

Efficient epoxidation over dinuclear sites in Titanium Silicalite-1

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Titanium Silicalite-1 (TS-1) shows an outstanding ability to catalytically epoxidize olefins with hydrogen peroxide (H₂O₂), leaving only water as byproduct.^{1,2} Despite the industrial use of the TS-1/H₂O₂ system for the production of more than one million tons of propylene oxide per year,³ the active site structure remains elusive, although it has been studied for almost 40 years by spectroscopic and computational methods.⁴⁻¹⁰ TS-1 is a zeotype of MFI structure in which a small fraction of Si-atoms (1-2 %) are substituted by Ti, and its catalytic properties are generally attributed to isolated Ti(IV) sites.¹ Herein, we analyze a series of highly active and selective TS-1 propylene epoxidation catalysts. By UV-Vis and Raman spectroscopy, as well as electron microscopy, we show that Ti is well-dispersed in all samples, with formation of small TiO_x clusters at high Ti-loadings. Most notably, irrespective of Ti-content, all samples show a characteristic solid-state ¹⁷O NMR signature when contacted with H₂¹⁷O₂, indicating the formation of bridging peroxo species on dinuclear Ti-sites. Using DFT (density functional theory) calculations, we propose a mechanism of propylene epoxidation on a dinuclear site, in which the cooperativity between two titanium atoms enables a low-energy reaction pathway where the key oxygen-transfer transition state bears strong resemblance to that of olefin epoxidation by peracids.

The active species in TS-1 are commonly proposed to be isolated Ti(IV) sites bearing peroxo¹¹ or hydroperoxo moieties,¹² although the involvement of terminal Ti-oxo and activated H₂O₂ on Ti(IV) has also been discussed (Fig. 1a,b).⁷ In contrast, the only homogeneous Ti-based epoxidation catalysts able to efficiently utilize H₂O₂ as primary oxidant are dinuclear, such as the Berkessel-Katsuki epoxidation catalyst **1** (Fig. 1c).¹⁴⁻¹⁹ While the structural characterization of molecular systems is well-established and has enabled the isolation of peroxo compounds,

obtaining information on the structure of Ti-sites in TS-1 with molecular-level precision has proven more challenging.

Recent work by some of us has shown that solid-state ^{17}O NMR spectroscopy is a powerful tool for understanding and assessing the reactivity of peroxo species.²⁰ Oxygen-17 is an NMR-active quadrupolar nucleus whose spectroscopic properties can be readily measured by solid-state NMR and computed by DFT. The NMR signature (chemical shift and quadrupolar coupling) is highly sensitive to the symmetry and electronic structure around the oxygen atoms. We thus reasoned that ^{17}O NMR spectroscopy would be a valuable tool to harness the signature of the active sites in TS-1 and thereby probe their structure. In this study, we investigate five TS-1 samples prepared in the BASF laboratories (Table 1).^{21,22} Two of these samples have a Ti-content of 1.9 wt%, one of which was prepared on hundred-kg scale (sample 1), the other three samples have Ti-loadings of 1.5 wt%, 1.0 wt%, and 0.5 wt%. The five samples have surface areas between 442 and 471 m^2g^{-1} and show typical MFI-structures, as confirmed by powder XRD (Extended Data Fig. 4). Importantly, irrespective of the Ti-content, all samples show high selectivity in propylene epoxidation (91-96%), thus maximizing the chances to capture the signature of species relevant to this reaction (see Methods for the detailed catalyst preparation, characterization, and catalytic testing). As we show in the next section, by ^{17}O NMR spectroscopy we evidence the activation of H_2O_2 on non-isolated sites in these TS-1 samples (Fig. 1d).

Spectroscopic investigations

The TS-1 samples^{21,22} were contacted with ^{17}O -labelled H_2O_2 under ambient conditions,²³ and studied by solid-state ^{17}O NMR spectroscopy at 100 K (Fig. 2a,b and Extended Data Fig. 1). This approach allows for the observation of reaction intermediates that originate from the activation of $\text{H}_2^{17}\text{O}_2$, while possible signal averaging due to dynamics is avoided at low temperature. The solid-state ^{17}O NMR spectra of $\text{H}_2^{17}\text{O}_2$ (Fig. 2e) and H_2^{17}O (Extended Data Fig. 1f) were also recorded as these molecules could likely be present in the catalyst sample. The solid-state NMR spectra of TS-1 at various Ti-loadings contacted with one equivalent (with respect to Ti) of a 1.6 M $\text{H}_2^{17}\text{O}_2$ solution for 2-3 hours show that $\text{H}_2^{17}\text{O}_2$ fully reacted in all cases and that two new main signals of comparable intensity appeared (Fig. 2a,b). One of them shows a relatively large anisotropy, indicating a rather anisotropic chemical shift tensor and/or a large quadrupolar coupling constant (C_Q), while the other signal shows a small C_Q and resembles the signal expected for H_2O or hydroxo species. This signature is related to the

presence of Ti in TS-1 since contacting a Ti-free MFI silicalite with H₂¹⁷O₂ only leads to the observation of the ¹⁷O NMR signature of H₂¹⁷O₂ (Extended Data Fig. 9).

