

Electronic Supplementary Information (ESI)

Highly efficient titanosilicate catalyst Ti-MCM-68 prepared using liquid-phase titanium source for the phenol oxidation

Satoshi Inagaki, Ryo Ishizuka, Yuya Ikehara, Shota Odagawa, Kai Asanuma, Shunsuke Morimoto, and Yoshihiro Kubota*

Experimental

1. Catalyst preparation

1.1. Preparation and dealumination of Al-MCM-68

The organic structure-directing agent (OSDA), *N,N,N',N'*-tetraethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium (designated as TEBOP²⁺) was synthesized as its iodide form, TEBOP²⁺(I⁻)₂, according to the reported procedure^{S1,S2} with some modifications^{S3-S5} 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 in detail elsewhere.^{S4,S5}

Al-MCM-68 was hydrothermally synthesized by known methods^{S1-S3} with slight modifications. Our typical procedure is as follows. Colloidal silica (Ludox HS-40, DuPont, 40 wt% SiO₂, 15.01 g (including 6.01 g of SiO₂), 100.0 mmol), deionized water (20 mL), and Al(OH)₃ (Pfaltz & Bauer, 780 mg, 10.0 mmol) were mixed in a 180-mL Teflon beaker and stirred for 10 min. Aqueous KOH solution (6.02 mmol g⁻¹, 6.23 g, 37.5 mmol) was added to the solution and stirred for further 30 min. Then, TEBOP²⁺(I⁻)₂ (10.0 mmol) and deionized water (20 mL) were added and the mixture was stirred for another 4 h. The resulting mixture with a molar composition: 1.0SiO₂-0.1TEBOP²⁺(I⁻)₂-0.375KOH-0.1Al(OH)₃-30H₂O was taken into a 125-mL Teflon-lined autoclave and kept statically at 160 °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 (5.72 g). To remove the OSDA occluded in the pores, the as-synthesized MCM-68 was kept in a muffle furnace, and calcined at 650 °C for 10 h after raising the temperature from room temperature to 650 °C with the ramping

rate of $1\text{ }^{\circ}\text{C min}^{-1}$. 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 (i.e., 4.0 g) was dealuminated by treating with 13.4 mol L^{-1} HNO_3 solution ($30\text{ mL g-sample}^{-1}$, i.e., 120 mL) in a 200-mL round-bottom flask under reflux conditions (oil bath temperature: $130\text{ }^{\circ}\text{C}$) for 24 h. The Si/Al ratios of the dealuminated samples were typically greater than 1000, which were designated as deAl-MCM-68.

1.2. Preparation of conventional [Ti]-MCM-68

A typical procedure for Ti-insertion to the dealuminated sample is as follows. The deAl-MCM-68 (300 mg) was loaded into a quartz reactor by holding with quartz wool and heated to $500\text{ }^{\circ}\text{C}$ in a flow of dry argon for 4 h. The temperature was then raised to $600\text{ }^{\circ}\text{C}$ and the sample was exposed to a flow ($30\text{ cm}^3\text{ min}^{-1}$) of argon bubbled through a vessel containing TiCl_4 maintained at room temperature. The TiCl_4 flow was continued for 60 min at $600\text{ }^{\circ}\text{C}$ unless otherwise noted. To remove the unreacted excess TiCl_4 inside the reactor, the argon flow was continued at $600\text{ }^{\circ}\text{C}$ for 60 min. The sample was washed thoroughly with distilled water to give [Ti]-MCM-68. [Ti]-MCM-68 was further calcined at $650\text{ }^{\circ}\text{C}$ for 4 h after raising the temperature from room temperature to $650\text{ }^{\circ}\text{C}$ with the ramping rate of $1\text{ }^{\circ}\text{C min}^{-1}$ to give [Ti]-MCM-68₆₅₀.

1.3. Preparation of Ti-MCM-68 using titanium(IV) chloride aqueous solution

1.3.1. Preparation at ambient temperature

Titanium(IV) chloride aqueous solution (Wako Chemical; Ti concentration, 3.45 mmol g^{-1} ; Cl/Ti molar ratio = 2.37–2.70; estimation based on the inspection certificate from the chemical supplier) was used for the liquid-phase treatment of deAl-MCM-68. In this paper, the solution is designated as $\text{Ti}^{4+}/\text{H}_2\text{O}$.

The deAl-MCM-68 (1.0 g) was suspended into the $\text{Ti}^{4+}/\text{H}_2\text{O}$ (6.67 g) in a 25-mL round-bottom flask at the ambient temperature ($18 \pm 2\text{ }^{\circ}\text{C}$) without using the temperature-controlled bath. The atmosphere in the flask was purged into argon, and then the treatment was performed at the ambient temperature for 60 min. The sample was washed thoroughly with distilled water to give Ti-MCM-68_{Ti⁴⁺/H₂O_rt} (ca. 0.83 g). A part of Ti-MCM-68_{rt} (0.38 g) was further calcined at $650\text{ }^{\circ}\text{C}$ for 4 h after raising the temperature from room temperature to $650\text{ }^{\circ}\text{C}$ with the ramping rate of $1\text{ }^{\circ}\text{C min}^{-1}$.

to give [Ti]-MCM-68_Ti⁴⁺/H₂O_rt_cal (0.36 g).

