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Project Title: Surface Termination of M1 Phase and Rational Design of Propane Ammoxidation Catalysts

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Summary

The overall objective of this research was to develop fundamental understanding of selective oxidation processes (oxidation, ammoxidation, and oxidative dehydrogenation) of lower alkanes (C₂-C₄) over complex Mo-V-M-O mixed metal oxides (M= Nb, Ta, Te, Sb, and their combinations, etc.) containing so-called “M1” and “M2” phases via the integration of theory and modeling; catalyst synthesis and characterization of its bulk and surface; microreactor studies; and catalyst optimization. Many exciting and important fundamental advances were made to date while pursuing the following specific objectives:

- *Establish roles of Mo-V-M-O M1 and M2 phases in propane ammoxidation*
- *Investigate Nb and Ta location in the M1 structure*
- *Elucidate surface *ab* plane termination in Mo-V-Te-Nb-O M1 catalysts*
- *Probe mechanism of propane ammoxidation over surface *ab* plane of Mo-V-Te-Nb-O M1 phase*

We demonstrated a synergy between the Mo-V-Te-Nb-O M1 and M2 phases at low propane conversion because this Nb-free M2 phase was much more active than the Nb-containing M1 phase in the ammoxidation of the propylene intermediate formed over the M1 phase (Korovchenko and Guliants 2007; Korovchenko et al. 2007; Guliants, 2008; Korovchenko et al. 2008). We also showed that at high propane conversion the Mo-V-Te-Nb-O M1 is the only phase required for propane ammoxidation to acrylonitrile (ACN) and oxidation to acrylic acid (Korovchenko et al. 2008) and that its surface *ab* planes are responsible for its activity and selectivity in propane (amm)oxidation (Guliants et al. 2005a; Guliants et al. 2005b; Guliants et al. 2006a; Guliants et al. 2006b; Trunschke et al. 2006). Redox VO_x sites present in the surface *ab* planes of the M1 phase activate C-H bonds in propane and propylene, whereas other surface MO_x species (Mo and Te) are responsible for the selectivity of the NH insertion into the allyl intermediate. Our XANES study confirmed that only VO_x species undergo reversible oxidation

state changes when the M1 catalyst is cycled between reducing (H_2/He) and oxidizing (O_2/He) environments (Shiju et al. 2007a; Shiju et al. 2008a).

Parallel structural studies of Mo-V-O, Mo-V-Te-O, Mo-V-Te-Nb-O and Mo-V-Te-Ta-O M1 phases revealed that the nature of substituting element (Nb, Ta, Mo or even V) at the pentagonal Site 9 (S9) has a significant impact on the vanadium occupancy in the proposed surface active center and its catalytic behavior in propane ammoxidation (Shiju et al. 2008b). ^{13}C -labeled propane ammoxidation to ACN over the Mo-V-Te-Nb-O M1 phase demonstrated that this reaction occurs directly via C_3 intermediates without their dimerization or skeletal rearrangement as was suggested previously for propane oxidation over other classes of mixed metal oxides (Shiju et al. 2007b). The Mo-V-Te-Nb-O M1 catalysts modified by atomic layer deposition (ALD) of alumina and silica and selectively exposing surface *ab* planes displayed much greater catalytic activity and selectivity in propane ammoxidation than the original Mo-V-Te-Nb-O M1 catalysts indicating that the surface *ab* planes contain the active and selective catalytic sites for this reaction (Shiju et al. 2008c).

