Supporting Information

High Activity and Stability in the Cross-Coupling of Aryl Halides with

Disulfides over Cu-doped Hierarchically Porous Zeolite ZSM-5

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1. Materials Synthesis

1.1 Synthesis of Cu-ZSM-5-M

Tetraethyl orthosilicate (TEOS), sodium aluminate (NaAlO₂), tetrapropylammonium hydroxide (TPAOH) and cupric nitrate (Cu(NO₃)₂•3H₂O) were purchased from Chinese Pharmic Group Chemical Co. Silane ($[(C_2H_5O)_3SiC_3H_6N(CH_3)_2C_{18}H_{37}]Br$, TPOAB) was obtained from Guangzhou Dymatic Investment Co. Cu-doped mesoporous zeolite ZSM-5 (Cu-ZSM-5-M) was synthesized from selfassembly of aluminosilicate gel with TPOAB mesoscale template. The molar ratio of various compositions was 1Al₂O₃/1.Na₂O/2.5CuO/69SiO₂/15.1 TPAOH/13.2TPOAB /1552H₂O. Typically, 0.16 g NaAlO₂ was dissolved into 18.0 mL of water followed by addition of 12.0 mL TPAOH and 15.0 mL TEOS. After stirring of the mixture at room temperature for 4.5 h, 0.6 g of Cu(NO₃)₂•3H₂O was then introduced and the reaction mixture was stirred at 75°C for another 5 h. Finally, 7.5 mL of TPOAB was added by dropwise and stirred for 1 h, the obtained aluminosilicate gel was transferred into Teflon-coated stainless-steel autoclave for static crystallization at 180 °C for 3 days. The resultant product was filtered, washed, dried at 120 °C overnight and calcined in air at 550 °C for 5 h. The Cudoped mesopore-free ZSM-5 (Cu-ZSM-5) and mesoporous zeolite ZSM-5 (ZSM-5-M) were also synthesized by the similar procedures except for the absence of the TPOAB and the Cu(NO₃)₂•3H₂O, respectively.

1.2 Preparation of Cu-ZSM-5-MI

The ZSM-5-M supported Cu catalyst (Cu-ZSM-5-MI) was prepared by incipient wetness impregnation of the support using cupric nitrate solution. After impregnation, the sample was exposed under ambient condition for 20 h, and further dried at 120 °C for 12 h and calcined in air at 550 °C for 5 h.

2. Characterization

X-ray powder diffraction (XRD) analysis was conducted on a RIGAKU Smart Lab diffractometer. using Cu K α radiation. Nitrogen adsorption-desorption isotherms were obtained using a Micromeritics ASAP2020M apparatus at the temperature of liquid nitrogen (-196 °C). Specific surface areas were calculated from the adsorption data, using the Brunauer-Emmett-Teller (BET) equation. The pore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) model. Scanning electron microscopy (SEM) images were obtained using a field-emission scanning electron microscope (SUPRA55) operating at an acceleration voltage of 5 kV. Transmission electron microscopy (TEM) images of the sample were obtained on a JEM-2100F microscope with a limited line resolution capacity of 1.4 Å, under a voltage of 200 kV. Before characterization by the TEM technique, the sample was cut into thin slices and dropped onto a Cu-grid coated with carbon membrane. To further investigate the location of Cu species in the Cu-ZSM-5-M catalyst, the additional TEM and EDS experiments were performed on a Tecnai G² F30 S-Twin Philips-FEI microscope with a limited line resolution capacity of 1.4 Å, under a voltage of 300 kV. Before characterization by TEM technique, the samples were dispersed ultrasonically in an ethanol solution and dropped onto a Ni-grid coated with carbon membrane. X-ray photoelectron spectroscopic (XPS) experiments were performed using an ESCALAB MK II system. The Cu content and the ratios of Si/Al were determined by the inductively coupled plasma optical emission spectroscopy (ICP-OES) with a Perkin-Elmer 3300DV emission spectrometer. UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded in Perkin-Elmer Lambda 25 spectrometer with an integration sphere. BaSO₄ was used as a reference sample to measure the baseline spectrum.

