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Article

Synthesis of $LaNiO_3$ Perovskite by the Modified Proteic Gel Method and Study of Catalytic Properties in the Syngas Production

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Este trabalho descreve um estudo sobre a síntese da perovsquita $LaNiO_3$ via método do gel proteico, variando quantidade de colágeno e sobre a atividade catalítica de $LaNiO_3$ e $LaNiO_3/Al_2O_3$ na produção de gás de síntese ($CO + H_2$). Os padrões de difração de raios X revelaram a formação da estrutura perovsquita em todas as amostras preparadas pelo método de síntese do gel protéico, variando a quantidade de colágeno e após calcinações a 700 ºC por 2 h. O catalisador $LaNiO_3/Al_2O_3$ preparado pelo método de impregnação mostrou picos de difração nos difratogramas atribuídos a $LaNiO_3$ e ao suporte (Al_2O_3). Este catalisador apresentou: área superficial específica de 46,1 $m^2\ g^{-1}$, dois picos de redução no perfil de redução à temperatura programada (RTP) e 46% de conversão do metano (através da oxidação parcial do metano utilizando oxigênio) depois de 18 h de reação.

This work describes a study on the synthesis of $LaNiO_3$ perovskites via the modified proteic gel method, varying collagen content and on the catalytic activity of $LaNiO_3$ and $LaNiO_3/Al_2O_3$ in the syngas ($CO + H_2$) production. X-ray diffraction patterns revealed the formation of perovskite structure in all samples prepared by proteic gel synthesis method, varying collagen content and after calcinations at 700 ºC for 2 h. $LaNiO_3/Al_2O_3$ catalyst prepared by the impregnation method showed diffraction peaks due to the perovskite structure and to the support (Al_2O_3). This catalyst presented: specific surface of 46.1 $m^2\ g^{-1}$, two reduction peaks in the temperature programmed reduction (TPR) profile and 46% of methane conversion (by the partial oxidation of methane using oxygen) after 18 h of reaction.

Keywords: $LaNiO_3$ perovskites, collagen, syngas production, partial oxidation of methane

Introduction

Perovskite mixed oxides are ceramic materials that combine metal elements with non-metallic ones, usually with the general formula ABO_3, where A represents a lanthanide or alkaline earth ion and B a trivalent ion of a transition metal.[1] $LaNiO_3$ perovskite oxides have been widely investigated among the rare earth perovskites containing Ni^{+3}. Nickel usually adopts a formal charge of Ni^{2+} but can (in rare earth or alkaline earth ternary metal oxides) form 3+ ions.[2] These materials can be considered extremely important due to their electronic, optic and catalytic properties, among others.[1-5]

In recent decades, many routes have been used for preparing mixed oxides with the perovskite structure such as the conventional ceramic powder technology, the Pechini process, the chelating precursor method, the proteic sol gel process and the combustion synthesis, among others.[5-9] In general, these methods aim at obtaining a material with high homogeneity, low amount of impurities, and phase, particle size and surface area suitable for different applications.[5-8] The effects of the routes of preparation and calcination

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temperature on the phase composition and crystalline structure of $LaNiO_3$ materials are considered important because of their effects on the electronic properties, which affect the conductivity and catalytic properties of the final product.[10]

Some researchers have used a synthetic route similar to the polymeric precursor method in which the gelatin replaces the ethylene glycol as the polymerizing agent to obtain nanoparticles.[11-13] This method consists in the formation of a metal-chelate complex system, including a chelating agent and a metal precursor, replacing the ethylene glycol and the citric acid or EDTA (ethylenediaminetetraacetic acid) by gelatin. The method is distinguished by its simplicity and ability to obtain crystalline materials with high purity and good control of stoichiometry. It is a new alternative for obtaining oxides with high efficiency and low cost. Oliveira *et al.*[13] evaluated the protein-gel method in the formation of the perovskite phase and observed the formation of a single phase material with the perovskite structure at 700 °C.

