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Oxidative reforming of diesel fuel over $LaCoO_3$ perovskite derived catalysts: Influence of perovskite synthesis method on catalyst properties and performance

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ABSTRACT

Oxidative reforming of diesel fuel was studied over Co/La_2O_3 catalysts derived from $LaCoO_3$ perovskite precursors synthesized by co-precipitation (COP), sol–gel (PEC) and combustion (SCS) methods. Physical–chemical characterization of perovskite precursors by N_2-adsorption isotherms, Hg-intrusion porosimetry, XRD, XPS, TPR and SEM showed that the method of preparation produced changes in the porosity and homogeneity both at bulk and surface levels of the $LaCoO_3$ perovskite precursors. The perovskite prepared by the SCS method achieved a higher development of the porous network as well as higher homogeneity in bulk and surface compared to COP and PEC counterparts. By contrast, the PEC and COP methods produced perovskites with lower porosity and with the presence of some secondary phases such as Co_3O_4 and $La(OH)_3$. The modifications of the characteristics of $LaCoO_3$ perovskites directly affected the structure and morphology of the catalytic materials derived from the thermal pre-treatment of perovskites before the activity tests. The differences in catalyst characteristics resulted from a different reduction and interaction between the gaseous reducing stream and the initial $LaCoO_3$ perovskites which occurred during the thermal pre-treatment. The activity of the samples at the beginning of the reaction test followed the order: PEC > SCS > COP. The latter could be related to the different interaction of the catalysts with the reactants as well as with the larger presence of the La_2CoO_4 phase produced during the thermal pre-treatment. The evolution of the catalysts for long times on stream resulted in the activity order: SCS > PEC > COP. Characterization of used samples disclosed the key role of the Co^0 exposure on the catalyst surface as concerns the achieved catalytic activities and the extent of the $La_2O_2CO_3$ phase on catalysts as regards the inhibition of coke deposition.

1. Introduction

In situ hydrogen generation by reforming of hydrocarbons from logistic fuels has been widely investigated in the last years as a way to overcome the known difficulties related to the storage and transport of pure hydrogen which limit its use in stationary and mobile fuel cells (FC) [1,2].

Among logistic fuels, diesel fuel presents a sufficiently high hydrogen density and acceptably low cost which make it interesting as H_2 source. From an operational point of view, among the conventional technologies available to produce hydrogen from the heavy hydrocarbons contained in diesel fuels, the oxidative reforming, a combination of the steam reforming (Eq. (1)) and partial oxidation (Eq. (2)) reactions, is the most attractive process since it has the simplest system design, has an acceptably high energy effectiveness and provides the better response to dynamic changes [2–7].

$$C_nH_m + nH_2O \rightarrow nCO + (n + m/2)H_2, \quad \Delta H^\circ > 0 \qquad (1)$$

$$C_nH_m + n/2O_2 \rightarrow nCO + m/2H_2, \quad \Delta H^\circ < 0 \qquad (2)$$

Oxidative reforming of diesel fuel is complicate because of the nature of the compounds present in its formulation (aromatics) that makes difficult the dehydrogenation reactions involved in the reforming process [8]. The main problems associated with the reforming of diesel fuel are derived from the catalyst degradation over time due to the high reaction temperature, that leads to thermal sintering and metal volatilization, as well as to the catalysts poisoning by coke and sulphur [9]. Catalyst formulations developed for this process typically consist in noble metals (Pt, Pd, Ru and Rh) [10,11] or non-noble metals (Fe, Ni and Co) [12]

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incorporated into carefully designed supports such as thermally stabilized doped alumina [13], mixed metal oxides [14] or oxide-ion-conducting substrates like ceria, zirconia or lanthanum gallate doped with gadolinium or samarium [10,15].

In the search for new catalysts with improved activity for the reforming process, perovskite oxides (ABO_3, where A and B are usually trivalent rare-earth cations and transition metals, respectively) have arisen as good catalyst precursors. The structure of these perovskite oxides decomposes, under the reductive conditions of the reforming process, to form finely dispersed active metal particles of B atoms supported on a highly stable oxide of A [16–19]. A previous work [20] pointed out $LaCoO_3$ as a very promising catalyst precursor for hydrogen production by diesel fuel reforming. This perovskite presented a high tolerance factor (0.883) which favours the formation of perovskite crystallites. This tolerance factor, calculated through the ionic radii of oxygen and both perovskite cations, is a measurement of the deviation from the ideal cubic structure which is obtained at high temperatures and present tolerance factors close to the unity [21].

The catalysts formed after $LaCoO_3$ reduction showed high reforming activity associated to the high dispersed Co particles and high reforming stability associated with lanthanum oxycarbonates, formed under reaction, that have a role in catalyst stability favouring coke gasification [22]. However, in spite of the advantages of $LaCoO_3$ as catalyst precursor, it is a bulk material, without internal porosity, which implies low specific surface areas [23] that strongly affect the derived catalysts' activity limiting the contact among reactants and active sites. To overcome this problem, important efforts were made in order to develop perovskite oxides with larger specific surface areas applying new routes of synthesis [23].

