



Dry reforming of methane on ceria prepared by modified precipitation route

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ARTICLE INFO

Article history:

Received 13 October 2014

Received in revised form 13 January 2015

Accepted 14 January 2015

Available online 22 January 2015

Keywords:

Ceria

Surfactant

Hydrogen peroxide

Precipitation method

Dry reforming of methane

ABSTRACT

Cerium oxide catalysts for fuel cells application were synthesized *via* precipitation and modified precipitation routes where the effect of H₂O₂ and/or cetyltrimethylammonium bromide (CTAB) addition in the precipitation step has been investigated. Microstructure and reduction–reoxidation properties of the oxides were analyzed by XRD, adsorption–desorption isotherms of N₂ at –196 °C, TG–DTA, Raman, SEM, TPR–H₂, TPR–CH₄ and TPO. The catalytic properties of CeO₂ samples were investigated in dry reforming of methane (DRM) between 750 and 900 °C under both stoichiometric (CH₄ and CO₂ in equal amounts) and oxidizing (excess of CO₂ with respect to CH₄) conditions. A material exploitable for applications in catalysis and solid oxide fuel cells (SOFCs) was obtained by modifying the precipitation route *via* the addition of H₂O₂ (CeO₂–H₂O₂). Compared to materials synthesized conventionally or by using CTAB, CeO₂–H₂O₂ exhibited the best thermal stability, least surface loss under high temperatures operation (e.g. 900 °C), superior stability with respect to bulk redox properties when alternating between oxidizing and reducing treatments, and highest catalytic activity and resistance to deposition of graphitic carbon.

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1. Introduction

Catalytic dry reforming of methane (CH₄ + CO₂) to synthesis gas (CO and H₂) has received considerable attention in recent years [1,2] due to the H₂/CO product ratio close to unity. This is suitable for the liquid hydrocarbon production *via* Fischer-Tropsch synthesis and, in conjunction with the water-gas-shift reaction lead to the production of H₂ for fuel cell applications [2]. Solid oxide fuel cells (SOFCs) are then used to convert chemical energy directly into electrical energy with high efficiency (up to 80%) and minimal emissions compared with the conventional combustion using biogas as fuel. As cathodes this methodology uses strontium-doped lanthanum manganite [3], while nickel yttria-stabilized zirconia (YSZ) cermet is the most investigated as anodes [4].

The main disadvantages of the currently SOFC systems operating with CH₄ + CO₂ are the anode redox instability, carbon deposition on the catalytic active sites and their poisoning with sulfur compounds, even at low levels [5]. The deterioration of the anode

performances decreases the electrical efficiency of the cell [6]. To avoid these disadvantages numerous studies have been focused on the identification of new materials [7]. Among them, cerium oxide was suggested as a promising candidate, due to its enhanced catalytic activity and stability against coke formation [6]. This capability has been attributed to some unique properties, such as the high oxygen storage capacity, the high oxygen mobility and the ability of cerium to switch easily between the oxidized and reduced states (Ce³⁺ ↔ Ce⁴⁺). All these properties are often associated to the presence of defects (oxygen vacancies) [8], and recommend cerium oxide as possible electrode material for SOFCs applications at intermediate temperature operation (600–800 °C) [9].

To achieve materials with required characteristics considerable efforts were invested in both the development of new synthesis routes and the optimization of the existent ones. The most investigated methods were: hydrothermal synthesis, homogenous precipitation, sol–gel and modified sol–gel processes, combustion, and reverse microemulsion [10–14].

Today, in spite of the much focused efforts, the preparation of ceria catalysts with sufficiently high surface area, high defects concentration and high thermal stability is still incompletely controlled. Moreover, when used in SOFCs, the catalytic efficiency may decrease due to sintering at high operating temperature causing the

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decrease of the surface area and the ability to store oxygen. Among other methods, the addition of hydrogen peroxide as oxidizer in the preparation stages of ceria nanomaterials led to an improvement of the morphological and structural properties (e.g. high surface area, improved redox properties) [15–17]. This positive effect was attributed to the conversion of Ce^{3+} to more reducible (hydrolyzable) Ce^{4+} species in the presence of H_2O_2 . Indeed, during the crystallization process, the formed cerium hydro peroxide complexes disrupt with the pre-synthesis of a compact Ce–O–Ce network, which favors the formation of highly dispersed nanocrystallites, than simple hydroxides, as oxide precursors [16].

This work is focused on the possibility to control the defects population in ceria based materials during preparation. In this scope, the effect of adding H_2O_2 during the synthesis, alone or in tandem with cetyltrimethylammonium bromide (CTAB), a template agent, on the morphologic and structural properties of synthesized ceria was revisited. The textural and structural features of the studied materials were determined in depth by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), isotherms of adsorption–desorption of nitrogen at -196°C , thermogravimetric and differential thermal analysis (TG–DTA) and Raman spectroscopy. Redox properties were determined by performing successive cycles of temperature programmed reduction experiments in CH_4 (TPR- CH_4) followed by temperature programmed oxidation in O_2 (TPO). The reduction behavior of CeO_2 in the presence of hydrogen (TPR- H_2) was also studied. Catalytic properties in methane dry reforming were investigated in view of the potential use of ceria materials as SOFC anodes operating on $\text{CH}_4 + \text{CO}_2$ mixtures such as in biogas.

