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Theoretical study of vanadium-catalyzed butane oxidation

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Abstract

The theoretical study on the mechanism of butane oxidation using model complexes of vanadyl pyrophosphate has been investigated using density functional theory (DFT) method. The monomeric complex $VO(OH)_2(OH_2)_2$ was selected as a fundamental structure. The complexes bearing one phosphoric residue were selected for clarifying the effect of pyrophosphoric moieties on the catalyst. The complexes having two vanadium units were selected as two-layer models of the catalyst for clarifying the influence of the presence or absence of lattice oxygen and the effect of the oxidation states of the inner vanadium atom.

The introduction of a phosphoric moiety on one of the hydroxy groups strongly stabilizes the lower oxidation states of the complexes. This result suggests that the surface vanadium species having the higher 5+ oxidation state should possess stronger oxidation ability. The presence of the vanadium (4+) atom at the lower layer relatively destabilizes the V^{3+} state of the upper vanadium complexes, and stabilizes the peroxo-vanadium (4+) complexes, which suggests that the lattice oxo-oxygen in vanadyl pyrophosphate may play an important role in the activation of molecular oxygen. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Density functional theory (DFT) calculation; Butane oxidation; Model complexes of VPO catalyst

1. Introduction

In the reaction course of the catalytic aerobic alkane oxidations, many fundamental processes such as C–H activation, hydrogen abstraction, hydrogen transfer, activation of oxygen, insertion, elimination, migration and so on, may take place on the catalyst. The theoretical study on the mechanism of alkane oxidation may be helpful for the development of more active and selective catalysts in this field. Here, we focused on the butane oxidation over vanadyl pyrophosphate, and studied the reaction profiles from butane to maleic anhydride via one-electron oxidations as well as the catalytic cycles of the vanadium model complexes.

2. Methods

2.1. Computational details

Schrödinger equations on the model compounds were solved using the hybrid density functional theory (DFT) method [1]. Becke's [2,3] three parameter functional incorporating the LYP correlation term (B3LYP) with a standard double-zeta quality basis set (LANL2DZ) [4] was used in the DFT calculation. The stability of SCF solution was always tested in single-point energy calculation. All computations were performed by the Gaussian 98 package [1].

All structures of organic species, including hydrogen and hydroxy radicals and water, were fully optimized by the theoretical calculations.

The partial structures cut-off from the X-ray crystallographic data of vanadium pyrophosphate

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$(VO)_2P_2O_7$ [5–7] were used in the present calculations for all the geometries of vanadium complexes except for the geometries of the considered reaction site.

3. Results and discussions

3.1. Reaction profiles from butane to maleic anhydride

The reaction pathway via one-electron oxidation from butane (**1**) to maleic anhydride (**18**) we assumed is shown in Scheme 1, where two cyclization pathways via crotonaldehyde (**7**) and 2-butene-1,4-diol (**9**) may be possible. All structures of the compounds **1**–**18**, hydrogen and hydroxy radicals, and water were optimized by DFT method [1] using B3LYP [2,3]/LANL2DZ [4] as a keyword and a basis set, respectively. The calculated energy differences of each step are shown in Scheme 1.

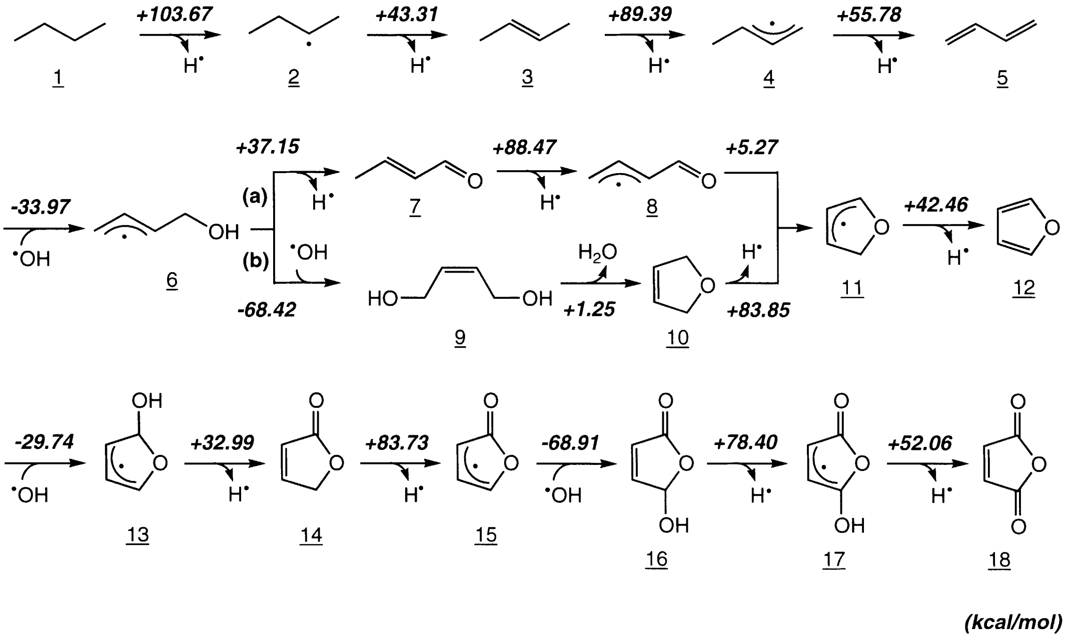
There are four characteristic features as follows:

