Oxidative Dehydrogenation of Propane by Monomeric Vanadium Oxide Sites on Silica Support

Xavier Rozanska, Rémy Fortrie, and Joachim Sauer*

Institut für Chemie, Humboldt Universität zu Berlin, Unter den Linden 6, D-10099 Berlin, Germany

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We investigate possible mechanisms of oxidative dehydrogenation of propane using density functional theory. Monomeric vanadium oxide species supported on silica are modeled by vanadyl-substituted silsesquioxane. Similarly to other catalysts with transition metal oxo bonds, the initial C–H bond activation step is hydrogen abstraction by the vanadyl (O=V) group yielding a diradical intermediate in which a propyl radical is bound to a HO–VIV site. This is followed by a propyl rebound mechanism yielding alkoxide or alcohol attached to a VIII(OSi)3 surface site from which propene can be formed. Propene is also directly obtained by a second hydrogen abstraction from the diradical intermediate. Desorption of propyl radicals leads to a stationary concentration of propyl in the gas phase and leaves reduced HO–VIV sites on the surface. Due to fast reoxidation their concentration is much smaller than the concentration of O=V sites. Therefore the rate of propene formation after readsorption on O=V sites is much larger than the rate of isopropyl alcohol (or propene) formation after readsorption on HO–VIV sites. Generation of surface propyl radicals by the first hydrogen abstraction becomes rate limiting. We predict that at 750 K the apparent activation energy is 123 (5 kJ/mol and the rate constant is about 0.26 s−1, in close agreement with experiments. The first hydrogen abstraction occurs exclusively on O=V sites, while the second hydrogen abstraction can also occur on V–O–Si bridging oxygen sites.

1. 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 (ODH) of lower alkanes to alkene by, for example, supported transition metal oxide catalysts1,2 and the oxidation of C–H bonds to C–OH groups by cytochrom P450.3 For transition metal oxide species there is experimental and computational evidence that the initial C–H activation is hydrogen abstraction by metal oxo bonds,4

\[ R-H + O=V \rightarrow R' + HO-V \quad (1) \]

with \( d^n \) denoting the occupation of nonbonding d-states on vanadium. The alkyl radical can directly form alkenes by losing another hydrogen atom,5 but it can also form an alcohol by a rebound mechanism as suggested for enzyme P450, see, e.g., ref 3 and references therein:

\[ R' + HO-V \rightarrow \text{H(R)}-OV \quad (2) \]

From the alcohol intermediate, an alkene can be obtained by elimination.

Alternative mechanisms suggest oxidative addition of the C–H bond onto the O=V bond as the initial step according to:6

\[ C_3H_8 + \text{O=V(O−)}_3 \rightarrow C_3H_6 + H_2O \cdot \text{V(O−)}_3 \quad (4) \]

\[ \text{O} \quad \text{H} \quad \text{OH} \]

\[ \text{M} \quad \text{CH}_2\text{R} \quad \text{M-CH}_2\text{R.} \quad (3) \]

\[ \text{SiO}_2 \]

which together with dimeric and oligomeric \( V_2O_5 \) species are present on catalyst surfaces with low \( V_2O_3 \) loadings.13 In the oxidative dehydrogenation of propane by supported transition metal oxide catalysts. Specifically we are interested in \( V_2O_5 \) supported on \( \text{SiO}_2 \) and consider monomeric O=V(O−)3 surface species,
kinetically separated from reoxidation of the catalyst, which is not the rate determining step in the oxidative dehydrogenation of alkane.\textsuperscript{14,15}

2. Models and Methods

To model monomeric vanadium oxide species on silicon oxide we use the cubic silsesquioxane $\text{HSi}_8\text{O}_{12}$ in which one $\text{Si} \equiv \text{H}$ group is replaced by a vanadyl group. This model has proven useful in previous studies.\textsuperscript{16,17} $\text{HSi}_8\text{O}_{12}$ mimics well the electronic structure of silica and is also sufficiently flexible to realistically simulate structural relaxations at reaction sites.\textsuperscript{18–21}

We apply density functional theory (DFT) with the hybrid B3LYP functional\textsuperscript{22} and triple-$\zeta$ plus polarization (TZVP) basis sets on all atoms\textsuperscript{23} and employ Turbomole 5.7.\textsuperscript{24} B3LYP gives vanadium oxide reduction energies in good agreement with more accurate quantum chemical methods and the few experimental results available.\textsuperscript{25} The optimized structures are characterized as minima or saddle points by frequency calculations. All reported energies are zero-point corrected unless otherwise stated. Finite temperature contributions to enthalpies and Gibbs free energies are estimated within the rigid rotor--ideal gas approximation.

