

Electronic Supplementary Information

Accessibility Enhancement of TS-1-Based Catalysts for Improving the Epoxidation of Plant Oil-Derived Substrates

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1 Synthesis of the Catalysts

1.1 Synthesis of meso-TS-1

The initial gel with a molar ratio of $n_{\text{Si}}/n_{\text{Ti}} = 43$ was prepared from tetraethylorthosilicate (TEOS, Aldrich, 98 %) and tetrabutylorthotitanate (TBOTi, Aldrich 97 %), distilled water and tetrapropylammonium hydroxide (TPAOH, Aldrich, 40 wt.-% aqueous solution) as a structure-directing agent. The TBOTi was added dropwise into the TEOS and stirred for 45 min prior to the addition of distilled water and TPAOH. After another 30 min, the CBP were added and the mixture was homogenized for 30 min. The final synthesis mixture with a molar composition 100 TEOS :

2.35 TBOTi : 25 TPAOH : 3700 H₂O : 680 CBP was hydrothermally crystallized in a polytetrafluoroethene (PTFE)-lined autoclave (90 cm³) at 175 °C for 90 h under agitation. After the hydrothermal synthesis, the zeolite was filtered off, washed with a copious amount of distilled water, dried at 85 °C and finally calcined in an air flow (150 cm³ min⁻¹) at 550 °C for 24 h using a temperature ramp of 2 °C min⁻¹.

1.2 Synthesis of layered TS-1

The TBOTi was added drop-wise into the TEOS and stirred for 30 min. Then, an aqueous solution of the surfactant (0.085 M) was added to the reaction mixture and homogenized at 60 °C for 3 h. Evaporated ethanol was replaced with the same volume of distilled water. The synthesis mixture of the molar composition 100 TEOS : 2.5 TBOTi : 6 C₁₈₋₆₋₆ : 5000 H₂O was hydrothermally crystallized in a 90 cm³ PTFE-lined autoclave at 160 °C for 236 h under agitation. After the hydrothermal synthesis, the zeolite was filtered off, washed with a copious amount of distilled water, dried at 80 °C and finally calcined (resulting in layered TS-1 catalyst) or subjected to the pillaring treatment (see section 2.1.3). Calcination was carried out in static air at 570 °C for 8 h using a temperature ramp of 1 °C min⁻¹.

1.3 Synthesis of Ti-MCM-36

To prepare Ti-MCM-22P Piperidine (Aldrich, 99 %, structure-directing agent, 0.307 mol) was added to distilled water and stirred for 15 min. The piperidine solution was divided into two equal parts and TBOTi (7.55 mmol) was added into one part while H₃BO₃ (Fluka, 99%, 0.287 mmol) was added to the other part. Both solutions were stirred for about 50 min. Then, equal amounts of pyrogenic SiO₂ (Cab-O-Sil M-5, Havel Composites, Czech Republic, total 0.214 mol) were slowly added into both solutions and stirred for another 60 min. Finally, both resulting slurries were mixed together and stirred for 60 min. The final gel of the molar composition 3.5 TBOTi : 134 H₃BO₃ : 143 piperidine : 100 SiO₂ : 1900 H₂O was charged into a PTFE-lined autoclave (90 cm³). The crystallization proceeded under agitation and the temperature was increased stepwise. The crystallization started at 130 °C for the first 24 h, then, the temperature was increased to 150 °C for another 24 h and finally, to 170 °C for 120 h. After the hydrothermal synthesis, the solid

product was collected by filtration, washed with distilled water and dried in an oven at 60 °C. To remove extra-framework Ti-species, the as-synthesized Ti-MCM-22P was stirred in a 2 M HNO₃ at 85 °C for 15 h (20 cm³ g⁻¹) and then filtered, washed with a copious amount of distilled water and dried at 60 °C again.

To transform the Ti-MCM-22P into Ti-MCM-36, the Ti-MCM-22P was swollen using 20 cm³ g⁻¹ of a 25 wt.-% aqueous solution of cetyltrimethylammonium hydroxide (C₁₆TMA-OH, prepared by ion-exchange from the chloride form (Aldrich)). The slurry was stirred at ambient temperature for 16 h. The swollen product Ti-MCM-22SW was separated by centrifugation, washed with distilled water and dried in air at 60 °C.

Pillaring of Ti-MCM-22SW was carried out with TEOS (50 cm³ g⁻¹) at 85 °C for 16 h under stirring. The solid product was isolated by centrifugation and dried at ambient temperature for 24 h. Subsequently, the material was hydrolyzed in water (100 cm³ g⁻¹) at ambient temperature for another 24 h. Finally, the solid product was separated again by centrifugation, dried at 60 °C and calcined in a flow of air at 550 °C for 10 h using a temperature ramp of 2 °C min⁻¹ resulting in Ti-MCM-36.

