ORIGINAL PAPER

Structures, Mechanisms, and Kinetics of Ammoxidation and Selective Oxidation of Propane Over the M2 Phase of MoVNbTeO Catalysts

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Abstract We report here first-principles-based predictions of the structures, mechanisms, and activation barriers for propane activation by the M2 phase of the MoVNbTeO multi-metal oxide catalysts capable of the direct conversion of propane to acrylonitrile. Our approach is to combine extensive quantum mechanical (QM) calculations to establish the mechanisms for idealized representations of the surfaces for these catalytic systems and then to modify the parameters in the ReaxFF reactive force field for molecular dynamics (MD) calculations to describe accurately the activation barriers and reaction mechanisms of the chemical reactions over complex mixed metal oxides. The parameters for ReaxFF are derived entirely from QM without the use of empirical data so that it can be applied to novel systems on which there is little or no data. To understand the catalysis in these systems it is essential to determine the surface structures that control the surface chemistry. High quality three-dimensional (3D) Rietveld structures are now available for the M1 and M2 phases of the MoVNbTeO catalysts. However the details of the chemical mechanisms controlling selectivity and activity have remained elusive because the catalytically important sites in these Rietveld structures are occupied by mixtures of Mo and V atoms, obscuring the actual distributions of the metals and oxides at the active sites. To solve this problem we use a supercell of the Rietveld structure sufficiently large that all atoms can be whole, then we use Monte Carlo techniques based on ReaxFF to resolve these partial occupations into the optimum configuration of whole atoms still consistent with the X-ray data. We will report the ReaxFF resolved 3D structures for the M2 phase of the MoVNbTeO system. Using the resolved 3D structures we consider the distribution of sites on the important surfaces and carry out ReaxFF Reactive Dynamics (RD) calculations to follow the initial steps of the reactions. Such studies provide insights into the chemical reaction steps on MMO catalysts that should be useful in designing more selective and more active systems. We find that this suggests the critical role of the Te^{IV} oxo chains for activating propene but not propane in the M2 phase. This suggests a new mechanism for this phase.

Dedicated to Dr. Robert Grasselli in honor of his 80th Birthday, whose every year has enriched us all.

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1 Introduction and Motivation

The last decade has seen quantum mechanics methods (particularly density functional theory) play an essential role in partnership with experiment to develop improved soluble catalysts for olefin polymerization and CH_4 activation, for some reactions on metal surfaces and some reactions in zeolites. However there has been far less progress on the very important but very complex reactions

on multi-metal oxide (MMO) catalysts. Most prominent among these are catalysts for ammoxidation of propene to acrylonitrile that are utilized for the production of 10 billion pounds of acrylonitrile annually [1]. An indication of the difficulty here is that the major breakthroughs in the 1990s by BP-America [2] (formerly SOHIO) and Mitsubishi [3] in discovering catalysts (e.g. MoVNbTeO$_x$) that convert propane (not propene) directly to acrylonitrile have not yet led to commercially viable catalysts. We claim that the essential reason for the lack of progress is that the active sites of these catalysts have proved impossible to characterize experimentally because of extensive disorder of chemically inequivalent metals in the structures extracted from Rietveld analysts of the crystals.

Figure 1 illustrates this for the very important M1 phase of the MoVNbTeO$_x$ catalysts, which is believed to be responsible for the propane activation step. Based on QM studies we have done on various V, Mo, Te, and Nb sites, we have concluded (see discussion below) that the sites responsible for activating the CH bond of propane are V=O bonds of V^V sites, whereas the site that can form the new CN bond, the key step in making acrylonitrile is a Mo containing a Mo=NH bond from prior reaction with NH$_3$. We believe that the process of the V=O bond activating propane, converts it to a V^{IV} and eventually to a V^{III} site (prior to reactivation by O$_2$) neither of which can react with the reaction product. This is good since we want this product to react with Mo=NH to initiate the formation of acrylonitrile.

Thus although the picture of the structure provided by the analysis is very pretty and symmetric, it does not provide any real clues as to which of these sites M1, M2, M3, M4, or M5, or M7 is important for the selective transformations and which play a role in the unwanted combustion of the intermediates to products. Moreover, correlations among these sites are clearly required to do these selective transformations, but no such information can be gathered from the structural studies. We claim that although the X-ray data does not provide this correlation information, that there are indeed such correlations and that they play a role in the selectivity (as discussed below).

We have carried out calculations described below that predict strong correlations perpendicular to the layers of the apparently disordered system, and we have also carried out calculations indicating that this ordering affects chemical processes involving the surface atoms. In order to obtain such information we have extended the crystallographic unit cell from the X-ray studies to a supercell sufficiently large to resolve the disorder and then we have used Monte Carlo techniques to find the optimum (lowest energy) distributions that are compatible with the Rietveld analyses (and hence would lead to the same diffraction pattern). For the M2 phases of the MoVNbTeO$_x$ catalyst, this requires a 2 × 3 supercell in the ab layer with 4 layers for a total of 24 times the Rietveld unit cell for a total of 672 atoms. We find (see discussion below) that it is good to start this Monte Carlo procedure with 20 independent starting points and that 50,000 Monte Carlo steps are required to obtain convergence. At each such MC step we do a limited energy minimization (50 Conjugate gradient steps) to allow the oxygen atoms to readjust for the new positions of the metal atoms.