Unrestricted Kohn–Sham (UB3LYP) is used for triplet or doublet spin state systems. Broken-symmetry calculations are performed for open-shell singlets.\textsuperscript{26} In this approach, the energy of the low spin state ($E_{\text{ls}}$) is obtained by spin projection from the energies of the broken-symmetry ($E_{\text{bs}}$) solution and the triplet ($E_{\text{tr}}$) solution for a given geometric structure:\textsuperscript{27}

$$E_{\text{ls}} = \frac{2E_{\text{bs}} - \langle S^2\rangle_{\text{bs}}E_{\text{pc}}^{\text{tr}}}{2 - \langle S^2\rangle_{\text{bs}}}$$ (5)

$\langle S^2\rangle_{\text{bs}}$ is the expectation value of the total-spin operator value for the broken-symmetry solution. $\langle S^2\rangle_{\text{bs}}$ is equal to one in the ideal case of non-interacting spins in equivalent orbitals. For cases in which $\langle S^2\rangle_{\text{bs}}$ significantly deviates from one, spin-projection has been questioned,\textsuperscript{28} and $E_{\text{ls}}$ should be taken as the upper limit estimate. Zero-point vibrational energy corrections are calculated for the broken-symmetry potential energy surface and, where appropriate, added to the spin-projected energy.

Classical transition state theory is used to calculate intrinsic rate constants, $k$,

$$k = \frac{k_B T}{h} \exp\left( -\frac{G_{\text{Ts}} - G_{\text{Int}}}{RT} \right) = \frac{k_B T q_{\text{Ts}}}{h} \exp\left( -\frac{E_{\text{Ts}} - E_{\text{Int}}}{RT} \right)$$ (6a)

and apparent rate constants, $k_{\text{app}}$,

$$k_{\text{app}} = K \cdot k = \frac{k_B T}{h} \exp\left( -\frac{G_{\text{Tx}} - G_{S+hc}}{RT} \right) = \frac{k_B T q_{\text{Ts}}}{h} e^{-\frac{E_{\text{Ts}} - E_{S+hc}}{RT}}$$ (6b)

with $G$ and $E_{\text{ZP}}$ being the Gibbs free energies and the zero-point energies, respectively, of transition structures (Ts), intermediates (Int), and hydrocarbon species in the gas phase separated from surface sites ($S+hc$). $K$ is the equilibrium constant for formation of the intermediate Int from $S+hc$. The partition functions for the gas-phase species are calculated within the harmonic oscillator–rigid rotor–ideal gas approximation including vibrational, rotational, and translational degrees of freedom. As part of a solid body, the surface species Ts, Int, and S do not have rotational or translational degrees of freedom. All $N = 6$ internal degrees of freedom, including internal hindered rotations, are treated as harmonic vibrations. Low frequencies (in cm$^{-1}$ in parentheses) are encountered for intermediates in which hydrocarbon species are weakly bound to the surface site: Int1 (3.2, 5.6), Int3(tr) (7.7), Int3(bs) (6.1), Ts7 (6.1, 5.9), and Ts13 (8.8). An error of 3 cm$^{-1}$ on a wavenumber of 5 cm$^{-1}$ and another error of 3 cm$^{-1}$ on a wavenumber of 10 cm$^{-1}$ cause a combined error of 3, 9, and 12 kJ/mol at 200, 600, and 800 K. We may take these as estimates of the uncertainty of our calculated Gibbs free energy values.

3. Results

3.1. Reaction Mechanisms on Isolated Sites. Figure 1 shows the different reaction routes for the oxidative dehydrogenation of propane at an isolated vanadium oxide site on the silica surface. Figures 2 and 3 show the geometric details of the intermediates and transition structures, respectively. The corresponding energies are reported in Table 1.

The first step is adsorption of propane onto the surface site leading to the van der Waals complex Int1. As other widely used functionals, B3LYP poorly describes dispersion, which is the major stabilizing contribution in van der Waals complexes.\textsuperscript{29,30} This explains the apparent absence of binding between propane and the surface site model. The enthalpy of adsorption of propane onto V$_2$O$_5$ at 298 K is 37 $\pm$ 5 kJ/mol,\textsuperscript{31} which constitutes a realistic estimate of the binding in Int1.

From Int1, two reaction routes can be followed, namely hydrogen abstraction by the oxygen atom of the vanadyl group through Ts1 or by one of the three bridging $\text{V} \equiv \text{O} \equiv \text{Si}$ oxygen atoms through Ts2. Which oxygen atom is involved in the activation of the first carbon–hydrogen bond is a question that has been frequently raised in the literature,\textsuperscript{9,12,15,32} but never unambiguously answered for supported transition metal oxide species. The products after Ts1 and Ts2, Int2 and Int3, respectively, are biradicals in which a propyl radical weakly interacts with a HO–$\text{V}^{IV}(\text{d}^1)$ site. Dissociation of $\text{C}_3\text{H}_7^+$ from the HO–$\text{V}^{IV}(\text{d}^1)$ site requires only 15 and 24 kJ/mol, respectively. The broken symmetry solution yields an energy within 1 kJ/mol of the triplet calculation, which implies that singlet and triplet states are almost degenerate.