1.3.2. Preparation at various elevated temperatures

The careful treatment of deAl-MCM-68 using the Ti⁴⁺/H₂O was performed by using a 40-mL glass pressure tube and immersing in an oil bath preheated at 25, 40 or 60 °C. The deAl-MCM-68 (1.0 g) was suspended into the Ti⁴⁺/H₂O (6.67 g) in a 40-mL glass pressure tube at room temperature (rt: 16–20 °C). The pressure tube was purged with argon, and then the treatment was performed at a predetermined temperature (25, 40 or 60 °C) for 60 min. The sample was washed thoroughly with distilled water to give Ti-MCM-68_Ti⁴⁺/H₂O_25, Ti-MCM-68_Ti⁴⁺/H₂O_40, or Ti-MCM-68_Ti⁴⁺/H₂O_60. A part of sample was further calcined at 650 °C for 4 h after raising the temperature from rt to 650 °C with the ramping rate of 1 °C/min to give Ti-MCM-68_Ti⁴⁺/H₂O_25_cal, Ti-MCM-68_Ti⁴⁺/H₂O_40_cal or Ti-MCM-68_Ti⁴⁺/H₂O_60_cal.

1.4. Ti-modification of dealuminated MCM-68 using TiCl₄/toluene

Titanium(IV) chloride toluene solution (TiCl₄/toluene, 1.0 mol/L, Aldrich) was used for the liquid-phase treatment of deAl-MCM-68.

The deAl-MCM-68 (0.50 g) was suspended in toluene (65 mL; Wako Chemical, special grade) in a 200-mL round-bottom flask at the ambient temperature. To ensure the dryness, azeotropic distillation with toluene (ca. 15 mL ×2) was performed using a 145 °C-oil bath. After cooling down the suspension (ca. 15 mL) to 45 °C, TiCl₄/toluene (0.2 mL, 0.2 mmol) was added and the whole mixture was stirred at 45 °C for 24 h under dried air by using a drying tube (CaCl₂). After evaporation *in vacuo*, the residue was washed thoroughly with distilled water to give Ti-MCM-68_TiCl₄/toluene (0.46 g). A part of Ti-MCM-68_TiCl₄/toluene (0.36 g) was further calcined at 650 °C for 4 h after raising the temperature from room temperature to 650 °C with the ramping rate of 1 °C min⁻¹ to give Ti-MCM-68_TiCl₄/toluene_cal (0.34 g).

1.5. Ti-modification of dealuminated MCM-68 using Ti(OPr^{*i*})₄/toluene

Titanium(IV) isopropoxide (Ti(OPr^{*i*})₄, Aldrich) was used for the liquid-phase treatment of deAl-MCM-68.

The deAl-MCM-68 (4.00 g) was suspended in toluene (100 mL; Wako Chemical, special grade)

in a 200-mL round-bottom flask at ambient temperature. To ensure the dryness, azeotropic distillation with toluene (ca. 15 mL \times 2) was performed using a 145 °C-oil bath. After the toluene amount was adjusted to 100 mL without heating, $\text{Ti}(\text{OPr}^i)_4$ (0.570 g, 2.01 mmol) was added to the suspension and the whole mixture was refluxed with stirring (oil bath temperature was 140 °C) for 24 h under argon atmosphere. The solid in the mixture was collected by suction filtration and washed thoroughly with toluene (150 mL) to give 4.1 g of $\text{Ti-MCM-68_Ti}(\text{OPr}^i)_4/\text{toluene}$. A part of $\text{Ti-MCM-68_Ti}(\text{OPr}^i)_4/\text{toluene}$ (0.37 g) was further calcined at 650 °C for 4 h after raising the temperature from room temperature to 650 °C with the ramping rate of 1 °C min^{-1} to give $\text{Ti-MCM-68_Ti}(\text{OPr}^i)_4/\text{toluene_cal}$ (0.34 g).

1.6. TS-1

TS-1 was obtained from the Asia Catalyst Project in collaboration with the Catalysis Society of Japan as an Asia-reference catalyst TS-1 (catalogue specification: Si/Ti = 35).

2. Characterization

All titanosilicates used in this study were characterized by powder X-ray diffraction (XRD, Ultima-IV, Rigaku) using $\text{Cu K}\alpha$ radiation at 40 kV and 20 mA. The morphology of the solid products was observed using field-emission scanning microscope (FE-SEM, SU8010, JEOL). The textural properties, specific surface area and micropore volume of titanosilicates were evaluated using the nitrogen (N_2) adsorption–desorption isotherm (Autosorb-iQ, Quantachrome Instruments) at -196 °C. The hydrophobic nature of titanosilicates were evaluated using the water adsorption isotherm (BEL-Max, MicrotracBEL) at 25 °C. The contents of Ti in titanosilicates were measured using inductively coupled plasma atomic emission spectrometry (ICP-AES, ICPE-9000, Shimadzu). The coordination and conformation of Ti species in a liquid phase were evaluated using Raman microscopy (inVia Reflex, Renishaw) with a 532 nm excitation wavelength laser beam. The coordination states of Ti species in the titanosilicates were evaluated using diffuse reflectance UV-vis spectroscopy (DR/UV-Vis, V-550 spectrometer, JASCO). The solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were obtained using an AVANCEIII 600 (Bruker) instrument operating at 600.1 MHz for ^1H and 119.2 MHz for ^{29}Si . All MAS NMR spectra were obtained in a 4 mm diameter ZrO_2 tube. Hexamethylcyclotrisiloxane (HMCS) was used as the secondary reference of the ^{29}Si chemical

shift at -9.66 ppm. The dipolar decoupling (DD) MAS NMR measurements were performed in a contact time of 30.0 s for 1024 scans at a spinning rate of 10 kHz.

