higher oxygen content, promoting the formation of CO<sub>2</sub> as well as maintaining the formation rate. The constant CO<sub>2</sub> formation rate is related to a constant oxygen concentration in

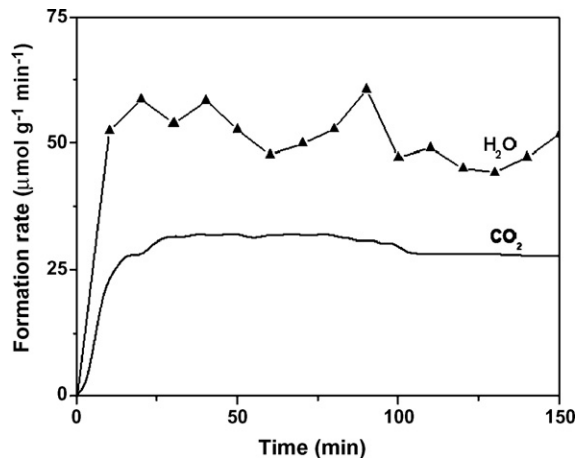


Fig. 5. Product formation profiles during methane reaction over pre-reduced 25 wt% Bi<sub>2</sub>O<sub>3</sub>-GDC at 600 °C.

the surface  $\text{Bi}_2\text{O}_3$ , via a process of quick oxygen replenishment from the bulk, which can occur because of the high oxygen conductivity of  $\text{Bi}_2\text{O}_3$  at  $780^\circ\text{C}$  [1,4]. Notably,  $\text{Bi}_2\text{O}_3$  is distributed over the surface. Additionally, the determining factor for  $\text{CO}_2$  formation is considered to be the existence of two neighboring oxygen species at the same time. Thus, a constant  $\text{CO}_2$  formation rate is possible if ample oxygen species present nearby. This constant supply of ample oxygen species is possible in the presence of the surface  $\text{Bi}_2\text{O}_3$ . In the temperature range considered in this work, the oxygen mobility is high enough to keep the surface  $\text{Bi}_2\text{O}_3$  with ample oxygen storage. Therefore, the surface  $\text{Bi}_2\text{O}_3$  acting as an oxygen reservoir is an important characteristic of the  $\text{Bi}_2\text{O}_3$ –GDC system.

During direct-methane SOFC operation, oxygen over the anode surface is constantly supplied from the cathode-side gas-phase via the bulk lattice of the oxygen-ion conducting electrolyte materials. In a traditional catalytic reactor, a long activity test over the  $\text{Bi}_2\text{O}_3$ –GDC system can deplete the O content to an extent that differs greatly from that of the anode catalyst. Therefore, a test period for the catalytic activity to just reach a pseudo-steady-state may be feasible for simulating the SOFC operation.

### 3.3. Effect of temperature on distribution of products of direct methane oxidation

For the following results,  $\text{Bi}_2\text{O}_3$ –GDC systems were pre-reduced at the reaction temperature to take advantage of the beneficial effect of pre-reduction on direct methane oxidation activity. Fig. 5 shows that, at  $600^\circ\text{C}$ , only  $\text{H}_2\text{O}$  and  $\text{CO}_2$  are formed and no  $\text{H}_2$  or  $\text{CO}$  is formed. Therefore, complete – not partial – oxidation of methane occurs. If it occurs over the SOFC anode, the converted methane fuel is fully utilized to generate the maximum possible amount of electrical current; nevertheless, syngas co-generation is not possible at this temperature. Huang and Wang [24] have observed that complete  $\text{CO}_2$  formation without  $\text{CO}$  formation may occur at a temperature below  $700^\circ\text{C}$  over GDC.