To assign the observed ¹⁷O NMR signal, we investigated the ¹⁷O NMR signatures of various proposed intermediates in the TS-1/H₂O₂ system by DFT calculations. Indeed, the calculated signatures of H₂O, H₂O₂ and **1-O₂** (Extended Data Fig. 1f, Fig. 2e, Fig. 2c, red line) reproduce very well the observed spectra, confirming that DFT calculations are suitable for that purpose. The DFT calculated signatures of mononuclear Ti-sites with oxo- and hydroxo-ligands (Fig. 2f) show much smaller anisotropies compared to the experimental spectrum of TS-1 contacted with H₂¹⁷O₂. On the other hand, side-on peroxo (Fig. 2g) or side-on hydroperoxo ligands (Fig. 2h) show significantly broader spectral signatures (see Extended Data Fig. 8 for further models including isolated sites in a defective zeolite framework). The unique feature observed in the experimental spectra (Fig. 2a,b) indicates the presence of a peroxo species whose oxygen atoms are in a rather symmetric environment. A probable assignment is a dinuclear Ti-peroxo species that resembles the side-on peroxo species (**1-O₂**) of the corresponding homogeneous dinuclear Ti-salalen epoxidation catalyst **1** (Fig. 1c), which indeed shows a similar experimental and calculated NMR signature (Fig. 2c). Indeed, the calculated signature of a dinuclear peroxo species in the MFI framework and H₂O matches the experimental spectra well (Fig. 2d).

Notably, the characteristic ¹⁷O NMR signature that we ascribe to the presence of non-isolated Ti-sites is observed irrespective of the Ti-loading (Extended Data Fig. 1). Even though the presented NMR spectra do not allow for accurate quantification, the observed dinuclear sites account for a significant amount of the ¹⁷O signal, suggesting that a large part of the titanium is present in non-isolated form. Even the TS-1 sample with only 0.5 wt% Ti shows a large amount of bridging peroxo species, suggesting that the presence of non-isolated sites is not due to the statistical distribution of Ti-atoms but is rather intrinsic to the incorporation of Ti in TS-1 during synthesis. This might in fact not be surprising, given that the molecular Ti-precursor used in the synthesis (tetraethyl orthotitanate) is known to form di- or tri-nuclear species in solution.²⁴

We additionally examined the UV-Vis spectrum of the TS-1 samples (Fig. 3a). Apart from an absorption below ca. 300 nm, that is typically attributed to charge transfer bands of Ti-sites, the UV-Vis spectra of the TS-1 samples with 1.5 wt% and 1.9 wt% Ti show a pronounced feature with a maximum at ca. 320 nm, which is absent in the samples with 0.5 wt% and 1.0 wt% Ti-loading. Such features are usually attributed to TiO_x agglomerates or anatase. We thus

further probed the presence of TiO_x clusters by Raman spectroscopy at 325 nm (Fig. 3b), since this wavelength yields resonance enhancement of signals associated with such clusters. Consistent with UV-Vis, the samples with 1.5 and 1.9 wt% Ti-loading show Raman modes at 149, 200, 398, 521, and 640 cm^{-1} , which likely originate from TiO_x clusters and are absent in the samples with lower loading, and small in one of the samples containing 1.9 wt% Ti (sample 1). Without resonance enhancement of TiO_x clusters (at 266 nm), all samples show similar Raman bands, independent of Ti-loading (Extended Data Fig. 5). By Powder XRD (Extended Data Fig. 4), traces of anatase could only be detected in sample 2 (with 1.9 wt% Ti), indicating that the TiO_x clusters in the other samples are small and/or amorphous. Further investigation by STEM-EDX (Scanning Transmission Electron Microscopy-Energy Dispersive X-ray Fig. 3c,d and Extended Data Fig. 2) revealed that, while overall Ti is well-distributed in all samples, small additional clusters are present in samples with loadings above 1.5 wt% Ti, consistent with UV-Vis and Raman spectroscopies. In addition, HR-TEM images of bulk and surface suggest some TiO_x agglomeration on the surface of the 1.5 wt% sample, which is absent in the sample with 1.0 wt% Ti (Extended Data Fig. 3). Overall, the complementary spectroscopic techniques described above indicate that all investigated samples (independent of their Ti-content and the presence of clusters) display one common spectroscopic signature: a characteristic signal in ^{17}O NMR spectroscopy that is consistent with a peroxo species as found in the molecular complex **1-O₂**, i.e. a $\mu^2\eta^2$ -peroxo species sandwiched in a dinuclear Ti site.

Epoxidation mechanism in TS-1

With strong spectroscopic evidence of dinuclear Ti-sites in TS-1, capable of activating H_2O_2 , we employed periodic DFT calculations to model the possible structure and reactivity of such an active site. Studies based on neutron diffraction suggest that Ti-atoms in TS-1 are mostly located in T6, T7 and T11 sites.²⁵ We thus modeled an MFI structure with Ti-substitution at the adjacent T7 and T11 positions as a prototypical dinuclear site and explored potential epoxidation pathways with this system.

