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Review

CO_2 reforming of CH_4 over Co–La-based perovskite-type catalyst precursors

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HIGHLIGHTS

- ► The precursors solids $La_{1-x}Sr_xCoO_3$ were synthesized by the auto combustion method.
- ► XRD *in situ* confirmed the thermal stability and transformations of the perovskite.
- ► Co^0 nanoparticles highly dispersed in $La_2O_2CO_3$–SrO are obtained by reduction process.
- ► The interaction between CO_2 and La_2O_3 produces $La_2O_2CO_3$ phase.
- ► The catalysts inhibit carbon formation despite the severe reaction conditions.

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ABSTRACT

A series of perovskite-type oxides based on La–Sr–Co ($La_{1-x}Sr_xCoO_3$) were synthesized by the auto combustion method and used as precursors for the catalytic methane dry reforming (MDR) at 1073 K, atmospheric pressure under continuous flow of reactant gases with a CH_4:CO_2 = 1:1 ratio. Catalysts were characterized by techniques such as X-ray diffraction (XRD), BET specific surface area, temperature-programmed reduction-oxidation (TPR–TPO) and scanning-transmission electron microscopy (SEM–TEM). Formation of La–Sr–Co–O solid solutions was confirmed by the more intense diffraction peaks and cell parameter measurements. It was observed that the activation/reduction process occurs through intermediary species producing Co^0 nano-size particles over the SrO and La_2O_3 phases, which are highly dispersed in the $La_2O_2CO_3$–SrO solid matrix responsible for the high activity and low carbon formation despite the severe reaction conditions used. The presence of Sr in doping quantities slightly promotes secondary reactions such as carbon formation and water–gas shift retarding partially the dry reforming reaction.

1. Introduction

The burnout of the world crude oil reserves will unchain some international conflicts on account of the natural resources access mainly of fossil origin; this situation will originate a serious economic crisis at world especially in the countries without technologies replaceable toward the energy generation. Similarly, the imminent danger of global warming partly caused by greenhouse gas emission from burning fossil fuels has driven both the scientific and industrial communities to search for environment-friendly energy sources [1]. This scenario suggests as an energetic strategy, a radical change of the vector energetic petroleum-based to an economy hydrogen-based which is the more efficient, clean and sure energy source considered. This situation convert natural gas (methane) as the excellent raw material for hydrogen production due to the existence of immense reserves at world level, high H/C ratio, less CO_2 emitted by unit of energy produced during its combustion, among others. In this sense, new technologies are required to efficiently transform natural gas to fuel and/or products chemicals that replace those coming from the petroleum [2].

Among natural gas reforming processes, the dry reforming of methane with CO_2 has recently increased interest because of the lower H_2/CO ratios produced (Eq. (1)) sometimes lower than unity due to the simultaneous occurrence of the reverse water–gas shift reaction (RWGS, Eq. (2)) that can be used industrially as raw material for the Fischer–Tropsch synthesis [3] and to valuable oxygenated chemicals (such as aldehydes, methanol, dimethyl ether, acetic acid, etc., and to unsaturated hydrocarbons) [4]. In addition, the dry reforming allows using natural gas reserves containing considerable quantities of CO_2, contributing to transform these

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greenhouse gases (CO_2 and methane). However, due to the fact that this reaction presents a high thermodynamic potential ($\Delta G_{298} = 174.6$ kJ mol^{-1}), it requires the use of high temperatures to revert its spontaneity (for example $\Delta G_{1073} = -44.76$ kJ mol^{-1}), condition which promotes simultaneously carbon formation (Eq. (3)) leading to catalysts deactivation.

$$CH_4 + CO_2 \leftrightarrows 2CO + 2H_2 \quad \Delta H^{\circ}_{298} = 247 \text{ kJ mol}^{-1} \tag{1}$$

$$CO + H_2O \leftrightarrows CO_2 + H_2 \quad \Delta H^{\circ}_{298} = -41.17 \text{ kJ mol}^{-1} \tag{2}$$

$$CH_4 \leftrightarrows C + 2H_2 \quad \Delta H^{\circ}_{298} = 74.85 \text{ kJ mol}^{-1} \tag{3}$$

Noble metal-based catalysts used in the reforming of CH_4 [5], are less sensitive to coking, contrary to Fe, Co and Ni based catalysts that show high activity but are rapidly deactivated [6]. However, the high cost of noble metals and their limited availability promote the development of Co and Ni-based catalytic systems that inhibit coke formation. As it has been shown [7], coke formation decreases with downsizing metallic particle on the support. An alternative is to use metal-based precursors with a well-defined structure, as perovskite-type oxides (ABO_3) which produce metallic particles in the order of nanometers under reducing atmosphere [8] diminishing coke formation and increasing the activity of the catalysts. Other advantage of perovskite-type oxides is its redox properties, due to the fact that a wide range of elements can be incorporated in the structure by partial substitution of A and/or B cations, giving rise to a combination of elements with different oxidation states [9].

In previous work we reported the physicochemical properties and the behavior of $La_{1-x}Sr_xNiO_3$ and $La_{2-2x}Sr_{2x}NiO_{4-\delta}$ as catalyst precursors in dry reforming of methane [10], which show high activity and resistance to coke deposition [11]. Recently we reported that ternary solid solutions $LaNi_{1-x}Co_xO_3$ [12] and quaternary $La_{1-x}Sr_xNi_{1-y}Co_yO_3$ [13] show high metallic dispersion and produces a synergetic effect between these particles to inhibit coke formation. The aim of the present work is to investigate the use of perovskite-type solid solutions $La_{1-x}Sr_xCoO_3$ as precursors of highly dispersed Co nanoparticles to avoid coke formation during the dry reforming of methane under continuous flow of reactive gases. We also investigated the possible carbon nanotubes formation.