2 Catalysts Characterization

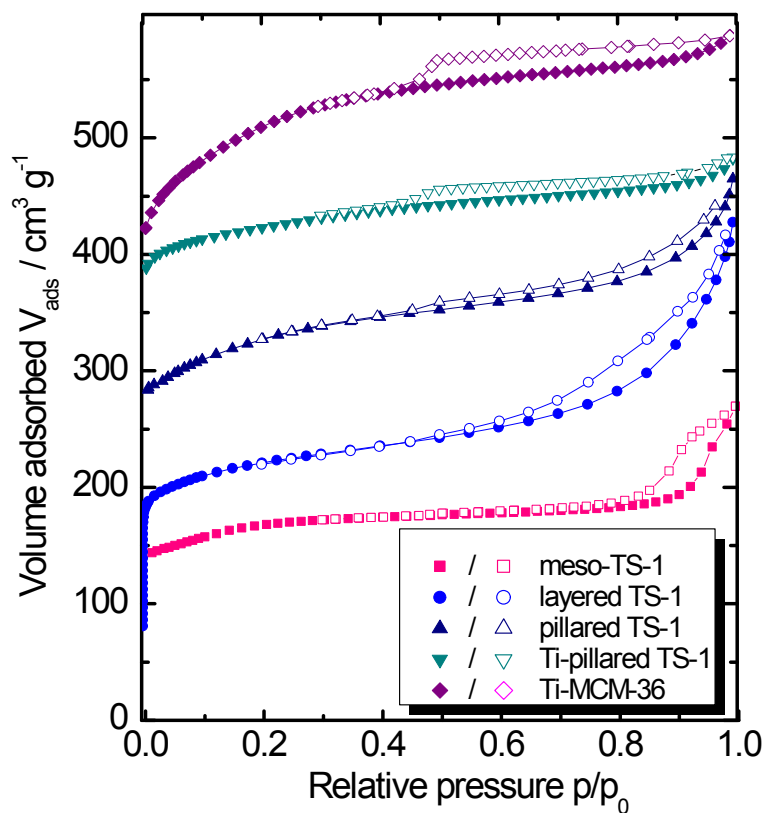


Fig. S1 Nitrogen adsorption (closed symbols) and desorption (open symbols) isotherms for meso-TS-1, layered TS-1, pillared TS-1, Ti-pillared TS-1, and Ti-MCM-36. For clarity, the isotherms are vertically displaced by $80 \text{ cm}^3 \text{g}^{-1}$.

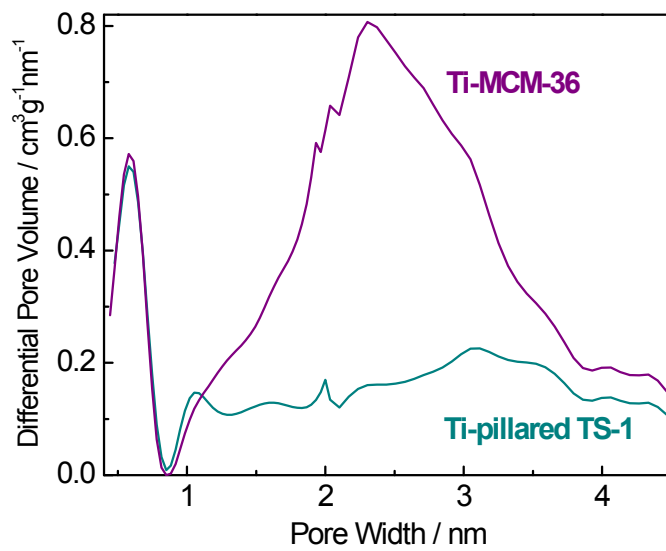


Fig. S2 NLDFT pore width distribution for Ti-MCM-36 and Ti-pillared TS-1 in the range from 0.3 to 4.5 nm.

SEM-EDX –maps of the pillared and Ti-pillared TS-1 as well as Ti-MCM-26 (Figure S3 - 5) were collected using a Hitachi S-4800 field emission scanning electron microscope at 25 kV with Noran EDX Six system.