In this study, the $LaNiO_3$ perovskite-type oxide was synthesized by a new route of the modified proteic gel method using collagen as organic precursor with the goal of studying the effect of the metal/collagen ratio on the structural properties of the material. Collagen was used as chelating agent that binds with metals through carboxylate and amine groups.[14] The prepared $LaNiO_3$ and $LaNiO_3/Al_2O_3$ catalysts were studied in the syngas production.

Experimental

Synthesis

The $LaNiO_3$ perovskite oxides were prepared by the modified proteic gel method, using nickel and lanthanum nitrates as starting materials and collagen powder as chelating agent. First, the nickel nitrate dissolution was performed in 100 ml of distilled water at temperature of 30 °C for 30 min under agitation, and afterwards, the solid lanthanum nitrate was added to the system under stirring at the temperature of 30 °C for 30 min. Then, the solution was heated up to 70 °C, and at this point, the collagen was added. The temperature was maintained constant for 1 h resulting in a viscous gel that was heat treated at 350 °C for 2 h with a heating rate of 10 °C min^{-1}. The resulting precursor powder was calcined in air at 700 °C during 2 h. The mass ratios of metal to collagen (Ni:collagen) were 1.0:5.0, 1.0:2.0, 1.0:1.0 and 1.0:0.5. It was chosen the material with a lower metal/collagen content to study the catalytic properties in order to use a material with potentially lower cost. The $LaNiO_3$ catalyst calcined at 700 ºC and synthesized with the 1.0:0.5 metal:collagen proportion was supported on alumina by excess solvent impregnation method using ethanol solution and followed by drying at 60 ºC for 1 h. The amount of $LaNiO_3$ loaded on Al_2O_3 used was of 5% (mass ratio), and the Al_2O_3 used contained the alpha and gamma phases.

Characterization

X-ray diffraction (XRD) measurements of calcined samples were performed on a Rigaku DMAX100 diffractometer using Cu K_α (λ = 1.5406 nm) radiation. The diffraction angle (2θ) range was from 10 to 60° with steps of 0.020°. The identification of crystalline phases was performed using data from the cards of JCPDS (International Center for Diffraction Data). The lattice parameters of the unit cell of orthorhombic perovskite structure were determined from the reflections of the planes (110) (200) and (220) of the material $LaNiO_3$ (1:0.5) and the values were *a* 0.545 nm and *c* 1.308 nm. The BET surface area was measured on a Quanta Chrome NOVA 1200 instrument using nitrogen adsorption. The analysis of the particle size was done to all samples using the Scherrer equation.[15] The TPR (temperature programmed reduction) profile was performed by heating of about 100 mg of the sample from 50 to 1000 ºC in a AutoChem II 2920 instrument under a heating rate of 10 ºC min^{-1} and H_2-N_2 (10.1% of H_2) in a quartz reactor. Before the catalytic test, the catalysts were activated with a hydrogen flow for 60 min at 500 ºC. Afterwards, the catalytic bed was heated from 500 to 800 ºC under a nitrogen flow at 10 ºC min^{-1}. The conditions used were: inlet temperature of 900 ºC, reaction temperature of 800 ºC, pressure of 1 atm, dynamic flow of 333 mL min^{-1} for CH_4 and 167 mL min^{-1} for O_2, catalyst mass equal to 100 mg and reaction time of 18 h. The catalytic tests were online conducted and the products were simultaneously analyzed using a gas chromatogtaph of the thermo Fisher Scientific.

