

Thermal resistance of perovskites with cerium for methane oxidation

M. A. Fraga, R. A. Pereira and M. C. Greca

INT/MCT - Laboratório de Catálise, Av. Venezuela 82/518 CEP 20081-312, Rio de Janeiro/RJ, Brazil,
mariacon@int.gov.br

Abstract – The influence of cerium in perovskites containing Co was studied. XRD analysis showed that the perovskite presented a cubic system but a phase transition may occur. SEM revealed that the morphology of powders was similar. Element mapping evidenced a homogeneous distribution of Co, Sr and Ce over CeSrCo and La CeCo. For LaSrCo sample a segregation of Sr was observed.

Catalytic combustion of methane has been widely investigated as an alternative technology for power generation [1]. Perovskite-type oxides, with general formula $A_xA'_{1-x}B_yB'_{1-y}O_3$, has been evaluated on catalytic combustion due to the good heat resistance and their rather promising activity at moderate temperatures. Since several cations can be settle in to the structure either on *A* or *B* position, a large number of perovskites can be obtained. Nevertheless, perovskites applications are claimed to be limited due to a strong tendency to sinter irrespective of their composition [2]. Preparation of ceramic oxides via a route known as combustion synthesis has been gaining reputation as a straightforward process to produce homogeneous, very fine and crystalline powders [3]. The aim of this contribution is to evaluate the influence of cerium in the *A* position in a perovskite containing cobalt ($A_xA'_{1-x}CoO_3$) obtained by the combustion synthesis methodology. The perovskites studied were $La_{0.8}Ce_{0.2}CoO_3$; $Ce_{0.8}Sr_{0.2}CoO_3$ and $La_{0.8}Sr_{0.2}CoO_3$ and they are identified herein by their composition, as for example LaCeCo. All perovskites were characterized as prepared by X-ray diffraction (XRD) and the perovskites thermal resistance was also investigated by this technique through heating from room temperature up to 1100 °C. Scanning electron microscopy (SEM) was carried out in these samples followed by element mapping with the objective of verifying any morphological or textural modifications.

The XRD analysis obtained at room temperature showed only basal reflection corresponding to a perovskite with a cubic crystal system. The diffractograms of LaCeCo and CeSrCo also present basal reflections corresponding to CeO_2 . These reflections are much more intense in the sample CeSrCo, consistent with the higher content of this lanthanide. As a matter of fact, it may be suggested that the formation of a CeO_2 isolated phase occurs in detriment of the perovskite over this sample. These results indicate that not the totality of cerium is introduced in the *A* position of the perovskite, revealing that there might be a limited content that is able to settle in this structure. Meanwhile, the formation of the perovskite phase could not be completed ruled out; it is possible that such a phase is present in low concentration and/or less than the limit observation of the technique. The diffractograms of LaSrCo obtained at 1100 °C is characteristic of a perovskite with an orthorhombic crystal system, showing a change in the perovskite structure at high temperatures. A different behavior can be observed for LaCeCo sample, to which only typical reflections of the cubic system of perovskites were detected. No evidence of the transition from cubic to orthorhombic structure could be registered, suggesting that the presence of cerium in *A* position leads to an improved structural stability. The basal reflections corresponding to the CeO_2 phase remain present in all diffractograms, evidencing that its inclusion in the perovskite structure after the synthesis does not occur even at high temperatures. The CeSrCo sample showed reflections compatible with perovskites of cubic system and CeO_2 phase. This evolution would thus suggest that the perovskite is formed during the synthesis by combustion reaction. Its absence in the diffractograms at room temperature is much likely due to its low concentration and particle dimension, as initially suggested.

The scanning electron microscopy in the combustion synthesis powders are similar and revealed small grains like fine fragments. At 1100 °C some changes in their morphology occurred and it was then possible to distinguish some isolated grains because of the de-sintering phenomenon [4]. In element mapping it is possible to observe the homogeneous distribution of Co, Sr and Ce in CeSrCo and Co, La and Ce in La CeCo. On the other hand, in LaSrCo sample a segregation of Sr can be observed while the homogeneity of Co and La is revealed.

In conclusion, the combustion synthesis technique allows obtaining perovskite with a cubic crystal system. High temperature promotes the transition of this structure to orthorhombic. The introduction of cerium partially replacing lanthanum in *A* position leads to an improved thermal stability of the cubic structure until temperatures up to 1100 °C. The Ce in the *A* position of the perovskite leads to more homogeneous powders. A segregation of Sr was observed for the structure containing both La and Co.

References

- [1] T.V. Choudhary, S. Banerjee, V.R. Choudhary, Appl. Catal. A, 1-23, 234 (2002).
- [2] J. Kirchnerova, M. Alifanti, B. Delmon, Appl. Catal. A, 65-80, 231 (2002).
- [5] M.A. Fraga, M.C. Greca, L.C. Appel, eds., R. Mallinson, M. Aresta, L. Chang-Jiu: Utilization of Greenhouse Gases (American Chemical Society, D.C. 2003).
- [4] F.F. Lange, Lecture Notes, Materials Department of California, CA 93106.