



ReaxFF Monte Carlo reactive dynamics: Application to resolving the partial occupations of the M1 phase of the MoVNbTeO catalyst

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ABSTRACT

Recently high quality structures have become available for the M1 and M2 phases of the MoVNbTeO multi-metal oxide (MMO) catalysts capable of selectively activating propane to form acrylonitrile and other important monomers for modern polymer materials. However the details of the chemical mechanisms controlling selectivity and activity have remained elusive because important sites in these structures are occupied by mixtures of Mo and V atoms, obscuring the actual distributions of the metals and oxides at the active sites. We have developed the ReaxFF-MC-RD computational approach to resolve such partial occupations of crystallographic sites, which we apply here to determine the atomistic arrangements in the M1 phase of the MoVNbTeO system. We find ordering of four distinct crystallographic sites with partial occupations in the z direction. There is a strong energetic preference for Mo–O–Mo and V–O–V interlayer bonding between adjacent M1 sites and also between adjacent M7 sites, leading to V=O V=O and M=O M=O chains perpendicular to the layers and bordering the heptagonal channels. On the other hand, for M3 sites in adjacent sites Mo–O–V bonding is preferred, while there is no observed energetic preference for different ordering between adjacent M2 sites. We consider that these ordered structures lead to local environments that strongly affect the reactivity of V and Mo atoms in the M1 catalyst, demonstrating the need to resolve the partial occupations from X-ray analysis into atomistic structures with whole atoms. The ReaxFF-MC-RD approach provides a means for accomplishing this resolution. We expect that such studies will provide additional insights into the chemical reaction steps on MMO catalysts that should be useful in designing more selective and more active systems.

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1. Introduction

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. While the most effective catalysts already have yields of better than 80% in the commercial process, there is great interest in replacing the relatively expensive propylene 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% [4].

The structures for three of the distinct phases composing the MoVTeNbO 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 to be 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 [5]. 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 [5,6]. As such, understanding the M1 phase is of primary interest in the search for improved catalysts.

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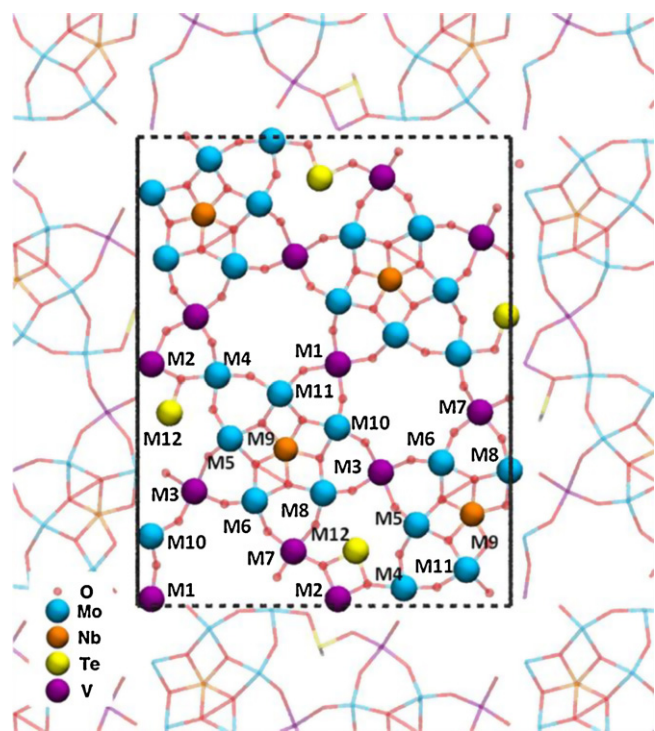


Fig. 1. Experimental structure for M1 catalyst, with 12 unique types of crystallographic sites labelled by color. Occupations are as follows: M1: $V_{0.26}Mo_{0.74}$, M2: $V_{0.62}Mo_{0.38}$, M3: $V_{0.42}Mo_{0.58}$, M4: Mo, M5: Mo, M6: Mo, M7: $V_{0.42}Mo_{0.58}$, M8: Mo, M9: Nb, M10: Mo, M11: Mo, M12: Te. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

