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Perovskite-type oxides in methane dry reforming: Effect of their incorporation into a mesoporous SBA-15 silica-host

Issarly Rivas, Juan Alvarez, Eglé Pietri, M. Josefina Pérez-Zurita, Mireya R. Goldwasser *

Escuela de Química, Centro de Catálisis, Petróleo y Petroquímica, Apartado 40600, Los Chaguaramos, Caracas 1020 A, Venezuela

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ABSTRACT

A series of Ni-based perovskite-type oxides $LaNiO_3$, $La_{0.8}Ca_{0.2}NiO_3$ and $La_{0.8}Ca_{0.2}Ni_{0.6}Co_{0.4}O_3$, were synthesized as catalyst precursors both bulk and built-in a highly ordered mesoporous SBA-15 silica-host with the aim of using them as heterogeneous catalysts in syngas production by the methane dry reforming with CO_2. The solids were characterized by means of FT-IR, XRD, BET surface area and TPR techniques. All synthesized oxides showed a perovskite-type structure. Incorporation of the oxides into the mesoporous silica-host generates a higher metal–support interaction increasing the Ni reduction temperature. A decrease in CH_4 and CO_2 conversion was observed when a second cation in A- and/or B-site was added to the bulk perovskite. The built-in of these solids in the SBA-15 mesoporous silica-host allows working at lower temperature with an increase in conversions and selectivity towards syngas which represent an attractive perspective for industrial application.

1. Introduction

Among all processes to transform methane to syngas, the CO_2 dry reforming of methane produces the lower molar ratio of H_2/CO, suitable to be transformed to more valuable products through various chemical processes such as Fischer Tropsch synthesis and oxo-synthesis. An alternative application of the dry reforming is the thermochemical storage and transmission of renewable energy sources. Specifically, the process Solchem [1] and the CLEA project [2] used the reaction of methane reforming with CO_2 and its reverse methanation reaction as a mean of converting solar energy into chemical energy, which is easier to store and carry. Besides, this reaction consumes CO_2 a greenhouse gas processing it to higher added value products [3–6].

Recently interest has arisen in perovskite-type oxides as precursors in the catalytic dry reforming of CH_4 with CO_2 [7–10]. These solids have high thermal and hydrothermal stability as well as high mechanical strength among other properties. However, the potential application of these oxides is limited by its small surface area, lower than 10 m^2/g [11] and the high reaction temperatures necessary to carry out the reforming due to its endothermicity [9–11].

One way to remedy this problem is to disperse the perovskite-type oxide in a medium that possesses a high specific surface area, thermal stability and prevent the sintering of the metal [12]. Energy consumption in the process of reforming of methane can be significantly reduced by optimizing the design of highly active and selective catalysts; the ordered SBA-15 mesoporous silica meets these features. Applications of ordered mesoporous silica as hosts for the preparation of mesoporous catalysts with chemically functionalized surfaces have been investigated [13–15].

We have previously reported the catalytic performance of a series of binary and ternary Ni-based perovskite-type oxides for dry reforming of methane [9–11,16–18]. Results showed that perovskite systems are good precursors for the dry reforming reaction since, in most cases, they present better catalytic properties quantified in terms of activity, selectivity and stability, comparable even with a catalyst commercially used in steam reforming [9]. The good performance shown by these systems in the reforming reaction has been attributed to the in situ formation of highly dispersed systems (metal particles from B-site cations/A-site cations oxides) as a result of drastic structural changes being experienced by the network of the original crystalline perovskite-type synthesized material after reduction. However, the specific surface area of these catalysts did not meet the requirements needed for industrialization.

The objective of the present work was to investigate the performance of perovskite-type oxides dispersed in an ordered SBA-15 mesoporous silica-host as catalyst precursors for the CO_2 reforming of CH_4 to syngas in order to increase surface area, prevent carbon formation and reduce the high temperatures needed for the reforming reaction lowering energy consumption. $AA'BB'O_3$ ($A = La^{3+}$, $A' = Ca^{2+}$, $B = Ni$ and $B' = Co$) perovskite-type oxides were used as catalysts precursors both bulk and built-in a

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* Corresponding author. Fax: +58 0212 6051265.
E-mail address: mireya.goldwasser@ciens.ucv.ve (M.R. Goldwasser).

