

In Silico Design of Highly Selective Mo-V-Te-Nb-O Mixed Metal Oxide Catalysts for Ammoxidation and Oxidative Dehydrogenation of Propane and Ethane

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S Supporting Information

ABSTRACT: We used density functional theory quantum mechanics with periodic boundary conditions to determine the atomistic mechanism underlying catalytic activation of propane by the M1 phase of Mo-V-Nb-Te-O mixed metal oxides. We find that propane is activated by Te=O through our recently established reduction-coupled oxo activation mechanism. More importantly, we find that the C–H activation activity of Te=O is controlled by the distribution of nearby V atoms, leading to a range of activation barriers from 34 to 23 kcal/mol. On the basis of the new insight into this mechanism, we propose a synthesis strategy that we expect to form a much more selective single-phase Mo-V-Nb-Te-O catalyst.

Selective heterogeneous oxidation catalysis produces about a quarter of industrial organic chemicals used in the manufacture of products and consumer goods, making it of vital importance to industrial economics. A particularly important catalytic oxidation process is the ammoxidation of propene to acrylonitrile, producing 10 billion pounds of acrylonitrile per year.¹ Replacing propene with the less expensive and more abundant propane as feedstock in this reaction would have dramatic economic advantages. Thus, the discovery by Mitsubishi Chemical Co. of Mo-V-Nb-Te-O mixed metal oxide catalysts for propane ammoxidation in the 1990s created great excitement.² However, after 20 years of development, the current yield for propane ammoxidation (61.8%) is still not sufficient for industrial application.³

We believe that, to dramatically improve these catalysts, it is essential to develop an atomistic reaction mechanism that explains the details of how the structure and composition combine to activate propane to form propene and then continue to add N to form acrylonitrile. This mechanism would provide guidelines for predicting how to modify the atomistic structure to improve the catalyst. In this work, we report an atomistic reaction mechanism that explains the activation of propane and the dehydrogenation to propene. On the basis of this mechanism, we propose modified synthesis strategies that we expect to increase selectivity.

Our approach uses the density functional theory (DFT: PBE functional,⁴ with GBRV ultrasoft pseudopotentials,⁵ and a plane-wave basis set (40.0 Ry cutoff), as implemented in the QUANTUM-ESPRESSO package⁶) form of quantum mechanics with a periodic surface slab to determine how the reactivity for activating propane depends on the distributions of atoms over the

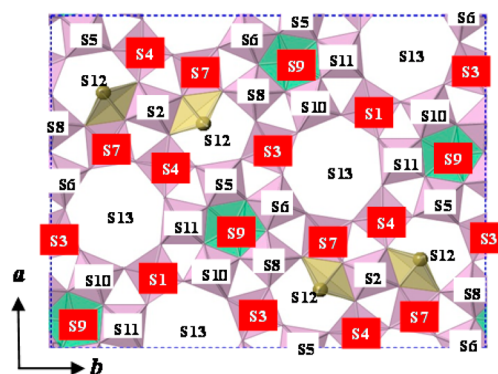


Figure 1. Structure adopted for the one-layer Mo-V-Nb-Te-O [001] model surface: red, oxo points down; white, oxo points up.

various crystal sites. We focus here on the [001] surface of the M1 phase of the Mo-V-Nb-Te-O catalyst, rather than the M2 phase, since various studies indicate that only the M1 phase can activate propane and that it leads to the initial production of propene.^{3,7} A single unit cell of M1 contains 160 atoms (assuming that the S13 site is empty, see Figure 1), making it computationally impractical to use a surface model containing more than one layer. Fortunately, M1 has a distinct layered structure along the *c* axis, with two adjacent layers connected only through coordinating bonds, i.e., M=O---M=O motifs (M = Mo, V, Nb, and Te).⁸ Thus, preparation of the one-layer surface model from the crystal structure is unambiguous (breaking only the longer M---O bond, while keeping the shorter M=O intact). The surface is arranged in such a way that the oxygens of the M=O bonds in sites S2, S5, S6, S8, S10, and S11 point in the same direction as that of Te=O at S12, while those of M=O in sites S1, S3, S4, S7, and S9 point in the opposite direction.

