

# Catalytic CO<sub>2</sub> reforming of methane over Ir/Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2-x</sub>

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## Abstract

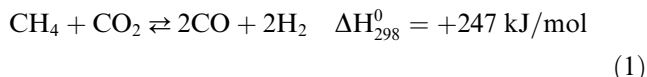
CO<sub>2</sub> reforming of methane over Ir loaded Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2-x</sub> (Ir/CGO) has been studied between 600 and 800 °C and for CH<sub>4</sub>/CO<sub>2</sub> ratios between 2 and 0.66 in order to evaluate its potential use as an anode material for direct conversion of biogas 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<sub>4</sub>/CO<sub>2</sub> ratios and temperatures were required to obtain the maximum H<sub>2</sub>/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<sub>4</sub>/CO<sub>2</sub> = 2). This carbon was found to be highly reactive towards O<sub>2</sub> upon TPO experiments.

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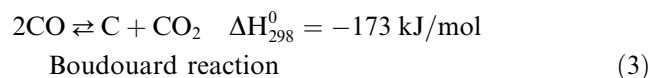
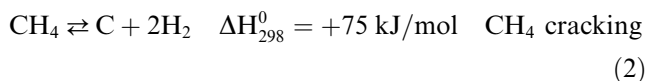
**Keywords:** Methane; Carbon dioxide; Reforming; Iridium; Gd-doped ceria; SOFC; Biogas

## 1. Introduction

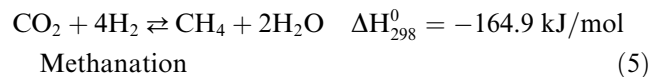
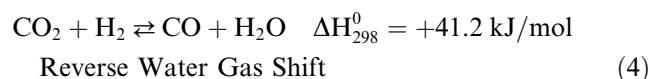
Solid oxide fuel cells (SOFCs) appear as an attractive “clean” technology to produce electricity from fuels such as biogas [1]. For proper operation of the fuel cell, CH<sub>4</sub>, which is the main component of the biogas, has to be converted into hydrogen, which is then electrochemically oxidized on the anode to produce electricity. Direct reforming of CH<sub>4</sub> on the anode is highly desirable [2]. In the case of a biogas mainly containing CH<sub>4</sub> and CO<sub>2</sub>, this can be achieved by dry reforming



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



In addition H<sub>2</sub> production can be affected by side reactions like



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



may compete with dry reforming and affect the H<sub>2</sub>/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  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-x}$ , and studying its catalytic activity in  $\text{CH}_4$  dry reforming for varying  $\text{CH}_4/\text{CO}_2$  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/ $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-x}$  (CGO) catalyst was prepared by conventional wet impregnation technique. A suspension of CGO powder (PRAXAIR 40.9  $\text{m}^2 \text{g}^{-1}$ ) in an aqueous solution of  $\text{H}_2\text{IrCl}_6 \cdot 4\text{H}_2\text{O}$  (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  $\text{min}^{-1}$ , 7 l  $\text{h}^{-1}$ ). The specific surface area of the catalyst after final calcination was 26.3  $\text{m}^2 \text{g}^{-1}$ .

### 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.%  $\text{CH}_4$ , variable  $\text{CO}_2$  concentration (12.5, 16.6, 25.0, and 37.5 vol.%) and  $\text{N}_2$  as balance. The total flow rate at reactor inlet was 6 l  $\text{h}^{-1}$ .

Before activity measurements the catalyst was pre-treated in situ at 800 °C under flowing  $\text{N}_2$  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  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2$ , and CO. The amount of  $\text{H}_2\text{O}$  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  $\text{N}_2$  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%  $\text{O}_2/\text{He}$  (1.8 l  $\text{h}^{-1}$ ) and heated up to 800 °C (linear heating rate of 5 °C  $\text{min}^{-1}$ ). The signals characteristic of  $\text{CO}_2$  ( $m/e = 44$ ),  $\text{O}_2$  ( $m/e = 32$ ) and  $\text{H}_2\text{O}$  ( $m/e = 18$ ) were continuously monitored as a function of time/temperature with a Pfeiffer Vacuum Omnistar quadrupole. CO was never formed during these experiments. Calibration of  $\text{O}_2$  and  $\text{CO}_2$  allowed quantitative measurements of  $\text{O}_2$  consumption and  $\text{CO}_2$  formation respectively.

## 3. Results and discussion

The  $\text{CH}_4$  and  $\text{CO}_2$  conversions over Ir/CGO were measured at steady state for various feed compositions and temperatures (Fig. 1). At 800 °C,  $\text{CH}_4$  conversion is the lowest for  $\text{CH}_4/\text{CO}_2 = 2$  (48%) and increases with decreasing  $\text{CH}_4/\text{CO}_2$  ratio up to a maximum value of 73% for  $\text{CH}_4/\text{CO}_2 = 1$ . Surprisingly further increase in  $\text{CO}_2$  concentration causes a slight decrease in  $\text{CH}_4$  conversion (69% under  $\text{CH}_4/\text{CO}_2 = 0.66$ ). Decreasing reaction temperature causes the decrease in  $\text{CH}_4$  conversion, while maintaining the volcano shape of  $\text{CH}_4$  conversion vs.  $\text{CH}_4/\text{CO}_2$  curves, i.e., at all temperatures  $\text{CH}_4$  is maximum for  $\text{CH}_4/\text{CO}_2 = 1$ . On the contrary to  $\text{CH}_4$ , at all temperatures,  $\text{CO}_2$  conversion continuously increases with increasing  $\text{CH}_4/\text{CO}_2$  ratio until reaching its maximum for  $\text{CH}_4/\text{CO}_2 \geq 1.5$  without exhibiting a volcano shape. At 800 °C,  $\text{CO}_2$  is totally consumed for  $\text{CH}_4/\text{CO}_2 \geq 1.5$ .

The observed decrease of  $\text{CH}_4$  conversion for  $\text{CH}_4/\text{CO}_2 < 1$  is in contradiction with data reported by Mark and Maier [10] with methane dry reforming over 1% Rh/ $\text{Al}_2\text{O}_3$ . On the Ir/CGO catalyst, large  $\text{CO}_2$  concentrations appear to inhibit  $\text{CH}_4$  conversion.

The catalytic activity for dry reforming at 600 °C ( $\text{CH}_4/\text{CO}_2 = 1$ ) on Ir catalysts supported on various supports was recently reported [7,10,11]. The rate of  $\text{CO}_2$  consumption varied from 0.2 up to 6 mol g  $\text{Ir}^{-1} \text{h}^{-1}$ . These values are very much lower than that obtained on Ir/CGO (36 mol consumed  $\text{CO}_2$  per gram of Ir and

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