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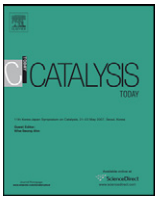

Screening of ceria-based catalysts for internal methane reforming in low temperature SOFC

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ABSTRACT

Ceria-based catalysts have been assessed for internal methane reforming at low temperature (400–600 °C) in Solid Oxide Fuel Cell (SOFC). A combinatorial library of 15 metal (Cu, Pt, Ni) supported ceria was prepared using wet impregnation method. The ceria-based oxides are undoped or doped with metal transition (Zr) or by rare earth (Gd or Pr). The effect of the metal, the dopant and the surface area on the catalytic performances was investigated in high-throughput manner using a 16-parallel reactor. The catalysts were assessed in two different conditions, (i) in CH_4 rich condition and (ii) in model reformate condition. Catalytic performances are very metal depending. In dry conditions, Cu-based catalysts do not produce H_2 whereas Ni-catalysts are very active despite low carbon balance. However, when water and CO_2 are added in the feed, the nature of the ceria plays an important role in the catalytic performances. At low temperature ($T < 550$ °C), most of Ni/ceria catalysts are not active under reformate conditions at low temperature while Pt catalysts appear more robust with respect to the conditions. From unsteady state parallel studies, we suggest that surface hydroxyl on ceria are the active species.

1. Introduction

Solid Oxide Fuel Cells (SOFCs) are considered as a very efficient technologies to produce electrical energy from H_2. However, H_2 storage and distribution issues make its use non-appropriate for transport, domestic and remote applications. On the other hand, the internal reforming is an attractive solution to overcome H_2 storage and distribution issues. The large resource, high H/C ratio and distribution infrastructure make natural gas the fuel of choice [1]. Unfortunately, direct hydrocarbon reforming in conventional SOFC causes long term issues due to coke formation over Ni/ZrO_2 based anodes [2]. Due to material limitations, conventional SOFC systems operate at very high temperatures (1000 °C). Intense R&D efforts aim at decreasing the operating temperature in order to limit ageing issues of the diverse components including interfaces and sealing. However, to the best of our knowledge, the development of catalysts for internal reforming of methane is scarce for low temperature (400–600 °C). In a previous high-throughput screening [3], we have identified ceria-based catalysts as potential candidates for H_2 production at low temperature. We found out that the performances in autothermal conditions were very influenced by the nature of the metal and ceria dopant.

The objective of this study is to assess ceria-based catalysts for the H_2 production from methane at low temperature in a SOFC. Among the questions that we have addressed: Can Ni, the usual reforming metal at high temperature, be active at low temperature? Can Cu be an alternative metal with reduced coking effects? What are the effects of H_2O and/or CO_2 on the catalytic performances and time on stream stability?

Among the various scenarios using natural gas as fuel [4], two technological options can be considered: (A) the anode is fed by methane stream. CO and H_2 can be obtained from selective oxidation while H_2O and CO_2 are produced in situ and then can be further used as reforming agents (steam and dry reforming). In this scenario, the main objective is to investigate methane activation on suitable catalysts enclosed into the anode layer in SOFC operating conditions, i.e. by simulating a continuous low flow of oxygen coming from the electrolyte. (B) The anode is fed directly by a process gas which is basically a methane rich mixture with variable amounts of H_2O and CO_2 corresponding to a downstream reformate feed (CO_2, H_2, CO, H_2O and CH_4) in domestic application [5] or a biogas composition obtained from biomass or municipal waste fermentation.

In this study, we report the synthesis and parallel testing of a wide range of modified metal impregnated ceria-based catalysts as potential SOFC anodes at low temperature through two potential scenarios (A and B).

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2. Experimental

2.1. Samples preparation

Five cerium-based powders were supplied by Rhodia (Ce-H, CeZr-H, CePr-H and CeGd-L) and purchased from Nextech Materials (CeGd-H). Compositions and surface area data are given in Table 1. For the same CGO composition, two samples with high (H) and low (L) surface area have been tested. The 15 supported catalysts were prepared by wetness impregnation by combining the 5 different supports and 3 metals (Pt, Ni, Cu) (Table 1). Typically, the wet impregnation was carried by the dissolution of appropriated metal salt in water at concentrations approaching saturation. The support was impregnated and water was added until all the powder is soaked. The slurry was vigorously stirred for 2 h, dried in oven at 100 °C for 1 h then calcined under static air at 500 °C for 8 h with a rate of 60 °C/h.

2.2. Samples characterization

Prior catalytic tests, all catalysts were characterized by X-ray diffraction (XRD) using a Bruker D5005 Diffractometer with the Cu Kα radiation. The amount of metal (Ni, Cu, Pt) was measured by ICP (Activa Horiba). Porous structural data are summarized in Table 1. Transmission electron microscopy (JEOL 2010 LaB6) studies were carried out on fresh Ce-H sample and Pt-Ce-H samples (after Pt impregnation and calcination). The specific surface areas (BET method) were determined by N_2 physisorption at 77 K (ASAP 2020 Micromeritics; desorption conditions 10^{-2} mbar; 300 °C for 3 h) for all samples at different stages; cerium-based supports as received and fresh catalysts (after impregnation and calcinations).

