Efficient hydrogen production from methane over iridium-doped ceria catalysts synthesized by solution combustion

Georgeta Postole [*], Thanh-Son Nguyen, Mimoun Aouine, Patrick Gélin,
Luis Cardenas, Laurent Piccolo [*]

Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS & Université Lyon 1, 2 Avenue Albert Einstein, 69626 Villeurbanne Cedex 9, France

ARTICLE INFO

ABSTRACT

This study reports on the investigations performed on an Ir-CeO$_2$ (0.1 wt% Ir) catalyst, prepared for the first time by one-step solution combustion synthesis (SCS) and submitted to a number of analyses: N$_2$ volumetry, elemental analysis, X-ray diffraction, scanning electron microscopy, aberration-corrected high-resolution transmission electron microscopy, X-ray photoelectron spectroscopy, and temperature-programmed methods. The catalyst was studied in the steam reforming of methane (SRM) at 750 °C, under water-deficient conditions (CH$_4$/H$_2$O ratio of 10) and in the presence of 220 ppm H$_2$S. The obtained catalytic performances were compared with those of an Ir/CeO$_2$ catalyst prepared by incipient wetness impregnation (IWI). The influence of the support and the metal was investigated through testing of Ir/SiO$_2$-Al$_2$O$_3$-IWI and Rh-CeO$_2$-SCS catalysts, respectively. Using CeO$_2$ as carrier, Ir-based catalysts are highly efficient in SRM and resistant to carbon and irreversible sulfur poisoning. The catalytic activity of Ir-CeO$_2$-SCS is superior to that of Ir/CeO$_2$-IWI. Unlike the Ir-CeO$_2$ catalyst, Ir/SiO$_2$-Al$_2$O$_3$ is completely deactivated in presence of sulfur, while Rh-CeO$_2$-SCS does not recover its initial activity after exposure to an H$_2$S-containing feed.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The main advantage of solid oxide fuel cells (SOFCs), operating at high temperatures (600–1000 °C) and using ceramic membranes that conduct oxygen anions, is their capacity to operate not only with hydrogen but also with hydrocarbon-based fuels, such as natural gas [1]. The operation of SOFCs fed with natural gas is based on the internal conversion of methane, on the anode side, to produce H$_2$ and CO by reforming reactions ("direct internal reforming"). Nickel–yttria-stabilized zirconia (Ni–YSZ) is the most commonly used material for fabricating SOFC anodes and works satisfactorily with H$_2$ because of the high electrocatalytic activity of Ni [2,3]. Unfortunately, with natural gas under cell operation conditions the dissociative adsorption of CH$_4$ on the anode surface competes with the desired reforming processes, resulting in uncontrolled carbon deposition [4]. Furthermore, S-containing compounds found as impurities in hydrocarbon-based fuels react with the nickel surface

to form very stable Ni$_x$S$_y$ compounds, which block reactant access to the Ni surface [5].

In order to mitigate the issue of carbon formation over Ni–YSZ anodes, the deposition of a catalytically active layer onto the anodic electrode was first applied for operation in CO$_2$/isooctane mixtures [6]. Strong improvements with respect to operation without the catalytic barrier could be achieved, but carbon formation on the catalyst could not be totally avoided. The concept was extended to the use of chemically inert barrier layers added to commercial Ni–YSZ anodes for operation with methane [7]. This architecture was successful to extend the range of coke-free operation, even with pure methane. The main role of the inert barrier layer is to impede the transport of electrochemically formed products from the three-phase region toward the fuel channel, thus inhibiting coking and facilitating the reforming process. It helps also preventing the direct contact of the Ni anode with high hydrocarbon concentrations. Further, a concept of gradual internal reforming (GIR) was proposed for SOFCs fed with hydrocarbon fuels (e.g. methane) [8,9]. The principle is that SRM and electrochemical oxidation of hydrogen can be self-sustained, because the latter reaction produces the water needed by the former one. The main advantages of GIR are a delocalization of the high endothermicity

* Corresponding authors. Tel.: +33 427465734.
E-mail addresses: georgeta.postole@ircelyon.univ-lyon1.fr (G. Postole), laurent.piccolo@ircelyon.univ-lyon1.fr (L. Piccolo).

of steam reforming and a potential operation in dry methane after initiation of the reforming reaction with a small amount of steam [8,9]. The practical applicability of such an SOFC architecture was demonstrated for a system continuously operated with hydrogen, methane, and ethanol, without water, O_2, or CO_2 additions, delivering a rather stable power output for nearly 400 h [10].

