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## Supporting Information

# Macroscopic macroporous titanosilicate constructed of micro-mesoporous ultrathin nanofilm

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#### **Experiment section**

#### Materials.

Bisphenol A epoxy resin was purchased from Nantong xingchen Synthetic Material Co., Ltd. Tetrapropylammonium hydroxide (TPAOH, 50%) was obtained from Shanghai Bangcheng Chemical Co., Ltd. Polyethylene glycol 1000 (PEG1000), polyethylene glycol 20000 (PEG20000), triethylene tetramine (TETA), ethyl orthosilicate (TEOS, 98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Titanium (IV) isopropoxide (TiPr, 98%), cetyltrimethylammonium bromide (CTAB) were obtained from Aladdin. T-butyl hydroperoxide (TBHP, ca 5.5 M in decane) were obtained from Sigma-Aldrich Company. 1-octene, and cyclohexene were from Sinopharm Chemical Reagent Co., Ltd. Cis-cyclooctene were purchased from Alfa Aesear (China) Chemicals Co., Ltd.

#### Synthesis of monolithic epoxy-based macroporous polymer (MEMP)

Monolithic epoxy-based macroporous polymers were synthesized according to the literature procedure<sup>1</sup>.

#### Preparation of MNCMM-TiSi

A titanosilicate precursor solution (designated as solution 1) was prepared by mixing 2 ml tetrapropylammonium hydroxide (TPAOH, 50%), 8 ml distilled water, 0.2 g titanium (IV) isopropoxide (TiPr) and 5 ml ethyl orthosilicate (TEOS) under stirring at 313 K for 3 h, followed by aging at 413 K for 3 h in an autoclave. 0.3 g cetyltrimethylammonium bromide (CTAB) was mixed with 20 ml deionized water and heated to 313 K until CTAB was completely dissolved (designated as solution 2). Subsequently, 1.0 g MEMP was added to solution 2 with stirring for 10 h at 313 K, and naturally dried after being taken out. Next, the MEMP to which CTAB were adsorbed was added to solution 1, stirred at room temperature for 24 h, and aged at 313 K for 24 h. Finally, the samples were taken out, dried, carbonized under nitrogen for 2 h, and calcined at 823 K for 6 h at a heating rate of 1 K min<sup>-1</sup>. Removal of MEMP and other organic matters led to the formation of the micro-mesoporous nanofilm constructed macroscopic macroporous titanosilicate, which was denoted as MNCMM-TiSi.

#### Catalytic tests

The catalytic activity was evaluated by the epoxidations of cyclohexene, ciscyclooctene and 1-octene with TBHP, which were carried out in 25 ml glass vials on an experimental digital heating thermostat magnetic stirrer.

For cyclohexene, 4.5 mmol cyclohexene, 5 ml acetonitrile, a certain proportion of TBHP (5.5 M in decane) and 60 mg catalyst were mixed in the vial under shaking and heated to 333 K. The molar ratio of cyclohexene to oxidant was 3:1, 2:1, 1:1 and 1:2, respectively. After 5 h of reaction, the reaction systems were cooled in ice-water.

For cis-cyclooctene, 2.6 mmol cis-cyclooctene, 5 ml acetonitrile and 60 mg catalyst were added to the reactor. When the reactor temperature reached to 333K, 1.3 mmol TBHP (5.5 M in decane) was added. After reaction for 0.5 h, 1 h, 2 h, 3 h, 5 h and 7 h, respectively, the reaction systems were cooled in ice-water.

For 1-octene, 2.6 mmol 1-octene, 5 ml acetonitrile and 60 mg catalyst were added to the reactor. When the reactor temperature reached to 333K, 1.3 mmol aqueous  $H_2O_2$  (35 wt.%)/TBHP (5.5 M in decane) was added. After 5 h of reaction, the reaction systems were cooled in ice-water.

For repeatability test, after the first time reaction, the catalyst was separated from the solution, washed with ethanol, and air-dried at room temperature for 24 h. According to the proportion of the first time reaction, the reused catalyst was used for the second, third, and fourth repeated experiments, while the reused catalyst was washed with ethanol and dried each time. Finally, the reused catalyst was calcined at 823 K for 6 hours, and subjected to a fifth repeated experiment.

The products were analyzed on a gas chromatograph (Shimadzu GC-14B) equipped with a capillary column and hydrogen flame ionization detector. 1-heptane was used as an internal standard.

#### Characterization

The compositions and phases of MNCMM-TiSi were analyzed by powder XRD on a Bruker D8 instrument with a Cu Ka radiation. Fourier transform infrared (FT-IR) spectra were tested by using a Nicolet 6700 spectrometer with KBr pellets. UV-vis spectra were measured on a Perkin Elmer Lambda 950 spectrophotometer in the region of 200-800 nm using BaSO<sub>4</sub> as a reference. Prior to analysis by XRD, FT-IR and UVvis measurements, the samples were ground to powders. The isotherms of nitrogen adsorption-desorption were recorded at liquid nitrogen temperature using Mike TriStar II 3flex analyzer. Mercury intrusion porosimetry (MIP) was performed on an American Max Prep AutoPore Iv 9510 instrument to analyze the pore properties of the materials such as macropore pore size, porosity and pore volume. The microstructure of the samples was characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S4800-type), and all the samples were treated with ion sputtering metal spraying process for 90s before the measurement. Transmission electron microscopy (TEM) images were taken on an FEI-T12 electron microscope. Si/Ti molar ratios were determined by elemental analysis using a Spectro Arcos mv inductively coupled Plasma optical emission spectrometer (ICP-OES).

