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Aberration-Corrected Scanning Transmission Electron Microscopy for Site Occupancy in M1 Selective Oxidation Catalyst

D. A. Blom[(1)*], W. D. Pyrz[(2)], T. Vogt[(3)], D. J. Buttrey[(2)], M. Sadakane[(4)] W. Ueda [(5)], and V. V. Guliants[(6)]

(1) Electron Microscopy Center and NanoCenter, University of South Carolina, Columbia, SC 29208, email:doug.blom@sc.edu
(2) Center for Catalytic Science and Technology, University of Delaware, Newark, DE 19716
(3) NanoCenter and Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208 USA
(4) Chemistry and Chemical Engineering, Graduate, School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, 739-8527 Japan
(5) Catalysis Research Center, Hokkaido University, N-21, W-10, Sapporo, 001-0021 Japan
(6) Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH 45221

* Corresponding author.

Abstract – The M1 selective oxidation catalyst is a complex metal oxide framework structure with an orthorhombic unit cell consisting of 11 cation sites in the framework and two types of channels into which additional species can intercalate. It has the potential to allow for the production of acrylonitrile (ACN) from propane feedstock rather than the currently used propene. Major energy and costs savings would accrue. Most of the cation sites are known to exhibit partial substitution from simultaneous Rietveld refinement of neutron and X-ray diffraction datasets [1]. Aberration-corrected HAADF STEM has been used to measure the extent of substitution at the various cation sites in a number of specimens. Comparisons with multislice image simulations yield good agreement with a simplified incoherent imaging model.

Selective oxidation catalysts are used extensively to produce either intermediate chemicals or final products incorporated into consumer goods. Acrylic acid and acrylonitrile are two products in high demand that are currently produced using propene feeds with multicomponent bismuth molybdate catalysts [2-3]. A multiphase MoVNbTeO catalyst is one of the most promising candidates to allow for the substitution of propane for propene and corresponding cost savings [4]. Extensive research has been undertaken to improve both the activity and selectivity of this complex system; however there are still a number of basic questions unresolved. Acrylonitrile yields for M1-type catalysts vary widely depending on the details of the synthesis method and extent of chemical substitution [2,3,5]. As a first approximation, the signal in a high angle annular darkfield (HAADF) STEM image exhibits a Z^2 dependence (Z being atomic number). Substitution of V for Mo in the framework cation sites has been found via detailed diffraction studies [1]. HAADF STEM image contrast provides agreement to within 10% with known site occupancies. Figure 1 shows the comparison for two specimens between estimated site occupancies from STEM using an incoherent imaging model and model structures derived from Rietveld refinement [1,6]. Figure 2 shows the results of multislice image simulations [7] of the model structure from [1]. Except for framework site 4, all the image intensities agree reasonably well with the experimental data and the incoherent model.

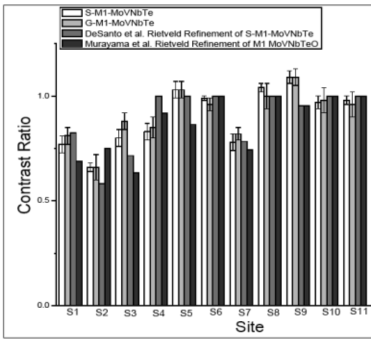

Figure 1: Experimental HAADF image relative contrast compared to incoherent image model.

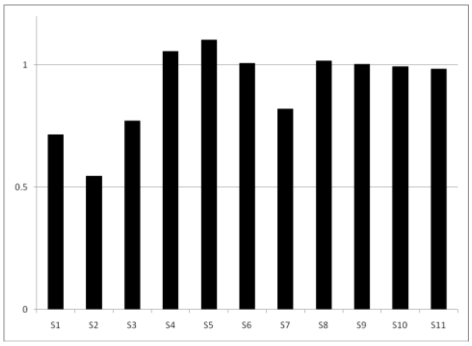

Figure 2: Multislice image simulation of cation site image contrast for an M1 structure 8 nm thick with 5µm C_s and defocus of 2nm.

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