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Catalytic CO_2 reforming of methane over $Ir/Ce_{0.9}Gd_{0.1}O_{2-x}$

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Abstract

CO_2 reforming of methane over Ir loaded $Ce_{0.9}Gd_{0.1}O_{2-x}$ (Ir/CGO) has been studied between 600 and 800 °C and for CH_4/CO_2 ratios between 2 and 0.66 in order to evaluate its potential use as an anode material for direct conversion of biogas at moderate temperatures in solid oxide fuel cells. The catalyst exhibited a superior catalytic activity compared to the support alone and other Ir based catalysts. High CH_4/CO_2 ratios and temperatures were required to obtain the maximum H_2/CO ratio, which could never exceed unity. Long-term experiments were carried out, showing the excellent stability of the catalyst with time on stream. Carbon formation was totally inhibited (in most experimental conditions) or very limited in the most severe conditions of the study (800 °C, $CH_4/CO_2 = 2$). This carbon was found to be highly reactive towards O_2 upon TPO experiments.

Keywords: Methane; Carbon dioxide; Reforming; Iridium; Gd-doped ceria; SOFC; Biogas

1. Introduction

Solid oxide fuel cells (SOFCs) appear as an attractive "clean" technology to produce electricity from fuels such as biogas [1]. For proper operation of the fuel cell, CH_4, which is the main component of the biogas, has to be converted into hydrogen, which is then electrochemically oxidized on the anode to produce electricity. Direct reforming of CH_4 on the anode is highly desirable [2]. In the case of a biogas mainly containing CH_4 and CO_2, this can be achieved by dry reforming

$$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2 \quad \Delta H^0_{298} = +247\ \text{kJ/mol} \tag{1}$$

However the major concern with this reaction is severe carbon formation by

$$CH_4 \rightleftarrows C + 2H_2 \quad \Delta H^0_{298} = +75\ \text{kJ/mol} \quad CH_4\ \text{cracking} \tag{2}$$

$$2CO \rightleftarrows C + CO_2 \quad \Delta H^0_{298} = -173\ \text{kJ/mol}$$
Boudouard reaction (3)

In addition H_2 production can be affected by side reactions like

$$CO_2 + H_2 \rightleftarrows CO + H_2O \quad \Delta H^0_{298} = +41.2\ \text{kJ/mol}$$
Reverse Water Gas Shift (4)

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \quad \Delta H^0_{298} = -164.9\ \text{kJ/mol}$$
Methanation (5)

Finally, since water can be produced via reactions (4) and (5), the steam reforming

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \quad \Delta H^0_{298} = +206\ \text{kJ/mol} \tag{6}$$

may compete with dry reforming and affect the H_2/CO ratio.

The formation of carbon deposits which may deactivate the catalyst is certainly the main drawback to internal reforming. This is the reason why new anode materials with the property of inhibiting carbon formation have to be used.

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To this respect it has been shown recently that ceria can be successfully used as a key component of the anode for SOFC operating directly on dry reforming with an excellent resistance to carbon formation [3–5]. However, the activity of ceria is too low to permit operation of the anode at intermediate temperatures (typically less than or equal to 800 °C). The activity of ceria has to be improved by the use of an adequate active phase. Noble metals were found to be more resistant to carbon formation than Ni [5–9].

The present work aimed at preparing a catalyst of Ir deposited on Gd-doped ceria (CGO), with the composition $Ce_{0.9}Gd_{0.1}O_{2-x}$, and studying its catalytic activity in CH_4 dry reforming for varying CH_4/CO_2 ratios in order to evaluate its potential use for SOFCs operating at intermediate temperatures with biogas.

Special attention was devoted to the formation of carbon deposits after long-term catalytic testing under various working conditions. TPO experiments were used to evaluate the nature, the reactivity and the amount of deposits which could have formed during testing.

2. Experimental

2.1. Materials

A 0.16% $Ir/C_{0.9}G_{0.1}O_{2-x}$ (CGO) catalyst was prepared by conventional wet impregnation technique. A suspension of CGO powder (PRAXAIR 40.9 $m^2\,g^{-1}$) in an aqueous solution of $H_2IrCl_6 \cdot 4H_2O$ (Alfa Aesar) was maintained under stirring at room temperature for 0.5 h, evaporated under reduced pressure at 70 °C, and dried at 120 °C overnight. Catalyst was finally calcined for 6 h at 800 °C in air (2 °C min^{-1}, 7 l h^{-1}). The specific surface area of the catalyst after final calcination was 26.3 $m^2\,g^{-1}$.