Our experimental studies during the last renewal period have focused on the synthesis and characterization of Ta- and Sb-substituted M1 and M2 phases. Pure reference Mo-V-Te-Ta-O M1 phases with different Ta content were successfully made for the first time by hydrothermal synthesis. The Ta-substituted M1 phases were used a model for the structurally and chemically similar Nb-M1 because Nb and Mo in the latter M1 phase could not distinguished by structural methods due to similar scattering factors of these 2 elements. The Ta-M1 phases were employed in a STEM study to directly image the Ta sites in the M1 structure and determine their partial occupancies from the analysis of the Ta atomic column contrast across many unit cells from the surface region to the crystal bulk (Yu et al. 2012). The same analysis was also applied to determine the Mo/V partial occupancies in 10 other metal lattice sites in the M1 phase. This analysis revealed that Ta was present only in so-called pentagonal bipyramidal Site 9 where its occupancy varied from 12 to 39%, the rest being Mo. Contrary to findings of an earlier study employing a Ta-M1 phase made by rapid slurry evaporation (Pyrz et al. 2009), the Ta content was constant from the surface region to the crystal bulk confirming that hydrothermal synthesis results in better-defined catalytic materials. A density functional theory (DFT) study of the model clusters of the Ta- and Nb-M1 phase further confirmed that Site 9 was by far the most preferred location for both Ta and Nb, thereby providing first concrete support for earlier hypothetical models of Nb location in the M1 phase (Yu et al. 2012).

The Ta-M1 phase with the highest Ta content (39% Site 9 occupancy) displayed slightly higher selectivity to ACN (87 vs. 84 mol. %) at optimal propane conversion (28%) as compared to the Nb-M1 phase with assumed 100% Nb occupancy at Site 9. A linear correlation was established between the selectivity to ACN and the Ta partial occupancy in Site 9 suggesting a beneficial active site isolation effect due to the presence of Ta at Site 9. Moreover, a volcano-shaped curve was suggested when the selectivity to ACN at optimal propane conversion (28%) was plotted against the probability of finding a single V^{5+} cation in the proposed active center (Woo et al. 2014). This is primarily explained by poor site isolation effect observed at very high concentration of active centers in a Mo-V-Te-O M1 catalyst. The maximum selectivity to ACN corresponded to ca. 49% probability of finding just one V^{5+} cation in the active center, which is the proposed active and selective site for propane activation to ACN over the *ab* planes of the M1 phase. This volcano plot is in good agreement with another volcano plot reported in our earlier study of the Mo-V-Te-O M1 phases where the ACN selectivity was plotted against the V

concentration in the topmost surface of these M1 phases found in a LEIS study (Gulianti et al. 2005a). Furthermore, a direct correlation was indicated between the selectivity to combustion products (CO_x) and the probability of finding only Mo in the active center. This correlation suggested that Mo^{6+} might be responsible for combustion reactions.

These very important findings provide support for the new concept of active site isolation that manifests itself on two length scales. On a shorter length scale, the isolated (single) V^{5+} cations present at the active centers are associated with high activity and selectivity of the M1 phase in propane ammoxidation to ACN. On a longer length scale, these active centers are further isolated from one another due to the presence of either Ta or Nb at Site 9 that are unable to activate propane and other C_3 intermediates. The active site isolation on a longer length scale further boosts the selectivity of the M1 phase catalysts towards acrylonitrile. These novel insights into the composition of the active centers and roles of constituent metal oxide species guided our theoretical studies of propane ammoxidation on the surface *ab* planes of the Mo-V-Te-Nb-O M1 phase.

Our theoretical studies of propane ammoxidation on the surface *ab* planes of the Mo-V-Te-Nb-O M1 phase (Govindasamy et al. 2010; Muthukumar et al. 2011; Yu et al. 2014a; Yu et al. 2014b) have yielded significant new insights into the elementary reaction steps that suggest different pathways from those advanced in current hypothetical models. Contrary to the hypothetical models, propane is activated over a surface $\text{V}=\text{O}$ species resulting in isopropyl radical and H atoms adsorbed on $\text{V}=\text{O}$ and $\text{Te}=\text{O}$, respectively, with a 1.15 eV barrier consistent with the experimental observations. Moreover, the second and third H abstraction steps were also found to occur over the surface $\text{V}=\text{O}$ and $\text{Te}=\text{O}$ sites. Contrary to the hypothetical model, ammonia is activated on an oxo-depleted Mo site, which is different from the sites for dioxygen and propane activation. Activation of NH_x ($x=1-3$) species over this Mo site is energetically downhill all the way to recombination of N atoms into gas-phase dinitrogen, making the surface imido ($\text{Mo}=\text{NH}$) the most stable H-containing N species. NH insertion from $\text{Mo}=\text{NH}$ into the allyl radical was found to be energetically favorable proceeding essentially without an energy barrier (0.09 eV). This observation suggests that the selectivity of this step would depend on relative abundance of surface $\text{Mo}=\text{NH}$ and various oxygen-containing metal oxide species.