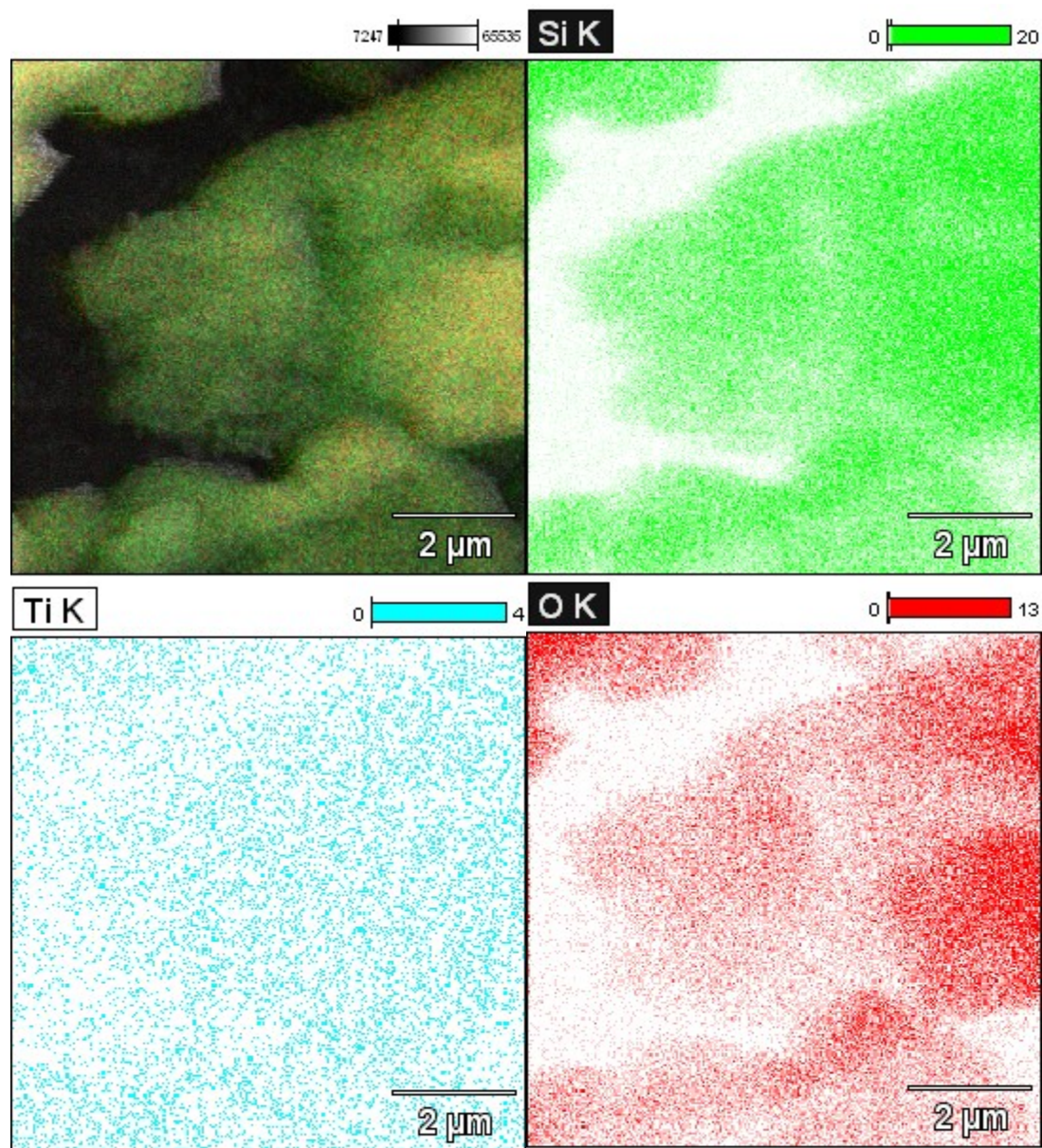


Fig. S3 Overlap of the SEM-EDX maps of silicon and oxygen and SEM-EDX maps for silicon (green), titanium (blue) and oxygen (red) of pillared TS-1.

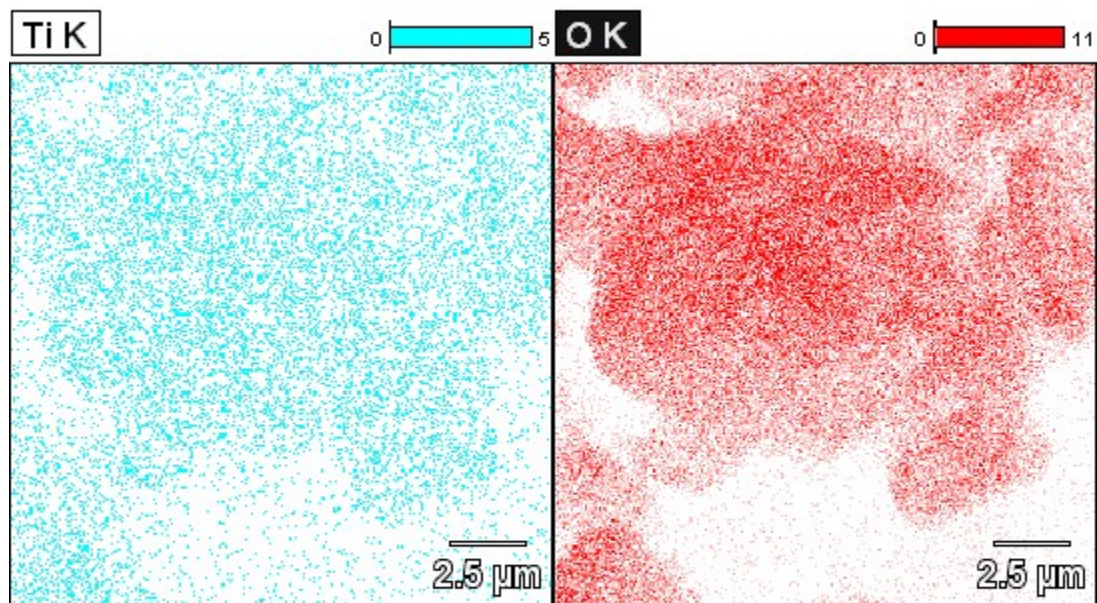
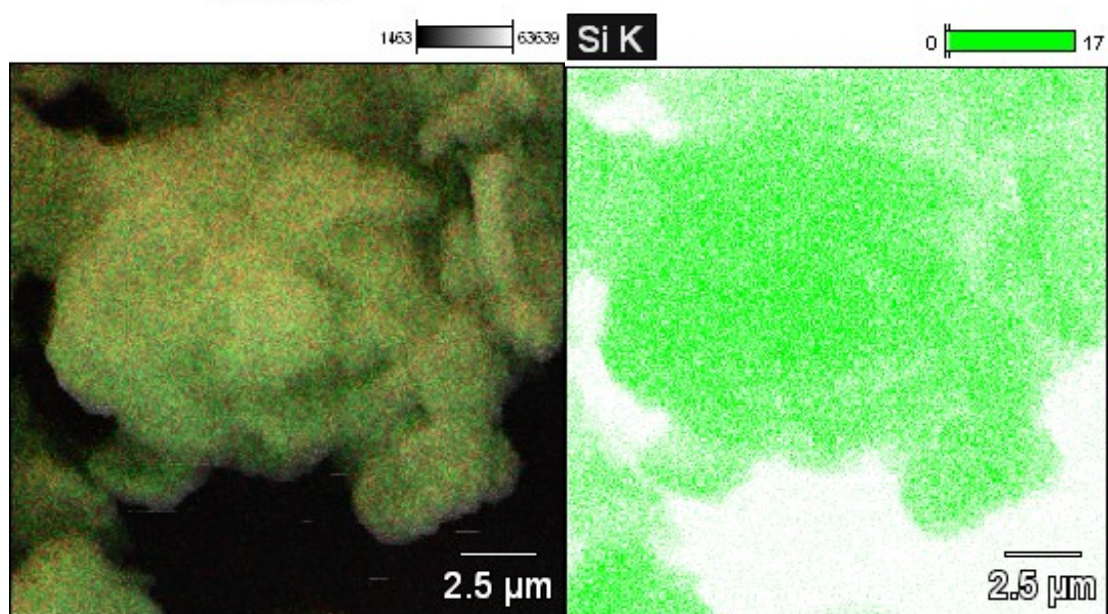


Fig. S4 Overlap of the SEM-EDX maps of silicon and oxygen and SEM-EDX maps for silicon (green), titanium (blue) and oxygen (red) of Ti-pillared TS-1.

