Electronic Supplementary Information (ESI) For

Construction of Unique Six-Coordinated Titanium Species with an Organic Amine Ligand in Titanosilicate and Their Unprecedented High Efficiency for Alkene Epoxidation

Le Xu, Da-Ding Huang, Chen-Geng Li, Xinyi Ji, Shaoqing Jin, Zhaochi Feng, Fei Xia,* Xiaohong Li,
Fengtao Fan,* Can Li and Peng Wu*

L. Xu, D. Huang, C. Li, X. Ji, Dr. F. Xia, Dr. X. Li, Prof. Dr. P. Wu,
Shanghai Key Laboratory of Green Chemistry and Chemical Processes
Department of Chemistry
East China Normal University
3663 North Zhongshan Road, Shanghai, 200062, China
E-mail: pwu@chem.ecnu.edu.cn, fxia@chem.ecnu.edu.cn

S. Jin, Prof. Dr. Z. Feng, Dr. Fengtao Fan, Prof. Dr. C. Li,
State Key Laboratory of Catalysis
Dalian Institute of Chemical Physics
Chinese Academy of Sciences
457 Zhongshan Road, Dalian, 116023, China
E-mail: ffan@dicp.ac.cn
Experimental section

Synthesis of catalysts

The Ti-MWW lamellar precursor was hydrothermally synthesized in the presence of boric acid using piperidine (PI) as the structure-directing agent (SDA). According to the method reported previously,[1] the gel with a molar ratio of 1.0 SiO\textsubscript{2} : 0.05 TiO\textsubscript{2} : 1.4 PI : 0.67 B\textsubscript{2}O\textsubscript{3} : 19 H\textsubscript{2}O was crystallized under rotation (10 rpm) at 443 K for 7 days. The obtained Ti-containing lamellar precursor was refluxed with 2 M HNO\textsubscript{3} aqueous solution and further calcined at 823 K for 10 h. Thus, Ti-MWW possessing the three dimensional (3D) MWW structure was obtained.

The 3D Ti-MWW was transformed to 2D lamellar structure by treating Ti-MWW in aqueous solution containing PI or hexamethyleneimine (HMI). The treatment was carried out at a PI/SiO\textsubscript{2} or HMI/SiO\textsubscript{2} molar ratio of 1.0 and an H\textsubscript{2}O/SiO\textsubscript{2} molar ratio of 10 at 443 K for 24 h. The resulting solid was collected by filtration, washed with deionized water and dried at 373 K overnight. Finally, the 2D Re-Ti-MWW-PI containing PI molecules or Re-Ti-MWW-HMI with HMI molecules was obtained.

The organic species occluded in Re-Ti-MWW-PI were totally burned off in air at 823 K for 10 h, which led to Re-Ti-MWW-cal catalyst.

The extruded titanosilicate catalysts were prepared as following: 80 g of Ti-MWW powder, 5 g of sesbania powder, 66.7 g of silica sol (30 wt.%) and 55 g of water were mixed vigorously with a blender for 2 h. The obtained solid mixture was extruded to generate the shaped catalyst of strip shape (Ø 1.8 mm). After calcination at 823 K, the shaped Ti-MWW catalyst was obtained. It was treated with aqueous PI solution using the same procedures mentioned above, then the shaped Re-Ti-MWW-PI and Re-Ti-MWW-cal catalysts were obtained.

Catalytic reactions

The epoxidation of various alkenes (1-hexene, cyclopentene, cyclohexene and cycloheptene) were carried out bathwise. A mixture of catalyst
(50 mg), alkene (10 mmol), oxidant (H₂O₂, 30 wt.% aqueous solution, 10 mmol) and acetonitrile (10 mL) was stirred vigorously at 333 K for 2 h. For the propylene epoxidations, the mixture of catalyst (30 mg), H₂O₂ (30 wt.% aqueous solution, 15 mmol) and methanol (10 g) was sealed in a Teflon-lined autoclave (100 mL). Then, propylene was charged into the reactor at a pressure of 0.4 MPa. After reaction at 333 K for 2 h, the reaction mixture was analyzed using a gas chromatograph (Shimadzu 2014, FID detector) equipped with a 30 m OV-1 capillary column and with cyclopentanone as the internal standard.