Of course such a calculation with 672 atoms per cell (and no symmetry within the cell because of resolving the disorder) for 20 times 50,000 steps with 50 steps of minimization is totally impractical with accurate QM. The reason we have been able to manage such calculations is

Fig. 1 The partial occupations observed from Rietveld analyses of the powder X-ray date of the M1 phase of MoVNbTeO$_x$
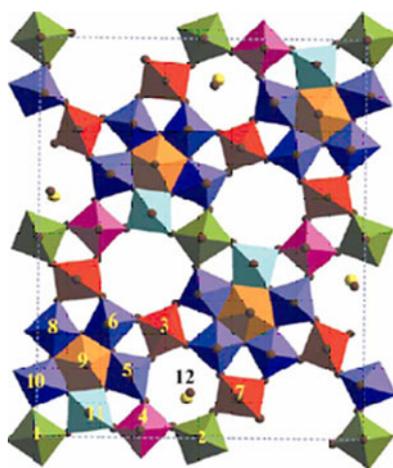
		2006	2004	2003
Tot	Mo : V	7.3: 1.7	7.8:1.2	7.5:1.5
1	Mo : V	0.46:0.54	0.74:0.26	0.8:0.2
2	Mo : V	0.63:0.37	0.38:0.62	0.8:0.2
3	Mo : V	0.46:0.54	0.58:0.42	0.5:0.5
4	Mo : V	0.88:0.12	1.0:0.0	1.0:0.0
5	Mo : V	0.80:0.20	1.0:0.0	1.0:0.0
6	Mo	1.0	1.0	1.0
7	Mo : V	0.62:0.38	0.68:0.32	0.5:0.5
8	Mo	1.0	1.0	1.0
9	Nb	1.0	1.0	1.0
10	Mo	1.0	1.0	1.0
11	Mo	1.0	1.0	1.0
12	Te	0.69	0.74	1.0
13	Te	0.0	0.2	0.0

H. Murayamai et al. *Applied Catalysis A* 318 (2007) 137. P. Desanto et al. *Z. Kristallogr. A* 219 (2004) 152. HP. DeSanto et al. *Topics in Catalysis* 23 (2003) 23.

with the development of the ReaxFF reactive force development by van Duin and Goddard over the last 10 years (also described below). We have shown that ReaxFF can give an accurate description of the detailed energy barriers and structures derived from QM for the reactions involved with ammoxidation, and we have shown that ReaxFF gives an accurate description of the various oxidation states involved (mostly the III, IV, and V oxidation states of V; the IV, V, and VI oxidation states of Mo, the V oxidation state of Nb, and the IV and III oxidation states of Te; but also describing these atoms all the way to the 0 oxidation state of each bulk metal).

Thus, progress on the MMO problem requires a mixture of accurate DFT (at the B3LYP or M06 level) to obtain accurate barriers, energetics, and structures for complex intermediates, combined with continued refinement in the ReaxFF methodology and parameterization, combined with improved strategies for the Monte Carlo structure optimization, a true multiparadigm, multiscale methodology.

We started working on the mechanism of the propene ammoxidation in the early 1980s and on the propane ammoxidation in the mid 1990s although never yet with government support (several proposals have been submitted over the years but we never convinced the reviewers that what we proposed to do could be accomplished). Nevertheless we have gradually made progress and believe that we are now starting to obtain real insight into the mechanism for selective ammoxidation of propane. We would hope that with such a mechanism in hand we could design experiments that could probe the structures predicted to be important. For example we might design multisite probes that could passivate or enhance certain sites or steps and ligands that might be decomposed or trapped by certain sites.

As elaborated below, we believe:

- the *structure* of disordered, multimetal oxides (as well as the structures of clusters grown on oxide supports in general) can be determined by our proposed methods combining reactive forcefields, Monte Carlo (MC) optimization, and quantum mechanical (QM) validation.
- the mechanism, that is the *collaborative roles* of constituent metals in determining reaction networks and product distributions of these multimetal catalysts will be determined using our ReaxFF MC resolved atomistic structures to determine barriers for various reaction steps related to the desired and deleterious reactions steps, which will be validated through QM cluster calculations as we discover the critical steps.
- We expect that the mechanisms derived for these catalytic processes (involving optimal combination of the CH activation, radical trapping, NH_3 activation and O_2 activation functions of existing catalysts) will allow

us to predict new heterogeneous and homogeneous multimetallic catalysts that might be suitable for selective transformations of other *hydrocarbons* and might even suggest new catalysts for *fuel cell anodes* (where we want complete combustion).

1.1 Review of Hydrocarbon Oxidation and Ammoxidation over Multi-Metal Oxides

Heterogeneous oxidation catalysis is responsible for about a quarter of the most important industrial chemicals produced worldwide. The ammoxidation of propylene to acrylonitrile is one such process, and is utilized for the production of 10 billion pounds of acrylonitrile annually [1]. Multi-metal oxide (MMO) catalysts for this process have been of commercial importance since they were invented at SOHIO in the mid 1950s. These systems have been optimized so that the most effective catalysts already have yields of better than 80% in the commercial process. Starting in the early 1980s [4] the Goddard group played an essential role in explaining the mechanism of these MMO propene ammoxidation catalysts, showing the critical role of spectator Mo=O and Mo=NH groups in the selectivity where later extensive DFT calculations [5, 6] validated the concepts for the early work and showed excellent agreement with the dramatic change in kinetics as the ratio of NH_3 is changed. This mechanism was summarized at Irsee III and IV [7]. In these papers we reported results showing that ReaxFF provides an excellent description of the various reaction events.