A major obstacle in understanding the reaction mechanism of the M1 phase is that 8 of the 13 distinct sites exhibit partial occupation by both molybdenum and vanadium.^{8,9} Since the chemistry related to Mo vs V at a site is likely to be dramatically different, we focus on how replacing Mo with V modifies the activation of propane.

To provide the reference state, we first predict the reactivity of oxygen on the surface with no vanadium (0 V, Figure 2a). Since the transition state for alkane C–H cleavage by a metal oxo site involves a structure in which the C··H··O is linear,¹⁰ leading to

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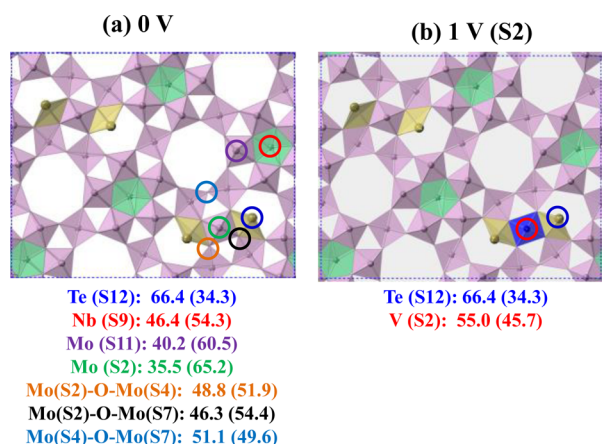


Figure 2. $D_{\text{O-H}}$ and $E_{\text{a,min}}$ (in parentheses) of $\text{M}=\text{O}$ sites on the M1 phase [001] surface for the case with zero (a) and one (b) vanadium per unit cell. The minimum reaction barrier for activating propane is calculated to be $E_{\text{a,min}} = 100.7 - D_{\text{O-H}}$, where 100.7 is the binding energy (in kcal/mol) of the methylene C-H bond of propane. The color code is Mo (pink), Nb (green), Te (brown), and V (blue), and the energy unit is kcal/mol.

formation of an O-H bond plus a carbon radical, we can estimate the minimum barrier as $E_{\text{a,min}} = D_{\text{C-H}} - D_{\text{O-H}}$, where for propane $D_{\text{C-H}} = 100.7$ kcal/mol.^{10,11} Thus, to have $E_{\text{a,min}} \approx 25.0$ kcal/mol (a plausible value for M1), the $D_{\text{O-H}}$ for bonding an H atom to the surface must be at least 75.0 kcal/mol. As a result, we only need to examine the $D_{\text{O-H}}$ bond energies for various sites to estimate the reactivity of the surface. For the VPO system, the estimated $E_{\text{a,min}}$ was within 3 kcal/mol of our full transition-state calculation.^{10b-d}

For the 0 V case (Figure 2a), we calculate $D_{\text{O-H}}$ bond energies to be 66.4 (Te=O, S12), 46.4 (Nb=O, S9), 40.2 (Mo=O, S11), and 35.5 kcal/mol (Mo=O, S2). We also investigated the possible role of bridging oxygen sites. We find $D_{\text{O-H}} = 48.8, 46.3,$ and 51.1 kcal/mol for Mo(S2)-O-Mo(S4), Mo(S2)-O-Mo(S7), and Mo(S4)-O-Mo(S7), respectively. Since the weakest C-H bond strength of propane is 100.7 kcal/mol, the most active site is Te=O, with $E_{\text{a,min}} = 34.3$ kcal/mol, far more active than Nb=O or Mo=O. This is consistent with the speculations that Nb=O and its surrounding Mo=O's are inactive to propane.¹² Although this 0 V system would not be active for propane, it should be active for propene, since the weaker $D_{\text{C-H}} = 86.3$ kcal/mol for propene leads to $E_{\text{a,min}} = 19.9$ kcal/mol. This result is consistent with our studies on the M2 phase of Mo-V-Nb-Te-O catalyst,¹³ where we found that only the Te=O site could activate propene; it is also consistent with other recent DFT studies on the M1 phase based on cluster models.¹⁴ This is in sharp contrast to all previously proposed mechanisms.³