The most recent experimental structure for M1 observed the orthorhombic unit cell to have sides of $a = 2.1116$ nm, $b = 2.6594$ nm, and $c = 0.4007$ nm [7]. The unit formula, with four formula units per cell, was found to be $Mo_{0.55}^{5+}Mo_{6.76}^{6+}V_{1.52}^{4+}V_{0.17}^{5+}Te_{0.69}^{4+}Nb_{1.00}^{5+}O_x^{2-}$ ($28.34 < x < 28.69$), 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.

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 [8,9] 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% to 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 [10].

The partial occupations of these materials make the examination of atomistic details of the chemical reactions processes difficult, 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 experimental means has been proposed to resolve this difficulty.

To solve this problem we developed the ReaxFF-MC-RD multiparadigm computational method to resolve partial occupations of crystallographic sites in such complex inorganic materials into optimized supercells containing whole atoms at each site. We demonstrate here the first application to the M1 phase of the MoVnbTeO MMO catalyst. This is expected to provide insight into how variations in the site occupations can be modified and controlled to develop improved catalysts.

2. The ReaxFF reactive force field

Over the last few years we have developed the first principle-based ReaxFF reactive force field method which has been demonstrated to be capable of reproducing the energy surfaces, structures, and barriers of materials, including hydrocarbons [11,12], nitramines [13], ceramics [14], metals and metal oxides [15], and metal/hydrocarbon systems [16], demonstrating that ReaxFF has the versatility required to capture the complexity of hydrocarbons reacting over mixed metal oxide catalysts. ReaxFF includes the following features:

- Time dependent atomic charge distributions.* The net charge on each atom is allowed to change as bonds are formed and broken. Thus a C bonded to H's is generally negative while a C bonded to an O is generally positive. The three universal ReaxFF charge parameters: electronegativity, hardness, and shielding for each element are optimized to reproduce QM charge distributions.
- Bond order dependent valence terms.* All valence terms (bonds, angles, and torsions) depend on the bond orders (BO) which are determined uniquely from the interatomic distances, allowing ReaxFF to describe smoothly the changes in connectivity during chemical reactions. All parameters describing the valence terms are derived directly from QM studies on a large number (1000s) of reactions (allowed and forbidden) and are universal.
- van der Waals (vdW) interactions.* Most critical in ReaxFF is to properly account for the short range repulsion and steric interactions arising directly from the Pauli principle. We use a simple Morse expression with 3 parameters optimized to fit the equation of state from QM for bulk phases involving a variety of coordinations.
- No discontinuities in energy or forces.* Even during reactions, ReaxFF provides a continuous energy and force description, allowing RD simulations.
- Transferable potential.* Each element is described by just one atom type, allowing transferability of the force field to new systems.
- No predefinition of reactive sites.* With ReaxFF, one does not predefine where and when reactions are expected, allowing unbiased simulations on reactive systems.

As reported previously [17] we have developed the ReaxFF parameters for metal oxides relevant to the M1 catalyst and their interactions with hydrocarbons. ReaxFF successfully reproduces the energy differences between the various oxidation states of Mo,

Nb, V and Te, and the redox chemistry relevant to these elements. Furthermore, it has been developed to describe the interactions of hydrocarbons with these metals and their oxides. Indeed, ReaxFF has been shown to accurately model the reactions—including all intermediates and reaction barriers—involved in the selective oxidation of propane by a V_4O_{10} cluster [18].