1. The hydrogen abstractions from neutral molecules to radical ones are extremely endothermic reactions (78.40–103.67 kcal/mol).
2. The hydrogen abstractions from radical molecules to neutral ones are moderately endothermic reactions (32.99–55.78 kcal/mol).
3. The introductions of hydroxy radicals into organic molecules are exothermic reactions (−29.74 to −68.91 kcal/mol).
4. The elimination of water (**9** to **10**) and the isomerization to cyclic compound (**8** to **11**) are slightly endothermic reactions (1.25 and 5.27 kcal/mol).

Overall, 11 hydrogen abstractions and three introductions of hydroxy radical (path a), or 10 hydrogen abstractions and four introductions of hydroxy radical (path b) should take place from butane to maleic anhydride.

3.2. Structures of selected vanadium model complexes

The partial structures cut-off from the X-ray crystallographic data of vanadyl pyrophosphate [5–7] was used for the geometries of vanadium complexes in the present calculations. The monomeric complex $VO(OH)_2(OH_2)_2$ (**AA**) was selected as a fundamental structure. The complexes bearing one



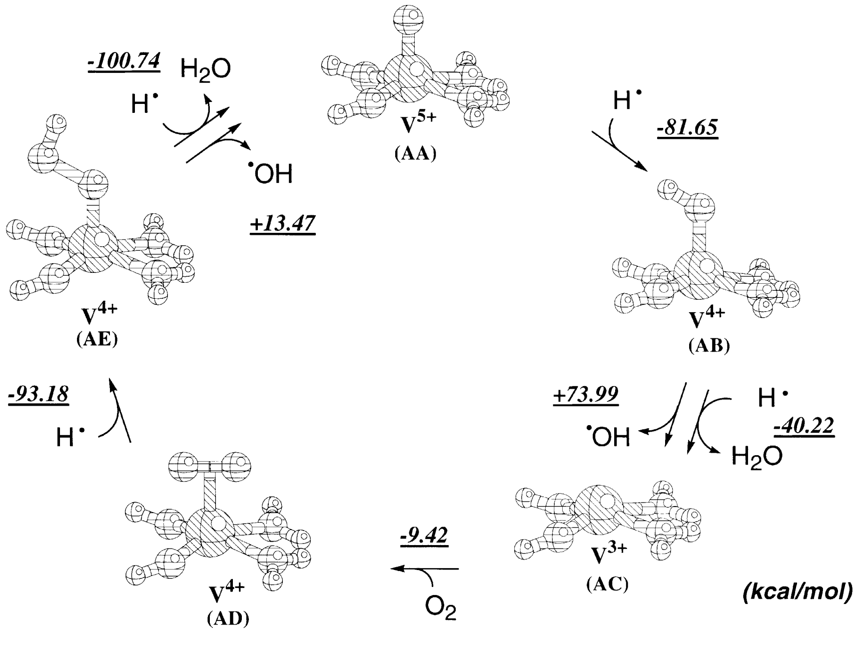
Scheme 1. One-electron oxidations of butane to maleic anhydride.

phosphoric residue (**BA** and **CA**) were selected for clarifying the effect of pyrophosphoric moieties on the catalyst. The complexes having two vanadium units were selected as two-layer models of the catalyst for clarifying the influence of the presence or absence of lattice oxygen and the effect of the oxidation states of the inner vanadium atom.