Noble metals (NMs) such as Pt-group ones, which are too expensive to be used in conventional industrial reformers, can be materials of choice for the barrier layer in the anode compartment of SOFCs integrating a GIR concept and directly fed with natural gas. NM-based catalysts present high activity in methane reforming, durability, low coking tendency, and resistance to poisoning by sulfur. Thus, they may be used for the production of synthesis gas at very low steam/carbon ratios [11–13]. As the use of GIR requires the development of specific catalysts moderately active in steam reforming but highly resistant to carbon deposition, the efficiency of NM-based catalysts with low metal loading (much lower than 30–40 wt% typically used for Ni-based steam reforming catalysts) can minimize the cost, making them versatile for this application. The literature concerning steam reforming of hydrocarbons on NM-based catalysts shows the use of 0.1 up to 5 wt% NM loadings. Furthermore, as seen in Table 1 which summarizes literature findings [11,13–24] for SRM over NM catalysts, most of these studies were performed under oxidative atmosphere (H_2O/C ratio higher than unity), between 350 and 750 °C. Even though a rigorous comparison of the data is difficult due to the variety of experimental conditions (temperature, pressure, reactant gas composition) and catalyst characteristics (metal dispersion, support type), these reports demonstrated that SRM proceeds with high activity and stability over metals such as Ru, Rh, Ir, Pd, Pt. Wei and Iglesia [17,21,23,24] have found that, whatever the nature of the NM, the SRM reaction rate increases linearly with CH_4 pressure, but it is not influenced neither by H_2O nor by the nature of the support. These observations are in line with those reported by Berman et al. [25] who carried out the reaction at high temperatures (700–900 °C) over a Ru-based catalyst. Conversely, at low temperatures (450–500 °C), the reaction order toward methane was found much less than unity. Gorte et al. [15,26] have found that ceria-supported NMs are much more active than NMs supported on inert oxides. Mortola et al. [22] have demonstrated that, when Pt is supported on a material containing CeO_2, its dispersion does not have a crucial influence on the number of converted CH_4 molecules. The stability and activity of the SRM catalysts depend on the balance between the rate of methane decomposition over the metal particles and the rate of carbon removal. Due to its redox properties, ceria promotes the oxidation of carbonaceous adsorbates [27].

This work is an extension of the studies dealing with the development of NM-based catalysts for hydrogen production from CH_4/H_2O mixtures, for both SOFC and automotive applications (CH_4 can be eliminated from automotive exhaust streams by SRM in reducing environments, and the produced H_2 can serve as a NO reductant [26]). Based on the preliminary experience acquired in the use of iridium-based catalysts for SOFC applications [9,28,29], this study has been focused on a non-conventional one-step method for the preparation of Ir-doped ceria, namely solution combustion synthesis (SCS). It is well known that the method of preparation and the applied treatment affect the strength of metal-support interaction and the metal dispersion, which in turn strongly influence the final performances of dispersed metal catalysts. SCS has been recently used to prepare catalysts for reforming and combustion reactions, and even to synthesize advanced materials for SOFCs [30,31]. To the best of our knowledge, the present work is the first attempt to synthesize Ir-based catalysts by such a method. It involves the one-pot combustion of cerium and metal salts in the presence of water and a fuel, and generates high degree of metal dispersion [32,33].