Based on Löwdin population analysis, we find that when Te=O binds with hydrogen to form Te-OH, the spin density (SD) of Te remains zero, while the SD of Mo at the adjacent S8 site increases from 0.08 to 0.53 e^- , and the SD of Mo at the adjacent S2 site decreases from 0.85 to -0.05 e^- . This shows clearly that, during the hydrogen transfer, the proton binds to Te=O while the electron is hosted by nearby Mo atoms. Thus, the M1 phase activates propane's C-H bonds through our recently discovered reduction-coupled oxo activation (ROA) mechanism.^{10b-d}

For the 1 V case, we replaced the Mo at S2 by V (Figure 2b), since experiments show that the probability of V at S2 is $\sigma = 58.0\%$, the highest among all sites.⁸ This leads to OH bond energies of $D_{\text{O-H}} = 66.4$ (Te=O, S12) and 55.0 kcal/mol (V=O, S2). Thus, $E_{\text{a,min}} = 34.3$ kcal/mol for Te=O, while $E_{\text{a,min}} = 45.7$ kcal/mol for

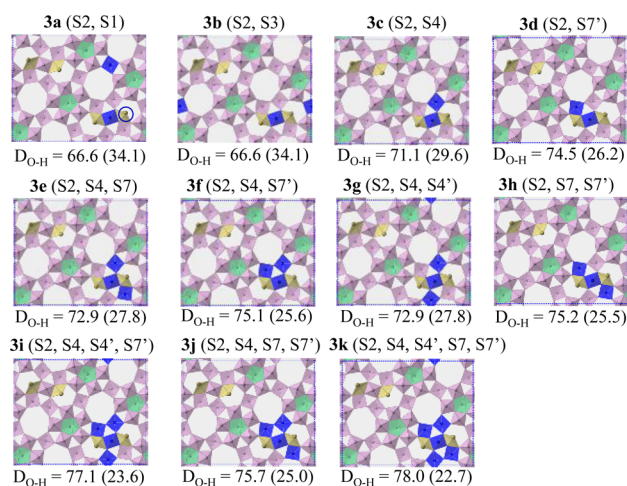


Figure 3. Calculated $D_{\text{O-H}}$ ($E_{\text{a,min}}$) for Te=O (S12) on the Mo-V-Nb-Te-O [001] surface with 2-5 V per unit cell. The best case is 5 V, with $E_{\text{a,min}} = 22.7$ kcal/mol.

V=O. Since it had been nearly universally accepted, from the literature, that the propane activating site was the partially occupied S4 and/or S7 sites,¹² we then examined another configuration for the 1 V case (not shown), in which Mo in S7 is replaced by V. $D_{\text{O-H}}$ of O=V(S7) is calculated to be only 48.5 kcal/mol, corresponding to $E_{\text{a,min}} = 52.2$ kcal/mol. Those results are in stark contrast to the general expectation that V=O is responsible for the high propane activity of the M1 phase.^{3,12} Again we find that forming the TeO-H bond leads to no change in the SD of Te, while the SD of Mo at the adjacent S5 site increases from 0.01 to 0.55 e^- —the signature of the ROA mechanism. We find that the SD of V at S2 increases slightly from 0.92 to 1.01 e^- , indicating that this vanadium remains in the +4 oxidation state.

Next, we focus on how this most reactive Te=O is affected by replacing additional nearby Mo atoms with vanadium (2 V-5 V, shown as 3a-3h in Figure 3). We replaced Mo with V only at the sites with the highest experimental V occupations: S2 (58%), S3 (43%), S1 (30%), S7 (24%), and S4 (20%).^{8,15} Since we bind the H to the Te=O in the S12 site in Figure 1, we distinguish between V's in the two sites adjacent to this Te, S4 and S7, and the two sites farther away, S4' and S7'.

For the 2 V cases (Figure 3, cases 3a to 3d), we investigated configurations in which one vanadium occupies S2 while the other occupies either S1 (3a), S3 (3b), S4 (3c), or S7' (3d). We calculate $E_{\text{a,min}} = 34.1$ kcal/mol for both 3a and 3b, similar to 34.3 kcal/mol for the 0 V and 1 V cases. This is reasonable, since these configurations have the second V too far from Te=O for ROA. However, the other two 2 V cases lead to $E_{\text{a,min}} = 29.6$ (S4, 3c) and 26.2 kcal/mol (S7', 3d), as expected for ROA. Thus, we will consider additional V's only in the S4, S4', S7, and S7' sites next to the target Te=O.

