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Short Communication

$Ce_{0.9}Zr_{0.1}O_2$ nanocatalyst: Influence of synthesis conditions in the reducibility and catalytic activity

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ABSTRACT

This paper analyzes the influence of synthesis conditions on the reducibility and catalytic behavior of $Ce_{0.9}Zr_{0.1}O_2$ mixed oxide synthesized by α-amino acid/metallic nitrate combustion processes, through stoichiometric and non-stoichiometric routes. We concluded that the α-amino acid selected and the α-amino acid/nitrate molar ratio strongly influence the reducibility and catalytic activity in the total combustion of methane. Thus, the $Ce_{0.9}Zr_{0.1}O_2$ catalyst synthesized by the stoichiometric route with glycine showed the higher catalytic activity, which, in conjunction with the well-known ionic and electronic conductivities of ceria-based oxides under reducing conditions, positions this solid as an appropriate anode material for methane-fuelled solid oxide fuel cells.

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1. Introduction

In recent years, the development of new technologies for power generation has attracted much attention. Solid oxide fuel cells (SOFCs) have emerged as a very promising technology for both stationary and mobile applications [1–4]. One of the biggest goals to achieve in this field is to reduce SOFCs operating temperature at values in the range of 600–800 °C. While electrolyte and cathode materials with excellent performances at intermediate temperatures have been developed, the remaining challenge is the development of anode materials that can operate in that temperature range, especially when hydrocarbons like methane are used in the feed. Conventional anodes are based on the catalytic activity of nickel in the reforming of hydrocarbons, but the system is only efficient at high temperatures. For lower temperatures, especially when hydrocarbons are fed to the anode chamber, it is necessary to develop new materials capable to oxidize the fuel molecule with its O^{2-} ions in accordance with Eq. (1)

$$CH_4(g) + 4O^{2-}(s) \rightarrow CO_2(g) + 2H_2O(g) + 8e^-. \qquad (1)$$

As a consequence, research and technological developments of active catalysts for methane total oxidation have gained a prominent place in the area of power generation. The material to be developed should be capable to easily deliver the oxygen of its structure in order to oxidize the methane molecule, preventing dehydrogenation processes of this molecule with the concomitant formation of carbonaceous deposits.

Additionally, if the material has mixed ionic/electronic conductivity in the reducing conditions of the SOFC anode atmosphere, the electro-oxidation of the hydrocarbon molecule would take place over the entire anode surface and not only in the Three-Phase-Boundary (TPB) [5–8].

Ceria derived catalysts appear to have outstanding features for the above mentioned applications. Many researchers have studied Ce–Zr–O mixed oxides of different compositions and synthesis methods in the combustion of methane [9,10]. The critical aspects of the use of Ce–Zr–O mixed oxides in the complete oxidation of methane are structure of the solid, morphology stability, and redox properties. All of these characteristics are strongly related to the synthesis process and the composition selected.

Many compositions and synthesis processes have been reported, leading to a wide scope of catalytic behaviors. In the last years, the synthesis of nanomaterials remarked the influence of the particle size over structural, electronic and chemical properties, especially of metal oxides. At nanometric size, the electronic properties of the oxides change, and the increment of the ionic character of the metal – oxygen bond is observed. When talking of nanoparticles, their surface could present extraordinary chemical characteristics because of the ease of vacancy accommodation and the presence of atoms with a much

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lower coordination than in the bulk [11]. These extraordinary features of nanoparticles are crucial in heterogeneous catalysis, due to the fact that the chemical processes are confined to the solid surface.

We have previously studied [12] the catalytic properties of Ce–Zr–O mixed oxides of different compositions, synthesized by the pH-controlled nitrate–citrate gel-combustion route, in the catalytic combustion of methane. These oxides have ionic/electronic conductivity in reducing atmospheres. We have found that the oxide of nominal composition $Ce_{0.9}Zr_{0.1}O_2$ presented the better catalytic performance with a maximum methane conversion value of ~30% at 700 °C, at the experimental operating conditions. While the results were promising, it was necessary to improve the synthesis conditions in order to enhance the catalytic activity of this oxide, reducing its particle size and improving its redox behavior.

In this paper we present the analysis of the influence of synthesis conditions on the reducibility and catalytic behavior of a Ce–Zr–O system with $Ce_{0.9}Zr_{0.1}O_2$ nominal composition, synthesized by α-amino acid/nitrate combustion processes, through stoichiometric and nonstoichiometric routes.

2. Experimental

$Ce_{0.9}Zr_{0.1}O_2$ nanopowders were synthesized by the gel-combustion method following different routes. Samples identified as GS, LS and AS, were synthesized by the α-amino acid/nitrate combustion method following stoichiometric routes with glycine, lysine and alanine as fuels, respectively. Samples identified as G3 and G8 correspond to a non-stoichiometric pH-controlled glycine–nitrate route starting with glycine/metal molar ratios of 3/1 and 8/1 respectively. After the synthesis, the samples were calcined at 600 °C in air in order to eliminate any vestige of carbonaceous residues. The full description of synthesis process and the influence of synthesis conditions on texture and morphology were presented in a previous work [13]. In this paper, Scanning Electron Microscopy (SEM) micrographies, reduction profiles and catalytic performances of the synthesized materials are presented. The SEM images were obtained with a Zeiss Electron Beam SEM-Supra 40. The samples were placed over double-sided adhesive carbon-filled conductive ribbon to avoid charging problems.