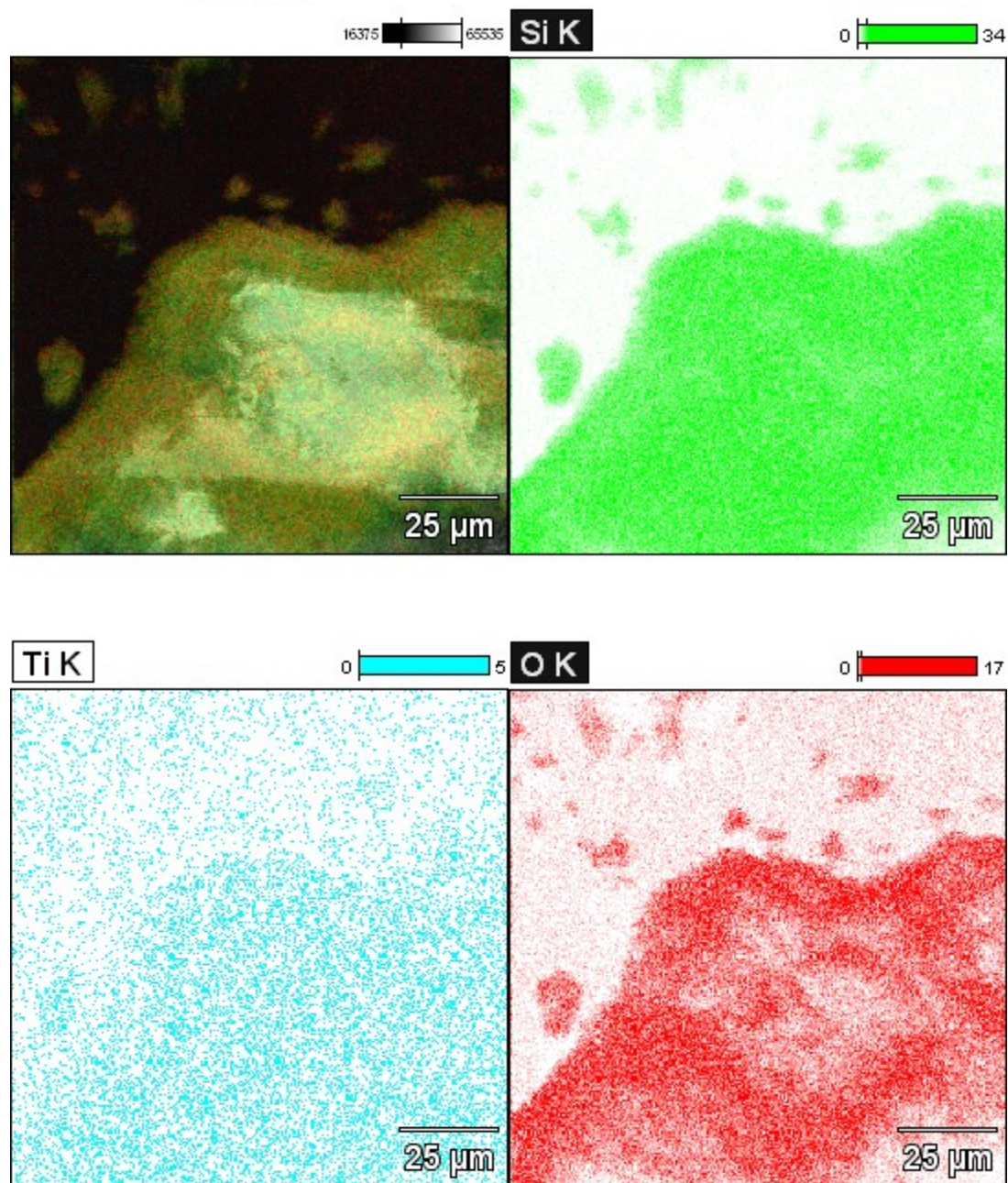


Fig. S5 Overlap of the SEM-EDX maps of silicon and oxygen and SEM-EDX maps for silicon (green), titanium (blue) and oxygen (red) of Ti-MCM-36.