3. Typical reaction procedure

3.1. Oxidation of phenol with H_2O_2

The oxidation of phenol with H_2O_2 was performed as follows. Catalyst (20 mg), phenol (2.00 g, 21.25 mmol) and a 30 wt% aqueous solution of H_2O_2 (466 mg, 4.25 mmol) were loaded into a 35 mL glass pressure tube. When the cosolvent was used, EtOH (4.0 g, 86.8 mmol) was added to the reaction mixture. The whole mixture was immediately immersed in a pre-heated oil bath to start the reaction. The reaction mixture was stirred at 100 °C for 10 min (in the absence of cosolvents) or at 70 °C for 60 min (with a cosolvent), and then immediately cooled in an ice bath to stop the reaction. Sulfolane (2.0 g as a suitable unreactive solvent for derivatization), anisole (225 mg, 2.0 mmol, as an internal standard), and the catalyst was removed from the reaction mixture by centrifugation. The supernatant (100 mg) was treated with an excess amount of acetic anhydride (ca. 200 mg, 2 mmol) and K_2CO_3 (ca. 300 mg) at 35 °C for 10 min to achieve exhaustive acetylation of the phenolic OH groups. After removing the residual inorganic solids by filtration through a membrane filter and adjusting the concentration to the one suitable for gas chromatography (GC) with chloroform, the GC analysis was performed on a Shimadzu GC-2014 instrument equipped with a flame ionization detector using a capillary column of DB-1 (30 m length, 0.25 mm diameter, and 1.00 μ m film thickness). The unreacted H_2O_2 was quantified using the iodometry method involving titration of a well-stirred solution of the reaction mixture (1.0 g) and KI (0.2 g) in 2.0 mol L^{-1} hydrochloric acid (50 mL) with 0.1 mol L^{-1} aqueous $Na_2S_2O_3$ solution.

[S1] D. C. Calabro, J. C. Cheng, R. A. Crane, Jr, C. T. Kresge, S. S. Dhingra, M. A. Steckel, D. L. Stern, S. C. Weston, U.S. Patent 6049018, **2000**.

[S2] D. L. Dorset, S. C. Weston, S. S. Dhingra, *J. Phys. Chem. B* **2006**, 110, 2045.

[S3] T. Shibata, S. Suzuki, K. Komura, Y. Kubota, Y. Sugi, J.-H. Kim, G. Seo, *Microporous Mesoporous Mater.* **2008**, 116, 216.

[S4] S. Inagaki, Y. Tsuboi, Y. Nishita, T. Syahylah, T. Wakihara, Y. Kubota, *Chem. Eur. J.* **2013**, 19,

7780.

[S5] M. Sasaki, Y. Sato, Y. Tsuboi, S. Inagaki, Y. Kubota, *ACS Catal.* **2014**, 4, 2653.

Table S1. Textural properties of MCM-68 samples prepared in this study

Sample	BET surface area ^a / m ² g ⁻¹	Micropore volume ^b / cm ³ g ⁻¹
Al-MCM-68	501	0.178
Dealuminated MCM-68	477	0.173
Ti-MCM-68_Ti ⁴⁺ /H ₂ O_rt	485	0.174
Ti-MCM-68_Ti ⁴⁺ /H ₂ O_rt_cal	495	0.175

^a The BET surface area was estimated from the N₂ adsorption isotherm in the relative pressure range of 0.001–0.01.^{S6}

^b The micropore volume was estimated using the *t*-plot method.^{S6}

[s6] M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K. S. W. Sing, *Pure Appl. Chem.*, **2015**, 87, 1051–1069.

Table S2. Oxidation of phenol with H₂O₂ over various titanasilicate catalysts^a

Run	Catalyst	Ti content ^b / mmol g ⁻¹	TON ^c	Yield ^d / %				<i>p</i> -Sel. ^e / %
				Total	HQ	CL	<i>p</i> -BQ	
1	Ti-MCM-68_Ti ⁴⁺ /H ₂ O_rt	0.201	91	8.7	2.1	4.2	2.4	51.7
2	Ti-MCM-68_Ti ⁴⁺ /H ₂ O_rt_cal	0.217	478	44.4	25.8	8.2	10.4	81.5
3	Ti-MCM-68_TiCl ₄ /toluene	0.378	–	<0.1	<0.1	<0.1	<0.1	–
4	Ti-MCM-68_TiCl ₄ /toluene_cal	0.417	12	2.5	1.6	0.9	<0.1	64.9
5	Ti-MCM-68_Ti(OPr ⁱ) ₄ /toluene_cal	0.620	–	0.2	<0.1	0.2	<0.1	–
6	TS-1 ^f	0.360	50	8.4	4.7	3.7	<0.1	56.0

a. Reaction conditions: catalyst, 20 mg; phenol, 21.25 mmol; H₂O₂, 4.25 mmol, H₂O, 17.9 mmol; temperature, 100 °C; time, 10 min.

b. The Ti content per a gram-catalyst was determined by ICP-AES analysis.

c. Turnover number = (moles of [HQ + CL + *p*-BQ] per mole of Ti site).

d. Product yields based on added H₂O₂.

e. Selectivity to *para*-isomers of dihydroxybenzenes and quinones (moles of [HQ + *p*-BQ] per moles of [HQ + CL + *p*-BQ]).

f. Data from ref. 29.