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SBA-15 mesoporous silica-host. Correlations between the effect of partial substitution of cations in A and/or B sites of the precursor perovskite and the catalytic activity and stability of in situ created Ni and Co nanoparticles in the mesoporous silica-host are discussed.

2. Experimental

2.1. Catalyst synthesis

2.1.1. Synthesis and characterization of SBA-15 mesoporous silica-host

Highly ordered SBA-15 mesoporous silica was synthesized according to the method described by Wang et al. [15]. A typical synthesis procedure is as follows: 12 g of TCP $EO_{20}PO_{70}EO_{20}$ triblock polymer (Aldrich) with a molecular weight of ~5800 g/mol was dissolved in 60 mL of HCl (35–37%) and 350 g of distilled water with stirring at 40 °C for 2 h to make a homogeneous clear solution. Then 29.5 g of the tetraethylorthosilicate (TEOS) was added into that solution and left for 48 h at 40 °C with vigorous stirring to form a solid precipitate, which was filtered and washed with distilled water until pH 7. The solid product was recovered, dried at 50–70 °C for 5 h and calcined at 520 °C for 6 h in air flow.

The SBA-15 mesoporous silica-host was characterized by FT-IR spectroscopy in a Perkin Elmer spectrometer, in the range of 4000–400 cm^{-1}, using potassium bromide (KBr) pellets with a sample/KBR ratio of 1:3. 75 scans were recorded at 20 °C with a resolution of 4 cm^{-1}.

XRD analysis at low angles was used to determine the hexagonal ordering of the mesoporous silica using a diffractometer Bruker Model D8 Advance, using nickel-filtered Cu Kα radiation with λ = 1.5406 Å, in the range of 0.5–5° (2θ).

Samples were characterized by N_2 adsorption/desorption isotherms to obtain the textural properties of the solid at liquid nitrogen temperature in an automated physisorption instrument (Micromeritics Tristar 3300). Prior to the analysis, the samples were outgassed in vacuum at 300 °C overnight.

2.1.2. Synthesis and characterization of perovskite-type catalyst precursors

The studied perovskite-type oxides $LaNiO_3$, $La_{0.8}Ca_{0.2}NiO_3$ and $La_{0.8}Ca_{0.2}Ni_{0.6}Co_{0.4}O_3$ were synthesized by fine chemical using a modification of the citrate sol–gel method investigated first by Pechini, as described elsewhere [9]. Adequate amounts of the precursor of the cation at B-site were dissolved under vigorous stirring in a solution of citric acid (99.5 Riedel-de Haën) with an excess of ethylene glycol (99.5 Riedel-de Haën) as the organic polydentate ligand. The citric acid/B-cation molar ratio was 4, while it was 1.38 for ethylene glycol/citric acid. The mixture was kept at 50–60 °C with mild continuous stirring until a clear solution was obtained. At this point, a stoichiometric quantity of the precursor of A-cation, $La(NO_3)_3·5H_2O$, was added while keeping the mixture at 60 °C. The evaporating process proceeded for 2 days until a viscous resin was formed. The resin was dried at 150 °C for 24 h and calcined in air at 700 °C for 5 h.

Perovskite-type oxides loaded into SBA-15 mesoporous silica-host were synthesized by the method described by Yin et al. [12]. Alcoholic solutions of the precursor cations under the nitrate form (La, Ca, Ni and/or Co) were dissolved in the minimum amount of ethanol (solution 1) to obtain the perovskite with a 10% (w/w) Ni in the catalyst. Citric acid was added to solution 1 until a citric acid/cations molar ratio equal to 1 (solution 2). Subsequently, the solution 2 was added to SBA-15 mesoporous silica, left to dry for 24 h and calcined at 600 °C for 6 h in an air flow (30 mL/min). SBA-15 loaded perovskite solids are referred as $LaNiO_3$/SBA-15, $La_{0.8}Ca_{0.2}NiO_3$/SBA-15 and $La_{0.8}Ca_{0.2}Ni_{0.6}Co_{0.4}O_3$/SBA-15.

