Supplementary Material (ESI) for Chemical Communications

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Synthesis and Catalytic Performance of Ti-MCM-68 for Effective Oxidation Reactions

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Experimental

Synthesis

TS-1 samples were synthesized basically according to the procedures reported by the Enichem group (M. G. Clerici, G. Bellussi, U. Romano, *J. Catal.* 1991, **129**, 159) except that $(NH_4)_2CO_3$ was added after removing alcohol (so-called YNU system; W. Fan, R.-G. Duan, T. Yokoi, P. Wu, Y. Kubota ,T. Tatsumi, *J. Am. Chem. Soc.* 2008, **130**, 10150). Ti-BEA was synthesized using 4,4’-trimethylene-bis(*N*-benzyl-*N*-methylpiperidinium) dihydroxide according to the reported procedure (R.J. Davis, Z. Liu, J.E. Tabora, W.S. Wieland, *Catal. Lett.* 1995, **34**, 101, and Ref. 10) with slight modification. Ti-MWW was synthesized according to the procedure described in ref. 17. The SDA, *N,N,N’,N’*-tetraethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium diiodide and Al-MCM-68 (Al-MSE) zeolite were synthesized exactly following the reported procedure.[22,25] The calcined Al-MSE (Si/Al = 10) was dealuminated by treating with *xM* HNO_3 solution (60 mL/g-sample) in a 200-mL round-bottom flask at 100ºC for 24 h. The Si/Al ratios of the dealuminated samples were typically 480 (*x*=6.0; designated as deAl-MSE-A) - 930 (*x*=13.4; designated as deAl-MSE-B). In a typical procedure for Ti-insertion, the dealuminated sample (deAl-MSE-A, 500 mg) was loaded into a quartz reactor by holding with quartz wool and heated to 500°C in a flow of dry argon for 4 h. The temperature was then raised to 600°C and the sample was exposed to a flow (30 ml/min) of argon bubbled through a vessel containing $TiC1_4$ (Wako, used as received) maintained at room temperature. The $TiC1_4$ flow was continued for 20 min at 600°C unless otherwise noted. To remove the unreacted excess $TiCl_4$ inside the reactor, the argon flow was continued at 600°C for 1 h. The sample was washed thoroughly with water to give Ti-MSE (designated as Ti-MSE-A; Si/Ti=95, Si/Al=480; the values slightly vary from batch to batch). Ti-MCM-68 derived from deAl-MSE-B by the same way was designated as Ti-MSE-B. Ti-MSE-A and Ti-MSE-B were further calcined at 600ºC for 4 h to give Ti-MSE-A-cal and Ti-MSE-B-cal, respectively.

Characterization

All titanosilicates used were characterized by X-ray diffraction (MAC Science MX Labo powder diffractometer using Cu Kα radiation), N_2-adsorption (BELSORP-max-1-N, Bel Japan), and UV-Vis spectroscopy (JASCO V-550 spectrometer). Elemental analyses were performed using inductively coupled plasma atomic emission spectrometry (Shimadzu ICP-8000E). The vapour-phase adsorption measurements of water on the selected samples were performed at 25ºC on BELSORP-18 (Bel Japan). Representative physicochemical properties are shown in Table S4.

Reaction procedures

Epoxidation reactions were performed in a 20 mL glass reactor immersed in a 60°C oil bath and used 31% hydrogen peroxide as the oxidant. The reactions were carried out with 25 mg catalyst, 5.0 mmol substrate and 5.0 mmol H_2O_2 in 5.0 mL acetonitrile with vigorous stirring for 2 h. Cycloheptanone was added as an internal standard after reactions. Reaction mixtures were analyzed by gas chromatography (GC) using a Shimadz GC-14B equipped with a WCOT silicone OV-1 (Shinwa Chemical Industries; 0.25 mm x 50 m) capillary column and a flame ionization detector (FID). Products were identified using commercial standards and GC/MS analysis (JEOL JMS-600Y). The amount of hydrogen peroxide left unreacted was determined by titration with $Ce(SO_4)_2$.

The oxidation of phenol was carried out in a 20-mL round-bottom flask equipped with a condenser. For a typical reaction run, 40 mg catalyst, 21.25 mmol phenol, and 4.25 mmol H_2O_2 as an oxidant were stirred vigorously at 100°C for 10 min. The relatively low H_2O_2 value was chosen intentionally to suppress the formation of tars and unproductive decomposition of H_2O_2. Anisole was added as an internal standard after reactions. The mixture was diluted with sulfolane (2.0 g) and filtered. To the filtrate, excess K_2CO_3 (0.3 g) and acetic anhydride (80 mg) were added (exothermic reaction occurred) and stirred for 20 min in order to convert all hydroxy groups into acetoxy groups. The derivatized products were analyzed by GC on the same instrument and equipments as mentioned above. The remaining H_2O_2 was determined by the iodometry method.