For the 3 V case, we find $E_{\text{a,min}} = 25.6$ (S2, S4, S7', 3f) and 25.5 kcal/mol (S2, S7, S7', 3h). We showed above that a single V at S2 does not improve the reactivity of the T=O. However, we find that, for the 3 V cases, changing the vanadium in S2 back to molybdenum leads to $E_{\text{a,min}} = 38.6$ (S4, S7') and 32.9 kcal/mol (S7, S7'). This indicates that, to achieve a reactive Te=O moiety, it is essential to ensure that S2 is occupied by vanadium.

For the 4 V and 5 V cases, we started from 3f and 3h, and then placed V at S4 or S7, leading to $E_{\text{a,min}} = 23.6$ (S2, S4, S4', S7, 3i), 25.0 (S2, S4, S7, S7', 3j), and 22.7 kcal/mol (S2, S4, S4', S7, S7',

3k). Thus, the 5 V case leads to a very favorable $E_{a,\min} = 22.7$ kcal/mol, making it a most active site. Again, replacing vanadium at S2 with molybdenum leads to $E_{a,\min} = 29.4$ kcal/mol, an increase by 6.7 kcal/mol, indicating that occupying S2 with V is crucial to maximize the rate of C–H activation by Te=O. Generally, surrounding Te=O by more V neighbors coupled by an O with the Te increases its reactivity. This discovery is consistent with experimental results showing that the rate of propane consumption is correlated with the surface concentration of vanadium in the M1 phase.¹⁶

Since the S2, S4, and S7 sites are only partially occupied by vanadium, at $\sigma = 58, 20,$ and 24% , respectively, we calculated the total probability of the configurations 3d, 3f, 3h, 3i, 3j, and 3k to be 13.54, 1.69, 1.69, 0.84, 1.06, and 0.13%, respectively. Convoluting these σ values with the $E_{a,\min}$, we expect that, in the M1 phase, configuration 3d plays a more important role than the others in activating propane, due to its low $E_{a,\min} = 26.2$ kcal/mol combined with the high $\sigma = 13.54\%$. While 3k possesses the smallest $E_{a,\min} = 22.7$ kcal/mol, we expect that its small $\sigma = 0.13\%$ makes it play a less important role in the current M1 phase.

We also evaluated the stability of all configurations by calculating their heat of formation (HOF, see the Supporting Information for details). We find that HOF = 456.0 kcal/mol for the 0 V case, decreasing to 426.7 kcal/mol for the 1 V case, 406.9–409.6 kcal/mol for the 2 V cases, 389.2–391.3 kcal/mol for the 3 V cases, 375.0–374.3 kcal/mol for the 4 V cases, and 360.8 kcal/mol for the 5 V case. This suggests that the system becomes more stable as more Mo's are replaced by V.

Next, we considered the 5 V configuration (3k), the most reactive Te=O case, to study oxidative dehydrogenation (ODH) of propane to propene. This process has been confirmed experimentally to be the first step of propane ammoxidation to acrylonitrile.¹⁷ To examine the overall energetics, we note that breaking the terminal C–H bond of isopropyl to form propene requires 41.6 kcal/mol, so the total energy for removing the two C–H bonds from propane to form propene is 142.3 kcal/mol. Thus, for ODH of propane to be exothermic, the surface must form two O–H bonds whose bond energies sum to 142.3 kcal/mol or higher. Thus, both H's must go to Te=O sites. Indeed, the M1 structure has exactly the surface structure with Te=O on both sides of the S2 site. (Since the occupation of S12 with Te is 71%, the probability of both being Te is 50%.) The reaction mechanism is shown in Figure 4.