The peroxo-species observed by ^{17}O NMR spectroscopy, generated from TS-1 and H_2O_2 , is stable for hours and hence likely a resting state of the catalyst. By analogy with the molecular peroxo-complex **1-O₂**, this structure is a $\mu^2\eta^2$ -peroxo-species with a bridging water molecule. The formation of this species (**TS1-O₂**) from the initial oxo (**TS1-O**) and H_2O_2 is very favorable with a reaction energy ΔE of -31.4 kcal mol^{-1} with respect to separated reactants, consistent with its observation by NMR (all energies and structures are given in Fig. 4a). The calculated

transition state energy for O-transfer (epoxidation of propylene) directly from this intermediate is relatively high ($\Delta E = 17.4 \text{ kcal mol}^{-1}$). **TS1-O₂** is hence not expected to significantly contribute to the epoxidation activity, in analogy to the molecular species **1-O₂**, which is inactive in epoxidation in the absence of H₂O₂.¹⁶ Indeed, by reaction with additional H₂O₂, **TS1-O₂** can form a bis-hydroperoxo species (**TS1-(OOH)₂**), which is only slightly higher in energy with respect to separate **TS1-O₂** and H₂O₂ ($\Delta E = 6.7 \text{ kcal mol}^{-1}$). This bis-hydroperoxo species shows a peculiar structure with one hydroperoxo group interacting with the adjacent framework Ti-O moiety via a hydrogen-bond in the large cavity of the zeolite structure, while the other hydroperoxo group points into the smaller cavity. Addition of propylene stabilizes the structure with respect to **TS1-(OOH)₂** (with empty pores) and propylene ($\Delta E = -5.9 \text{ kcal mol}^{-1}$), likely due to non-covalent interactions between propylene and the zeolite framework. This physisorption is in line with experimental studies²⁶ and similar stabilizations are calculated for propylene-interaction with **TS1-O** and **TS1-O₂**. The transition state for propylene epoxidation from **TS1-(OOH)₂+propylene** is found at $\Delta E^\ddagger = 7.4 \text{ kcal mol}^{-1}$, in good agreement with the experimentally determined initial activation energy of $6.2 \text{ kcal mol}^{-1}$.²⁷ During the epoxidation, the hydroperoxo H-atom is transferred to the adjacent Si-O group, generating a Ti-O-Ti moiety with a coordinated silanol Si-OH ligand (**TS1-(OOH)(O)**); this intermediate lies at $\Delta E = -18.6 \text{ kcal mol}^{-1}$ below **TS1-(OOH)₂+propylene**. The rearrangement of this structure to a bridging hydroxo moiety (**TS1-(OOH)(OH)**) is exoenergetic by $\Delta E = -14.3 \text{ kcal mol}^{-1}$. A direct proton transfer has a calculated energy barrier (ΔE^\ddagger) of $14.2 \text{ kcal mol}^{-1}$. This accessible transition state is likely significantly lowered in protic medium, due to the ease of solvent-mediated proton transfer. The regeneration of the active bis-hydroperoxo species **TS1-(OOH)₂+propylene** by reaction with propylene, H₂O₂ and release of water is exoenergetic by $\Delta E = -16.7 \text{ kcal mol}^{-1}$ (this number refers to the overall energy of the multistep process). Notably, every step in the catalytic cycle is exoenergetic, reflecting the overall exothermicity of the epoxidation process. In contrast to the mechanism proposed in Fig. 4, similar O-transfer mechanisms involving only one Ti-atom are found to be energetically much less favorable, mainly because the Ti-hydroxo and Ti-hydroperoxo intermediates are significantly higher in energy and above separate reactants (Extended Data Fig. 7a,b). Such high-energy species would likely be unobservable by ¹⁷O NMR spectroscopy, as they would merely be present in minute quantities. A previously proposed mechanism involving an isolated Ti-hydroperoxo species adjacent to a defect site in the framework²⁸ is more favorable, with an energy barrier

for the key transition state of 8.3 kcal mol⁻¹. However, in that case, no thermodynamic driving force for formation of the hydroperoxo intermediate exists (its generation from the corresponding hydroxo species and H₂O₂ is an almost isoenergetic process with $\Delta E = 0.1$ kcal mol⁻¹ – Extended Data Fig. 7c). In addition, such a hydroperoxo species is inconsistent with the experimental NMR spectra (Extended Data Fig. 8c). We want to emphasize however that our work does not exclude the presence of isolated Ti-sites in TS-1, but rather shows that dinuclear sites, evidenced in the studied samples by ¹⁷O NMR, are particularly efficient in propylene epoxidation and should be considered in the development of improved catalysts.

The transition state structure for the oxygen-transfer from the dinuclear Ti-site in TS-1 is reminiscent of that with peracids, which are efficient stoichiometric epoxidation agents.²⁹ Peracids show a similar hydrogen-bonding, enabled by the carbonyl group that facilitates H-transfer. In TS-1, this role is taken by the framework Ti-O-Si moiety. As recently pointed out, this arrangement is key for a facile oxygen transfer in epoxidation: the hydrogen-bonding forces the oxygen lone-pairs into a co-planar arrangement, raising the energy of the filled $\pi^*(\text{O}-\text{O})$ orbital, hence leading to a stronger interaction with the olefin $\pi^*(\text{C}=\text{C})$ orbital during O-transfer (Fig. 4d).²⁰