When a  $\text{Bi}_2\text{O}_3$ –GDC system is used, in the presence of surface  $\text{Bi}_2\text{O}_3$  and given its high content of mobile oxygen, the concentration of oxygen species existing over the catalyst surface can be increased. Therefore, the rate of  $\text{CO}_2$  formation is increased and the probability of complete  $\text{CO}_2$  formation increases. Notably,  $\text{CO}_2$  formation over GDC is associated with the surface lattice oxygen [24]. Notably, also, the GDC surface over  $\text{Bi}_2\text{O}_3$ –GDC provides the major activity for methane oxidation, given the large activity difference between  $\text{Bi}_2\text{O}_3$  and GDC, as also indicated in Table 1. Baker and Metcalfe [27] reported that, with direct methane oxidation over a perovskite oxide  $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ , complete oxidation of methane occurs at approximately  $400$ – $600^\circ\text{C}$  but only over the pre-oxidized catalyst. This finding is consistent with the association between the  $\text{CO}_2$  formation and the existing surface lattice oxygen.

As the reaction temperature increases to  $700^\circ\text{C}$ , both complete oxidation and partial oxidation of methane occur, as shown in Fig. 6. An induction period of about 2 min applies for  $\text{CO}$  for-

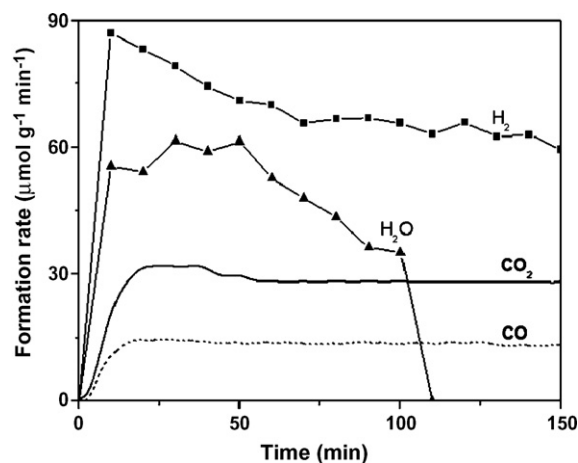


Fig. 6. Product formation profiles during methane reaction over pre-reduced 25 wt%  $\text{Bi}_2\text{O}_3$ –GDC at  $700^\circ\text{C}$ .

mation, because  $\text{CO}$  formation is related to bulk lattice oxygen species, similar to that over GDC [24]. Since a certain time is needed for the bulk lattice oxygen to be extracted to the surface for the reaction, an induction period without  $\text{CO}$  formation applies.

Fig. 6 also reveals that the  $\text{H}_2\text{O}$  formation suddenly declines to zero at about 120 min; however, the rate of  $\text{H}_2$  formation can be maintained roughly constant, because the formation of  $\text{H}_2\text{O}$  depends on the presence of hydrogen species at an active site. As observed by Huang and Huang [18], during direct methane oxidation over a Ni–YSZ anode in SOFC at  $800^\circ\text{C}$ , the active sites can be completely covered by the deposited carbon species such that no hydrogen can have presence at an active site. Furthermore, the interaction between the C species and the surface O species is stronger than that of the H species. Consequently, during methane decomposition, the produced C species is preferentially adsorbed over the active sites and thus, when the active sites are fully occupied by the C species, the produced H species can no longer be adsorbed to react with the surface lattice oxygen to form  $\text{H}_2\text{O}$ . Fig. 6 shows also that the  $\text{H}_2\text{O}$  formation rate declines gradually before a quick drop to zero, while both  $\text{CO}_2$  and  $\text{CO}$  formation rates remain roughly constant. This result indicates the preferential adsorption of the C species for oxidation with the lattice oxygen species.

As reported by Huang and Huang [28], at  $800^\circ\text{C}$  in an SOFC with Ni–YSZ anode and under both close- and open-circuit conditions,  $\text{H}_2\text{O}$  formation declines quickly, i.e. in about 10 min, to nearly zero but  $\text{H}_2$ ,  $\text{CO}$  and  $\text{CO}_2$  production rates are still substantial. This is similar to the above observation that  $\text{H}_2\text{O}$  formation rate declines quickly to zero, noting that the condition of this work is equivalent to open-circuit and the GC measurement interval is 10 min in this work. Notably, the H atoms are considered to be stored as interstitial H species. Bessler et al. [29] pointed out that the interstitial protons in bulk YSZ are known to be present in relatively high concentration with high enough diffusivity. The interstitial H species can associate to form  $\text{H}_2$  [30].

