VO$^{1-4}$ 阳离子与 $n$-$C_mH_{2m+2}$ ($m = 3, 5, 7$) 烷烃的反应性研究：氧含量和碳链长度的影响

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Table S1 Products, Pseudo-First-Order Rate Coefficients (k), and Reaction Efficiencies (Φ) for the Reactions Investigated.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Products/Equations</th>
<th>k, (cm³ molecule⁻¹ s⁻¹) × Φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO⁺ + C₃H₈</td>
<td>VOC₂H₄</td>
<td>100% (S1a)</td>
</tr>
<tr>
<td></td>
<td>VOC₂H₆</td>
<td>42% (S2a)</td>
</tr>
<tr>
<td>VO⁺ + n-C₅H₁₂</td>
<td>VOC₂H₄ + 2H₂</td>
<td>38% (S2b)</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>20% (S2c)</td>
</tr>
<tr>
<td>VO₂⁺ + C₃H₈</td>
<td>VO₂C₂H₆</td>
<td>49% (S3b)</td>
</tr>
<tr>
<td></td>
<td>VO₂C₂H₆ + C₃H₈</td>
<td>1% (S3c)</td>
</tr>
<tr>
<td></td>
<td>VO₂C₂H₆ + C₃H₈</td>
<td>6.54 × 10⁻¹⁰/0.60</td>
</tr>
<tr>
<td>VO₂⁺ + n-C₅H₁₂</td>
<td>VOC₂H₆ + C₃H₈</td>
<td>28% (S4b)</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>14% (S4c)</td>
</tr>
<tr>
<td></td>
<td>VOC₂H₆ + C₃H₈ + H₂</td>
<td>5% (S4d)</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>10% (S4e)</td>
</tr>
</tbody>
</table>
\[
\begin{align*}
\text{VO}_3 + \text{C}_3\text{H}_6 & \quad \text{VO}_3\text{C}_3\text{H}_6 \quad 82\% \ (S5a) \quad 4.79 \times 10^{-10} / 0.45 \\
\text{VO}_3 + \text{C}_3\text{H}_4 & \quad \text{VO}_3\text{C}_3\text{H}_4 \quad 18\% \ (S5b) \quad 7.76 \times 10^{-10} / 0.63 \\
\text{VO}_3 + n\text{-C}_3\text{H}_6 & \quad \text{VO}_3\text{C}_3\text{H}_6 \quad 62\% \ (S6a) \quad 1.21 \times 10^5 / 1.18 \\
\text{VO}_3 + n\text{-C}_3\text{H}_4 & \quad \text{VO}_3\text{C}_3\text{H}_4 \quad 88\% \ (S6b) \quad 2.23 \times 10^5 / 1.88 \\
\text{VO}_3 + \text{C}_2\text{H}_4 & \quad \text{VO}_3\text{C}_2\text{H}_4 \quad 88\% \ (S7a) \quad 1.21 \times 10^5 / 1.16 \\
\text{VO}_3 + \text{C}_2\text{H}_6 & \quad \text{VO}_3\text{C}_2\text{H}_6 \quad 80\% \ (S7b) \\
\end{align*}
\]

\[
\begin{align*}
\text{Others} & \quad 2\% \ (S5b) \quad 7.76 \times 10^{-10} / 0.63 \\
\text{Others} & \quad 1\% \ (S7c) \quad 2.23 \times 10^5 / 1.88 \\
\text{Others} & \quad 5\% \ (S8d) \\
\end{align*}
\]

\[
\begin{align*}
\text{VO}_2 + \text{C}_3\text{H}_6 & \quad \text{VO}_2\text{C}_3\text{H}_6 \quad 88\% \ (S5a) \quad 4.79 \times 10^{-10} / 0.45 \\
\text{VO}_2 + \text{C}_3\text{H}_4 & \quad \text{VO}_2\text{C}_3\text{H}_4 \quad 12\% \ (S5b) \\
\text{VO}_2 + n\text{-C}_3\text{H}_6 & \quad \text{VO}_2\text{C}_3\text{H}_6 \quad 88\% \ (S6a) \quad 1.21 \times 10^5 / 1.16 \\
\text{VO}_2 + n\text{-C}_3\text{H}_4 & \quad \text{VO}_2\text{C}_3\text{H}_4 \quad 80\% \ (S6b) \\
\text{VO}_2 + \text{C}_2\text{H}_4 & \quad \text{VO}_2\text{C}_2\text{H}_4 \quad 12\% \ (S7a) \quad 1.21 \times 10^5 / 1.16 \\
\text{VO}_2 + \text{C}_2\text{H}_6 & \quad \text{VO}_2\text{C}_2\text{H}_6 \quad 80\% \ (S7b) \\
\end{align*}
\]