In conclusion, the combination of ¹⁷O NMR, UV-Vis and Raman spectroscopy, as well as electron microscopy and DFT calculations provides robust spectroscopic evidence for the presence of non-isolated Ti-sites in the industrially used TS-1 epoxidation catalyst. The proposed dinuclear sites closely resemble the observed resting state of homogeneous Ti-based epoxidation catalysts. Such dinuclear sites enable the low-energy epoxidation of propylene, where the O-transfer transition state bears a remarkable resemblance to that of electrophilic epoxidation by peracids. The dinuclear Ti-site in the zeolite framework pre-organizes the hydroperoxo moiety to enable an efficient reaction with olefins. This cooperativity of metal atoms in TS-1 seems essential for efficient catalysis and draws parallels with Cu-containing zeolites that enable the selective oxidation of methane to methanol.³⁰

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Table 1. Overview of the TS-1 materials studied in this work.

Ti-content [wt%]	BET surface area [m ² g ⁻¹]	PO concentration [wt%] ^a	selectivity for PO [%] ^b
1.9 (sample 1)	471	8.0	94
1.9 (sample 2)	442	8.0	91
1.5	448	8.2	96
1.0	450	7.7	94
0.5	443	3.7	96

^a Propylene oxide in the product solution; the theoretical maximum concentration is approximately 15 wt% (see Methods for details of catalytic test). ^b Calculated based on ratio of propylene oxide to the total amount of propylene oxide, mono propylene glycol, hydroperoxypropanols, and methoxypropanols formed in the reaction.

Fig. 1. The TS-1 epoxidation catalyst. **a**, Representation of Titanium Silicalite-1 (TS-1), used industrially in the epoxidation of propylene with H₂O₂. In TS-1, a small fraction of Si-atoms in the 12 crystallographically inequivalent T-sites (shown by colored spheres) of the MFI framework are isomorphically replaced by Ti-atoms (additional framework atoms are shown in red (oxygen) and beige (silicon)). **b**, Proposed active species in the TS-1/H₂O₂ system. **c**, Molecular dimeric Berkessel-Katsuki catalyst **1**, able to epoxidize olefins with H₂O₂ as terminal oxidant and corresponding peroxy species **1-O₂**. **d**, Dinuclear site proposed in this work, based on ¹⁷O NMR and periodic DFT calculations (blue spheres: titanium, red spheres: oxygen, white spheres: hydrogen).

Fig. 2. Experimental and calculated solid-state ^{17}O NMR spectra. **a**, ^{17}O NMR spectrum of sample with 1.9 wt% Ti (sample 1) contacted with $\text{H}_2^{17}\text{O}_2$ (1 equivalent with respect to Ti). **b**, corresponding spectrum of sample with 0.5 wt% Ti. **c**, ^{17}O NMR spectrum (blue) and calculated spectrum (red) of the dinuclear molecular $\mu^2\eta^2$ -peroxo compound **1-O₂**. **d**, DFT calculated ^{17}O NMR signature of a dinuclear Ti-peroxo species and H_2^{17}O (solid blue lines on top of shaded experimental spectrum). **e**, Experimental (blue) and calculated spectrum (red) of $\text{H}_2^{17}\text{O}_2$. **f-h**, Calculated spectra for Ti-oxo, Ti-hydroxo, Ti-peroxo (the two O-atoms are inequivalent in the MFI structure) and Ti-hydroperoxo species in the MFI framework. The experimental spectrum of the TS-1/ H_2O_2 system is shaded in the background. Spectra of the other TS-1 samples and H_2^{17}O are shown in Extended Data Fig. 1.

Fig 3. Complementary characterization of TS-1 materials. **a**, UV-Vis spectra and **b**, Raman spectra measured at 325 nm of the investigated TS-1 samples (the same color-code is used in both figures). The spectra are shifted vertically to enable a comparison between the various samples. The UV-Vis band below 370 nm in samples with 1.5 wt% and 1.9 wt% Ti coincides with Raman peaks indicative of TiO_x clusters. **c**, STEM EDX of TS-1 with 1.9 wt% Ti (sample 2) and **d**, 0.5 wt% Ti (Stem EDX of all samples is shown in Extended Data Fig. 2).

Fig. 4. Mechanistic Investigations. **a**, Calculated energy surface of propylene epoxidation at a dinuclear Ti-site (electronic energies in kcal mol^{-1}). **b**, Calculated structures of selected stationary points of the mechanism. In this model, the two Ti-atoms (blue spheres) are located at the adjacent T7 and T11 sites of the MFI structure. **c**, Key transition state of olefin epoxidation which is assisted by a framework O-atom and related transition state of olefin epoxidation with peracids. **d**, Main orbital interactions involved in the epoxidation process with co-planar lone-pairs on oxygen.

Methods

Preparation of Sample 1 (1.9 wt%)²¹

In a reaction vessel, 400 kg tetrapropylammonium hydroxide (TPAOH) were added to 550 kg of deionized water under stirring. After 1 hour of stirring, the resulting mixture was transferred to a suitable vessel. The reaction vessel was washed twice with 2,000 L of deionized water in total. In the washed reaction vessel, a mixture of 80 kg tetraethyl orthosilicate (TEOS) and 16 kg tetraethyl orthotitanate (TEOT) was added to 300 kg of TEOS under stirring. Subsequently, an additional 340 kg TEOS were added. The TPAOH solution was then added, and the resulting mixture was stirred for another hour. Then, the reaction vessel was heated and the ethanol obtained was separated by distillation. When the internal temperature of the vessel had reached 95 °C, the reaction vessel was cooled. 1,143 kg deionized water were added to the resulting suspension in the vessel, and the mixture was stirred for another hour. Crystallization was performed at 175 °C within 24 hours at

autogenous pressure. The obtained TS-1 crystals were separated, dried, and calcined at a temperature of 500 °C in air.