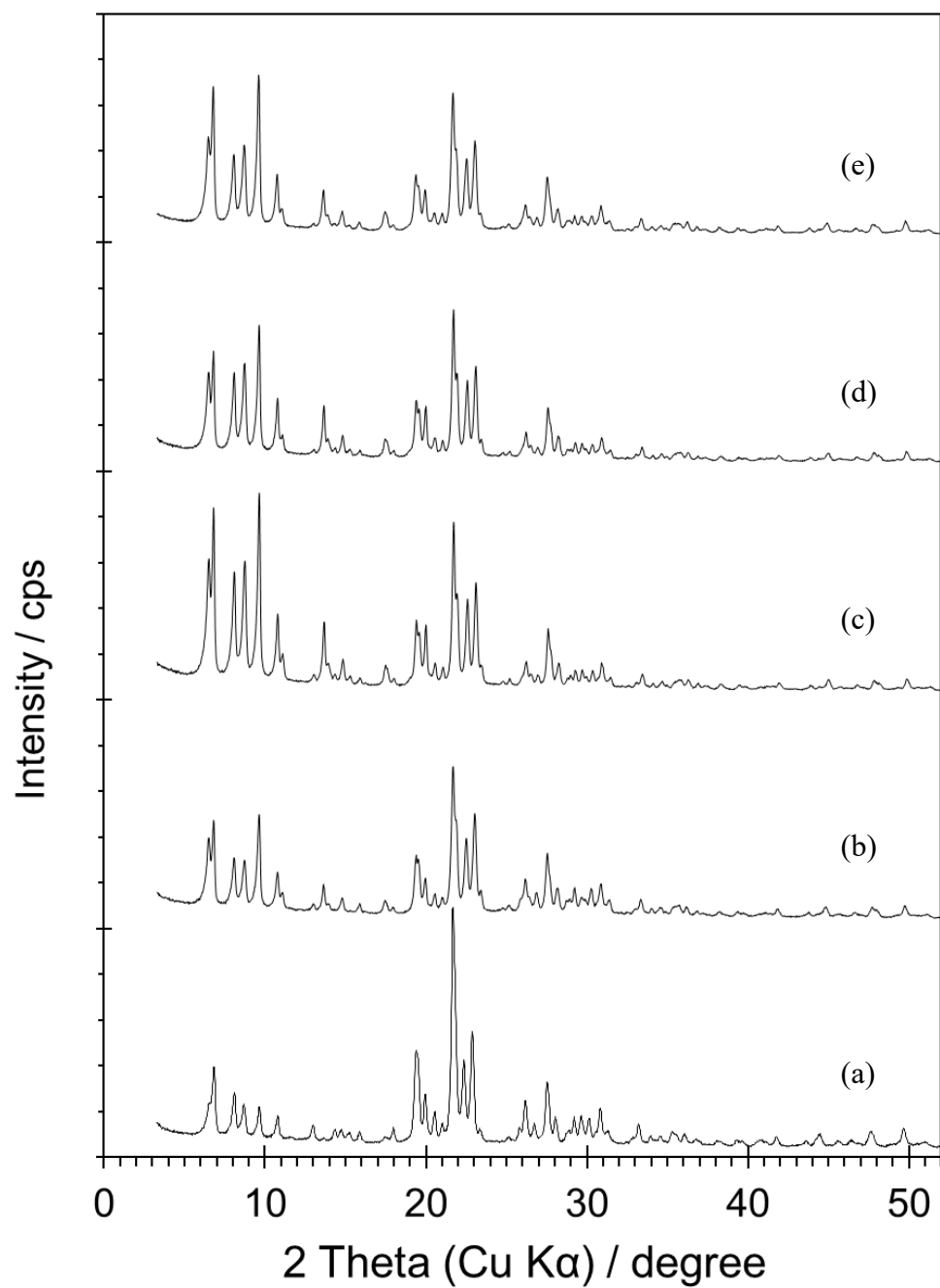
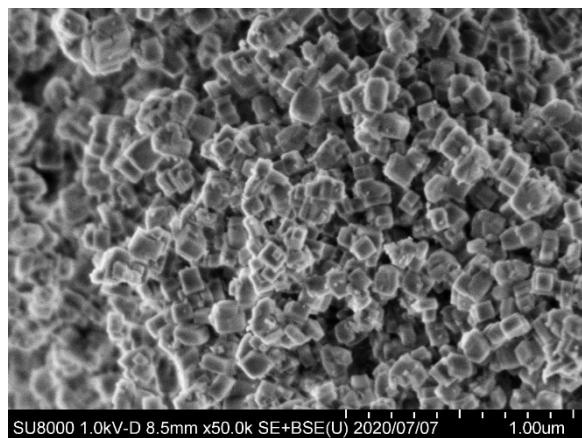


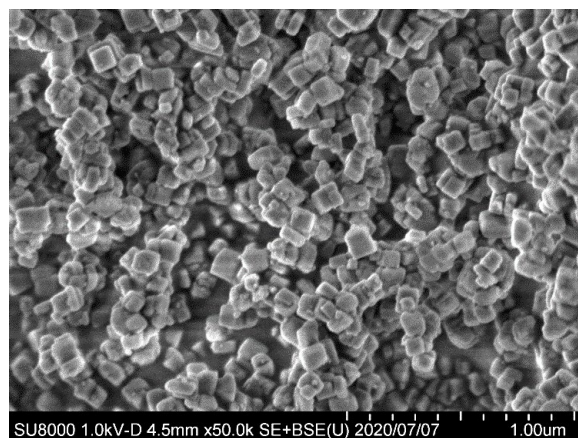
Figure S1. Powder XRD patterns of (a) as-prepared Al-MCM-68, (b) calcined Al-MCM-68, (c) dealuminated MCM-68, (d) [Ti]-MCM-68_Ti⁴⁺/H₂O_rt, and (e) [Ti]-MCM-68_Ti⁴⁺/H₂O_rt_cal.

