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Hydrogen production by autothermal reforming of methane over lanthanum chromites modified with Ru and Sr

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ABSTRACT

The partial substitution of La by Sr in lanthanum chromites ($\text{La}_{1-y}\text{Sr}_y\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$, $y = 0.01, 0.02, 0.05$) produced changes in the size, insertion degree of Ru and oxygen vacancies of the perovskite structure. The surface and structural modifications of the $\text{La}_{1-y}\text{Sr}_y\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$ perovskites brought about by substitution of La by Sr directly affected the catalytic behaviour of the perovskites in the autothermal reforming of methane (ATR). It was found that all $\text{La}_{1-y}\text{Sr}_y\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$ perovskites showed excellent ATR activity that it increased with the Sr substitution degree in the perovskite. The most active Sr-substituted chromite also showed high stability and thiotolerance in the long ATR durability test in the presence of 50 ppm of sulphur. Characterization of used samples revealed not only good structural stability of the Sr-substituted perovskites under the ATR conditions but also absence of carbon deposition on the surface of used catalyst in the ATR reaction.

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Introduction

In the short-medium term, the hydrogen generation from catalytic technologies based on fossil hydrocarbons reforming or partial oxidation processes will play a key role for the establishment of the first stages in the production, distribution and use of hydrogen [1–4]. Large-scale, industrial hydrogen can be extracted from the natural gas, oil and coal.

Approximately 96% of the hydrogen is generated directly from fossil fuels sources. The natural gas is doubtless the most commonly fuel used in the industrial hydrogen production, with about 49%, followed by the oil (29%) and carbon (18%) [3]. The hydrogen generation from natural gas can be carried out by means of catalytic technologies such as steam methane reforming (SMR), catalytic partial oxidation (CPO) and autothermal reforming (ATR). The autothermal

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reforming technology combines the SMR and CPO reactions to produce hydrogen in such a manner that the global process is almost thermally neutral or slightly exothermic, thus achieving a major efficiency for heat exchange and a great operating temperature control that reduce the hot spots formation to prevent the catalyst deactivation by sintering or coking. In addition, the ATR has a short start-up and shut-down response time in compact size reactors and presents more rapid response to changes in hydrogen-on-demand [2–6]. The operation conditions of ATR creates a severe environment for the catalysts respect to carbon formation, sulphur poisoning and thermal stability that require improved resistance of the catalysts to sintering or vaporization of metals used as active phases since the rates for both phenomena increase exponentially with the temperature. Traditionally, catalytic systems used for ATR of methane are based on metals (Pt, Rh for oxidation reactions and Ni, Co and Ru for reforming) supported on carefully formulated oxide substrate such as Al_2O_3 , CeO_2 , ZrO_2 , La_2O_3 ,... in order to provide high surface area and high thermal and mechanical resistance [7,8]. Despite the advances achieved in traditional supported catalysts formulations for the ATR of methane, the development of reforming catalysts with significantly improved activity and resistance to sulphur remains a worthwhile goal.

Perovskite-type mixed oxides have become increasingly studied in the reforming of hydrocarbons because of the ability to substitute different metals into their structure, thus modifying their characteristics and reforming activity [9–11]. Lanthanum chromites (LaCrO_3) have recorded high stability and activity for the reforming of hydrocarbons to produce hydrogen [12–14]. Nevertheless, this unsubstituted perovskite formulation shows relatively low hydrogen yields as compared to other unsubstituted lanthanum perovskites such as LaCoO_3 or LaNiO_3 [15–17]. A strategy to improve the activity of the unsubstituted LaCrO_3 is to introducing structural modifications in the perovskite by means of the partial substitution of Cr by other transition metals with high reforming activity (Ni, Co, Ru, etc.) [12,18,19]. Among the transition metals that can be introduced in the structure of the LaCrO_3 , ruthenium is of particular interest because it is highly effective in the catalytic reforming of hydrocarbons [20–23]. Another way to achieve more active and stable perovskite catalysts is to tailor catalytic properties by producing structural defects through partial substitution of La by alkaline or alkaline-earth metal cations (Li, Na, K, Rb, Ca, Sr, etc.); such defects, typically oxygen vacancies, can influence the catalytic activity since their presence could favour reactants chemisorption or other relevant catalytic steps involving oxygen transport, electron transfer processes, etc. [10,13].