Results and Discussion

The XRD patterns of the $LaNiO_3$ powders calcined at 700 °C (Figure 1a-1d) indicated the formation of a crystalline phase of perovskite type. Peaks corresponding to secondary phases attributed to the NiO and La_2O_3 were also found in some samples. In the diffraction patterns, it can be observed that the intensities of the peaks of the secondary phases decreased according to the amount of collagen, except for the sample with a metal/collagen ratio of 1.0:0.5. Moreover, it is suggested that the metal/collagen ratio of 1.0:1.0 is the best one in the formation of the perovskite single phase, whereas the peaks related to secondary phases disappeared. The perovskite structure of the samples was confirmed by the very intense peaks at $2\theta = 32.8°$, $47.3°$ and $58.1°$. All perovskite peaks were attributed to rhombohedral structure (JCPDS 34-1028). The XRD pattern of the $LaNiO_3/Al_2O_3$ sample (Figure 1e) showed very intense peaks attributed to phases of alumina and less intense peaks related of the main peaks of the $LaNiO_3$ perovskite phase. Then, the material maintained the structure suggesting that the alumina can be used as support because it did not change the perovskite structure, as expected by the preparation method. Although the XRD profiles for pure perovskite ($LaNiO_3$) indicated the presence of NiO content in samples prepared with the metal/collagen 1.0:0.5, the XRD pattern of this sample supports ($LaNiO_3/Al_2O_3$) did not clearly indicate the presence of this oxide due to the fact that the diffraction peaks referent to this phase (NiO) are overlapped by peaks of Al_2O_3.

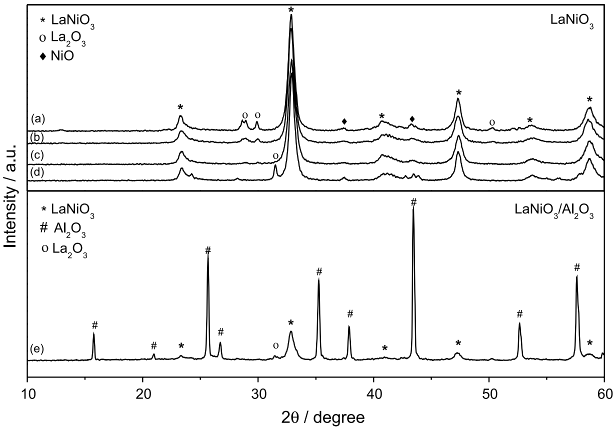

Figure 1. XRD patterns for $LaNiO_3$ perovskite with metal:collagen ratio of (a) 1.0:5.0, (b) 1.0:2.0, (c) 1.0:1.0 and (d) 1.0:0.5, and (e) $LaNiO_3/Al_2O_3$.

The crystallite size was calculated by Scherrer laws,[15] and the results for the samples with different metal:collagen ratio are shown in Table 1. The crystallite sizes were practically not much influenced by the collagen content. The sample with the lower metal/collagen ratio (1.0:0.5) showed a lower crystallinity and a larger crystallite size (13.0 nm) among the samples. These results showed that the smaller content of collagen used in the synthesis contributed for the larger crystallite size of perovskite. The sample with the lower metal/collagen ratio (1.0:0.5) showed crystallinity equal to 89%, which is the lowest one among all samples synthesized. This suggests that a smaller amount of the substrate (chelating agent) can be used for the synthesis. However, this influences the crystallinity because it affected the particle size and ordering of the structure. The specific surface area did not show linear relation with crystallite size.

Table 1. Specific surface area (SSA), crystallite size (D) and crystallinity for $LaNiO_3$ perovskite with different metal:collagen (M:C) ratio and for $LaNiO_3/Al_2O_3$

Catalysts, M:C ratio	SSA / ($m^2 g^{-1}$)	D / nm	Crystallinity / %
LaNiO, 1.0:5.0	18.5	12.9	92
$LaNiO_3$, 1.0:2.0	18.0	11.3	100
$LaNiO_3$, 1.0:1.0	18.2	11.8	97
$LaNiO_3$, 1.0:0.5	25.3	13.0	89
$LaNiO_3/Al_2O_3$	46.1	10.1	–

The specific surface areas (SSA) for $LaNiO_3$ perovskite with the lower metal/collagen ratio (1.0:0.5) calcined at 700 °C and supported in Al_2O_3 ($LaNiO_3/Al_2O_3$) were 25.3 and 46.1 $m^2 g^{-1}$. The $LaNiO_3$ presented higher SSA than the characteristic SSA of perovskite type oxides. The material supported on alumina ($LaNiO_3/Al_2O_3$) presented high area values because the alumina presents a porous structure.

