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Comparison of two Different Synthesis Methods of Perovskites, $SrCo_{0.5}FeO_3$ Type, Aiming at Evaluating their Use as Membranes for Partial Oxidation of Methane

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In this work two different synthesis methods of perovskites, $SrCo_{0.5}FeO_3$, were compared: combustion synthesis and oxides mixture aiming at evaluating their use as membranes for partial oxidation of methane. The combustion synthesis method explores an exothermic, generally very fast and self-sustaining chemical reaction between the desired metal salts and a suitable organic fuel, which is ignited at a temperature much lower than the actual phase formation temperature. The oxides mixture are based on a physical mixture of the powder oxides followed by calcination to obtain the desired phase. In order to obtain the membranes, we studied the conformation of bodies and the temperatures of sintering in the two powders synthesized. The powders were analyzed by density and grain size distribution and characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). After conformation, in cylindrical form, the green bodies were analyzed by density. After sintering at 1150 °C, the membranes were analyzed by density and they were characterized by XRD and SEM. The powder obtained by combustion synthesis shows lower density and fine grains than the other obtained by oxides mixture. The membranes obtained present very different morphology depending on the precursor powder synthesis. The sintered membranes obtained by combustion method also present a very uniform morphology without segregation.

Keywords: *Perovskite synthesis, powders characterization, membranes characterization*

1. Introduction

The partial oxidation of methane is one of the alternative routes for syngas production, a mixture of CO and H_2 . In this process, the presence of oxygen promotes the removal of carbon deposit on the catalyst surface at high temperatures and, therefore, it is possible to extend the catalyst useful life. The problem of this process is the high investments costs required by the cryogenic units[1] used to separate the oxygen from air.

Dense ceramic membranes highly selective to oxygen (≈ 100%) offer a potential solution to such problems in methane conversion[2]. They allow the use of air as the oxidant precluding thus the need for the costly oxygen plant. Recent reports in the literature[1] suggest that perovskites ceramic membranes can successfully separate oxygen and nitrogen at flux rates that could be considered commercially feasible[3-11]. However, one of the challenges of this process is the development of materials that are stable under the reaction conditions.

Several techniques can be used to prepare advanced ceramic materials and the combustion synthesis route can be highlighted among them all[12]. Recently, this method has been attracting increasing interest as a straightforward preparation process to produce homogeneous, very fine, crystalline and unagglomerated powders with good

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sintering behavior. It explores an exothermic, generally very fast and self-sustaining chemical reaction between the desired metal salts (nitrates, chlorides, sulfates) and a suitable organic fuel (such as urea), which is ignited at a temperature much lower than the actual phase formation temperature[13-19]. The key feature is that the heat required to drive the chemical reaction and accomplish the compound synthesis is supplied by the reaction itself and not by an external source. However, dense ceramic membranes are not usually prepared by the combustion method.

The objective of this work is to compare two different synthesis processes of $SrCo_{0.5}FeO_3$ perovskites: combustion synthesis and the conventional oxides mixture aiming at evaluating their use as membranes for partial oxidation of methane. The powders were analyzed by density (picnometry method) and by grain size distribution and characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). After conformation in cylindrical form the green bodies were analyzed by density (geometrical method) and the percentage of the real density was calculated. The membranes were also characterized after sintering at 1150 °C.

2. Experimental Procedure

Combustion Synthesis

A detailed description of the methodology used to prepare the powder by combustion reaction has been described elsewhere[13]. Briefly, in the combustion synthesis the appropriate amounts of the cations precursors (nitrates) and an organic fuel (urea) were dissolved in water, heated in a wide-mouth vitreous silica basin up to boiling and self-ignition. The basin was then transferred to a muffle furnace preheated at 600 °C and kept for 30 min producing a dry fragile foam that easily crumbles into powder. The molar proportions of the reactants in combustion synthesis were calculated in order to obtain the formula $SrCo_{0.5}FeO_3$ and are listed in Table 1.

The powder was moisturized and homogenized in a ball milled (16 h at 90 rpm) with ethanol, dried at 100 °C and sieved with 0,074 mm. This material will be identified as SCF-C.

Oxides Mixture Synthesis

The conventional synthesis of oxides mixture[12] is based on the physical mixture of the powders oxides followed by calcination (Table 2). After the mixture, the powder was submitted to the same treatment used in the combustion synthesis method. Nevertheless, after homogenization, the material was put into a furnace and heated at 1000 °C/2 h in order to obtain the $SrCo_{0.5}FeO_3$ phase. This material will be identified as SCF-O.