2. Experimental

2.1. Synthesis of cerium oxide

Ceria powders were prepared by additives-assisted precipitation method. The desired amount of cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) was dissolved in hot ultra-pure distilled water to obtain a 0.1 mol/L. At this solution were added different additives (H_2O_2 , CTAB, and $\text{H}_2\text{O}_2/\text{CTAB}$) under vigorous stirring and then drop-wise ammonium hydroxide (NH_4OH 25%, precipitation agent) 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 alcohol to remove the unreacted species. The precipitate was then dried at 60°C under vacuum for 5 h and at 120°C overnight under air. These materials are denoted as *as-synthesized* samples. The obtained powders were further calcined in air, for 5 h, at 500 and 900°C , respectively (with a heating rate of $10^\circ\text{C}/\text{min}$). The samples were denoted in relation with the additive used: CeO_2 ; $\text{CeO}_2\text{-CTAB}$; $\text{CeO}_2\text{-H}_2\text{O}_2$; $\text{CeO}_2\text{-CTAB-H}_2\text{O}_2$.

2.2. Characterization

Surface area and porosity analysis. The characterization of the porous texture of the as-synthesized and calcined samples was performed by N_2 adsorption at -196°C using a Micromeritics instrument (ASAP 2010). The Brunauer–Emmett–Teller (BET) method was used to calculate the surface area from the data obtained at P/P_0 between 0.01 and 0.995. Prior to surface area determination, the samples were outgassed at 150°C for 5 h. The pore size distribution of each sample was determined from the desorption branch of the N_2 isotherm.

Scanning electron microscopy (SEM). The morphology of the different samples have been examined using images obtained from a JEOL 2010 microscope.

X-ray diffraction analyses were carried out on a Shimadzu XRD-7000 diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation with $\lambda = 1.5418 \text{ \AA}$. The tube source was operated at 40 kV and 30 mA. Scans were taken in the 2θ range of $10\text{--}80^\circ$ with a step size of 0.02° and scan time of $2^\circ/\text{min}$. Crystalline phase were identified by the comparison of the XRD patterns with the JCPDS database. The crystallite sizes were calculated from (1 1 1) peak using Scherrer's formula $D = k\lambda/\beta \cos \theta$, where D is the average crystallite size, k a constant equal to 0.89, λ the wavelength of X rays and β is the corrected half width.

The *differential thermal and thermogravimetric analysis* of the as-synthesized powders were carried out by using a TG–DTA analyzer Shimadzu DTA-60 instrument. The experiments were performed in nitrogen atmosphere from room temperature to 900°C with a heating rate of $10^\circ\text{C}/\text{min}$, by using alumina as reference and 5–10 mg of CeO_2 sample.

Raman spectra were obtained by using a Jobin Ivone Raman microprobe instrument, with an excited wavelength of 514.54 nm laser radiation. All the spectra were recorded between 200 and 4000 cm^{-1} with a $\times 50$ objective which focuses the laser beam in a spot of $100 \mu\text{m}$.

Temperature programmed experiments (TPR- H_2 , TPR- CH_4 and TPO). The temperature programmed reduction measurements in hydrogen atmosphere (TPR- H_2) were conducted on a Micromeritics, AutoChemII 2920 apparatus. Approximately 20 mg samples were pretreated at 150°C (in an air flow of 30 mL/min for 1 h) and then cooled to room temperature in argon gas flow before reduction. A hydrogen–argon mixture (10% H_2), was used to reduce the samples at a flow rate of 50 mL/min. The temperature was linearly raised at a rate of $10^\circ\text{C}/\text{min}$ up to 950°C .

The temperature programmed reduction in CH_4 (TPR- CH_4) experiments coupled with the temperature programmed oxidation measurements (TPO) were performed in a custom-made apparatus equipped with a U-shaped quartz tube micro-reactor surrounded by a furnace controlled by a programmed heating system. For each experiments 20 mg of sieved CeO_2 powder ($40 < \phi < 75 \mu\text{m}$) were used. The TPR- CH_4 was performed with a mixture of 1% CH_4 in He, and the oxidizing gas for TPO was a mixture of O_2/He (1% O_2). The gas flow rate during these experiments was 30 mL/min and a heating rate of $10^\circ\text{C}/\text{min}$ was used. The procedure for an experiment consisted in the following steps: (1) the fresh catalyst sample calcined at 500°C was treated under He for 2 h at 900°C , cooled to 100°C in the same atmosphere, and then switched from pure He to the CH_4/He mixture; (2) the temperature of the system was then increased from 100 to 900°C in the CH_4/He flow, maintained at 900°C for 2 h, switched from CH_4/He to pure He and then cooled down to 80°C ; (3) the sample was further exposed to the O_2/He flow at 80°C (TPO experiment), the temperature was linearly increased up to 800°C , the O_2/He atmosphere was replaced by the carrier He and the system was cooled down at 100°C ; (4) following the same procedure as in (2) and (3) another TPR- $\text{CH}_4/\text{TPO}/\text{TPR-CH}_4$ cycle was performed. The analysis of the inlet/outlet gases was carried out by using a Pfeiffer Omnistar quadrupole mass spectrometer (QMS). The calibration of CH_4 , CO_2 , CO and H_2 was performed before each experiment making possible the quantitative analyses of CH_4 and respectively of O_2 consumed during TPR/TPO experiments and of H_2 , CO, and CO_2 produced. The characteristic signals of H_2 ($m/e = 2$), CH_4 ($m/e = 15$), CO ($m/e = 28$), CO_2 ($m/e = 44$), O_2 ($m/e = 32$), H_2O ($m/e = 18$) and He ($m/e = 4$) were continuously monitored as a function of time and temperature.

The series of temperature programmed experiments performed are further denoted as follows: TPR- CH_4 -1/TPO-1 – the first cycle, TPR- CH_4 -2/TPO-2 – the second cycle, and TPR- CH_4 -3 – the final reduction step.

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