3. Activity Assessment

All reagents unless otherwise noted were obtained from commercial sources (purity > 99%) and used without further purification. The typical experimental procedure for the cross-coupling reaction was as

S3

followed: 30 mg catalyst, 0.6 mmol aryl halides, 0.2 mmol disulfides and 2 mL of solvent were placed into a 15 mL glass vessel, and purified by nitrogen. The reaction was proceeding at setting temperature for 12 h. After the reaction finished, the catalyst was separated by centrifugation and filtered to obtain the liquid phase. The liquid products were analyzed by an Agilent 7890A gas chromatograph equipped with a flame ionization detector. The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (60-90 °C) and ethyl acetate as eluents. Compounds described in the literature were characterized by comparing their ¹H and ¹³C NMR spectra and MS data to the reported data. The ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) were recorded with spectrometers at 20 °C using CDCl₃ as the solvent. Chemical shifts were given in parts per million relative to TMS as the internal standard at room temperature.

4. General Procedure for the Recyclability Experiment

The resulting mixture was treated with ethyl acetate and H_2O (3×5 mL). The catalyst was recovered from the solution by centrifugation, dried under vacuum, and reused for the next run. The combined organic layer was detected by GC-FID, and some residual K₂CO₃ was the new K₂CO₃ (42 mg, 0.3 mmol), diphenyl disulfide (0.1 mmol), iodobenzene (0.3 mmol), and DMSO (1 mL) under an atmosphere of nitrogen for the next run.

5. The mechanical and chemical stability of Cu-ZSM-5-M catalyst

The XRD, ICP, N₂ adsorption-desorption experiments for the reused Cu-ZSM-5-M catalyst were performed to survey its mechanical and chemical stability, and the results are listed in Fig. 1a, Fig. S7 and Table S1. To obtain the desired amount of the reused Cu-ZSM-5-M catalyst, the magnified experiment was carried out as followed: 210 mg catalyst, 4.2 mmol aryl halides, 1.4 mmol disulfides and 14 mL of solvent were placed into a 100 mL round-bottom flask. And the general procedure for the

recyclability experiment is the same as the process that was described above.

6. Figures



Fig. S1. TEM images of the thin-sectioned Cu-ZSM-5-M and Cu-ZSM-5-MI samples. (a) overview,(b) high resolution image showing mesopores, (c) high resolution image of the selected area in the Fig.S1b of the Cu-ZSM-5-M sample. (d) TEM image of the thin-sectioned Cu-ZSM-5-MI sample.



Fig. S2 TEM image of the (a) thin-sectioned microporous Cu-ZSM-5 sample and (b) the magnified SEM image of the selected area in (a). (The selected zone is analyzed by element mapping, as shown in

Fig. S3).



Fig. S3 The element mapping and EDS analysis of O, Al, Si and Cu in the selected area marked in Fig. S2a.



Fig. S4 TEM image of the (a) thin-sectioned mesoporous Cu-ZSM-5 sample and (b) the magnified SEM image of the selected area in (a). (The selected zone is analyzed by element mapping, as shown in

Fig. S5).



Fig. S5 The element mapping and EDS analysis of O, Al, Si and Cu in the selected area marked in Fig. S4a.



Fig. S6 (a) Low and (b) high resolution TEM images of the thin-sectioned Cu-ZSM-5-M sample (the selected zone as same as the zone in Fig. S4a after destruction of the zeolite framework by the electron

beam).



Fig. S7 N₂ adsorption isotherm of the reused Cu-ZSM-5-M sample (inset: pore size distribution of the sample).

7. Tables

Sample	S_{BET}^{a}	\mathbf{S}_{ext}^{b}	V _{mic} ^c	$V_{mes}{}^d$	Si/Al ^e	$\mathrm{W}_{\mathrm{Cu}}(\mathrm{wt.\%})^{f}$
	(m^{2}/g)	(m ² /g)	(cm^{3}/g)	(cm^{3}/g)		
Cu-ZSM-5-M	337	168	0.08	0.45	32	1.3
Cu-ZSM-5	329	67	0.10	0.06	37	1.4
Cu-ZSM-5-MI	339	164	0.10	0.46	35	1.8
Reused Cu-ZSM-5-M	320	160	0.08	0.42	33	1.2

Table S1 Textural parameters of the different samples.

^{*a*} BET surface area. ^{*b*} External surface area. ^{*c*} Microporous pore volume. ^{*d*} Mesoporous pore volume.

^e The Si/Al ratio is obtained by ICP.^f The Cu content is detected by ICP.