The continuous epoxidation of 1-hexene was carried out in a 40 mL three-neck fixed-bed glass reactor under reflux. For a typical run, a desired amount of the catalyst extrude (1 g), inert stuff (polytetrafluoroethylene tube, Ø 3 mm, 15 g) and 20 mL of CH₃CN were added in the reactor and heated at 333 K. The mixture of 1-hexene, CH₃CN and H₂O₂ aqueous solution (25 wt.%) were fed into the reactor with micro-pumps. The molar ratio of H₂O₂/1-hexene was 0.66. The feeding rate of the mixture was kept constant at 30.5 mL h⁻¹. With the reaction proceeding, the reaction mixture overflowed from the outlet filter and the catalyst remained in the reactor. The liquid solution was analyzed on a gas chromatograph (Shimadzu 2014) with a flame ionization detector and a OV-1 capillary column to calculate the yield and the selectivity of epoxide.

**Characterization methods**

The X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer using Cu-Kα radiation (λ=1.5405 Å). The amount of Si, Ti, and B were quantified by inductively coupled plasma (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer, while C, N elemental analysis was carried out with an Elementar Vario EL III analyzer. The thermogravimetric and differential thermal analysis were performed on a NETZSCH STA 449 F3 Jupiter Thermal Analyzer. The SEM images were taken on a Hitachi S4800 Scanning electron microscope. Solid-state NMR spectra were recorded on a VARIAN VNMRS-400MB NMR spectrometer. UV-visible diffuse reflectance spectra
were recorded on a Shimadzu UV-2700 spectrophotometer by using BaSO\textsubscript{4} as a reference. N\textsubscript{2} adsorption and desorption measurements were carried out on BELSORP-MAX instrument after the evacuation at 363 K for 5 h for Ti-MWW and Re-Ti-MWW-cal. For Re-Ti-MWW-PI, the sample was evacuated at 363 K for 3 h. UV-Raman spectroscopy with excitation line at 266 nm was recorded on UV Raman spectrograph and using a Jobin-Yvon T6400 triple-stage spectrograph with a spectral resolution of 2 cm\textsuperscript{-1}. The line at 266 nm from the double-frequency of a DPSS 532 model 200. The power of 266 nm line at samples were below 1.0 mW. XPS spectra were recorded with a PHI 5000 Versa probe equipment by using monochromatic Al K\textalpha radiation.

**Cluster Models and Theoretical Calculations**

In order to explore the Ti octahedron configurations in Re-Ti-MWW-PI and Re-Ti-MWW-cal, the density functional theory (DFT) calculations were carried out based on the constructed clusters models of Ti-MWW, Re-Ti-MWW-PI and Re-Ti-MWW-cal. The detailed structures of Ti-MWW, Re-Ti-MWW-PI and Re-Ti-MWW-cal are shown in Figure 4 (b)-(d). Since the T3 site is known to be the most possible active site in Ti-MWW zeolite\cite{2}, the cluster models mainly involving the T3 sites were constructed by truncating the Si-O bonds in the crystal structure of Ti-MWW, as shown in Figure 4a. The oxygen atoms at the boundary of cluster models were saturated with hydrogen atoms to eliminate the effect of dangling bonds. To construct the initial structures of titanium species in Re-Ti-MWW-PI and Re-Ti-MWW-cal, two Si-O bonds connecting with the central Ti in Ti-MWW were substituted by two hydroxyls to form Ti-OH species. The Ti atoms in the active sites could accommodate two water molecules or one water molecule as well as one piperidine molecule to form a novel six-coordinated pattern, as shown in Figure 4 (c) and (d), respectively.

To calculate the Raman spectra of titanium species in Re-Ti-MWW-PI and Re-Ti-MWW-cal, the hybrid functional B3LYP combined with
the basis set 6-311+G(d,p) was employed to optimize the constructed cluster models. The method of B3LYP/6-311+G(d,p) gives an accurate description of Raman spectra for TS-1 zeolite, which has been demonstrated in the previous study.[2] In the process of structural optimization, we followed the strategy proposed in the previous study.[3] The positions of hydrogen atoms at the boundary in the clusters models were firstly optimized with all the heavy atoms in the backbone fixed. Next, the heavy atoms of backbone were relaxed with the hydrogen atoms fixed. Such a strategy avoids the possible structural distortion that might be caused by a direct full optimization of cluster models. Based the optimized structures, the frequency analyses of Raman spectra were performed. The charges from electrostatic potentials (CHELP) of Ti atoms in Ti-MWW, Re-Ti-MWW-PI and Re-Ti-MWW-cal were evaluated according to the method proposed by Chirlian et al.[4] All the calculations were performed in the computational chemistry software Gaussian 09.[5]

Reference:
Fig. S1 (A) XRD patterns of parent Ti-MWW (a), Re-Ti-MWW-PI (b), and Re-Ti-MWW-cal (c). (B) Schematic description of structurally rearrangement Ti-MWW with PI treatment and further calcination.