3. The ReaxFF Monte Carlo reaction dynamics (ReaxFF-MC-RD) method

Using the ReaxFF we have developed a Monte Carlo (MC) strategy for resolving the partial occupations of X-ray crystal structures which can then be used in reactive dynamics (RD) simulations of the reactive processes [19]. Our method begins by expanding the structure to a supercell of the crystallographic unit cell that is large enough to resolve the partial occupations into whole atoms. Atoms can then be distributed over the partial occupation sites so that the average population of each distinct crystallographic site matches the experimental fractional occupations. Then this starting structure is optimized using reactive dynamics (RD) and its optimized energy is computed. Next, two atoms of different elemental types, but occupying the same type of crystallographic site are randomly selected and swapped (i.e. exchange locations). The new structure is optimized and its energy calculated. If the system energy has improved following the swap, the new structure is retained. If the energy has not improved, we use a Monte Carlo (MC) criterion to determine whether or not to keep the new structure.

For the M1 catalyst we can match the experimental partial occupations for Mo/V sites reported in [9] within 2% by expanding to super-cell four times larger than the crystallographic unit cell, for example, a $(1 \times 1 \times 4)$ unit cell. The result is 640 atoms per super-cell with 12,825,612,800 unique configurations corresponding to different ways to distribute the different elements in the partial occupation sites. This is far too many possibilities to test each one explicitly! A MC method provides an efficient means for optimizing the configuration without testing each combination explicitly. Nevertheless, anywhere from 100,000 to 10,000,000 MC + RD steps are needed to find the optimal family of configurations depending on the exact system and computational setup. At present, such large systems and numbers of iterations are impractical for quantum mechanics (QM) calculations. However, they are practical for the ReaxFF reactive force field.

As a proof of concept we recently reported the ReaxFF-MC-RD method for resolving the configurations of partial occupation sites and its application to the Mo_3VO_x catalyst [19]. This is a much simpler problem than M1 since only one site is disordered. However this study showed that the V atoms form chains in the z direction, so that V–O–V and Mo–O–Mo bonding is preferred over V–O–Mo bonding. The various sites on the resulting structure were then analyzed for their reactive properties, revealing that crystallographically equivalent sites play different catalytic roles because of their distinct chemical environments and properties.

4. Application of ReaxFF-MC-RD to the M1 phase

Experimental work examining the effect of grinding the M1 catalyst on catalytic activity indicates that the (001) surface contains the active sites [20]. ReaxFF has been utilized to probe this surface for the active sites by examining the reactivity of the various surface sites [17]. After the location of surface oxo groups was determined by comparing the binding energy of O at the various metal sites on the surface to the binding energy of O_2 , the energy for binding H to each of these oxo groups was calculated. The most reactive oxo group was bonded to Mo^{6+} at an M4 site. The next four most reactive sites are: Mo^{6+} at an M6, site, Mo^{6+} at an M5 site, Mo^{6+} at an

M5, site, and V^{5+} at an M7 site. The wide variation in these sites suggests that the local environment of the metal it is attached to plays an important role in determining the reactivity of an oxo group. Thus, resolving the partial occupations by determining the configuration of the atoms in the partial occupation sites is essential for understanding the catalytic reaction mechanism.

Here we consider early applications of the ReaxFF-MC-RD procedure toward resolving these partial occupations. Because there are multiple sites with partial occupations, two basic approaches are possible. The first approach is to optimize the partial occupations at all distinct crystallographic sites with partial occupations simultaneously (not in the sense of swapping an M3 atom with an M7 atom, but of swapping M3 atoms at some iterations and M7 atoms at other iterations, etc.). An alternative approach is to use the ReaxFF-MC-RD procedure to optimize the configuration of one site at a time. Here we have taken an intermediate approach in which we fix the configuration of atoms in a set of crystallographically indistinguishable sites (e.g. M3) to fit a particular structural motif we wish to model, and then simultaneously optimize the configurations of the remaining partial occupation sites to find the lowest energy configuration given the particular structural motif of interest. By applying this same procedure to another structural motif for the same crystallographic site we can compare the energies of the basic structural motifs associated with each site.

