Supporting information

For

Interaction of vanadium oxide cluster anions with water: an experimental and theoretical study on reactivity and mechanism

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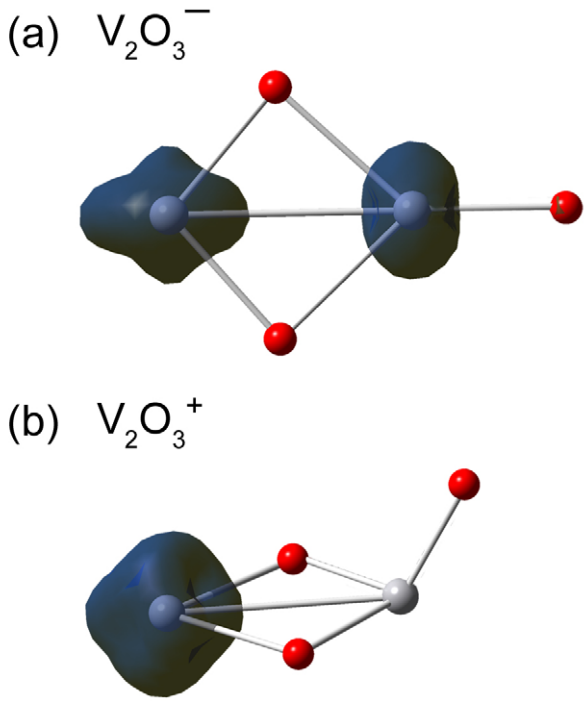

Fig. S1 Spin density distribution of the $V_2O_3^-$ (a) and $V_2O_3^+$ (b) clusters.

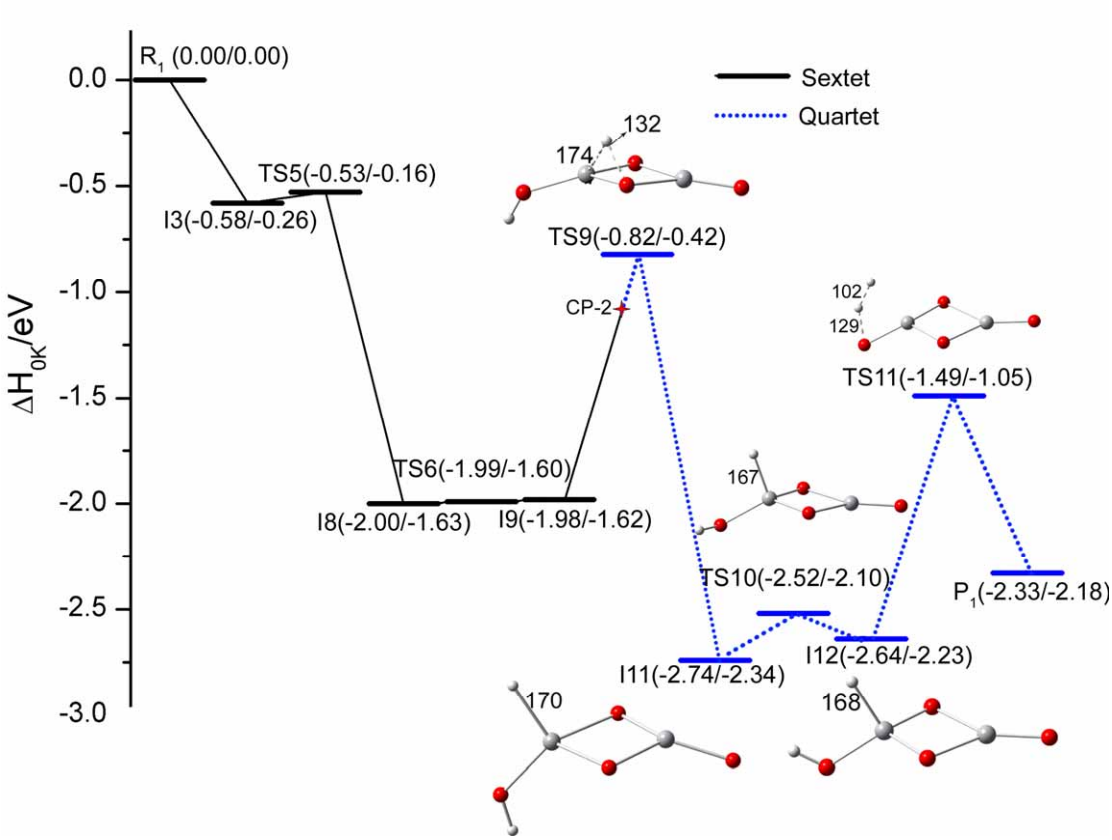

Fig. S2 Density functional theory calculated potential energy profile for $V_2O_3^-$ + H_2O → $V_2O_4^-$ + H_2. The $\Delta H_{0K}/\Delta G_{298K}$ energies in eV with respect to the separated reactants are given in parentheses. A sextet to quartet conversion point is marked with an asterisk and denoted as CP-2. Bond lengths are given in pm.