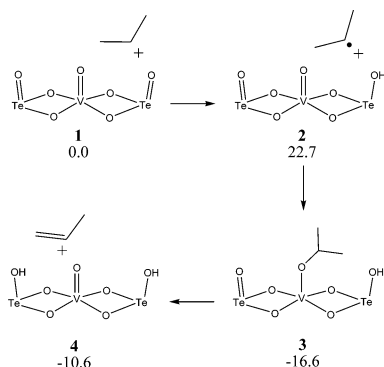


Figure 4. Potential energy surface for oxidative dehydrogenation of propane to propene using the 5 V configuration 3k (electronic energy only, in kcal/mol). An atomic description of the active center can be found in Figure S1.

First, it is uphill by 22.7 kcal/mol to use Te=O of 1 to break the secondary C–H bond of propane, while forming intermediate 2 plus isopropyl. Next, the isopropyl radical is trapped by V=O(S2), leading to intermediate 3, which is 16.6 kcal/mol more stable than the reactant. Finally, the second Te=O cleaves the terminal C–H bond of the isopropyl to form species 4 plus propene. Although the overall reaction is downhill by 10.6 kcal/mol, the reaction energy for the final step is uphill by 6.0 kcal/mol. This final step leads to propene release, providing a very favorable increase in entropy and hence a favorable Gibbs free energy surface at reaction temperatures (~ 700 K).

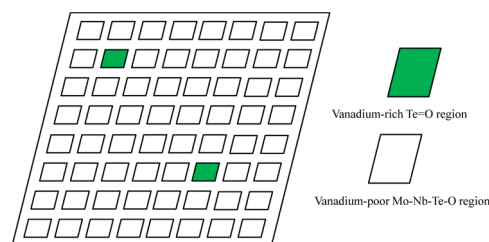


Figure 5. Landscape of the proposed single-phase Mo-V-Nb-Te-O mixed metal oxide catalyst synthesized by combining TeVO_4 and MoNbTeO_y nanoparticles.

Experimentally, the best Mo-V-Nb-Te-O mixed metal oxide catalysts consists of 60% M1 phase and 40% M2 phase.^{3,8,9a,18} It is speculated that, to achieve the highest selectivity, propene produced by ODH of propane on M1 must migrate to M2 for subsequent functionalization to acrylonitrile.¹² This migration process is thought to be essential for achieving a high selectivity, because with its ability to activate strong propane C–H bonds (100.7 kcal/mol), M1 might over-oxidize propene, with its much weaker allylic C–H bond (86.3 kcal/mol).¹² Indeed, experiments have shown that the selectivity increases for catalysts with smaller grains, which should reduce the time for propene to transfer from M1 to M2.¹² However, it is difficult to control the spacings and oxidation levels of such two-phase regions, making it difficult to ensure the highest selectivity.

Since we now understand how the reactivity of Te=O depends on the surrounding vanadium distribution, we suggest an ideal single-phase MMO catalyst. We propose maximizing the probability of having $\text{Te}_2\text{V}_5\text{O}_x$ sites as in 3k but arranging them to be maximally distant from each other, while minimizing the probability of having V on all other Te. This would lead to $E_{a,\min} = 22.7$ kcal/mol for the propane activation to form propene, but then the propene would see only MoNbTeO_y sites like Figure 2a, with $E_{a,\min} = 86.3 - 66.4 = 19.9$ kcal/mol for activating propene to form allyl. This allyl would, in turn, react with the Mo=O or Mo=NH bonds to form acrolein or acrylonitrile, as shown previously.¹⁹ Here we want the $\text{Te}_2\text{V}_5\text{O}_x$ regions to be well separated from the MoNbTeO_y regions, as illustrated in Figure 5.

As a synthetic strategy for achieving such a single phase, we suggest that nanoparticles with TeVO_4 stoichiometry be synthesized separately²⁰ and then incorporated into a matrix with MoNbTeO_y composition (no V) in appropriate ratios and blended to obtain a uniform mixture. In this case, we can expect that the TeVO_x regions activating propane to propene are well separated by intervening MoNbTeO_y regions that are just active enough to form allyl from propene ($E_{a,\min} \approx 20$ kcal/mol). Here, one should vary the ratio of the Te-V-rich nanoclusters and the Mo-Nb-Te-rich materials for optimum selectivity. We plan future

computational experiments using ReaxFF reactive molecular dynamics²¹ to explore this proposal.