\[
\begin{align*}
\text{Others} & \quad 3\% \ (S7c) \\
\text{Others} & \quad 5\% \ (S8c) \\
\end{align*}
\]
Fig. S2  Variations of the relative intensities of the reactant and product cations in the reactions between (a) VO$^+$ and n-C$_5$H$_{12}$ with respect to the n-C$_5$H$_{12}$ pressures for 1.3 ms, (b) VO$^+$ and n-C$_7$H$_{16}$ with respect to the n-C$_7$H$_{16}$ pressures for 1 ms, (c) VO$_2^+$ and C$_3$H$_8$ with respect to the C$_3$H$_8$ pressures for 1 ms, (d) VO$_2^+$ and n-C$_5$H$_{12}$ with respect to the n-C$_5$H$_{12}$ pressures for 0.8 ms, (e) VO$_2^+$ and n-C$_7$H$_{16}$ with respect to the n-C$_7$H$_{16}$ pressures for 1 ms, (f) VO$_3^+$ and C$_3$H$_8$ with respect to the C$_3$H$_8$ pressures for 0.8 ms, (g) VO$_3^+$ and n-C$_5$H$_{12}$ with respect to the n-C$_5$H$_{12}$ pressures for 0.8 ms, (h) VO$_3^+$ and n-C$_7$H$_{16}$ with respect to the n-C$_7$H$_{16}$ pressures for 1 ms, (i) VO$^+$ and n-C$_5$H$_{12}$ with respect to the n-C$_5$H$_{12}$ pressures for 0.8 ms, and (j) VO$^+$ and n-C$_7$H$_{16}$ with respect to the n-C$_7$H$_{16}$ pressures for 1 ms.

The solid lines are fitted to the experimental data points derived with the approximation of the pseudo-first-order reaction mechanisms.
Fig. S3  DFT-calculated potential energy surface for the reaction of VO$_2^+$ with n-C$_5$H$_{12}$. Some bond lengths are given in pm. The zero-point vibration corrected energies ($\Delta H_{	ext{ZPE}}$ in eV) of the reaction intermediates, transition states, and products with respect to the separated reactants are given.

The superscripts indicate the spin states.

The PES of path from IS1 to IS2 is similar to that shown in Fig. 4 of the main text, which is not discussed herein. In path a, Intermediate IS4 is formed involves two H atom transfer process through IS2 $\rightarrow$ TS2$'$ $\rightarrow$ IS3 $\rightarrow$ TS3$'$ $\rightarrow$ IS4 and H$_2$ is generated. Through transition state TS4$'$, the HAT process happens with the generation of H$_2$O and yields intermediate IS5. Intermediate IS5 further dissociates into VOC$_5$H$_8^+$ (PA) under the evaporation of H$_2$ and H$_2$O with a barrier of 1.75 eV. In path b, through IS1$\rightarrow$TS1$'$ $\rightarrow$ IS2 $\rightarrow$ TS5$'$ $\rightarrow$ IS6, two hydrogen atoms are successively transferred to two oxygen atoms, respectively. Intermediate IS6 is formed and then dissociates into VO$^+$H$_2^+$ (PB) and C$_5$H$_{10}$. 

Fig. S4  DFT-calculated potential energy surface for the reaction of VO\textsuperscript{3+} with n-C\textsubscript{5}H\textsubscript{12}. Some bond lengths are given in pm. The zero-point vibration corrected energies (\(\Delta H_0\) in eV) of the reaction intermediates, transition states, and products with respect to the separated reactants are given. The superscripts indicate the spin states.

The PES of path from 18 to 19 is same as that shown in Fig. 5 of the main text, which is not discussed herein. As the HAT occurs, resulting in the formation of H\textsubscript{2}O in intermediate IS\textsubscript{7} via TS\textsubscript{6}. Then a H atom in IS\textsubscript{7} transfers from the methylene group to the C atom (IS\textsubscript{7} \(\rightarrow\) TS\textsubscript{7} \(\rightarrow\) IS\textsubscript{8}), generating a C\(\cdots\)O bond in the most stable structure (IS\textsubscript{8}). Through transition state TS\textsubscript{8}, the C\(\cdots\)C bond of intermediate IS\textsubscript{8} ruptures and yields intermediate IS\textsubscript{9}. Intermediate IS\textsubscript{9} has enough energy to dissociate into VO\textsubscript{2}C\textsubscript{2}H\textsubscript{4}\textsuperscript{+} (P\textsubscript{C}), C\textsubscript{3}H\textsubscript{6} and H\textsubscript{2}O.