Because the ReaxFF-MC-RD procedure involves both structure and configuration optimization, there are several approaches for coupling these. On one hand, full structural optimization between each of the MC iterations would allow one to compare the lowest energy available for each configuration. Nevertheless, this procedure is computationally expensive and inefficient for such a large structure. Furthermore, unless one returns to the original, “unbiased” coordinates at the beginning of each geometry optimization procedure there is a possibility of being trapped in a local minimum for the present configuration that is similar to the global minimum for the previous configuration. On the other hand, minimal geometry optimization between each of the MC iterations, runs the risk of comparing energies for the various configurations that are not reflective of the actual energy differences, which results in either unreliable results or requires excessive numbers of MC iterations for convergence. Here we take an intermediate approach in which we perform a maximum of 15 steps of conjugate gradient minimization between MC iterations. To determine which energetically unfavourable swaps to accept we use a MC temperature of 5000 K. The crystallographic site from which to choose the pair of atoms to swap is selected randomly at each iteration.

5. Results

We consider partial occupations in the M1, M2, M3 and M7 sites as reported by [9]. At present, for the sake of simplicity, we treat the M12 Te sites as fully occupied (rather than partially at 0.94) in agreement with [8]. As noted above, experiments show variation in the partial occupations reported due to the difficulty of exactly reproducing the preparation procedures and the sensitivity of the partial occupation sites to slight variations in these preparation conditions. To resolve the partial occupations we use a $(2 \times 2 \times 2)$ super-cell. The sixteen M1 sites are filled with 12 Mo and 4 V atoms, giving an average of 0.75 Mo and 0.25 V per site to correspond to the experimental fractions of 0.74 Mo and 0.24 V. The sixteen M2 sites are filled with 6 Mo and 10 V atoms, giving an average of 0.63 Mo and 0.38 V per site to correspond to the experimental fractions of 0.62 Mo and 0.38 V. The thirty-two M3 sites are filled with 18 Mo and 14 V atoms, giving an average of 0.44 Mo and 0.56 V per site to correspond to the experimental fractions of 0.42 Mo and 0.58 V. Finally, the thirty-two M7 sites are filled with 18 Mo and 14 V

atoms, giving an average of 0.44 Mo and 0.56 V per site to correspond to the experimental fractions of 0.42 Mo and 0.58 V. Thus, our model matches the experimental partial occupations within 2%.

Because correlation is typically an indication of strong interactions, the distance between partial occupation sites, in terms of the smallest number of M–O bonds connecting a pair of partial occupation sites, provides a rough measure of how likely there is to be a pattern in how their partial occupations are resolved. For the M1 site, the next nearest partially occupied site in the same metal oxide plane is an M3 site, which is four M–O bonds away. However, each of the metal oxide planes above and below contains an M1 site which is only two M–O bonds away. Thus, we expect the atomic configuration of the M1 sites to be primarily influenced by coupling among adjacent M1 sites in vertical columns, perpendicular to the metal oxide planes. Under these assumptions, the simplest structural motifs for columns of M1 sites would be

- homogeneous columns, having only one type of atom (either Mo or V) in each column;
- alternating columns, containing both Mo and V atoms.

The ratio of Mo:V for M1 sites is 3:1, so for the homogeneous column idealized case there would be one column of V for every three columns of Mo, while in the second case we might consider equal numbers of pure Mo columns and columns with alternating Mo and V atoms. This second case would have an entropic advantage with three times as many configurations as the first. Now we can use the MC technique to compare their energies by optimizing the configurations of the atoms at the other partial occupation sites (M2, M3, and M7), while keeping the M1 configuration fixed. After 25,000 MC iterations (Figs. 2 and 3), the energy for the configuration based on the M1 homogeneous motif is 291 kcal/mol more stable than the energy of the M1 alternating motif. This suggests an energetic advantage for ordering the M1 sites in columns of like atoms.