3 Catalysts Stability and Regeneration

3.1 Catalyst Reuse and Regeneration

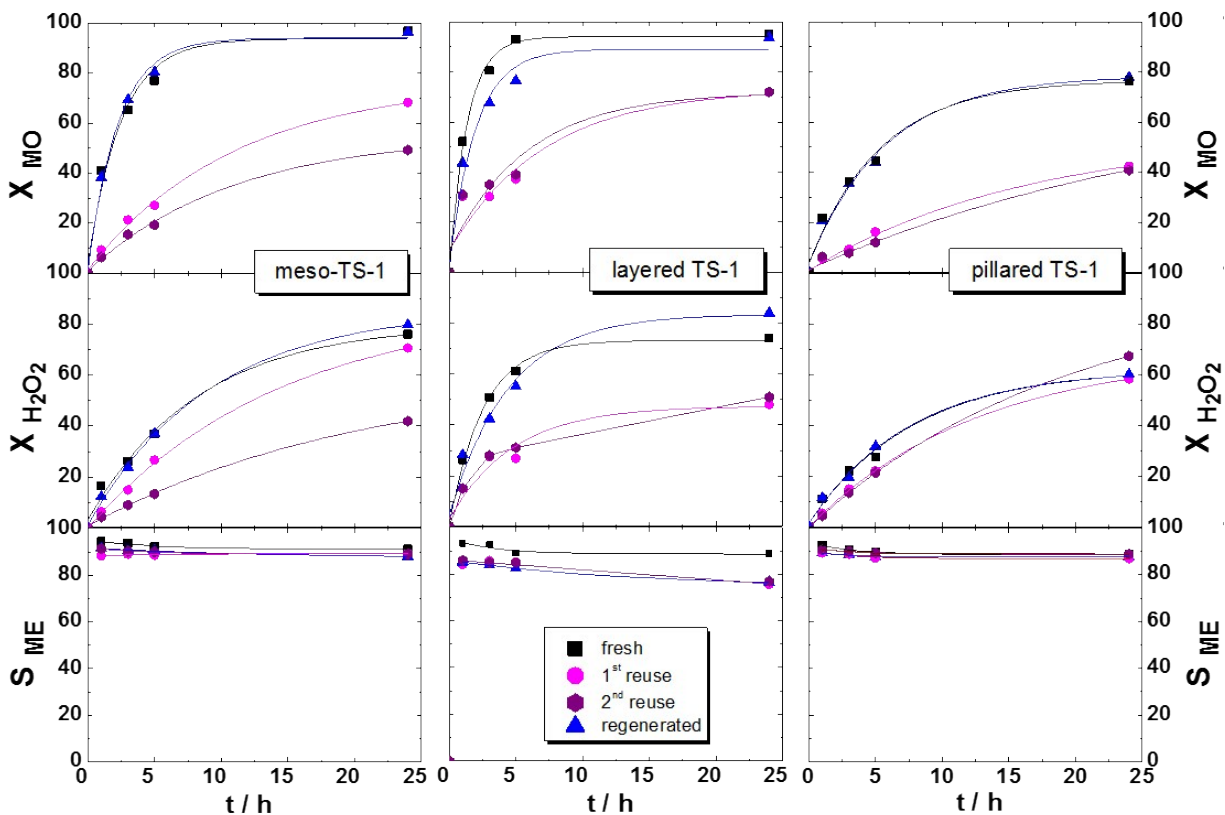


Fig. S6 Conversion of methylolate X_{MO} , conversion of hydrogen peroxide $X_{H_2O_2}$, and epoxide selectivity S_{ME} as a function of reaction time in the epoxidation of methylolate over the catalysts meso-TS-1 (left part), layered TS-1 (middle) , and pillared TS-1 (right part) fresh, reused and regenerated ($V_{acetonitrile} = 10 \text{ cm}^3$, $c_{MO} = 0.03 \text{ mol L}^{-1}$, $n_{H_2O_2}/n_{MO} = 5 \text{ mol mol}^{-1}$, $m_{cat} = 150 \text{ mg}$, $T = 50^\circ\text{C}$).

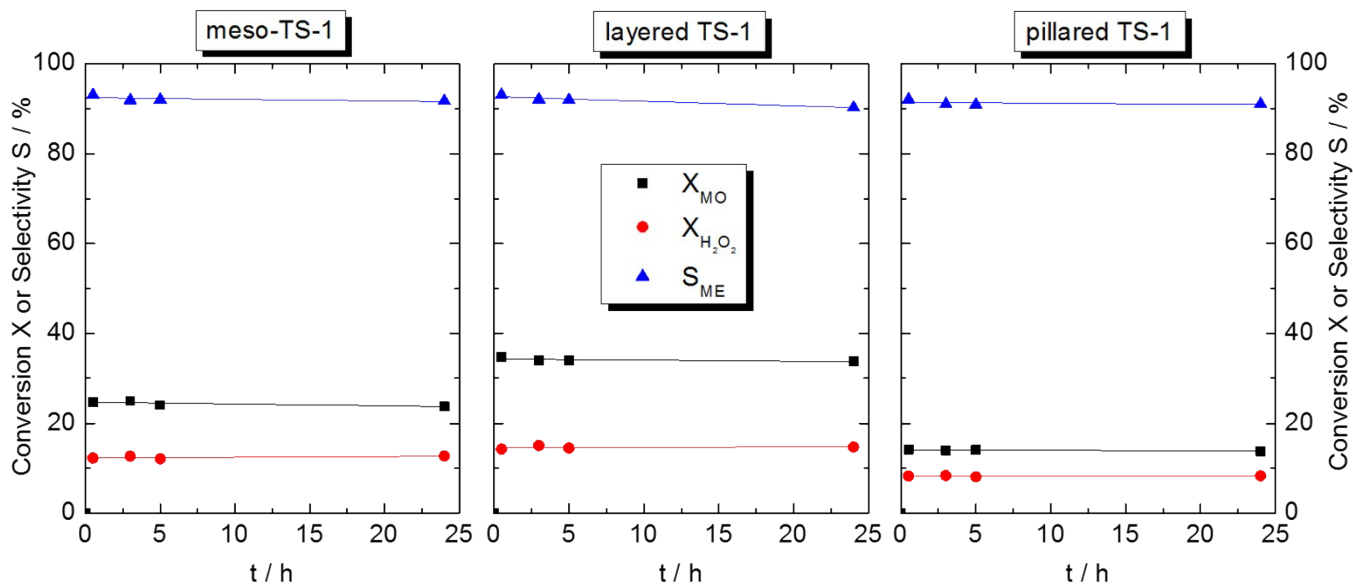


Fig. S7 Conversion of methyloleate X_{MO} , conversion of hydrogen peroxide $X_{H_2O_2}$, and epoxide selectivity S_{ME} as a function of reaction time in the epoxidation of methyloleate over the catalysts meso-TS-1, layered TS-1, and pillared TS-1. The catalysts were removed by hot filtration after 30 min of reaction ($V_{acetonitrile} = 10 \text{ cm}^3$, $c_{MO} = 0.03 \text{ mol L}^{-1}$, $n_{H_2O_2}/n_{MO} = 5 \text{ mol mol}^{-1}$, $m_{cat} = 150 \text{ mg}$, $T = 50^\circ\text{C}$).

