

Oxidative Dehydrogenation of Propane by Supported Transition Metal Oxide Species

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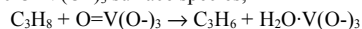
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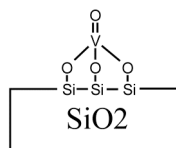
Introduction

The catalytic activation of C-H bonds is of fundamental interest, because it is the crucial step in important technological processes and also in many enzymatic reactions. Examples are the oxidative dehydrogenation of lower alkanes to alkenes by, e.g., supported transition metal oxide catalysts [1], and the oxygenation of C-H bonds to C-OH groups by cytochrom P450. Among the different mechanistic proposals for the initial C-H activation is hydrogen abstraction by metal oxo bonds [2], $\text{RH} + \text{O}=\text{M}(\text{d}^n) \rightarrow \text{R}^\bullet + \text{HOM}(\text{d}^{n+1})$, or oxidative addition of the C-H bond onto the metal oxo bond, $\text{R-H} + \text{O}=\text{M} \rightarrow \text{HO-M-R}$ [3]. We examine possible reaction mechanisms for the oxidative dehydrogenation of propane by supported transition metal oxide catalysts.

Specifically we are interested in V_2O_5 supported on SiO_2 [4,5] and consider the oxidative dehydrogenation of propane at monomeric $\text{O}=\text{V}(\text{O}-)_3$ surface species,



In this reaction vanadium(V) gets reduced to $\text{V}^{\text{III}}(\text{d}^2)$ and its spin changes from singlet to triplet.



Materials and Methods

We model monomeric vanadium oxide species by the cubic silsesquioxane in which one Si-H is replaced by $\text{O}=\text{V}$ [6]. We apply density functional theory with the B3LYP functional and TZVP basis sets. The Turbomole 5.7 code is employed. The use of the broken symmetry approach for intermediates with diradical or transition structures with diradicaloid electronic structures proved to be essential. Gibbs free energies for the surface sites and the surface species are calculated from DFT energies and harmonic vibrational frequencies. For the gas phase species, translational and rotational degrees of freedom are also considered.

Results and Discussion

Similarly to other catalysts with transition metal oxo bonds, the initial C-H bond activation step is hydrogen abstraction by the vanadyl ($\text{V}=\text{O}$) group yielding a diradical intermediate in which a propyl radical is attached to a $\text{HO} \cdot \text{V}^{\text{IV}}(\text{d}^1)(\text{O}-)_3$ site (see Figure). From here there are many different routes for the second hydrogen abstraction that lead to propene formation. Both the H-O-V oxygen atom of the (former) vanadyl group or the V-O-Si interphase oxygen of the $\text{O}=\text{V}(\text{OSi})_3$ sites may be involved. The Figure shows two examples. Propene is either directly obtained by a second hydrogen abstraction from the diradical intermediate, or a surface alkoxide or alcohol is obtained first from the intermediate by a propyl rebound mechanism from which propene can be formed. The second hydrogen abstraction is rate-limiting if it occurs at the same site as the first H abstraction (isolated sites). Energy barriers for the second hydrogen abstraction are lower if it occurs at another $\text{V}=\text{O}$ group (cooperating sites). In this case the first hydrogen abstraction becomes rate-limiting. For

isolated sites vanadium(III) is reached from $\text{V}(\text{V})$, while for cooperating sites we have a $\text{V}(\text{IV})/\text{V}(\text{V})$ redox cycle. For isolated and cooperating sites we predict apparent energy barriers in the range of 142 ± 16 and 107 ± 5 kJ/mol, respectively, and rate constants (at 800 K) of about $2 \cdot 10^{-4}$ to $6 \cdot 10^{-3} \text{ s}^{-1}$ and $9 \cdot 10^{-1} \text{ s}^{-1}$, respectively.

The energy and free energy barriers for C-H addition on the $\text{V}=\text{O}$ bond are much higher. Comparison with a study on the $\text{V}_2\text{O}_5(001)$ crystal surface [7] shows that such sites are more active than monomeric vanadia sites, but only a fraction of them is accessible.

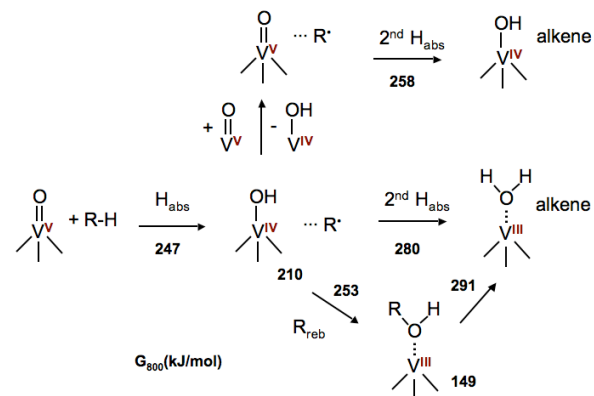


Figure 1. Main steps in the oxidative dehydrogenation of propane by monomeric vanadia sites on silica. The numbers show the Gibbs free energies at 800 K.

Significance

For the first time the complex mechanism of an important class of selective oxidation reactions has been revealed. Long debated issues for supported oxide catalysts such as which type of oxygen species is involved and how does the activity of a supported oxide species differ from that of a bulk oxide could be answered.

References

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