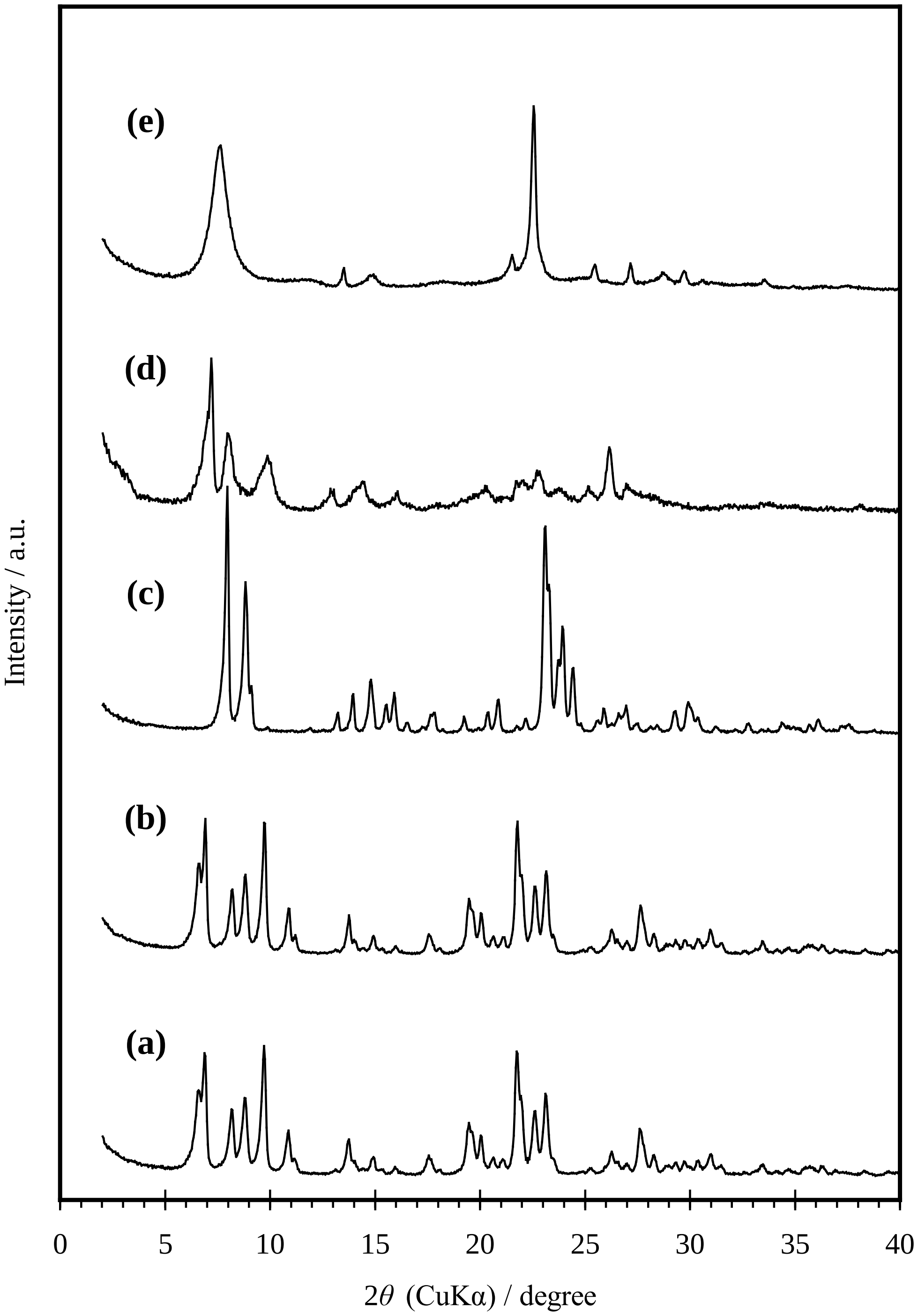


Figure S1

XRD patterns of (a) Ti-MSE-A, (b) Ti-MSE-A-cal, (c) TS-1, (d) Ti-MWW, and (e) Ti-BEA.