2. Experimental

2.1. Synthesis of perovskite-type oxides

The ternary perovskite-type $La_{1-x}Sr_xCoO_3$ were synthesized by the auto combustion method [14], which consist of adding glycine ($H_2NCH_2CO_2H$) to an aqueous solution of metallic nitrates [$La(NO_3)_3 \bullet 6H_2O$, $Co(NO_3)_2 \bullet 6H_2O$, $Sr(NO_3)_2$] to obtain a $NO_3^-/NH_3 = 1$ M ratio. The resulting solution is formed by dissolving the salts in their own occluded water at ~323 K with constant stirring. The solvent is then slowly evaporated at ~373 K until a resin is formed. The glycine acts as metal complexing agent and as a pyrophoric substance. The increase of the heating temperature up to ~523 K producing a spontaneous exothermic reaction (auto combustion) that allows the formation of the precursor powder which is then calcined in air (973–1173 K, 2 h) to remove any carbon residue.

2.2. Characterization

The solids were characterized by means of techniques such as X-ray diffraction (XRD), BET surface area, temperature-programmed reduction and oxidation (TPR–TPO) and scanning-transmission electron microscopy (SEM–TEM).

The *ex situ* XRD analysis were conducted in a Siemens D500 diffractometer with Cu K_α radiation ($\lambda = 1.5418$ Å, 40 kV, 30 mA). The acquisition of the data were performed according to the required study; e.g. the scanning of the angular zone from 10° to 90° 2θ (0.05 2θ step, 27 s) were used to obtain the initials phases and cell parameters, and the angular zone between 32° and 35° 2θ (0.02 2θ step, 30 s) was used to confirm the solid solution formation. Samples were prepared by the powder chamber method, which consists of finely crushing the solid (0.05–0.1 g) to ensure a homogeneous and abundant size of the grain, and placed on the sample holder and irradiated with X-rays. The *in situ* XRD analyses were performed to study the effect of degassing and of the reduction temperature on the crystal structure; the finely crushed sample on methanol was placed on a platinum plate. Heating was conducted increasing the temperature at 4 K min^{-1} from room temperature to 1173 K under Ar or H_2 atmospheres according to the analysis to be performed. The diffractograms were recorded at different temperatures every 50 K in order to determine the temperature at which phases transformations occur. Phase's recognition was obtained by comparison with JCPDS files using the database PDF2 and software EVA 3.30 programs. The particle size diameter was calculated by the Scherrer equation using the more intense diffraction peaks [15].

The specific surface areas were determined by N_2 adsorption at 77 K, using 0.1–0.2 g of sample previously out gassed at 623 K for 2 h, with a $N_2/Ar = 30/70$ ratio on a Micromeritics Flow Sorb II. The TPR experiments were carried out in a quartz reactor loaded with 0.05 g of the solid. Pulses of hydrogen (12 μmol H_2) were injected every 2 min while the temperature was risen from room to 1173 K at 4 K min^{-1}. The TPR experiments were followed by temperature programmed oxidation (TPO) in order to study the reversibility of the reduction. After cooling to room temperature, the reduced sample was exposed to He diluted O_2 pulses. The temperature program was similar to that described for TPR experiments. Prior to redox cycles, samples were heated at 873 K for 2 h under Ar.

The morphological and elemental analyses were performed by means of a SEM S-500 microscope coupled to energy dispersive X-ray (EDX) at 20 kV and 3.1×10^{-9} A, on samples covered with Au or C respectively. Metal dispersion after reduction and carbon

Table 1
Chemical analysis, phases and textural properties of $La_{1-x}Sr_xCoO_3$ solids.

Stoichiometry		Tcalc. (K)	SA_{BET} (m^2 g^{-1})	XRD phases (as-synthesized)	Particle size (nm)	XRD phases (after TPR/TPO)	XRD phases (after catalytic test)
(Nominal)	(Experimental)						
$LaCoO_3$	$La_{0.99}CoO_3$	973	5	$LaCoO_3$	19	$LaCoO_3$	Co, La_2O_3
$La_{0.9}Sr_{0.1}CoO_3$	$La_{0.89}Sr_{0.06}CoO_3$	973	8	$La_{0.9}Sr_{0.1}CoO_3$	19	$La_{0.9}Sr_{0.1}CoO_3$	
$La_{0.8}Sr_{0.2}CoO_3$	$La_{0.76}Sr_{0.13}CoO_3$	973	12	$La_{0.8}Sr_{0.2}CoO_{3-x}$	19	$La_{0.9}Sr_{0.1}CoO_3$	Co,
		1073	10		20		$La_2O_2CO_3$
		1173	5		21		SrO
$La_{0.7}Sr_{0.3}CoO_3$	$La_{0.68}Sr_{0.21}CoO_3$	1073	14	$La_{0.6}Sr_{0.4}CoO_3$	18	$La_{0.8}Sr_{0.2}CoO_{3-x}$	
$La_{0.6}Sr_{0.4}CoO_3$	$La_{0.63}Sr_{0.22}CoO_3$	1073	18	$La_{0.6}Sr_{0.4}CoO_3$	17	$La_{0.6}Sr_{0.4}CoO_3$	