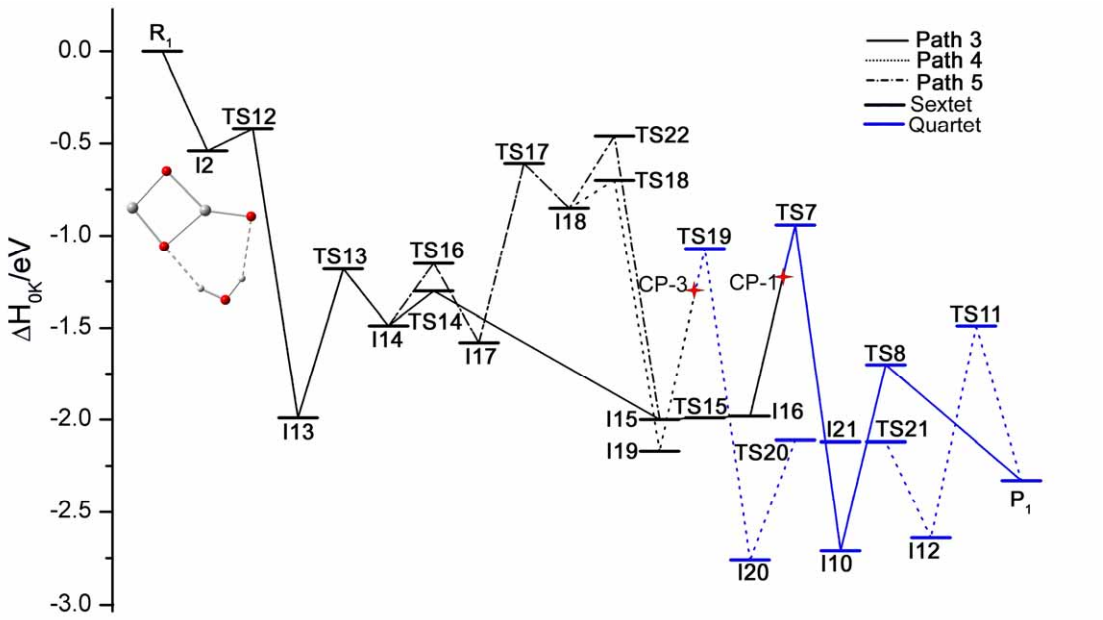

Fig. S3 Potential energy profile following the $V_2O_3^-$ +H_2O →$V_2O_4^-$ +H_2 reaction paths (Path 3 −5) from encounter complex I2.