The transition structures Ts1 and Ts2 are found only on the broken-symmetry surface. The energy barriers are 144 and 204 kJ/mol, respectively. After spin-projection, these values are 27 and 12 kJ/mol lower, respectively. The intermediates Int2 and Int3 are only 12 and 24 kJ/mol below the respective transition structures, which points to the “late” nature of the latter. Because Ts2 is 60 kJ/mol above Ts1 only the vanadyl group will be involved in the initial activation of propane. Consideration of the free energies of Ts1 and Ts2 at different temperatures (Table 1) does not change the dominance of the route through Ts1.

Different consecutive reaction steps toward propene formation can take place from Int2 and Int3 and all transition structures have triplet electronic states. For some of them, the existence
of broken-symmetry solutions was also examined. It was indeed possible to localize broken-symmetry transition structures, but they all had higher energies than the corresponding triplet transition structures, usually around 60 kJ/mol after spin-projection. Vanadium is in a VIII (d$^2$) triplet state in all the intermediates and products reached after the transition structures from Int2 and Int3. Crossing from the singlet potential energy surface to the triplet surface occurs in the region of the biradical intermediates Int2 and Int3, where the two surfaces are largely parallel over an extended range and only a few kilojoules per mole apart from each other.$^{33}$

We consider first the reaction pathways from Int2 toward propene formation. A second hydrogen abstraction from a CH$_3$ group of C$_3$H$_7$ via Ts3 or Ts5 leads directly to propene. The route via Ts3 yields water attached to a V III (O$-$)$_3$ site. The route via Ts5 leaves the abstracted hydrogen on the oxygen atom of a V$-$O$-$Si group and the V$-$O bond opens. The energies of Ts3 and Ts5 are 178 and 184 kJ/mol, respectively. The propyl radical can also rebind to an oxygen atom of the HOVIII (O$-$)$_3$ surface site, either to the V$-$O$-$Si bond via Ts4 or to the VOH bond via Ts6. With $+173$ and $+161$ kJ/mol Ts4 and Ts6 respectively are lower than both Ts3 and Ts5. The route through Ts6 is kinetically dominant whatever the temperature.

From Int4, which is reached after Ts3, desorption of propene costs 23 kJ/mol (Int10$+$propene), and the water binding to the V$^{IIII}$V(0$-$)$_3$ site is 86 kJ/mol. The energy of Int4 is $+72$ kJ/mol with respect to Int1. The exothermic conversion of propene and oxygen to propene and water is not sufficient to compensate for the endothermic conversion of V$^+$ to V$^{II}$ and oxygen.$^{25}$ The energy of the alkoxy species Int5 that is reached after Ts4 is only 3 kJ/mol higher than that of Int4. However, its free energy increases more strongly with increasing temperature due to its more constrained structure. Removal of propene from Int6 that is reached after Ts5 requires only 15 kJ/mol. When temperature increases, the free energy of this complex increases similarly to that of Int4. Among the intermediates attainable from Int2, Int7 that is reached via Ts6 has the lowest energy. Its structure corresponds to isopropyl alcohol attached to the V$^{III}$O$-$ site. The interaction energy of isopropyl alcohol with V$^{III}$O$-$ is 102 kJ/mol, comparable with the interaction between water and the V$^{III}$O$-$ site in Int10. The OH stretching vibration frequencies of isopropyl alcohol when adsorbed onto the V$^{III}$O$-$ site and when in gas phase are 3724 and 3807 cm$^{-1}$, respectively. Apart from Int1, this intermediate has the lowest energy in the whole reaction network. Only at high temperature does its free energy become more positive than that of the product Int4.

We consider now the reaction pathways from Int3 toward propene. Int6 and Int7 can also be reached from Int3 through two-step mechanisms with prohibitively high barriers. Int2 and Int3 are connected by the high-energy transition structure Ts7. The energies of Ts7 and Int3 relative to Int2 are little affected by the interaction of the propyl radical with the surface model. When we optimize Int2, Ts7, and Int3 in the absence of the propyl radical, we find that the surface models in the doublet state of Ts7 and Int3 are 143 and 60 kJ/mol, respectively, above that of Int2.

From Int3 two reaction routes yield propene by abstraction of a second hydrogen atom from the propyl radical. Int6 is reached when hydrogen is transferred to the vanadyl oxygen atom via Ts9. The energy of Ts9 is $+251$ kJ/mol with respect to Int1. Hydrogen transfer to the oxygen atom in one of the two V$-$O$-$Si bonds yields the high-energy intermediate Int9 via a prohibitively high barrier (Ts10). The alkoxy species Int8

Figure 1. Reaction network of the oxidative dehydrogenation of propane by vanadyl-exchanged silsesquioxane. Values are zero-point energy (in kJ/mol). ($S^2$) of the open-shell singlets are indicated. All systems except Int1, Ts1, Ts2, Int2(bs), and Int3(bs) are triplet.
that is reached from Int3 through Ts8 is rather stable. Ts8 has a rather high energy, but it is the lowest one from Int3 toward propene formation at any temperature.

