

Propane Oxidative Dehydrogenation on Vanadium Oxide Molecules and Supported Clusters: A Density Functional Study

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Introduction

Currently there is much interest in using supported vanadium oxide (VO_x) catalysts, prepared by anchoring VO_x species on a metal oxide support such as anatase TiO₂, for oxidative dehydrogenation (ODH) of light alkanes. 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. 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.

To model propane ODH by supported VO_x/TiO₂ catalysts, we have calculated the geometries and relative energies of a variety of monomeric, dimeric, and tetrameric VO_x catalyst structures on the (001) anatase TiO₂ surface. We found the most stable VO_x species to be the “molecular” monomer or dimer structures, which consist of VO₄H₃ or V₂O₇H₄ molecules that graft onto the TiO₂ surface while maintaining 2 or 4 V-O-H bridges. We then used these models for the catalytic active sites to calculate possible reaction pathways for propane ODH. To better understand the catalyst-support interaction, we calculated analogous reaction pathways for propane ODH on the VO₄H₃ and V₂O₇H₄ gas phase molecules. Comparisons between the results obtained using gas phase and supported molecular catalysts help us determine the influence of the support on the ODH reaction kinetics.

Computational Methods

To model supported monomeric and dimeric VO_x species, we used a Ti₄O₁₆H₁₆ cluster to represent the (001) surface of anatase TiO₂. In all calculations constrained geometry optimizations were performed, in which the terminal OH and OH₂ groups were fixed. The terminal O atoms were frozen at positions given by the density functional calculations of Lazzeri et al. [1], 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) V₂O₅ surface [2], 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. Transition state structures connecting local energy minima along the ODH reaction pathway were optimized using conjugate-gradient techniques implemented in GAUSSIAN 03 as well as the nudged elastic band (NEB) method [3].

Results and Discussion

The propane ODH reaction pathway is similar for all four models of the active site considered. The reactants, with V in the 5+ oxidation state, are most stable in the singlet electronic state. First the vanadyl O atom abstracts a H atom from the secondary C in propane. This breaks the vanadyl double bond and forms an intermediate structure with a V-OH linkage. However, at this point the triplet state is much more stable than the singlet, so the intermediate is a triplet with one unpaired spin on the V and one on the secondary C. The V is now in the +4 oxidation state, and the C₃H₇ fragment is a nearly neutral radical. A subsequent rotation of the newly-formed OH group allows formation of a C-OH linkage and thereby breaks the V-O bond, producing a propanol-like adduct and leaving V in the +3 oxidation state. Subsequent transfer of a terminal H from the hydrocarbon to a surface O atom is followed by removal of H₂O and propene. Energetically downhill adsorption and dissociation of O₂ fills the O vacancy in the catalyst and completes the catalytic cycle, returning the system to the singlet state and V to the +5 oxidation state. The initial H transfer step is found to be rate-limiting in all cases. Activation energies for both gas phase and supported VO₄H₃ and V₂O₇H₄ are shown in Table 1, relative in each case to the singlet state reactants (system + C₃H₈).

Table 1. Activation energies for propane ODH on various VO_x species (kcal/mol)

Catalyst System	ΔE (kcal/mol)
VO ₄ H ₃	61.8
VO ₄ H ₃ /TiO ₂	49.1
V ₂ O ₇ H ₄	49.8
V ₂ O ₇ H ₄ /TiO ₂	33.5
Monolayer VO _x /TiO ₂ expt. [4]	≈ 20

These results show two important effects. First, a dimeric active site, whether in the gas phase or supported, has an activation energy 12-15 kcal/mol less than that of a monomeric site. Secondly, interaction with an oxide support lowers the activation energy of both monomers and dimers by 13-16 kcal/mol and thus enhances the catalytic activity of the site. Underlying reasons for these effects will be discussed in terms of the partial charges on the atoms in the VO_x unit and the singlet-triplet energy difference for the catalyst. The phenomenon of “spin-acceleration” revealed in this study of VO_x ODH catalysis may extend to other reactions and other transition metal oxide catalyst systems.

References

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