However for the last 15 years there has been great interest in replacing the relatively expensive propene feed with more abundant propane [1]. There were major breakthroughs in this area in 1989 by BP-America [2] and in 1994 by Mitsubishi [3]. While intensive efforts have been made to improve these catalysts, further advances are required to make these processes commercially viable. Thus, Grasselli estimates that at least 70% selectivity would be required for this, whereas the most promising catalysts—MMOs including at least four metallic elements: Mo, V, Te, Nb—currently have a selectivity of around 60% [8].

Rietveld X-ray structures for three of the distinct phases composing the MoVNbTeO MMO catalyst have been reported based on X-ray powder diffraction data. Two of these phases are believed to play important roles in catalyzing the ammoxidation of propane. The orthorhombic phase, known as the M1 phase, is believed to be responsible for all paraffin activation, while also capable of the alpha hydrogen abstraction and NH insertion steps required to selectively convert the activated propylene to acrylonitrile. The hexagonal phase, known as the M2 phase, is also thought capable of carrying out the alpha hydrogen

abstraction and NH insertion steps necessary for the selective conversion of propylene to acrylonitrile while it is unable to activate propane [9]. Indeed experimental studies suggest a symbiosis or synergism between the M1 and M2 phases, whereby the M2 phase is inactive in the absence of the M1 phase, while the M1 phase is self-sufficient in the absence of the M2 phase [9, 10]. As such, understanding the M1 phase is of primary interest in the search for improved catalysts.

The most recent experimental structure for M1 observed an orthorhombic unit cell [11] with four formula units per cell, with composition $Mo_{0.55}^{5+}Mo_{6.76}^{6+}V_{1.52}^{4+}V_{0.17}^{5+}Te_{0.69}^{4+}Nb_{1.00}^{5+}O_x^{2-}$ ($28.34 < x < 28.69$), resulting in 44 metal atoms and 116 oxygen atoms per unit cell. As shown in Fig. 1, the metal atoms are distributed among 12 distinct crystallographic sites in layers of metal oxide, while the oxygen atoms are distributed among 30 distinct crystallographic sites forming either M–O bonds within a metal oxide plane or bridging between metal atoms in identical crystallographic sites in adjacent planes. Pentagonal, hexagonal and heptagonal channels, formed by Mo, V and O run in the c direction perpendicular to the metal oxide planes. It is believed that Te occupies the hexagonal channels while Nb is in the pentagonal channels, leaving the heptagonal channels empty Figs. 2, 3, 4, and 5.
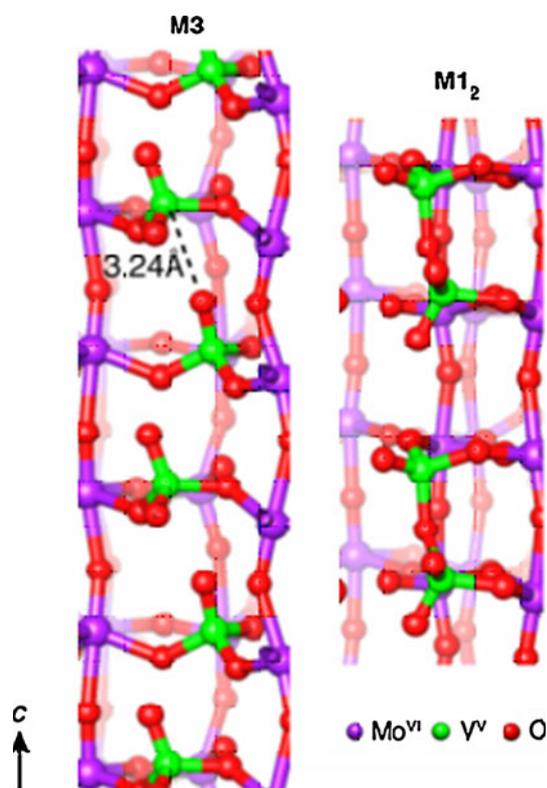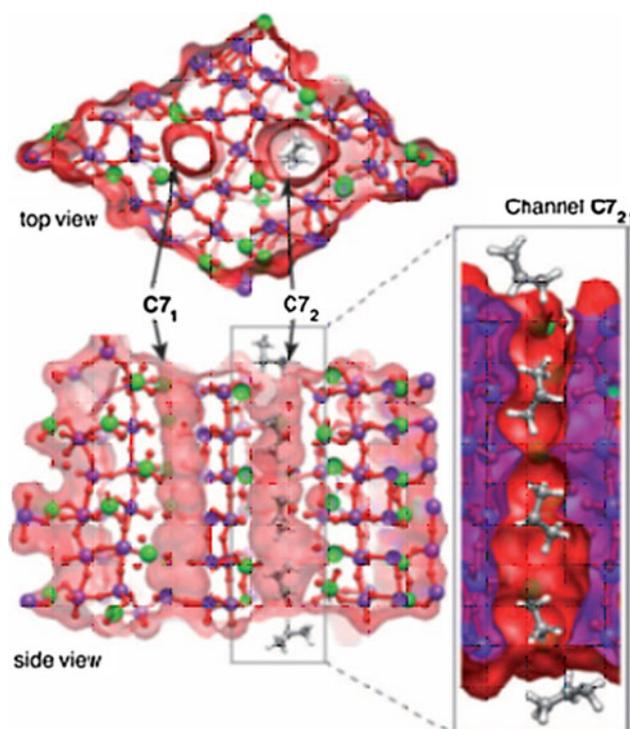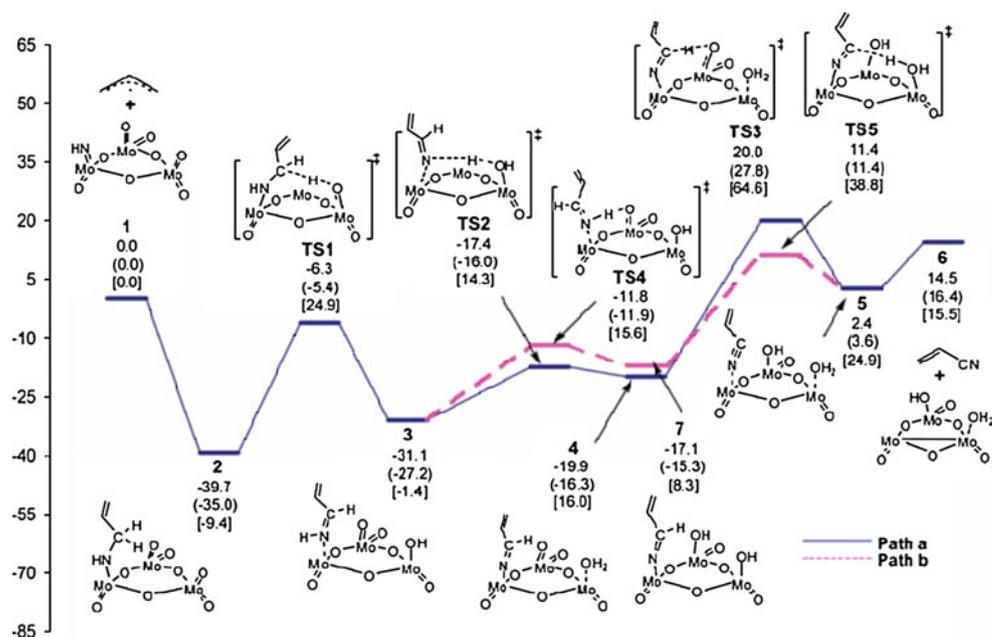