All reaction intermediates in the oxidative dehydrogenation of propane by \( \text{O} = \text{V(OSi)}_3 \) sites are described now, but there are two additional groups of transition structures. Ts11, Ts12, and Ts14 are transition structures that lead to propene from alkoxide or alcohol. Ts13, Ts15, and Ts16 are transition structures for hydrogen exchange between oxygen atoms.

In Int5, a hydrogen atom of one of the \( \text{CH}_3 \) groups can jump to an oxygen atom of the surface yielding propene in two ways. Water can be formed through Ts11 (+181 kJ/mol), or a bridging hydroxyl (Int6) can be formed via Ts12, which is 18 kJ/mol above Ts11. The free energy difference between Ts11 and Ts12 increases with temperature. From Int7, only one transition structure leading to propene was found. Ts14 links Int7 to Int6 (+173 kJ/mol). A transition structure corresponding to the elimination of water from isopropyl alcohol (connecting Int4 and Int7) “collapses” to a transition structure similar to Ts3.

The second group of transition structures connects Int6 to Int4, Int8 to Int7, and Int9 to Int6. A hydrogen atom attached to oxygen in a \( \text{V} – \text{O} – \text{Si} \) bridge jumps to the oxygen atom originating from the vanadyl group (see Ts13, Ts15, and Ts16). Ts13 has a much lower energy than any other transition structure accessible from Int6, and a fast conversion of Int6 into Int4 occurs. This remains valid when temperature is considered.

Ts15, which connects the two reaction intermediates of lowest energy, namely Int8 and Int7, has the lowest energy of all transition structures.

3.2. Cooperating Monomeric Sites. The mechanism described so far proceeds via a diradical intermediate in two subsequent hydrogen abstraction steps of which the second has significantly higher barriers. Monomeric vanadium oxide sites can be more active if the second hydrogen abstraction occurs on a different, “unreacted”, monomeric vanadia site. In this case, two \( \text{HO} – \text{V}^\text{IV}(d^1) \) species are reached at the end of the reaction instead of one \( \text{H}_2\text{O} – \text{V}^\text{III}(d^2) \) species. The dominant reaction pathways for this situation are shown in Figure 4, and the energies are reported in Table 2. Details of the structures can be found in Figures 5 and 6.

Once the intermediate Int2 is formed, the propyl radical may desorb from the \( \text{HOVIV}(d^1) \) site and re-adsorb to an unreacted \( \text{OV}V^\text{IV}(d^0) \) species elsewhere (Int13). Diffusion on the surface is also possible instead of desorption/readsorption steps. Table 2 shows that \( \text{C}_3\text{H}_7^\text{a} \) desorption is thermodynamically feasible at reaction temperature, and the free energy of Int12 + \( \text{C}_3\text{H}_7^\text{a} \) is lower than the free energies of Ts2 and Ts17. This also remains true if the increment of 37 ± 5 kJ/mol mentioned above is added to the energy of Int12 + \( \text{C}_3\text{H}_7^\text{a} \) to correct for missing dispersion contributions. After \( \text{C}_3\text{H}_7^\text{a} \) has re-adsorbed to an unreacted active \( \text{O} = \text{V(O)h} \) site (Int13), the latter abstracts another hydrogen atom yielding \( \text{C}_2\text{H}_6 \). As we saw before, the

Figure 2. Stable structures of different pathways for the oxidative dehydrogenation of propane. The labels are the same as in Figure 1. The distances are in picometers.
vanadyl oxygen atom is much more active than a bridging $\text{V}-\text{O}-\text{Si}$ oxygen site, and we can safely consider only two reaction routes. In the first, $\text{C}_3\text{H}_6$ is formed in a single step (Int14) by hydrogen abstraction from $\text{C}_3\text{H}_7^*$ (Ts17). In the second, $\text{C}_3\text{H}_7^*$ attaches to the vanadyl oxygen atom (Ts18), forming isopropoxide (Int15). $\text{V}^\text{V}(d^0)$ is reduced to $\text{V}^\text{IV}(d^1)$ in both cases.