3.3. Catalytic cycle of $V^{(5+)}O(OH)_2(OH_2)_2$

When the hydrogen radical was attracted to the oxo-oxygen atom from the opposite side to the coordinated waters of the complex **AA**, the total energy was minimized at the O–H bond length of 0.98 Å and the V–O bond length of 1.80 Å. The energy difference of this stage was calculated to −81.65 kcal/mol. The conformer where the hydrogen radical was attracted from the same side to the coordinated waters was found to be less stable by 5.53 kcal/mol. The energy in the formation of the complex **AC** by the attack of the hydrogen radical to the complex **AB** with the elimination of water was calculated to be −40.22 kcal/mol, which also shows that the removal of hydroxy radical from **AB** might be endothermic reaction by +73.99 kcal/mol. The approach of the molecular oxygen to **AC** gave the stable structure **AD**, in which the bond lengths of O–O and O–V were obtained to be 1.40 and 2.00 Å, respectively. The approach of hydrogen radical to **AD** gave the stable complex **AE**, in which the bond lengths of O–O and O–V were calculated to be 1.52 and 1.80 Å, respectively. Again, the conformer having hydroperoxy group same side to the waters was calculated to be less stable by 0.85 kcal/mol. The regeneration of **AA** from **AE** was calculated to be +13.47 kcal/mol with the elimination of hydroxy radical or to be −100.74 kcal/mol by the attack of hydrogen radical with the formation of water (Scheme 2).

As mentioned above, there are three or four introductions of hydroxy radical into organic molecules in the butane oxidation. These introductions can easily proceed in the step of **AE** to **AA** as totally exothermic reactions. The step of **AB** to **AC** may participate in the hydrogen abstractions from radical molecules to neutral ones. The activation of molecular oxygen can be done in the step of **AC** to **AD** without difficulty.



Scheme 2. Catalytic cycle of $V^{(5+)}O(OH)_2(OH_2)_2$.

3.4. Catalytic cycle of $V^{(5+)}O(OH)_2(OHP(OH)_3)(OH_2)$

The results of the single-point energy calculations of the structures **BA**–**BE**, which possess a phosphoric moiety on one of the coordinated water molecules of the complexes **AA**–**AE**, are shown in Scheme 3.

The introduction of a phosphoric moiety on one of the coordinated waters stabilizes the lower oxidation states to some extent. This lower effect may be attributed to the longer V–O bond length (2.154 Å), which is selected from the crystallographic data between vanadium atom and the bridged oxygen atom.

3.5. Catalytic cycle of $V^{(5+)}O(OH)(OP(OH)_2(OH_2))(OH_2)_2$

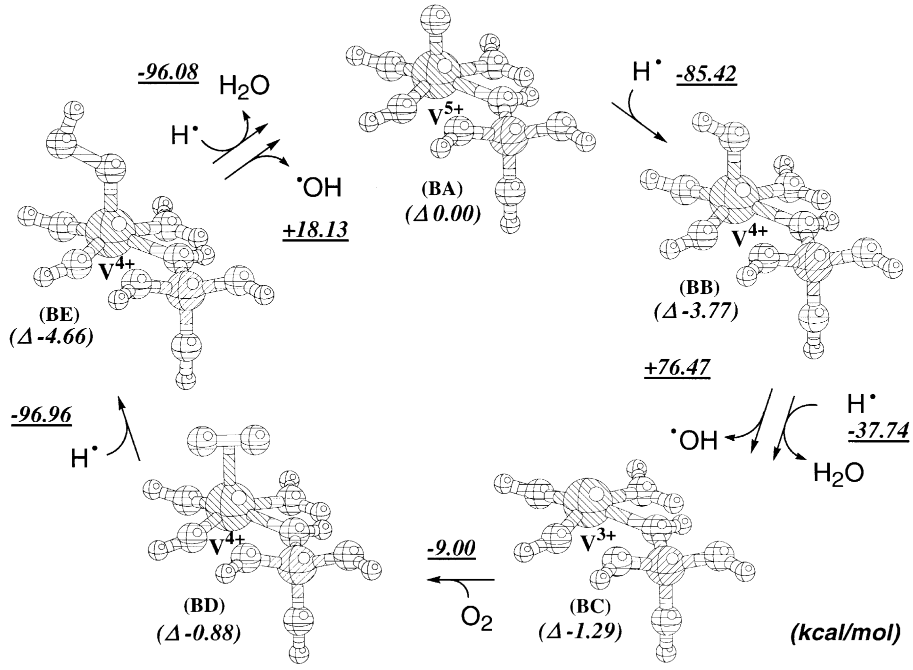
The results of the single-point energy calculations of the structures **CA**–**CE**, which possess a phosphoric moiety on one of the hydroxy groups of the complexes **AA**–**AE**, are shown in Scheme 4. In the structures **CB** and **CE**, the conformers having hydroxy and hydroperoxy groups opposite side to a phosphoric moiety were found to be more stable because of the steric effects.