(a)



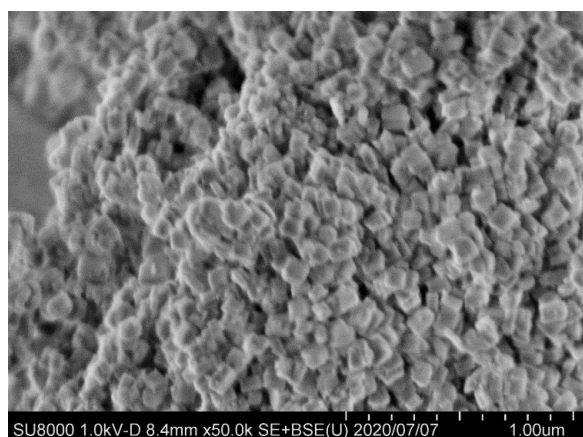
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(b)



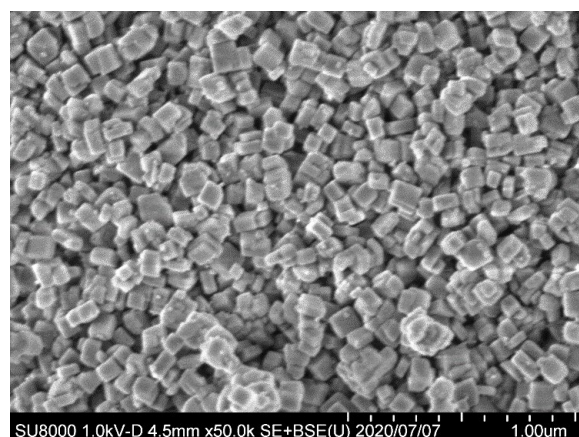
200 nm

(c)



200 nm

(d)



200 nm

Figure S2. Typical FE-SEM images of (a) calcined Al-MCM-68, (b) dealuminated MCM-68, (c) [Ti]-MCM-68_Ti⁴⁺/H₂O_rt, and (d) [Ti]-MCM-68_Ti⁴⁺/H₂O_rt_cal.

