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Reforming of Diesel Fuel for Hydrogen Production over Catalysts Derived from $\text{LaCo}_{0.8}\text{M}_{0.2}\text{O}_3$ (M = Ni, Ru, Fe, Ga)

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1 Introduction

In recent years, the need to reduce pollutant emissions to atmosphere has favored the development of new technologies for the production of energy. The use of hydrogen is a feasible choice for energy production, being less contaminant and more efficient than internal combustion engines, especially when it is associated to fuel cells [0,0]. One of the main ways to produce hydrogen is by catalytic reforming of fossil fuels. Nowadays, there is an increasing interest in the development of technologies for the conversion of liquid hydrocarbons in hydrogen rich gas mixtures as a way to overcome the current technical limitations in hydrogen supply and storage. The use of diesel as a source of hydrogen offers advantages such as its high volumetric hydrogen density and well-established delivery infrastructure; however, the reforming of this fuel needs very active catalysts for the reforming of hydrocarbons of different nature and resistant to high temperatures, to sulphur poisoning and also, to coke formation [0]. An alternative to traditional catalysts based on transition metals supported over oxides doped with rare earths are perovskites (ABO_3), that present high resistance at elevated temperatures and to sulphur poisoning and produce, under reaction, a highly dispersed transition metal (B^0) over the oxide (A_2O_3). Previous works have point to LaCoO_3 as a very promising catalyst precursor for hydrogen production by hydrocarbons reforming, where lanthanum oxycarbonates, formed under reaction, have a role in catalyst stability favoring coke gasification [0,0,0]. In the present work, oxidative reforming of diesel fuel was studied over catalysts derived from perovskite $\text{LaCo}_{0.8}\text{M}_{0.2}\text{O}_3$ (M = Ni, Ru, Fe, Ga) precursors. It has been analyzed the influence of the partial substitution of Co by the above cations over modifications in cell parameters, average crystallite size, surface area, reducibility, morphology and surface composition, establishing a relationship of those physicochemical characteristics with catalytic activity and stability.

2 Experimental

Perovskite precursors were synthesized by a modified citrate sol-gel method [0]. Aqueous nitrate solutions containing the precursors cations were added to a solution of citric acid and ethylenglycol (molar ratio 1:1 and citric acid/A+B= 2.5). The mixture was stirred and heated

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at 343 K for 5 h. The obtained resin was charred at 573 K for 2 h and calcined at 1023 K during 4 h.

Fresh, pretreated and used samples (after 24 h of reaction) were characterized by means of different techniques. The BET surface area of fresh and pretreated catalysts was calculated from the nitrogen adsorption-desorption isotherms at 77 K, measurements performed with a Micromeritics ASAP 2100 apparatus. Photoelectron Spectroscopy analyses were recorded using a Escalab 200R spectrometer equipped with a hemispherical electron analyzer using monochromatic Al K α (1486.6 eV). XRD patterns were recorded using a Seifert 3000P vertical diffractometer and nickel-filtered Cu K α radiation. Hydrogen temperature-programmed reductions (H₂-TPR) were conducted using a Micromeritics 2900 instrument by heating the sample under a 10 % H₂/Ar flow (50 mL/min) up to 973 K at a linearly programmed rate of 10 K/min.

Perovskite samples were activated, before diesel oxidative reforming reaction, with a reductive stream (H₂(10%)/N₂) at 973 K for 1 h. Afterwards, activity tests were performed in a fixed-bed reactor at 1023 K, to avoid complete conversion. Reactants were fed at a molar ratio of H₂O/O₂/C equal to 3/0.5/1. The gas flow rate was kept at 75 mL/min (GHSV = 20,000 h⁻¹).