Fig. 3 After allowing 20 propane molecules to react with Mo_3VO_x, we find that 3 have penetrated one of the 7-fold channels and that one has lost an H to a V=O at a M1 site

Fig. 2 The ordering in the M3 site from the ReaxFF-MC RD resolution of The Mo_3VO_x crystal leads to ordered chains of V=O perpendicular to the sheets

Of the ten distinct crystallographic sites containing Mo or V, at least four of these sites have partial occupations in V and Mo, while the remainder of these ten types of sites are occupied solely with Mo. The variation between studies [12, 13] in the partial occupation sites and fractions (either four or six distinct crystallographic sites have been reported to have partial occupations, with variations in the partial occupation fractions for the sites ranging from 5–20%) reflects the sensitivity of the catalyst to small variations in the preparation conditions. Many factors in the preparation methods, including the calcination conditions, lead to variabilities in catalyst performance resulting in poor reproducibility. These variations do not alter the crystal structure, but they do affect the partial occupations which seem to have a significant impact on the activity and selectivity of the catalyst. Indeed, it has been noted that because the M1 phase is particularly susceptible to changes in the partial occupation fractions, this flexibility might be used cleverly for catalytic advantage [14].

The partial occupations of these materials make difficult the examination of atomistic details of the chemical reactions processes, obscuring the reaction mechanisms involved in catalytic processes. Because Mo and V have very different reactivities and local oxygen environments, equivalent crystallographic sites containing a V will lead to very different chemistry than when the site is populated

with a Mo. These uncertainties are multiplied considerably because there are four different sites with partial occupations leading to astronomical numbers of combinations of site populations, greatly increasing the number of possible chemical environments on the catalyst surface. No

Fig. 5 Pourbaix diagram fo trans-(bpy)Ru(OH)2: *red*: experimental results (Dobson and Meyer Inorg. Chem. 27,19(1988). *Blue*: QM results for oxidation potentials and pK$_a$'s based on Lite M06 DFT and PBF Poisson-Boltzmann aqueous solvation

experimental means has been proposed to resolve this difficultly (Fig. 2).

To solve this problem we developed the ReaxFF-MC-RD multiparadigm computational method to resolve such partial occupations of crystallographic sites in such complex inorganic materials into optimized supercells containing whole atoms at each site [15]. We published this concept with the applications to the Mo₃VO$_x$ catalysts of Ueda. Although not as selective, this system involved just one site with disorder, making the problem tractable. Indeed we found that the Mo and V atoms ordered themselves as to have V=O chains perpendicular to the layers (see Fig. 2) in much the same way as for the V₂O₅ catalysts. But it is the V=O at the M1 site that points into the 7-fold channel that we find does the activation. Using ReaxFF we were able to carry out reactive dynamics (RD) studies using periodic boundary conditions with a 6-layer slab of the catalyst and 20 molecules of propane. We observed that three propanes invaded one of the 7-fold channels, containing a chain of V^V=O bonds with the result that the H from one of the CH bonds was extracted by a V=O unit to form a V–OH, leaving a propyl radical (see Fig. 3). This is the first step of the selective process which we believe may be selective within these 7-fold pores because the V=O is deactivated, whereas at the surface there would be others that might lead to combustion.

