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Electrospun lanthanide bimetallic oxide nanoparticles and nanofibers for partial oxidation of methane

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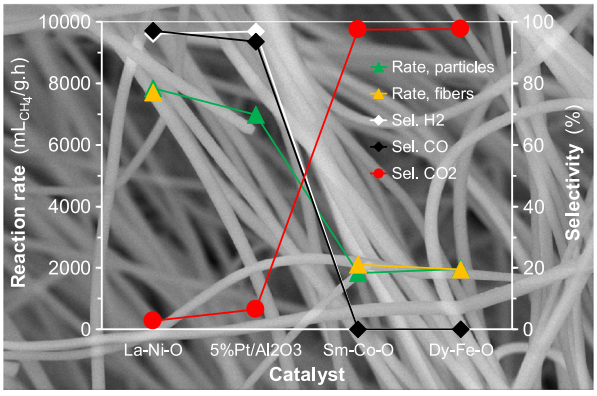
HIGHLIGHTS

- Synthesis of bimetallic oxides nanoparticles and nanofibers.
- Use of electrospinning technique.
- Preparation of perovskites of the type $LaNiO_3$, $SmCoO_3$ and $DyFeO_3$.
- Tested as catalysts for the partial oxidation of methane aiming the production of syngas.
- Best results obtained over nickel based catalyst; comparable to that of 5 wt% Pt/Al_2O_3 used as reference.
- Catalysts present also an unusual long stability in the gaseous stream.

GRAPHICAL ABSTRACT



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ABSTRACT

The preparation of nanoparticles and nanofibers of bimetallic oxides containing *f* block element perovskites of the type $LaNiO_3$, $SmCoO_3$ and $DyFeO_3$ was undertaken. They were obtained by electrospinning and its formation simply tuneable in the subsequent oxidation step-heating rate. These bimetallic oxides were tested as catalysts in the partial oxidation of methane aiming the production of syngas. The best results were those obtained over the nickel-based catalysts, which have an activity and selectivity comparable to that of a commercial catalyst used as reference (5 wt% Pt/Al_2O_3). The catalysts present also an unusual long catalytic stability in the gaseous stream. These perovskites type bimetallic oxides were characterized by different techniques (XRD, SEM/EDS, H_2-TPR). To our knowledge, it is the first time that these results are reported in the literature.

1. Introduction

The synthesis of bimetallic lanthanide oxides, namely nanocrystalline perovskites containing lanthanides is an important material goal [1–7]. Lanthanide perovskite oxides, $REMO_3$ general formula (RE, rare earth and M, 3*d* transition metal), have a pseudo cubic structure with the largest RE ions positioned at the corners, the smaller M ions occupying the center of the cube and the oxygen ions located at the centers of the cubic faces. The M–O bonds play a central role in the perovskite oxides properties [8,9].

Bimetallic lanthanide oxides are widely used in different areas, such has electronics, optics or catalysis [10]. $LaNiO_3$, $SmCoO_3$ and $DyFeO_3$ are three important examples of lanthanide perovskite oxides. $LaNiO_3$ is a typical perovskite oxide with good electrocatalytic

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activity that can be used as gas sensor, among other applications [11,12]. $SmCoO_3$ is known due to properties such as low temperature magnetic behavior [9,13], high temperature thermoelectric properties [14] and applications in solid state fuel cells technology [15,16]. $DyFeO_3$ has received a lot of attention in the last decades, particularly due to its spin structure and spin reorientation [17–21]. All these perovskite oxides were also used has catalysts in some important environmental reactions [22–24].

The properties of nanocrystalline perovskites are strongly influenced by the preparation technique. Many of them depend on the grain size, which can be tuned in a controlled way. It is the case of their catalytic activity that increases as a consequence of the increase of the porosity and decrease of the grain size (increase of specific surface area) [25,26]. Other example of such grain dimension effect is the wavelength of luminescent materials that depends on it due to quantum confinement effects [10].

Ball milling [27,28], co-precipitation [29] and hydrothermal [30,31] are chemical methods commonly used in the synthesis of perovskites. Other routes include the sol–gel or the autocombustion method that offer advantages such as good product homogeneity, purity and fast reaction [32,33]. It is also known that the same product can be obtained using different methods but, usually, with different grain shapes and sizes. Therefore, the optimization of a suitable, inexpensive and reproducible technique operating at or close to room temperature, allowing the tuning of the perovskite crystallite size and shape is one of today's main goals. Accordingly, electrospinning is a straightforward and versatile technique capable of generating submicron structures [34]; including fibers, ribbons, beads, globules, filled and hollow tubes [35]. These products can have extremely high specific surface areas, very high porosity; tuneable crystallite sizes and shapes, among others characteristics. It is also a low cost and effective preparation technique. Details about this technique can be found elsewhere [26,36]. Recently, electrospinning was successfully used to obtain material precursors [37–39], which after a high temperature treatment under air allows the production of bimetallic oxides [40,41].