Sample 1 was found to contain 1.9 wt% Ti and 43 wt% Si, and showed a BET surface area of 471 m² g⁻¹.

Preparation of Sample 2 (1.9 wt%)²²

Tetraethyl orthosilicate (TEOS) (500 g) and tetraethyl orthotitanate (TEOT) (15 g) were added to a round bottom flask. 5,200 g of a 20 wt% solution of allyl-tripropylammonium hydroxide (ATPAOH) was added under stirring. A yellow blurry solution was obtained after mixing all the components. The mixture was stirred for 1 hour until the hydrolysis of the silica and titanium sources was finished and the temperature of the mixture was held constant at 54 °C. The ethanol resulting from the hydrolysis of TEOS and TEOT was separated by distillation from the synthesis mixture at 95 °C for 2 hours, during which the solution was continuously stirred at 100 rpm. After the distillation, 600 g of distilled water were added to (about 530 g) of the residue and the solution was stirred for another hour at room temperature. Finally, the suspension was transferred to a 2.5 L stainless steel autoclave equipped with mechanical stirring. The autoclave was heated to 175 °C and kept for 16 hours under continuous stirring (200 rpm). After 16 hours, the autoclave was cooled to room temperature and distilled water was added to the suspension in a volumetric ratio of 1:1 (pH of the resulting solution was about 12). The suspension was then filtered on a Buchner filter and the solid was washed several times with water. The white solid was dried for 4 hours at 120 °C and calcined for 5 hours at 490 °C under air, using the following calcination program: 60 min to 120 °C, 240 min at 120 °C, 370 min from 120 to 490 °C and 300 min at 490 °C.

Sample 2 was found to contain 1.9 wt% Ti and 45 wt% Si, and showed a BET surface area of 442 m² g⁻¹.

Preparation of Sample 3-5 (1.5 wt%, 1.0 wt%, and 0.5 wt%)

Tetraethyl orthosilicate (TEOS) (500 g) was added together with tetraethyl orthotitanate (TEOT) (11.25 g, 7.5 g, and 3.75 g for the samples with 1.5 wt%, 1.0 wt%, and 0.5 wt% Ti, respectively) to a round bottom flask. 220 g of a 40 wt% solution of tetrapropylammonium hydroxide (TPAOH) was mixed with 300 g of distilled water and then added under stirring to the flask containing the Si and Ti source. The mixture was further kept under stirring for 1 hour

until the hydrolysis of the silica and titanium sources was finished and the temperature of the mixture was held constant at 60 °C. The ethanol resulting from the hydrolysis of TEOS and TEOT was separated by distillation from the synthesis mixture at 95 °C for 2 hours, during which the solution was continuously stirred with 200 rpm. After the distillation, 546 g of distilled water were added and the solution was stirred for another hour at room temperature. Finally, the suspension was transferred to a 2.5 L stainless steel autoclave equipped with mechanical stirring. The autoclave was heated to 175 °C and kept for 16 hours under continuous stirring (200 rpm). After 16 hours, the autoclave was cooled to room temperature and distilled water was added to the suspension in a volumetric ratio of 1:1 (pH of the resulting solution was about 12). The suspension was brought to a pH of around 7 by the addition of a solution of 10 wt% HNO₃. The suspension was then filtered on a Buchner filter and the solid was washed several times with water. The white solid was dried for 4 hours at 120 °C and calcined for 5 hours at 490 °C under air, using the following calcination program: 60 min to 120 °C, 240 min at 120 °C, 370 min from 120 to 490 °C and 300 min at 490 °C.

Sample 3 (11.25 g TEOT) was found to contain 1.5 wt% Ti and 42 wt% Si, and showed a BET surface area of 448 m² g⁻¹.

Sample 4 (7.50 g TEOT) was found to contain 1.0 wt% Ti and 43 wt% Si, and showed a BET surface area of 450 m² g⁻¹.

Sample 5 (3.75 g TEOT) was found to contain 0.5 wt% Ti and 44 wt% Si, and showed a BET surface area of 443 m² g⁻¹.

Characterization of TS-1 Materials

Extended Data Fig. 2 shows STEM EDX (energy-dispersive X-ray) images of the 5 TS-1 samples. These images show that Ti is well dispersed over the samples in all cases. However, in the case of samples with Ti-loadings of 1.5 and 1.9 wt% Ti, small TiO_x clusters can be seen in addition. This is consistent with the UV-Vis and Raman spectra presented in Fig. 3a-b.

Extended Data Fig. 3a,b shows SEM and HR-TEM images of the two samples with 1.9 wt% Ti, showing well dispersed nanoparticles and a well-ordered MFI structure.