2.2. Activity tests

Activity tests were carried out in a conventional flow system at atmospheric pressure, using 200 mg Ir/CGO catalyst introduced in a U-shaped quartz micro-reactor. The reaction mixture consisted of 25 vol.% CH_4, variable CO_2 concentration (12.5, 16.6, 25.0, and 37.5 vol.%) and N_2 as balance. The total flow rate at reactor inlet was 6 l h^{-1}.

Before activity measurements the catalyst was pretreated in situ at 800 °C under flowing N_2 for 2 h. Two kinds of experiments were then performed: (i) the conversion was measured at decreasing temperature from 800 °C down to 600 °C by steps of 50 °C, after reaching the steady state at each step, (ii) long-term experiments were carried out for 22 h at 800 °C, to study the stability of catalytic activity with time on stream.

The exit gases were analyzed using a gas chromatograph (Varian CP 2003 QUAD), equipped with TCD in order to measure the concentrations of CH_4, CO_2, H_2, and CO. The amount of H_2O formed during reaction was measured with an Edge Tech Dew Prime I hygrometer.

2.3. TPO experiments

After long-term experiments, the catalysts were purged in N_2 at 800 °C, cooled down to room temperature, and recovered for performing subsequent temperature programmed oxidation (TPO) experiment to characterise eventual deposits formed during reaction. Typically 50 mg of catalyst were introduced in a U-shaped quartz reactor flowed with 1% O_2/He (1.8 l h^{-1}) and heated up to 800 °C (linear heating rate of 5 °C min^{-1}). The signals characteristic of CO_2 ($m/e = 44$), O_2 ($m/e = 32$) and H_2O ($m/e = 18$) were continuously monitored as a function of time/temperature with a Pfeiffer Vacuum Omnistar quadrupole. CO was never formed during these experiments. Calibration of O_2 and CO_2 allowed quantitative measurements of O_2 consumption and CO_2 formation respectively.

3. Results and discussion

The CH_4 and CO_2 conversions over Ir/CGO were measured at steady state for various feed compositions and temperatures (Fig. 1). At 800 °C, CH_4 conversion is the lowest for $CH_4/CO_2 = 2$ (48%) and increases with decreasing CH_4/CO_2 ratio up to a maximum value of 73% for $CH_4/CO_2 = 1$. Surprisingly further increase in CO_2 concentration causes a slight decrease in CH_4 conversion (69% under $CH_4/CO_2 = 0.66$). Decreasing reaction temperature causes the decrease in CH_4 conversion, while maintaining the volcano shape of CH_4 conversion vs. CH_4/CO_2 curves, i.e., at all temperatures CH_4 is maximum for $CH_4/CO_2 = 1$. On the contrary to CH_4, at all temperatures, CO_2 conversion continuously increases with increasing CH_4/CO_2 ratio until reaching its maximum for $CH_4/CO_2 \geqslant 1.5$ without exhibiting a volcano shape. At 800 °C, CO_2 is totally consumed for $CH_4/CO_2 \geqslant 1.5$.

The observed decrease of CH_4 conversion for $CH_4/CO_2 < 1$ is in contradiction with data reported by Mark and Maier [10] with methane dry reforming over 1% Rh/Al_2O_3. On the Ir/CGO catalyst, large CO_2 concentrations appear to inhibit CH_4 conversion.

The catalytic activity for dry reforming at 600 °C ($CH_4/CO_2 = 1$) on Ir catalysts supported on various supports was recently reported [7,10,11]. The rate of CO_2 consumption varied from 0.2 up to 6 mol g Ir^{-1} h^{-1}. These values are very much lower than that obtained on Ir/CGO (36 mol consumed CO_2 per gram of Ir and