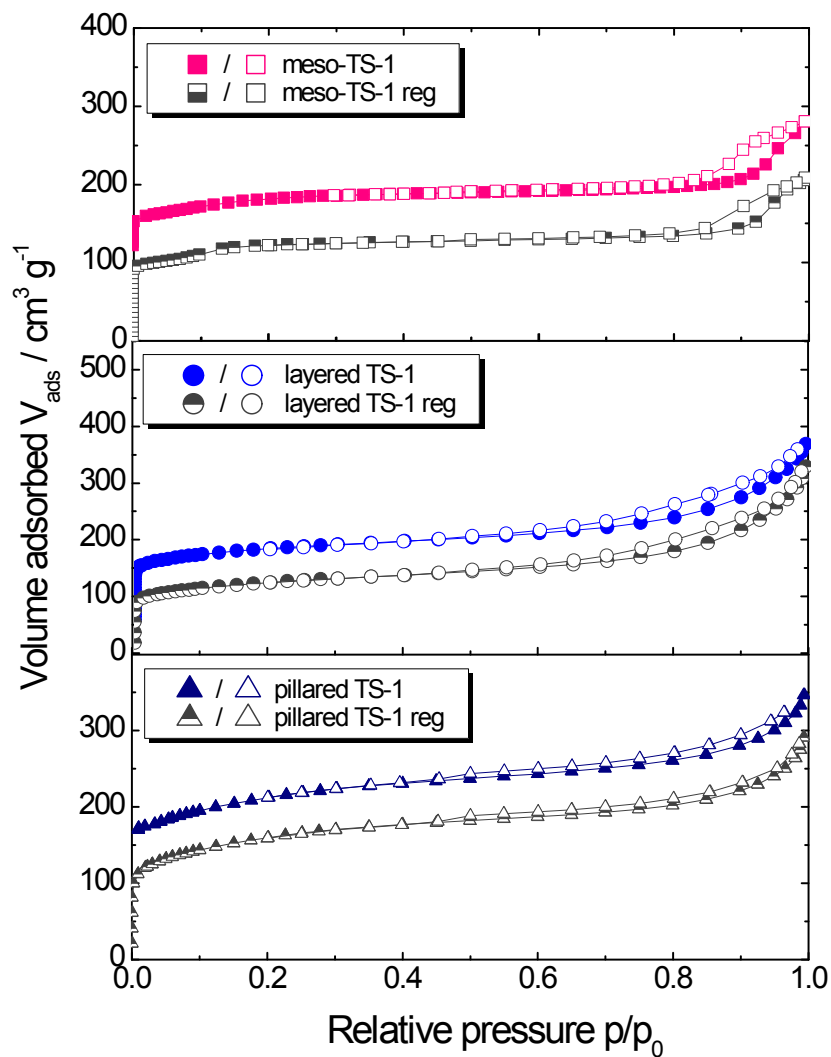


Fig. S8 Nitrogen adsorption (closed or partially filled symbols) and desorption (open symbols) isotherms for the fresh and regenerated (reg) catalysts meso-TS-1, layered TS-1, and pillared TS-1. For clarity, the isotherms of the fresh catalysts are vertically displaced by $50 \text{ cm}^3 \text{g}^{-1}$.

Tab. S1 Specific BET surface area S_{BET} , external surface area S_{ext} , micropore volume V_{micro} and total pore volume V_{total} of the fresh and regenerated (reg) catalysts meso-TS-1, layered TS-1, and pillared TS-1 as determined from nitrogen sorption analysis.

Titanosilicate	$S_{\text{BET}} /$ $\text{m}^2 \text{g}^{-1}$	$S_{\text{ext}} /$ $\text{m}^2 \text{g}^{-1}$	$V_{\text{micro}} /$ $\text{cm}^3 \text{g}^{-1}$	$V_{\text{total}} /$ $\text{cm}^3 \text{g}^{-1}$
meso-TS-1	465	239	0.10	0.16
meso-TS-1 reg	459	231	0.09	0.15
layered TS-1	508	256	0.12	0.48
layered TS-1 reg	457	222	0.10	0.35
pillared TS-1	595	384	0.09	0.46
pillared TS-1 reg	589	378	0.09	0.45