Extended Data Fig. 3c,d shows HR-TEM images of the samples with 1.5wt% and 1.0 wt% Ti, indicating that a decoupling of the surface occurs in the former sample, but not in the latter.

Extended Data Fig. 4 shows the powder-XRD pattern of the 5 TS-1 samples studied in this work. In all cases, the observed pattern is consistent with a highly crystalline TS-1 zeolite. Traces of anatase can only be detected in one sample with 1.9 wt% Ti (sample 2).

Extended Data Fig. 5 shows additional Raman spectra of all 5 samples, measured at 266 nm. At this wavelength, where the Raman bands of TiO_x clusters are not resonance-enhanced, all samples show bands at similar Raman shifts.

Extended Data Fig. 6 shows the FT-IR-spectra of the 5 TS-1 samples. In addition to the typical MFI bands, the spectra show a band at around 960 cm^{-1} which is typical for TS-1.

Catalytic Tests

The 5 TS-1 samples were tested using the following procedure:

0.5 g TS-1 zeolite powder and 45 mL methanol were introduced in a 250 mL glass reactor. The reactor was closed and cooled to $-25\text{ }^\circ\text{C}$. 20 mL of liquid propylene (at $-25\text{ }^\circ\text{C}/10\text{ bar}$ pressure) was added to the vessel under vigorous stirring. The reactor was heated to $0\text{ }^\circ\text{C}$. 18 g of H_2O_2 (30 wt% aqueous solution) were subsequently fed by means of an HPLC pump. The reaction was run for 5 hours at $0\text{ }^\circ\text{C}$ under vigorous stirring. After 5 hours, the reaction was stopped, the mixture was depressurized, and the reactor was heated to room temperature. The liquid phase was collected and analyzed by gas-chromatography. The products were quantified both by internal standard and by a calibration curve. The results of the catalytic tests are shown in Table 1.

Sample preparation for NMR measurements

TS-1 samples with ^{17}O labelled H_2O_2 were prepared by impregnating 50 mg of TS-1 with one equivalent (with respect to Ti) of a 1.6 M aqueous solution of ^{17}O labelled H_2O_2 .²³ The samples were left to equilibrate for 2-3 hours before spectroscopic measurements. ^{17}O NMR measurements of freshly impregnated samples (no equilibration time) show significant amounts of unreacted $\text{H}_2^{17}\text{O}_2$, which obscures the spectrum. The reaction is complete after around 2-3 hours, however, longer reaction times do not significantly change the NMR spectra, illustrating the stability of the peroxo species.

Compound **1-O₂** was generated by reacting the Berkessel-Katsuki epoxidation catalyst **1** with a 1.6 M aqueous solution of ^{17}O labelled H_2O_2 . Catalyst **1** was prepared as described in literature.¹⁶

¹⁷O NMR Spectroscopy

All NMR measurements were obtained on a Bruker Avance III 600 MHz NMR spectrometer (14.1 T) at low temperatures (110 K) using a 3.2 mm probe. The magnetic field was externally referenced by setting the signal of liquid H₂O (at RT) to 0 ppm. Measurements were performed in a 3.2 mm zirconia rotor closed with a VESPEL drive cap, or in a 3.2 mm sapphire rotor closed with a zirconia cap.

Static WURST-CPMG³¹ (Wideband, Uniform Rate, and Smooth Truncation pulse with CPMG echo-train acquisition) experiments were performed to obtain the ¹⁷O NMR spectra. Details of the WURST pulse are as follows: 50 μs length, 80 steps, 0.5 MHz sweep width, sweeping from low to high frequency. SPINAL64 with 100 kHz rf-frequency was used for ¹H decoupling. The spectra shown in Fig. 2a and Fig. 2b are averaged over 97,472 scans and 113,320 scans, respectively. The spectra shown in Extended Data Fig. 1b, 1c, and 1d are averaged over 84,224 scans, 13,576 scans, and 14,768 scans, respectively. Simulations of the spectra were performed using the QUEST software.³²

Powder XRD

Powder X-ray diffraction (PXRD) data was collected using a diffractometer (D8 Advance Series II, Bruker AXS GmbH) equipped with a LYNXEYE detector operated with a Copper anode X-ray tube, running at 40 kV and 40 mA. The geometry was Bragg-Brentano, and air scattering was reduced using an air scatter shield.

For measurements, the samples were homogenized in a mortar and then pressed into a standard flat sample holder provided by Bruker AXS GmbH for Bragg-Brentano geometry data collection. The flat surface was achieved using a glass plate to compress and flatten the sample powder. The data was collected from the angular range 2° to 70° 2Θ, with a step size of 0.02° 2Θ, while the variable divergence slit was set to an angle of 0.1°. The crystalline content describes the intensity of the crystalline signal to the total scattered intensity.

SEM

For surface analysis, the sample material (powder) was applied on conductive C-tabs and coated by 9 nm of Pt using a sputter coater (Balzers SCD 050). The acceleration voltage for the

SEM-Images was 3 kV and the SE-detector (ETD) was used. The instrument was a Ultra55 (high resolution scanning electron microscope from Carl Zeiss AG).

