Diffraction imaging of catalytic materials under operating conditions – unrevealing the solid-state chemistry with full pattern Rietveld refinement

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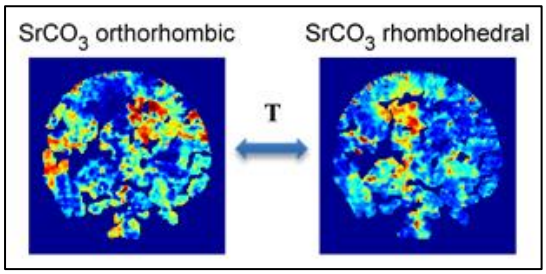
X-ray diffraction computed tomography is a technique that combines powder X-ray diffraction (PXRD) with computed tomography (CT). In contrast to conventional X-ray absorption-contrast computed tomography (CT), which is based on the difference in the attenuation of X-rays from the components present in the sample, XRD-CT is based on the difference in the diffraction signals from the crystalline materials present in the sample. Therefore, additional physico-chemical information is obtained. In the reconstructed image, each pixel corresponds to a complete diffraction pattern, and thus different crystalline chemical species can be mapped inside the cross section of a bulk object [1]. XRD-CT technique is most often applied in synchrotrons (such as the ESRF and the ID15A beamline), due to the remarkable properties (high flux, monochromatic beam, state-of-the-art detector, etc.) and was found to be a very promising technique for *in situ* studies of heterogeneous catalysts, providing high temporally and spatially-resolved data [2]. A diffraction pattern can provide a great number of information not only about the chemical composition but also about the unit cell parameters and crystallite sizes for each crystalline component present in the sample under investigation. These can be extracted by performing a full pattern Rietveld analysis that can be also applied to XRD-CT data [3]. Such information is highly desirable to understand the relationship between the catalyst structure and its role in chemical reaction (structure-function relationships). Since the structure/composition of solid catalysts is rarely uniform, single point measurements are usually insufficient to capture the evolving solid-state chemistry occurring during the chemical process inside the catalytic reactor.



The purpose of this work is to demonstrate the principles of the XRD-CT technique and the batch full profile Rietveld analysis on data collected during the *operando* study of catalytic materials. As an example, a La-Sr/CaO catalyst was studied during the oxidative coupling of methane reaction with XRD-CT. The results obtained from the Rietveld analysis of the XRD-CT data allowed us to capture the transition between two polymorphs of the $SrCO_3$ phase (orthorhombic and rhombohedral). The derived phase distribution maps, which could only be observed by the combination of XRD-CT technique and Rietveld analysis, are directly linked to local temperature gradients inside the catalyst bed as well as the gas-phase composition (partial pressure of CO_2) [3]. We therefore show, for the first time, that the XRD-CT technique coupled with Rietveld analysis can provide unprecedented spatially-resolved physico-chemical information from working reactors and functional materials.

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