## **Electronic Supplementary Information**

Enhancement of *para*-selectivity in the phenol oxidation with  $H_2O_2$  over Ti-MCM-68 catalyst

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## **Experimental Section**

## Preparation of catalysts

*N*,*N*,*N*',*N*'-Tetraethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium diiodide (TEBOP<sup>2+</sup>( $\Gamma$ )<sub>2</sub>) as the organic structure-directing agent (organic SDA) was synthesized according to the reported procedure<sup>S1–S3</sup> with some modifications from commercially available bicyclo[2.2.2]oct-7-ene-2,3:5,6-tetracarboxylic dianhydride (Aldrich) by three steps in *ca*. 60% overall yield. Our typical procedures are described elsewhere.<sup>S4,S5</sup>

Al-MCM-68 was hydrothermally synthesized by known methods<sup>S1-S3</sup> with slight modifications. Our typical procedure <sup>S6</sup> is as follows. Colloidal silica (Ludox HS-40, DuPont, 40 wt% SiO<sub>2</sub>, 6.01 g, 100.0 mmol), deionized water (40 mL), and Al(OH)<sub>3</sub> (Pfaltz & Bauer, 780 mg, 10.0 mmol) were mixed in a 180-mL Teflon beaker and stirred for 10 min. Aqueous KOH solution (5.93 mmol/g, 6.32 g, 37.5 mmol) was added to the solution and stirred for further 30 min. Then, TEBOP<sup>2+</sup>( $\Gamma$ )<sub>2</sub> (10.0 mmol) was added as the SDA and the mixture was stirred for another 4 h. The resulting mixture with a molar composition:  $1.0SiO_2-0.1TEBOP^{2+}(I)_2-0.375KOH-$ 0.1Al(OH)<sub>3</sub>-30H<sub>2</sub>O was taken into a 125-mL Teflon-lined autoclave and kept statically at160 °C for 16 days in a convection oven. After cooling the autoclave to room temperature, the mixture was centrifuged, and then the solid obtained was washed several times with deionized water and dried overnight. The as-synthesized MCM-68 was obtained as a white powder (6.04 g). To remove the SDA occluded in the pores, the as-synthesized MCM-68 was kept in a muffle furnace, and heated stepwise as follows: the temperature was raised from room temperature to 650 °C under 1 °C/min of the ramping rate and maintained at the same temperature for 10 h. Finally, the sample was cooled down to room temperature to give a calcined sample as a white powder (Si/Al = 10–12).

The calcined Al-MCM-68 (Si/Al = 10) was dealuminated by treating with 13.4 mol/L HNO3 solution (60 mL/g-sample) in a 200-mL round-bottom flask at 100°C for 24 h. The Si/Al ratios of the dealuminated samples were typically greater than 1000, which were designated as deAl-MCM-68.

A typical procedure for Ti-insertion to the dealuminated sample is as follows. The deAl-MCM-68 (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 TiCl<sub>4</sub> maintained at room temperature. The TiCl<sub>4</sub> flow was continued for 20 min at 600 °C unless otherwise noted. To remove the unreacted excess TiCl<sub>4</sub> inside the reactor, the argon flow was continued at 600 °C for 1 h. The sample was washed thoroughly with water to give Ti-MCM-68. Ti-MCM-68 was further calcined at 600 °C for 4 h to give Ti-MCM-68\_cal.

A portion of the dealuminated sample (deAl-MCM-68) was silvlated *before* Ti-insertion. In a typical procedure, 1.40 g of deAl-MCM-68 was suspended in 70 mL of toluene under Ar atmosphere in a 300-mL round-bottom flask. A trace of water possibly adsorbed on the solid surface was removed by azeotropic distillation using an oil bath at 150 °C prior to the silvlation. After adjusting the toluene amount to 70–80 mL and cooling down to room temperature, Ph<sub>2</sub>SiCl<sub>2</sub> (709 mg, 2.59 mmol) was added and the whole mixture was refluxed for 24 h. After cooling down, the solid was filtered off , washed thoroughly with toluene (300 mL), and dried at room temperature to give 1.48 g of the silvlated sample (denoted Ph<sub>2</sub>Si-MCM-68) as a white powder.

The Ti-insertion to the  $Ph_2Si$ -MCM-68 was performed according to the same procedure as described above. The resultant solid was designated as  $Ph_2Si$ -[Ti]-MCM-68, which was further calcined at 650 °C for 4 h to give the sample denoted as Si/[Ti]-MCM-68\_cal.

For comparison, Ti-beta was synthesized using 4,4'-trimethylenebis(1-benzyl-1-methylpiperidinium) dihydroxide as an SDA according to the reported procedure <sup>S7,S8</sup> with slight modifications.