These results show that the introduction of a phosphoric moiety on one of the hydroxy groups strongly stabilizes the lower oxidation states of the complexes. The shorter bond length (1.914 Å) between vanadium and oxygen atoms makes clearer the substitution effects than the previous one. This effect relatively destabilizes the higher 5+ oxidation state of vanadium atom, and the step **CE** to **CA**, which may act as an important key step of the introduction of OH moiety into organic molecules, becomes much difficult (more than 16 kcal/mol).

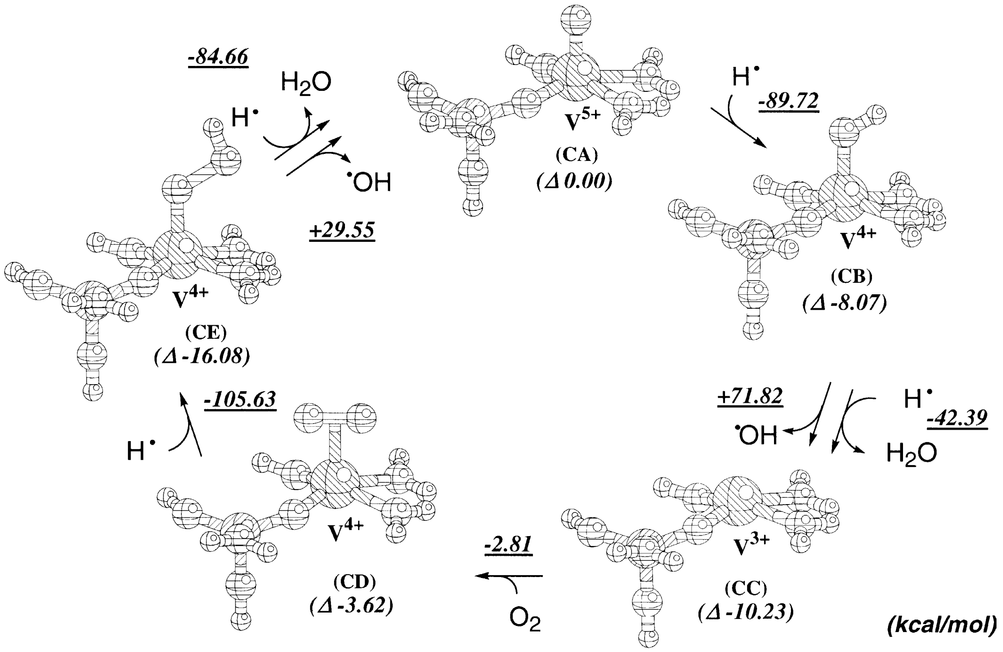
In vanadyl pyrophosphate, there are four phosphoric moieties around one vanadium atom, and these stabilization effects in the lower oxidation state can be expected to be much stronger. In other words, the surface vanadium species having the higher 5+ oxidation state in vanadyl pyrophosphate should possess stronger oxidation ability.