In order to characterize the redox behavior of the catalysts, temperature programmed reduction (TPR) experiments were performed in a Micromeritics AutoChem II 2720. Prior to beginning the experiments, the samples were heated in a He flow of 50 cm^3 (STP)/min with a heating rate of 10 °C/min starting at ambient temperature and ending at 300 °C. This pretreatment was performed to eliminate any humidity absorbed and to displace the adsorbed gasses from the surface of the samples. Then, the sample was cooled down in order to begin with the reduction process. A flow of 50 cm^3(STP/min) with a composition of 5 vol.% H_2 in Ar was fed to the reactor containing the sample and heated up to 900 °C with a heating rate of 10 °C/min.

The TPR is a powerful technique for characterizing the reducibility of oxides. Each profile is like a “fingerprint” of oxygen reactivity in the solid. Nevertheless, transport phenomena at the gaseous-solid interphase could have a strong influence on the reduction kinetics. The selection of an adequate set of experimental conditions has shown to be important in order to get useful results. Our experimental conditions were selected in order to minimize the influence of mass transfer on the profiles [14].

The catalytic activity in total oxidation of methane of fresh solids was evaluated in a fixed bed reactor, laboratory scale, operated at atmospheric pressure. The mass of catalyst was 100 mg in all cases, and the catalytic bed was diluted with inert material in a mass ratio inert/catalyst = 6/1, to avoid the formation of hot spots. The catalytic bed was placed between two layers of quartz wool in a quartz reactor with 10 mm of inner diameter. The reactor was placed in a temperature controlled oven. The catalyst bed temperature was measured with a type K thermocouple placed axially and within the catalyst bed. The experiments were performed in the 400 °C to 800 °C temperature range, with steps of 100 °C. After reaching a set temperature value, the effluent composition was checked at least three times in order to confirm the stable behavior of the catalyst. Then, the temperature was again increased to the following temperature value. The feed was a mixture of 2% CH_4, 4% O_2 and N_2 balance with a total volume flow of 333 cm^3 (STP) min^{-1}. The CH_4:O_2 molar ratio in the feed corresponds to the stoichiometric molar ratio of the total oxidation reaction represented in (Eq. 2)

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g). \qquad (2)$$

Preliminary catalytic tests were performed to ensure that in the operating conditions, the contribution of homogeneous phase reaction was negligible and there were no diffusional and inter particles limitations. The feed and reactor effluent compositions were determined by on-line gas chromatography with a Perkin Elmer Clarus 500, equipped with an automatic injection valve, a CTR1 column and a Temperature Conductivity Detector (TCD), with He as carrier. Methane and oxygen conversions were calculated as

$$\text{Methane conversion} : X_{CH4} = (F^{i}_{CH4} - F^{o}_{CH4}).(F^{i}_{CH4})^{-1}.100\%$$

$$\text{Oxygen conversion} : X_{O2} = (F^{i}_{O2} - F^{o}_{O2}).(F^{i}_{O2})^{-1}.100\%$$

where F^{i}_{CH4} and F^{i}_{O2} are the molar flows fed to the reactor, and F^{o}_{CH4} and F^{o}_{O2} are the molar flows in the effluent.

3. Results and discussion

The main results of our previous work [13] are summarized in Table 1. All the samples exhibited the cubic fluorite-type crystal structure (spatial group *Fm3m*), with no secondary phases or indications of compositional inhomogeneities. The broad diffraction peaks reveal the nanocrystalline nature of the solids. Crystallite sizes (D_{XRD}) in Table 1 were calculated with the Scherrer equation. The degree of agglomeration, D_{BET}/D_{XRD}, was also reported. Particle sizes were calculated from the values of specific surface area using the formula $D_{BET} = 6/(\rho.A)$, where ρ is the theoretical density of the material. After the calcination step carbon elemental analyses were performed. Negligible carbonaceous residues were observed. Elemental analysis performed by Rutherford Back Scattering (RBS) technique confirmed the nominal composition within the error margin of this technique (2 mol%).

From Table 1 it is clear that there is a profound effect of the type of the amino acid used in the synthesis on the specific surface area, pore volume, crystallite size and degree of agglomeration. Sample GS presents the largest specific surface area and pore volume while sample LS shows the smallest values. We claimed that the differences are related with the length of the hydrocarbon chain of the amino acid molecule used in the synthesis, which is strongly related to the volume of evolved gasses and the rate of the combustion process. Besides, observing the results obtained for samples GS, G3 and G8, it is possible to conclude that higher specific surface area values and a lower crystallite sizes are observed at the stoichiometric glycine/nitrate ratio, while further

Table 1
Structural and morphological properties.

Sample	Structure	D_{XRD} (nm)	A ($m^2.g^{-1}$)	V ($cm^3.g^{-1}$)	D_{BET}/D_{XRD}
GS	*Fm3m*	8.6 (4)	45 (2)	0.086 (4)	2.2 (1)
AS	*Fm3m*	8.6 (3)	13.2 (7)	0.028 (1)	7.4 (3)
LS	*Fm3m*	7.9 (4)	4.9 (3)	0.011 (6)	22 (1)
G3	*Fm3m*	27 (2)	20 (1)	0.066 (3)	1.5 (1)
G8	*Fm3m*	35 (2)	16 (1)	0.072 (4)	1.5 (1)