2.3. Testing equipments and methods

Catalytic tests were carried out on the Switch 16 parallel reactor (AMTEC GmbH-CNRS) as described in [6]. This multi-channel device consists of 16 parallel reactors in Inconel^{TM} with two independent feeding systems. In this study, the switching 16 port valve allows (i) to regenerate catalysts under air after gas chromatography (GC) sampling is achieved; (ii) to perform unsteady state testing by switching the feed from air to methane and recording on-line. Exhaust gases were analysed on-line by gas chromatography (GC HP 6950 and 6980). Water introduced or produced during the reaction was condensed in a Peltier cooler placed before the GCs. For unsteady state experiments, the analyses were performed with an on-line mass spectrometer (Inficon IPC-400). Prior catalytic runs, catalysts were stabilized at 600 °C for 4 h under test conditions and then cool down to 400 °C. When the targeted reaction temperature is reached, the downstream stream is analysed in an empty reactor in order to measure blank activity. Then, one reactor is fed by the inlet stream (see below) while the 15 reactors are regenerated under air (50 mL/min) conditions. In order to ensure that the catalytic performances are measured under steady state conditions, duplicate samplings at different time were carried out, i.e. after 12 and 22 min of time on stream. In all cases, the analyses differ less than 1% showing that the catalysts are equilibrated. The reported values correspond to the average of these two analyses. Then, a subsequent reactor is selected for a catalytic run. After all runs are completed at a given temperature, the temperature is heated up to the next plateau, from 400 to 600 °C every 25 °C at atmospheric pressure. The 15 reactors are filled with 100 mg of catalysts and the last reactor is free of catalysts and used as a blank test. Scenario A is simulated with a methane-to-oxygen ratio of 15:2 (7.5:1 mL/min), argon as balance (41.5 mL/min) and a total flow of 50 mL/min. Scenario B was studied as previously with a feed consisting in 20% of steam (10 mL/min) and then 20% of steam (10 mL/min) and 5% of carbon dioxide (2.5 mL/min) added to the former CH_4-O_2 mixture. Unsteady state experiments over Pt-CePr-H and Ni-CePr-H were performed to investigate reaction mechanism. Diluted methane was fed on fully oxidized catalysts and a flow of 5% of methane diluted in argon was fed for 4 min.

For all cases, the methane conversion and H_2 yield are calculated as:

$$X_{CH_4} = \left(1 - \frac{CH_{4_{outlet}}}{CH_{4_{inlet}}}\right) \times 100 \quad \text{and}$$

$$Y_{H_2} = \frac{H_{2_{outlet}}}{2CH_{4_{inlet}} + H_2O_{inlet}} \times 100$$

The carbon balance was defined as the fraction of all the carbon atoms recovered at the reactor outlet over all the carbon atoms fed into the reactor: $Z = \frac{\sum_{Compounds} C_{outlet}}{\sum_{Compounds} C_{inlet}}$.

A value below 1 means a carbon loss (carbonaceous species deposition).

CO selectivities were calculated by:

$$S_{CO} = \frac{CO_{outlet}}{CO_{inlet} + CO_{2_{outlet}}} \times 100$$

The thermodynamic equilibrium data were calculated on the basis of the inlet gas composition and including all the potential products formation under various atmosphere conditions. The Gibbs free energy was minimized by using the software Outokumpu HSC (ver. 4.1). These calculations were conducted for temperatures between 400 and 600 °C and at a total pressure of 1 bar. The relevant species are CH_4, O_2, H_2, CO, CO_2 and H_2O for the gas phase and graphitic carbon for the solid phase. The considered reactions which can take place under the present operating conditions are (ΔH values are given for T = 298 K):

Methane total and selective oxidations:

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad \Delta H = -798\ \text{kJ/mol} \tag{1}$$

and

$$CH_4 + (1/2)O_2 = CO + 2H_2 \quad \Delta H = -58\ \text{kJ/mol} \tag{2}$$

Methane steam and dry reforming:

$$CH_4 + H_2O = CO + 3H_2 \quad \Delta H = 206\ \text{kJ/mol} \tag{3}$$

and

$$CH_4 + CO_2 = 2CO + 2H_2 \quad \Delta H = 261\ \text{kJ/mol} \tag{4}$$

Water gas shift reaction:

$$CO + H_2O = CO_2 + H_2 \quad \Delta H = -41\ \text{kJ/mol} \tag{5}$$

Two sets of reactions have to be considered for carbon formation and/or consumption:

$$\text{Methane cracking}: CH_4 = C + 2H_2 \quad \Delta H = 75\ \text{kJ/mol} \tag{6}$$

Carbon steam and dry reforming (Boudouard reactions):

$$CO + H_2 = C + H_2O \quad \Delta H = -133\ \text{kJ/mol} \tag{7}$$

and

$$2CO = C + CO_2 \quad \Delta H = -172\ \text{kJ/mol} \tag{8}$$

3. Results

3.1. Catalysts characterization

Whatever the ceria substitution, the fluorite structure is maintained for all samples as evidenced by X-ray diffraction. The absence