Fig. 7 shows that, as the reaction temperature increases from  $500^\circ\text{C}$  to  $700^\circ\text{C}$ , the  $\text{CO}_2$  formation rate of this pre-reduced

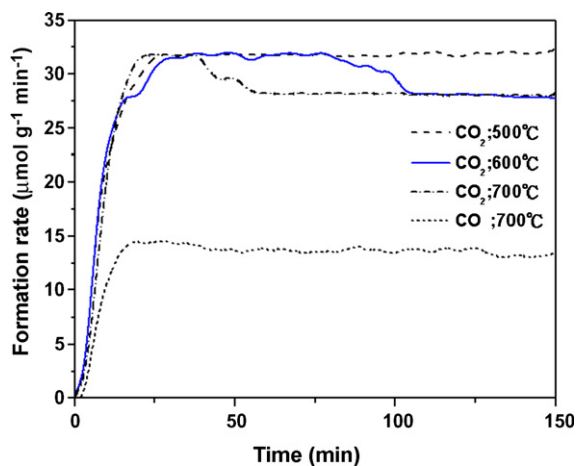


Fig. 7. CO<sub>2</sub> and CO formation profiles during methane reaction at various temperatures over pre-reduced 25 wt% Bi<sub>2</sub>O<sub>3</sub>–GDC.

catalyst jumps up with roughly the same extent, between 500 °C and 700 °C profiles, and its highest value is also roughly the same. This result differs from that over the un-reduced catalyst, as presented in Fig. 2, where both the peak height and the jumping speed vary markedly with temperature. This fact again verifies the presence of surface oxygen species on the catalyst without pre-reduction, whose oxidation rate increases with increasing temperature.

Fig. 7 also indicates that the pseudo-steady-state CO<sub>2</sub> formation rate declines slightly as the reaction temperature increases from 500 °C to 700 °C. The slight decrease or approximate constancy of the pseudo-steady-state CO<sub>2</sub> formation rate with increasing temperature over the pre-reduced catalysts is similar to that over the catalysts that had not been pre-reduced, as presented in Fig. 2. This result is thought to follow from the fact that, although a higher temperature means faster methane decomposition to surface C species, the mobility of the surface lattice oxygen species also becomes higher, reducing the probability of the existence of two oxygen species close to the surface C species; consequently, the rate of CO<sub>2</sub> formation declines. Huang and Huang [19] found that a higher oxygen-supply rate retards CO<sub>2</sub> formation, because CO<sub>2</sub> formation requires two O species in the vicinity of the C species. Notably, an increase in the oxygen-supply rate means an increase in the mobility of O species [19]. As the oxygen species becomes increasingly mobile, its contact time with the surface C species declines and thus the probability that two O species react with the surface C species to form CO<sub>2</sub> falls. However, the probability of CO formation increases.

The above results and discussion reveal that, under conditions under which intermediate-temperature direct-methane SOFCs can be simulated, the Bi<sub>2</sub>O<sub>3</sub>–GDC system completely oxidizes methane to form CO<sub>2</sub> and H<sub>2</sub>O at temperatures of around 600 °C or lower, while partial oxidation of methane to form CO and H<sub>2</sub> can occur only at a temperature of about 700 °C or higher. Therefore, the Bi<sub>2</sub>O<sub>3</sub>–GDC system can be applied to design SOFC anode materials for complete electrical generation at low temperature.

#### 4. Conclusions

Temperature-programmed and fixed-temperature reaction of direct methane oxidation, in the absence of gas-phase oxygen, were carried out over Bi<sub>2</sub>O<sub>3</sub>–GDC system. The results lead to the following conclusions:

1. Adding Bi<sub>2</sub>O<sub>3</sub> to GDC can promote the catalytic activity for direct methane oxidation.
2. A Bi<sub>2</sub>O<sub>3</sub> loading of 25 wt% in the Bi<sub>2</sub>O<sub>3</sub>–GDC system maximized the activity of direct methane oxidation.
3. Possible carbon deposition after the reaction of direct methane oxidation can be negligible over Bi<sub>2</sub>O<sub>3</sub>–GDC.
4. The methane oxidation activity is promoted with pre-reduction.
5. At temperatures of about 600 °C or lower, only CO<sub>2</sub> and H<sub>2</sub>O are produced.
6. CO and H<sub>2</sub> are produced only at a temperature of about 700 °C or higher.

