

# Developing Structural Models for Mo-based Selective Oxidation Catalysts Using High-Resolution Scanning Transmission Electron Microscopy (STEM)

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## Introduction

In our work, we use high-angle annular dark-field (HAADF) STEM imaging to develop preliminary structural models for several Mo-V-M-O (M=Nb, Ta, Te, or Sb) complex oxide catalysts used for the selective oxidation of light alkanes. Current processes used to produce high-demand C3 derivatives, namely acrylic acid and acrylonitrile, require the use of multicomponent bismuth molybdates with propene as the feed [1-2]. Significant cost savings can be achieved by replacing propene with propane. Top candidates for this replacement are based on the multiphase Mo-V-O based materials and the current formulation is the MoVTenbO complex oxide system [1-2]. The optimal MoVTenbO catalysts with respect to selectivity and activity are two-phase mixtures comprised of an orthorhombic network bronze (M1) and a hexagonal tungsten bronze (HTB)-type phase (M2) [1-2]. Recently, significant variations in the activity and selectivity towards acrylic acid or acrylonitrile upon the addition or removal of various elements to/from the M1 framework have been observed [3].

## Materials and Methods

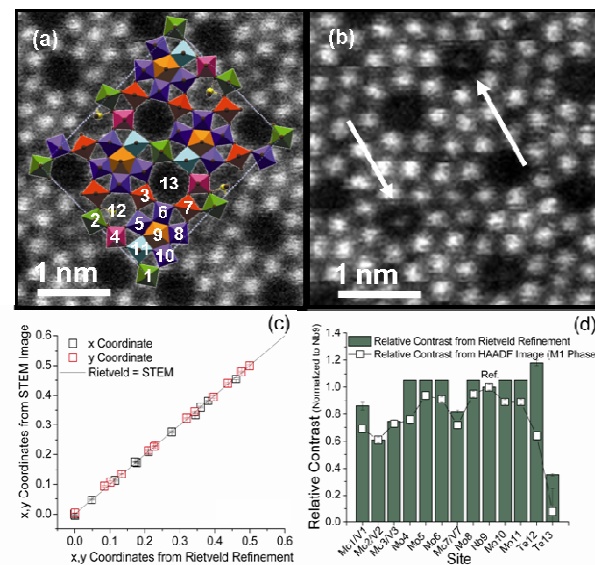
Nearly phase-pure samples of the M1 phase were prepared using either slurry or hydrothermal techniques. HR-STEM was completed on a JEOL 2100F equipped with an aberration-corrector (from CEOS GmbH, Germany) on the illumination system. Samples were prepared for TEM by grinding the as-prepared catalyst and dipping a holey-carbon-coated Cu grid into the powder.

## Results and Discussion

By using high-resolution HAADF imaging and applying the  $Z^2$  contrast approximation [4], we are able to evaluate several catalyst formulations and estimate the chemical composition of individual atomic columns, the atomic coordinates of the metal framework, and the occupancy of the intercalation species enclosed within polyhedral rings [5]. An HAADF image of the MoVTenbO catalyst is shown in Figure 1a, 1b. Direct measurement of the fractional coordinates (Figure 1c), and estimates for site occupancies (Figure 1d) based on the observed image contrast were consistent with our previous studies based on the refinement of high-resolution X-ray and neutron powder diffraction data. After validating the image interpretation algorithm using the well-characterized MoVTenbO, this method was used to develop structural models for several different Mo-V-M-O (M=Nb, Ta, Te, or Sb) catalyst formulations. Using these models, we can begin to develop structure-property relationships that connect catalytic performance to trends in crystal structure, active site composition, or the inclusion/exclusion of various substitutional elements.

## Significance

These HAADF-derived models can be developed in short periods of time (~1-2 weeks) and can serve as starting models for rigorous refinements that otherwise may require several months or even years to complete due to difficulties in estimating the large number of parameters necessary for full structure refinement. Rapid evaluation of complex catalyst formulations can assist with efficient assessment of relationships between crystal chemistry, structure, and catalyst performance.



**Figure 1.** (a) HAADF image of the MoVTenbO 'M1' catalyst with a rendering of our diffraction-based atomic model superimposed on the image showing good agreement [5]. (b) HAADF image showing the occupied heptagonal channels [5]. (c) Plot showing the measured x,y coordinates compared to the refined coordinates from the Rietveld refinement [5]. (d) Plot showing the comparison of the expected relative contrast for each atomic framework site to the measured values based on the HAADF image for the M1 phase [5].

## References

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