The crystalline phase detection of the as-synthesized perovskites were determined using a Philips diffractometer model PW 1830 using Cu Kα radiation with λ = 1.5406 Å, between 10° and 80° (2θ) and compared with JCPDS standard files software using the program database PCPDFWIN. Surface areas were measured by a multiple-point BET procedure using nitrogen–argon adsorption at liquid nitrogen temperature with 30% N_2 in Ar in a Micromeritics Tristar 3300 system. The reducibility of these precursor mixed-oxide perovskites was studied by TPR analysis performed in a Thermo-Quest TPD/TPR 1100 system using 0.07 g of the sample in 10% H_2 in Ar stream (20 mL/min). The temperature was raised from room temperature to 1000 °C at a rate of 10 °C/min.

2.2. Activity test

The variation of activity/selectivity patterns as a function of the composition of the mixed-oxide precursors, the influence of activation procedure and reaction parameters were monitored between 600 and 700 °C with a 24 L h^{-1} g^{-1} hourly space velocities using 200 mg of catalyst in a 20-mm i.d. quartz reactor at atmospheric pressure operated in a fixed-bed continuous flow system with feed molar ratio CH_4/CO_2 = 1, using argon as diluents gas with $CH_4/CO_2/Ar$ = 1:1:8, as previously described [9].

The reaction mixture was fed at a total flow rate of 80 mL/min. Before the catalytic tests, the solids were reduced in H_2 flow (20 mL/min, T = 700 °C, 8 h). After reduction, the system was swept with Ar for 15 min and adjusted to reaction temperature. The water produced during reaction, was condensed before passing the reactants and products to the analyzing system, which consisted of an on-line gas chromatograph (Perkin-Elmer Clarus 500) equipped with a TCD detector and provided with a Carbosieve SII 80/100 column (12 ft, 1/8 in. o.d. SS), as previously described [16]. The CH_4 and CO_2 conversions are defined as the CH_4 and CO_2 converted per total amount of CH_4 and CO_2 fed, respectively. The selectivity to CO was calculated based in carbon balance and defined as $S_{CO}\,(\%) = \eta_{CO}/[\eta_{CH_4(c)} + \eta_{CO_2(c)}] \times 100$; while hydrogen selectivity was calculated as $S_{H_2}\,(\%) = [\eta_{H_2}/2\eta_{CH_4(c)}] \times 100$, where η_{CO} and η_{H_2} are the moles of CO and hydrogen produced and $\eta_{CH_4(c)}$ and $\eta_{CO_2(c)}$ are the amounts of methane and carbon dioxide converted, as described elsewhere [17]. Stability tests were performed at 700 °C for 24 h.

3. Results and discussion

3.1. FT-IR and XRD analysis of SBA-15 mesoporous silica

Evidence of SBA-15 mesoporous silica synthesis was followed by FT-IR and low angle XRD analysis. Fig. 1 shows the FT-IR spectrum of SBA-15 mesoporous silica. Characteristic bands are

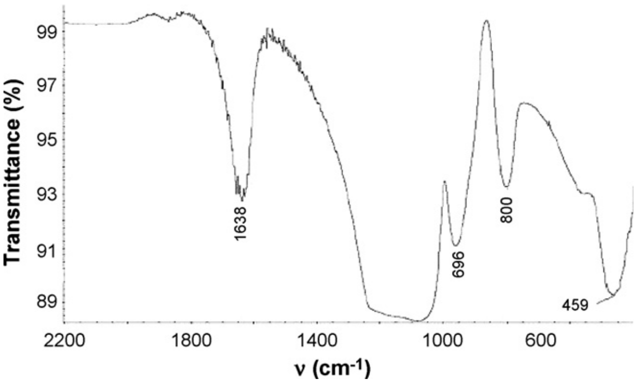

Fig. 1. FT-IR spectrum of SBA-15 mesoporous silica-host.