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STEM-XEDS spectrokinetic analysis of oxygen: a tool to understand redox processes in nanostructured oxide catalysts

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Background

Understanding the details of oxygen exchange processes becomes key to understand the performance of catalysts used in redox processes as well as to fix the most convenient pretreatment conditions to activate the catalyst prior to reaction. At macroscopic level, hydrogen temperature programmed experiments (H_2-TPR) are the most commonly used tool to propose the different phases and processes resulting from this activation step. Nevertheless, the interpretation of these TPRs becomes cumbersome and most of the times rather speculative.

A reliable determination of the actual phases appearing during the different oxygen evolution processes involved in these TPRs requires a precise quantification of the oxygen content of the materials at different steps of the reduction process. Such information, combined with structural analysis at local level provides the necessary information to interpret the H_2-TPR trace at quantitative level on solid backgrounds.

Regarding the compositional aspects. STEM-XEDS stems as a possible technique to face the quantification of the oxygen content at nanoscale in oxides with interest in redox catalysis. However, such approach requires to overcome two major difficulties: (a) dealing with absorption effects in the quantification of the oxygen signal; (b) disentangling the influence of beam reduction effects, which are particularly relevant in the case of high surface area, beam sensitive oxide nanostructures.

This contribution illustrates how combining time-resolved STEM XEDS experiments recorded during the in-situ reduction under the electron-beam performed on an aberration-corrected microscope equipped with large area detectors; an O-quantification scheme based on the use of the so-called ζ-factors method [1] and modeling of the kinetics of oxygen evolution, it is possible to determine with high accuracy the composition of the intermediate phases involved in the oxygen exchange processes of oxide nanostructures. In particular, the methodology is applied to the quite challenging case of nanorods of a complex, extremely beam sensitive, multicationic K-modified manganese oxide with hollandite type structure highly active in CO oxidation.

Methods

The starting K0.11MnO2-δ nanoxide was prepared from Mn(SO4)2, HNO3 and KMnO4 solutions under reflux over 24 h. This oxide was characterized at microscopic and macroscopic levels by Electron Probe Microanalysis (EPMA) and Neutron Diffraction (ND). The implementation of the ζ-factors method was done starting from Electron Tomography experiments performed in a Titan Themis 60-300 microscope operated at 80 kV. For reconstruction, a methodology based on TVM3D algorithms was employed to ensure high accuracy in the determination of local thickness values the oxide nanostructures [2]. XEDS maps were acquired with a Super-X G2 detector, using a beam current ranging between 135 and 145 pA. Maps were recorded in both single and multiple frames modes setting a pixel dwell time between 0.128 and 5.000 ms respectively. These conditions result in a frame acquisition time of approximately 3-100s, after which the drift was corrected using cross correlation. XEDS line profiles were extracted using Velox 3.1 and the quantification was carried out using home-made scripts coded in Matlab.

Hydrogen temperature-programmed reduction (H_2-TPR) experiments were performed in an AutoChem II 2920 automated characterization system, equipped with a calibrated thermal conductivity detector (TCD).

Results

The quantitative analysis of XEDS spectra recorded at different irradiation times under the electron beam allowed us tracking the evolution of the O/Mn molar ratio of different oxide nanostructures, Figure 1 (left). Extrapolation to t=0 of the O/Mn ratio vs t plot provided an estimate of K0.13MnO1.98 stoichiometry for the pristine material. Full agreement with the K/Mn ratio determined by EPMA (K/Mn=0.125) and with the composition obtained by ND (K0.11MnO1.96) and H_2-TPR (K0.13MnO1.99) validated the oxygen quantification procedure proposed by us.

Formation of K0.13MnO1.61 as steady-state product of the electron-beam reduction process, which could be perfectly fitted to a contracting-volume kinetics, suggested that oxygen evolution proceeds in steps of 1/3 of the oxygen located at the O1 or O2 positions of the unit cell.

Taking this experimental observation into account and analysing in quantitative terms the deconvolution of the H_2-TPR experiments, Figure 1 (middle), all the steps involved in the reduction under hydrogen of this type of oxides could be perfectly interpreted and the corresponding intermediate phases proposed (Figure 1, right).

Combination of these results with those coming from DFT calculations allowed us confirming that the usual pre-reduction procedures used to activate these oxides lead to the elimination of all the oxygen residing at the O2 sites of the hollandite structure, rather than just all the oxygen sites (O1 and O2) at the surface of the oxide nanorods, as it has been proposed on speculative basis in the existing literature.

Likewise, it was possible to determine that the formation of MnO concludes at 553°C after the so-called δ step, rather than after the γ one, just at 423°, as it has also been proposed in literature. Moreover, it has been possible to clarify that the intensity of this δ step is totally determined by the initial K content of the hollandite, this suggesting that oxygen evolution in this peak is related to O at the interface between Mn and K.

Conclusions

A novel methodology to implement the ζ-factors scheme to quantify with high accuracy the oxygen content in multi-cationic, beam sensitive, materials has been developed [3]. This methodology has been fruitfully applied to analyse in full quantitative terms time-resolved STEM-XEDS experiments recorded during the in-situ e-beam irradiation of nanorods of a potassium-modified manganese oxide with hollandite-type structure.

The quantitative results obtained at nanoscopic level fully agree with reference data obtained at macroscopic level by EPMA, ND and H_2-TPR, which supports the reliability of the developed approach. Moreover, from the nanoscopic results and the deconvolution of the TPR diagram on the basis of α step processes, it has been possible to determine the composition of the different intermediate phases involved in the reduction of the oxide under hydrogen, avoiding erroneous assignments in the literature.

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Graphic:

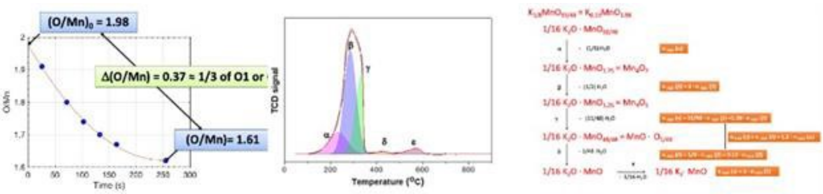

Figure 1. (left) O/Mn molar ratio vs t curve as determined from ζ-factors quantification of time-resolved STEM-XEDS in-situ e-beam reduction experiments; (middle) Deconvolution of the H_2-TRP diagrams of the hollandite oxide; (right) Scheme depicting the different oxygen evolution processes and intermediate phases during the reduction of the hollandite under hydrogen.

Keywords:

Time-resolved-STEM-XEDS, oxygen-stoichiometry, quantitative-XEDS-at-nanoscale, beam-sensitive-materials, ζ-factors

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