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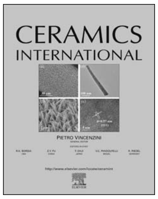

Synthesis and characterization of mesoporous NiO_2/ZrO_2-CeO_2 catalysts for total methane conversion

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ABSTRACT

This work reports the synthesis and characterization of mesoporous NiO/ZrO_2-CeO_2 composites. These materials are still being developed due to their excellent morphological and structural properties, especially for solid oxide fuel cells (SOFCs) anodes. A soft chemical route using a polymeric template was utilized to synthesize the samples. The structure after two different calcination processes at 400 °C and 540 °C was studied by X-ray diffraction and Rietveld refinement, before and after NiO loading. Nitrogen adsorption, scanning/transmission electron microscopy and small angle X-ray scattering revealed a nanocrystalline bi-phasic porous material. Temperature programmed reduction experiments showed higher Ni and Ce reduction values for samples calcined at 400 °C and 540 °C, respectively. Methane conversion values in the temperature range studied were similar for both calcination temperatures, showing 50% CH_4 conversion around 550 °C and 80% around 650 °C. However, a sample calcined at 400 °C exhibited better morphological and textural properties leading to an enhancement in NiO and CeO_2 reducibility that might be responsible for an improvement in oxygen surface exchange and gasification of carbon species in catalytic experiments.

1. Introduction

Ceria-based materials are well known for excellent catalytic performance due to the cerium oxide redox/oxygen storage properties [1–6]. Specially, ceria-zirconia solid solutions are used in many catalytic and electrocatalytic applications such as automotive three-way catalysts (TWCs) [7], oxidation and reforming catalysts [5,8–14], electrode materials in solid oxide fuel cells (SOFCs) [15–17] and constitutive materials in electrocatalytic devices [18–20].

The synthesis of mesoporous (2 < pores sizes < 50 nm) ceria-zirconia materials via soft template methods is a useful strategy to produce these solids since they are more versatile and are conducted at lower temperature, compared to other synthesis procedures [6,12,21–25]. Several attempts to synthesize zirconia doped ceria (ZDC) with better textural/structural properties were reported in the last decades [8,26–28]. This material is a mixed ionic-electronic conductor (MIEC) under reducing atmosphere, which is an important feature for SOFC applications because the fuel oxidation reaction takes place over the entire anode surface of the material and not only in the triple phase boundary (TPB) as in the case of the electronic conductors [28]. The synthesis by the gel-combustion, citrate and freeze-drying methods provide materials with suitable properties for many applications [29–37]. Given the fact that the electronic conductivity of ZDC is relatively low, it is typically used in composites with a metal conductor. Nickel is the most common choice due to its lower cost and high catalytic activity for methane oxidation [11,35,36,38].

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Ni/Yttria-stabilized zirconia (YSZ) anode is the most studied and tested in SOFCs, providing high power density values when operating at temperatures between 750 °C and 850 °C [39–41], using H_2 and CH_4 as the fuel source. It was found that the conversion rate of methane is strongly dependent on the specific surface area of the anode [41], indicating the importance to control the morphology of the anode in order to achieve better device performance. Many recent studies have focused on the investigation of the mechanisms responsible for the anode degradation, such as Ni grain growth by sintering, carbon coking, sulfur poisoning and redox cycling [42,43]. In addition, different anode compositions have been studied, modifying both, the metallic phase, through metal substitution and, the support, employing samarium and gadolinium cermets, in order to avoid degradation, decrease of the operation temperature, increase of the cell performance and extend the type of fuel that can be used [44–58].

Another strategy investigate the possibility to avoid metal impregnation in the anodes, by synthesizing mixed ionic and electronic conductors (MIEC) perovskites, such as lanthanum strontium chromium manganites/ferrites, sintered at high temperatures (> 1000 °C) [40,43,59]. However, these anodes do not present high catalytic activity for methane oxidation; neither high electronic conductivity nor stability, therefore, the development of novel compositions or combinations of material structures is still an open area for research, motivated by the use of natural gas fuels [43].

The aim of this work was to synthesize and characterize ZDC with 90 mol% CeO_2, using a polymeric template route and two different calcination temperatures, in order to obtain porous ceramics, preferentially with a single crystalline phase. The ceramics impregnated with NiO were analyzed to evaluate their applicability in catalysis and as anodes of intermediate temperature solid oxide fuel cells (IT-SOFCs).

2. Materials and methods

2.1. Sample preparation

The ZDC synthesis used 0.5 g of Pluronic P-123 (BASF) for 5 mmol of Ce/Zr (molar ratio of 9/1). The polymer was previously stirred with 10.7 mL of 2 mol L^{-1} HCl solution before the addition of $CeCl_3 \cdot 7H_2O$ (Aldrich) and $ZrCl_4$ (Aldrich). The gel was stirred for 2 h and its pH was adjusted to 3 by adding concentrated NH_4OH. The hydrothermal treatment of the resulting mixture was performed in a Teflon autoclave for 48 h at 80 °C. The sample was dried at 60 °C for 1 day.