The M3 sites are similar to the M1 sites in that their closest neighbours in the metal oxide plane are M1 and M7 sites, which are four M–O bonds away. The partial occupation sites closest to them are the M2 sites in the metal oxide planes directly above and below them. Because the ratio of Mo:V for M3 sites is 9:7 the simplest motifs would be nine homogeneous columns of Mo for every seven columns of V on the one hand, or two homogeneous columns of Mo for every seven columns of alternating V and Mo. In this case we

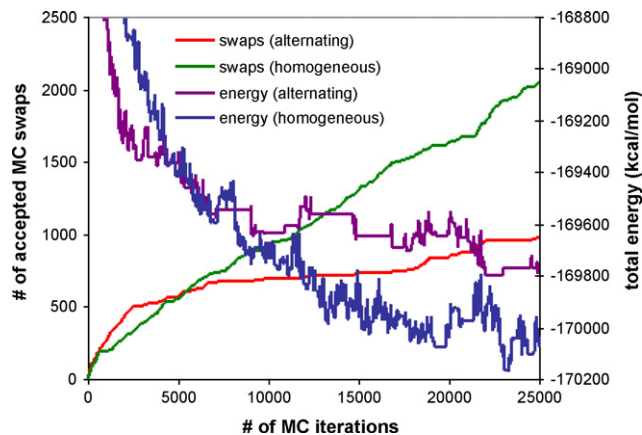


Fig. 2. System energy (kcal/mol) and number of successful swaps for 25,000 iterations of ReaxFF-MC-RD simulations on alternating (Mo–O–V–O) and homogeneous (Mo–O–Mo–O and V–O–V–O) configurations for M1 M1 catalyst. These calculations used a MC temperature of 5000 K and a $(2 \times 2 \times 2)$ super-cell.

find that the alternating motif has an energetic advantage of 401 kcal/mol after 25,000 MC iterations.

Unlike the M1 and M3 sites, we expect each M2 site to be not only coupled with other M2 sites in the metal oxide layers directly above and below it, but also with the two M7 sites, each only two M–O bonds away, each M2 site is sandwiched between in the metal oxide plane. Nevertheless, allowing the M7 sites (along with the M1 and M3 sites) to optimize around basic M2 structures, we can consider the correlation of M2 sites by themselves as long as we remember that the occupations of the surrounding M7 sites probably plays an important role in the final analysis. Thus for the M2 sites, which have a Mo:V ratio of 5:3 the simplest motifs are five homogeneous columns of V for every three columns of Mo on the one hand, or two homogeneous columns of V for every six columns of alternating V and Mo. Here we find that the alternating columns are only preferred by a mere 12 kcal/mol after 25,000 MC iterations, making the two motifs essentially indistinguishable with respect to their energy.

Finally, columns of M7 sites come in pairs. So we must consider four motifs for groups of four M7 sites forming a column on either side of a column of M2 sites. The M7 columns can be either homogeneous or alternating. In the case of homogeneous columns the