3.6. Catalytic cycle of $V^{(5+)}O(OH)_2(OH_2)_2$–$V^{(4+)}O(OH)_2(OH_2)_2$

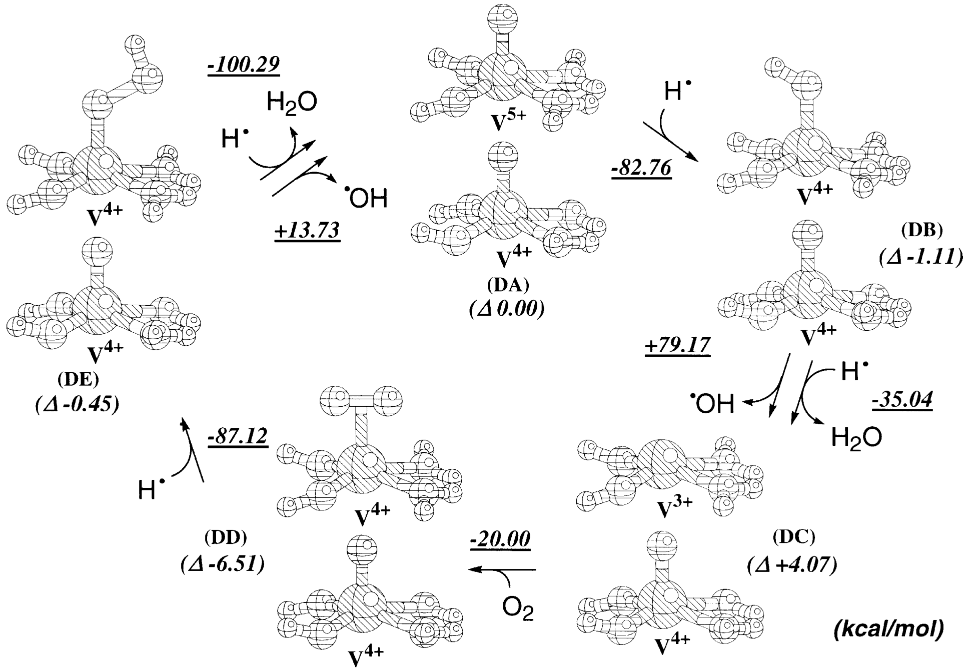
The complexes having two vanadium units, in which the lower vanadium atom has the 4+ oxidation state,



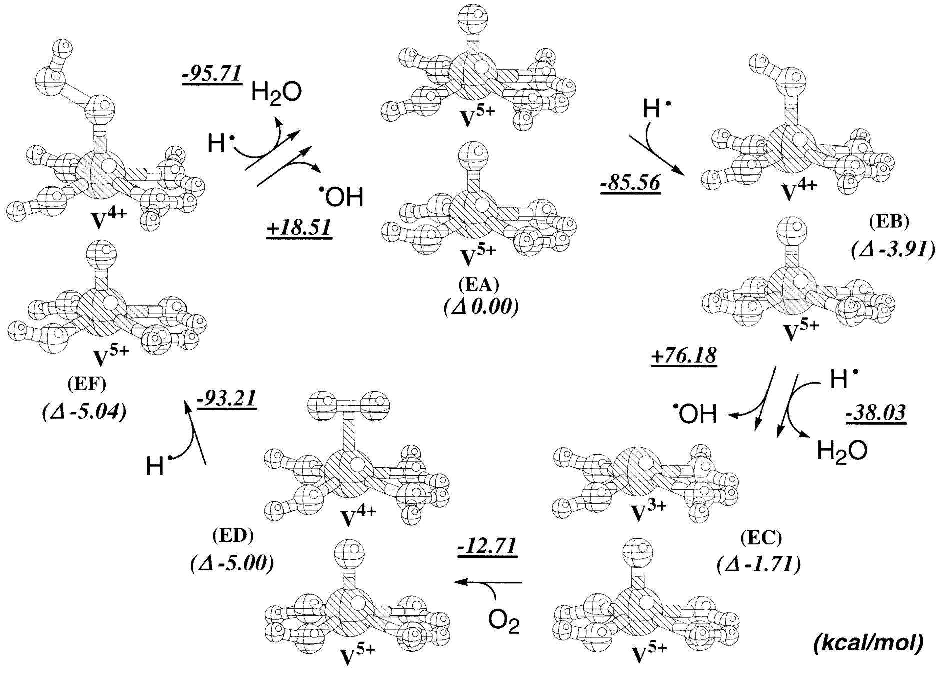
Scheme 3. Catalytic cycle of $V^{(5+)}O(OH)_2(OHP(OH)_3)(OH_2)$.