#### References

- [1] N.M. Sammes, G.A. Tompsett, H. Nafe, F. Aldinger, *J. Eur. Ceram. Soc.* 19 (1999) 1801.
- [2] R. Irmawati, M.N. Noorfarizan Nasriah, Y.H. Taufiq-Yap, S.B. Abdul Hamid, *Catal. Today* 93–95 (2004) 701.
- [3] M. Mehring, *Coord. Chem. Rev.* 251 (2007) 974.
- [4] P. Shuk, H.D. Wiemhofer, U. Guth, W. Gopel, M. Greenblatt, *Solid State Ionics* 89 (1996) 179.
- [5] Y. Zeng, Y.S. Lin, *J. Catal.* 182 (1999) 30.
- [6] Y. Zeng, Y.S. Lin, *Appl. Catal. A: Gen.* 159 (1997) 101.
- [7] Y. Zeng, Y.S. Lin, *J. Catal.* 193 (2000) 58.
- [8] C. Xia, M. Liu, *Solid State Ionics* 144 (2001) 249.
- [9] Y.J. Leng, S.H. Chan, S.P. Jiang, K.A. Khor, *Solid State Ionics* 170 (2004) 9.
- [10] A.A. Yaremchenko, A.A. Valente, V.V. Kharton, I.A. Bashmakov, J. Rocha, F.M.B. Marques, *Catal. Commun.* 4 (2003) 477.
- [11] J.B. Wang, J.C. Jang, T.J. Huang, *J. Power Sources* 122 (2003) 122.
- [12] Y. Lin, Z. Zhan, J. Liu, S.A. Barnett, *Solid State Ionics* 176 (2005) 1827.
- [13] T.J. Huang, C.H. Wang, *Chem. Eng. J.* 132 (2007) 97.
- [14] V.R. Choudhary, S. Banerjee, A.M. Rajput, *Appl. Catal. A: Gen.* 234 (2002) 259.
- [15] J.B. Wang, Y.S. Wu, T.J. Huang, *Appl. Catal. A: Gen.* 272 (2004) 289.
- [16] T.J. Huang, T.C. Yu, *Catal. Lett.* 102 (2005) 175.
- [17] T.J. Huang, H.C. Lin, T.C. Yu, *Catal. Lett.* 105 (2005) 239.
- [18] T.J. Huang, M.C. Huang, *J. Power Sources* 168 (2007) 229.
- [19] T.J. Huang, M.C. Huang, *Chem. Eng. J.* (2007), doi:10.1016/j.cej.2007.03.015.
- [20] M. Ihara, K. Matsuda, H. Sato, C. Yokoyama, *Solid State Ionics* 175 (2004) 51.
- [21] N. Jiang, E.D. Wachsman, S.H. Jung, *Solid State Ionics* 150 (2002) 347.
- [22] V. Gil, J. Tartaj, C. Moure, P. Duran, *J. Eur. Ceram. Soc.* 27 (2007) 801.
- [23] K. Otsuka, Y. Wang, E. Sunada, I. Yamanaka, *J. Catal.* 175 (1998) 152.
- [24] T.J. Huang, C.H. Wang, *Catal. Lett.*, in press.
- [25] W.P. Dow, T.J. Huang, *J. Catal.* 147 (1994) 322.
- [26] W.P. Dow, T.J. Huang, *J. Catal.* 160 (1996) 171.
- [27] R.T. Baker, I.S. Metcalfe, *Appl. Catal. A: Gen.* 126 (1995) 297.
- [28] T.J. Huang, M.C. Huang, *Chem. Eng. J.* (2007), doi:10.1016/j.cej.2007.07.057. 2007.
- [29] W.G. Bessler, J. Warnatz, D.G. Goodwin, *Solid State Ionics* 177 (2007) 3371.
- [30] K.V. Hansen, K. Norrman, M. Mogensen, *J. Electrochem. Soc.* 151 (2004) A1436.