Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information for

Structure and catalytic cctivity of a newly proposed titanium species in Ti-YNU-1 zeolite: a density functional theory study

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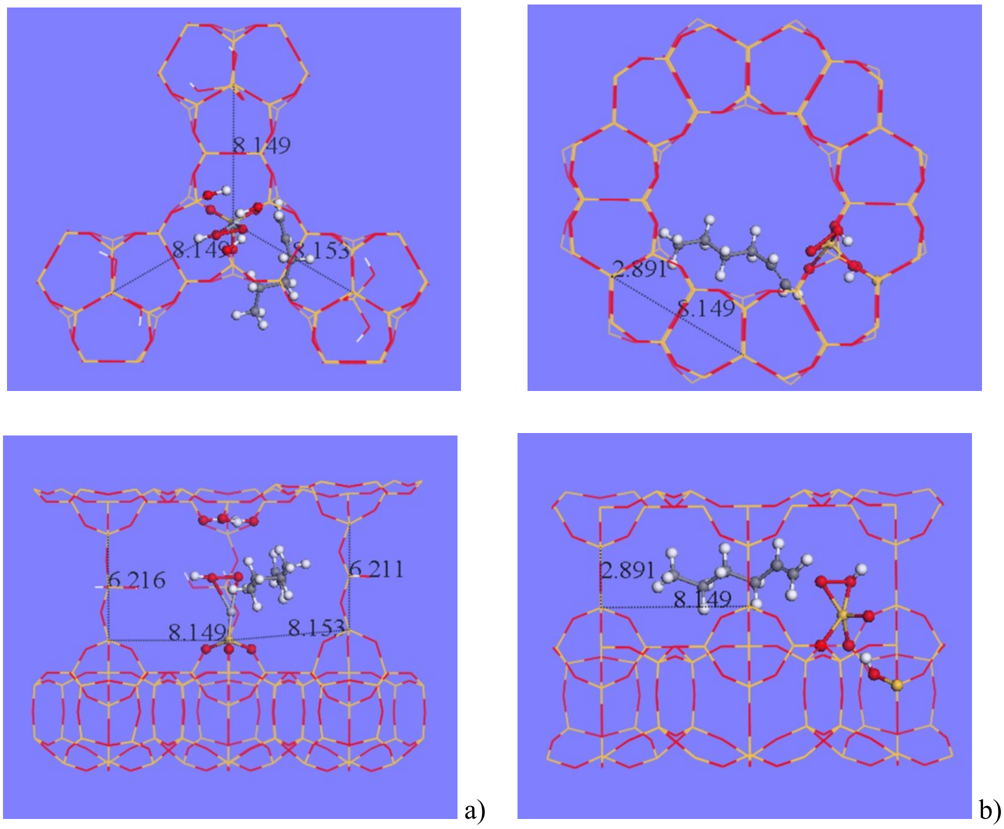
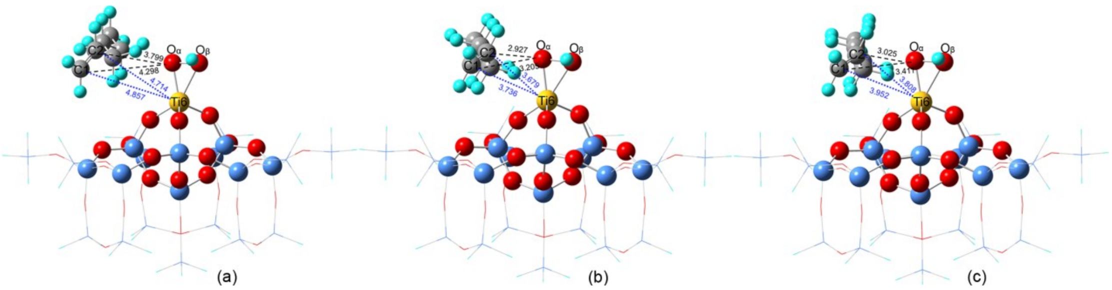


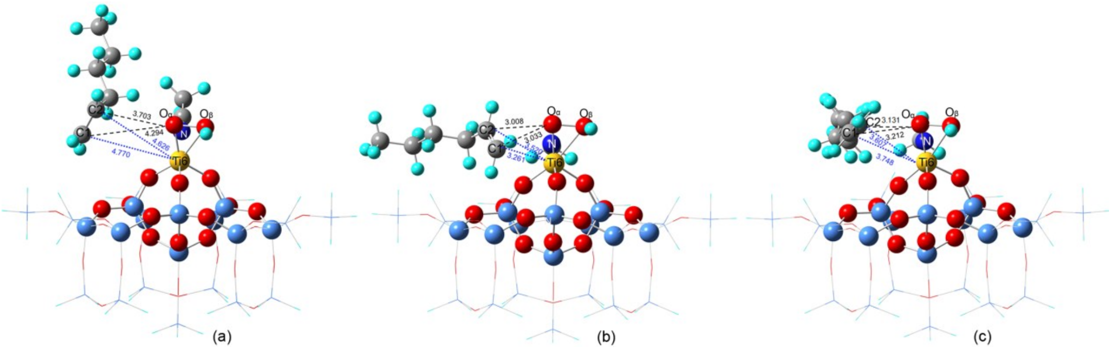
Figure S1 Schematic drawings for the locations of the transition state complex in the framework of a) Ti-YUN-1 and b) Ti-MWW zeolites illustrated as top view (up) and side view (down).