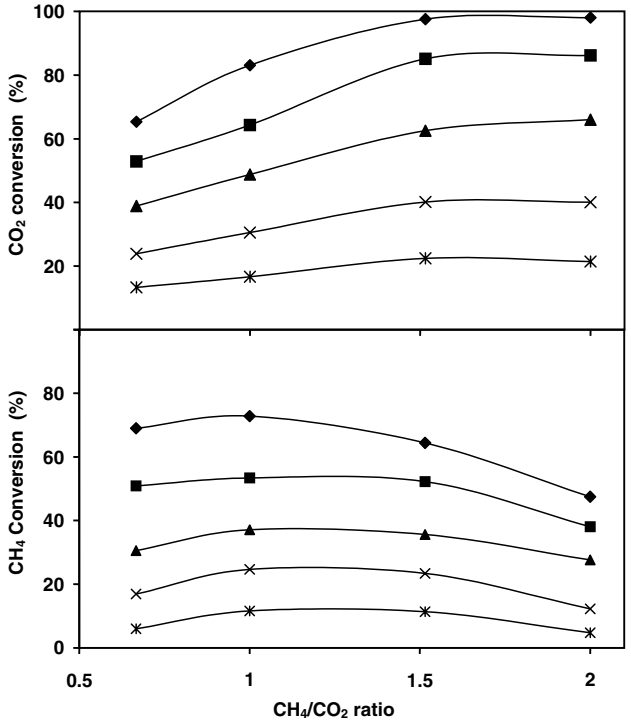

Fig. 1. Effect of CH_4/CO_2 ratio on CH_4 and CO_2 conversions at different temperatures: 800 °C (◆), 750 °C (■), 700 °C (▲), 650 °C (×), 600 °C (✳). Reaction conditions: catalyst weight = 0.2 g, flow rates: CH_4 = 1.5 l/h, CO_2 variable (0.75–2.25 l/h), N_2 balance, total = 6.0 l/h.

per hour). The Ir dispersion was shown to influence catalytic activity of Ir/Al_2O_3 catalysts [10]. It turned out that the catalytic activity in dry reforming over Ir/CGO at 600 °C was as high as that of a highly dispersed 0.5% Ir/Al_2O_3 (50% dispersion) reported earlier at a temperature 150 °C above [10]. Therefore dispersion effects cannot explain alone the highest activity of Ir/CGO. It is suggested that the CGO support strongly enhances the catalytic activity. A promoting effect with MgO was previously proposed to explain the enhanced activity of a mechanical mixture of MgO and Rh/SiO_2 [12,13]. In this study, CO_2 dissociation was thought to be the rate determining step of the reaction, being promoted by CO_2 enrichment on Rh surface due to improved adsorption on MgO. Bifunctional pathways involving metal and support have also been proposed for CH_4 dry reforming over Pt catalysts [14,15].

The results presented in Fig. 2 show that over Ir/CGO catalyst the molar H_2/CO ratio depends strongly on the temperature of the process as well as feed composition. In all cases the H_2/CO ratio was lower than the stoichiometric ratio of unity. The highest value ($H_2/CO = 0.98$) is observed at 800 °C with CH_4 in excess ($CH_4/CO_2 > 1$). At all temperatures, increasing CO_2 concentration in the feed lowers the H_2/CO ratio. All these data agree well with previous findings for Ir catalysts [10,11]. The decrease in reaction temperature causes the decrease of this effect.

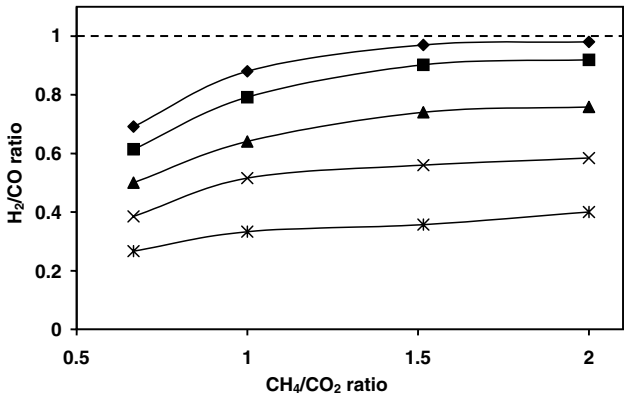

Fig. 2. Effect of CH_4/CO_2 ratio on H_2/CO ratio at different temperatures: 800 °C (◆), 750 °C (■), 700 °C (▲), 650 °C (×), 600 °C (✳). Reaction conditions as in Fig. 1.

Methanation reaction (reaction 5) could explain H_2/CO ratios lower than unity. We performed catalytic testing over Ir/CGO in the same range of temperatures using equimolar CO_2 and H_2 concentrations. CH_4 formation was never observed. This ruled out this reaction as an explanation for such behaviour. Therefore H_2/CO ratios lower than unity could be attributed to the significant contribution of the Reverse Water Gas Shift reaction (RWGS, reaction 4) in the overall process in agreement with other studies [7,16,17]. On the other hand, since water is produced via RWGS, steam reforming reaction has also to be considered. But this reaction seems to be slower than RWGS at lower temperatures.

