Electronic Supplementary Information

Enhancement of para-selectivity in the phenol oxidation with H₂O₂ 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 (TEBOP²⁺(I⁻)²) as the organic structure-directing agent (organic SDA) was synthesized according to the reported procedure⁹¹–³ 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.⁹⁴,⁹⁵

Al-MCM-68 was hydrothermally synthesized by known methods⁹¹–³ with slight modifications. Our typical procedure⁹⁶ is as follows. Colloidal silica (Ludox HS-40, DuPont, 40 wt% SiO₂, 6.01 g, 100.0 mmol), deionized water (40 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 (5.93 mmol/g, 6.32 g, 37.5 mmol) was added to the solution and stirred for further 30 min. Then, TEBOP²⁺(I⁻)² (10.0 mmol) was added as the SDA and the mixture was stirred for another 4 h. The resulting mixture with a molar composition: 1.0SiO₂–0.1TEBOP²⁺(I⁻)²–0.375KOH–0.1Al(OH)₃–30H₂O was taken into a 125-mL Teflon-lined autoclave and kept statically at 160 ºC 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 ºC under 1 ºC/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 100ºC 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 TiCl₄ maintained at room temperature. The TiCl₄ flow was continued for 20 min at 600 °C unless otherwise noted. To remove the unreacted excess TiCl₄ 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 silylated 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 silylation. After adjusting the toluene amount to 70–80 mL and cooling down to room temperature, Ph₂SiCl₂ (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 silylated sample (denoted Ph₂Si-MCM-68) as a white powder.

The Ti-insertion to the Ph₂Si-MCM-68 was performed according to the same procedure as described above. The resultant solid was designated as Ph₂Si-[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 with slight modifications.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area $^a$ / m$^2$ g$^{-1}$</th>
<th>Micropore volume $^b$ / cm$^3$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-MCM-68</td>
<td>460</td>
<td>0.169</td>
</tr>
<tr>
<td>deAl-MCM-68</td>
<td>527</td>
<td>0.195</td>
</tr>
<tr>
<td>Ti-MCM-68</td>
<td>551</td>
<td>0.200</td>
</tr>
<tr>
<td>Ti-MCM-68_cal</td>
<td>517</td>
<td>0.193</td>
</tr>
<tr>
<td>Si/Ti-MCM-68_cal</td>
<td>528</td>
<td>0.202</td>
</tr>
<tr>
<td>TS-1</td>
<td>446</td>
<td>0.185</td>
</tr>
</tbody>
</table>

$^a$. 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 \( \text{H}_2\text{O}_2 \) 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  $^1$H CP MAS NMR spectrum of Ph$_2$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 Ph₂Si-modified Ti-MCM-68. The analysis was performed under air flow (30 cm³ min⁻¹) with 10 °C min⁻¹ of a ramping rate.
Fig. S6  Size comparison of the pore-entrance of MSE framework with the Corey-Pauling-Koltun (CPK) models of TiCl₄ and Ph₂SiCl₂.

View along [001]
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$^3$ (S.T.P.) g$^{-1}$, respectively. Filled and unfilled symbols indicate adsorption and desorption, respectively.
Fig. S8  Plausible mechanism of phenol oxidation with H$_2$O$_2$ over a titanosilicate catalyst to form hydroquinone (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.