- [S1] D. C. Calabro, J. C. Cheng, R. A. Crane, Jr, C. T. Kresge, S. S. Dhingra, M. A. Steckel, D. L. Stern and S. C. Weston, *US Pat.*, 2000, 6 049 018.
- [S2] D. L. Dorset, S. C. Weston, and S. S. Dhingra, J. Phys. Chem. B, 2006, 110, 2045–2050.
- [S3] T. Shibata, S. Suzuki, K. Komura, Y. Kubota, Y. Sugi, H. Kim and S. Gon, *Micropor. Mesopor. Mater.*, 2008, **116**, 216–226.
- [S4] S. Inagaki, Y. Tsuboi, Y. Nishita, T. Syahylah, T. Wakihara and Y. Kubota, *Chem. Eur. J.*, 2013, **19**, 7780–7786.
- [S5] M. Sasaki, Y. Sato, Y. Tsuboi, S. Inagaki and Y. Kubota, ACS Catal., 2014, 4, 2653–2657.
- [S6] Y. Kubota, S. Inagaki, Y. Nishita, K. Itabashi, Y. Tsuboi, T. Syahylah and T. Okubo, *Catal. Today*, 2015, 243, 85–91.
- [S7] R.J. Davis, Z. Liu, J.E. Tabora, W.S. Wieland, Catal. Lett. 1995, 34, 101–113.
- [S8] J. C. van der Waal, P. J. Kooyman, J. C. Jansen and H. van Bekkum, *Micropor. Mesopor. Mater.*, 1998, 25, 43–57.

Table S1	Textural properties of MCM-68 and 15-1	
Sample	BET surface area <sup>a</sup>	Micropore volume <sup>b</sup>
	$/ m^2 g^{-1}$	$/ \text{ cm}^3 \text{ g}^{-1}$
Al-MCM-68	460	0.169
deAl-MCM-68	527	0.195
Ti-MCM-68	551	0.200
Ti-MCM-68_cal	517	0.193
Si/Ti-MCM-68_cal	528	0.202
TS-1	446	0.185

partias of MCM 68 Table S1  $\mathbf{T}_{c}$ **r**01 and TS 1

*a*. BET surface area was estimated from the adsorption branch in  $P/P_0 = 0.01-0.10$ .

*b*. Micropore volume was estimated by the *t*-plot method.



Fig. S1 Reaction pathways of (a) oxidation of aniline to *p*-benzoquinone followed by reduction, (b) environmentally benign route developed by Upjohn, and (c) oxidation of phenol with  $H_2O_2$  to hydroquinone (HQ) and catechol (CL) and subsequent reactions.



Fig. S2 Schematic diagram of the preparation of Ti-MCM-68 from Al-MCM-68.



Fig. S3 FT-IR spectra of (a) Ti-MCM-68 (0.235 mmol-Ti  $g^{-1}$ ), (b) Ti-MCM-68\_cal (0.241 mmol-Ti  $g^{-1}$ ), (c) Si/Ti-MCM-68\_cal (0.300 mmol-Ti  $g^{-1}$ ), and (d) TS-1 (0.373 mmol-Ti  $g^{-1}$ ). The sample disk was prepared by pressing the titanosilicate sample (ca. 1 mg) diluted with KBr powder (ca. 100 mg). The spectra were collected at room temperature under atmospheric conditions.



Fig. S4  $^{13}$ C CP MAS NMR spectrum of Ph<sub>2</sub>Si-modified MCM-68 sample.

Conditions: reference, glycine; magic angle spinning rate, 10 kHz; recycle time, 4.0 s; accumulation, 2000 times.

The asterisk symbols indicate spinning side bands.

The sample involves residual toluene used for silylation.



Fig. S5 TG-DTA curves of Ph<sub>2</sub>Si-modified Ti-MCM-68. The analysis was performed under air flow (30 cm<sup>3</sup> min<sup>-1</sup>) with 10 °C min<sup>-1</sup> of a ramping rate.



Fig. S6 Size comparison of the pore-entrance of MSE framework with the Corey-Pauling-Koltun (CPK) models of  $TiCl_4$  and  $Ph_2SiCl_2$ .



Fig. S7 Nitrogen adsorption-desorption isotherms at 77 K of (a) calcined Al-MCM-68, (b) deakuminated MCM-68, (c) Ti-MCM-68, (d) Ti-MCM-68\_cal, (e) Si/Ti-MCM-68\_cal, and (f) TS-1. The isotherms (b), (c), (e), and (f) are offset vertically by 400, 800, 400 and 800 cm<sup>3</sup> (S.T.P.)  $g^{-1}$ , respectively. Filled and unfilled symbols indicate adsorption and desorption, respectively.



Fig. S8 Plausible mechanism of phenol oxidation with  $H_2O_2$  over a titanosilicatte catalyst to form hydroquinohe (HQ). The brown-colored curly arrows are so-called "arrow pushing" illustrating the movement of electrons as bonds are cleaved and new bonds or charges are formed. For simplicity, proton-transfer via acid-base equilibrium is omitted.