#### Mensuration of surface hydroxyl number

This experimental method is referenced from the literature<sup>2</sup>. Firstly, weigh 0.1 g of material, 12.5 ml of absolute ethanol and 37.5 ml of NaCl solution (20 wt.%) into a 100 ml beaker and stir well. Then use 0.1 mol/L HCl solution or 0.1 mol/L NaOH solution to adjust the pH to 4.0. Finally, slowly add 0.1mol/L NaOH solution to raise the pH to 9.0 for 20 s and keep the pH unchanged. Calculate the number of hydroxyl groups (N) on the surface of the material per nm<sup>2</sup> according to the formula (1).

$$N = \frac{CVN_A \times 10^{-3}}{Sm} \tag{1}$$

Where C is the concentration of NaOH (0.1 mol/L), V is the volume (ml) of 0.1 mol/L NaOH solution consumed when the pH value rises from 4.0 to 9.0,  $N_A$  is Avogadro's

constant, S is the specific surface area of the material  $(nm^2/g)$ , m is the mass of the material (g).

Sample	Pore size (nm)	Micropore V (cm <sup>3</sup> g <sup>-1</sup> )	Mesopore V (cm <sup>3</sup> g <sup>-1</sup> )	Macropore V $(cm^3 g^{-1})^a$	Porosity (%) <sup>a</sup>	Surface area (m <sup>2</sup> g <sup>-1</sup> )
MEMP	500~1500 <sup>a</sup>	-	-	1.20	67.5	2.29 <sup>a</sup>
MNCMM -TiSi	0.57, 3.53, 300~1200 <sup>a</sup>	0.08	0.18	3.78	92.8	504
Ti-MCM- 41	3.60	0.01	0.78	-	-	857

**Table S1** The textural properties and specific surface areas of MEMP, MNCMM-TiSi and Ti-MCM-41.

<sup>*a*</sup> determined by MIP.



Fig.S1 FT-IR spectra of MEMP and MEMP covered with titanosilicate layer.



Fig. S2 TEM images of grinded MNCMM-TiSi.

sample	diameter/mm	thickness/mm	Compressive strength/MPa
1	9.92	~2.0	4.31
2	9.90	~2.0	4.00
3	9.90	~2.0	2.58
average value			3.63

**Table S2** The mechanical strength of MNCMM-TiSi.



Fig. S3 XRD patterns of TS-1, Ti-MCM-41 and MNCMM-TiSi.



Fig. S4 The micropore distribution of MNCMM-TiSi.



**Fig. S5** Mercury intrusion curve of MNCMM-TiSi and corresponding macropore size distribution curve.



Fig. S6 SEM images of Ti-MCM-41(M) and TS-1(N).

sample		N(-OH/nm <sup>2</sup> )								
	TS-1	Ti-MCM-41	MNCMM-TiSi							
1	0.129	0.351	0.788							
2	0.165	0.442	0.716							
average value	0.147	0.395	0.752							

**Table S3** The number of hydroxyl groups (N) on the surface of TS-1, Ti-MCM-41 andMNCMM-TiSi.

Catalyst		Conversion (%)	
	cyclohexene	cis-cyclooctene	1-octene
MNCMM-TiSi	10.0	10.8	13.7
TS-1	1.4	2.7	5.0
Ti-MCM-41	4.5	4.9	4.7

**Table S4** The catalytic conversion in the epoxidation of cyclohexene, cis-cyclooctene and 1-octene with TBHP after 0.5 hour.

TOF = moles of alkene converted per mole Ti of the catalyst per hour, calculated according to the conversion after 0.5 h of reaction.

$$TOF = \frac{n_0 \times X}{n_{Ti} \times T}$$

Where  $n_0$  and  $n_{Ti}$  represent the initial molar amounts of reactant and Ti of catalyst, respectively. *X* stands for the conversion of reactant. *T* is the reaction time (0.5 h).

Oxidant	Catalyst	Si/Ti <sup>b</sup>	Conv. (%) <sup>c</sup>	TOF (h <sup>-1</sup> ) <sup>d</sup>
H <sub>2</sub> O <sub>2</sub>	MNCMM-TiSi	42.8	23.2	27.8
	<b>TS-1</b>	35.1	11.2	9.7
	Ti-MCM-41	65.2	12.9	16.3
ТВНР	MNCMM-TiSi	42.8	25.1	31.7
	<b>TS-1</b>	35.1	12.1	9.5
	Ti-MCM-41	65.2	18.1	16.2

**Table S5** The catalytic performance in the epoxidation of 1-octene with aqueous  $H_2O_2$ and TBHP<sup>a</sup>.

<sup>a</sup> Reaction conditions: 5 ml acetonitrile, 2.6 mmol 1-octene, 1.3 mmol aqueous  $H_2O_2$  (35 wt.%)/TBHP (ca. 5.5 M in decane), 60 mg catalyst, 333 K, 5h.

<sup>b</sup> Molar ratios measured by ICP-OES.

<sup>c</sup> The theoretical maximum conversion achievable under the employed reaction conditions is 50%.

 $^{d}$  TOF = moles of 1-octene converted per mole Ti of the catalyst per hour, calculated according to the conversion after 0.5 h of reaction.



**Fig. S7** Reusability of MNCMM-TiSi for the epoxidation of 1-octene with TBHP (the fifth conversion is the result of catalysis after re-calcination of MNCMM-TiSi).

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