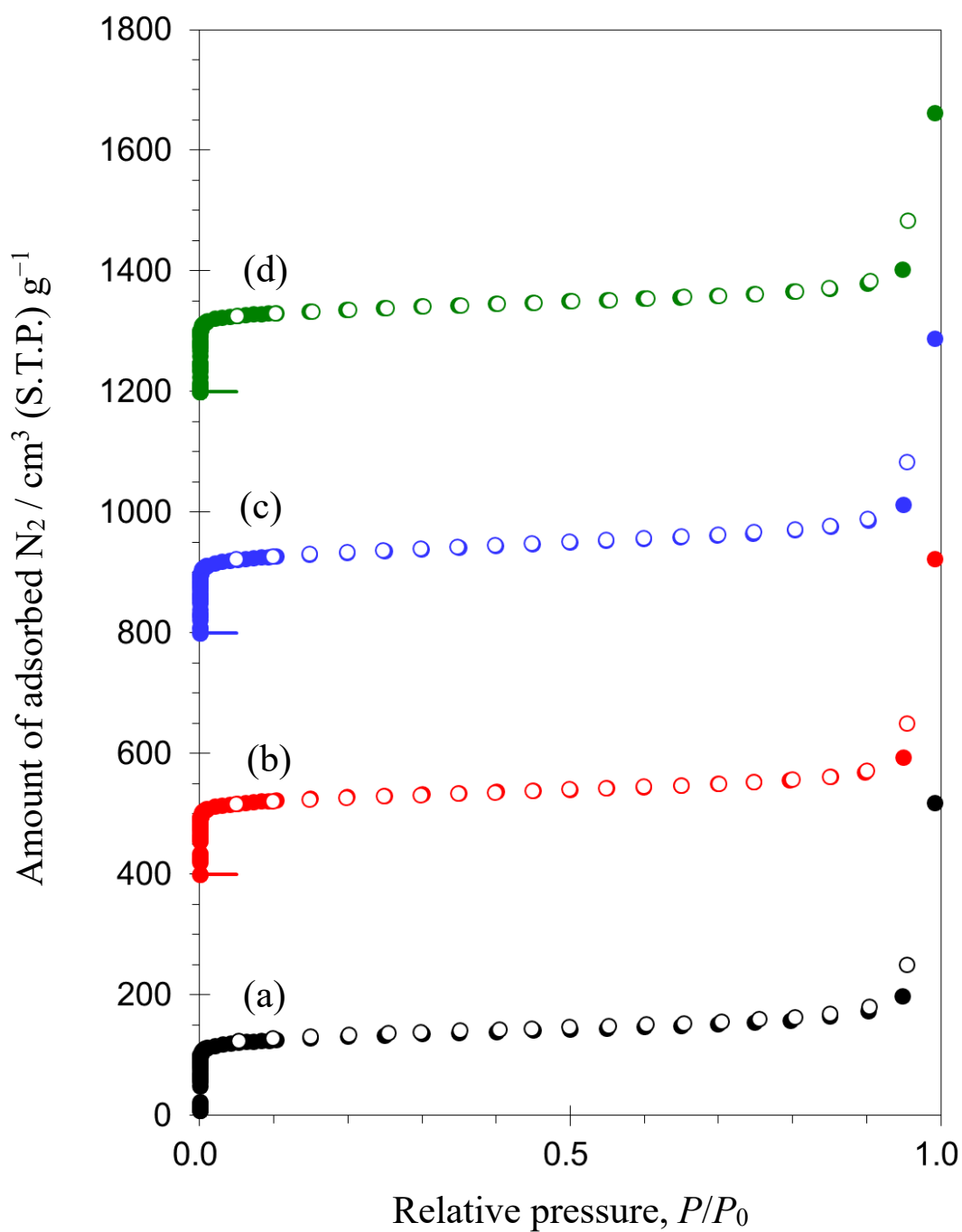


Figure S3. N_2 adsorption-desorption isotherms of (a) Al-MCM-68, (b) dealuminated MCM-68, (c) Ti-MCM-68_Ti⁴⁺/H₂O_rt, and (d) Ti-MCM-68_Ti⁴⁺/H₂O_rt_cal.

The isotherms of (b), (c) and (d) were offset vertically at 400, 800 and 1200 $\text{cm}^3 \text{ g}^{-1}$, respectively. Filled and unfilled symbols indicate adsorption and desorption branches, respectively.

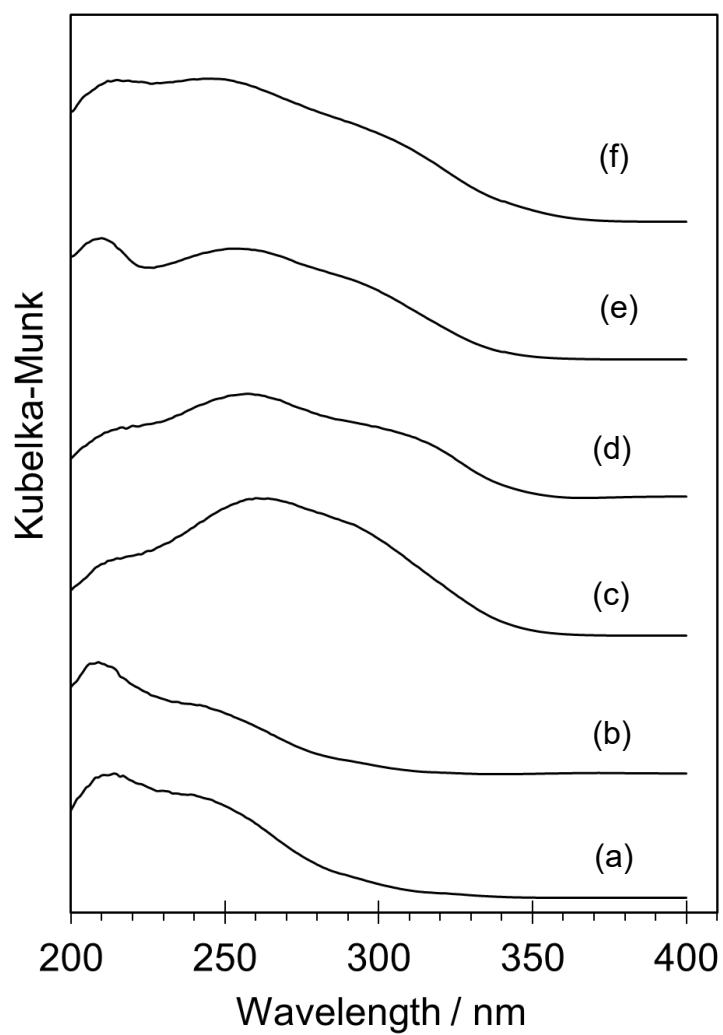


Figure S4. DR/UV-vis. spectra of (a) Ti-MCM-68_Ti⁴⁺/H₂O_rt, (b) Ti-MCM-68_Ti⁴⁺/H₂O_rt_cal, (c) Ti-MCM-68_TiCl₄/toluene, (d) Ti-MCM-68_TiCl₄/toluene_cal, (e) Ti-MCM-68_Ti(OPrⁱ)₄/toluene, and (f) Ti-MCM-68_Ti(OPrⁱ)₄/toluene_cal.

