

Structural Characterization of Acrylonitrile Catalysts

Acrylonitrile is not a household word, but products made from it are ubiquitous in our homes. Acrylic fibers made from acrylonitrile are used to make our clothing and carpets; they even reinforce paper products.

Acrylonitrile-based plastics are often impact resistant and are used for computer and video-cassette cases. It is also formulated into nitrile rubber products, which are impervious to most solvents and thus are products of choice to contain gasoline or as protective gloves for lab use.

Worldwide, approximately 10 billion pounds of acrylonitrile are made each year through the reaction of ammonia and propylene. However, there is considerable interest in production of acrylonitrile from the reaction of ammonia and propane, since the latter compound is cheap enough to burn. Several multi-component mixtures have been tried as potential catalysts for this reaction, known as propane ammoxidation. The best of these mixtures contains molybdenum oxides doped with various transition metals. Neither the chemical structures nor the mechanism of operation of the various phases in the catalyst was previously understood.

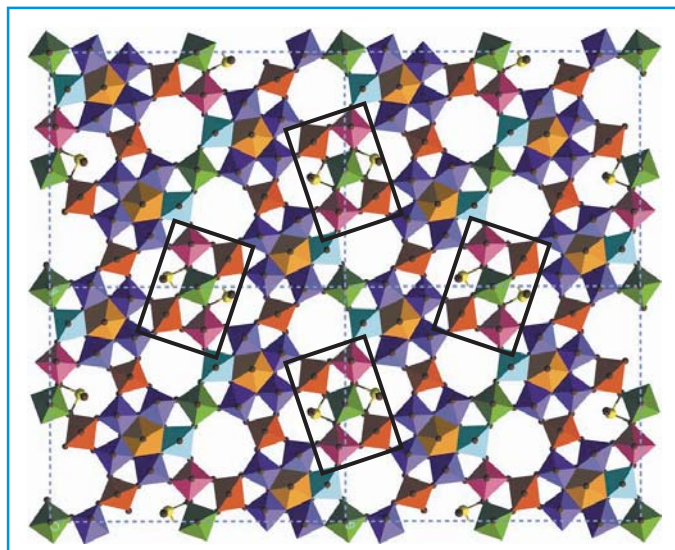


Fig. 1. A view of four unit cells of the M1 propane ammoxidation catalyst viewed along the *c*-axis. O atoms are shown as brown spheres and polyhedra are color coded by cation type: Mo⁶⁺ = purple, Mo⁵⁺ = pink, Mo⁶⁺/ Mo⁵⁺ = light blue, Mo⁶⁺/ V⁵⁺ = red, Mo⁵⁺/V⁴⁺ = green, Te⁴⁺ = yellow. The regions believed to be active sites for catalysis are shown in rectangular boxes [3].

In 2001, workers at CNRS and Elf Atochem, both in France, used electron microscopy to study the most effective known propane ammoxidation catalyst, a (Mo, V, Nb, Te) oxide, and determined that it was composed of two chemical phases, an orthorhombic phase, labeled M1 and a hexagonal phase, known as M2. [1] They were even able to propose schematic structures for these materials. These models, however, do not indicate which cation is found at a particular site and thus provide no knowledge of cation coordination or valence state. Thus, these schematic structures provide little insight into the catalysis function of the materials.

The M1 and M2 compounds are not simple phases. They have large unit cells and do not form single crystals. Therefore, detailed structural information can come only from powder diffraction studies. However, materials of this form, with 40+ atoms in the asymmetric unit are at the limit of where powder diffraction can be used to resolve individual atoms. Further, deviations from crystallinity are seen readily in the electron microscope. The presence of these “errors” in crystallization reduces the long-range ordering in the material and degrades the diffraction pattern, which reduces the amount of structural information that can be obtained. Structural analysis from a mixture of the M1 and M2 phases is not possible. With the advent of combinatorial synthesis, collaborators at Symyx Technologies, Inc. were able to find ways to synthesize the M1 and M2 phases separately. [2] With reasonably pure phases it becomes possible to consider structure determination to learn how the materials function. With those questions answered, there is hope to create even better catalysts, that will further improve the industrial production of acrylonitrile from the desired starting materials.

The usefulness of x-ray diffraction for structure elucidation for these phases is also limited, because the scattering from O is almost negligible in the presence of heavy elements such as Mo, Nb and Te. For that matter, Mo and Nb are virtually indistinguishable with x-rays. With neutron powder diffraction, however, O scattering is comparable to the other atom types and Mo and Nb can potentially be distinguished. However at natural abundance, V is invisible to neutron diffraction.