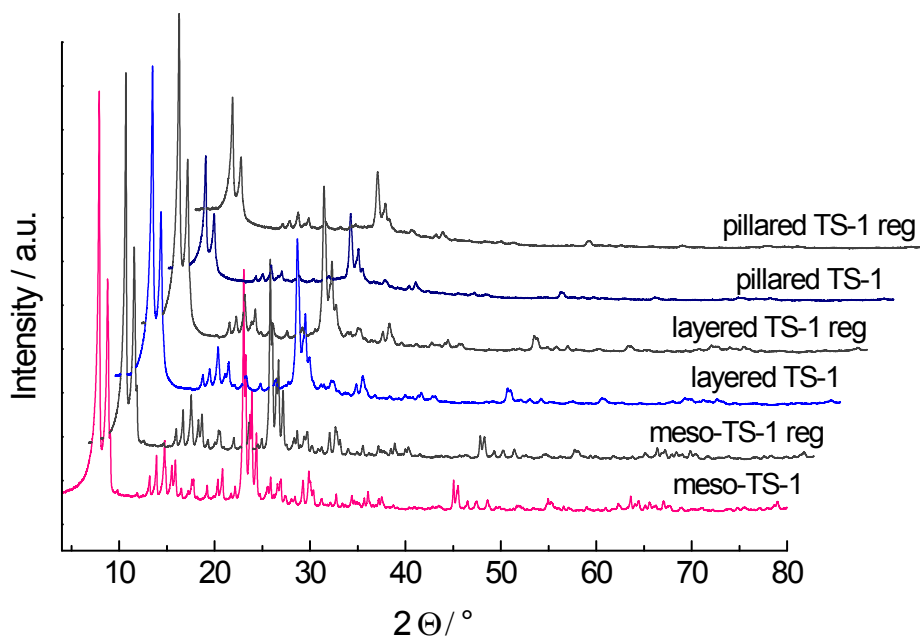


Fig. S9 Powder X-ray diffraction patterns of the fresh and regenerated (reg) catalysts meso-TS-1, layered TS-1, and pillared TS-1.

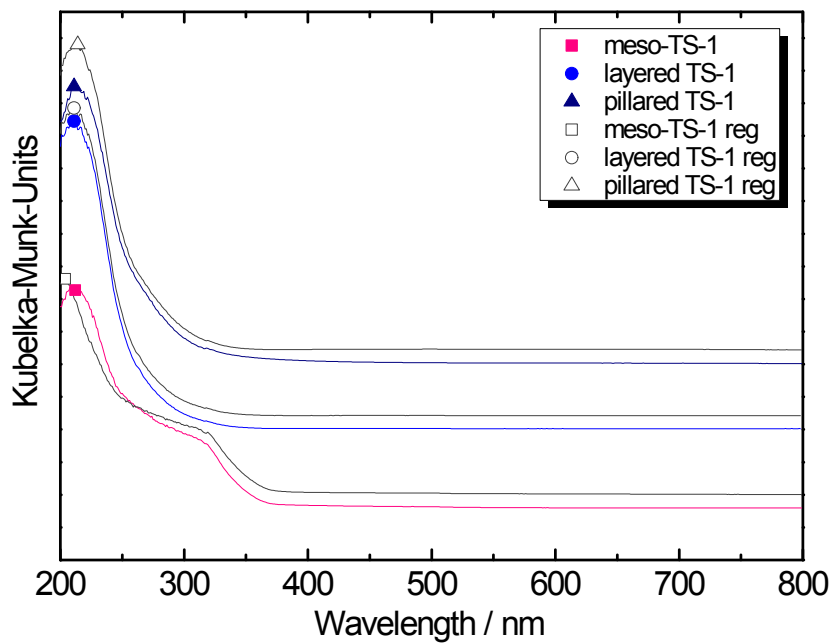


Fig. S10 DR-UV-Vis spectra of the fresh and regenerated catalysts meso-TS-1, layered TS-1, and pillared TS-1. For clarity, the spectra of the regenerated materials (reg) were vertically displaced.

