Electronic Supplementary Information (ESI)

"Switching Catalytic Reaction Conducted in Pore Void of Mesoporous Material by Redox Gate Control"

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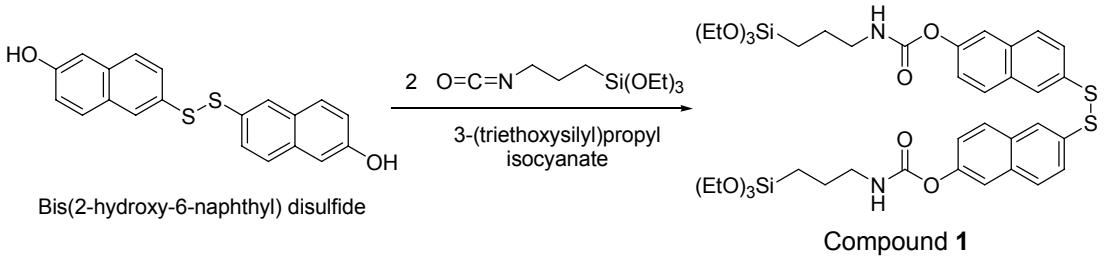
Experimental Procedures

Mesoporous silica (sample: MS): Mesoporous silica material (MS) was synthesized by a modified method based on reported one [Martin, T.; Galarneau, A.; Renzo, F. D.; Fajula, F.; Plee, D. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 2590.]. To a solution of NaOH (2.84 g; 71.1 mmol) and n-hexadecyltrimethylammonium bromide (9.86 g; 27.1 mmol) in 97 mL of deionized water, 16.24 g of silica (Merck Silica-Gel 60) was added and the resulting silica-suspended solution was stirred for 2 h. This solution was placed under hydrothermal conditions using a Teflon-lined autoclave at 115 °C for 20 h. The obtained material was filtered off, washed with deionized water, and dried at 120 °C for 20 h. This as-synthesized material was calcined at 550 °C for 6 h.

Al-loaded mesoporous silica (sample: Al-MS): 9.0 g of calcined mesoporous silica (MS) was added to the toluene solution (50 mL) of $Al(acac)_3$ (2.59 g; 8.0 mmol). This suspension was refluxed for 2 h. The volatiles were removed under reduced pressure, and the residual solid was dried at 120 °C for 3 h, and calcined at 550 °C for 7 h (9.54 g).

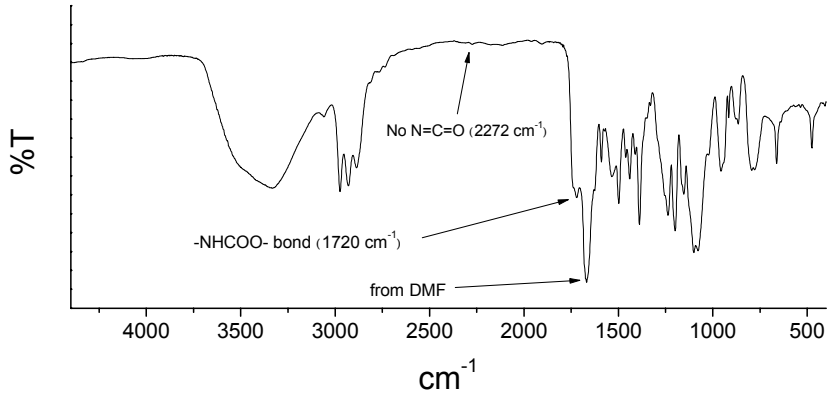
Disulfide-modified Al-loaded mesoporous silica [sample: (SS)Al-MS]: Compound **1** was obtained by the reaction of 6-hydroxy-2-naphthyl disulfide (0.350 g; 1.00 mmol) and 3-(triethoxysilyl)propyl isocyanate (0.498 g; 2.01 mmol) both from Aldrich at 100 °C for 40 h in 5 mL of dry DMF as shown below. The complete consumption of silane isocyanate was ensured by the disappearance of infrared characteristic band at 2272 cm^{-1}. All portion of this DMF solution was diluted with dry toluene, to fix the concentration of compound **1** as 0.1 M. This mixed solution (1.5 mL; as compound **1**: 0.15 mmol; 0.127 g) was added to 60 mL of dry toluene, and next 6.0 g of Al-MS was mixed. This solution was refluxed for 20 h. Volatiles were removed under reduced pressure. This solid thus obtained was washed with benzene (400 mL) two times, and finally dried under air at 60 °C for 18 h (6.2 g).



Bis(2-hydroxy-6-naphthyl) disulfide

Compound **1**

Infrared spectrum of the DMF solution of compound **1**



Thiol-modified Al-loaded mesoporous silica [sample: (SH)Al-MS]: 5.0 g of (SS)Al-MS was added to the aqueous solution (100 mL) of dithiothreitol (DTT: 1.686 g, 10.9 mmol) and this suspension was stirred for 16 h at room temperature. The solid was filtered and thoroughly washed with deionized water, and dried under vacuum at room temperature for 3 h (4.84 g).

Regenerated disulfide-modified Al-loaded mesoporous silica-2 [sample: (SS)*Al-MS]: 0.5 g of (SH)Al-MS was mixed with 0.067 g of I_2 in H_2O (12.5 mL) and AcOH (12.5 mL). This resulting solution was stirred at room temperature for 20 h. After filtration, the solid was washed thoroughly using deionized water (1 L) and EtOH (5 L), because remained HI (as a by-product) and I_2 promotes AMS dimerization (0.37 g of dried sample was obtained).