Energy barriers and reaction energies for the second hydrogen abstraction are all lower if it occurs on an “unrecracted” $\text{O}=\text{V}^\text{V}$ site instead of a $\text{HO}=\text{V}^\text{IV}$ site. Ts17 is the analogue of Ts3, except that two $\text{V}^\text{IV}(d^1)$ species are reached in the former case, and a $\text{V}^\text{III}(d^2)$ species in the latter case. The energy is only 6 kJ/mol lower for Ts17 than for Ts3, but the free energy difference between the two transition structures increases with temperature and reaches 22 kJ/mol at 800 K. The same trend applies to Ts18 and Ts6, which are the transition structures for formation of surface propoxides. The energy and free energy differences are 10 and 23 kJ/mol at 0 and 800 K, respectively. The products are around 30 kJ/mol more stable when two HO-$\text{V}^\text{IV}(d^1)$ are reached (Int14 and Int15) instead of $\text{H}_2\text{O}+\text{V}^\text{III}(d^2)$. The free energy increases with temperature are equivalent for the intermediates Int4-Int14 and Int7-Int15. The same holds after $\text{C}_3\text{H}_6$ has desorbed.

3.3. Heterolytic Bond Dissociation. It was suggested that oxidative dehydrogenation can be achieved through heterolytic bond dissociation (CH addition on the $\text{V}=\text{O}$ bond).\textsuperscript{6,32} We investigated the closed-shell singlet reaction pathways (Figure 7) and found that the reaction intermediates and transition structures have significantly higher energies than for the open-shell singlet reaction pathways. This was also found before by Fu et al.\textsuperscript{7} for the reaction of propane with the $\text{Mo}_3\text{O}_9$ cluster. The closed and open-shell potential energy surfaces never intersect. Therefore, spin-crossover as described\textsuperscript{10,11} for propane dehydrogenation by $\text{VO}_2^+$ or $\text{V}_3\text{O}_7^+$ does not occur. This is one of many reactivity differences between charged vanadium oxide species in the gas phase and neutral vanadium oxide species on surfaces. Another critical difference is that the oxidation part of the catalytic cycle, that is, formation of propene and $\text{H}_2\text{O}$, is endothermic for the surface species studied here (Table 1), whereas it is strongly exothermic with $\text{VO}_2^+$. The energy of $\text{C}_3\text{H}_8+\text{VO}_2\text{H}_2^+$ is $-347$ kJ/mol with respect to $\text{C}_3\text{H}_6+\text{VO}_2^+$.\textsuperscript{10} The corresponding difference for the $\text{O}=\text{V}(\text{O})$ surface site, that is, the energy difference between Int4 and Int1, is $-74$ kJ/mol. This difference in reaction energies is in agreement with the difference in oxygen defect formation energies between charged gas phase and neutral vanadium oxide.
species on the surface. In propane dehydrogenation by \( V_3O_7+ \), the barrier for the CH addition onto the V=O bond is only marginally higher than the barrier for the first hydrogen atom abstraction from propane, which is the rate-determining step.

### 4. Discussion

#### 4.1. Comparison with Calculations for Bulk \( V_2O_5 \) Surfaces.

Very recently, Fu et al. studied oxidative dehydrogenation of propane on single-crystal \( V_2O_5(001) \) surfaces, which also exhibit vanadyl (O\(_d\)V) sites, albeit in a different environment. At these sites propene can be formed by a two-step hydrogen-abstraction mechanism leading to surface propoxy species similar to Int\(_8\). The barriers for the two steps are about the same, of the order of 110 kJ/mol. The propoxy species can also be reached with similar barriers by inserting the vanadyl oxygen into the C-H bond of propane. Bridging V-O-V sites which are also present on the \( V_2O_5(001) \) crystal surface have also been found active in propane ODH (oxo-insertion mechanism).

Unfortunately, the density functional used in ref 9 (PW91) was different from the one we use (B3LYP). B3LYP was applied in a study of propane ODH on cluster models of the \( V_2O_5(001) \) crystal surface, but since broken-symmetry solutions were not considered the H-abstraction mechanism was not found in ref 8b and much too high barriers were obtained for the oxo-insertion mechanism. PBE (which yields virtually the same results as PW91) has been found to yield larger energies for oxygen defect formation of vanadia (both supported and crystalline), and test calculations for Ts3 showed that PBE barriers can be higher than B3LYP barriers for propene formation on supported vanadia species. This implies that sites on \( V_2O_5(001) \) crystal surfaces could be significantly more active in the ODH of propane than monomeric vanadia species on silica support. The smaller apparent turnover frequencies observed for \( VO_x/SiO_2 \) and \( VO_x/Al_2O_3 \) catalysts at vanadia loadings high enough that \( V_2O_5 \) crystallites are present (above 8 V/nm\(^2\))

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**TABLE 1: Electronic and Zero-Point Energies and Gibbs Free Energies of the Intermediates and Transition States in the Oxidative Dehydrogenation of Propane**

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<td>72</td>
<td>62</td>
</tr>
<tr>
<td>Int11+H(_2)O+propene</td>
<td>198</td>
<td>180</td>
<td>151</td>
<td>79</td>
<td>42</td>
</tr>
<tr>
<td>Int11+isopropyl alcohol</td>
<td>141</td>
<td>142</td>
<td>139</td>
<td>131</td>
<td>127</td>
</tr>
</tbody>
</table>

\( a \) \( E_{el} \), \( E_{ZP} \), and \( G_T \) are electronic energy, zero-point energy, and Gibbs free energy at standard pressure, respectively, in kJ/mol. The temperature is in K. The numbers in parentheses are spin-projected energies. \( b \) To get an estimate of the van der Waals contribution to the reaction, the energies of Int0+propane, Int10+propene, Int11+H\(_2\)O+propene, and Int11+isopropyl alcohol can be increased by 37 ± 5 kJ/mol.

