Supporting information for

Insight into the stereoselectivity of TS-1 in epoxidation of cis/trans-2-hexene: a computational study

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Contents:

Scheme S1 Generation processes of Ti-hydroperoxo intermediates and the equations for calculation of the formation energies of the Ti-hydroperoxo intermediates.

Table S1 The total electronic energies of optimized molecules and models at the theoretical level of ωB97XD/6-31G(d, p).

Fig. S1 Optimized transition state structures of cis-2-hexene (a-d) and trans-2-hexene (e-f) on different active centers: (a, e) Ti-η{sup}(OOH), (b, f) Ti-η{sup}(OOH)-H_2O, (c, g) Ti-η{sub}(OOH)-(H_β)H_2O, and (d, h) Ti-η{sub}(OOH)-H_2O-(H_β)H_2O.

Fig. S2 Optimized structures of the epoxide products of cis-2-hexene (a-d) and trans-2-hexene (e-f) adsorbed on different active centers: (a, e) Ti-η{sup}(OOH), (b, f) Ti-η{sup}(OOH)-H_2O, (c, g) Ti-η{sup}(OOH)-(H_β)H_2O, and (d, h) Ti-η{sup}(OOH)-H_2O-(H_β)H_2O.
Scheme S1 Generation processes of Ti-hydroperoxo intermediate in TS-1/H2O2/H2O.

The formation energies of the Ti-hydroperoxo intermediates are calculated according to following equations: (1) for Ti-$\eta^2$(OOH); (2) for Ti-$\eta^2$(OOH)-H2O; (3) for Ti-$\eta^2$(OOH)-(Hβ)H2O; (4) for Ti-$\eta^2$(OOH)-H2O-(Hβ)H2O.

\[
\Delta E = E[\text{Ti-}\eta^2(\text{OOH})] + E(\text{H}_2\text{O}) - E(\text{Ti-\text{OH}}) - E(\text{H}_2\text{O}_2) \quad (1)
\]

\[
\Delta E = E[\text{Ti-}\eta^2(\text{OOH})-\text{H}_2\text{O}] - E(\text{Ti-\text{OH}}) - E(\text{H}_2\text{O}_2) \quad (2)
\]

\[
\Delta E = E[\text{Ti-}\eta^2(\text{OOH})-(\text{H}_\beta)\text{H}_2\text{O}] - E(\text{Ti-\text{OH}}) - E(\text{H}_2\text{O}_2) \quad (3)
\]

\[
\Delta E = E[\text{Ti-}\eta^2(\text{OOH})-\text{H}_2\text{O}-(\text{H}_\beta)\text{H}_2\text{O}] - E(\text{Ti-\text{OH}}) - E(\text{H}_2\text{O}_2) - E(\text{H}_2\text{O}) \quad (4)
\]

Here, $E(\text{H}_2\text{O})$ and $E(\text{H}_2\text{O}_2)$ are the total electronic energies of optimized H2O and H2O2 molecules, respectively, and $E(\text{Ti-\text{OH}})$, $E[\text{Ti-}\eta^2(\text{OOH})]$, $E[\text{Ti-}\eta^2(\text{OOH})-\text{H}_2\text{O}]$, and $E[\text{Ti-}\eta^2(\text{OOH})-(\text{H}_\beta)\text{H}_2\text{O}]$ denote the total electronic energies of optimized models (136T) for Ti-OH, Ti-$\eta^2$(OOH), Ti-$\eta^2$(OOH)-H2O, and Ti-$\eta^2$(OOH)-(Hβ)H2O, respectively.

Table S1 The total electronic energies of optimized molecules and models at the theoretical level of oB97XD/6-31G(d, p).

<table>
<thead>
<tr>
<th>Model</th>
<th>Energy (a.u.)</th>
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<tbody>
<tr>
<td>H2O</td>
<td>-76.39790</td>
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<td>H2O2</td>
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<td>Ti-OH</td>
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<td>Ti-$\eta^2$(OOH)</td>
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<td>Ti-$\eta^2$(OOH)-(Hβ)H2O</td>
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<tr>
<td>Ti-$\eta^2$(OOH)-H2O-(Hβ)H2O</td>
<td>-57750.95010</td>
</tr>
</tbody>
</table>
Fig. S1  Optimized transition state structures of *cis*-2-hexene (a-d) and *trans*-2-hexene (e-f) on different active centers: (a, e) Ti-$\eta^2$(OOH), (b, f) Ti-$\eta^2$(OOH)-$\text{H}_2$O, (c, g) Ti-$\eta^2$(OOH)-(H$_\beta$)H$_2$O, and (d, h) Ti-$\eta^2$(OOH)-H$_2$O-(H$_\beta$)H$_2$O.
Fig. S2 Optimized structures of the epoxide products of cis-2-hexene (a-d) and trans-2-hexene (e-f) adsorbed on different active centers: (a, e) Ti-η²(OOH), (b, f) Ti-η²(OOH)-H₂O, (c, g) Ti-η²(OOH)-(H₂)H₂O (Hβ)H₂O, and (d, h) Ti-η²(OOH)-H₂O-(Hβ)H₂O.