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Steam reforming and oxidative steam reforming of ethanol over $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ perovskite as catalyst precursor for hydrogen production

M. Morales*, M. Segarra

Centre DIOPMA, Departament de Ciència dels Materials i Enginyeria Metal·lúrgica, Facultat de Química, Universitat de Barcelona, Martí i Franquès, 1, E-08028, Barcelona, Spain

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ABSTRACT

The catalytic activity and stability of the $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ perovskite, as a catalyst precursor, for the hydrogen production by steam reforming of ethanol (SRE) and oxidative steam reforming of ethanol (OSRE) were investigated. The resistance to sintering and carbon deposition of the catalyst for these reactions were explored. For this purpose, the catalytic activity of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ was studied as a function of the temperature and the time-on-stream. Before and after testing, the catalyst precursor was characterized by temperature programed reduction (TPR), X-ray diffraction, SEM-EDX and specific surface area (BET). The results evidenced that the catalyst was highly selective to hydrogen with a good stability for OSRE reaction. The cobalt ions in the perovskite could be reduced to nanoparticles of metallic cobalt under reducing atmospheres. The precursor could be totally regenerated to the initial perovskite structure under a specific thermal treatment, leading to its high resistance to the sintering.

1. Introduction

Steam reforming of ethanol (SRE) is an important way for the hydrogen production that can be used as fuel for fuel cells [1]. Ethanol can be easily obtained from the renewable resources, such as biomass, which may not contribute to net CO_2 emissions. In addition, it presents low toxicity and contains no sulfur derivate. The bioethanol derived from renewable resources generally contains water that can be used for SRE, as this process is a reaction of ethanol and water to produce H_2-rich gases [2]. As a result, the production of hydrogen from bioethanol *via* SRE is an interesting process.

The steam reforming of ethanol is an endothermic reaction that produces CO_2, a global warming gas, as a by-product (Eq. (1)):

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \qquad \Delta H_{(298K)} = 41.6 \text{Kcalmol}^{-1} \tag{1}$$

In a partial oxidation reforming, the steam is replaced by oxygen, and the hydrogen is produced by exothermic reaction (Eq. (2)):

$$C_2H_5OH + 3/2H_2O \rightarrow 3H_2 + 2CO_2 \, \Delta H_{(298K)} = -132.0 \text{Kcalmol}^{-1} \tag{2}$$

Adding oxygen to SRE, the process is an oxidative steam reforming of ethanol (OSRE) that could be an autothermic reaction (Eq. (3)):

$$C_2H_5OH + 2H_2O + 1/2O_2 \rightarrow 5H_2 + 2CO_2 \, \Delta H_{(298K)} = -68.5 \text{Kcalmol}^{-1} \tag{3}$$

Therefore, OSRE does not require any external heat to be supplied as the thermal energy generated in the partial oxidation of ethanol is used for steam reforming. Thus, it is also well-known as Auto-thermal steam reforming [3,4].

A large number of catalysts, including oxide catalyst [5–8], Ni-based catalysts [9–12], Co-based catalysts [13–15], and noble metal catalysts [16–18], have been investigated for the hydrogen production by both the SRE and OSRE. The oxide catalysts exhibit low prices, but they also present a poor catalytic activity and an easy deactivation by carbon deposition. Nickel-based and cobalt-based catalysts show high conversion and good selectivity to hydrogen. However, they may present several problems related to the sintering of metal particles, thus decreasing the specific surface area, and the formation of carbon deposition. Although noble metal catalysts show high catalytic activity and selectivity, they present a high price, and tend to deactivate by carbon deposition and sintering of the active metal nanoparticles.

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* Corresponding author. Tel.: +34 618420415.
E-mail addresses: mmorales@ub.edu, mmoralescomas@yahoo.es (M. Morales).

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A suitable support and the addition of a metallic active phase are two important factors that play a crucial role to enhance the ethanol conversion and hydrogen production for SRE, and decrease the deactivation caused by carbon deposition or sintering of the active component. Several researchers have proposed various preparation methods to produce highly dispersed metal particles. One example is the use of perovskite-type oxides (ABO_3) as catalyst precursors, which can form catalysts with finely segregated active metals onto a matrix of metal oxides generated from an oxide precursor after reduction [19]. In addition, their catalytic properties may be tuned by partial substitution of cations in A and B positions. While the cation A is responsible for the thermal resistance of the catalyst, cation B influences on the catalytic activity [20]. The highly dispersed metal particles decrease the deactivation of the perovskite-type oxide catalysts for the partial oxidation of hydrocarbon like methane with O_2 and/or CO_2 [21]. Chen et al. [22] studied the effect of the cation B on the performance of $LaBO_3$ (B = Co, Fe, Mn, Ni) perovskite-type oxides derived catalysts for OSRE. While $LaMnO_3$ presented a low catalytic activity attributed to its low reducibility, the reduced $LaCoO_3$ catalyst was active and selective to H_2. The partial substitution of the A ion by another one at a lower oxidation state may affect to the thermal stability under reducing atmosphere, increasing the mobility of oxide ion vacancies. The oxide vacancies, generated during the catalytic oxidation reaction, can be refilled by regenerating the oxygen-deficient perovskite oxides in oxygen or air, returning to the normal stoichiometry composition [23]. The continuous generation and regeneration form a cyclic operation to directly convert methane to syngas.