In Ti-YUN-1 zeolite, the Ti6-η^2(OOH) species is located at a defective pillar site in the intersection between three 12-MR supercages. In Ti-MWW zeolite, the Ti1-η^2(OOH) species is located at the rim of the 12-MR supercage, and the transition state complex inserts into the intersection between the 12-MR supercage and the 10-MR channel window. There are huge spaces for the reaction, and the confinement of framework on the transition state complexes would be negligible.

Ti6-η^2(OOH)



Ti6-η^2(OOH)-CH_3CN



Ti6-η^2(OOH)-H_2O

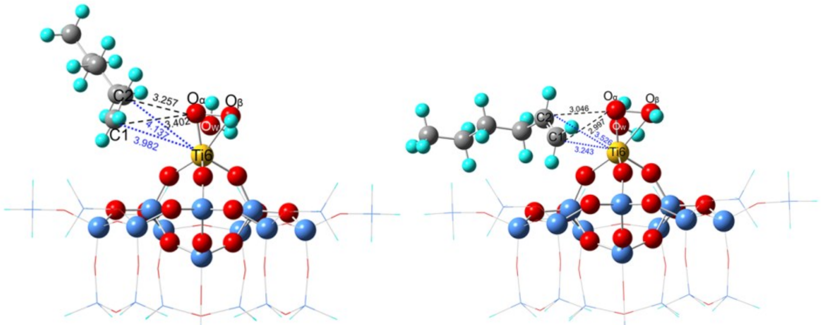


Figure S2 Optimized structures of the adsorption complexes of 1-hexene on Ti6-η^2(OOH), Ti6-η^2(OOH)-CH_3CN, and Ti6-η^2(OOH)-H_2O active centers calculated at different theoretical levels: a) B3LYP; b) B3LYP-D3; c) wB97XD. The 6-31G(d,p) basis set was selected for all atoms. All distances are given in Å unit.

Table S1 Adsorption energies of 1-hexene on different active centers calculated at different calculated at different theoretical levelswith the basis set 6-31G(d,p) for all atoms (energy in kJ/mol).

active center	B3LYP	B3LYP-D3	ωB97XD
Ti6-η^2(OOH)	−8.2 (3.0)[a]	−53.2 (−34.7)	− 40.3 (−25.5)
Ti6-η^2(OOH)-H_2O	−7.6 (3.7)	−65.3 (−41.2)	---
Ti6-η^2(OOH)-CH_3CN	−7.0 (4.3)	−64.1 (−41.3)	−47.5 (−32.4)

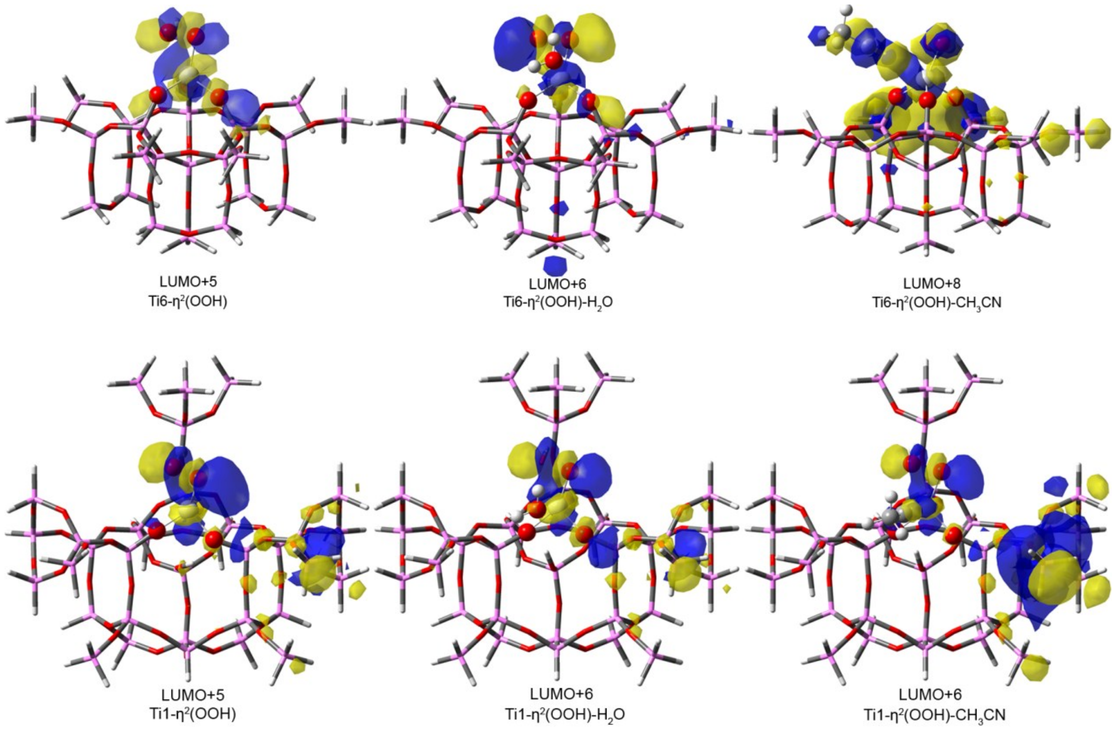
[a]Data in parenthesis are the adsorption energies corrected with BSSE.