Ti-MWW had a typical XRD pattern of 3D MWW structure (Fig. S1Aa). Re-Ti-MWW-PI, prepared from 3D Ti-MWW by hydrothermal treatment in PI aqueous solution at 443 K, showed the [001] and [002] diffractions in the 2θ range of 3-7°, which are the characteristic of a layered structure along c-direction (Fig. S1Ab). After further calcination, the layer-related [001] and [002] diffractions disappeared. It is clear to see that 3D MWW structure transfer to its 2D precursor during hydrothermal treatment, in which PI molecules inserted into the interlayer of adjacent MWW nanosheets.
Fig. S2 $^{29}\text{Si}$ MAS NMR spectra of Ti-MWW (a), Re-Ti-MWW-PI (b) and Re-Ti-MWW-cal (c).

The parent Ti-MWW showed two obvious resonances at -96.5 and -100 ppm attributed to $Q^3$ site. It indicated that the majority of Ti sites was in close tetrahedral coordinated state, while parts of them is in open state [Ti(OSi)$_3$(OH)]. Compared with Ti-MWW sample, Re-Ti-MWW-PI showed very similar resonances due to $Q^4$ sites but a much intensive resonance of $Q^3$ site (-94.5, -97.9 ppm) and an additional $Q^2$ site (-90.4 ppm), indicating more hydroxyl groups (silanols or titanols) generated during PI treatment. After calcination, a portion of defect sites disappeared, and the $Q^3$ sites decreased obviously, indicating the majority of open Ti sites were transformed back to close sites during calcination.
Fig. S3 Scanning electron micrographs of parent Ti-MWW (a, b), Re-Ti-MWW-PI (c, d) and Re-Ti-MWW-cal (e, f).

The morphology, thickness and orientation of Ti-MWW samples did not change during structural rearrangement with PI and calcination process, implying that the crystals were kept intact without dissolution and recrystallization. Any structural changes took place within interlayers of the MWW nanosheets.
Element analysis and $^{13}$C MAS NMR spectra of Re-Ti-MWW-PI indicated that the PI molecules were incorporated and remained intact without decomposition. Re-Ti-MWW-PI showed two stages of weight loss in TG analysis curve (Fig. S5). The weight loss above 573 K were attributed to the PI molecules incorporated into the intralayer sinusoidal 10-MR channels of MWW sheets (7.5 wt.%), whereas the loss below 573 K belonged to those PI molecules located between adjacent layers (7.4 wt.%). The PI treatment affected negligibly the Ti amount but made Ti-MWW deboronated slightly. These changes have little influence on the catalytic behavior. Re-Ti-MWW-PI possessed extremely low specific surface area (61 m$^2$ g$^{-1}$) and pore volume (0.001 cm$^3$ g$^{-1}$) because of pore-blocking effect by PI molecules. A further calcination reopened the pores, making the textual properties of Re-Ti-MWW-cal comparable to those of pristine Ti-MWW.
Fig. S4 $^{13}$C MAS NMR spectra of as-made Re-Ti-MWW-PI sample.

$^{13}$C MAS NMR spectra of Re-Ti-MWW-PI indicated that the PI molecules were incorporated and remained intact without decomposition.
Fig. S5 TG-DTA profiles of as-made Re-Ti-MWW-PI sample.
Table S2 The catalytic activity of the epoxidation of alkenes with different molecular size over titanosilicates.\(^a\)