The TPR profiles of pure perovskite and of perovskite supported on aluminia are shown in Figure 2. $LaNiO_3$ pure catalyst was reduced at least in two stages: the first one with a maximum peak at 368 ºC and the second one with a maximum peak at 482 ºC. These peaks correspond to successive changes in the perovskite structure, which are related to reduction of Ni^{3+} to Ni^{2+} resulting in the $La_2Ni_2O_5$ oxide and the second peak is attributed to reduction of Ni^{2+} to Ni^0, resulting in nickel metallic species, lanthanum oxide and water as reaction products. The maximum temperatures of the first and second reduction peaks of the perovskite structure change to 348 and 443 ºC, respectively, in the perovskite supported on alumina oxide. This decrease in temperature reduction can be attributed to good dispersion of the perovskite phase on the support and due to the low interaction of the perovskite phase with the support. The reduction of NiO phase present in the $LaNiO_3$

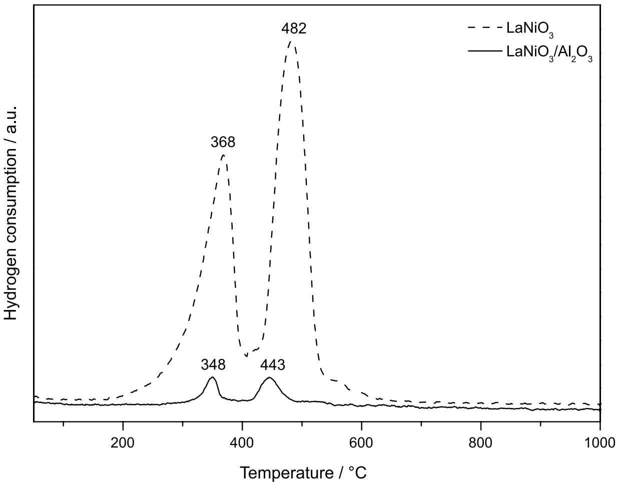

Figure 2. TPR profile for $LaNiO_3$ and $LaNiO_3/Al_2O_3$.

sample with metal/collagen ratio of 1.0:0.5 is probably simultaneously occurring during the steps of the nickel reduction of the perovskite structure.

The catalytic activity of the $LaNiO_3$ and $LaNiO_3/Al_2O_3$ catalysts were evaluated in the partial methane oxidation. The activity of the catalysts was based on the methane conversion, which was made by means of the carbon mass balance without considering the formed coke. It was assumed that all methane after the reaction should appear as CO, CO_2 and non-reacted CH_4. Conversion values (X%) were calculated from the equation:

$$X\% = \frac{nCH_4^{\,0} - nCH_4^{\,s}}{nCH_4^{\,0}} 100 \qquad (1)$$

where X% is the methane conversion, nCH_4^s the number of moles of methane on the reactor output and nCH_4^0 the number of moles of methane on the reactor input.

All evaluated catalysts showed activity on the methane conversion and selectivity to the syngas production (Figure 3). Figure 3 shows the conversion values in the partial methane oxidation for the catalysts studied. $LaNiO_3$ catalyst showed 51% of conversion after 18 h of reaction time, while the $LaNiO_3/Al_2O_3$ catalyst showed 46% of conversion after 18 h of reaction time. The results also showed that the catalyst stabilities during the catalytic test were different. $LaNiO_3$ catalyst showed several changes on activity during the 7 h of reaction, while the $LaNiO_3/Al_2O_3$ catalyst maintained its activity constant after 2 h of reaction until the total period of 18 h. The lower activity of $LaNiO_3/Al_2O_3$ catalyst in relation to the $LaNiO_3$ catalyst can be explained by the lower amount of active sites available for reaction since the supported samples contains only 5% of perovskite.

