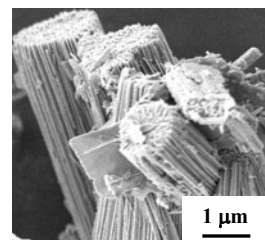


Fundamental Studies of Propane Ammoxidation over Model Bulk and Supported V-Mo-Te-O Catalysts

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The proposed interdisciplinary research program will combine novel methods of synthesis with detailed atomic scale characterization and theoretical modeling in a study of model V-Mo-Te-based mixed metal oxide catalytic technology for one-step transformation of propane into acrylonitrile. Through these methods we will gain fundamental insights into the behavior of these materials and advance the science of catalysis to replace the current fluid catalytic cracking of hydrocarbons to propylene intermediate, which is a major source of environmental pollution. These advances will, in turn, lead to a quantum leap in the development of new environmentally benign petrochemical technologies with very significant economic advantages over the existing technology. The research program will be undertaken by a team of two co-PIs with unique and complementary expertise in heterogeneous catalysis, molecular modeling and microstructural characterization, and will also involve international (the Netherlands, Japan, Spain), Argonne National Laboratory and industrial (Rohm & Haas, BP) collaborations. The specific objectives of this proposed research are:



Hydrothermal VMoTeO catalysts

- Develop synthesis methods for model V-Mo-Te-(Nb)-O oxides
- Establish the bulk and surface molecular structure-reactivity/selectivity relationships for propane ammoxidation over model V-Mo-Te-(Nb)-O oxides
- Develop molecular models for propane ammoxidation over model V-Mo-Te-(Nb)-O oxides

The preliminary studies by the co-PIs indicated that the bulk V-Mo-Te-(Nb)-O catalysts represent a well-defined model system for elucidating the bulk microstructures of the novel nanocrystalline M1 and M2 phases proposed as active and selective in propane ammoxidation, as well as the surface molecular structure-reactivity/selectivity relationships in propane ammoxidation to acrylonitrile. The V-Mo-Te-(Nb)-O synthesis and phase equilibria will be systematically explored in order to obtain the M1 and M2 phases, investigate their crystal

Surface Active Sites Present in Model V-Mo-Te-O and V-Mo-Te-Nb-O Catalysts

Catalyst	N_s^{\ddagger} $\mu\text{mol}/\text{m}^2$	Redox Sites at. %	Acid Sites at. %	C_3H_8 Conversion [§] mol. %	AA Yield [§] mol. %
$\text{Mo}_6\text{V}_3\text{Te}_1$	9.9	52	48	48	12
$\text{Mo}_5\text{V}_4\text{Te}_1$	4.0	45	55	65	38
$\text{Mo}_{5.8}\text{V}_{2.4}\text{Te}_{1.2}\text{Nb}_{0.6}$	8.4	35	65	68	45

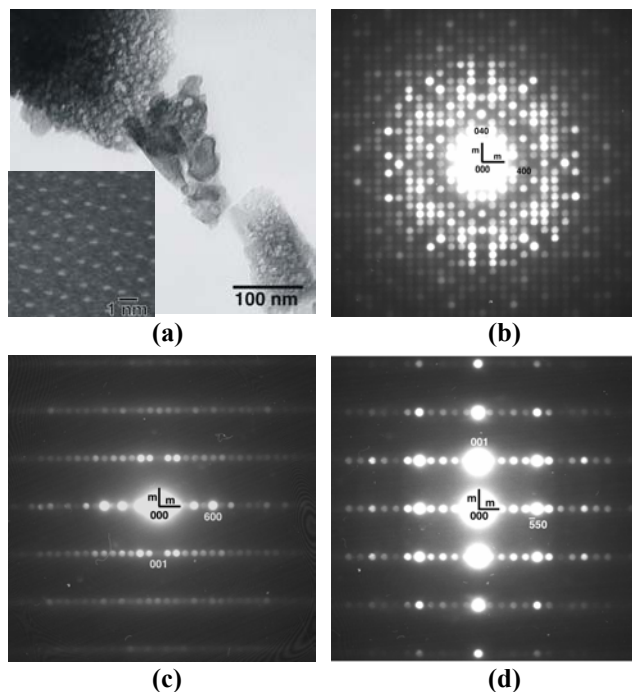
[†] N_s , the total number of surface sites,

[§] Acrylic acid (AA) yield at 653K in 6.3 vol. % C_3H_8 /9.4 vol. % O_2 /47.9 vol. % H_2O /balance He.

structures and local chemical composition by high-resolution TEM, EDS, etc. and the surface composition by ion-scattering and XPS. In addition, *in situ* molecular spectroscopies (IR, Raman, UV-Vis DRS) in combination with surface chemical probes (water, methanol, etc.) will be employed to determine (1) the roles of M1 and M2 in propane ammoxidation; (2) the role of

unique M2 micropores recently discovered by the co-PIs; (3) the M1 and M2 crystal size and surface area effect; (4) the nature, number, structure and specific activity of surface redox, acidic and basic sites; (5) the surface composition of the outermost surface layer; and (6) provide direct structural information about the active surface sites. Additional fundamental insights will come from molecular modeling studies of structure and reactivity of surface $M'O_x$ ($M=V, Mo, Te$ and Nb) species. The molecular structure-reactivity/selectivity relationships from this research will be used to design improved catalysts and the development of fundamental mechanistic models for alkane ammoxidation over mixed metal oxide catalysts.

The *broad impacts* of the proposed program are many. Firstly, this research will advance the science of catalysis by developing new multifunctional catalysts that reduce the number of process stages; super-selective catalysts exploiting nano- and meso-scale structured environments; and result in materials substitutions and process alternatives that prevent or reduce environmental harm. On a utilitarian level, the proposed program is expected to lead to an environmentally benign technology for propane oxidation, thereby addressing the long-term EPA research goal in Pollution Prevention and New Technologies under the Green Chemistry and Engineering area: **develop new catalysts that improve reactions and prevent formation of hazardous by-products**. The third area of impact is in the education and outreach process. A new course on *Environmentally Benign Engineering* will be developed for graduate and undergraduate students, and industrial scientists will be involved in the work of the students. Significant efforts will also be made to recruit underrepresented students, which will be integrated with NSF REU program at the University of Cincinnati. Students who work on this project will gain valuable experience in cutting-edge research and coursework in advanced materials and green engineering and have the opportunity to interact with scientists from industry. This training will give them a competitive advantage in their search for fruitful careers in chemical processing in academia and industry.



TEM images of Mo-V-Te-O system: (a) BF image of M2 phase (inset: HRTEM image of M2 along [001] showing the presence of small pores); (b) [001], (c) [010] and (d) [110] CBED patterns from the M2 particles.