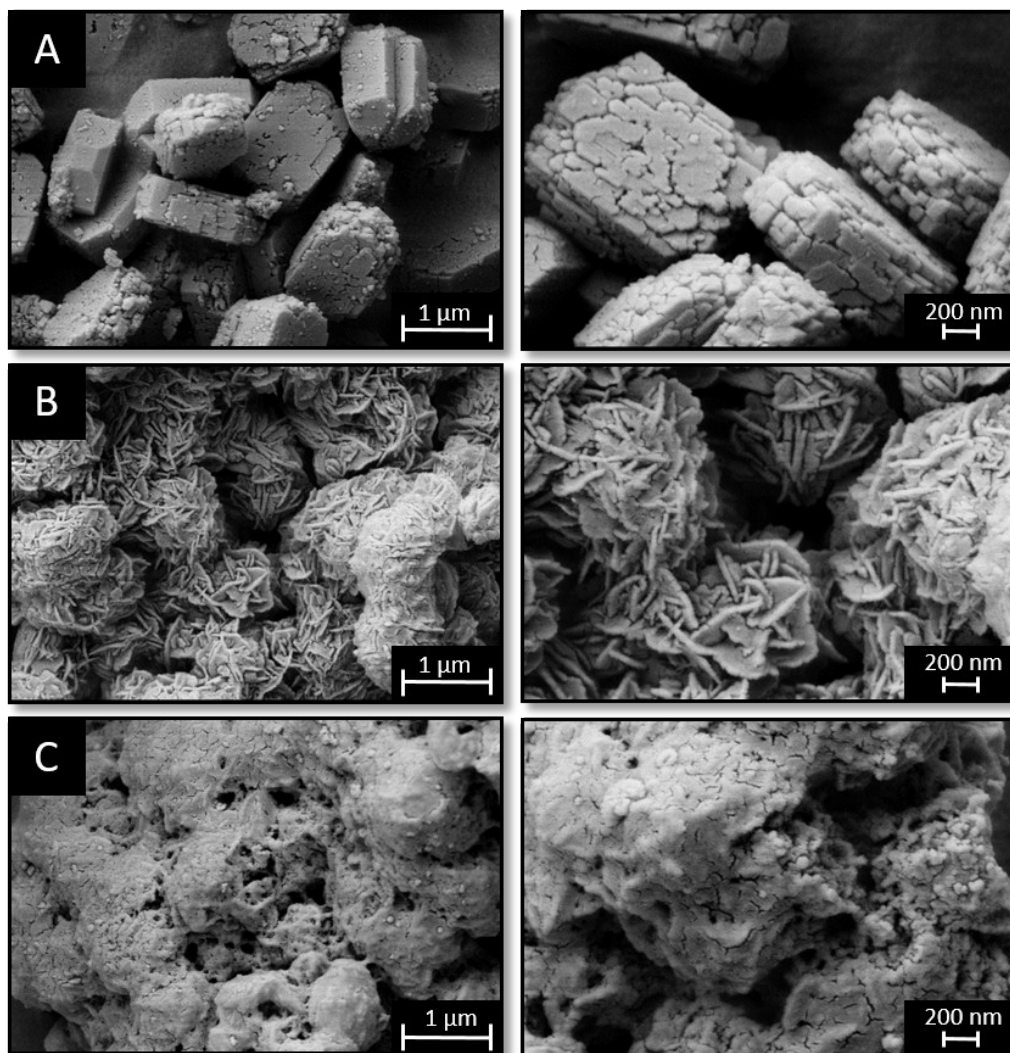


Fig. S11 SEM images of the regenerated catalysts meso-TS-1 (A), layered TS-1 (B), and pillared TS-1 (C) at different magnifications.

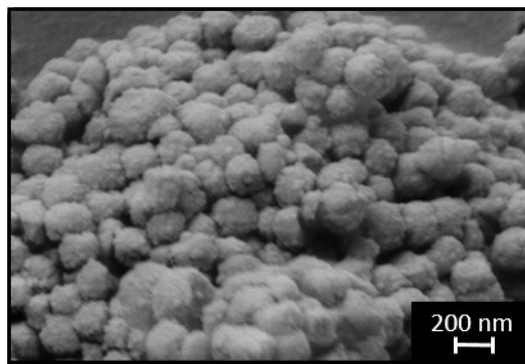


Fig. S12 SEM image of conventional TS-1.

3.2 Carbonaceous Compounds Leading to Deactivation of Conventional TS-1

In order to examine which compounds lead to the observed catalyst deactivation, 500 mg of the conventional TS-1 catalyst (after the 2nd reuse) were extracted first with 5 cm³ of tetrachloromethane (99.9 %, Sigma-Aldrich) and, then, with 5 cm³ dichloromethane (99.5 %, Sigma-Aldrich) at room temperature (cf.¹). The extracts were combined, concentrated by evaporating the solvent in vacuum at 40°C and analyzed by electrospray ionization - mass spectrometry (ESI-MS) on an API 2000 ESI- Triple Quadrupol MS, AB SCIEX. Two fragments with $m\ e^{-1} = 791$ und $m\ e^{-1} = 963$ were observed. For the epoxidation of propene over TS-1, Thiele et al.² and Wang et al.³ reported that the deactivation can be attributed to the blocking of the micropores by bulky organic deposits formed by consecutive reactions such as dimerization and/or oligomerization of propene oxide. The deposition of organic compounds was also observed for the epoxidation of methyloleate over TS-1.⁴ In accordance with these observations, we propose a mechanism for the formation of oligomers in the epoxidation of methyloleate with H₂O₂ over conventional TS-1 as shown in Figure S10. Referring to the fragments observed by ESI-MS, these can be assigned to di- and trimers originating from the ring-opening product of the epoxide. The unavoidable acidic properties of the active Ti-OOH species as well as of the Ti-sites themselves play a key role for the activity loss of TS-1 during the epoxidation of methyloleate. As can be seen from Figure S10, the diol is obtained by hydrolysis of the epoxide catalyzed by the Brønsted-acidic Ti-hydroperoxo-species and/or the weak Lewis-acidic Ti-sites and nucleophilic

addition of H₂O. Subsequently, the epoxide can undergo a nucleophilic attack by the formed diol which leads to the formation of oligomers.

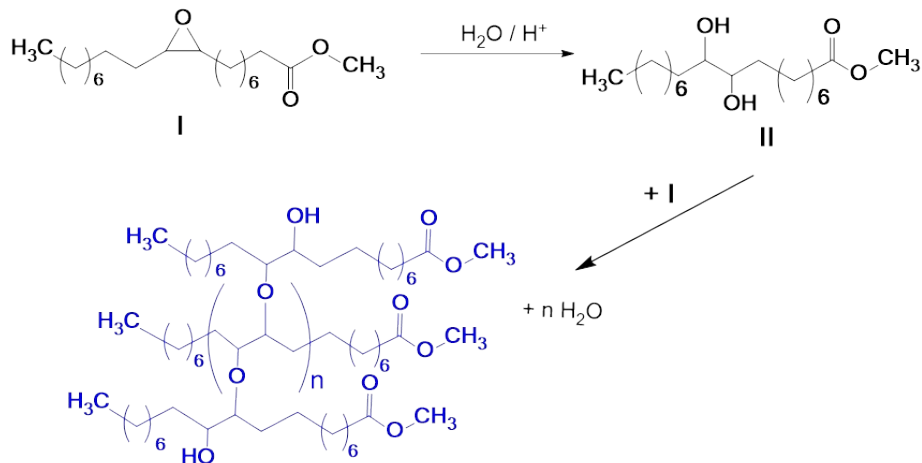


Fig. S13 Proposed reaction scheme for the formation of oligomers by consecutive reactions of the epoxide (I) and further condensation with the diol (II).

References

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2. G. F. Thiele and E. Roland, *J. Mol. Catal. A: Chem.*, 1997, **117**, 351.
3. Q. F. Wang, L. Wang, J. X. Chen, W. Wu and Z. T. Mi, *J. Mol. Catal. A: Chem.*, 2007, **273**, 73.
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