Over the last 2 years we have been continuing at a modest pace with similar studies on M1 and M2 phases of the MoVNbTeO MMO catalyst. We already have some tantalising results for the M2 phase, but M1 will require much more work. This is already providing insight into the mechanism for these catalysts.
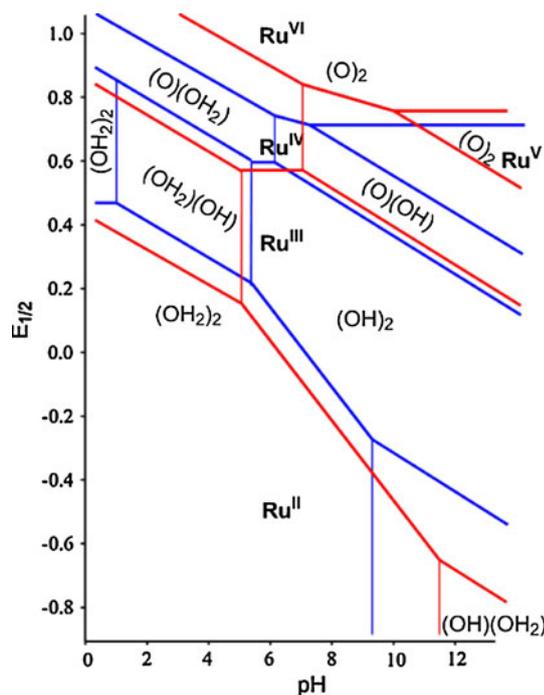
1.2 The ReaxFF Reactive Forcefield

The first principles-based ReaxFF reactive force field has been under development over the last 10 years, primarily with support from DARPA, ARO, and ONR because of its proven ability to capture the reactions of propellants and energetic materials undergoing shocks severe enough to cause detonation. These ReaxFF RD simulation methods have been incorporated into LAMMPS for convenient use by other groups and are being used by many research groups around the world. We are continuing to develop and refine the methods. Thus, we have now demonstrated that ReaxFF is capable of reproducing the energy surfaces, structures, and barriers from accurate QM calculations for reactive systems. ReaxFF studies have been reported for a wide range of materials, including hydrocarbons [16], nitramines [17], ceramics, Si/SiO_2, metals and metal oxides [18, 19], metal/hydrocarbon interactions [20] and metal hydrides [21] demonstrating that ReaxFF has the versatility required to capture the complexity of the mixed metal catalyst system. Critical components of ReaxFF are:

- *Environmentally dependent charge distributions on atoms*. Since atoms make and break bonds in ReaxFF, it is not possible to exclude the huge Coulomb interactions between bonded atoms as in ordinary FF. Thus we allow the Coulomb interaction between atoms to be shielded using the size of the atom to determine the magnitude of the shielding. In addition we allow charge transfer using generalized atomic electronegativity and hardness parameters, allowing the charges to polarize as the systems react.

- *Bond order dependent valence terms*. In ReaxFF we assume a sigmoid Bond order dependence on bond distance, and an power dependence of bond energy on bond order where the parameters are derived directly from QM studies on a large number (1000s) of reactions (allowed and forbidden). This same dependence is used in the other valence interactions (3 and 4 body to ensure proper dissociation as bonds are broken.

- *Universal non-bond or van der Waals interactions*. Since atoms make and break bonds in ReaxFF, it is not possible to exclude the huge vdw interactions between bonded atoms as in ordinary FF. To properly account for the short range repulsion and steric interactions arising directly from the Pauli principle, we use the equation of state from QM for bulk phases involving a variety of coordinations. Thus for metals we typically include coordinations of 12 (fcc and hcp), 8 (bcc), 6 (simple cubic), 4 (diamond), and mixed (A15). We use a Morse function (3 parameters) to describe the short range repulsion (exponential 6 and LJ 12-6 are too stiff in the inner wall region). In principle this accounts for the long range attraction; however, we

have found that the optimization of the vdw terms instead is determined more by the 1–3 interactions, which are dominated by Pauli Repulsion. Thus we have now started the implementation of the low-gradient form for long range London dispersion developed by Yi and Goddard for improving the description of vdw interactions in DFT theory (PBE and B3LYP) [22, 23]. We find that this improves the accuracy of the densities and binding energies of molecular crystals while not modifying the short range valance interactions already well described with ReaxFF. These nonbonding interactions are included between *every* atom pair, independent of connectivity.

- Furthermore, the following guiding principles were adopted during the development of the ReaxFF reactive potentials:

- *No discontinuities in energy or forces*. Earlier attempts at FF to describe reactions resorted to various cut-offs that lead to discontinuities. However, all terms in ReaxFF are continuous allowing proper reactive dynamics (RD) simulations.

- *Transferable potential*. Normal force fields use hybridization dependence in the parameters (e.g. sp3 C, sp2 C etc.). ReaxFF eschews such distinctions treating each element with just one atom type, allowing good transferability of the force field to new systems and avoiding modifications of the atom types during reactions.