Among relevant environmental reactions, the study of the partial oxidation of CH_4 using O_2 as oxidant aiming the production of syngas (CO and H_2) has attracted also a lot of attention [42,43]. Noble metal (Pt, Pd, Rh and particularly Ru) or Ni-based compounds are between the most important catalysts for the activation of methane [44]. Despite being highly active, noble metal-based catalysts are very expensive which limits any industrial application. Ni-based compounds are an alternative due to their low cost [44–47]. However, the main drawback of the catalysts used in this reaction is its poor stability due to catalyst poisoning, e.g., by carbon deposition (Boudouard reaction).

Herein, we present for the first time the synthesis of nanoparticles and nanofibers of bimetallic oxides containing perovskites of the type $LaNiO_3$, $SmCoO_3$ and $DyFeO_3$ by electrospinning ($LaNiO_3$.4NiO, $3SmCoO_3.4Co_3O_4$ and $DyFeO_3$. Fe_2O_3). They were tested as catalysts in the partial oxidation of methane aiming the production of syngas. These nanocrystalline lanthanide perovskites were characterized by powder X-ray diffraction (XRD) and scanning electron microscopy energy dispersive X-ray detection (SEM/EDS) for structural characterization, BET and temperature programmed reduction under hydrogen (H_2-TPR) to characterize the lability of the oxygen species on the bimetallic oxides aiming their use in catalysis.

2. Experimental

2.1. Catalysts preparation

Nanoparticles and nanofibers of bimetallic oxides containing perovskites of the type $LaNiO_3$, $SmCoO_3$ and $DyFeO_3$ were prepared by a two-step methodology: (i) electrospinning of the appropriate solution containing a mixture of metal chlorides (Aldrich, purity 99.9%), followed by (ii) controlled oxidation under air (Air_Liquide, Alphagaz 2 purity). All the reagents were used without further purification. Solutions were prepared by mixing metal chlorides hexahydrate (1:5, molar ratio using La/Ni and Sm/Co chlorides; 1:3 molar ratio using Dy/Fe chlorides) with 40 wt. % PVP40 (Aldrich, average mol wt 40,000) in a solution of absolute ethanol (Fischer-Scientific, purity >99.9%). The solutions were stirred at 60 °C for 30 min to dissolve the metal chlorides, cool down to room temperature and collected in a syringe with a ~0.5 mm interior diameter stainless steel flat tip needle. To start the electrospinning experiments (step 1), the solution is pumped continuously using a syringe pump (KW scientific) at a rate of 0.8 cm^3/h and an electric field of 20–25 kV applied between the syringe tip needle and a grounded aluminum plate placed 10 cm from the needle tip and used as a collector. After the electrospinning step, the electrospun materials were subsequently calcined (step 2) in a dry atmosphere of air (Airliquide, O_2 / N_2 (20:80%), Alphagaz 2 purity) at 900 °C for 3 h and at a heating rate of 1 or 10 °C/min.

2.2. Catalyst characterization

The X-ray diffraction measurements were performed on a PANalytical X'Pert Pro diffractometer (Cu Kα-radiation) with Bragg–Brentano geometry. Step-scanning mode diffractograms were taken in the 20–80 ° 2θ region using the θ/2θ configuration, a step scan of 0.03 °and a counting time per step of 15 s. For identification purposes, the relative intensities (I/I_0) and the d-spacing (Å) were compared with standard JCPDS powder diffraction files [48]. Theoretical powder patterns were also simulated with the help of the Powder-Cell program [49]. Crystalline sizes were calculated using the Scherrer's equation.

The surface morphology and the particle size of the samples were obtained using a FE-SEM JEOL JSM-6500F, operating at 15–20 keV and 80 μA. The chemical composition was determined by coupled EDS system. Nitrogen gas adsorption/desorption measurements were carried out using a Micrometrics ChemiSorb 2720–ChemiSoft TPx system (30% N_2 in Helium, Air Liquid 99.9995%). The samples were adsorbed at 77 K and desorbed at room temperature, the specific surface area being determined from the desorption isotherms by the Brunauer—Emmett—Teller (BET) method.

Thermogravimetric analysis (TGA) of the electrospun material was performed on a TA STA 409 system from room temperature to 750 °C at a heating rate of 10 °C/min and under dry air atmosphere (flux of 50 cm^3/min). Sample weight ~10 mg. Temperature programmed reduction studies under hydrogen (H_2-TPR) were performed on a Micromeritics ChemSorb 2720 instrument equipped with a high temperature module option (APX). The samples were placed in a specific Micromeritics quartz type U reactor and reduced under a 10%H_2/ argon mixture (0–1000 °C, at 10 °C/min, flow 20 mL/min). Quantitative H_2-uptakes were evaluated by integration of the experimental H_2-TPR curves, based on previous calibration measurements with CuO powder (Aldrich, 99.99995% purity). Optimized resolution was obtained by careful choice of the sample weight (10–20 mg).

2.3. Catalytic measurements

The catalytic behavior of the nanoparticles and nanofibers of bimetallic oxides containing perovskites of the type $LaNiO_3$, $SmCoO_3$ and $DyFeO_3$was studied at atmospheric pressure in a U-shaped quartz plug-flow reactor (9 mm internal diameter; 1 mm wall thickness), with a fixed bed (quartz wool) and an internal volume of 7 cm^3. Catalysts grain size was controlled using a 200 Mesh sieve (0.074 mm), m=10–15 mg (max. 1 mm bed thickness).

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