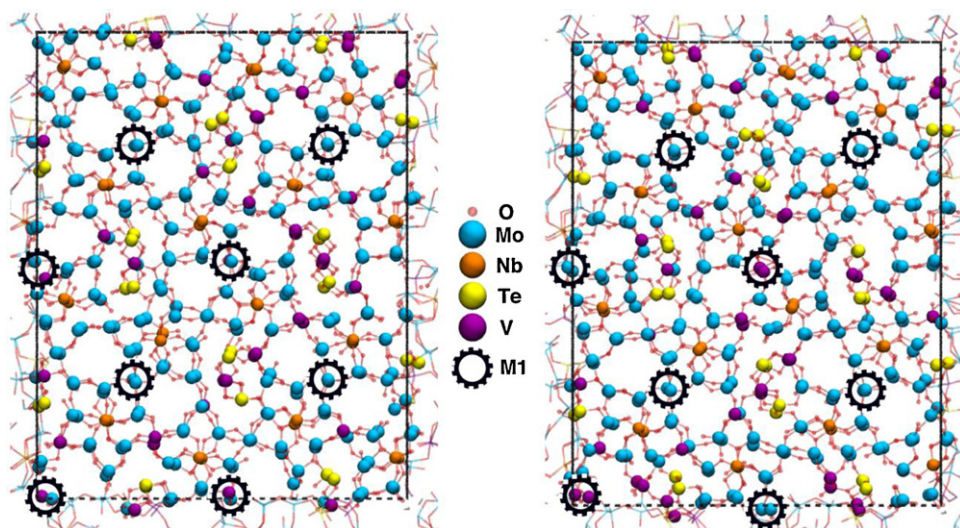


Fig. 3. Structure after 15,000 MC iterations of ReaxFF-MC-RD on the $(2 \times 2 \times 2)$ unit cell of the M1 catalyst ($\text{Mo}_{246}\text{V}_{42}\text{Nb}_{32}\text{Te}_{32}\text{O}_{928}$), with the configuration of the M1 sites fixed in alternating columns (left) or homogeneous columns (right), while the configurations of M2, M3 and M7 sites are optimized.

columns can be composed of like atoms to form a block of all V or all Mo around a column of M2 sites, or else one homogeneous column of each type, one on each side of the M2 column. In the case of alternating columns the atoms at M7 sites in adjacent columns in the same metal oxide layer can either be the same, forming layers of like atoms or different forming a checker pattern. After 25,000 MC iterations the lowest energy configuration has homogenous columns of opposite type adjacent to each other. However, blocks of like atoms surrounding each column of M2 sites are only 76 kcal/mol higher in energy. Forming alternating columns with layers of like atoms is 231 kcal/mol higher in energy than the column motif, while a checker board pattern lies 342 kcal/mol in energy relative to the column motif. Thus, we find that columns of homogeneous atoms are preferred for the M7 sites over columns of alternating atoms.

The above analysis is not meant to provide the final configuration for the M1 phase but rather to show how ReaxFF-MC-RD is used to prepare reasonable possible starting points. A more robust structural study would require either proof that structure/configuration coupling does not pose a problem for finding the global minimum (i.e. the final configuration does not depend on the initial configuration) or the development of improved sampling methods guaranteed to find the global minimum configuration. Here, as an important step in developing these methods we selected a simple scheme for finding a minimum energy configuration that would be appropriate for well behaved systems. Additional, work is required to demonstrate that the system of interest is indeed well behaved. Nevertheless, on the assumption that the M1 phase is well behaved, the plausible structural motifs for the M1, M2, M3 and M7 sites suggested here lead to some initial structural insights.

6. Discussion

The catalytic properties of the M1 phase have previously been rationalized in terms of active centres, groups of metal atoms on the catalyst surface containing the necessarily elements to carry out all steps of the catalytic process. It has been proposed that these assemblies include the surface metal atoms in a single metal oxide layer, surrounding each M2 site. Thus, two M4 sites containing Mo^{5+} or Mo^{6+} , two M7 sites containing Mo^{6+} or V^{5+} , two M12 sites containing Te^{4+} , and one M2 site containing Mo^{5+} or V^{4+} make up each active centre [6]. The V^{5+} at the M7 sites was suggested to be responsible for activating propane, the Te^{4+} at the M12 sites for the alpha hydrogenation abstraction steps, and the Mo^{6+} at either an M4 or M7 site enable NH insertion. The Mo sites (M5, M6, M8, and M11) surrounding each active centre isolate the active centres from each other, allowing each one to carry out the entire catalytic process independent from the other sites.

In considering the catalytic capabilities of these proposed active sites, the occupations of the M7 sites are particularly important. Because of the high reactivity of V^{5+} at the M7 sites, waste products resulting from additional dehydrogenation are likely to result from active centres with V occupying both M7 sites. On the other hand, active sites with Mo^{6+} at both M7 sites will be inactive, because they cannot activate propane. Thus, it is likely that active centres containing V^{5+} at only one of the M7 sites will result in the desired product, while active centres with no V^{5+} at the M7 sites will be inactive, and active centres with V^{5+} at both M7 sites will lead to waste products. Based on these mechanistic assumptions Grasselli et al. [10] computed the distribution of active, inactive and waste sites assuming a random distribution of atoms in the partial occupation sites based on the experimental partial occupations. They determined that 44% of the centres should be active sites, 46% should be inactive, and 10% should be waste. Based on this distribution of sites the maximum selectivity ought to be 81%.

