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Methane steam reforming in water deficient conditions on Ir/$Ce_{0.9}Gd_{0.1}O_{2-x}$ catalyst: Metal-support interactions and catalytic activity enhancement

S.K. Cheah[a,b], L. Massin[a], M. Aouine[a], M.C. Steil[b], J. Fouletier[b,*], P. Gélin[a,*]

[a] Univ Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, F-69626, Villeurbanne, France
[b] Univ. Grenoble Alpes, CNRS, Grenoble INP, LEPMI, 38000 Grenoble, France[1]

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ABSTRACT

This work reports on the study of steam reforming of methane under water deficient conditions over Ir/$Ce_{0.9}Gd_{0.1}O_{2-x}$ (Ir/CGO) catalyst with very low Ir loading (0.1 wt% Ir). The catalyst surface was studied before and after testing by X-ray photoelectron spectrometry (XPS) and aberration-corrected high-resolution transmission electron microscopy (HRTEM) with 1 Å best resolution. Ir/CGO was pretreated at 1173 K in He flow with less than 0.5 ppm O_2 prior to catalytic testing. This led to the formation of Ir metal nanoparticles (NPs) with narrow-size distribution (2.5–6 nm, mean size of 4 nm in diameter). Ir/CGO slowly activated during reaction until reaching a steady state with tenfold increase of CH_4 conversion rate. The initial catalytic activity was consistent with surface metal sites being the main active sites and the CGO support having no effect on the CH_4 conversion rate except the inhibiting influence on the thermodynamically favoured carbon accumulation. After completion of the activation during reaction, Ir was present in the form of metallic NPs with smaller mean size (ca. 1.7 nm) than before testing, and oxidized Ir in 3 + /4 + states. Metal support interactions were thought to be responsible for Ir oxidation and redispersion at the CGO surface during reaction. It is proposed that the improved catalytic activity is due to a synergy between highly dispersed Ir species and the CGO substrate through delocalization of the catalytic reactions in the vicinity of the Ir metal particles.

1. Introduction

Internal reforming is an attractive technology to be implemented in Solid Oxide Fuel Cells feed with natural gas or alternative hydrocarbon fuels, for extending their applicability. Direct Internal Reforming (DIR) is generally achieved using conventional Ni-cermets, which requires large excess of water vapour, including often oxygen and/or carbon dioxide, to avoid carbon deposition [1–4]. Moreover, owing to the endothermicity of the reforming process, a local cooling of the cell is observed inducing thermal gradient and mechanical stress that dramatically lowers the lifetime of the cells [5,6].

Various alternatives have been proposed to overcome these difficulties. A first way of research has been to propose anode components, which are less sensitive to carbon deposition than nickel, *i.e.*, ceria-containing anodes [7,8], ceria-doped catalysts [9–11], *etc.* Vernoux et al. [12] have proposed a new concept, *i.e.*, the Gradual Internal Reforming (GIR), in which the two anode functions *i.e.*, the steam reforming of the fuel and its electrochemical oxidation producing water vapour, are separated. The production of water vapour is used for the fuel reforming all along the anode channel. Consequently, only a small quantity of water vapour is required at the inlet of the cell. This concept has been experimentally demonstrated [13], and applied for other gases than methane [14–16]. More recently, using an original anode microstructure, state of the art anode materials, *i.e.* Ni-YSZ cermet, has been tested over 2000 h without noticeable deterioration of the performance of the cell feed with pure and dry hydrocarbons [17,18]. This feature was obtained, both by deposition of a catalytic layer onto the anode and by the design of an original current collector.

