Supporting information for

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

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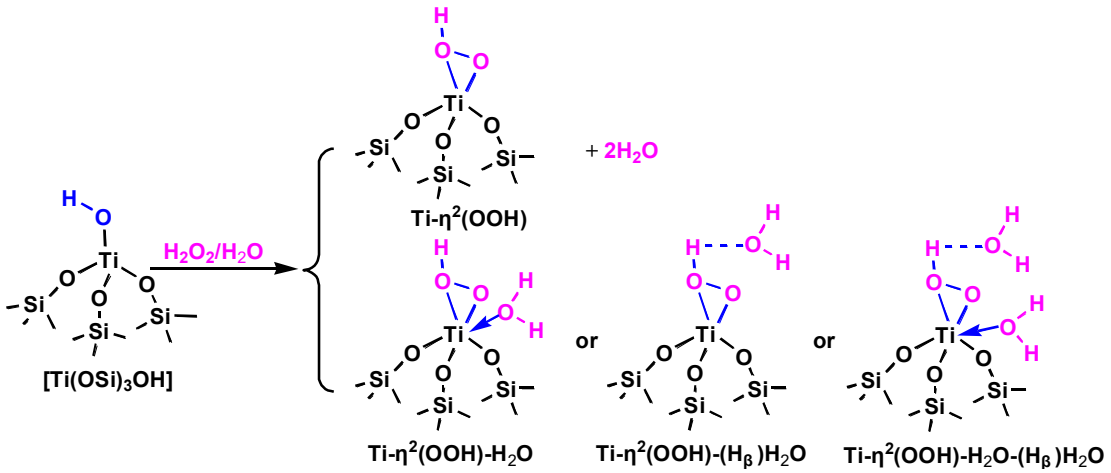

Scheme S1 Generation processes of Ti-hydroperoxo intermediate in TS-1/H_2O_2/H_2O.

The formation energies of the Ti-hydroperoxo intermediates are calculated according to following equations: (1) for Ti-η^2(OOH); (2) for Ti-η^2(OOH)-H_2O; (3) for Ti-η^2(OOH)-(H_β)H_2O; (4) for Ti-η^2(OOH)-H_2O-(H_β)H_2O.

$$\Delta E = E[\text{Ti-}\eta^2\text{(OOH)}] + E(H_2O) - E(\text{Ti-OH}) - E(H_2O_2) \quad (1)$$

$$\Delta E = E[\text{Ti-}\eta^2\text{(OOH)-}H_2O] - E(\text{Ti-OH}) - E(H_2O_2) \quad (2)$$

$$\Delta E = E[\text{Ti-}\eta^2\text{(OOH)-}(H_\beta)H_2O] - E(\text{Ti-OH}) - E(H_2O_2) \quad (3)$$

$$\Delta E = E[\text{Ti-}\eta^2\text{(OOH)-}H_2O\text{-}(H_\beta)H_2O] - E(\text{Ti-OH}) - E(H_2O_2) - E(H_2O) \quad (4)$$

Here, $E(H_2O)$ and $E(H_2O_2)$ are the total electronic energies of optimized H_2O and H_2O_2 molecules, respectively, and E(Ti-OH), E[Ti-η^2(OOH)], E[Ti-η^2(OOH)-H_2O], and E[Ti-η^2(OOH)-(H_β)H_2O] denote the total electronic energies of optimized models (136T) for Ti-OH, Ti-η^2(OOH), Ti-η^2(OOH)-H_2O, and Ti-η^2(OOH)-(H_β)H_2O, respectively.

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

Model	Energy (a.u.)
H_2O	-76.39790
H_2O_2	-151.49520
Ti-OH	-57522.97953
Ti-η^2(OOH)	-57598.08494
Ti-η^2(OOH)-H_2O	-57674.52100
Ti-η^2(OOH)-(H_β)H_2O	-57674.51584
Ti-η^2(OOH)-H_2O-(H_β)H_2O	-57750.95010