Our MC simulations on the structure of the M1 catalyst suggest that the maximum selectivity may be even better. We find

that columns of M7 sites show a strong preference for having like atoms in adjacent layers forming columns of like atoms rather than columns of alternating atoms. Thus, the vast majority of M7 sites are likely to have adjacent M7 sites above and below with identical occupations. For such homogeneous columns of M7 sites, we find a modest energetic preference (76 kcal/mol) for having the two M7 sites in each active centre occupied by one Mo and one V. Such a preference would suggest that there may be more active sites than expected from a random distribution, simply because they are energetically more favourable. This possibility provides additional motivation for seeking to extend the experimental selectivity beyond the present maximum realized selectivity of 72%.

7. Comparison with recent simulations on Mo_3VO_x catalyst and implications

Recently we reported similar ReaxFF-MC-RD studies on the simpler but related Mo_3VO_x catalyst [19]. This catalyst has structural motifs similar to the M1 phase with heptagonal and hexagonal channels. For the Mo_3VO_x catalyst there was only one site with partial occupation so that it was possible to more completely optimize the structure. We found similar results to those reported here for M1, with $\text{V}=\text{O}$ chains forming columns separate from $\text{Mo}=\text{O}$ chains. As was pointed out in ref [19] such $\text{V}=\text{O}$ chains are observed in the V_2O_5 and VPO systems both of which can activate CH bonds of saturated alkanes.

We were able to carry out reactive dynamics on the Mo_3VO_x system exposed to a gas of propane and found that three propane molecules entered into one of the heptagonal channels. We also found that one of the propanes was activated inside the channel. After such activation, the $\text{V}=\text{O}$ chain may be inactive toward additional reactions allowing subsequent steps along the pathway for selective oxidation to occur in the somewhat protected environment inside the channel. This suggests that the sites for selective oxidation might be within the channels (but perhaps not too far from the surface). It could be that activation at the surface may be less favourable because the termination of the $\text{V}=\text{O}$ chains leads to deactivation of the terminal $\text{V}=\text{O}$ groups. Moreover it could be that activating the propane at the surface to form propene might expose the propene to additional active sites that could lead to combustion and formation of CO_2 , instead of the desired products. If this were true, it might be possible to increase selectivity by irreversibly blocking the surface $\text{V}=\text{O}$ sites with bulky groups that could not penetrate the heptagonal channels.

8. Summary

We have applied the ReaxFF-MC-RD procedure to resolve the partial occupations in the M1 catalyst for the ammoxidation of propane. For the sixteen M1 sites (Mo_{12}V_4 in our model) we find a correlation between M1 sites in adjacent (001) metal oxide planes, so that separate columns of Mo and V are preferred over mixed columns of alternating Mo and V. This leads to chains of $\text{V}=\text{O}$ $\text{V}=\text{O}$ similar to those found in Mo_3VO_x and in V_2O_5 and VPO, that we believe might be important in activating CH bonds of alkanes.

In contrast, for the thirty-two M3 sites ($\text{Mo}_{18}\text{V}_{14}$ in our model), we find that columns in which Mo and V alternate are preferred. The sixteen M2 sites (Mo_6V_{10} in our model) show no significant preference for alternating as opposed to homogeneous chains.

Finally, the thirty-two M7 sites ($\text{Mo}_{18}\text{V}_{14}$ in our model) come in pairs of columns on either side of the M2 columns. The most stable configuration for the M7 sites is for the columns in pair to be homogeneous columns of different type of atom (i.e. one pure Mo column and one pure V columns). Homogeneous column of the same type is the next best, while mixed columns of alternating Mo and V atoms are high energy configurations.

This analysis is just the start. We will continue to extend the ReaxFF investigation on the M1 and M2 systems to more fully resolve the partial occupations. As the structures are refined with ReaxFF-MC-RD and the refined structures are used in reactive dynamics (RD) with propane, O₂, and NH₃ present, we expect to obtain a much improved understanding of the mechanisms, with the hope that our new knowledge will suggest strategies for improving selectivity and activity. Thus, ReaxFF-MC-RD provides a powerful tool for examining complex catalytic systems and obtaining the atomistic insights into these systems needed to optimize them for better selectivity and activity.