Conformation and Sintering Temperature Study

The behavior of the densification during the sintering was studied over cylindrical green bodies with 1.5 cm in diameter and 0.09; 0.13 and 0.17 cm in thickness, using uniaxial pressure until ~600 MPa (Ceramic Instruments, 10 ton). Then, the green density by geometrical method and the percentage of the real density were calculated.

The compacts were submitted to thermal treatments at different times and temperatures such as: 1150 °C for 1 h; 1150; 1170 and 1250 °C for 2h and 1150 °C for 3 h.

The membranes obtained by combustion synthesis were identified as SCF-C_s and the others obtained by oxides mixture, as SCF-O_s.

Powders Characterization

The powders were characterized by density (Micromerits helium picnometry model 1330); grain size distribution (Micromerits sedigraph); X-ray diffraction (Siemens diffractometer, CuKα = 1.5450 Å, 40 kV, 40 mA, 2θ =10 ° to 80 °) and scanning electron microscopy (Zeiss West Germany model DSM940A with 25 kV, after Au coating).

Membranes Characterization

The membranes were analyzed by density (Archimedes method), the percentage of the real density was calculated, the apparent porosity was investigated and they were characterized by X-ray diffraction at the same condition of the powders after breaking up one cylindrical membrane. The scanning electron microscopy was carried out in one polished cylindrical membrane in order to obtain a polished surface.

3. Results and Discussion

Real Density of Powders

The measurement of real density of the powders showed that the value obtained for the combustion synthesis sample (4.73 g/cm^3 ± 0.01 g/cm^3) was lower than that obtained for the oxides mixture (5.24 g/cm^3 ± 0.01 g/cm^3).

Grain Size Distribution

The average grain size distribution of combustion synthesis samples showed that 50% was less than 13 µm while for the oxides mixture powders 50% was less than 31 µm. The powders were found submicron and presented a monomodal grain size distribution.

Conformation and Sintering Temperature

The behavior of the densification during the sintering of both powders was similar. The ideal pressure for the green bodies with 0.13 and 0.17 cm thickness was around 477 MPa while, for the green bodies with 0.09 cm it was around 570 MPa.

After conformation in cylindrical bodies, the density and the percentage of the real density were calculated, as showed in Table 3.

The study of the sintering temperature showed that the ideal temperature for the powder synthesized by combustion reaction was 1150 °C for 2h for every thickness studied and to the oxides mixture it was 1150 °C for 3 h for every thickness as well.

After sintering, as showed in Table 4, the density, the percentage of the real density and the apparent porosity were calculated in the membranes.

XRD

Figure 1 shows the XRD patterns of the two powders and membranes obtained by these precursors.

The SCF-C presents only the basal reflection corresponding to the family of perovskites with general formula ABO_3. The diffractograms demonstrated non identified basal reflections which probably corresponds to a new phase, that will be studied later. Over the membrane SCF-C_s after intering at 1150 °C/2 h, it is possible to verify the increase in the crystallinity level as well as the disappearance of the non identified phase in the SCF-C powder.

The SCF-O powder and the SCF-O_s membrane showed only the basal reflections related to perovskites family and it is possible to see the increase in the crystallinity level after the sintering at 1150 °C/3 h.

SEM

The scanning electron microscopy (Fig. 2) revealed that

Table 1. Molar proportions of the reactants in combustion synthesis.

Sample	$Sr(NO_3)_2$	$Co(NO_3)_2.6H_2O$	$Fe(NO_3)_3.9H_2O$	$CO(NH_2)_2$
SCF-C	5.24	3.60	10	10

Table 2. Contents of the pure oxides.