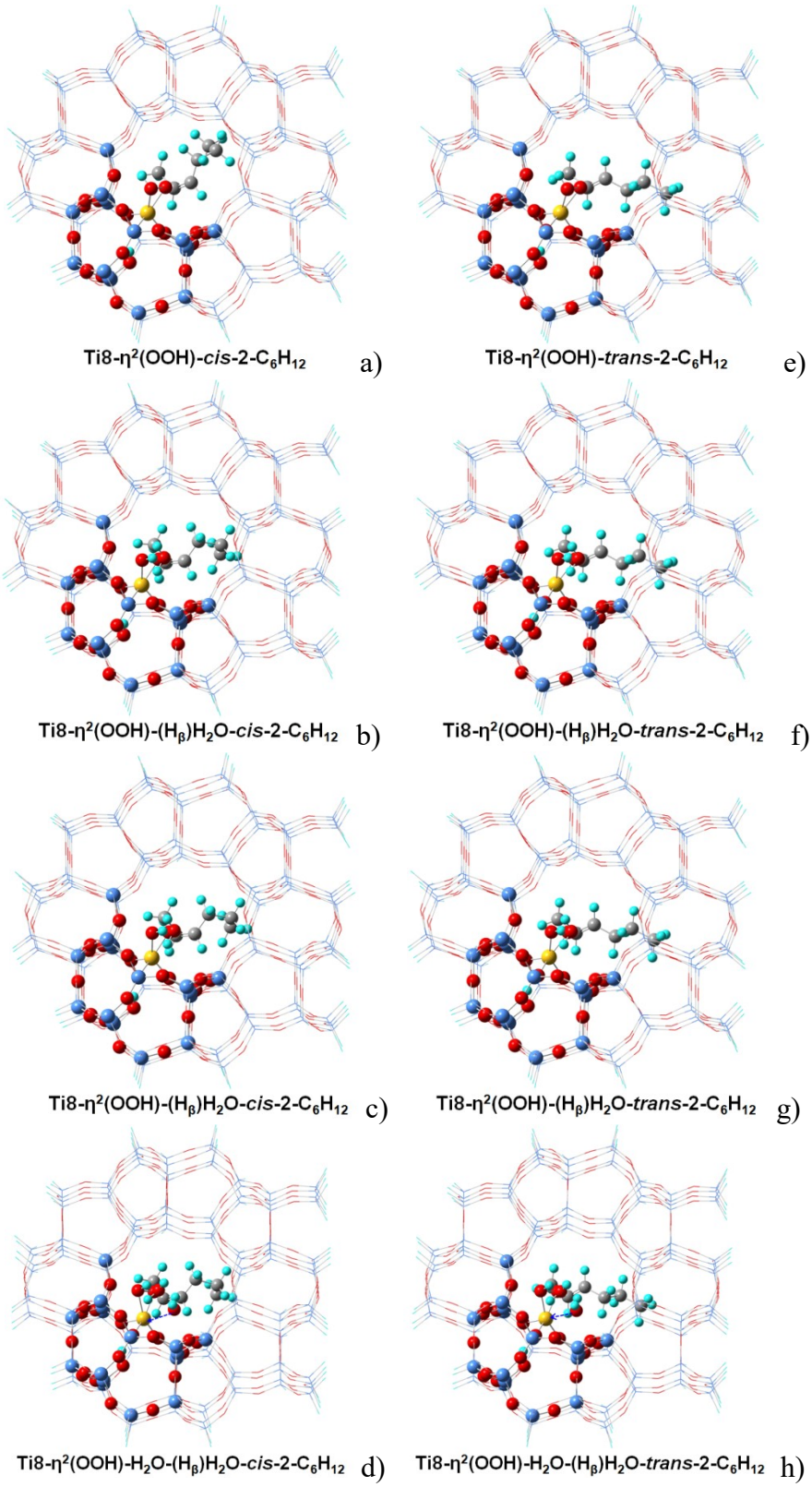

Fig. S1 Optimized transition state structures of *cis*-2-hexene (a-d) and *trans*-2-hexene (e-f) on different active centers: (a, e) Ti-η^2(OOH), (b, f) Ti-η^2(OOH)-H_2O, (c, g) Ti-η^2(OOH)-(H_β)H_2O, and (d, h) Ti-η^2(OOH)-H_2O-(H_β)H_2O.