3 Results and Discussion

XRD analyses indicated that all the prepared materials showed a perovskite structure with rhombohedral symmetry. However, it was found that the substitution of Co by Ni, Ru, Fe and Ga produced structural modifications in lattice parameters and mean crystallite size (table 1), that are more evident for the sample with Ru. XRD pattern of LaCo_{0.8}Ru_{0.2}O₃ also support these results, since it shows a shift in the diffraction lines and a disappearance of the typical doublet around 33° associated to above symmetry. These facts are attributed to the greater size of Ru³⁺ cation, that difficult its introduction in the perovskite lattice [0]. Partial substitution of Co by above elements also produces some increase in surface area (table 1).

The activation process produces a complete transformation of the perovskite structure which derives in a well dispersed phase of Co⁰ and most likely of M⁰ particles - although these last ones haven't been detected by XRD, probably due to their small size - over a matrix of La₂O₃. The absence of diffraction lines of Co⁰ in the Ru-containing activated sample is explained by the small mean size of these particles. It has been also found a greater size of Co⁰ and La₂O₃ crystallites in activated systems with Ni and Ga (table 2), which could give to a lesser development of Co-Ni-La and Co-Ga-La interactions that have an important role in the reaction [0,0] and that may be the cause of the low conversion values observed in these samples (figure 1).

Table 1: Lattice parameters, particle size and surface area of perovskite precursors.

Perovskite precursors	Lattice Parameters (Å)		Particle size (nm)	BET surface area (m ² /g)
	a = b	c		
LaCoO ₃	5.46	13.07	54	1.1
LaCo _{0.8} Ni _{0.2} O ₃	5.45	13.12	43	2.7
LaCo _{0.8} Ru _{0.2} O ₃	5.24	5.24	20	2.9
LaCo _{0.8} Fe _{0.2} O ₃	5.46	13.06	34	6.0
LaCo _{0.8} Ga _{0.2} O ₃	5.51	13.08	52	2.0

XPS results derived from activated samples indicates a low Co+M/La surface ratio in the Ru-containing sample; however binding energies indicate a greater reduction degree of these phases that are in accordance with TPR profiles. The better surface reduction together with the higher proportion of La₂O₃, M⁰ (Ru⁰) and Co⁰ in the surface will explain the better performance of this system at the beginning of the reaction.

XPS surface analyses of the activated samples also indicate that the proportion of cobalt species increases when cobalt is partially substituted by the different M cations, with the exception of the sample with Ru (Table 2). It is worth mentioning that a surface enrichment of the modifiers elements is produced in samples with Fe, Ru and Ga, especially in the sample containing Ga (Table 2).

Table 2: Particle size and surface Co/La, M/La (XPS) for the perovskite elements reduced and after reaction.

Precursor perovskites	Reduced				After reaction			
	XRD		XPS		XRD		XPS	
	Particle size La ₂ O ₃ (nm)	Particle size Co ⁰ (nm)	Co/La	M/La	Particle size La ₂ O ₂ CO ₃ (nm)	Particle size Co ⁰ (nm)	Co/La	M/La
LaCoO ₃	23	20	0.27 (1)	-	33	19	0.43 (1)	-
LaCo _{0.8} Ni _{0.2} O ₃	28	27	0.42 (0.8)	0.19 (0.2)	38	24	0.85 (0.8)	n.d.
LaCo _{0.8} Ru _{0.2} O ₃	18	n.d.	0.08 (0.8)	0.26 (0.2)	29	14	0.56 (0.8)	0.34 (0.2)
LaCo _{0.8} Fe _{0.2} O ₃	18	15	0.36 (0.8)	0.34 (0.2)	22	17	0.64 (0.8)	0.44 (0.2)
LaCo _{0.8} Ga _{0.2} O ₃	31	22	0.37 (0.2)	0.59 (0.2)	30	18	0.24 (0.8)	0.12 (0.2)

M: Ni, Ru, Fe or Ga; n.d.: not detected; (...): nominal values

From the activity results, presented in figure 1 and related to mean conversions and products distributions values after 24 hours of reaction, could be derived that the lowest hydrogen yield and the greater selectivity to combustion, is shown by the catalyst with Ga, which is

explained by the lesser surface exposition of cobalt and gallium observed in this sample (table 2).