With this background, the present work deals with the effect of the preparation method (co-precipitation, sol–gel and combustion) on the properties of $LaCoO_3$ perovskite as precursor of catalysts for oxidative reforming of diesel fuel. Textural, structural and surface properties of $LaCoO_3$ precursors synthesized by co-precipitation, sol–gel and combustion were analyzed, trying to establish a relationship between the physical–chemical characteristics of perovskite precursors and the activity and stability of the derived catalysts.

2. Experimental

2.1. Catalysts' preparation

$LaCoO_3$ perovskite precursors were prepared by three different methodologies: co-precipitation, sol–gel and combustion. The salts $La(NO_3)_3 \cdot 6H_2O$ (99.9%, Johnson Matthey) and $Co(NO_3)_2 \cdot 6H_2O$ (97.7% minimum, Johnson Matthey) were always used as $LaCoO_3$ precursors. The preparation of the perovskite by co-precipitation (COP sample) was carried out by simultaneous precipitation of cobalt and lanthanum ions using K_2CO_3 as precipitating agent [24]. The lanthanum and cobalt nitrates were dissolved in distilled water to obtain 1 M solutions. Both solutions were mixed together under vigorous stirring. Then, an aqueous solution of K_2CO_3 (99% minimum, Johnson Matthey) with a concentration 10% higher than the stoichiometric value was added to that of nitrate salts until achieving basic conditions (pH > 9). After co-precipitation, water was partially evaporated by heating around 343 K. After filtering, the precipitate was washed with ice-cooled distilled water until the pH of the filtrate became neutral. The filtrate was dried at 383 K for 4 h and calcined in air at 1023 K for 4 h; the calcination temperature was attained by heating the dried filtrate at a rate of $2\ K\ min^{-1}$.

$LaCoO_3$ prepared by the modified sol–gel method [25,26] (PEC sample) was obtained from 1 M aqueous solutions of lanthanum and cobalt nitrates. Both solutions were mixed under vigorous stirring with a 1 M aqueous solution of citric acid (CA) in a ratio CA to metal cations of 1:1 (molar). After that, ethylene glycol (EG) was added to this solution in a molar ratio of 2:3 with respect to CA. The solution was stirred and heated at 363 K for 2 h until excess of water was removed and therefore a resin containing the metal cations inside a polymeric network was obtained. A following step of heating at 673 K for 4 h was needed to char the resin. The obtained solid was milled into a fine powder before being dried at 383 K for 4 h and calcined at 1023 K for 4 h, reaching this temperature with a heating rate of $2\ K\ min^{-1}$.

$LaCoO_3$ prepared by the combustion method [27–34] (SCS sample) was obtained from lanthanum and cobalt nitrates mixed with glycine (99.9% glycine, Sigma–Aldrich) as suitable fuel [35]. As this method consists in an oxidising/reducing balance of the mixture of metal salts and the glycine fuel, the global reaction among metal nitrates and glycine to form the $LaCoO_3$ perovskite can be written as:

$$La(NO_3)_3 + Co(NO_3)_2 + 8/3C_2H_5NO_2 \rightarrow LaCoO_3 + 20/3H_2O + 23/6N_2 + 16/3CO_2 \qquad (3)$$

In our synthesis a 0.16 M aqueous solution of lanthanum and cobalt nitrates was used with 3.2 g of glycine; it was stirred on a heating plate to ensure proper homogeneity. These proportions were selected according to the optimal results obtained by Civera et al. [36] to synthesize perovskite powders with high crystallinity. The mixture was placed into a preheated oven at 773 K for a few minutes to perform the combustion. In this step the mixture ignited and a fast and explosive reaction took place reaching high temperatures and producing CO_2, N_2 and H_2O [36–38]. The resultant solid was subsequently crumbled to obtain a fine powder which was calcined at 1023 K for 4 h, attaining this temperature with a heating rate of $2\ K\ min^{-1}$.

2.2. Characterization

The BET surface area of the prepared perovskite precursors was calculated from N_2 adsorption–desorption isotherms obtained at 77 K, taking a value of $0.162\ nm^2$ for the cross-section of N_2 molecule adsorbed at this temperature. These measurements were performed with a Micromeritics ASAP 2100 apparatus on samples previously out-gassed at 423 K for 12 h.

Mercury intrusion porosimetry experiments were carried out with a CE Instruments Pascal 140/240 apparatus. Starting from vacuum and raising the pressure to 200 MPa, pore diameters from 150 μm down to 7.5 nm can be determined. In this method, the non-wetting liquid Hg is forced into the pores of a dry sample and the volume of intruded Hg is measured as a function of applied pressure. The analysis of mercury data is based on the Washburn equation for cylindrical pores:

$$r = \frac{2\gamma \cos\theta}{P} \qquad (4)$$

where γ is the surface tension, θ is the contact angle and P is the pressure applied to Hg to penetrate cylindrical pores of radius r. Constant values for γ ($0.485\ Nm^{-1}$) and θ (140°) are generally assumed. Mercury porosimetry was also used to evaluate the open porosity of the samples.

X-ray diffraction patterns were recorded using a Seifert 3000P vertical diffractometer and nickel-filtered Cu Kα radiation ($\lambda = 0.1538$ nm) under constant instrumental parameters. For each sample, Bragg angles between 5° and 80° were scanned; a rate of 5 s per step (step size: $0.04^\circ\ 2\theta$) was used during the continuous scan. Using the Scherrer equation, the mean $LaCoO_3$ particle size was then estimated from X-ray line width broadening, taken as the