Calcination process at 400 °C was performed in a tubular oven, with a temperature heating rate of 1 °C min^{-1}, with an isotherm of 4 h at 400 °C, in air (sample named Z90C-c400). The other calcination used the same heating rate, until 540 °C in N_2 atmosphere, an isotherm at 540 °C with 2 h in N_2 and 2 h in air (sample named Z90C-c540). This last process was previously established for calcined ordered mesoporous silica [60].

The NiO was incorporated by incipient wetness impregnation (IWI) of $Ni(NO_3)_2 \cdot 6H_2O$ solution with anhydrous ethanol (99.99% purity). The solution with nickel nitrate and the ZDC solid was mixed in a proportion to obtain 60 (w/w)% of NiO after calcination. The impregnated solid was dried in an oven for 4 h and calcined until 350 °C with a heating rate of 1 °C min^{-1} and maintained at this temperature for 4 h.

2.2. ZDC and Ni/ZDC characterization

The X-ray diffraction measurements were performed with a Bruker D8 Discover-DaVinci equipment with a copper tube (Cu Kα radiation, λ=1.5418 Å), Ni filter and a Lynx-eye detector, operating at 40 kV and 30 mA, with 2θ from 20° to 100°, a 0.02° step and counting time of 10 s/step. The Rietveld's powder structure refinement analysis was performed using Fullprof software [61]. The peak shape was assumed as an asymmetric pseudo-Voigt function. The background of each pattern was fitted by a polynomial function (degree 5). The least-square method was adopted to minimize the difference between the observed and the simulated powder diffraction patterns.

Nitrogen adsorption isotherms (NAI) were obtained with an ASAP 2020 Micromeritics porosimeter. Thermal treatment was made during 12 h at 200 °C and the measurements were taken at 77 K (N_2). The pore size distribution (PSD), pore volume and pore diameter were calculated using the BJH (Barrett-Joyner-Halenda) method [62]. The specific surface area was calculated using the BET (Brunauer–Emmett–Teller) method [63]. Scanning electron microscopy (SEM) images were obtained with a field emission electron microscope JEOL JSM-7401F with 5.0–10.0 kV of acceleration tension, SEI secondary electron detector, working distance ranging from 2.0 to 6.0 mm and 1.0 nm resolution. Transmission electron microscopy (TEM) images and Energy Dispersive X-ray Spectroscopy (EDS) maps were collected at a JEOL model JEM-2100 with 50 kV of acceleration tension, resolution of 0.25 nm and sample inclination of ±30°.

The small angle X-ray scattering (SAXS) measurements were carried out with a Bruker NANOSTAR sealed Cu tube (Cu Kα radiation, λ=1.5418 Å) operating at 40 kV and 30 mA, with a multi-filament Hi-STAR two-dimensional detector. The point focus geometry was used; the system was collimated by 3 pinholes and a cross-coupled Goebel-mirror system. The set up holds a vacuum path between the sample chamber and the detector. The sample to detector distance was 650 mm, therefore with q values ranging from 0.012 $Å^{-1}$ to 0.35 $Å^{-1}$. All the data were normalized by the measuring time and were corrected for the absorption effects. The inverse Fourier transform (IFT) method was used to perform the particle size distribution function in order to evaluate the porous structure of the samples, using the PCG software [64].

Temperature-programmed Reduction (TPR) was performed with a Micromeritics Chemisorb 2720. The samples were placed in a quartz reactor and prepared by heating in a He gas flow (50 mL min^{-1} at STP) until 300 °C for 1 h to eliminate water and other impurities. After the samples were cooled down to room temperature, then they were heated with a 10 °C min^{-1} ramp with 50 mL min^{-1} at STP gas flow mixture with 5 mol% H_2 in Ar balance. The thermocouple was placed inside the reactor, just above the catalyst bed, in order to avoid heat transfer limitations. H_2 consumption was monitored by the change in the thermal conductivity of the reactor exit gas flow with a thermal conductivity detector (TCD). The catalytic test for total methane oxidation was carried out in fixed-bed quartz tubular reactor with internal 10 mm diameter containing 50 mg of catalyst samples without any pretreatment. It was used a feed gas flow of 333 cm^3 min^{-1} at STP, consisted of CH_4 2 mol%, O_2 4 mol% and N_2 balance. Composition of feed and exhaust reactor gas flows were determined by on-line gas chromatography. A Clarus 500 (Perkin Elmer) equipped with a thermal conductivity detector and automatic injection valve was used. The reaction temperature was monitored by a thermocouple placed in the middle of the catalyst bed. Methane and oxygen conversions and carbon dioxide production were calculated according to the following expressions:

$$X_{CH4} = \frac{(F^{i}_{CH4} - F^{o}_{CH4})}{F^{i}_{CH4}} 100\% \tag{1}$$

$$X_{O2} = \frac{(F^{i}_{O2} - F^{o}_{O2})}{F^{i}_{O2}} 100\% \tag{2}$$

F^{i}_{CH4} and F^{i}_{O2} are the methane and oxygen molar flow in the feed, and F^{o}_{CH4} and F^{o}_{O2} are the molar flow in the exit. The CO_2 production is:

$$P_{CO2} = \frac{F^{p}_{CO2}}{F^{i}_{CH4}} 100\% \tag{3}$$

F^{p}_{CO2} corresponds to the molar flow of CO_2 in the exit.

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