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References

- [1] R.K. Grasselli, J.D. Burrington, D.J. Buttrey, P. DeSanto Jr., C.G. Lugmair, A.F. Volpe, T. Weingard, *Top. Catal.* 23 (2003) 5.
- [2] U.S. Patents 4,746,641 (1988), 4,788,317 (1988), 4,843,055 (1989) assigned to the Standard Oil Company.
- [3] T. Ushikubo, K. Oshima, V. Kayo, T. Umezawa, T. Kiyono, I Sawaki, Mitsubishi Kasei Corporation. US Patent # 5,281,745, 1994.
- [4] R.K. Grasselli, 234th ACS National Meeting, Boston, MA, August 19–23, 2007.
- [5] M. Baca, A. Pigamo, J.L. Dubois, J.M.M. Millet, *Top. Catal.* 23 (2003) 39.
- [6] R.K. Grasselli, D.J. Buttrey, J.D. Burrington, A. Andersson, J. Holmberg, W. Ueda, J. Kubo, C.G. Lugmair, F. Volpe Jr, *Top. Catal.* 38 (2006) 7.
- [7] H. Murayama, D. Vitry, W. Ueda, G. Fuchs, M. Anne, J.L. Dubois, *Appl. Catal. A* 318 (2007) 137.
- [8] P. DeSanto Jr., D.J. Buttrey, R.K. Grasselli, C.G. Lugmair, A.F. Volpe, B.H. Toby, T. Vogt, *Top. Catal.* 23 (2003) 23.
- [9] P. DeSanto Jr., D.J. Buttrey, R.K. Grasselli, C.G. Lugmair, A.F. Volpe Jr, B.H. Toby, T. Vogt, *Z. Kristallogr.* 219 (2004) 152.
- [10] R.K. Grasselli, D.J. Buttrey, P. Desanto Jr., J.D. Burrington, C.G. Lugmair, A.F. Volpe Jr, T. Weingard, *Catal. Today* 91–92 (2004) 251.
- [11] A.C.T. van Duin, S. Dasgupta, F. Lorant, W.A. Goddard III, *J. Phys. Chem. A* 105 (2001) 9396.
- [12] K. Chenoweth, A.C.T. van Duin, W.A. Goddard III, *J. Phys. Chem. A* 112 (2008) 1040.
- [13] A. Strachan, A.C.T. van Duin, S. Dasgupta, D. Chakraborty, W.A. Goddard III, *Phys. Rev. Lett.* 91 (2003) 098301.
- [14] A.C.T. van Duin, A. Strachan, S. Stewman, Q. Zhang, W.A. Goddard III, *J. Phys. Chem. A* 107 (2003) 3803.
- [15] Q. Zhang, T. Cagin, A.C.T. van Duin, W.A. Goddard III, *Phys. Rev. B* 69 (2004) 045423.
- [16] K.D. Nielson, A.C.T. van Duin, J. Oxgaard, W. Deng, W.A. Goddard III, *J. Phys. Chem. A* 109 (2005) 493.
- [17] Goddard W.A. III, K. Chenoweth, S. Pudar, A.C.T. van Duin, M.J. Cheng, *Top. Catal.* 50 (2008) 2.
- [18] K. Chenoweth, A.C.T. van Duin, P. Persson, M.J. Cheng, J. Oxgaard, W.A. Goddard III, *J. Phys. Chem. C* 112 (2008) 14645.
- [19] K. Chenoweth, A.C.T. van Duin, W.A. Goddard III, *Angew. Chem. Int. Ed.* 48 (2009) 7630.
- [20] P. DeSanto Jr., D.J. Buttrey, R.K. Grasselli, C.G. Lugmair, A.F. Volpe Jr., B.H. Toby, T. Vogt, *Top. Catal.* 23 (2003) 23.