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La_xFeO_3, $La_{0.95}Sr_{0.05}FeO_3$ and $Nd_{0.95}FeO_3$ (x= 0.95 or 1.00) perovskites for the partial oxidation of methane.

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Highlights

- Fresh LF, L0.95F, LSF and NF perovskites were refined by Rietveld method.
- All perovskites presented a high value for the H_2/CO ratio.
- $Nd_{0.95}FeO_3$ presents better CH_4 conversion than $La_{0.95}FeO_3$.

1. Introduction

Search for clean and low-cost fuel to substitute petroleum is a popular research focus in the energy field. Methane (CH_4) can be converted into syngas (H_2 + CO), which can be directly used as a fuel or can be converted into liquid fuel or other chemicals through the Fischer-Tropsch synthesis method [1]. In this sense, the partial oxidation of CH_4 (POM) has several advantages such as moderate exothermic reaction requiring a small reactor, low energy consumption and high efficiency [1]. Perovskite-type oxides with ABO_3 structure have attracted significant interest in catalysis. The high metal dispersion of perovskites is an alternative for the usual metal supported catalyst in the POM reaction [2]. $LaFeO_3$, for example, is an attractive oxygen carrier due to its high oxygen mobility and its capability of hosting large concentrations of vacancies in its structure [3]. This work is focused in the synthesis of La_xFeO_3, $La_{0.95}Sr_{0.05}FeO_3$ and $Nd_{0.95}FeO_3$ (x= 0.95 or 1.00) perovskites and investigation of its efficiency in the POM reaction for syngas production as well as the effect of the non-stoichiometry and the substitution of La by Nd on the catalytic performance.

2. Methods

$LaFeO_3$ (LF), $La_{0.95}FeO_3$ (L0.95F), $La_{0.95}Sr_{0.05}FeO_3$ (LSF) and $Nd_{0.95}FeO_3$ (NF) perovskites were prepared by the Pechini method. Metal precursors employed were $La(NO_3)_3.6H_2O$ (VETEC, P.A.), $Nd(NO_3)_3.6H_2O$ (Sigma-Aldrich, 99,9%), $Fe(NO_3)_3.9H_2O$ (Sigma-Aldrich, ≥ 98%) and $Sr(NO_3)_2$ (VETEC, P.A.). A citric acid solution (CA) was added to the metal precursors solution mixture and the temperature was raised up to 60 °C for 30 min. Ethyleneglycol (EG) was added at AC:EG ratio of 3:2 and the temperature was increased up to 90°C for approximately 3 h. The obtained resins were dried at 110 °C for 19 h and then calcined in a muffle in 2 steps: a) the first one was performed at 500°C for 30 min at a heating rate of 1°C/min and b) the second one at 700°C for 3 h at a heating rate of 5°C/min both steps under static air. The crystalline structures were examined by X-ray diffraction. The powder X-ray diffraction was recorded on a Miniflex X-ray Diffractometer (Rigaku) equipped with a Cu tube (λ= 1.5418 Å). Data was collected at 30 kV, 15 mA, in the range $10° \leq 2\theta \leq 90°$, with step size of 0.05° and count time of 6 seconds per step.

The catalysts were evaluated in the POM reaction. The continuous gas flow reactor consists of a U quartz tube surrounded by a resistive furnace. The catalyst was positioned between two quartz wool layers. All tests were carried out at atmospheric pressure. The total mass was 100 mg. Before the reaction tests, the catalysts were reduced with a H_2 flow of 50 cm^3/min at 650 °C and heating rate of 10 °C/min, remaining at this temperature for 1 h. The tests were carried out at 700°C, feed CH_4:O_2 proportions of 2. The exit gases were analyzed by gas chromatography Perkin Elmer N2000, equipped with a thermal conductivity detector (TCD). The product analyzes were obtained using a capillary column (Carboxen 1010) with He as carrier gas. The main products identified from the POM reaction were H_2, CO, CO_2, ethene and ethane.

3. Results and discussion

Fresh LF, L0.95F, LSF and NF perovskites were examined by XRD and the diffraction data were refined by Rietveld method. In Figure 1(a), it is shown the refined diffractogram of the LF perovskite. It is observed that the LF sample exhibited peaks consistent only with the orthorhombic structure of $LaFeO_3$ in the standard from JCPDS. The average crystallite size was calculated as 35 nm for the LF sample by Scherrer's equation.

Figure 1(b) shows the CH_4 conversion at 700°C over the perovskites. L0.95F catalyst indicated a relatively high value, while the LF sample showed a low value. Perovskite with an atomic ratio of the A-site/B-site < 1 revealed a high mobility of the lattice oxygen due to the production of oxygen vacancies as a result of the A-site deficiencies [4], wich promotes the CH_4 reform performance. The catalyst with neodymium presents better CH_4 conversion than lanthanum. $La_{0.95}Sr_{0.05}FeO_3$ presented the best conversion among all the catalysts.

In terms of product selectivity, the catalysts produced mainly H_2, CO, CO_2, ethane and ethene, as shown in Figure 1(d). Product distribution practically did not vary with the perovskite type catalyst under the conditions tested. However, it was found that the introduction of Sr (LSF) and the substitution of La by Nd (NF) showed a slightly higher conversion of methane and lower tendency to ethane and ethene formation compared to LF and L0.95F perovskites. All perovskites presented a high value for the H_2/CO ratio (Figure 1(c)), meaning that other reactions prevailed over the POM reaction.

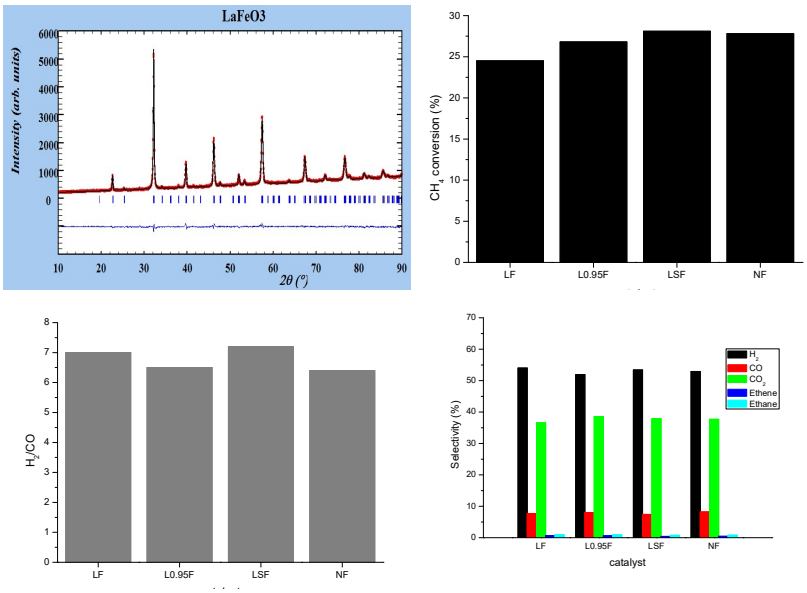

Figure 1. (a) Diffractogram of the LF sample, (b-d) Conversions and selectivities at 700°C in the POM reaction.

4. Conclusions

Perovskites were investigated in the POM reaction for syngas. The catalyst with neodymium presents better CH_4 conversion than lanthanum. $La_{0.95}Sr_{0.05}FeO_3$ presented the best conversion among all the catalysts. Product distribution practically did not vary with the perovskite type under the conditions tested.

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Keywords
Perovskite, methane, syngas, POM.