<table>
<thead>
<tr>
<th>No.</th>
<th>Catalyst</th>
<th>Si/Ti</th>
<th>SA /m² g⁻¹</th>
<th>1-hexene conv. / %</th>
<th>cyclopentene conv. / %</th>
<th>cyclohexene conv. / %</th>
<th>cycloheptene conv. / %</th>
<th>TON</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ti-MWW</td>
<td>49</td>
<td>536</td>
<td>48.8</td>
<td>293</td>
<td>11.9</td>
<td>71</td>
<td>1.3</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>Re-Ti-MWW-PI</td>
<td>51</td>
<td>61</td>
<td>92.8</td>
<td>680</td>
<td>96.8</td>
<td>710</td>
<td>6.9</td>
<td>51</td>
</tr>
<tr>
<td>3</td>
<td>Re-Ti-MWW-HMI(^c)</td>
<td>50</td>
<td>79</td>
<td>90.5</td>
<td>667</td>
<td>94.1</td>
<td>694</td>
<td>6.4</td>
<td>47</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: cat., 50 mg; alkene, 10 mmol; H₂O₂ (30 wt.%), 10 mmol; CH₃CN, 10 mL; temp., 333 K; time, 2 h.

\(^b\) TON in mol (mol Ti)⁻¹. The oxide product selectivity was over 99 % for all the reactions, which is thus omitted for clarity.

\(^c\) The relative weight of the organic species in Re-Ti-MWW-HMI is 17.1 wt.%.
Fig. S6 UV-Raman spectra excited at 220 nm UV line of Ti-MWW (a), Re-Ti-MWW-PI (b) and Re-Ti-MWW-cal (c).
Fig. S7 a) Plots of apparent activation energy in the 1-hexene epoxidation. b) The reuse of Re-Ti-MWW-PI in 1-hexene epoxidation.
Table S3: Catalytic results of propylene epoxidation over several Ti-MWW and related catalysts.\textsuperscript{a}

<table>
<thead>
<tr>
<th>No.</th>
<th>Catalyst</th>
<th>Conv. ( \text{H}_2\text{O}_2 ) (%)</th>
<th>Yield PO (%)</th>
<th>Yield others (%)</th>
<th>( \text{U}^b \text{H}_2\text{O}_2 ) (%)</th>
<th>Sel. PO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ti-MWW</td>
<td>19.4</td>
<td>11.9</td>
<td>4.4</td>
<td>84.1</td>
<td>73.1</td>
</tr>
<tr>
<td>2</td>
<td>Re-Ti-MWW-PI</td>
<td>84.4</td>
<td>71.0</td>
<td>1.6</td>
<td>86.0</td>
<td>97.8</td>
</tr>
<tr>
<td>3</td>
<td>Re-Ti-MWW-cal</td>
<td>22.4</td>
<td>9.8</td>
<td>9.9</td>
<td>87.7</td>
<td>49.8</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: cat., 30 mg; CH\textsubscript{3}OH, 10 g; propylene, 0.4 MPa; H\textsubscript{2}O\textsubscript{2} (30 wt.%), 15 mmol; temp., 333 K; time, 2 h. \textsuperscript{b} Utilization efficiency of hydrogen peroxide.

The propylene epoxidation was carried out using methanol as solvent. It has been demonstrated that the best solvent for Ti-MWW in alkenes epoxidation is acetonitrile, in which the target product epoxide selectivity is maintained over 99%. The epoxide is expected to undergo easily ring-opening solvolysis reaction to yield alcohol ether byproducts in methanol.

It was concerned that the epoxide selectivity may be influenced by the acidic property of silanols or titanols in open Ti sites. However, Re-Ti-MWW-PI showed a much higher PO yield than the other two catalysts. Although more hydroxyl groups were generated during hydrothermal treatment, the presence of amine ligand with basic property in Ti micro-environment neutralized the acidity of the hydroxyl groups, and then improved the PO selectivity. Therefore, the presence of PI in Ti octahedron configurations not only enhanced the catalytic activity but also suppressed the acidity of titanols. On the other hand, the Re-Ti-MWW-cal catalyst possessing open Ti sites (\( \text{H}_2\text{O} \)) exhibited the lowest PO selectivity owing to a higher acidity. The phenomenon is very similar to that observed previously on TS-1.
Fig. S8 The proposed reaction pathway of alkenes epoxidation on close Ti site (left) and open Ti (PI) site (right).
Fig. S9 Catalytic performance of the shaped Ti-MWW (a), Re-Ti-MWW-cal (b) and Re-Ti-MWW-PI (c) catalysts in continuous epoxidation of 1-hexene on a fixed-bed reactor. Reaction conditions: see experimental section.