

Perovskite-type $\text{La}_{1-x}\text{Ce}_x\text{MO}_3$ (M=Co,Mn) as catalysts: Synthesis and Characterization

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$\text{La}_{1-x}\text{Ce}_x(\text{Co},\text{Mn})\text{O}_3$ perovskites, prepared by the co-precipitation method, have been studied by EDS-SEM, surface area-BET method, X-ray diffraction (XRD), temperature programmed reduction (TPR), and have been catalytically tested for CO-preferential oxidation. The purpose of this work is to verify structural changes on the perovskites due to the presence of Ce and correlate these changes with their catalytic behavior. The samples prepared were $\text{La}_{1-x}\text{Ce}_x(\text{Mn},\text{Co})\text{O}_3$ ($x = 0, 0.05, \text{ and } 0.10$) and their catalytic activities were tested over the temperature range of 100–230°C in a fixed-bed tubular glass micro-reactor, with 200mg of catalyst with feed stream was 65mL min⁻¹ (2.5% CO, 5% O₂, 33% H₂ and N₂ to 100%). The amounts of the constituent metals obtained by EDS were in agreement with the expected values; the presence of cerium did not change the surface area of the samples with Mn (26-27m² g⁻¹), but the samples with Co presented an increase in surface area (12 to 16 m² g⁻¹). The XRD patterns corresponded to cubic LaMnO_3 and rhombohedral LaCoO_3 structures; the replacement of La did not change significantly the diffractograms. The peaks of cerium oxide were not observed for any samples, suggesting the incorporation of Ce ions into the perovskite lattice. The presence of cerium in the LaCoO_3 structure caused an enhancement in the thermal stability of Ce³⁺ ions, prevented their reduction, and facilitated the reduction of Co²⁺ ions due to a possible interaction between these ions and Ce ions [1,2]. The $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ samples presented an increase in thermal stabilization of Mn³⁺ ions, and Mn⁴⁺ species that were reduced at lower temperatures. Probably, a reduction of cerium ions occurred, but this was difficult to observe because of the low amount of this metal [1]. The average grain sizes, observed by SEM, for $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ samples practically did not change with the addition of cerium, having values within 53-70nm. However, the $\text{La}_{1.9}\text{Ce}_{0.1}\text{MnO}_3$ sample presented a range of size distribution and grain shapes more homogeneous than the other ones. For the $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ series, the average grain sizes were lower (43-56 nm), the size distribution was homogeneous compared to the other series of perovskites. It was observed that cerium caused a decrease in the average grain size and this effect was more significant for the $\text{La}_{1.9}\text{Ce}_{0.1}\text{MnO}_3$ sample, suggesting that the high levels of cerium in this series caused changes in their structures. The catalytic tests showed that cerium had a promoter effect at low temperatures (100-150°C) for $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ samples and all samples with Ce had the same catalytic behavior; for the Co series, high temperatures favored the CO conversion for samples with Ce, and the best catalytic behavior was observed for the $\text{La}_{1.95}\text{Ce}_{0.05}\text{MnO}_3$ sample.

Keywords: perovskites, CO oxidation, cerium, lanthanum, cobalt, manganese, catalysts.

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