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## Doped ceria prepared by precipitation route for steam reforming of methane

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### ABSTRACT

The reactivity of methane on pure- and doped (Gd, Pr)-ceria catalysts has been investigated under highly deficient steam conditions ( $\text{CH}_4/\text{H}_2\text{O} = 10$ ) at  $750^\circ\text{C}$ . The physico-chemical properties of the prepared samples were studied by XRD, adsorption-desorption isotherms of  $\text{N}_2$  at  $-196^\circ\text{C}$ , and temperature programmed reduction in  $\text{H}_2$ . The doping process led to an increase in the surface area and changes in the surface properties. Thus, doping by Pr enhanced the redox and, consequently, the catalytic properties while doping by Gd improved the catalysts stability against deactivation processes.

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### 1. Introduction

Steam reforming of hydrocarbons is the most widely used route for the production of hydrogen [1–3]. Among these, methane as the main constituent of the natural gas and biogas is more convenient. To reach this goal, different oxide catalytic formulations were investigated and  $\text{NiO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$  and  $\text{CuO}$  supported on various supports such as alumina, silica, or zirconia were suggested as the most efficient methane steam reforming (MSR) candidates. These catalysts fitted quite well the required criteria (e.g. high activity, reasonable lifetime, good heat transfer, low pressure drop, high thermal stability and excellent mechanical strength) [4,5].

Developments on the MSR process were also applied for the hydrogen production in the technology of solid oxide fuel cells (SOFC) operated on methane. The direct electrochemical oxidation of  $\text{CH}_4$  being difficult at the anode, it is necessary to convert  $\text{CH}_4$  into hydrogen, which is made possible by the presence of the catalyst at the anode: this is the so called direct internal reforming (DIR). In this respect, nickel-yttria stabilized zirconia cermets (Ni-YSZ), used as a conventional anode in SOFCs, are considered as

analogous to the supported MSR nickel catalysts [1]. The main issue is the possible deposition of carbon depending on the varying conditions along the anode, which may lead to the final collapse of the cell. Excess of steam has to be used to overcome this issue but this severely affects the lifetime of the cell. Gradual Internal Reforming (GIR) has been proposed as an alternative to DIR [6]. The two anode functions are separated, i.e., the steam reforming of the fuel and its electrochemical oxidation producing water vapour. 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. In this mode, the activity of the catalyst in MSR has to be moderate and its resistance against carbon formation high, which definitely excludes Ni catalysts.

Due to their tunable ionic conduction behavior doped- $\text{CeO}_2$  materials attracted, in the last decades, a special interest as component of SOFC [7–9]. The high oxygen storage capacity, the mixed ionic-electronic conductivity in reducing atmospheres and the satisfactory thermal and mechanical resistance recommended it for these applications. Doping ceria was indicated as a tool of tuning these properties. The effect of the type and amount of the dopant, and of the preparation method onto the morphology and conductivity of these materials, has been reviewed by several reports [9,10]. Examples of dopants used are Gd ( $\text{Ce}_{0.6}\text{Gd}_{0.4}\text{O}_{1.8}$  [11]), Nb [12], Gd-Sm ( $\text{Ce}_x\text{Gd}_y\text{Sm}_z\text{O}_2$  [13]) etc. The high resistance of these systems against carbon deposition in MSR compared with Ni-YSZ

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suggested the ceria-based materials as more promising solutions for electrodes in SOFCs operated on methane [11,14–16], especially in GIR mode.

The aim of the present work was to investigate Gd- and Pr-doped-ceria materials versus pure CeO<sub>2</sub> as reforming catalysts for the MSR reaction with potential application as anode component material in SOFCs. Gd exhibits a stable valence (+3) while Pr may easily adopt the +3 and +4 oxidation states. These materials were prepared by a coprecipitation method and characterized by XRD, adsorption-desorption isotherms of N<sub>2</sub> at –196 °C and temperature programmed reduction in H<sub>2</sub>. The synthesized powders were tested in CH<sub>4</sub>/H<sub>2</sub>O reaction at 750 °C under highly deficient water conditions (CH<sub>4</sub>/H<sub>2</sub>O = 10), in order to evaluate their potential use in SOFCs operated in GIR mode.

## 2. Experimental

Ceria based materials (Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2</sub>, Ce<sub>0.9</sub>Pr<sub>0.1</sub>O<sub>2</sub>, Ce<sub>0.9</sub>Gd<sub>0.05</sub>Pr<sub>0.05</sub>O<sub>2</sub>) were prepared by a coprecipitation method. All chemicals were provided by Sigma-Aldrich. The desired amounts of cerium nitrate hexahydrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O), gadolinium nitrate hexahydrate (Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O) and praseodymium nitrate hexahydrate (Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O) were dissolved separately in hot ultra-pure distilled water to obtain a 0.1 mol/L solution. The solutions were mixed together under vigorous stirring and then ammonium hydroxide (NH<sub>4</sub>OH 25%, precipitation agent) was added drop-wise until the pH value was about 9. The obtained suspension was stirred at 60 °C for 1 h. Then the precipitate was separated by centrifugation, washed three times with distilled water and one time with ethanol to remove the unreacted species. The precipitate was dried at 60 °C under vacuum for 5 h and at 120 °C overnight under air and finally calcined in air, for 5 h, at 500 °C and 900 °C (with a heating rate of 10 °C min<sup>-1</sup>). For comparison the ceria sample was prepared without adding dopant. The samples were denoted in relation with the used dopant: CeO<sub>2</sub>, CGO (gadolinium-doped sample), CPO (praseodymium-doped sample) and CGPO (co-doped gadolinium and praseodymium sample).