In this paper, after a brief report on structural aspects (this part will be detailed elsewhere [34]), it will be shown how the catalyst can be best activated for SRM and how it compare to other types of catalysts (preparation method, support, metal) in terms of activity, stability and resistance to irreversible sulfur poisoning. In addition, the role of Ir doping and of S reacted with the catalyst are revealed by temperature-programmed reduction with methane and X-ray photoelectron spectroscopy.

2. Experimental

2.1. Materials synthesis

For the preparation of pure CeO_2, the solution contained $(NH_4)_2Ce(NO_3)_6$ [Sigma Aldrich, 99.99%] and NH_2CH_2COOH [Sigma Aldrich, 99%] (glycine, used as the fuel) in the molar ratio 1:2.67. These values were chosen to obtain stoichiometric proportions of oxidizer and fuel, i.e., with the oxidizing/reducing valence ratio of the redox mixture equal to 1 [35]. For the preparation of 0.1 wt% Ir-CeO_2, 10^{-3} mol% of $(NH_4)_2IrCl_6$ [Strem Chemicals, 99%] was additionally employed. Practically, a 300 cm^3 borosilicate beaker containing a mixture of $(NH_4)_2Ce(NO_3)_6$ (5.00 g) and glycine (1.82 g) without/with $(NH_4)_2IrCl_6$ (4 mg for 0.1 wt% Ir-CeO_2), and 30 mL of deionized water, was introduced into a muffle furnace (Carbolite ELF 11/6) maintained at 350 °C. At the point of complete dehydration (within 5–10 min), the solution started to boil with frothing and foaming, and ignition took place after a few seconds with rapid increase of the temperature (up to ca. 1000 °C) simultaneously to the evolution of a large quantity of gases. This yielded a voluminous solid product within a few minutes. In order to verify the reproducibility of the SCS preparation, three different batches of Ir-CeO_2 catalysts were similarly synthesized and named: Ir-CeO_2, Ir-CeO_2(2) and Ir-CeO_2(3).

On the basis of thermogravimetric measurements (see Section 3), CeO_2 could be used as-prepared for the catalytic investigations, while for Ir-CeO_2 a thermal treatment was required. In this work, four different thermal treatments were applied to the Ir-CeO_2 reference sample, as described in Table 2. In all cases, the temperature was increased with a heating rate of 5 °C min^{-1} up to the desired value, and a total flow rate of 7 L_{NTP} h^{-1} was used, irrespective of the atmosphere chosen for the pretreatment.

For comparison, a Rh-CeO_2 catalyst was prepared by SCS using the same procedure and $RhCl_3$ [Aldrich, 38–40% in water] as the NM precursor. The as-prepared powder containing 0.05 wt% Rh (number of metal atoms similar as in the 0.1 wt% Ir) was submitted to an oxido-reducing treatment, as described for the Ir-CeO_2-oxred catalyst. The obtained catalyst is denoted Rh-CeO_2-oxred.

In addition, an Ir/CeO_2 catalyst was prepared by conventional IWI of ceria, itself prepared by SCS. For the impregnation step, $Ir(C_5H_7O_2)_3$ (acetylacetonate, Sigma-Aldrich, purity 97%) was dissolved in toluene using the concentration needed to obtain the desired Ir loading (0.1 wt%, measured loading 0.14 wt%). The sample was allowed to maturate in ambient conditions for 2 h and dried at 120 °C overnight, then treated under pure hydrogen flow at 500 °C for 6 h. This led to well-dispersed iridium particles with sizes in the same range as found for the SCS catalysts, i.e. 1–3 nm (Table 3). The obtained powder is denoted Ir/CeO_2-IWI.

Finally, a so-called Ir/ASA catalyst was prepared by IWI of amorphous silica–alumina (Sasol SIRAL-40, 500 m^2 g^{-1}, pre-calcined in air at 550 °C for 3 h), using the same impregnation-reduction procedure. The catalyst loading was 0.22 wt% and the Ir particle size was 1.4 ± 0.3 nm.