Spin Crossing Enhancement of Propane Oxidative Dehydrogenation on Supported Vanadium Oxide Catalysts: A Density Functional Study

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Introduction

Supported vanadium oxide (VO_x) catalysts, prepared by anchoring VO_x species on a metal oxide support, show great promise 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 catalysts, we have calculated geometries and relative free energies of a variety of monomeric and dimeric VO_x catalyst structures on the (001) anatase TiO_2 surface and the (010) surface of θ-Al_2O_3. Under reaction conditions, we found the most stable VO_x species to be the bidentate and tridentate monomer structures, in which a VO_4H_3 molecule grafts onto the oxide surface while forming either 2 or 3 V-O-Ti/Al bridges. The corresponding dimer structure is formed by a fusion of two adjacent bidentate monomers and formation of a V-O-V bridge. We then used these models for the catalytic active sites to calculate possible reaction pathways for propane ODH.

Computational Methods

To represent the (001) surface of anatase TiO_2, we used a $Ti_4O_{16}H_{16}$ cluster, while the (010) surface of θ-Al_2O_3 was modeled by a $Al_{18}O_{36}H_{18}$ 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 experimental positions, and the H atoms were frozen at an OH distance of 0.96Å along the direction pointing toward the nearest Ti/Al 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 [1], the 6-31G(*) basis set 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 [2].

Results and Discussion

Our results, in agreement with those of previous studies [3], indicate that the rate-limiting step of the propane ODH reaction is the initial abstraction of H from the hydrocarbon. The reactants are in the singlet spin state, but the transition state (TS) structure for the H abstraction step is in the triplet state. Previous studies did not attempt to identify the spin crossing point for this step; however, in Figure 1 we have mapped the H abstraction process to find its approximate location. The distance between the vanadyl O and the H on the secondary C of propane is used as the reaction coordinate. From this graph it is clear that the minimum energy reaction path will *not* pass through the triplet TS; instead, the singlet-triplet crossing occurs at an energy that is approximately 6 kcal/mol *lower* than the TS. Although Figure 1 shows only the results for the VO_x monomer, the results for the dimer structure are nearly identical. This results in a *spin crossing enhancement* of the ODH reaction rate. It is especially noteworthy, since our calculated triplet TS energy for the VO_x/TiO_2 dimer is 33.5 kcal/mol, somewhat higher than the experimental result of approximately 20 kcal/mol for monolayer VO_x coverage [4]. The 6 kcal/mol correction results in a value of 27.5 kcal/mol, in much better agreement with experiment. The remaining discrepancy is likely due to the greater activity of the VO_x/TiO_2 monolayer compared to the dimer model used in our calculations.

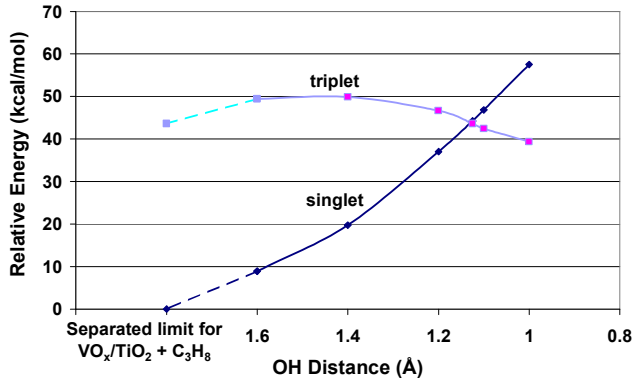

Figure 1. Energy vs. reaction coordinate for H abstraction from C_3H_8 by the VO_x/TiO_2 catalytic site. Energies for the separated reactants are shown for reference.

References

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