The respective contributions of Reverse Water Gas Shift and steam reforming reactions as a function of temperature and CH_4/CO_2 ratio were evaluated by measuring the H_2O concentration in the products (Fig. 3). Irrespective of the feed composition it can be observed that H_2O concentration increases with increasing temperature until reaching a maximum value and then decreases at higher temperatures. At low temperatures, the increase in H_2O concentration can be attributed to the increasing contribution of RWGS reaction without significant influence of steam reforming. As temperature increases, the reaction rate of steam reforming increases more than RWGS, which leads to an increasing consumption of H_2O and causes the observed maximum and then the decrease in H_2O concentration with increasing temperatures. This effect is more pronounced at high CH_4 concentration (high CH_4/CO_2). This is expected since steam reforming rate depends on CH_4 concentration. Interestingly, steam reforming reaction is faster than RWGS for $CH_4/CO_2 = 2$ at 800 °C. Water is then consumed as it is formed and the overall process can be described by CO_2 reforming only. As a result H_2/CO is highest, being equal to unity.

Fig. 4 illustrates the catalytic activity of Ir/CGO as a function of time on stream for two feed compositions, respectively $CH_4/CO_2 = 1$ and 2. The relative conversion

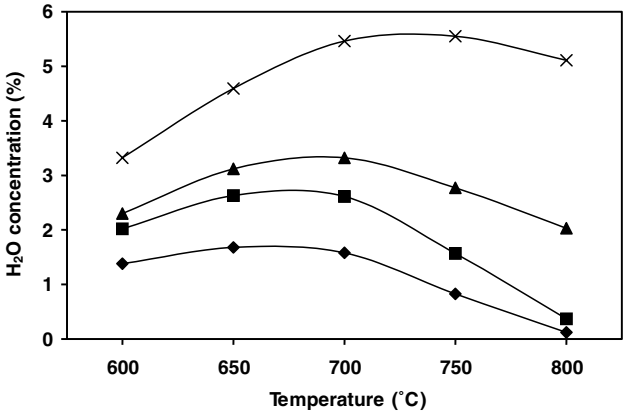

Fig. 3. Influence of the temperature on the formation of H_2O at varying CH_4/CO_2 ratios: $CH_4/CO_2 = 2$ (◆), 1.5 (■), 1 (▲), 0.67 (×). Reaction conditions as in Fig. 1.

$Conv/Conv_{max}$ of CH_4 and CO_2 ($Conv_{max}$ being the maximum conversion measured during the experiment) and the H_2/CO ratio are plotted. For all experiments the catalyst is observed to exhibit an activation period after which the maximum conversion is reached and no change in activity is further observed. The stability of the activity after the activation period is confirmed by the constant H_2/CO ratio. Under stoichiometric conditions, it takes about 11 h for Ir/CGO to reach steady state activity. This period is much shorter (5 h) when carrying out the reaction under CH_4 excess. Very long activation periods were also reported for CeO_2 and ZrO_2 supported Rh catalysts [18]. This phenomenon is not fully understood. Some variation in the oxidation state of the support with time on stream, being dependent on the CH_4/CO_2 ratio and being responsible for the improved catalytic activity, was proposed.

The most striking feature of the study is that no carbon deposition was observed after long-term testing over Ir/CGO below 800 °C irrespective of the CH_4/CO_2 ratio. This highlights the superior resistance of Ir/CGO to carbon formation with respect to other catalysts for which stoichiometric or oxidising (excess of CO_2) conditions are necessary to avoid carbon deposition [19,20].

It is worth to mention that the only case we observed carbon deposition in our experiments was after testing at 800 °C with $CH_4/CO_2 = 2$, that is under highly reductive conditions. Fig. 5 shows the CO_2 and O_2 profiles during TPO experiment after this test. The CO_2 evolution exhibits a maximum at 360 °C, coincidently with the maximum in O_2 consumption profile. The total amounts of consumed O_2 and released CO_2 derived from the profiles are found both equal to 125 μmol g of catalyst. This excludes any catalyst re-oxidation during TPO experiment. Moreover since no H_2O was formed simultaneously to O_2 consumption/CO_2 release, it can be stated that carbonaceous deposits are mainly in the form of carbon. The amount of carbon corresponds to 0.13 wt%, which is very small. The low temperature of combustion of this carbon (360 °C) indicates this carbon is highly reactive, which excludes the formation of graphite [15]. Recently after reacting CH_4 over CGO