The findings gained in these experimental and theoretical studies are particularly significant due to unique ability of the M1 phase among mixed metal oxides to selectively catalyze several alkane transformation reactions, e.g., propane ammoxidation to ACN (Gulianti *et al.* 2006a), propane oxidation to acrylic acid (Gulianti et al. 2004; Gulianti et al. 2005a; Gulianti et al. 2005b; Trunschke et al. 2006; Gulianti et al. 2006b), selective oxidation of *n*-butane to butadiene and maleic anhydride and *i*-butane to methacrolein, and oxidative dehydrogenation (ODH) of ethane (Botella et al. 2004). Therefore, fundamental advances made in understanding the surface molecular structure – reactivity relationships for this unique system offer a possibility of not only rational design of propane ammoxidation catalysts, but also expanding the scope of selective alkane oxidation beyond the limited number of feedstocks that have met with technological and commercial success.

Researchers Supported During the Current Grant Period

J. Woo, Ph.D. student, Chemical Engineering, University of Cincinnati (2007-2015)

J. Yu, Ph.D. student, Chemical Engineering, University of Cincinnati (2009-2015)

Publications (2010-2015) resulting from DE-FG02-04ER15604

J. Yu, Y. Xu and V. V. Guliants, "Propane Ammoxidation over Mo-V-Te-Nb-O M1 Phase: Density Functional Theory Study of Propane Oxidative Dehydrogenation Steps", *Catalysis Today* 238 (2014) 28-34.

J. Yu, Y. Xu and V. V. Guliants, "Propane Ammoxidation over Mo-V-Te-Nb-O M1 Phase Investigated by DFT: Elementary Steps of Ammonia Adsorption, Activation and NH Insertion into π -Allyl Intermediate", *Topics in Catalysis* 57 (2014) 1145-1151.

J. Yu, J. Woo, A. Borisevich, Y. Xu and V. V. Guliants, "A Combined HAADF STEM and Density Functional Theory Study of Tantalum and Niobium Locations in the Mo-V-Te-Ta(Nb)-O M1 Phases", *Catal. Commun.* 29 (2012) 68-72.

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submitted:

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in preparation:

J. Yu, Y. Xu and V. V. Guliants, "Selective and Unselective Transformation Pathways During Propylene Ammoxidation: N Insertion vs. Oxidation Steps".

J. Yu, Y. Xu and V. V. Guliants, "Quantum Chemistry Based Microkinetic Modeling of Complex Catalytic Processes: Propane Ammoxidation over Mo-V-Te-Nb-O M1 Phase".

J. Woo, A. Borisevich, Q. He, V.V. Guliants, "Quantitative Analysis of Partial Occupancies of Metal Sites in the MoVTaO M1 Phase Determined on the Basis of HAADF STEM Imaging".

J. Woo and V.V. Guliants, "Probability Models of Propane Ammoxidation Behavior of MoVTaO M1 Phases Based on Quantitative Analysis of Partial Occupancies of Metal Sites from HAADF STEM Imaging".

J. Woo and V.V. Guliants, "New Insights into the Origins of M1/M2 Phase Synergy for Mo-V-(Nb, Ta)-(Te, Sb)-O Compositions".

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