- *No predefinition of reactive sites*. With ReaxFF, one does not need to predefine where and when they expect reactions to occur. We typically heat a gas of molecules near a surface and allow the reactions to proceed, allowing unbiased simulations on reactive systems. Indeed ReaxFF has been used to describe pyrolysis and oxidation of complex molecules to derive mechanisms which were subsequently checked with QM calculations and found to be correct [24].

1.3 Quantum Mechanical Calculations

For this project QM calculations play a critical role in establishing the fundamental reaction steps. A typical example is shown in Fig. 4 which shows the important reaction steps in allyl conversion to acrylonitrile over the Mo_3O_8NH cluster (appropriate for low partial pressure of ammonia).

The top energy parameter (kcal/mol) is the ΔE from QM, the middle is ΔH^{0K} ($\Delta E + \Delta ZPE$), and the bottom is ΔG^{673K}. There are two alternative pathways for going from 3 to 5: solid line shows path a, and the dashed line shows path b. We find that step 4 to form 5 is much more favorable when species 4 or 7 is first oxidized. All reported values are for the doublet state ($M_s = \frac{1}{2}$) [25].

Potential energy surfaces are required for the parameterization of ReaxFF, and direct QM mechanistic investigations require free energies with predictive accuracy. To meet these needs in our heterogeneous and organometallic catalysis work we have developed combinations of (1) finite and periodic electronic structure calculations with (2) suitably augmented ≥triple zeta basis sets and (3) density functionals validated against the most relevant reference data, (4) Poisson-Boltzmann polarizable continuum solvation [26] and (5) statistical mechanics. An example of the power of these methods is the prediction of the Pourbaix diagram, illustrated in Fig. 5 for aqueous solutions of *trans*-(bpy)$_2$Ru(OH)$_2$ [27] (in V vs SSCE) to determine the species present at various electrode potentials as a function of pH. For catalysts this is useful for understanding how methods of preparation determine the surface species (metal oxo, metal hydroxide, bridging oxygen etc.)

To make these QM calculations reliable it is important test and validate our predicted free energies against experimental gas and solution phase thermochemical data. We find that standard basis sets often provide an adequate description of metals and main group elements in only one formal oxidation state. However, to predict accurate redox chemistry (including metals and hypervalent main group oxidants), we must augment common basis sets with additional polarization, diffuse, or compact basis functions. We optimized f-functions for third row metals using small molecules but found our results in agreement with Martin [28], so we use the Gaussian-type f-functions taken from this reference. We also optimized d- and f-functions for relevant main group elements to achieve the density functional limit of accuracy with the smallest basis possible.

We have found that as basis sets are expanded, gas phase heats of formation calculated using the B3LYP [29, 30] functional compare to experimental reference values to within 5–10% of reaction energies. (Often these gas phase reactions are a stricter test for electronic energies than the elementary reactions involved in catalysis studies, which by design involve incremental changes. Several bonds may be broken and formed in gas phase test reactions, and error tends to scale with the amount of change in the wavefunction.) New functionals appear regularly, and the meta-GGA functionals of Truhlar's M06 suite [31] have surpassed the accuracy of B3LYP across a broad range of chemical changes (e.g. ionizations, covalent bonding, van der Waals and hydrogen bonding). Thus we are including these in our validation work and are migrating our electronic energy calculations to the newer functionals accordingly.

The periodic QM calculations used to train ReaxFF have been performed using the SeqQuest program. This uses the PBE GGA exchange–correlation functional. The Gaussian basis sets were optimized at the core-valence double-zeta contraction level. All QM calculations were performed for all plausible spin states. For open-shell systems, QM calculations were performed using the spin unrestricted DFT (UDFT). ReaxFF does not employ the concept of multiple spin states and is parameterized to reproduce the energy corresponding to the lowest energy spin state.

To take advantage of hybrid functionals in periodic calculations, we also employ the CRYSTAL [32] and Quantum ESPRESSO [33] codes. Jaguar [34], Q-Chem [35] and GAMESS [36] are available for cluster calculations and analysis.

2 New Results

We are applying the ReaxFF-MC-RD methodology to

- extract whole atom super cells of the bulk M1 and M2 structures.
- determine the important surface structures for these systems.
- consider how these surfaces are modified by exposure to O$_2$, H$_2$O, and hydrocarbons.
- determine the mechanisms from ReaxFF based RD for these systems exposed to propane (and propene) along with O$_2$, NH$_3$, H$_2$O etc. at typical reaction temperatures (450 °C).

2.1 Computational Structure Determination: Application to MoVNbTaTeO$_x$

As we discover plausible reaction steps, we reexamine any new ones with QM to validate the accurate of the ReaxFF for these new steps.

