

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF $\text{LaMnO}_{3+\delta}$ AND $\text{La}_{0.8}\text{AE}_{0.2}\text{MnO}_{3+\delta}$ (AE=Ca, Sr, Ba) PEROVSKITES FOR CATALYTIC OXIDATION OF VOLATILE ORGANIC COMPOUNDS

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Perovskite oxides have the general formula ABO_3 , where A is typically an alkaline earth (AE) or a lanthanide and B is a transition-metal. This family of compounds is probably the most studied one in the last decades since understanding the structure-properties correlation is of fundamental and technological interest [1]. Despite the simplicity of the crystalline structure, the size variation of A and B cations creates an immense structural variety and generates deviations respect the ideal structure through changes in the crystal symmetry, that leads to the appearance of interesting properties. These properties are the origin of multiple applications, mostly related to energy conversion, adsorption and catalysis, among others.

Volatile Organic Compounds (VOCs) are a group of carbon-based chemicals considered not only as major contributors to air pollution but also one of the main hazardous substances for human health. Due to the great impact they provoke, the scientific community has been in search of an economically viable solution in order to control VOCs emissions. A few decades ago, the catalytic oxidation process arose as an interesting alternative to previously proposed methods, because it achieves greater conversions to CO_2 and H_2O at lower temperatures, is easier to control and less expensive in the long term. An additional complication of VOCs is that these group includes a wide range of compounds with very different physicochemical properties, what makes it difficult to find a single catalyst for the effective elimination of the majority of them.[2]

Transition metal oxides, specially manganites, have been tested for VOCs oxidation and proved active at low temperatures for several molecules. Among them, manganites with perovskite-like structure are the ones that have exhibited the best performances. This can be attributed to the redox properties of the manganese and the mobility of oxygen in the lattice.[3]

In this work, perovskites LaMnO_3 and $\text{La}_{0.8}\text{AE}_{0.2}\text{MnO}_3$ (AE=Ca, Sr, Ba) have been prepared by a simple one-step auto-combustion method and were characterized by X-ray powder diffraction and N_2 adsorption-desorption method in order to apply them as catalysts in the complete catalytic oxidation of volatile organic compounds. The studied phases show the expected orthorhombic and rhombohedral perovskite crystal structures, being as-prepared materials stoichiometric oxides that transform irreversibly into $(\text{La}_{1-x}\text{AE}_x)_{1-\varepsilon}\text{Mn}_{1-\varepsilon}\text{O}_3$ during a calcination in air at 750°C . The catalytic experiments, performed using acetone as model VOC, show almost no dependence on the state of the initial sample or AE cation. As-prepared stoichiometric samples slowly convert to cation deficient phases between 200 and 300°C as supported by in-situ thermo-diffraction experiments. This suggests that the most important factor for the activity of these oxides as catalysts, if not the only one, is the $\text{Mn}^{4+}/\text{Mn}^{3+}$ molar ratio in the surface of the samples.

References:

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