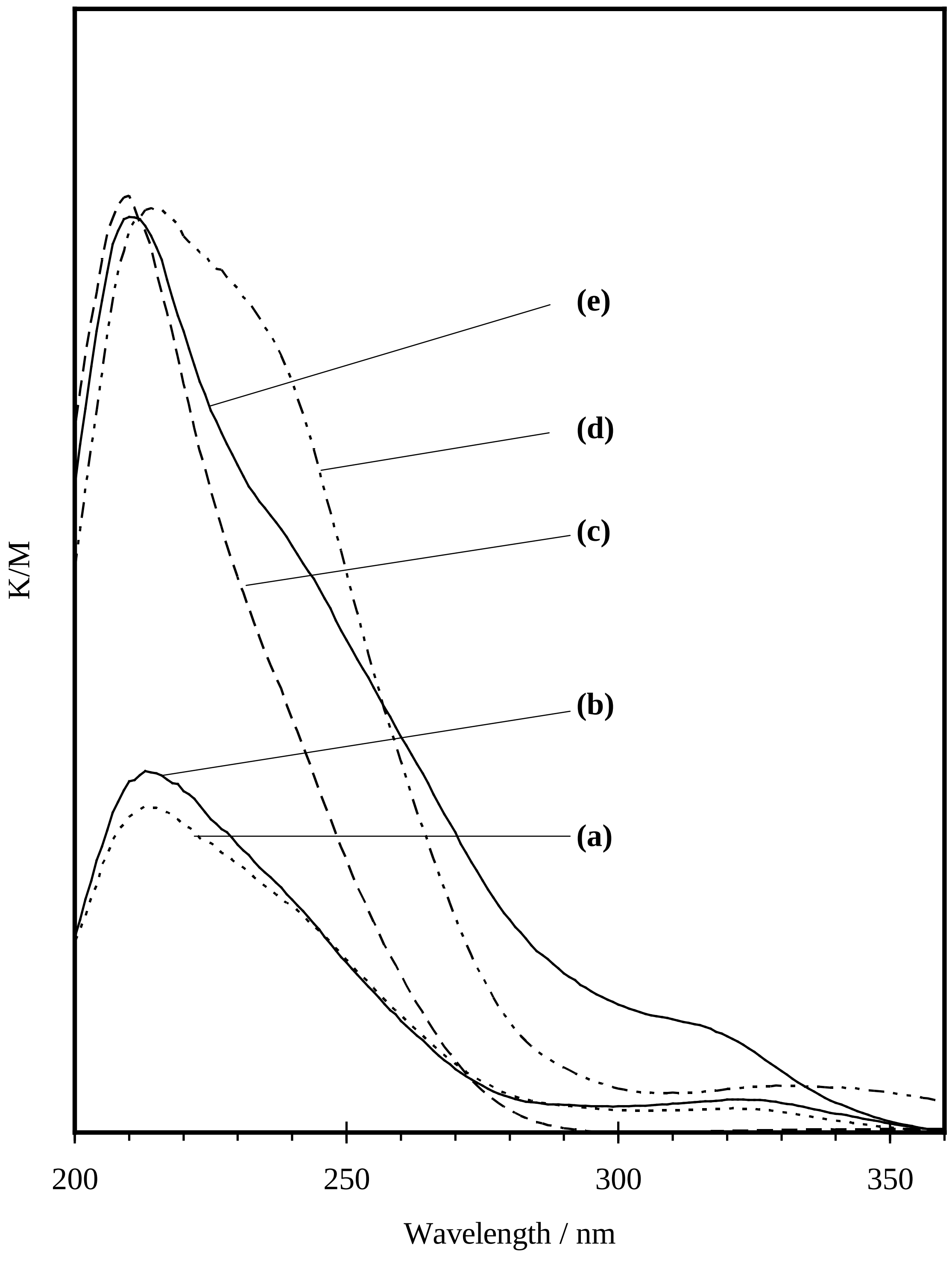


Figure S2

UV-vis spectra of (a) Ti-MSE-A, (b) Ti-MSE-A-cal, (c) TS-1, (d) Ti-MWW and (e) Ti-BEA.