We will summarize here some studies on the M2 system (Figs. 6, 7), which has partial occupations as shown in the Table 1. With the 2 × 3 × 4 supercell we can reproduce all occupations to less than 1.5% difference. The experiments cannot distinguish between the Nb and Mo occupation in the M5 site so we examined the various distributions favored by ReaxFF. We found a strong preference for the Nb to be in the same column (perpendicular to the layers). Then we examined the distribution of Mo and V among the M3 and M4 sites for two cases: only Mo in site M5 and only Nb. We found that Mo in M5 strongly favors the V in site M3 and M4 to align in columns (Fig. 7), while Nb column in M5 disperse the V column (Fig. 8). We do not yet know the implications of this, but clearly there may be an optimum ratio of Nb and Mo. Experimentally it has been hard to control this ratio because the fraction going into the crystal is not the same as in the original slurry.
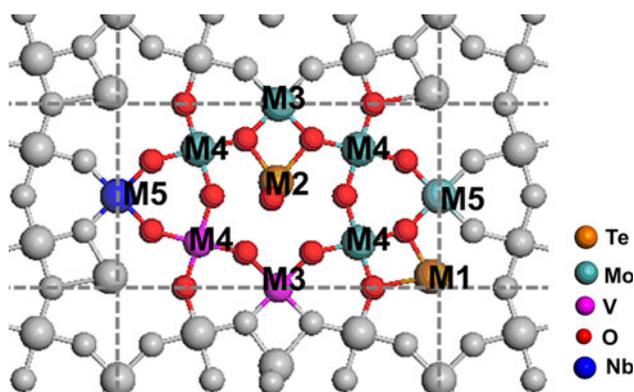
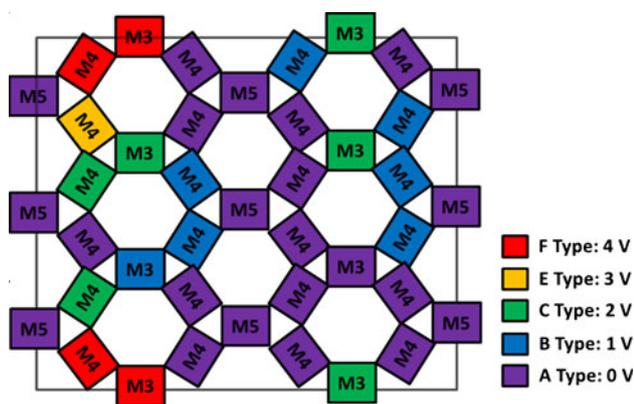Fig. 6 Crystal structure of M2 phase in MoVNbTeO$_x$

Fig. 7 Top view of 2 × 3×4 supercell of the Reitveld analysis of the M2 structure for MoVNbTeO$_x$, showing the M3, M4, and M5 sites. For the case of no Nb in M5: the *red squares* indicate that all 4 layers have V while the *orange squares* indicate ¾ V

Then we examined the Te which in the X-ray has linear Te–O chains in the center of the channel. We find some of the Te–O chains are spiral and the others are cis-trans. In both cases the Te are really Te^{IV}, with hypervalent bonding along the chain direction and two partially ionic covalent bonds to oxygen atoms bridging to Mo or V in the plane perpendicular to the chain axis. Starting with this ReaxFF

structure we carried out QM calculations and found two similar energy structures shown here. One has chains of bridging Te–O-Te–O bonds terminating in an OH while the other has Te=O bonds in the chain direction terminating in a Te=O on one surface and a H$_2$O on the other (Fig. 9). We then used QM to examine the reaction with propane and propene. We found that only propene was favorable leading to a reaction step shown in Fig. 10. Thus the exposed Te=O bond can extract the allylic H from the propene to form an OH that is stabilized because the other atoms in the Te–O chain can shift to the bridging Te–O–Te form in which all are still Te^{IV} (no formation of Te^{III}). Indeed the M2 phase is believed to only activate propene not propane, just as we find Figs. 10 and 11.

Next we created a surface. With ReaxFF this is straightforward since we merely stretch the unit cell and let the atoms break in their most favored way. However in practice such catalysts are calcined (heated to high temperature in O$_2$) so we did the same with ReaxFF, allowing all surfaces to add or subtract surface O depending on the bond energy relative to O$_2$. Then we probed the reactivity of all surface O atoms by allowing a single H atom to bind to the surface O. The results are plotted in Fig. 11 where the horizontal line corresponds to the CH bond energy of propene. Thus just the O atoms below the line can activate propene. We find that all of these sites are surface Te=O. None of the surface Mo=O or V=O can activate the propene. However just one site was reactive enough to break the CH bond of propane. This is quite consistent with current beliefs about M2. This is the first time that anyone has suggested that the Te might play a role in the activation, but now it seems reasonable because on the BiMoO$_x$ catalyst it is known that propene is activated by Bi–O sites while Mo=O or Mo=NH sites do the rest of the chemistry. Next we plan to look at what happens to the allyl radical. It can react with either M3, M4, or M5 sites, but we believe that it may be a combination of M3 and M4 sites.