With this background, this work was undertaken with the aim to study the influence of partial substitution of La by Sr on the surface and structural properties of the $\text{La}_{1-y}\text{Sr}_y\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$ ($y = 0.01, 0.02, 0.05$) perovskites and its effect on the performance for the ATR reaction of methane. Careful investigation of both surface and structural characteristics of the fresh and used catalysts has been conducted in order to know the origin of the different ATR catalytic behaviour of the mentioned catalysts.

Experimental

Perovskites preparation

$\text{La}_{1-y}\text{Sr}_y\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$ ($y = 0.01, 0.02, 0.05$) perovskites were synthesized by a modified citrate sol–gel method [24]. Basically, 1 M aqueous solutions of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9% Alfa Aesar), $\text{Sr}(\text{NO}_3)_2$ (99% Alfa Aesar), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99% Sigma–Aldrich) and RuCl_3 (38% Ru, Alfa Aesar) were added to a solution of citric acid (Merck) and ethylene glycol (Riedel-de Haën) in appropriate amounts (citric acid/(A-cation + B-cation) = 2.5 (mol), and ethylene glycol/citric acid = 1 (mol)). The aqueous mixture was stirred and slowly heated to 70 °C for 5 h. The resultant resin which contains the metal cations inside a polymeric network was charred at 300 °C for 2 h with a heating rate of 0.5 °C/min. After that, the resin was milled to obtain a fine powder and calcined at 750 °C for 4 h with a heating rate of 2 °C/min. Table 1 shows the nominal chemical composition, expressed as relative atomic composition, and the code of the perovskites prepared for this study.

Characterization of fresh and used perovskites

The specific area of the perovskite samples was calculated by the BET method from the adsorption/desorption isotherms of nitrogen recorded at –196 °C, taking a value of 0.162 nm² for the cross-section of N₂ molecule adsorbed at this temperature. These measurements were performed with a Micromeritics ASAP 2100 apparatus on samples previously degassed at 200 °C for 16 h. The experiments were performed at liquid nitrogen temperature (–196 °C) using quasi-Gemini method to minimize errors in the measurement of low area samples.

XRD patterns of fresh and used perovskites were recorded using a X'Pert Pro PANalytical diffractometer and Cu-K α radiation (λ Cu-K α_1 = 0.1540598 nm and λ Cu-K α_2 = 0.1544426 nm with a $K\alpha_1/K\alpha_2$ ratio = 0.5). The X-ray source operated at 45 kV and 40 mA. For each sample, Bragg angles between 4° and 90° were scanned, a step size of 0.0335° and accumulation time of 19.685 s was used during a continuous scan in the above-mentioned range. The crystallite size was estimated from X-ray line width broadening using the Scherrer equation. Width (t) was taken through the full width at half maximum intensity of the most intense and least overlapped peaks.

Hydrogen temperature-programmed reduction (H₂-TPR) of perovskites was performed using a Micromeritics TPD/TPR 2900 apparatus in a U-shaped quartz reactor. Samples were treated in helium at 110 °C for 15 min and then cooled down to room temperature followed by TPR study to 1000 °C at 10 °C/min using 10% H₂/Ar flow (50 mL_N/min).

Table 1 – Nominal atomic composition and nomenclature of the $\text{La}_{1-y}\text{Sr}_y\text{Cr}_{0.85}\text{Ru}_{0.15}\text{O}_3$ perovskites.

Nomenclature	Atomic ratio La/Sr/Cr/Ru
LCrRu15	1/0/0.85/0.15
LSr1CrRu15	0.99/0.01/0.85/0.15
LSr2CrRu15	0.98/0.02/0.85/0.15
LSr5CrRu15	0.95/0.05/0.85/0.15

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