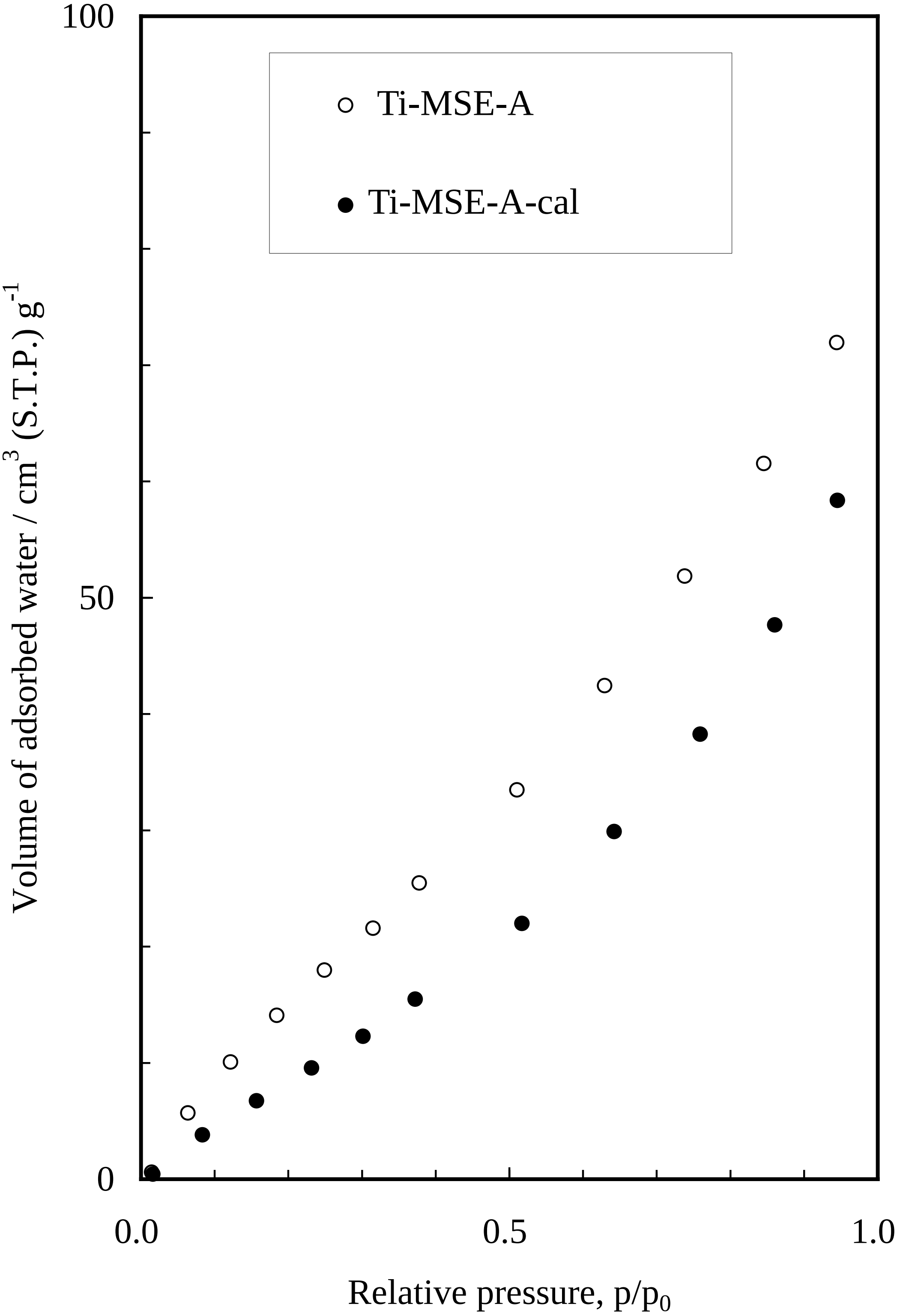


Figure S3

Effect of calcination after Ti-insertion as detected by water adsorption isotherms.

Table S1 Catalyst recycle in the oxidation of 1-hexene with H_2O_2 [a]

Reaction run [b]	Si/Al ratio	Si/Ti ratio	Conversion (%)	Selectivity (%)		TON [c]	H_2O_2	
				Epoxide **2**	Diol **3**		Conv. (%)	Eff. (%) [d]
1st	561	82	36.7	>99	0	370	37.3	>99
2nd	n.d.	n.d.	40.6	>99	0	n.d.	38.4	>99
3rd	n.d.	n.d.	34.2	>99	0	n.d.	31.1	>99

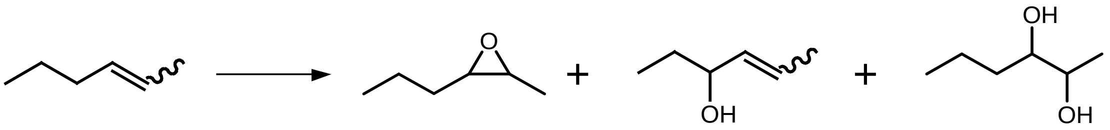
[a] Reaction conditions: 1-hexene (**1**), 5.0 mmol; catalyst (equivalent to Ti-MSE-A), 25 mg; CH_3CN, 5.0 ml, H_2O_2; 5.0 mmol; temperature, 60°C; time, 2.0 h.