These results are still preliminary. We need to follow up with real ReaxFF RD at the typical reaction temperatures to follow the dynamical processes. However I believe that this

Positions	Element	Num of sites/unitcell	Occupation ration[a]	Num of sites in 2 × 3×4 supercell
M1	T$_e$	1	0.948	23
M2	T$_e$	1	0.872	21
M3	Mo	1	0.54	13
	V		0.46	11
M4	Mo	4	0.78	75
	V		0.22	21
M5[b]	Mo	1	0.65	16
	Nb		0.33	8

Table 1 Experimental partial occupations for the M1 phase of MoVNbTeO$_x$ from the Rietveld analysis of the powder X-ray structure and number of sites in 2 × 3×4 supercell

[a] From experiments

[b] Nb occupation ration in M5 are not clearly refined in Expt

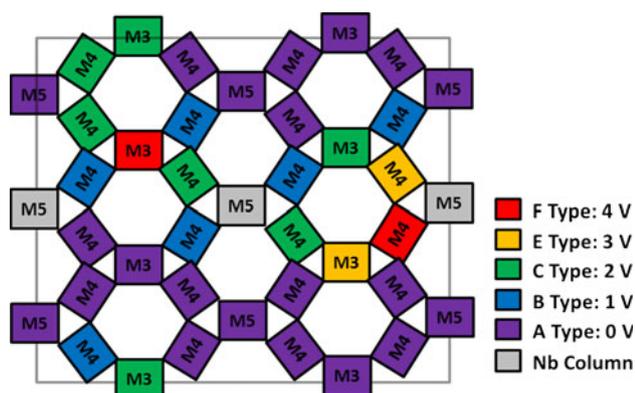**Fig. 8** Top view of 2 × 3 × 4 supercell of the Reitveld analysis of the M2 structure for MoVNbTeO$_x$, showing the M3, M4, and M5 sites. For the case of 1/3 Nb in M5: *gray square* indicate the Nb column; the *red squares* indicate that all 4 layers have V while the *orange squares* indicate ¾V
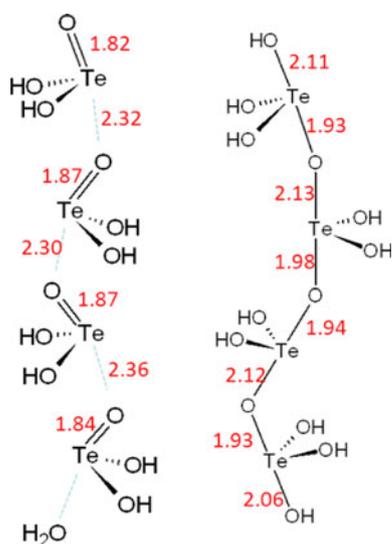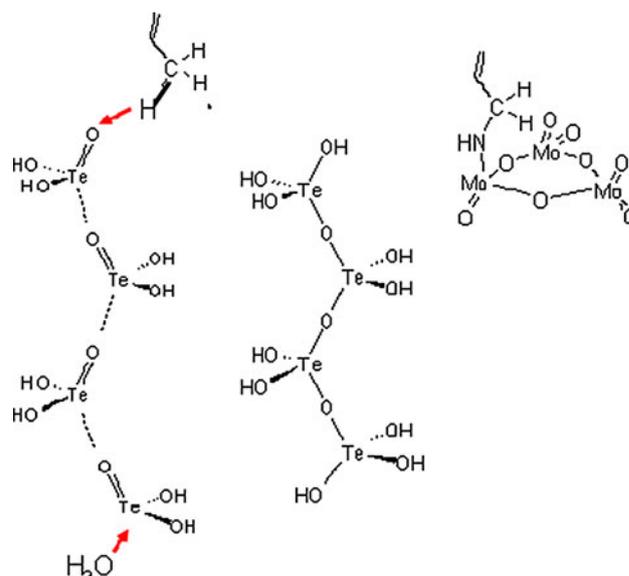

Fig. 10 Reaction of propene with Te oxygen chain. At *left* the propene reactant. At *right* the H is extracted by the Te=O while the iPr radical is trapped by a Mo=NH bond to form a new C–N bond

Fig. 9 Results of QM calculations for a model of the hypervalent Te^{IV} oxygen chains. The *left* shows chains of Te^{IV}=0 while the *right* shows Te^{IV}–0–Te^{IV}–O, with similar energy

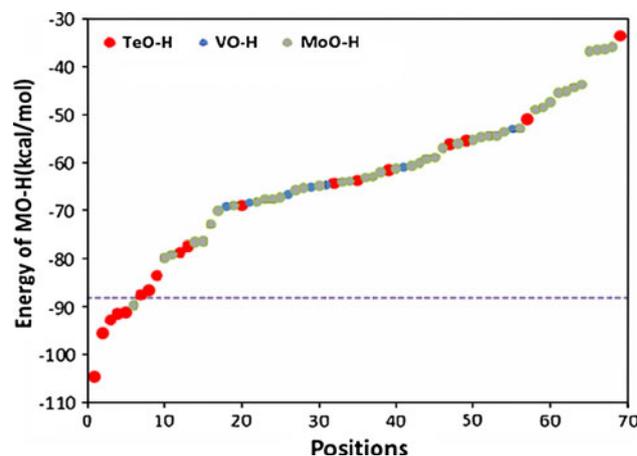**Fig. 11** Bond energy of H atom to M=O bonds of the surface of the 2 × 3×4 supercell of the Rietveld structure of the M2 phase of MoVNbTeO$_x$ after calcining in pure O$_2$. The *line* shows the energy needed to extract the H from propene to yield a surface MOH and an allyl radical. All cases below this *line* can extract this bond. We find that these sites are all Te=O bonds

illustrates how the combination of QM and ReaxFF along with the RD and MC can provide new insights into the mechanisms. Under this proposal we plan to proceed to work out this chemistry. We would expect that the elucidation of the mechanism would lead to suggestions of experimental tests.

Much more effort will be required for M1. It has many more partially occupied sites. We expect that by Irsee VI we should have a good working mechanism.

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