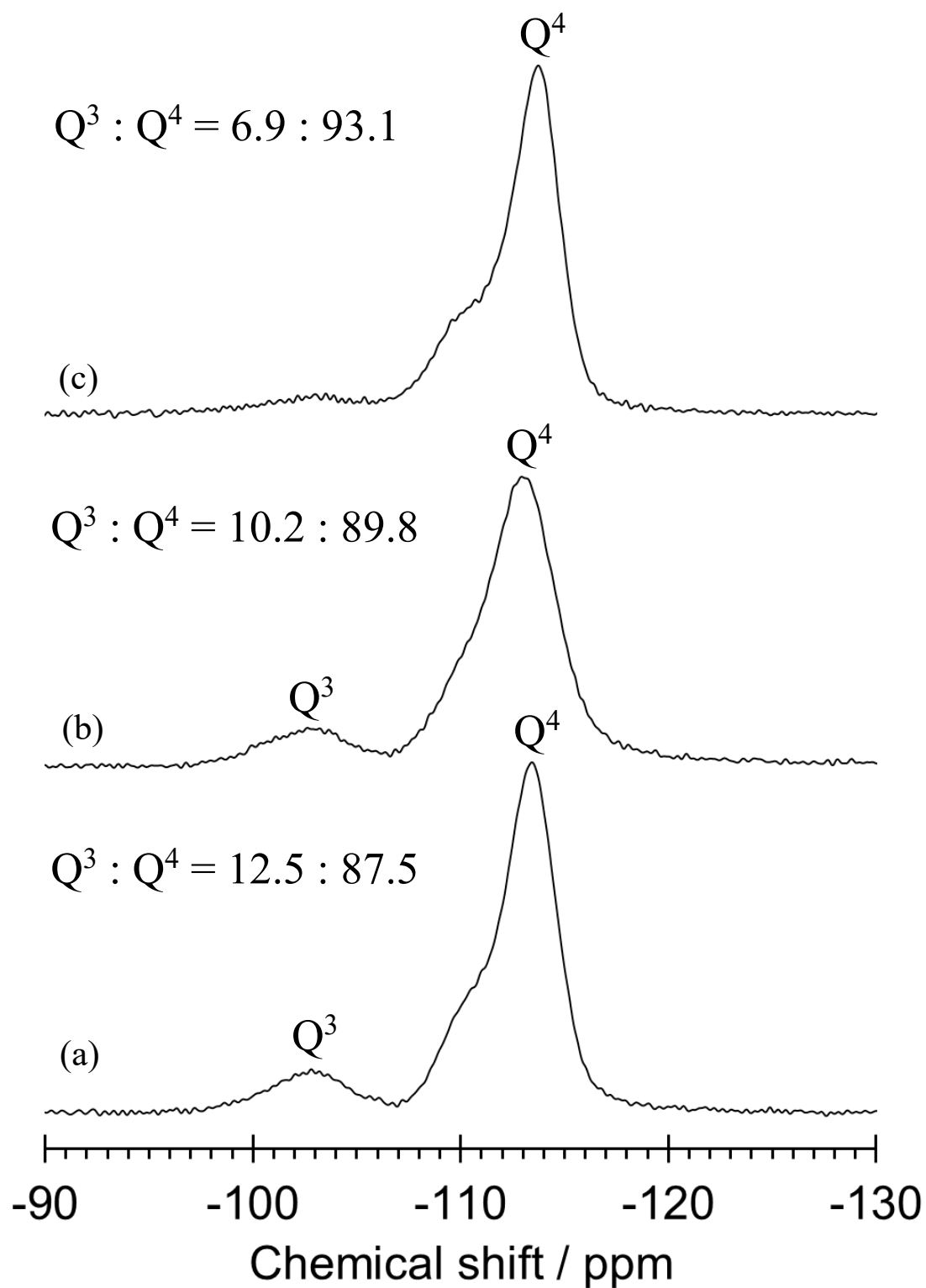


Figure S5. ^{29}Si DD MAS NMR spectra of (a) dealuminated MCM-68, (b) Ti-MCM-68_ $\text{Ti}^{4+}/\text{H}_2\text{O}$ _rt, and (c) Ti-MCM-68_ $\text{Ti}^{4+}/\text{H}_2\text{O}$ _rt_cal.