In summary, we used DFT to determine the reaction mechanism for activation of propane by the M1 phase of the Mo-V-Nb-Te-O mixed metal oxide catalysts. We found that the C–H bond of propane is activated by Te=O sites via the ROA mechanism, in which the Te=O bond accepts the proton while the electron goes to adjacent reducible V or Mo sites. With no nearby V, this leads to $E_{a,\min} = 34.3$ kcal/mol for propene but 19.9 kcal/mol for propene. Most important is that replacing Mo with V at S2, S4, and S7 sites adjacent to the Te dramatically increases the C–H activation ability of Te=O, leading to $E_{a,\min}$ as low as 22.7 kcal/mol for the case with five vanadiums in the S2, S4, and S7 sites adjacent to the Te=O. Our discovery that the activation of the alkane C–H bond is due to Te=O sites coupled to V=O centers is consistent with our results on the conversion of *n*-butane to maleic anhydride, catalyzed by VPO,^{10b} and with our study of the activation of propene by Te=O centers in the M2 phase of the MoVNbTeO_x.¹³ However, it is in sharp contrast to previous suggestions for vanadium²² and molybdenum oxides,²³ that oxygen bound directly with V or Mo is responsible for the initial alkane C–H activation.

On the basis of these discoveries, we propose a synthesis strategy of mixing nanoparticles of TeVO₄ with clusters of MoNbTeO_y to form a single-phase catalyst, in which the vanadium-rich Te=O active sites that can activate propane to form propene are well separated by MoNbTeO_y regions that can only activate the propene. We expect that such a well-controlled single-phase catalyst would lead to the highest possible selectivity, making commercialization feasible.

Although these studies were motivated by an interest in developing very selective propane ammoxidation catalysts, the ODH mechanism we propose should be very effective for converting the massive amounts of ethane and propane produced from petroleum fracking to the much more valuable ethene²⁴ and propene. We would also eliminate the Te in the MoNbO_x phase to minimize subsequent activation of propene. This catalyst should be particularly effective for ethane ODH, with $E_{a,\min} = 103.0 - 78.0 = 25.0$ kcal/mol. Here, the 3k site would not be able to activate the ethene product ($D_{C-H} = 115.6$ kcal/mol), so that one could do multiple passes to increase conversion.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07073.

