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Surface chemistry of Co3O4 and CoMn2O4 sputtered high-textured thin films in the CO catalytic oxidation: An operando NAP-XPS study

Content

The Co3O4 spinel-type material has a particular structure with Co2+ and Co3+ cations tetrahedrally and octahedrally coordinated, respectively, with O2- anions. This fact confers to Co3O4 special characteristics in the Co-O bond and consequently some properties of this spinel start to be important in application in engineering and science fields. Nevertheless, these properties can be modulated by changing the cation composition of the spinel using other transition metals (i.e. Fe, Mn, Cu, Ni, etc.). Incorporation of Mn species in Co3O4 has demonstrated improvement in its applicable capabilities, especially in the catalytic one. In this sense, several Co-Mn based-spinels systems have been widely studied since the synergistic effect between Co and Mn depends on the Co/Mn ratio [1][2].

The main purpose of this work is to investigate the surface chemistry of both Co3O4 and CoMn2O4 during the catalytic oxidation of CO and, to describe some interaction between reactants molecules and surface catalysts in function of the presence of Mn species in the catalyst. For this, two thin film samples were prepared by means of radiofrequency (RF) magnetron-assisted sputtering, using STO (100) as substrate and lab-made sputtering targets with composition of Co3O4 and CoMn2O4. The conditions for the thin film preparation were set to get a thickness up to 20 nm. After that, surface chemistry of samples was measured during a CO catalytic oxidation experiment using the Near-Ambient Pressure X-ray Photoelectron Spectrometry (NAP-XPS) facility located at the university research headquarters (SIU-UdeA) University of Antioquia in Medellín (COL). The reaction was carried out in a temperature range between room temperature (RT) and 673 K and, under a total chamber pressure of 0,5 mbar having a gas mix reactants of CO:O2 with relation of 1:3. Moreover, the residual gas composition was constantly monitored by mass spectrometry to follow the production of CO2. The results suggested that incorporation of Mn cations was completed successfully replacing the Co3+ cations by Mn3+ cations in the octahedral sites of the spinel. This substitution seemed to regulate the cyclical redox activity of Co species on surface during the reaction; what modify notoriously the capability to generate oxygen vacancies and consequently the catalytic performance became different.

References.

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