The synthesized materials were characterized by N<sub>2</sub> adsorption volumetry, X-ray diffraction (XRD) and temperature programmed reduction experiments (TPR-H<sub>2</sub>). The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area from the data obtained at P/P<sub>0</sub> between 0.01 and 0.995. The crystalline phases of the powder catalysts were examined by X-ray powder diffraction (XRD). Diffractograms were collected at 2θ between 5 and 80° and the crystal planes of the deposited films were identified according to the JCPDS crystallographic database. X-ray diffraction was also used to estimate the crystallite size of the catalyst particles, which allowed estimating the particle size with a reasonable accuracy.

$$D = \frac{0.9\vartheta_{Cu}}{\beta_{1/2} \cos \theta}$$

where  $\vartheta_{Cu}$  is the X-ray wavelength,  $\beta_{1/2}$  is the line broadening a half maximum intensity (FWHM) in radians, and  $\theta$  is the Bragg angle. In temperature programmed reduction measurements in hydrogen atmosphere (TPR-H<sub>2</sub>), approximately 20 mg samples were

pretreated at 150 °C (in an air flow of 30 mL min<sup>-1</sup> for 1 h) and then cooled to room temperature in argon gas flow before reduction. The details of the apparatus and procedures were described elsewhere [15,16]. The concentrations of Gd and Pr were determined by ICP-OES (Activa instrument from Horiba Jobin Yvon) by dissolving the samples in a mixture of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> at 250 °C. Chemical analysis indicated that the targeted compositions of doped samples (Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2</sub>, Ce<sub>0.9</sub>Pr<sub>0.1</sub>O<sub>2</sub>, Ce<sub>0.9</sub>Gd<sub>0.05</sub>Pr<sub>0.05</sub>O<sub>2</sub>) were obtained.

Catalytic activity experiments were carried out in a continuous flow system at atmospheric pressure and 750 °C using a reactant mixture consisting of 50 mol% CH<sub>4</sub> and 5 mol% H<sub>2</sub>O in N<sub>2</sub> as balance, at a total dry flow rate of 7 L<sub>NTP</sub> h<sup>-1</sup>. Prior to the catalytic tests, the samples (0.1 g) were treated in N<sub>2</sub> (7 L<sub>NTP</sub> h<sup>-1</sup>) at 900 °C for 2 h. The setup for MSR tests and details of calculated CH<sub>4</sub> conversion (X<sub>CH4</sub>), CH<sub>4</sub> consumption rate and H<sub>2</sub>, CO, and CO<sub>2</sub> formation rates were described in a previous article [17]. It has to be mentioned that CH<sub>4</sub> conversions obtained (typically lower than 1%) fulfill differential reactor conditions, allowing thus to determine rates of CH<sub>4</sub> disappearance. As in [16], it was checked that mass transport was not limiting.

## 3. Results and discussion

### 3.1. Physicochemical characterization

Table 1 summarizes the surface areas, pore volumes, crystallite sizes for the prepared samples at different temperatures. The doping process leads to an increase in the surface area values of the as-synthesized samples, compared to the pure as prepared CeO<sub>2</sub> sample. This tendency is the same after calcination at 500 °C. Such a behavior could be due to the presence of praseodymium and gadolinium in the solid solution, which avoids sintering of ceria [18,19]. Increasing further the calcination temperature induces the severe decrease of the surface area of all samples and differences between samples tend to level off. These findings are correlated with the pore volume and crystallite size values. After calcination at 900 °C, Pr-doped samples exhibit the highest surface areas and the lowest crystallites sizes of the series.

The shape of the N<sub>2</sub> adsorption-desorption isotherms for samples calcined at 500 °C (Fig. 1a) is almost similar for all samples, being characterized by a hysteresis loop at higher partial pressures. This kind of isotherm (type IV according to IUPAC) is specific to mesoporous solids. The initial part of the isotherm is attributed to monolayer-multilayer adsorption and the hysteresis loop is associated with capillary condensation taking place in mesopores. The pore sizes distributions derived from the presented desorption isotherms show a broad pore size distribution for the CeO<sub>2</sub> sample with average value around 20 nm, while in Gd and Pr doped samples, the pore size is diminishing, around 10 nm (inset of Fig. 1a).

In Fig. 1b are gathered the N<sub>2</sub> adsorption-desorption isotherms for samples calcined at 900 °C. The thermal treatment influences the shape of the isotherms, which are specific to nonporous solids, type II according to IUPAC.

All samples show the typical diffraction pattern of the CeO<sub>2</sub> pure cubic fluorite structure (Fig. 2) regardless the thermal treatment, with the reflections corresponding to (111), (200), (220), (311),

**Table 1**  
Physicochemical properties of the pure- and doped-ceria catalysts.

	Surface area (m <sup>2</sup> g <sup>-1</sup> )			Pore volume (cm <sup>3</sup> g <sup>-1</sup> )			Crystallite size by XRD (nm)		
	as-synthesized	500 °C	900 °C	as-synthesized	500 °C	900 °C	as-synthesized	500 °C	900 °C
CeO <sub>2</sub>	36.7	25.1	5.6	0.159	0.155	0.049	26.8	29.0	78.1
CGO	70	46	4.4	0.189	0.183	0.049	15.3	15.5	44.3
CPO	73.4	51.7	9.1	0.201	0.162	0.098	22.5	23.9	53.5
CGPO	140.0	66.1	8.9	0.360	0.182	0.091	18.4	20.0	59.9

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