HR-TEM (shown in Extended Data Fig. 3a,b)

Transmission Electron Microscopy (TEM) samples were prepared by the drop-on-grid-method on carbon support grids. The samples were imaged by TEM using a probe-corrected Themis Z 3.1 machine (Thermo-Fisher, Waltham, USA) under both High-Angle Annular Dark-Field (HAADF) Scanning Transmission Electron Microscopy (STEM) and integrated Differential Phase Contrast (iDPC) – STEM conditions. The acceleration voltage was set to 300 kV, the resolution was tuned on an Au cross grating sample, and the beam current was set to 1 pA for iDPC-STEM imaging. The chemical composition was analyzed with the integrated SuperX G2 Energy-Dispersive X-Ray Spectroscopy (EDXS) detectors (Thermo-Fisher, Waltham, USA). Data was analyzed using the Velox 2.9.0.889 software (Thermo-Fisher, Waltham, USA).

HR-TEM (shown in Extended Data Fig. 3c,d) and STEM-EDX

TEM and STEM-EDX analysis were performed using a double-corrected JEOL JEM-ARM 200CF microscope operated at 200 kV and equipped with a large angle SDD-EDS system of 0.7 sr and a detection area of 100 mm². For the HR-TEM imaging, a Gatan OneView 4Kx4K camera was used. All EDS maps were acquired with 33 pA probe current and 30 minutes acquisition time.

FT-IR

FT-IR spectra were acquired on a PIKE GladiATR FT-IR spectrometer using the Attenuated Total Reflectance (ATR) technique. Spectra shown are averaged over 16 scans and were recorded with a resolution of 0.5 cm⁻¹.

Raman spectroscopy

UV Raman spectra were recorded using a TriVista TR557 spectrometer (S&I Spectroscopy & Imaging GmbH), equipped with a confocal Raman microscope and a liquid nitrogen cooled CCD detector (PyLoN:2K; Princeton Instruments). For the spectra shown in Fig. 3, a He-Cd laser with a 325 nm wavelength and a maximum power of 1.80 mW was used. For the spectra shown in Extended Data Fig. 5, a continuous wave laser source (FQCW 266) from CryLaS with a 266 nm wavelength and a maximum power of 1.30 mW on the sample was used. The spectra

were acquired over 30 seconds and 60 to 80 accumulations, with a resolution of around 2 cm^{-1} . The displayed Raman spectra have been normalized to the respective most intense signal.

UV-Vis spectroscopy

UV-Vis spectra were obtained on an Agilent Cary 5,000 UV-Vis-NIR spectrometer, measuring the absolute %R under double beam mode with a scan rate of 600 nm min^{-1} and a data interval of 1 nm.

UV-Vis spectra related to the Berkessel-Katsuki catalyst were obtained on a Perkin Elmer Lambda 35 UV-Vis spectrometer, measuring the absorption at a scan rate of 480 nm min^{-1} and a data interval of 1 nm.

Computational Details

Periodic DFT calculations were carried out with the Vienna Ab Initio Simulation Package (VASP) code³³⁻³⁵ using the Projector Augmented Wave (PAW)³⁶ method with a cut-off energy of 600 eV. The Generalized Gradient Approximation (GGA) was used with the revised Perdew-Burke-Ernzerhof (RPBE) functional.³⁷ Dispersive interactions were taken into account with the DFT-D3 correction method.³⁸ For zeolitic materials, the use of GGA DFT is well established and is typically the method of choice.^{39,40} While hybrid functionals would be expected to give more accurate energies,⁴¹ their use in this work is impeded by their high computational cost. The Brillouin zone was sampled with a spacing between k-points of 1 \AA^{-1} and the grid was centered at the Γ -point. Electronic occupancies were determined with an energy smearing of 0.2 eV. The convergence criterion for the electronic structure was set to 10^{-5} eV. Ground-state geometries were relaxed until the forces acting on each atom were converged below 0.01 eV \AA^{-1} . Transition state geometries were optimized with the DIMER method,⁴² until the forces acting on each atom were converged below 0.03 eV \AA^{-1} . The vibrational modes were calculated by diagonalization of the Hessian matrix, using the central finite difference approximation with displacements of 0.015 \AA . All reported energies correspond to electronic energies extrapolated to an energy smearing of 0 eV.

The NMR spectroscopic parameters used to simulate the spectra in Figure 2 and Extended Data Fig. 1 were obtained within the GIAO framework using ADF 2014⁴³ with the PBE0 functional⁴⁴ and Slater-type basis sets of triple- ζ quality (TZ2P). The molecular peroxo-compound **1-O₂** was calculated using a double- ζ basis set; in addition, to simplify the

calculation, the C₆F₅ groups were replaced by CH₃ groups. Relativistic effects were treated by the 2 component zeroth order regular approximation (ZORA).⁴⁵⁻⁴⁹

For molecular systems (H₂O₂, H₂O and the $\mu^2\eta^2$ -peroxo compound **1-O₂**), the geometries used for the NMR calculations were optimized with the Gaussian09 package⁵⁰ at the PBE0⁴⁴ level. Ti was represented by a lanl2dz core potential and the associated basis set.⁵¹ The remaining atoms (H, C, N, O, and F) were represented by a Def2-TVZP basis set.⁵²

For periodic systems (Ti-oxo, Ti-hydroxo, Ti-hydroperoxo, Ti-peroxo, and the dinuclear $\mu^2\eta^2$ -peroxo species), the NMR calculations were carried out on clusters, cut out from periodic DFT calculated structures and capped with F-atoms. The structures used to calculate the NMR signatures in Fig. 2 and Extended Data Fig. 1 are shown in Extended Data Fig. 8.