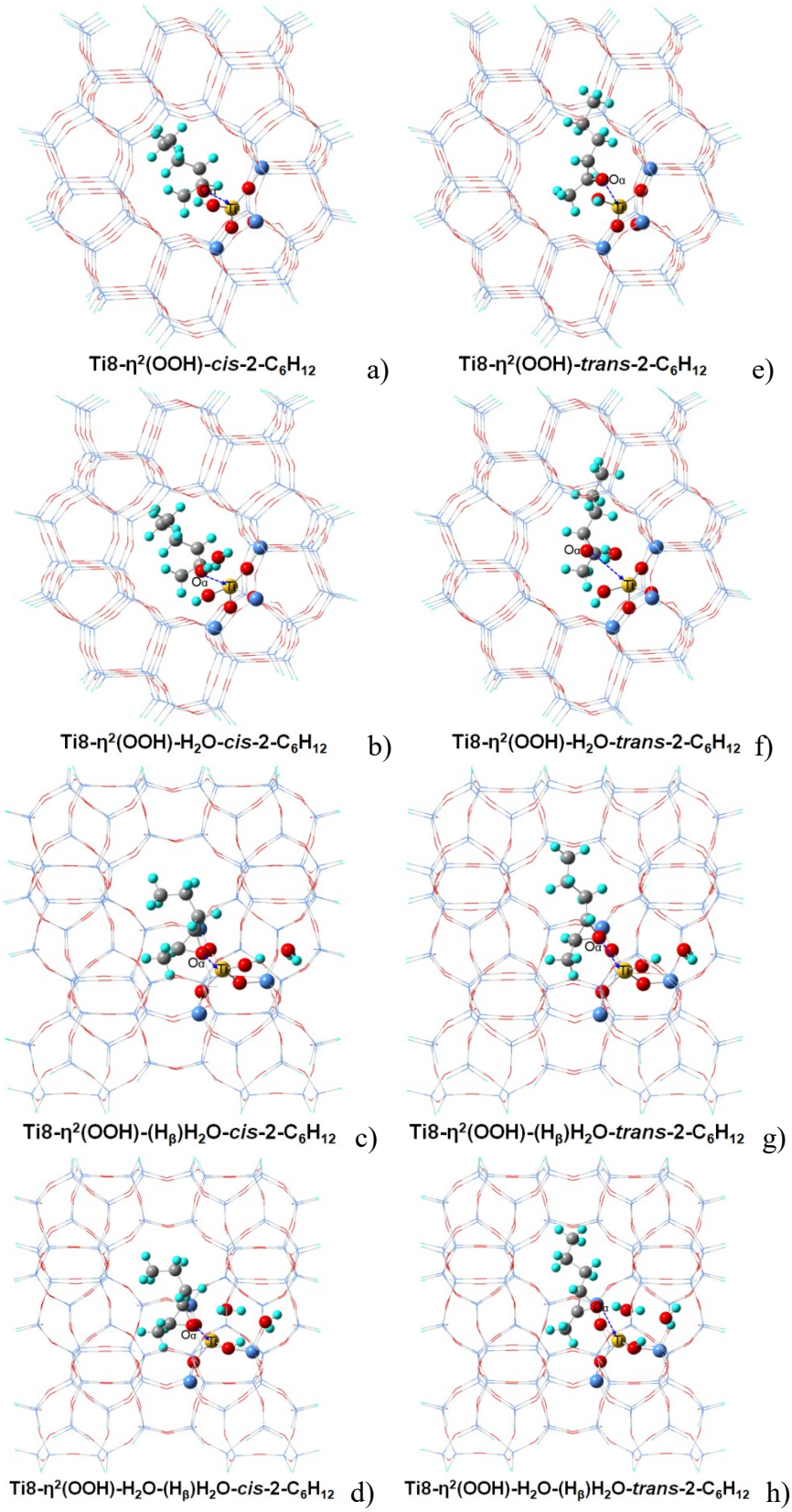

Fig. S2 Optimized structures of the epoxide products of *cis*-2-hexene (a-d) and *trans*-2-hexene (e-f) adsorbed on different active centers: (a, e) Ti-η^2(OOH), (b, f) Ti-η^2(OOH)-H_2O, (c, g) Ti-η^2(OOH)-(H_β)H_2O, and (d, h) Ti-η^2(OOH)-H_2O-(H_β)H_2O.