---

Figure 4. Reaction pathways in the ODH of propane by two cooperating active sites. V\(^V\)/V\(^V\) indicates the oxidation states X and Y of the two sites. The numbers are zero-point energies (in kJ/mol).
are not in contradiction. The majority of vanadia sites are inside the bulk of V₂O₅ crystallites and not accessible in such three-dimensional vanadia particles.

4.2. Kinetic Considerations. Hydrogen abstraction by the vanadyl oxygen atom is the initial step in the oxidative dehydrogenation of propane by supported vanadium oxide species. The diradical intermediate that is reached via the diradicaloid transition structure Ts1 consists of a propyl radical attached to a HO-V(O⁻)3 site and has similar energies in the singlet and triplet states (Int2). Spin-crossing to the triplet state most likely occurs in this step. For the second hydrogen abstraction there are many possible pathways that lead to propene formation. First, we consider cases in which the second hydrogen abstraction occurs at the same site as the first one, yielding a H₂O⁢V⁢III⁢(O⁻)₃ site (Figure 1). To ease the discussion, we consider the most significant reaction intermediates and calculate from the data in Table 1 the rates relative to the fastest route using classical transition state theory (eq 7).

Table 3 shows the results. For instance, Ts3, Ts4, Ts5, Ts6, and Ts7 can be crossed from Int2. Instead of giving all reaction rates, only the ratios are given for Ts3, Ts4, Ts5, and Ts7 with respect to the fastest route, Ts6. The only product that can be formed at low temperature from Int2 is Int7 through Ts6. With increasing temperature, the relative rates for conversion of Int2 through Ts3, Ts4, and Ts5 become larger (Table 3). The only route that can be excluded at all temperatures is the one through Ts7. Conversion between Int7 and Int8 is many orders of magnitude faster than the other routes from these intermediates. Int7 and Int8 can then be considered to be permanently at equilibrium. Because Int8 is the less stable among them, it is not further considered. From Int6, the conversion into Int4 via Ts13 is also many orders of magnitude faster than the other reactions, and, therefore, Int6 does not need to be considered as a separate species. This way it is possible to simplify the reaction network for the oxidative dehydrogenation of propane as shown in Figure 8. Surface alcohol and alkoxy species such...
TABLE 3: Most Favorable Kinetic Routes from the Different Reaction Intermediates in the Oxidative Dehydrogenation of Propane by an Isolated Site as a Function of Temperature (K)

<table>
<thead>
<tr>
<th>structurea</th>
<th>ratio of reaction ratesb</th>
<th>T</th>
<th>200</th>
<th>600</th>
<th>800</th>
</tr>
</thead>
<tbody>
<tr>
<td>Int2</td>
<td>r_{Int2} / r_{Int1}</td>
<td></td>
<td>1 x 10^{-5}</td>
<td>8 x 10^{-3}</td>
<td>2 x 10^{-2}</td>
</tr>
<tr>
<td>Int5</td>
<td>r_{Int5} / r_{Int1}</td>
<td></td>
<td>6 x 10^{-5}</td>
<td>6 x 10^{-3}</td>
<td>1 x 10^{-2}</td>
</tr>
<tr>
<td>Int6</td>
<td>r_{Int6} / r_{Int1}</td>
<td></td>
<td>4 x 10^{-7}</td>
<td>3 x 10^{-5}</td>
<td>8 x 10^{-3}</td>
</tr>
<tr>
<td>Int7</td>
<td>r_{Int7} / r_{Int1}</td>
<td></td>
<td>3 x 10^{-31}</td>
<td>9 x 10^{-10}</td>
<td>4 x 10^{-7}</td>
</tr>
<tr>
<td>Int8</td>
<td>r_{Int8} / r_{Int1}</td>
<td></td>
<td>3 x 10^{-3}</td>
<td>3 x 10^{-2}</td>
<td>4 x 10^{-2}</td>
</tr>
<tr>
<td>Int9</td>
<td>r_{Int9} / r_{Int1}</td>
<td></td>
<td>5 x 10^{-9}</td>
<td>3 x 10^{-7}</td>
<td>8 x 10^{-5}</td>
</tr>
<tr>
<td>Int10</td>
<td>r_{Int10} / r_{Int1}</td>
<td></td>
<td>6 x 10^{-18}</td>
<td>3 x 10^{-6}</td>
<td>4 x 10^{-4}</td>
</tr>
<tr>
<td>Int11</td>
<td>r_{Int11} / r_{Int1}</td>
<td></td>
<td>2 x 10^{-41}</td>
<td>8 x 10^{-15}</td>
<td>2 x 10^{-11}</td>
</tr>
<tr>
<td>Int12</td>
<td>r_{Int12} / r_{Int1}</td>
<td></td>
<td>2 x 10^{-21}</td>
<td>3 x 10^{-6}</td>
<td>3 x 10^{-4}</td>
</tr>
</tbody>
</table>