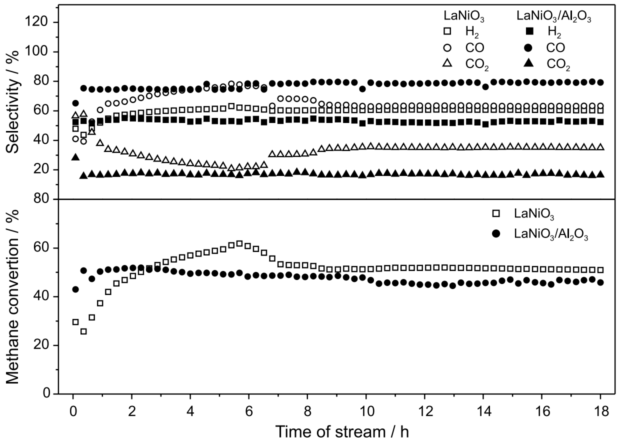

Figure 3. Selectivity products and conversion values for $LaNiO_3$ and $LaNiO_3/Al_2O_3$ catalysts in the partial methane oxidation. Parameters: temperature of 800 °C, pressure of 1 atm, CH_4 and O_2 as reactants, catalyst mass of 100 mg and reaction time of 18 h.

The selectivity products identified were CO, CO_2, H_2 and H_2O. According to the carbon balance, the product selectivity for CO and CO_2 can be represented by the equations:

$$CO\% = \frac{nCO^{S}}{nCO^{S} + nCO_2^{\,S}} 100 \qquad (2)$$

$$CO_2\% = \frac{nCO_2^{\,S}}{nCO^{S} + nCO_2^{\,S}} 100 \qquad (3)$$

where nCO^s is the number of moles of carbon monoxide on the reactor output and nCO_2^S the number of moles of carbon dioxide on the reactor output.

The selectivity to the H_2 and H_2O products can be described by the following equations:

$$H_2\% = \frac{nH_2^{\,S}}{nH_2^{\,S} + nH_2O^{S}} 100 \qquad (4)$$

$$H_2O\% = \frac{nH_2O^{S}}{nH_2^{\,S} + nH_2O^{S}} 100 \qquad (5)$$

where nH_2^s is the number of moles of hydrogen on the reactor output and nH_2O^S the number of moles of water on the reactor output.

In the catalytic tests of the partial oxidation of methane several reactions occur: complete combustion of methane, formation of syngas and steam reforming of methane unreacted. When the reaction of steam reforming of methane occurs, there is an increased on the CO amount until to stabilization, but the CO_2 amount presents an opposite profile. This fact is clearly observed for the sample $LaNiO_3$ and little observed for the sample $LaNiO_3/Al_2O_3$. The low amount of CO_2 formed in the supported catalyst ($LaNiO_3/Al_2O_3$) compared to the unsupported ($LaNiO_3$) can be an indication of the higher fraction of the Ni reduced phase than one oxidized phase, which (oxidized and reduced phases) can act as a catalyst in the reaction cycle.

The selectivity values to syngas (CO and H_2) were of 63.3% (CO) and 60.1% (H_2) using the $LaNiO_3$ catalyst and 79.3% (CO) and 52.4% (H_2) using $LaNiO_3/Al_2O_3$ catalyst. The results of selectivity to synthesis gas and conversion data of the catalysts studied compare favorably with other published data.[16]

Conclusions

The evidence of this study provides strong support for use of collagen, which is a low-cost, non-toxic organic material, very good chelating agent in the formation of the $LaNiO_3$ perovskite structure. X-ray diffraction patterns indicated the formation of the rhombohedral perovskite structure in all samples. Some sample also showed secondary phases, exception the sample with a metal/collagen ratio of 1.0:1.0 the formed a single phase material. These facts confirm that oxides with $LaNiO_3$ perovskite type structure can be obtained at low ratio of metal to chelating agent. The perovskite phase was identified in the material supported ($LaNiO_3/Al_2O_3$), although their peaks appeared in low intensities. The $LaNiO_3/Al_2O_3$ catalyst presented a specific surface are of 46.1 $m^2\ g^{-1}$ and showed two reduction peaks in the TPR profile. It was also observed that the methane conversion was approximately 46% and the selectivity to syngas was of 79.3% (CO) and 52.4% (H_2). In all cases, a low selectivity to CO_2 was verified, using $LaNiO_3$ and $LaNiO_3/Al_2O_3$ catalysts.

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