



Short communication

B-cation partial substitution of double perovskite $\text{La}_2\text{NiTiO}_6$ by Co^{2+} : Effect on crystal structure, reduction behavior and catalytic activityPablo V. Tuza¹, Mariana M.V.M. Souza*

Escola de Química, Universidade Federal do Rio de Janeiro (UFRJ), Centro de Tecnologia, Bloco E, Sala 206, CEP 21941-909 Rio de Janeiro, RJ, Brazil

ARTICLE INFO

Keywords:

Double perovskite
Cobalt
Nickel
Quantitative phase analysis
Reduction

ABSTRACT

$\text{La}_2\text{NiTi}_{0.9}\text{Co}_{0.1}\text{O}_6$ and $\text{La}_2\text{Ni}_{0.9}\text{Co}_{0.1}\text{TiO}_6$ perovskites were obtained by partial substitution of either Ti^{4+} or Ni^{2+} from double perovskite $\text{La}_2\text{NiTiO}_6$ by Co^{2+} . The Rietveld analysis demonstrated that all as-synthesized samples have orthorhombic symmetry and space group *Pbnm*. Quantitative phase analysis using Rietveld refinement of XRD profiles after temperature programmed reduction showed that the reduction of $\text{La}_2\text{NiTiO}_6$ was modified by partial substitution of either Ni^{2+} or Ti^{4+} by Co^{2+} , being more evident for the $\text{La}_2\text{NiTi}_{0.9}\text{Co}_{0.1}\text{O}_6$. The activity of all catalysts for steam reforming of methane was attributed to both the reduction degree of two-valence metals and the metal-support interaction.

1. Introduction

Perovskites are oxides that can be represented by the formula ABO_3 [1], where A is a rare earth, alkali or alkaline earth metal and B is a transition metal [2]. Perovskite structure can be illustrated by B cations in the center of octahedra sharing corners, whose vertices are occupied by oxygen atoms (BO_6), and thus forming a framework that contains the A cations in the center of the cavities between layers of BO_6 octahedra. Double perovskites (DPs) are represented by the formula $\text{A}_2\text{B}'\text{B}''\text{O}_6$ [3] or $\text{A}'\text{A}''\text{B}'\text{B}''\text{O}_6$ [4] and the B-cation sublattice types known for DPs are rock salt, layered and random [4]. In rock salt ordering, $\text{B}'\text{O}_6$ and $\text{B}''\text{O}_6$ octahedra are ordered like Na and Cl atoms in NaCl structure. Layered ordering occurs when layers composed of either $\text{B}'\text{O}_6$ or $\text{B}''\text{O}_6$ octahedra are placed one above other. Random ordering is characterized by the absence of $\text{B}'\text{O}_6$ and $\text{B}''\text{O}_6$ octahedra sequence in the structure formed by octahedra sharing corners. Therefore, the rock-salt and layered present an ordered arrangement [4], which characterizes compounds known as ordered DPs.

DPs show interesting physical and chemical properties such as superconductivity, ferroelectricity, antiferroelectricity, piezoelectricity, magnetic properties and optical properties or a combination of both magnetic and electric interactions [5,6]. These materials have been used as electrode in fuel cells [7,8] as well as catalysts [9] and catalyst precursors [10].

The reduction of catalyst precursors is important for catalytic reactions because it is associated with the formation of metal active sites and the crystalline phases composing the support. Reducibility of

cations varies according to its respective redox potential, e.g., copper, nickel or cobalt are more difficult to reduce than iridium, rhodium or ruthenium, and can be modified by the neighboring anions in the crystalline structure since it is also influenced by the coordination number and precise location of the cations [11]. Concerning perovskites, the reduction of LaNiO_3 was well detailed in the literature [12,13]. The reduction of the $\text{La}_2\text{NiTiO}_6$ DP was reported in our previous work, as well as its catalytic activity for steam reforming of methane [14].

To the best of our knowledge, the influence of partial substitution of B-cations of the $\text{La}_2\text{NiTiO}_6$ DP has not been studied yet. Therefore, the main objective of this work is to partially substitute either Ti^{4+} or Ni^{2+} from $\text{La}_2\text{NiTiO}_6$ by Co^{2+} for obtaining $\text{La}_2\text{NiTi}_{0.9}\text{Co}_{0.1}\text{O}_6$ and $\text{La}_2\text{Ni}_{0.9}\text{Co}_{0.1}\text{TiO}_6$ perovskites, respectively, and then to evaluate the crystal structure after synthesis, crystalline phases after reduction and the catalytic activity of the prepared samples.

2. Experimental

2.1. Synthesis

$\text{La}_2\text{NiTi}_{0.9}\text{Co}_{0.1}\text{O}_6$ ($\text{LNT}_{0.9}\text{Co}_{0.1}\text{O}$), $\text{La}_2\text{Ni}_{0.9}\text{Co}_{0.1}\text{TiO}_6$ ($\text{LN}_{0.9}\text{Co}_{0.1}\text{TO}$) and $\text{La}_2\text{NiTiO}_6$ (LNTO) were prepared by modified Pechini method [15]. Steps related to citrate and the preparation of the polyester solution with subsequent resin formation and its calcination were detailed in our previous work [14]. The weak sponge-like structure obtained was mixed and ground in agate mortar, calcined in air at

* Corresponding author.

E-mail address: mmattos@eq.ufrj.br (M.M.V.M. Souza).¹ Present address: Universidad Nacional de Loja, Carrera Químico Biológicas, Av. Pío Jaramillo Alvarado y Reinaldo Espinoza, Sector La Argelia, Loja, Ecuador.