a The labels used to designate the structures are the same as in Figure 1. b See eq 7 and Table 1 for the values of the Gibbs free energies.

Figure 8. The dominant reaction pathways in oxidative propane dehydrogenation on vanadia sites. The numbers are zero-point energies and Gibbs free energies at 800 K (in kJ/mol).

Table 2 shows the corresponding apparent reaction rate constants for different routes of the second hydrogen abstraction. The numbers are zero-point energies and from Int7 via Ts14. All four of these routes for the second hydrogen abstraction are included, because their energies are low, and they constitute the predominant addition intermediate. The numbers are zero-point energies and from Int7 (at an “unreacted” O═V(O═)3 site and undergo further oxidation to ketone, eventually leading to total oxidation of the alkene to CO and water.1,2,3 Apparent zero-point energy barriers for oxidation of alcohols to aldehydes (or ketones) are around 125 and 113 ± 3 kJ/mol when catalyzed by silica and alumina, respectively. Desorbed isopropyl alcohol could also re-adsorb at an “unreacted” site (see below), and the path toward higher oxidized products most likely goes through propane.

The following kinetic scheme takes desorption of the isopropyl radical from Int2 leaving an Int12 site (V IV ) into account (k1),

\[ \text{Int0} + \text{C}_3\text{H}_7 \rightarrow \text{Int12} + \text{C}_3\text{H}_7^* \]

K \text{Int0} + \text{C}_3\text{H}_7^* \rightarrow \text{Int11} + \text{C}_3\text{H}_5\text{O} \quad \text{(8)}

Readsorption can occur on the same type of site Int12, yielding either propane back via Ts6 (k_{1r}) or leading to isopropyl alcohol via Ts6 (k1), but readsorption can also occur at an “unreacted” Int0 site yielding propane via Ts17 or Ts19 (k1). For a stationary concentration of propyl radicals in the gas phase, and if we further assume (in accord with the Mars–van Krevelen mechanism) that the fraction of active sites that are in the reduced state is small, [Int12][Int0] \ll 1, the expression for the rate of propene formation becomes

\[ k_{\text{app}}(T) = k_0(2) \exp \left( \frac{E_{\text{IEP}} - E_{\text{IEP}}(\text{IEP})}{T} \right) \]

\[ k_{\text{app}}(T) = k_0(2) \exp \left( \frac{E_{\text{IEP}} - E_{\text{IEP}}(\text{IEP})}{T} \right) \]

\[ k_{\text{app}}(T) = k_0(2) \exp \left( \frac{E_{\text{IEP}} - E_{\text{IEP}}(\text{IEP})}{T} \right) \]

\[ k_{\text{app}}(T) = k_0(2) \exp \left( \frac{E_{\text{IEP}} - E_{\text{IEP}}(\text{IEP})}{T} \right) \]

\[ k_{\text{app}}(T) = k_0(2) \exp \left( \frac{E_{\text{IEP}} - E_{\text{IEP}}(\text{IEP})}{T} \right) \]
Oxidative Dehydrogenation of Propane

\[
\frac{d[C_3H_8]}{dt} = \frac{k_1k_2[\text{Int0}][C_3H_8]}{(k_1 + k_3)[\text{Int12}]/[\text{Int0}]} + k_2 \approx k_1[\text{Int0}][C_3H_8]
\]

(9)

This shows that under such conditions step 1 is rate determining. The apparent rate for the first hydrogen abstraction is included in Table 4.

The rate of propyl alcohol formation relative to the rate of propene formation is proportional to the concentration of reduced sites Int12 relative to the concentration of non-reduced sites Int0.

\[
\frac{d[C_3H_7OH]}{d[C_3H_8]} = \frac{k_2}{k_1} \frac{[\text{Int12}]}{[\text{Int0}]} \ll 1
\]

(10)

Since the latter is very small and \(k_1\) and \(k_2\) are comparable, only a tiny fraction of isopropyl alcohol is formed.