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Data Availability

All data leading to the conclusions drawn in this work are available within the manuscript, in the supplementary information files (raw data files are provided for Fig. 2 and Fig. 3), or from the corresponding author on reasonable request.

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Author Contributions C.P.G performed NMR measurements, DFT calculations, and lead the writing process. H.E. prepared the salalen ligand and the Berkessel-Katsuki catalyst **1**. A.-N.P. prepared the TS-1 sample analyzed in this study. A.S.T. performed Raman measurements, M.P. did STEM-EDX measurements. T.L. was involved in STEM-EDX and Raman measurements. All authors contributed to the design of the project, as well as to data interpretation and writing.

Competing Interests The authors declare no competing interests.

Additional Information

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Extended Data Fig. 1. Solid-state ¹⁷O NMR spectra of all TS-1 samples and H₂¹⁷O. Solid-state ¹⁷O NMR spectra of TS-1 samples with **a**, 1.9 wt% Ti (sample 1), **b**, 1.9 wt% Ti (sample 2), **c**, 1.5 wt% Ti, **d**, 1.0 wt% Ti, and **e**, 0.5 wt% Ti. **f**, Solid-state ¹⁷O NMR spectrum of H₂¹⁷O (red line: DFT calculated spectrum).

Extended Data Fig. 2. STEM EDX images. STEM EDX images of the 5 investigated TS-1 samples: **a**, 1.9 wt% Ti (sample 1), **b**, 1.9 wt% Ti (sample 2), **c**, 1.5 wt% Ti, **d**, 1.0 wt% Ti, and **e**, 0.5 wt% Ti.

Extended Data Fig. 3. SEM and HR-TEM images. **a**, SEM image (left) and HR-TEM image (right) of the TS-1 sample with 1.9 wt% Ti (sample 1). **b**, SEM image (left) and HR-TEM image (right)

of the TS-1 sample with 1.9 wt% Ti (sample 2). **c**, HR-TEM image of the TS-1 sample with 1.0 wt% Ti. **d**, HR-TEM image of the TS-1 sample with 1.5 wt% Ti.

Extended Data Fig. 4. Powder-XRD Patterns. Powder-XRD of the 5 investigated TS-1 samples (after calcination): **a**, 1.9 wt% Ti (sample 1), **b**, 1.9 wt% Ti (sample 2) with signs of an anatase phase marked by arrows, **c**, 1.5 wt% Ti, **d**, 1.0 wt% Ti, and **e**, 0.5 wt% Ti.

Extended Data Fig. 5. Additional Raman spectra. Raman spectra of the 5 TS-1 samples measured at a wavelength of 266 nm. At this wavelength, the signals associated with TiO_x clusters are not resonance-enhanced, and hence similar features are observed in all spectra.

Extended Data Fig. 6. FT-IR spectra. FT-IR spectra of the 5 investigated TS-1 samples. The spectra are shifted in steps of 20% on the vertical axis to enable a direct comparison.

Extended Data Fig. 7. Additional investigated mechanisms. **a**, Calculated potential energy surface for propylene epoxidation on a mononuclear Ti-site, via a bis-hydroperoxo species. **b**, Analogous mechanism via a hydroperoxo species. **c**, Potential energy surface for propylene epoxidation from a hydroperoxo species on an isolated Ti-site with an adjacent vacancy. Relative electronic energies are given in kcal mol^{-1} .

Extended Data Fig. 8. Models used for calculating NMR spectra. **a**, Cluster models used for calculation of the NMR signatures shown in Fig. 2. **b**, Structure and simulated spectrum (red) of a mononuclear peroxy species with adjacent vacant site (the experimental spectrum of TS-1 impregnated with $\text{H}_2^{17}\text{O}_2$ is shown in blue). **c**, Structure and simulated spectrum (red and purple) of a mononuclear hydroperoxo species with an adjacent vacant site (experimental spectrum shown in blue). **d**, Structure and simulated spectrum (red and purple) of mononuclear hydroperoxo species, in which the hydroperoxo ligand is oriented differently as compared to the structure used to calculate the spectrum shown in Fig. 2 (experimental spectrum shown in blue).

Extended Data Fig. 9. Additional ^{17}O NMR spectra. **a**, Solid-state ^{17}O NMR spectrum of TS-1 (1.9 wt%, sample 1) contacted with H_2^{17}O . **b**, Solid-state ^{17}O NMR spectrum of Ti-free MFI contacted with $\text{H}_2^{17}\text{O}_2$.

Extended Data Fig. 10. UV-Vis spectra related to Berkessel-Katsuki catalyst. UV-Vis spectra of the Berkessel ligand (blue), the Berkessel-Katsuki catalyst **1** (red), and the corresponding peroxy species **1-O₂** (green). The spectra were acquired in dichloromethane solution, with concentrations of $0.049 \text{ mmol L}^{-1}$, $0.022 \text{ mmol L}^{-1}$, and $0.022 \text{ mmol L}^{-1}$, respectively.