Sample	SrO	CoO	Fe_2O_3
SCF-O	19.44 g	11.25 g	23.8 g

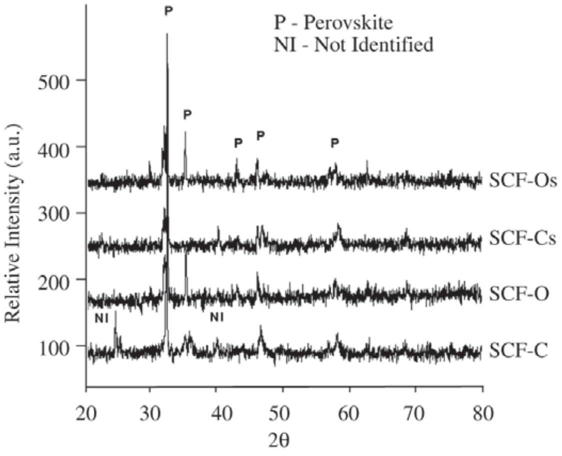

Figure 1. XRD patterns of the powders (SCF-C and SCF-O) the membranes (SCF-C_s and SCF-O_s).

Table 3. Characteristics of the green bodies compacted as cylindrical bodies after pressing.

	SCF-C			SCF-O		
ρ (g/cm^3)	2.95	2.98	2.99	3.07	3.11	3.12
ρ_R (%)	62.25	62.95	63.16	58.69	59.42	59.51
Initial thickness (cm)	0.09	0.13	0.17	0.09	0.13	0.17
Pressing (MPa)	570	477	477	570	477	477

Table 4. Characteristics of the membranes obtained by the two precursors.

	SCF-C_s			SCF-O_s		
ρ (g/cm^3)	4.51	4.53	4.52	4.86	5.01	4.95
ρ_R (%)	95.26	95.74	95.54	92.74	95.65	94.61
Apparent Porosity	0.010	0.019	0.010	0.001	0.002	0.005
Final thickness (cm)	0.08	0.11	0.14	0.08	0.10	0.13
Final diameter (cm)	1.27	1.28	1.28	1.27	1.27	1.27

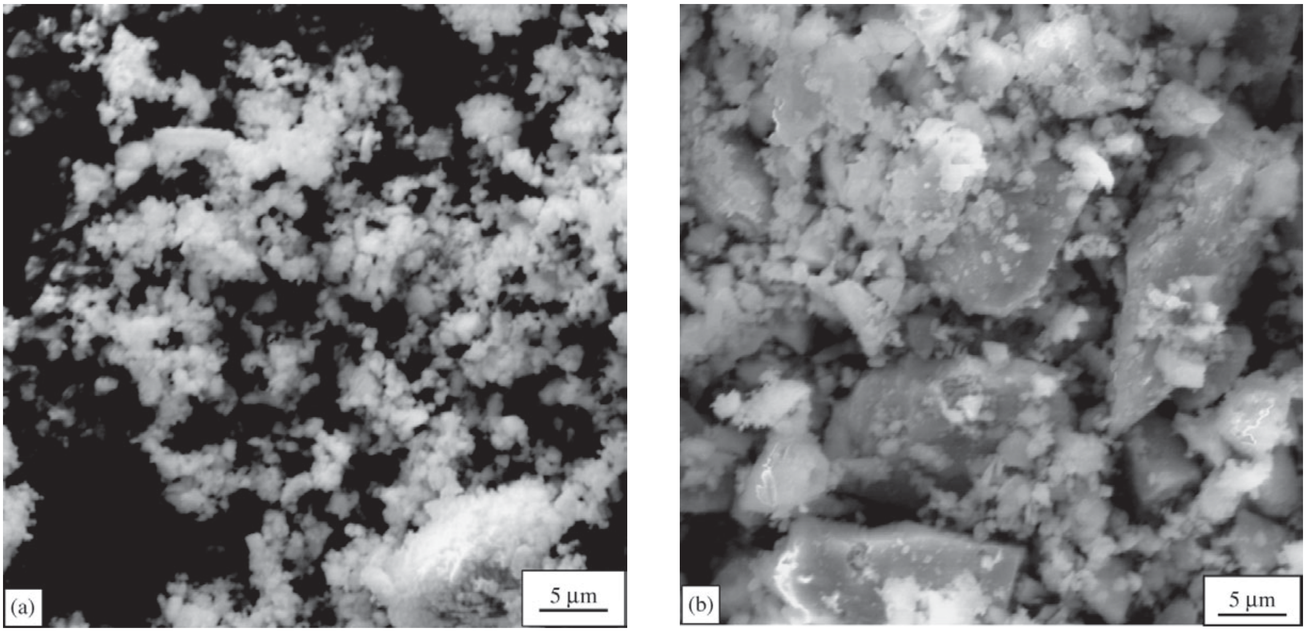

Figure 2. Scanning electron microscopy of the powders synthesized by: a) combustion reaction; b) oxide mixture (1500×).