In summary, the surface propyl radical is the central intermediate and its formation is the rate-determining step (Ts1). Desorption of propyl radicals leads to a stationary concentration of propyl in the gas phase and leaves reduced HO–V\(IV\) sites (Int12) on the surface. Due to fast reoxidation their concentration is much smaller than the concentration of O=V\(V\) sites (Int0). Therefore the rate of propene formation after readsorption on O=V\(V\) sites (Ts17) is much larger than the rate for isopropyl alcohol (or propene) formation after readsorption on HO–V\(IV\) sites via Ts6 (or Ts3). Going beyond these qualitative considerations requires a microkinetic modeling of a reaction network such as shown in Figure 8. Numerical solutions will be obtained for realistic conditions such as temperature, loading of the catalyst surface with active species, and partial pressure of propane. This will be done in a future publication that also considers larger vanadium species.\(^{45}\)

### 4.3. Comparison with Experimental Data

For V\(2\)O\(5\)/SiO\(2\) catalysts with vanadium surface coverages below 3 Vnm\(^{-2}\) (i.e., below the limit at which V\(2\)O\(5\) crystallites start to appear) turnover frequencies (TOF) of around 0.01 s\(^{-1}\) (748 K)\(^{37}\) and 0.3 \(\times\) 10\(^{-3}\) s\(^{-1}\) (623 K)\(^{38}\) have been observed for propene formation. The calculated apparent rate constants for the first hydrogen abstraction (Ts1) are 0.26 s\(^{-1}\) at 750 K and 1.7 \(\times\) 10\(^{-3}\) s\(^{-1}\) at 600 K (Table 4), that is, they are about 26 times (750 K) and 5 times (600 K) larger than the experimental numbers. For V\(2\)O\(5\)/SiO\(2\) catalysts with vanadium surface coverages below 0.5 Vnm\(^{-2}\) (MCM-41), apparent activation energies of 122 \(\pm\) 20 kJ/mol have been measured for propene formation,\(^{37,39}\) while values of 101 \(\pm\) 15 and 112 \(\pm\) 15 kJ/mol have been obtained for butane conversion.\(^{40}\) For V\(2\)O\(5\)/Al\(2\)O\(3\) and V\(2\)O\(5\)/ZrO\(2\) catalysts the apparent activation energies for propene formation are between 120 and 110 kJ/mol\(^{41}\) and around 99 kJ/mol,\(^{42}\) respectively. The upper limit estimate from the calculations for 750 K, \(E_a(T) = (H_{X_1} - H_{S_1 = \text{bc}}) + RT = 123 \pm 5\) kJ/mol for the first hydrogen abstraction, which includes the \(\pm 5\) kJ/mol uncertainty of the experimental adsorption energy,\(^{31}\) but not the DFT uncertainty, is close to the most directly related experimental value of 122 kJ/mol.\(^{37,39}\)

Comparison of both TOF and activation energies shows that the mechanistic details we suggest are compatible with known observations.

### 5. Conclusions

We analyzed possible reaction mechanisms for the oxidative dehydrogenation of propane by monomeric vanadium oxide species on silica. The initial step is hydrogen abstraction from propane by the vanadyl oxygen atom leading to a diradical intermediate, namely, C\(3\)H\(_4\)*:HO–V\(IV\)–O=0. The corresponding transition state is only found by broken-symmetry calculations. All reaction steps after the first hydrogen atom abstraction that occur at the same active site proceed on the triplet potential energy surface.

Desorption of propyl radicals leads to a stationary concentration of propyl in the gas phase and leaves reduced HO–V\(IV\)-O=0 sites on the surface. Due to fast reoxidation the concentration of the latter is much smaller than the concentration of regenerated (or unreacted) O=V\(V\)-O=0 sites. This has two consequences: (i) The rate of propene formation after readsorption on O=V\(V\)-O=0 sites is much larger than the rate for isopropyl alcohol (or propene) formation after readsorption on HO–V\(IV\)-O=0 sites. (ii) Formation of propyl radicals by the first hydrogen abstraction from propane becomes rate-limiting.

The mechanism suggested is compatible with turnover frequencies and activation energies available, while other suggestions (C–H addition onto the metal oxo bond)\(^{6,22}\) are not supported by the calculations.

With regard to the type of active oxygen species in the reaction, we find that only vanadyl sites are involved in the rate-determining step, but the second hydrogen abstraction may occur also at V=O−Si bridging oxygen sites without changing the overall kinetics of the reaction.

Comparison with recent DFT calculations for V\(2\)O\(5\)(001) crystal surfaces\(^{9}\) indicates that vanadyl sites may be significantly more active in the ODH of propane if they are part of the bulk surface and not supported as monomers on silica. However, apparent turnover frequencies may be lower for V\(2\)O\(5\) crystallites on the surface because only a fraction of sites is accessible in three-dimensional particles.

The detailed mechanism presented in this study is a firm basis for future analysis of different kinds of experiments and will be used in microkinetic models. Further work should address the selectivity problem.

### Acknowledgment

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### References and Notes

(39) Kondratenko, E. V.; Baerns, M. Private communication.