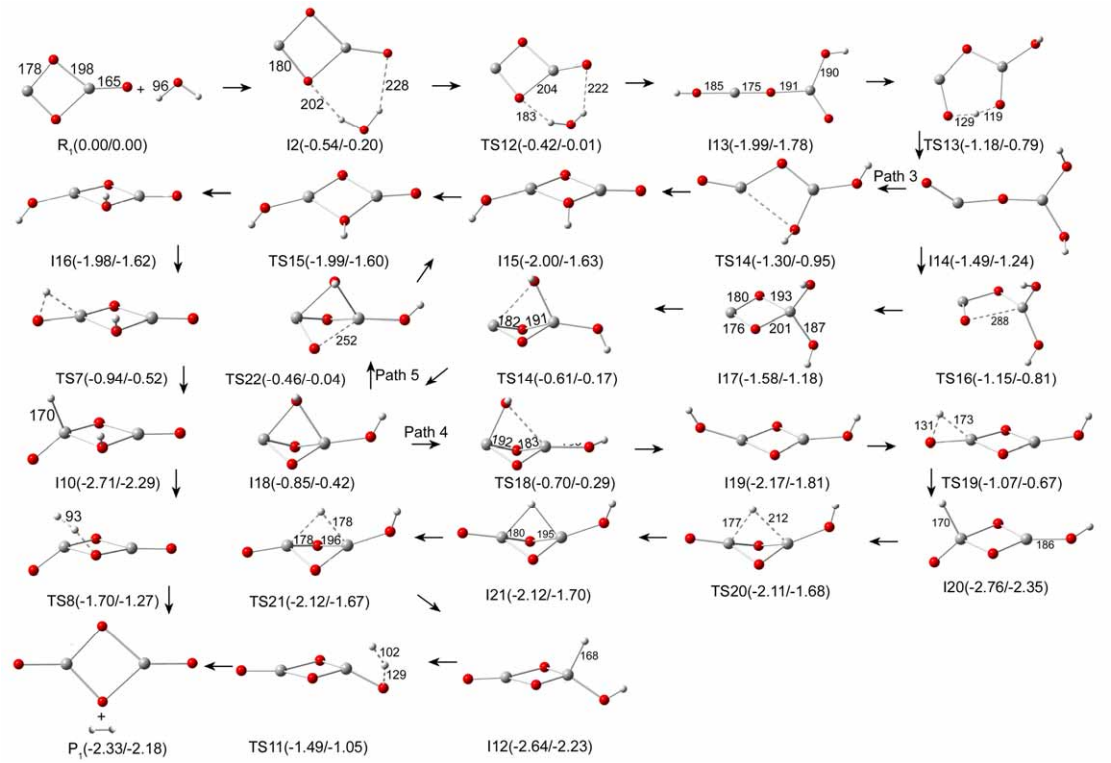

Fig. S4 The optimized structures of the reactants, products, reaction intermediates, and transition states for reaction $V_2O_3^- + H_2O \rightarrow V_2O_4^- + H_2$. The $\Delta H_{0K}/\Delta G_{298K}$ energies in eV with respect to the separated reactants are given in parentheses. Critical bond lengths are given in pm.

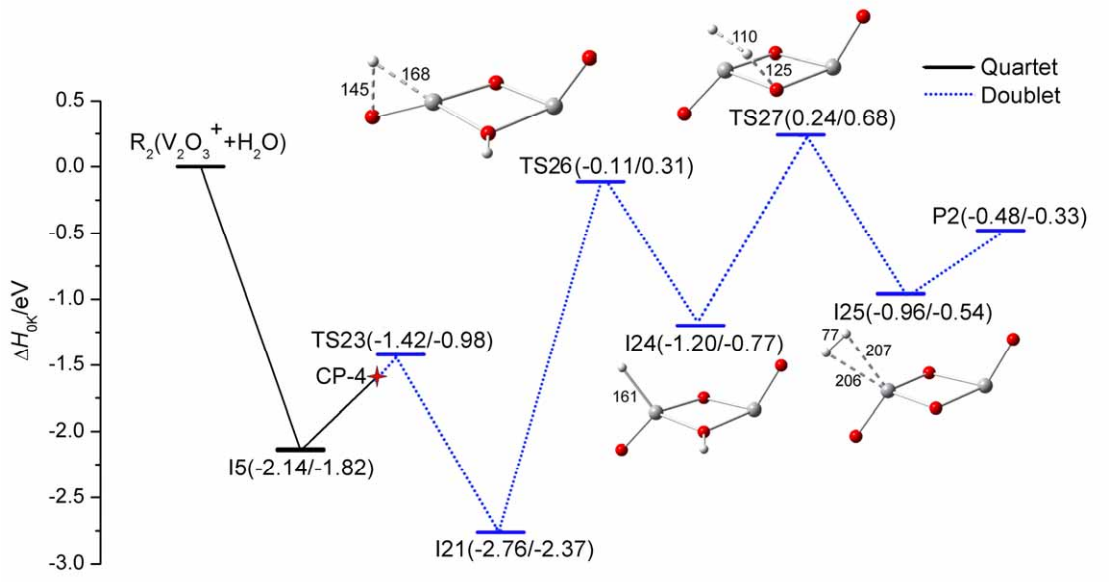

Fig. S5 Density functional theory calculated potential energy profile for $V_2O_3^+ + H_2O \rightarrow V_2O_4^- + H_2$. The $\Delta H_{0K}/\Delta G_{298K}$ energies in eV with respect to the separated reactants are given in parentheses. A sextet to quartet conversion point is marked with an asterisk and denoted as CP-4. Bond lengths are given in pm.

Detailed discussion for the reaction of $V_3{}^{18}O_y^-$ with D_2O is listed below.