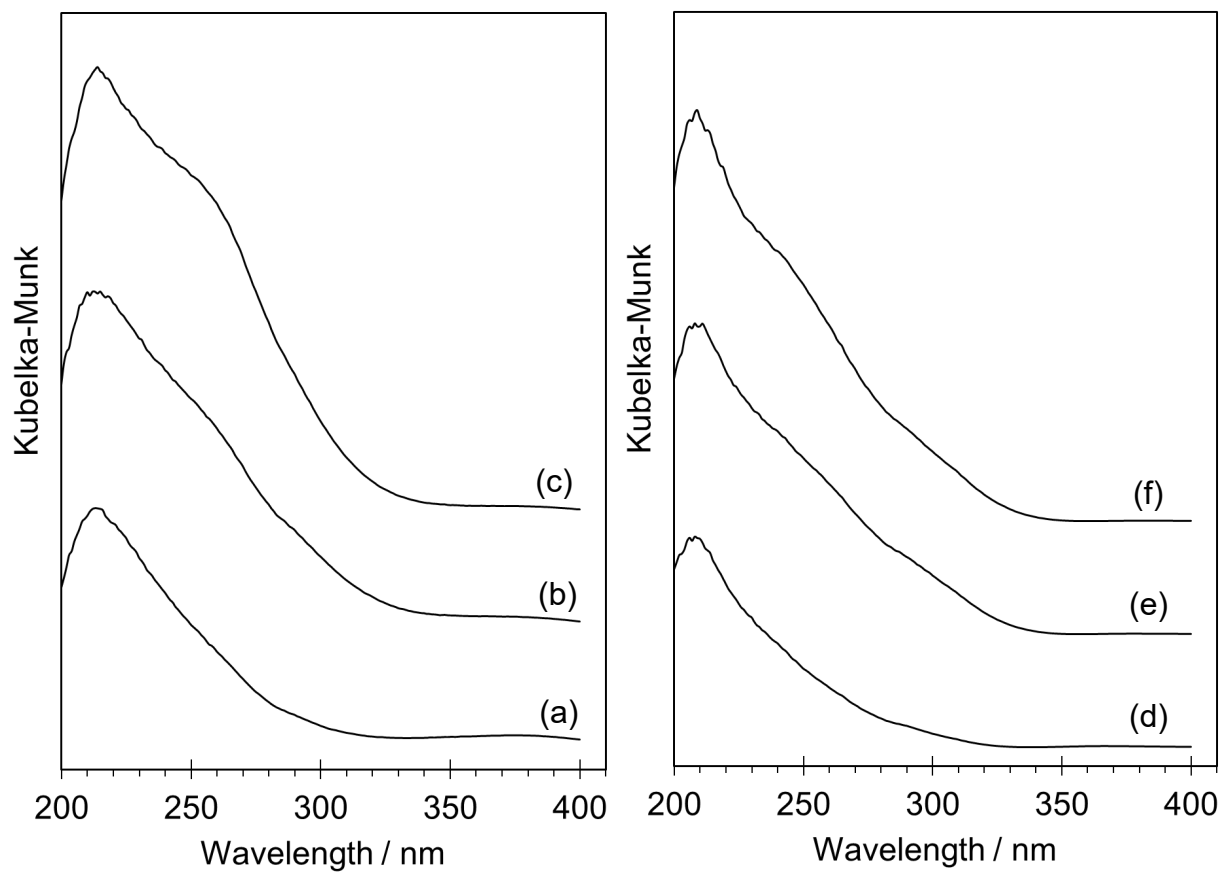


Figure S6. DR/UV-visible spectra of (a) Ti-MCM-68_Ti⁴⁺/H₂O_25, (b) Ti-MCM-68_Ti⁴⁺/H₂O_40, (c) Ti-MCM-68_Ti⁴⁺/H₂O_60, (d) Ti-MCM-68_Ti⁴⁺/H₂O_25_cal, (e) Ti-MCM-68_Ti⁴⁺/H₂O_40_cal, and (f) Ti-MCM-68_Ti⁴⁺/H₂O_60_cal.

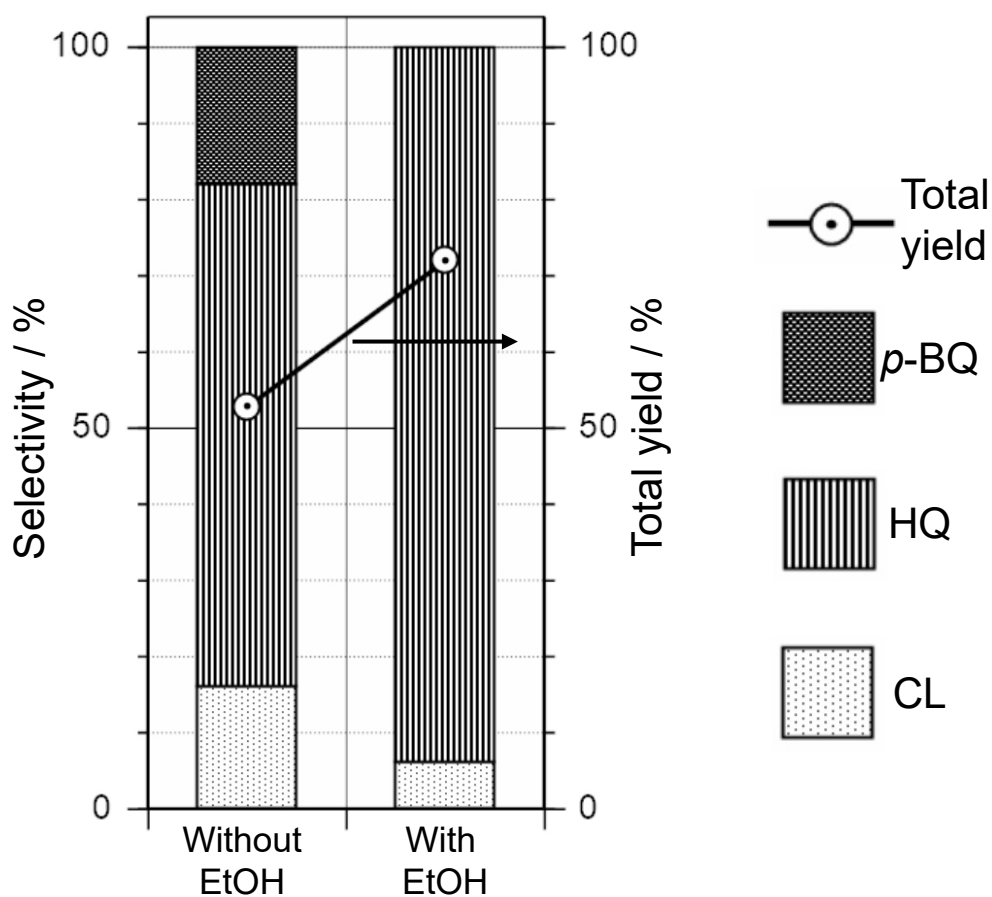


Figure S7. Typical effect of ethanol (EtOH) as a cosolvent exemplified by the phenol oxidation reaction over Ti-MCM-68_Ti⁴⁺/H₂O_40_cal. Reaction conditions: catalyst, 20 mg; phenol, 21.25 mmol; H₂O₂, 4.25 mmol, H₂O, 17.9 mmol; EtOH (cosolvent), 0 or 86.8 mmol (4.0 g); temperature, 70 °C; time, 60 min.