Due to the complexity of these structures, even with neutron and x-ray powder diffraction data combined, it

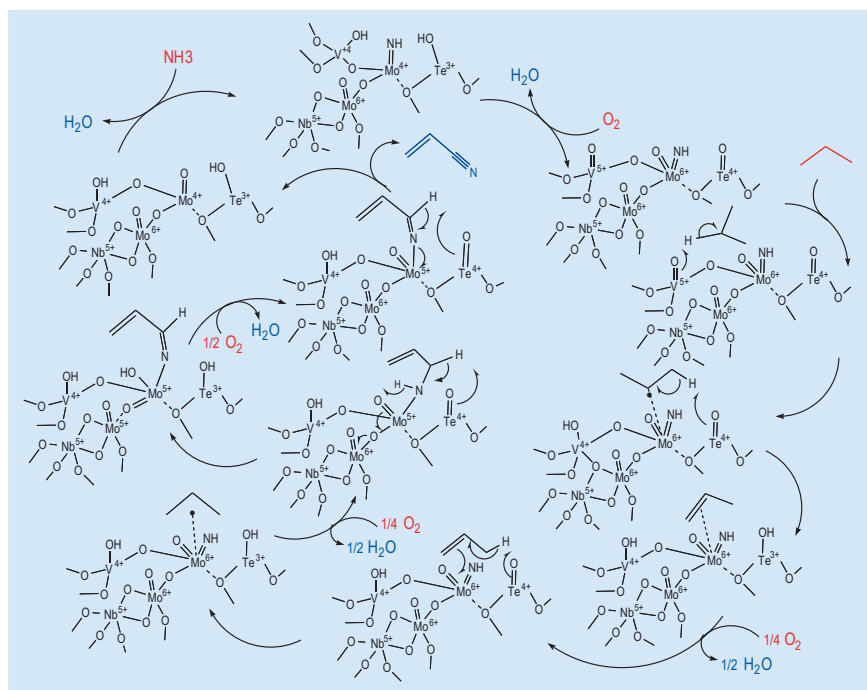


Fig. 2. A schematic mechanism for propane ammoxidation by the M1 catalyst that details the cation centers believed to be responsible for reactive process [3].

would still be very difficult and perhaps impossible to determine the structures *ab initio*. However, using unit cell dimensions and schematic models from electron microscopy, it was possible to build and test atomistic models against the neutron and x-ray powder diffraction data sets individually and in final stages, the two data sets combined. Using this approach, the structure of the M1 phase was determined (see Fig. 1). Work on the structure of the M2 phase, which turns out to be also orthorhombic, is nearly complete.

The result for the M1 phase shows that the material has a layer structure with two sets of channels, one approximately hexagonal, the other roughly heptagonal. The channels allow for the accommodation of large metal cations. This is where the large Te^{4+} cation atom sits. The large channel provides access to the cation's lone pair electrons, which is likely quite important in the ammoxidation reaction. Structural results also provide details of the metal atom coordination, which can then be used to determine the most likely oxidation state for each atom, as is indicated in the figure. Based on these structural results, it becomes possible to explore how the catalyst functions, as is outlined in Fig. 2 [3]. The active sites for propane oxidation to propylene are most likely the bridging lattice oxygen between V^{5+} cations and neighboring V^{4+} or Mo^{5+} . The subsequent addition of ammonia then occurs at a Mo^{6+} cation that neighbors the sites where propane is converted to propylene. Presumably, abstrac-

tion of hydrogen is carried out at Te^{4+} centers. The chemical function of the M2 phase will be more clear when the structure of that material is fully determined. However, it is clear that the M2 phase plays a role in the conversion of incompletely reacted intermediates that desorb from the M1 catalyst prior to the completion of the propane ammoxidation reaction.

Predicted oxidation states of V and Mo in M1 from the refined structure are consistent with those observed in XPS and EPR studies. The Te environment is consistent with those observed by Millet *et al.* using EXAFS in mixed-phase samples [4].

Only with the combination of numerous techniques was it possible to solve this propane ammoxidation catalyst puzzle.

Neutron powder diffraction was essential for refinement of metal and oxygen coordinates and determination of metal-oxygen bond lengths, which was pivotal to calculating cation oxidation states and characterizing the chemical nature of the surrounding oxygen atoms.

References

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