Proper GIR operation requires that the catalyst layer exhibits the following specific properties: (i) sufficiently high catalytic activity towards methane steam reforming (MSR), and (ii) high resistance against the thermodynamically favoured carbon formation due to high CH_4/H_2O (C/S) molar ratio at the anode (near to 10/1). In addition, decreasing operation temperatures of SOFCs (from 900 to 650 °C) is one of the main current objectives to improve the lifetime of the cells [19]. Ni is a commonly used MSR catalyst. It could meet the requirement (i). However, it prones to deactivate in water deficient conditions due to carbon formation [20,21]. Noble metals (Pt, Ru, Ir, Pd and Rh) are considered to be good substitutes for Ni: they are moderately active for steam reforming but highly resistant to carbon deposition [22]. These

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* Corresponding authors.
E-mail addresses: jacques.fouletier@lepmi.grenoble-inp.fr (J. Fouletier), patrick.gelin@ircelyon.univ-lyon1.fr (P. Gélin).
[1] Institute of Engineering Univ. Grenoble Alpes Univ. Savoie Mont Blanc, LEPMI, 73000 Chambery, France.

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metals are, obviously, expensive; however the metal loading is noticeably lower than 30–40 wt% typically used in Ni-YSZ cermets. Postole et al. [23] have given an overview of the literature data dealing with MSR on noble metal based catalysts. It should be pointed out that, in most of the studies, the noble metal loading was in the range 1–5 wt% and the C/S ratio was less than 1, which is not the GIR condition. It has also been shown that pure ceria and doped ceria are active for CH_4/H_2O reactions and particularly resistant to carbon formation under GIR conditions [10,24]. Even if these materials revealed a poor catalytic activity for methane reforming, they are interesting owing to this specific property.

Interestingly, it has been shown that doping a Gd-doped ceria ($Ce_{0.9}Gd_{0.1}O_{2-x}$) by trace amount (0.1 wt%) of iridium (referred to as Ir/CGO) improves by more than two orders of magnitude the catalytic activity while maintaining the resistance to carbon formation under GIR conditions [11,18]. The improvement is not simply due to the Ir addition because it has been shown that the same amount of Ir supported on alumina catalyst does not induce the same activity [11]. This feature has also been pointed out by Gorte et al. with other noble metals as catalysts [25,26]. Consequently, the synergetic role of Ir catalyst and CGO support has been suggested [11]. However, since the Ir amount is very low and approaching the sensitivity limits of physicochemical characterization techniques, the mechanistic study on the catalytic process is difficult and the conclusions often speculative because the nature of the catalytic sites involved in the reaction steps of the mechanism are not known so far.

On the basis of thermodynamic calculations, it has been shown that, above 650 °C, the catalytic conversion of methane by water vapour is essentially governed by steam reforming, methane cracking, and water gas shift (WGS) reactions:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{1}$$

$$CH_4 \rightarrow C + 2H_2 \tag{2}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{3}$$

The water deficient conditions are thermodynamically favourable to carbon formation [21,27]. However, it has been shown that the nature of the catalytic layer has an important role on carbon deposition, which indicates that the reactions proceed via kinetic control over the catalyst and not by thermodynamic control. It is well admitted that Ni-YSZ cermets cannot be used as anodes in SOFCs fed with dry methane, owing to the high catalytic activity of nickel for carbon deposition. It has also been observed that carbon deposit does not form over ceria-based anodes [11,24,28].

It has been proposed that CGO catalyst activates methane with formation of reactive CH_x species, which reduce Ce(IV) to Ce(III) and produces CO and H_2 [10]. There has been a general agreement in the literature to conclude that the mechanism of CH_4/H_2O reaction over ceria based materials proceeds according to the following two steps, *i.e.*, a reduction of ceria by adsorbed molecules of methane, and a step involving H_2O inducing the re-oxidation of Ce^{3+} ions:

$$CH_4 + 2\,Ce_{Ce}^{X} + O_O^{X} \rightarrow 2\,Ce'_{Ce} + V_O^{\bullet\bullet} + 2\,H_2 + CO \quad \text{(step 1)} \tag{4}$$

$$2\,Ce'_{Ce} + H_2O + V_O^{\bullet\bullet} \rightarrow 2Ce_{Ce}^{X} + O_O^{X} + H_2 \quad \text{(step 2)} \tag{5}$$