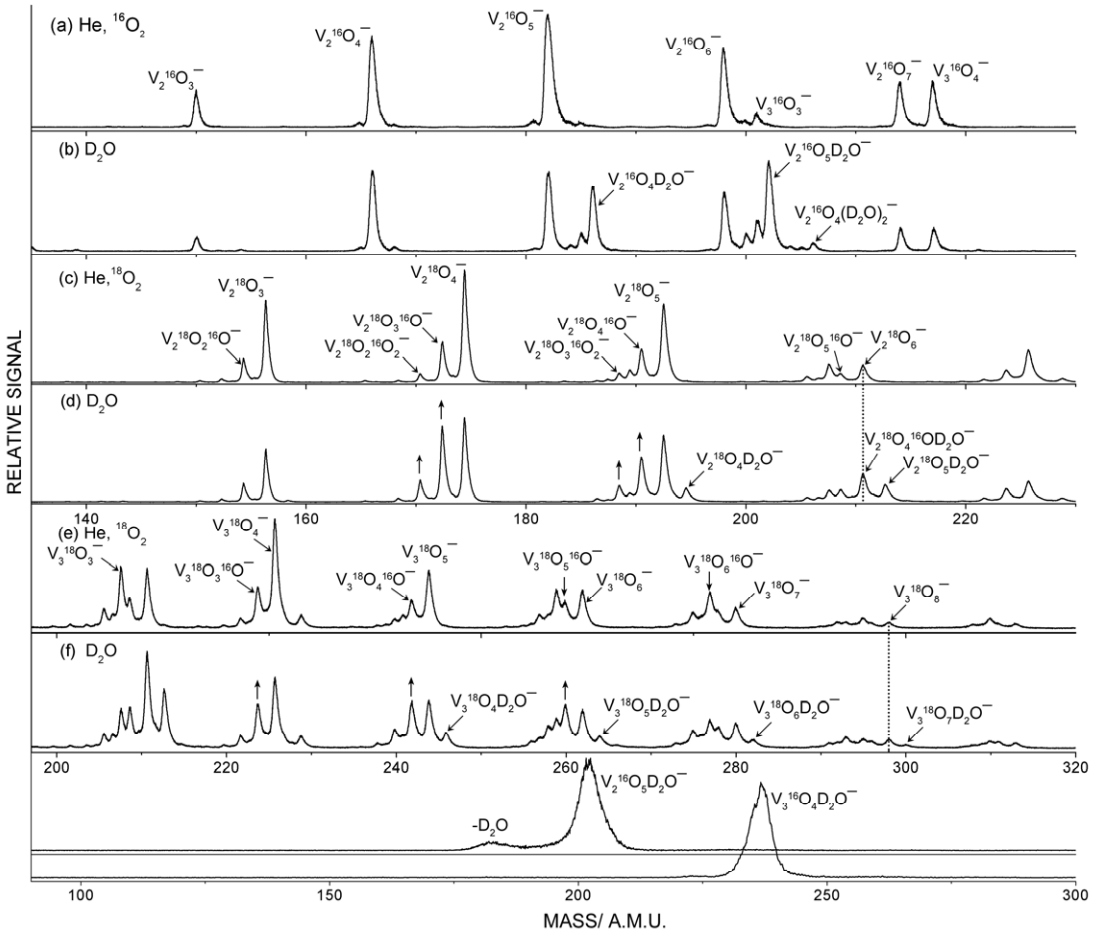

Fig. 1

Fig. 1e and 1f show that the apparent signal decrease of $V_3{}^{18}O_3^-$ and signal increase of $V_3{}^{18}O_3{}^{16}O^-$, and no appearance of water association product $V_3{}^{18}O_3D_2O^-$ indicate that the D_2 elimination is the only reaction channel for $V_3{}^{18}O_3^-$ with D_2O. For $V_3{}^{18}O_4^-$ and $V_3{}^{18}O_5^-$, both signals of $V_3{}^{18}O_{4,5}{}^{16}O^-$ increase and the water association product $V_3{}^{18}O_{4,5}D_2O^-$ appear, which indicates that both the D_2 elimination and D_2O association channels are possible for $V_3{}^{18}O_4^-$ and $V_3{}^{18}O_5^-$. Fig. 1f also shows that the water association peaks $V_3{}^{18}O_{6,7}D_2O^-$ appeare and the increase of $V_3{}^{18}O_{6,7}{}^{16}O^-$ can be negligible, which reveals the only water association channel for $V_3{}^{18}O_6^-$ and $V_3{}^{18}O_7^-$. The reaction of $V_3{}^{18}O_8^-$ with water can not be observed in the experiment.