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Effect of the type of ceria dopant on the performance of Ni/CeO_2 SOFC anode for ethanol internal reforming

A.A.A. da Silva[a,b], N. Bion[c], F. Epron[c], S. Baraka[c], F.C. Fonseca[d], R.C. Rabelo-Neto[a], L.V. Mattos[e], F.B. Noronha[a,b,*]

[a] National Institute of Technology, Catalysis Division, Av. Venezuela 82, Rio de Janeiro, 20081-312, Brazil
[b] Military Institute of Engineering, Chemical Engineering Department, Praça Gal. Tiburcio 80, Rio de Janeiro, 22290-270, Brazil
[c] Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), University of Poitiers, CNRS, 4 rue Michel Brunet, TSA51106, F86073, Poitiers Cedex 9, France
[d] Instituto de Pesquisas Energéticas Nucleares, IPEN-CNEN/SP, Av. Lineu Prestes 2242, São Paulo, 05508-000, Brazil
[e] Fluminense Federal University, Chemical Engineering Department, Rua Passo da Pátria, 156, Niterói, 24210-240, Brazil

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ABSTRACT

This work studied the effect of the type of ceria dopant on the performance of Ni/CeO_2 SOFC anode for ethanol conversion reaction. Ni-based catalysts supported on CeO_2 doped with different cations (Gd, Y, Pr, Zr, Nb) were prepared by the hydrothermal method. The addition of dopant to ceria led to the formation of the solid solutions during calcination for all samples, except for CeNb sample due to the low solubility limit. In spite of the high oxygen mobility of ceria-based supports, all catalysts deactivated for ethanol decomposition reaction at 1123 K due to carbon deposition. The large Ni^0 and CeO_2 crystallites formed during calcination at high temperature reduced the effectiveness of the mechanism of carbon removal because of the low metal-support interfacial area. The lowest formation of carbon on Ni/CeNb catalyst was attributed to the presence of $NiNb_2O_6$ phase. The reduction of this phase leads to the formation of Ni particles covered by NbO_x species, which inhibits carbon formation.

1. Introduction

The ethanol obtained from biomass has been considered as a promising alternative for energy generation, since it does not contribute to CO_2 emissions. Furthermore, in countries like Brazil and USA, the ethanol production and distribution infrastructure are well established.

Ethanol can be directly fed into the anode of solid oxide fuel cells (Direct Internal Reforming Solid Oxide Fuel Cells; DIR-SOFC) and reformed to H_2 and CO without the use of an external reformer, which reduces the complexity and cost of the fuel cell systems. Moreover, the H_2 produced at the anode side through ethanol reforming is consumed by the fuel cell electrochemical reaction, promoting the ethanol conversion and leading to high efficiency [1–3]. Therefore, in order to obtain good DIR-SOFC performance, anodes must have high electronic and ionic conductivity, high catalytic activity and stability in the operating conditions.

Anodes for SOFC systems are usually based on Ni/yttria-stabilized zirconia (YSZ) cermets [4–7]. When Ni/YSZ anodes operate directly with pure (dry) hydrocarbons or ethanol, a significant carbon deposition has been detected [8]. However, there are only few studies on pure bio-ethanol [8–18] or bio-ethanol/water mixture [19–26] fueled SOFC, and stability tests are rarely found.

Therefore, the major challenge of the DIR-SOFC is the development of an anode that is resistant to carbon deposition under SOFC operation conditions [8].

The traditional SOFC anode contains a high Ni content (at least 30 vol.%) in order to obtain high electronic conductivity. The high Ni loading as well as the high temperature required for sintering the ceramic components (electrodes and electrolyte) during the fabrication of SOFC leads to relatively large NiO particle size. Moreover, NiO has a less refractory character and exhibits faster mobility/coarsening than YSZ (and ceria) at high temperature. Such a behavior is more pronounced after reduction, when metallic Ni particles tend to sinter at relatively low temperatures. The relatively large Ni particles favor carbon formation, when hydrocarbons or bio-ethanol are used directly as a fuel in SOFC. The formation of carbon over metallic particles during steam reforming of ethanol reaction is significantly affected by the crystallite size of metal-

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* Corresponding author at: National Institute of Technology, Catalysis Division, Av. Venezuela 82, Rio de Janeiro, 20081-312, Brazil.
E-mail address: fabio.bellot@int.gov.br (F.B. Noronha).

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lic particles [8,27]. Silva et al. [27] reported that the deactivation rate decreased with decreasing Co particle size. This was due to the lower amount of carbon deposition over the smallest Co particles. They demonstrated that the small metallic particles contained a lower fraction of exposed terraces atoms, which are responsible for the initiation of carbon deposition.

One strategy to avoid carbon deposition is to reduce the Ni content of anodes. Decreasing Ni content increases metal dispersion, which reduces the formation of carbon, improving the performance of SOFC [28,29]. However, the use of conventional technology to prepare anodes with metal content below 30 vol.% did not provide materials with appropriate conductivity to SOFC applications [30]. Therefore, the use of alternative methods to prepare Ni based anodes with high activity, high stability, high conductivity, and low metal content has been proposed [29,30]

Jasinski et al. [30] prepared Ni/Sm-doped ceria cermets (with Ni content below 15 vol.%) by a net-shape procedure. Electrical measurements revealed that the cermet with 7.5 vol.% exhibited a much higher conductivity (10 S/cm) than the cermet prepared by conventional techniques (0.1 S/cm). For the anode with 14 vol.%, the conductivity (200 S/cm) was like that observed for a cermet with 35 vol.% Ni prepared by a conventional technique. The high dispersion and low sintering temperatures of net-shape technique preserved high surface area and nanocrystalline size of Ni particles. Such features promoted a stable framework of well-connected Ni particles, which percolate at volume fractions below the ones expected for classical percolation theory (∼30 vol.%). Therefore, the microstructural properties of the cermets resulted in high electrical conductivity at relatively low volume fraction of Ni (<30 vol.% Ni), as compared to traditional methods. Moreover, the low Ni loading also reduced the volume change during reduction and oxidation of the anode.