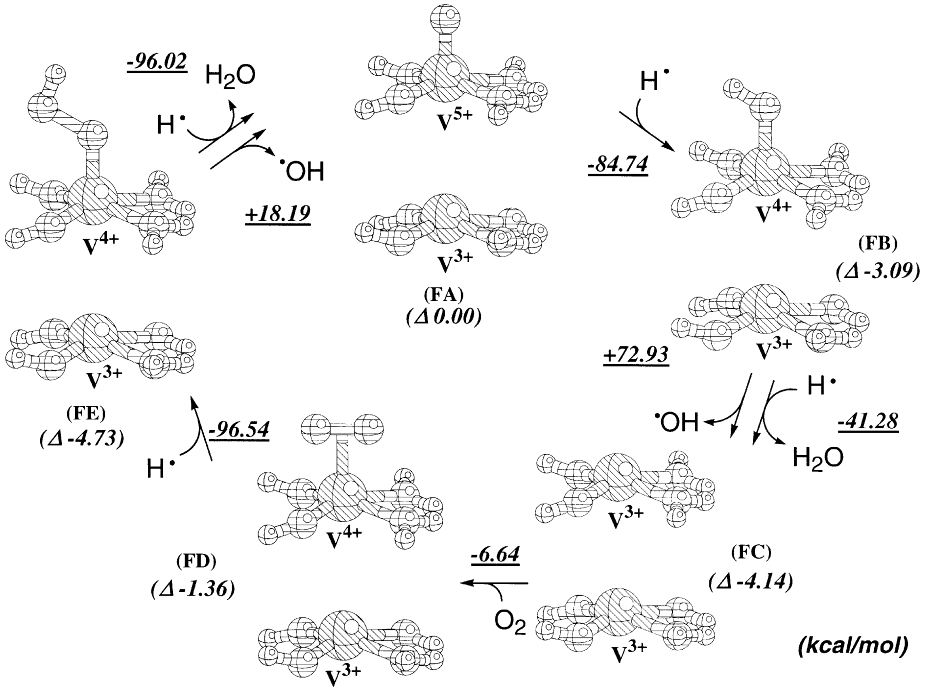
Scheme 4. Catalytic cycle of $V^{(5+)}O(OH)(OP(OH)_2(OH_2))(OH_2)_2$.



Scheme 5. Catalytic cycle of $V^{(5+)}O(OH)_2(OH_2)_2$–$V^{(4+)}O(OH)_2(OH_2)_2$.



Scheme 6. Catalytic cycle of $V^{(5+)}O(OH)_2(OH_2)_2$–$V^{(5+)}O(OH)_2(OH_2)_2$.



Scheme 7. Catalytic cycle of $V^{(5+)}O(OH)_2(OH_2)_2$–$V^{(3+)}(OH)_2(OH_2)_2$.

were selected as two-layer models of the catalyst. The results of the single-point calculations are shown in Scheme 5.

The presence of the vanadium (4+) atom at the lower layer relatively destabilizes the V^{3+} state of the upper vanadium complex, and stabilizes the peroxo-vanadium (4+) complex. Therefore, the activation step of oxygen becomes 10 kcal/mol easier than unsubstituted ones. These results suggest that the lattice oxo-oxygen in vanadyl pyrophosphate may play an important role in the activation of molecular oxygen.

3.7. Catalytic cycle of $V^{(5+)}O(OH)_2(OH_2)_2$–$V^{(5+)}O(OH)_2(OH_2)_2$

The results of the single-point calculations of the complexes having two vanadium units, in which the lower vanadium atom has the 5+ oxidation state, are shown in Scheme 6.

The vanadium atom in the lower layer having the 5+ oxidation state tends to stabilize the 4+ oxidation state of the upper vanadium; however, the energy differences are rather small.

3.8. Catalytic cycle of $V^{(5+)}O(OH)_2(OH_2)_2$–$V^{(3+)}(OH)_2(OH_2)_2$

The complexes having two vanadium units, in which the lower vanadium atom lacks the lattice oxo-oxygen and has the 3+ oxidation state, were selected as two-layer models of the lattice defective catalyst. The results of the single-point calculations are shown in Scheme 7.

The vanadium atom in the lower layer without the lattice oxo-oxygen also tends to stabilize the lower oxidation state of the upper vanadium to some extent. However, there are little energy differences because of the lack of bond between two vanadium atoms.

4. Conclusion

Here, we considered the effect of pyrophosphoric moieties on the catalyst, the influence of the presence or absence of lattice oxygen, and the effect of the oxidation states of the inner vanadium atom. We found that the introduction of a phosphoric moiety on one of the hydroxy groups strongly stabilizes the lower oxidation states of the complexes. As there are four phosphoric moieties around one vanadium atom in vanadyl pyrophosphate and so the surface vanadium species having the higher 5+ oxidation state should possess stronger oxidation ability.

The lack of the lattice oxo-oxygen atom showed little influence on the catalytic cycles; however, the presence of the vanadium (4+) atom at the lower layer relatively destabilizes the V^{3+} state of the upper vanadium complexes, and stabilizes the peroxo-vanadium (4+) complexes. These results suggest that the lattice oxo-oxygen in vanadyl pyrophosphate may play an important role in the activation of molecular oxygen.

Acknowledgements

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