[b] For each repeated run, the catalyst was calcined at 600ºC before use.

[c] TON = Turnover number (moles of [epoxide **2**+ diol **3**] per mole of Ti site).

[d] Eff. = Efficiency of H_2O_2 utilization (moles of [epoxide **2**+ diol **3**] per mole of H_2O_2 converted).

Table S2 Oxidation of 2-hexene with H_2O_2 over various titanosilicate[a]



2-hexene epoxide (**I**) (**II**) diol (**III**)

Catalyst	Si/Al ratio[b]	Si/Ti ratio[b]	Conversion (%)	Selectivity (%)			*cis* /*trans* ratio of (**I**)		TON[c]	H_2O_2	
				(**I**)	(**II**)	(**III**)	*cis*	*trans*		Conv. (%)	Eff. (%)[d]
Ti-MSE-A-cal	524	98	36.7	99	1.0	0	79	21	437	26.3	>99
Ti-MSE-B-cal	979	67	60.1	99	1.0	0	72	28	494	53.5	>99
TS-1	∞	43	26.1	>99	0	0	67	33	139	27.5	95
Ti-BEA	∞	45	35.9	99	0.4	0.6	68	32	199	46.0	77

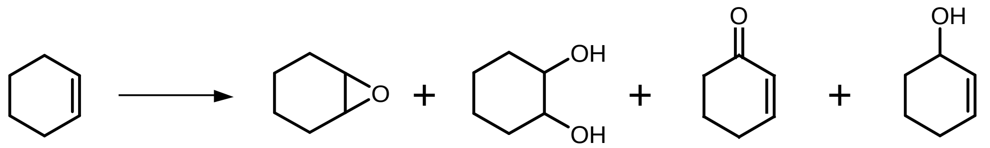
[a] Reaction conditions: 2-hexene (*cis*:*trans*=32:68), 5.0 mmol; catalyst, 25 mg; CH_3CN, 5.0 ml, H_2O_2; 5.0 mmol; temperature, 60°C; time, 2.0 h.

[b] Determined by ICP analysis.

[c] Turnover number (moles of [epoxide (**I**) + diol (**III**)] per mole of Ti site).

[d] Efficiency of H_2O_2 utilization (moles of [epoxide (**I**) + diol (**III**)] per mole of H_2O_2 converted).

Table S3 Oxidation of cyclohexene with H_2O_2 over various titanosilicate[a]



cyclohexene epoxide (**IV**) diol (**V**) (**VI**) (**VII**)

Catalyst	Si/Al ratio[b]	Si/Ti ratio[b]	Conversion (%)	Selectivity (%)			TON[c]	H_2O_2	
				(**IV**)	(**V**)	(**VI**)+(**VII**)		Conv. (%)	Eff. (%)[d]
Ti-MSE-A-cal	534	91	14.4	73.6	18.2	8.2	159	8.6	>99
Ti-MSE-B-cal	979	67	18.3	87.3	7.4	5.3	151	19.7	93
TS-1	∞	43	4.2	31.4	56.3	14.3	22	n.d.	
Ti-BEA	∞	45	28.5	58.5	36.3	5.2	159	42.6	67

[a] Reaction conditions: cyclohexene, 5.0 mmol; catalyst, 25 mg; CH_3CN, 5.0 ml, H_2O_2; 5.0 mmol; temperature, 60°C; time, 2.0 h.

[b] Determined by ICP analysis.

[c] Turnover number (moles of [epoxide (**IV**) +diol (**V**)] per mole of Ti site).

[d] Efficiency of H_2O_2 utilization (moles of [epoxide (**IV**) +diol (**V**)] per mole of H_2O_2 converted).

Table S4 Chemical compositions and textural properties of various titanosilicates used in this work

Sample	Si/Ti ratio	BET surface area /m^2 g^{-1}	Micropore volume /cm^3 g^{-1}
Ti-MSE-A	95	537	0.188
Ti-MSE-A-cal	91	543	0.190
Ti-MSE-B	67	540	0.192
Ti-MSE-B-cal	67	539	0.190
TS-1	43	460	0.177
Ti-BEA	45	770	0.306
Ti-MWW	42	500	0.172