This mechanism is consistent with the first order rate of the H_2 production with respect to methane partial pressure [24,29]. The rate of methane reforming is controlled by the slow reaction of methane with oxygen on doped-ceria (step 1), and the rapid reaction between water vapour and reduced CGO (step 2) [24]. However, it has also been shown that doping CGO with Ir, even in a very small amount, increased considerably the rate of methane consumption with only small amounts of carbon deposit. Consequently, a three-step mechanism involving Ir sites and CGO surface sites has been suggested, using Kröger-Vink notation [30]:

- the partial decomposition of CH_4 molecules over Ir sites (referred to as s) to form H_2 and $CH_{4\text{-}x}$ species (step 1'):

$$CH_4 + s \rightarrow CH_{4\text{-}X}\text{-}s + \frac{X}{2}H_2 \tag{6}$$

- the reaction of $CH_{4\text{-}x}$ species with reactive oxygen species on the CGO surface producing CO and H_2, with partial reduction of the ceria surface (step 2'):

$$CH_{4\text{-}x}\text{-}s + O_O^{\times} + 2\,Ce_{Ce}^{\times} \rightarrow CO + \frac{(4\text{-}x)}{2}H_2 + V_O^{\bullet\bullet} + 2\,Ce_{Ce}^{'} + s \tag{7}$$

- a final step of regeneration of the oxygen ions of CGO lattice, involving H_2O (step 3'):

$$H_2O + V_O^{\bullet\bullet} + 2\,Ce_{Ce}^{'} \rightarrow H_2 + 2\,Ce_{Ce}^{\times} + O_O^{\times} \tag{8}$$

In the absence of water vapour, the ceria substrate is progressively reduced by methane (steps 1' and 2'). Under GIR conditions with dry methane, the electrochemical oxidation of methane provides the water vapour needed for the substrate oxidation (step 3') avoiding the poisoning of the anode by graphitic carbon deposition.

In order to improve the performance of the catalyst, it is necessary to determine the nature of the active sites and to identify the parameters influencing their formation or degradation. It should be pointed out that the step 1' of the proposed mechanism, which involves surface Ir^0 sites, does not explain satisfactorily the high increase of the rate of methane conversion with addition of only trace amounts of noble metals on CGO support. Noble metal on alumina support does not perform equally well as the one with CGO support.

The present work consisted in (i) studying an Ir/CGO catalyst containing as low as 0.1 wt% Ir in the methane steam reforming reaction for potential use as anode material in SOFCs operated in GIR mode (water deficient conditions); (ii) obtaining experimental characterizations, which allow describing more precisely the active sites and explaining the catalytic behaviour. To this purpose, special care was paid to controlling the level of O_2 impurity present in the gases used for both activation and reaction in order to identify the key parameters influencing the activity. The samples were thoroughly analysed by XPS and ETEM before and after CH_4/H_2O reaction under water deficient conditions (GIR mode). The catalytic activity of the Ir/CGO catalyst was observed to be improved by one order of magnitude during one-day testing. Changes in the oxidation state and the dispersion of the iridium were clearly evidenced. The existence of metal support interactions between the noble metal and the CGO support was discussed to account for the strong improvement of the catalytic activity in methane steam reforming.

2. Experimental

2.1. Samples preparation

The powder sample was Ir/CGO (0.1 wt% Ir) prepared by impregnation of $Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO from Praxair, 43 $m^2\,g^{-1}$) with a solution of iridium acetylacetonate (Aldrich) in toluene. After complete evacuation of the solvent under reduced pressure, the catalyst was dried overnight at 393 K and calcined in flowing O_2 at 623 K for 6 h so as to obtain the so-called fresh Ir/CGO sample.

2.2. Physicochemical characterization

An FEI TITAN ETEM G2 80–300 kV instrument (0.085 nm resolution) equipped with an objective Cs aberration corrector was used for the observations of the catalyst. The microscope was also equipped with an energy dispersive X-ray (EDX) analyzer (SDD X-Max 80 m m^2 from Oxford Instruments) and a Gatan Imaging Filter Tridiem ERS (Gatan Instruments). The samples were crushed in ethanol and the solution was ultrasonically stirred before dropping it on a holey carbon-covered