Computational details; coordinates and cell parameters for the surface models (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Grasselli, R. K. *Top. Catal.* **2002**, *21*, 79.
- (2) Hinago, H.; Komada, Y. (Mitsubishi Chem Corp.). Ammoxidation catalyst for use in producing acrylonitrile or methacrylonitrile from propane or isobutane by ammoxidation. U.S. Patent 6,063,728, May 16, 2000.
- (3) Grasselli, R. K.; Burrington, J. D.; Buttrey, D. J.; DeSanto, P.; Lugmair, C. G.; Volpe, A. F.; Weingand, T. *Top. Catal.* **2003**, *23*, 5.
- (4) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (5) Garrity, K. F.; Bennett, J. W.; Rabe, K. M.; Vanderbilt, D. *Comput. Mater. Sci.* **2014**, *81*, 446.
- (6) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; et al. *J. Phys.: Condens. Matter* **2009**, *21*, 395502.
- (7) Holmberg, J.; Grasselli, R. K.; Andersson, A. *Appl. Catal., A* **2004**, *270*, 121.
- (8) Li, X.; Buttrey, D. J.; Blom, D. A.; Vogt, T. *Top. Catal.* **2011**, *54*, 614.
- (9) (a) DeSanto, P.; Buttrey, D. J.; Grasselli, R. K.; Lugmair, C. G.; Volpe, A. F.; Toby, B. H.; Vogt, T. *Z. Kristallogr. - Cryst. Mater.* **2004**, *219*, 152. (b) Pyrz, W. D.; Blom, D. A.; Shiju, N. R.; Gulians, V. V.; Vogt, T.; Buttrey, D. J. *J. Phys. Chem. C* **2008**, *112*, 10043. (c) Pyrz, W. D.; Blom, D. A.; Vogt, T.; Buttrey, D. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 2788.
- (10) (a) Cheng, M. J.; Chenoweth, K.; Oxgaard, J.; van Duin, A.; Goddard, W. A. *J. Phys. Chem. C* **2007**, *111*, 5115. (b) Cheng, M. J.; Goddard, W. A. *J. Am. Chem. Soc.* **2013**, *135*, 4600. (c) Cheng, M. J.; Fu, R.; Goddard, W. A. *Chem. Commun.* **2014**, *50*, 1748. (d) Cheng, M. J.; Goddard, W. A.; Fu, R. *Top. Catal.* **2014**, *57*, 1171.
- (11) (a) Tyo, E. C.; Yin, C. R.; Di Vece, M.; Qian, Q.; Kwon, G.; Lee, S.; Lee, B.; DeBartolo, J. E.; Seifert, S.; Winans, R. E.; Si, R.; Ricks, B.; Goergen, S.; Rutter, M.; Zugic, B.; Flytzani-Stephanopoulos, M.; Wang, Z. W.; Palmer, R. E.; Neurock, M.; Vajda, S. *ACS Catal.* **2012**, *2*, 2409. (b) Yu, J.; Xu, Y.; Gulians, V. V. *Catal. Today* **2014**, *238*, 28.
- (12) Grasselli, R. K.; Buttrey, D. J.; DeSanto, P.; Burrington, J. D.; Lugmair, C. G.; Volpe, A. F.; Weingand, T. *Catal. Today* **2004**, *91–92*, 251.
- (13) Goddard, W. A.; Liu, L. C.; Mueller, J. E.; Pudar, S.; Nielsen, R. J. *Top. Catal.* **2011**, *54*, 659.
- (14) Govindasamy, A.; Muthukumar, K.; Yu, J. J.; Xu, Y.; Gulians, V. V. *J. Phys. Chem. C* **2010**, *114*, 4544.
- (15) It should be noted that those V partial occupation numbers were reported for the bulk structure. However, some experimental studies have shown that vanadium is enriched on the surface, e.g.: Wachs, I. E.; Jehng, J.-M.; Ueda, W. *J. Phys. Chem. B* **2005**, *109*, 2275. Since the V partial occupation numbers are not available for the [001] surface, we used the numbers from the bulk structure.
- (16) Gulians, V. V.; Bhandari, R.; Brongersma, H. H.; Knoester, A.; Gaffney, A. M.; Han, S. *J. Phys. Chem. B* **2005**, *109*, 10234.
- (17) Oliver, J. M.; Nieto, J. M. L.; Botella, P. *Catal. Today* **2004**, *96*, 241.
- (18) Zhu, Y. H.; Wang, Q. X.; Zhao, L.; Teng, B. Y.; Lu, W. M.; Han, Y. *Chem. Mater.* **2012**, *24*, 3269.
- (19) (a) Goddard, W. A.; Chenoweth, K.; Pudar, S.; van Duin, A. C. T.; Cheng, M. J. *Top. Catal.* **2008**, *50*, 2. (b) Pudar, S.; Oxgaard, J.; Goddard, W. A. *J. Phys. Chem. C* **2010**, *114*, 15678. (c) Jang, Y. H.; Goddard, W. A. *J. Phys. Chem. B* **2002**, *106*, 5997. (d) Jang, Y. H.; Goddard, W. A. *Top. Catal.* **2001**, *15*, 273.
- (20) Meunier, G.; Darriet, J.; Galy, J. *J. Solid State Chem.* **1973**, *6*, 67.
- (21) van Duin, A. C. T.; Dasgupta, S.; Lorant, F.; Goddard, W. A. *J. Phys. Chem. A* **2001**, *105*, 9396.
- (22) Gartner, C. A.; van Veen, A. C.; Lercher, J. A. *ChemCatChem* **2013**, *5*, 3196.
- (23) Fu, G.; Xu, X.; Lu, X.; Wan, H. L. *J. Phys. Chem. B* **2005**, *109*, 6416.
- (24) Nieto, J. M. L.; Botella, P.; Vazquez, M. I.; Dejoz, A. *Chem. Commun.* **2002**, 1906.