Table S2. The adsorption energies and activation barriers of 1-hexene epoxidation over Ti6-η^2(OOH) active center calculated at different theoretical levels (energy in kJ/mol).

	[a]E_R	ΔE_{ads}	ΔE_{TS}(re. rea)	ΔE_{TS}(re. ads)
B3LYP	(0.0)	−8.2	33.5	41.7
B3LYP-D3	(0.0)	−53.2	−21.6	31.6
ωB97XD	(0.0)	−40.3	23.2	63.5

[a]E_R is the sum of the electronic energies of the model of Ti6-η^2(OOH) and that of 1-hexene.

For the adsorption complex optimized at B3LYP level, the shortest distances from C=C double bond to O_α and Ti are 3.799 and 4.714 Å, respectively, and the adsorption energy is only −8.2 kJ/mol (Table S1), indicating a weak physisorption between 1-hexene and the Ti6-η^2(OOH) active center. Optimizing with the B3LYP-D3 and ωB97XD functionals containing dispersion correction, the 1-hexene molecule is closer to the Ti6-η^2(OOH) active center, and the shortest distances from C=C double bond to O_α / Ti are 2.927 / 3.679 Å at B3LYP-D3 and 3.025/ 3.808 Å at ωB97XD , respectively. The adsorption energies are −53.2 and −40.3 kJ/mol, respectively, which are much larger than that from B3LYP, indicating the effect of dispersion force. With respect to the activation energies, the intrinsic activation energy, ΔE_{TS} (re. ads), at B3LYP-D3 level is 31.6 kJ/mol, lower than that of B3LYP by 10 kJ/mol, but similar to the apparent activation energy ΔE_{TS} (re. rea) of B3LYP. The ωB97XD functional overestimates the intrinsic activation energy.



LUMO+5 Ti6-η^2(OOH)

LUMO+6 Ti6-η^2(OOH)-H_2O

LUMO+8 Ti6-η^2(OOH)-CH_3CN

LUMO+5 Ti1-η^2(OOH)

LUMO+6 Ti1-η^2(OOH)-H_2O

LUMO+6 Ti1-η^2(OOH)-CH_3CN

Figure S3 Contours of the $\sigma(O_\alpha{-}O_\beta)$ antibonding orbital in different Ti-hydroperoxo intermediates (isovalue: 0.02).

Table S3 The frontier molecular orbital energies of the Ti hydroperoxo intermediates and 1-hexene, the energy gaps between σ*(O_α–O_β) and HOMO of 1-hexene, and the activation barriers calculated at B3LYP/6-31G(d,p).

	FMO	*E*(a.u.)	σ*(O_α–O_β)	*E*(a.u.)	ΔE_{gap} (eV)	ΔE_{TS} (kJ/mol)
Ti6-η^2(OOH)	LUMO	−0.093	LUMO +6	−0.021	6.12	33.5
Ti6-η^2(OOH)-H_2O	LUMO	−0.091	LUMO +5	−0.014	6.40	35.1
Ti6-η^2(OOH)-CH_3CN	LUMO	−0.087	LUMO +8	−0.003	6.70	43.9
Ti1-η^2(OOH)	LUMO	−0.084	LUMO +5	−0.016	6.34	28.1
Ti1-η^2(OOH)-H_2O	LUMO	−0.083	LUMO +6	−0.011	6.48	45.4
Ti1-η^2(OOH)-CH_3CN	LUMO	−0.083	LUMO +6	−0.008	6.56	52.3
Ti1-η^1(OOH)	LUMO	−0.081	LUMO +5	−0.020	6.23	107.2
1-hexene			HOMO	−0.249	–	–