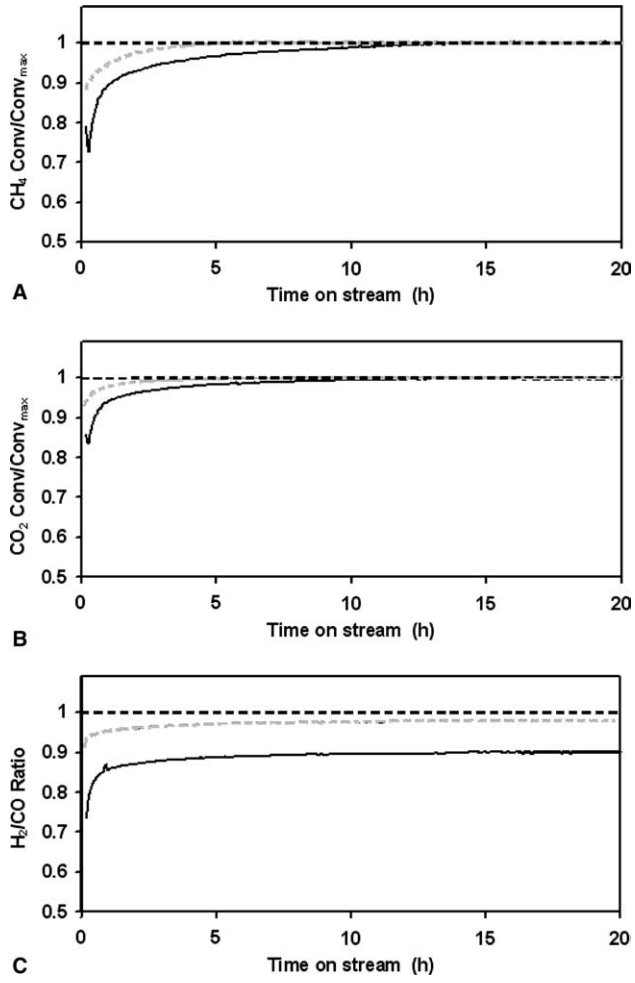

Fig. 4. Effect of time on stream on relative conversions of CH_4 (A), CO_2 (B), and on H_2/CO (C) for $CH_4/CO_2 = 2$ (black line) and 1 (grey dashed line). Reaction conditions as in Fig. 1.

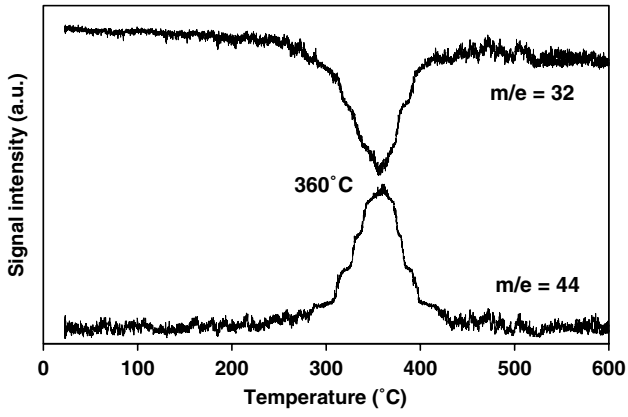

Fig. 5. CO_2 ($m/e = 44$) and O_2 ($m/e = 32$) profiles during TPO of Ir/CGO after 22 h reaction at 800 °C and $CH_4/CO_2 = 2$. TPO conditions: 1% O_2 in He, catalyst weight = 50 mg, flow rate = 1.8 l/h.

at 900 °C, Ramirez-Cabrera et al. [21] observed the formation of carbon exhibiting similar reactivity towards O_2. Thus our results confirm the high resistance of ceria based supports against carbon deposition.

4. Conclusions

Ir/CGO catalyst has useful methane dry reforming activity at temperatures lower than or equal to 800 °C, producing CO, H_2 and eventually some water. The varying production of water is explained by a competition between steam reforming of methane and Reverse Water Gas Shift reactions, depending on CH_4/CO_2 ratio and temperature. These side reactions explain also the variation of the H_2/CO ratio. This ratio cannot exceed unity and this is obtained when carrying out the reaction at 800 °C and in the presence of large CH_4 excess ($CH_4/CO_2 = 2$). The Ir/CGO catalyst shows a fairly high stability for CO_2 reforming of CH_4. This can be related to its very high resistance to carbon formation. This catalyst appears then as a good candidate for anode material in view of the direct conversion of biogas in SOFCs applications.

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