Among lanthanum cobaltite perovskites, strontium-substituted lanthanum cobalt oxides ($La_{1-x}Sr_xCoO_{3-\delta}$) have presented a great interest, because of their excellent performances as an oxygen electrode for solid oxide fuel cells (SOFCs) [24–26] and solid oxide electrolyser cells (SOECs) [27,28], and as a cathode for single-chamber SOFCs under methane and air mixtures [29,30]. Up to now, only a few studies on the catalysis of $La_{1-x}Sr_xCoO_{3-\delta}$ perovskite have been reported for different catalytic applications: the oxidation of carbon monoxide, propane and methanol over $La_{1-x}Sr_xCoO_3$ [31,32], the soot oxidation activity over $La_{1-x}Sr_xCoO_{3-\delta}$ [33], the toluene combustion over 8 wt.% $Co_3O_4/La_{0.6}Sr_{0.4}CoO_{3-\delta}$ [34]. Recently, Morales et al. [35] reported the performance and stability of the perovskite $La_{0.5}Sr_{0.5}CoO_{3-\delta}$, as a potential catalyst precursor, for the synthesis gas production by partial oxidation of methane. The results evidenced a remarkable catalytic activity due to the stability of the Co particles, which were in a highly disperse state, in its reduced state for partial oxidation of methane at temperatures as high as 900 °C.

Based on the ideas commented above, the $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ perovskite was prepared by the sol–gel citrate method and used as a catalyst precursor for hydrogen production by SRE and OSRE. The performance and stability of this catalyst precursor was investigated as a function of temperature, time-on-stream and feed composition under SRE and OSRE conditions. Before and after the stability tests, the LSC was characterized by temperature programed reduction (TPR), X-ray diffraction (XRD), scanning electron microscope equipped with an energy dispersive X-ray (SEM–EDX) detector, and the specific surface area by the BET method in order to correlate its catalytic and microstructural properties.

2. Experimental

2.1. Catalyst preparation

According to our previous studies [36], $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ perovskite was synthesized by the sol–gel citrate method, starting from a solution of La, Sr and Co nitrates in stoichiometric amounts mixed to a solution of ethylenediaminetetraacetic acid and citric acid at 50%. The solvent was evaporated and the resulting gel calcined at 550 °C for 5 h in air, to remove the organic fraction. Finally, the solid precursor was homogenized in an agate mortar, calcined in air at 900 °C for 5 h and finally oxygenated at 300 °C for 10 h.

2.2. Catalytic tests and treatments of reduction/oxidation/regeneration

Catalytic activities for the SRE and OSRE were evaluated in a fixed-bed quartz tubular reactor (5-mm i.d.) at atmospheric pressure. 50 mg LSC were diluted with inactive SiC (3.0 wt.% SiC/catalyst) and placed in the center of the reactor using quartz wool. The reactor was kept in a tubular furnace. Two K-type thermocouples were used, one outside the reactor to control the furnace temperature and another one in contact with the catalyst to measure the bed temperature. Before catalyst testing, several blanks were performed (without catalyst) to confirm the absence of direct oxidation reactions in the reactor. After that and prior to reaction, the samples were pre-reduced under 5 vol% H_2–Ar (30 ml min^{-1}) at 700 °C for 1 h, and then cooled under N_2 (30 ml min^{-1}) to the initial testing temperature of 450 °C.

Afterwards, the effect of temperature and time-on-stream on ethanol conversion and product selectivities were investigated under SRE and OSRE conditions. For catalytic tests under SRE, a mixture of vaporized water–ethanol, with a H_2O/C_2H_5OH molar ratio of 3, and nitrogen carrier gas were co-fed to the reactor. The reaction gas mixture was composed of 80 vol% N_2 and 20 vol% ($EtOH + H_2O$). The water–ethanol solution was continuously dosed by a peristaltic pump, and the nitrogen gas was fed by a mass flow controller. The resultant gas hourly space velocity (GHSV) of the total gas mixture was 40 000 cm^3 g^{-1} h^{-1}. For catalytic tests under OSRE, oxygen was added to the reaction mixture, using a mass flow controller, with an O_2/C_2H_5OH molar ratio of 0.5. The other conditions were similar to those of SRE. Thus, the reaction gas mixture was composed of 80 vol% N_2 and 20 vol% ($EtOH + H_2O + O_2$) and the GHSV was 40 000 cm^3 g^{-1} h^{-1}. The effluent gases were analyzed by on-line gas chromatography (Agilent Micro GC 3000 A) equipped with three channels, using a molecular sieve, a Poraplot, and QV-1 column, and three thermal conductivity detectors (TCD). The ethanol conversion and selectivity to products were determined as follows:

$$X_{EtOH} = \frac{\text{moles}(EtOH_{in}) - \text{moles}(EtOH_{out})}{\text{moles}(EtOH_{in})} \times 100 \tag{4}$$

$$S_i = \frac{\text{moles}(P_i)}{\sum_{i=1}^{n} \text{moles}(P_i)} \times 100 \tag{5}$$

where moles P_i are the produced amount of hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, acetaldehyde and acetone. The moles of water produced are not included.

In addition to the catalytic tests, reduction and oxidation treatments of LSC precursor were performed under 5% H_2–Ar and synthetic air at 700 °C for 1 h, respectively. In order to investigate the *in situ* regeneration of the LSC precursor under reforming conditions, the catalyst was re-oxidized by decreasing of the reaction temperature from 700 °C to room one under SRE and OSRE. Regeneration experiments of LSC precursor were also carried out under synthetic air at 900 °C for 12 h and subsequently at 300 °C for 72 h, in a similar way to that described previously [35].

2.3. Catalyst characterization

Temperature programmed reduction (TPR) of the LSC perovskite was carried out in a reactor equipped with a thermal conductivity detector (TCD). A gas mixture of 5% H_2–Ar (30 ml min^{-1}) was used