

A Density Functional Study of the Structures and Energies of Vanadium Oxide Clusters on a (001) Anatase Support

Stan A. Zygmunt^{1*}, Paul C. Redfern², Peter Zapol², Michael Sternberg², and Larry A. Curtiss²

¹Dept. of Physics and Astronomy, Valparaiso University, Valparaiso, IN 46383 (USA)

²Materials Science and Chemistry Divisions, Argonne National Laboratory,

Argonne, IL 60439 (USA)

*stan.zygmunt@valpo.edu

Introduction

Supported vanadium oxide catalysts, prepared by anchoring vanadium oxide (VO_x) species on a metal oxide support such as anatase TiO_2 , are used industrially for reactions like the selective oxidation of o-xylene to phthalic anhydride. The proper combination of a specific support oxide and a level of coverage of VO_x surface species can often be used to produce a catalyst system with a desirable activity and selectivity. Currently there is much interest in using supported VO_x catalysts for oxidative dehydrogenation (ODH) of light alkanes. However, the influence of the support oxide and the coverage of VO_x species on catalytic performance is not fully understood at a molecular level.

Raman spectroscopy has been used to show the dependence of vibrational spectra on VO_x coverage of the anatase TiO_2 surface [1]. However, few experimental studies have obtained quantitative geometrical information about the VO_x active sites, which are especially difficult to probe in the sub-monolayer coverage regime. Proposals for the structure of monomeric sites include di-oxo species as well as mono-oxo species bound to the support by either one, two or three V-O-Ti bridges. A previous computational study by Vittadini and Selloni considered some but not all of these possibilities [2].

Thus, in order to study the different structural possibilities in a unified way, and as a first step in modeling propane ODH by supported VO_x catalysts, we have calculated the geometries and relative energies of a variety of monomeric, dimeric, and tetrameric VO_x/TiO_2 catalyst structures. These include structures modeled by Vittadini and Selloni but also include several additional candidate structures, among which is an intriguing proposal for an “upside-down VO_4 ” unit by Keller et al [3]. We have also calculated vibrational frequencies for each structure in order to compare our results to previous experimental studies.

Computational Methods

To model supported monomeric and dimeric VO_x species, we used a $\text{Ti}_4\text{O}_{16}\text{H}_{16}$ cluster to represent the (001) surface of anatase TiO_2 . The tetrameric VO_x species was modeled using a larger $\text{Ti}_6\text{O}_{23}\text{H}_{22}$ cluster. In all calculations constrained geometry optimizations were performed, in which the terminal OH and OH_2 groups were fixed. The terminal O atoms were frozen at positions given by the density functional calculations of Lazzeri et al. [4], and the H atoms were frozen at an OH distance of 0.96Å along the direction pointing toward the nearest Ti atom in the experimental structure.

All of our calculations utilize the B3LYP/6-31G(*) hybrid density functional method as implemented in GAUSSIAN 03. As we reported in an earlier study of propane ODH on cluster models for the (010) V_2O_5 surface [5], the 6-31G(*) basis set includes polarization functions on all non-hydrogen atoms but omits f-functions on V in the interest of computational efficiency.

Results and Discussion

Relative energies of a series of monomeric and dimeric VO_x/TiO_2 species are shown in Table 1. Energies are calculated relative to the fully hydroxylated (001) TiO_2 surface cluster plus two gas phase VO_4H_3 molecules ($\text{TiO}_2 + 2 \text{VO}_4\text{H}_3$). On a fully hydroxylated surface, the formation of each V-O-Ti bridge requires the elimination of one H_2O molecule.

Table 1. Relative energies of VO_x/TiO_2 surface species (kcal/mol)

Supported VO_x Species	E (kcal/mol)
$\text{TiO}_2 + 2 \text{VO}_4\text{H}_3$	0.0
Monodentate + $\text{VO}_4\text{H}_3 + \text{H}_2\text{O}$	-6.9
Bidentate + $\text{VO}_4\text{H}_3 + 2\text{H}_2\text{O}$	-11.1
Tridentate + $\text{VO}_4\text{H}_3 + 3\text{H}_2\text{O}$	15.3
Di-oxo + $\text{VO}_4\text{H}_3 + 2\text{H}_2\text{O}$	5.5
“Upside-down” + $\text{VO}_4\text{H}_3 + \text{H}_2 + 2\text{H}_2\text{O}$	73.2
Molecular monomer + $\text{VO}_4\text{H}_3 + \text{H}_2\text{O}$	-19.5
Dimer + $5\text{H}_2\text{O}$	-2.0
Molecular dimer + $3\text{H}_2\text{O}$	-19.9

It is noteworthy that the tridentate structure, which is often used in schematic depictions of monomeric VO_x catalytic sites, is energetically unfavorable compared to other monomer sites. And it is also clear that the “upside-down VO_4 ” monomer is energetically very unfavorable on the (001) TiO_2 support, although it was originally proposed as a monomer site on an Al_2O_3 support. The most stable VO_x species are the “molecular” monomer or dimer structures, which consist of VO_4H_3 or $\text{V}_2\text{O}_7\text{H}_4$ molecules that graft onto the TiO_2 surface while maintaining 2 or 4 V-O-H bridges. It seems likely that both of these species are present in significant concentrations under conditions of low VO_x coverage. These models for the catalytically active sites form the basis for our computational study of the propane ODH reaction.

References

1. Went, G. T., Oyama, S. T., Bell, A. T., *J. Phys. Chem.* **1990**, *94*, 4240.
2. Vittadini, A., Selloni, A., *J. Phys. Chem. B* **2004**, *108*, 7337.
3. Keller, D. E., de Groot, F. M. F., Koningsberger, D. C., Weckhuysen, B. M., *J. Phys. Chem. B* **2005**, *109*, 10223.
4. Lazzeri, M., Vittadini, A., Selloni, A., *Phys. Rev. B* **2001**, *63*, 155409.
5. Redfern, P. C., Zapol, P., Sternberg, M., Adiga, S. P., Zygmunt, S. A., Curtiss, L. A., *J. Phys. Chem. B* **2006**, *110*, 8363.

This work was supported by the U. S. Department of Energy, Basic Energy Sciences, under contract DE-AC02-06CH11357, and by the Indiana Space Grant Consortium.