S.S.	+	$\frac{\text{Catalyst, K}_2\text{CO}_3}{\text{DMSO, 110 °C, 12 h}}$			
Entry	Recycle	Yield (%)			
	Recycle	Cu-ZSM-5-M	Cu-ZSM-5-MI		
1	run 1	100	77		
2	run 2	94	70		
3	run 3	95	66		
4	run 4	94	61		
5	run 5	91	54		
6	run 6	92	50		
7	run 7	88	47		
8	run 8	84	45		
9	run 9	93	50		
1 2 3 4 5 6 7 8 9	run 1 run 2 run 3 run 4 run 5 run 6 run 7 run 8 run 9	100 94 95 94 91 92 88 84 93	77 70 66 61 54 50 47 45 50		

 Table S2 Recycle experiment of the Cu-ZSM-5-M and Cu-ZSM-5-MI catalysts.

8 Compound Characterization Data



(1) Diphenylsulfane: Colorless liquid ¹; ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.32 (m, 4H), 7.32-7.28 (m, 4H), 7.26-7.23 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 135.76, 131.02, 129.17, 127.02.



(2) phenyl(p-tolyl)sulfane: Colorless liquid¹;¹H NMR (500 MHz, CDCl₃) δ 7.50-6.78 (m, 9H),
2.26 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 137.56, 137.11, 132.25, 131.30, 130.04, 129.78, 129.01,
126.38, 21.10.



(3) (4-methoxyphenyl)(phenyl)sulfane: Colorless liquid¹;¹H NMR (500 MHz, CDCl₃) δ 7.37-7.32 (m, 2H), 7.18-7.13 (m, 2H), 7.11-7.04 (m, 3H), 6.85-6.80 (m, 2H), 3.75 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 159.81, 138.57, 135.34, 128.90, 128.18, 125.74, 124.29, 114.96, 55.35.



(4) (4-nitrophenyl)(phenyl)sulfane: Yellow solid, m. p. 55-56 °C; ¹H NMR (500 MHz, CDCl₃) δ
8.37-8.32 (m, 2H), 8.16-8.12 (m, 2H), 7.96-7.95 (m, 2H), 7.66-7.62 (m, 1H), 7.59-7.54 (m, 2H); ¹³C
NMR (125 MHz, CDCl₃) δ 150.41, 147.37, 140.03, 134.12, 129.69, 128.97, 128.03, 124.52.



(5) (4-bromophenyl)(phenyl)sulfane: Yellow liquid, ¹H NMR (500 MHz, CDCl₃) δ 7.42-7.38 (m, 2H), 7.37-7.34 (m, 2H), 7.34-7.30(m, 2H), 7.30-7.28 (m, 1), 7.19-7.16 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 135.44, 134.77, 132.17,132.02, 131.50, 129.32, 127.51, 120.81.



(6) (2-nitrophenyl)(phenyl)sulfane: Yellow solid, m. p. 80-81 °C; ¹H NMR(500 MHz, CDCl₃) δ
8.16 (dd, J = 8.0, 1.0 Hz, 1H), 7.53-7.50 (m, 2H), 7.44-7.40 (m, 3H), 7.28-7.24 (m, 1H), 7.16-7.12 (m, 1H), 6.79 (dd, J = 8.5, 1.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 139.44, 135.89,133.36, 131.05, 130.087, 129.98, 129.02, 128.32, 125.72, 124.9.



(7) naphthalen-1-yl(phenyl)sulfane: Colorless liquid ¹;¹H NMR (500 MHz, CDCl₃) δ 8.40-8.36
(m, 4H), 7.90-7.84 (m, 2H), 7.67 (dd, J = 7.0, 1.0 Hz, 1H), 7.54-7.49 (m, 2H), 7.44 (dd, J = 8.5, 7.5 Hz, 1H), 7.24-7.20 (m, 2H), 7.20-7.13 (m, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 136.89, 134.21, 133.57, 132.55, 131.19, 129.19, 129.05, 128.98, 128.54, 126.92, 126.41, 126.11, 125.80, 125.61.



(8) 2-((phenylthio)methyl)furan: Yellow liquid, ¹H NMR (500 MHz, CDCl₃) δ 7.36-7.33 (m, 3H), 7.31-7.25 (m, 3H), 7.23-7.19 (m, 1H), 6.27 (dd, J = 3.0, 1.5 Hz, 1H), 6.09 (dd, J = 3.5, 0.5 Hz, 1H), 4.10 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 150.99, 142.13, 135.49, 130.59, 128.84, 126.77, 110.44, 107.84, 31.66.











210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10





10 200 190 140 130 120



9. References

(1) J. Y. Mao, T. Z. Jia, G. Frensch and P. J. Walsh. Org. Lett., 2014, 16, 5304.