

# Sparse X-ray hyperspectral tomography for nanoscopic compositional analysis of VPO catalysts

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**Abstract:** We introduced a novel X-ray measurement and reconstruction method that allows the acquisition of high-resolution hyperspectral tomograms. We applied it for compositional analysis of VPO catalysts which lead to a reevaluation of their working mechanisms. © 2021 The Author(s)

## Main text

### 1. Introduction

The key to understanding and improving the performance of functional materials lies often in the characterization of nanoscopic heterogeneities found distributed throughout their volume. Recently, the combination of X-ray absorption near-edge spectroscopy (XANES) and computed tomography has emerged as a powerful tool for compositional analysis at the nanoscopic level. However, conventional approaches are often hindered by the long acquisition time required for these measurements. We introduced a method based on X-ray near-edge spectroscopy, ptychographic X-ray computed tomography (PXCT), and sparsity techniques, termed sparse x-ray transmission near-edge spectrotomography (XTNES) [1], which allows the acquisition of quantitative hyperspectral tomograms of representative sample volumes at sub-30 nm half-period spatial resolution while reducing the acquisition time almost 10 times compared to conventional methods. PXCT is used as imaging modality for its quantitateness of contrast and high spatial resolution [2]. We used XTNES to investigate the transformation of vanadium phosphorus oxide (VPO) catalysts with industrial use and observed changes that led to a reevaluation of these catalysts used in the production of plastics worldwide [1].

### 2. Material and methods

Conventional X-ray spectral tomography measurements requires acquiring at each X-ray energy tomographic projections at different sample rotation angles. The number of required projections is determined by the Crowther criterion [3]. This results in lengthy acquisition times when aiming for nanoscale resolution of representative sample volumes. In our approach we leverage sparsity to measure only 1/8 of the conventionally required projections/angles at each energy, as shown in Fig 1B. Therewith substantially reducing XTNES acquisition times. Such a reduction is possible, because signal variation across the spectral dimension is heavily correlated. Our reconstruction leverages this correlation to relax the required measurements.

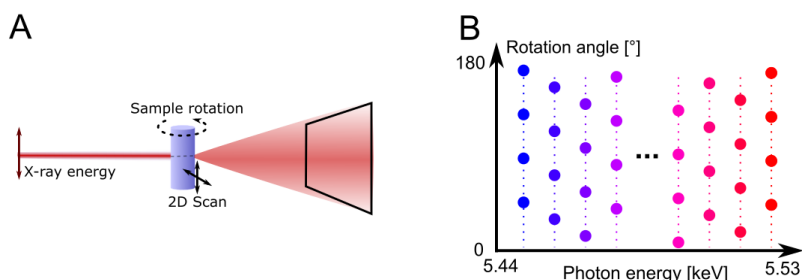


Fig. 1. (A) Schematic of XTNES measurement. (B) Graphical illustration of the acquisition scheme of tomography angular orientations versus X-ray photon energy. For each energy, the Crowther criterion is indicated by small dots, while larger dots indicate angularly sparse measured projections. At each energy, an offset to the angle based on a golden ratio is added to each projection to maximize the available information diversity.

Both a pristine and used VPO catalyst body, the later extracted from an industrial reactor, were analyzed. The bodies were shaped into pillars of 14-16  $\mu\text{m}$  in diameter using focused ion beam (FIB) milling. XTNES tomography measurements were performed at the Vanadium *K*-edge at 5.48 keV and carried out at the cSAXS beamline of the Swiss Light Source. The method relies on a simultaneous tomographic reconstruction of all hyperspectral projections, as described in detail in [1]. The reconstruction provides a hyperspectral tomogram containing one XANES spectrum per voxel in the imaged sample volume of 20\*20\*15  $\mu\text{m}$ , as shown in Fig 2A.

## 2. Result and discussion

From the hyperspectral tomogram we can extract various chemical quantities for each voxel: (i) local electron density [2] (ii) local vanadium concentrations retrieved from the edge jump magnitude, (iii) local vanadium oxidation states determined by the position of the absorption edge, and (iv) local vanadium coordination geometries inferred from pre-edge peak intensity variations. These quantities are shown in Fig 2B.

These extracted chemical quantities enable microstructural analysis, local structure optimization, and defect identification in the measured volume, which ultimately allows for a general description of the restructuring process of the catalyst during industrial use. Further, and locally detected was a selected crystallographic defect. This defect creates unsaturated P=O bonds on the surface of the used catalyst. The latter were so far only theorized to exist and recently suggested to be, in part, responsible for the catalytic activity.[4, 5] This work provide insights towards improved design of VPO catalysts or increasing the lifetime of existing catalysts.

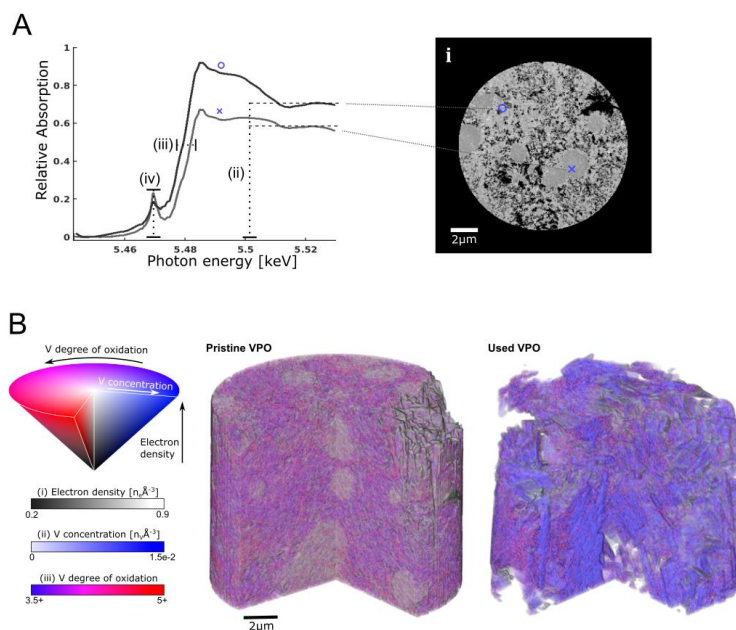


Fig. 2. XTNES results. (A) XANES spectra of two voxels in the pristine catalyst sample, from these spectra we extract (ii) vanadium concentration, (iii) vanadium oxidation state, and (iv) pre-peak intensity. (B) 3D volume rendering of the pristine and used catalyst sample based on the 3D color map used for the combined visualization of electron density, vanadium concentration, and vanadium oxidation state.

## Reference

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