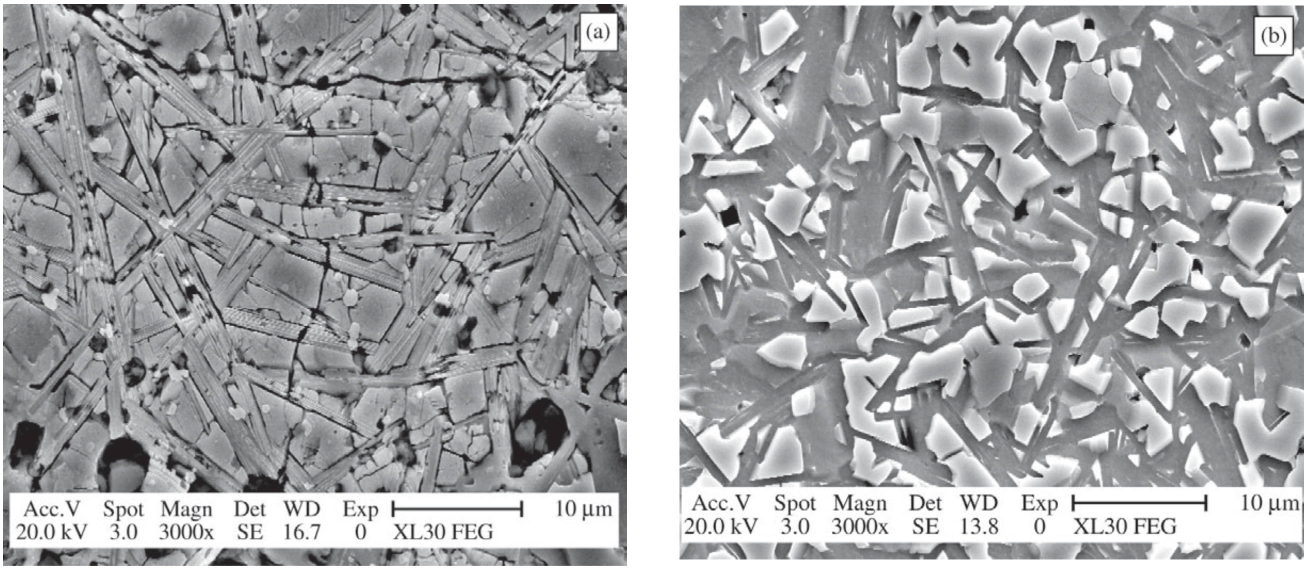

Figure 3. Scanning electron microscopy of the membranes after chemical attack with Keller's etching reagent starting with: a) combustion reaction; b) oxides mixture (3000×).

the morphology of the two powders are quite different. The grains in the powder synthesized by oxide mixture (SCF-O) are individual and it is possible to observe several dimensions and morphologies (Fig. 2b). On the other hand, over the SCF-C the individual grains are not identified in the fine fragments, Fig. 2a.

SEM analysis of the membranes, SCF-C_s and SCF-O_s, showed that they also have different morphologies but both are very similar to a metallic material even after thermal treatment at 1000 °C for 30 min.

Therefore, aiming at verifying the morphology of the membranes, a chemical attack with Keller's etching reagent (1%HF; 1.5%HCl; 2.5%HNO_3; 95%H_2O) was performed and they were again observed by SEM. The morphologies were still quite distinct for the two precursor, (Fig. 3) but it was possible to observed the phase segregation on the oxides mixture sample (Fig. 3b).

In order to verify the composition of the segregated phase a qualitative microanalysis (EDS) was carried out. It revealed that the matrix (dark phase) was constituted by strontium, iron and cobalt and the other phase (white phase) was, fundamentally, constituted by cobalt. Finally, the quantitative analysis by optical microscopy (Olympus BX 60M) was also performed and the content was 31.53 and 68.47%for the dark and for the white phase respectively.

4. Conclusion

The combustion synthesis leads to fine powders with lower real density than the oxides mixture indicating that it is possible to expend less sintering time. The percentage of the real density of the membrane synthesized by combustion reaction was about 95% but the apparent porosity was high indicating that the porosity was open. Furthermore, the membranes synthesized by combustion reaction present a very uniform morphology without phase segregation.

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