By the contrary, the relatively small size of lanthanum oxycarbonate and metallic cobalt, and the high surface proportion of both phases (table 2) in Fe and Ru-containing systems would increase the contact between them, increasing its activity and stability, thus inhibiting the formation of coke. The formation of these smaller crystallites should be a consequence of a deeper modification of the original LaCoO_3 perovskite structure, in the partial substitution of cobalt by the above elements, whose ionic size is more dissimilar with respect to cobalt ion. This fact together with the high intrinsic activity of Ru for reforming/partial oxidation reactions are key factors that make $\text{Co}^0\text{-Ru}^0/\text{La}_2\text{O}_3$ catalyst derived from the $\text{LaCo}_{0.8}\text{Ru}_{0.2}\text{O}_3$ precursor a good candidate for hydrogen production by oxidative reforming of heavy hydrocarbons.

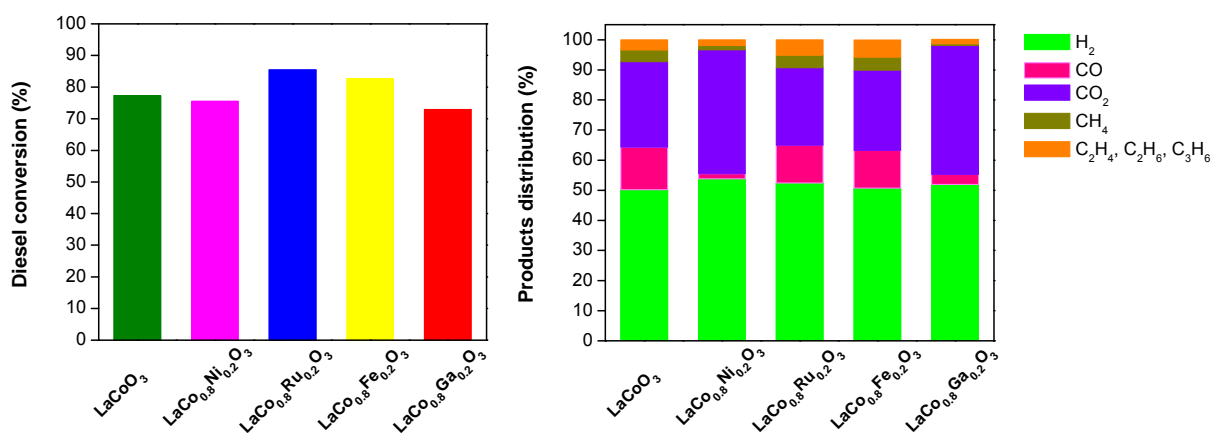


Figure 1: Diesel conversion and products distribution during oxidative reforming of diesel over LaCoO_3 , $\text{LaCo}_{0.8}\text{Ni}_{0.2}\text{O}_3$, $\text{LaCo}_{0.8}\text{Ru}_{0.2}\text{O}_3$, $\text{LaCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$ and $\text{LaCo}_{0.8}\text{Ga}_{0.2}\text{O}_3$ derived catalysts (1023 K, 20,000 h^{-1} , $\text{H}_2\text{O}/\text{O}_2/\text{C}=3/0.5/1$).

4 Conclusions

Physicochemical characterization of samples revealed that the substitution of Co by Ni, Ru, Fe and Ga produced modifications in cell parameters, average crystallite size, surface area and reducibility. These changes lead to different surface expositions of Co M, and La_2O_3 phases on catalysts derived from the reduction of perovskite precursors. The catalyst derived from $\text{LaCo}_{0.8}\text{Ru}_{0.2}\text{O}_3$ was the most active and stable for the production of hydrogen due to the high exposition of Co^0 , the intrinsic activity of Ru and the small crystallite size of La_2O_3 which improves the contact between this phase and Co-Ru, favouring the gasification of coke deposits. In the other extreme, the catalyst with Ga presents the lowest reforming activity as consequence of its high selectivity towards combustion.

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