The use of hydrothermal method to prepared Ni- based anodes with low metal contents (5 wt.% Ni and 5 wt.% Ru) inhibited the formation of carbon during oxidative steam reforming (OSR) of propane under SOFC operation conditions [29].

In order to suppress carbon formation and improve the electrical conductivity, some authors [10,11,31] have also proposed the use of redox supports in the composition of SOFC anodes, such as ceria based oxide. In this case, authors claim that the high oxygen mobility of ceria supports promotes the mechanism of carbon removal, which in turn should contribute to the stability of the catalysts on ethanol conversion reactions [32]. Furthermore, doping with cations such as Gd^{3+}, Y^{3+}, Pr^{3+} and Zr^{4+} enhances the mobility of oxygen in ceria and then, increases the oxygen storage capacity (OSC) of the support [33].

Nobrega et al. [13] reported a stable operation of a single SOFC containing an Ir/gadolinium-doped ceria (GDC) catalytic layer under pure ethanol for 150 h. Augusto et al. [15] studied the performance of Ni/GDC both as the anode current collector layer and as a catalytic layer in a single SOFC operating directly on pure ethanol. Carbon deposition was not detected in single cells with Ni/GDC catalytic layer after 50 h of continuous operation under direct (dry) ethanol. This result was attributed to the catalytic properties of the Ni/GDC layer and the operation mechanism of gradual internal reforming, in which the oxidation of hydrogen provides the steam for ethanol reforming, thus avoiding carbon deposition.

The addition of dopants to ceria, such as Gd, Zr, Pr, Y, also improves the ionic and electronic conductivity of ceria [34–36]. The use of Nb as a dopant also increases the electronic conductivity of cerium oxide.

However, most of the studies investigated the performance of Gd-doped ceria based catalysts for the ethanol conversion reactions. There is no systematic study about the effect of the type of ceria dopant on the performance of Ni supported catalysts for ethanol conversion reactions.

Therefore, the aim of this study is to investigate the effect of the type of ceria dopant on the catalytic performance of Ni/CeO_2 under operating conditions of a SOFC anode for ethanol internal reforming (1123 K). The hydrothermal method was used to prepare the Ni/dopant-CeO_2 (dopant = Gd, Zr, Pr, Y, Nb) SOFC anodes with 18 wt.% Ni. The oxygen mobility and the reducibility of the samples were obtained by temperature-programmed reduction (TPR) and isotopic exchange of $^{18}O_2$ with $^{16}O_2$. In situ X-ray diffraction analyses (XRD) were performed to follow the changes on catalyst structure during the reduction and ethanol decomposition (ED) reaction, which might shed light on the mechanism of catalyst deactivation. In addition, the amount and the nature of carbon formed during ethanol decomposition was determined by thermogravimetric analysis (TG) and scanning electron microscopy (SEM).

2. Experimental

2.1. Catalyst preparation

Doped-ceria support was obtained by a hydrothermal method previously described [15]. An aqueous solution containing cerium (IV) ammonium nitrate and the dopant precursor salts (nitrate of gadolinium, yttrium, praseodymium and zirconium; ammonium niobium oxalate) was prepared with a Ce/dopant molar ratio of 9/1. Then, cerium and the dopant hydroxides were co-precipitated through the addition of an excess of ammonium hydroxide. The precipitate was transferred to an autoclave and it was heated to 453 K for 4 h. Then, the precipitate was washed with distilled water and calcined at 573 K for 2 h in a muffle furnace. Ni was added to doped-ceria support by wet impregnation using an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ to obtain 18 wt.% of Ni. After impregnation, the sample was dried at 393 K and calcined under air (50 mL/min) at 1073 K according to the following temperature program: (i) from room temperature to 673 K at 0.5 K/min; (ii) from 673 to 1073 K at 2 K/min and (iii) remained at final temperature for 5 h. The following samples were synthesized: Ni/CeO_2; Ni/CeGd; Ni/CeY; Ni/CePr; Ni/CeZr; Ni/CeNb.

A $NiNb_2O_6/CeO_2$ sample was prepared according to the procedure previously described in the literature [37], by conventional wet impregnation of the CeO_2 support (prepared as mentioned above) with an aqueous solution containing $Ni(NO_3) \cdot 6H_2O$ and ammonium niobium oxalate (CBMM) in a rotary evaporator. The solution was heated at 343 K under continuous stirring for 1 h. Then, the solvent was removed by evaporation under reduced pressure at 363 K, and the resulting solid was dried overnight at 393 K and calcined in synthetic air at 1073 K and 1273 K for 5 h.

2.2. BET surface area

The BET surface area of the samples was measured using a Micromeritics ASAP 2020 analyzer by nitrogen adsorption at the boiling temperature of liquid nitrogen.

2.3. $^{18}O_2/^{16}O_2$ isotopic exchange

Oxygen Isotopic Exchange (OIE) reaction experiments were carried out in a closed recycling system connected to a Pfeiffer Vacuum quadrupole mass spectrometer and a vacuum pump, as described elsewhere [38]. The samples (c.a. 20 mg) were placed into a quartz U-form reactor and pre-treated prior to the experiment: the samples were oxidized under pure $^{16}O_2$ flow (20 mL/min, 973 K, 1 h) and evacuated for 1 h. A treatment under pure H_2 at 973 K was carried out to study the behavior of the reduced samples. After the pre-treatment, samples were cooled down to the reaction temperature.