Reaction conditions for AMS (α-methylstyrene) Dimerization

To a suspension of a catalyst (20 mg) in 5 mL of dry toluene, 1 mmol of AMS (α-methylstyrene) was added. The resulting solution was stirred vigorously at 80 or 120 °C for 2 h or 6 h. After cooling, the catalyst was filtered, and bibenzyl as GC internal standard was added to filtrate. The amounts of AMS recovered and AMS dimers were analyzed by capillary GC (Shimadzu GC-1700).

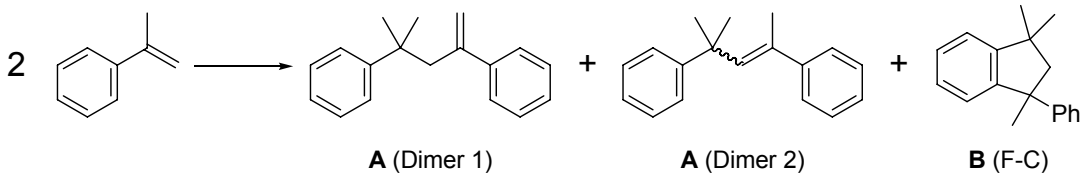
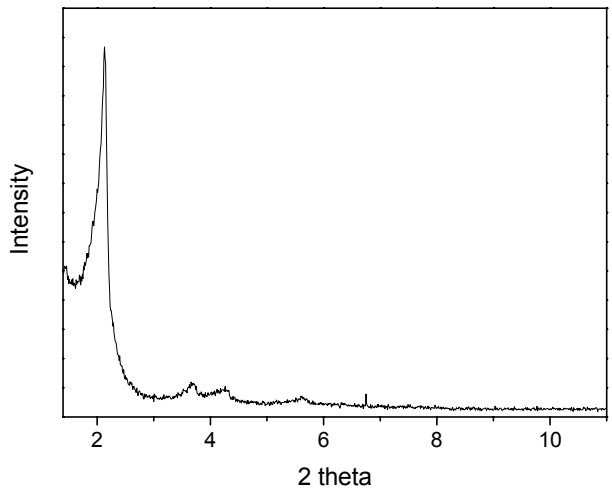


Table S1. Yields of AMS Dimerization

Catalyst	Conditions	**A** (Dimer 1)	**A** (Dimer 2)	**B** (F-C)
MS	120 °C, 2 h	0.1	<0.1	<0.1
Al-MS	120 °C, 2 h	<0.1	<0.1	>99.0
	80 °C, 2 h	1.9	6.7	85.5
(SS)Al-MS	120 °C, 2 h	<0.1	0.4	<0.1
	120 °C, 6 h	<0.1	0.9	<0.1
(SH)Al-MS	120 °C, 2 h	0.7	1.0	97.1
	80 °C, 2 h	16.9	42.8	37.5
(SS)*Al-MS	120 °C, 2 h	0.1	<0.1	<0.1
	120 °C, 6 h	1.5	<0.1	0.2

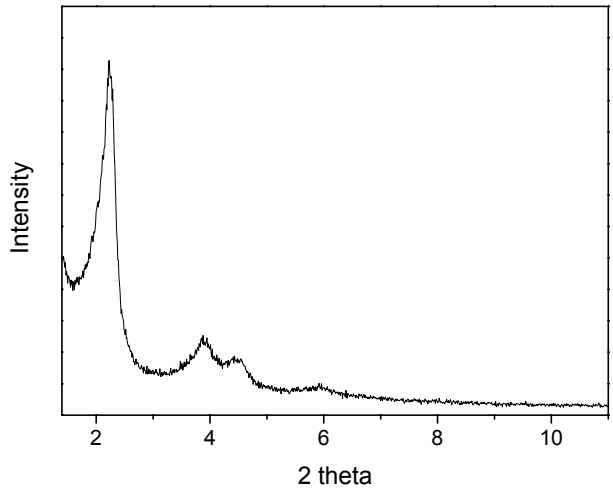
XRD patterns

As-synthesized MS (before calcination)



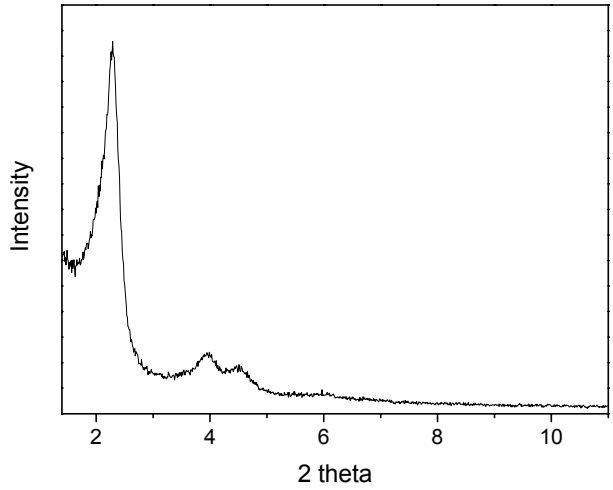
$d_{100:}$ 2.14 (2 theta); 4.13 (nm)

MS (after calcination)



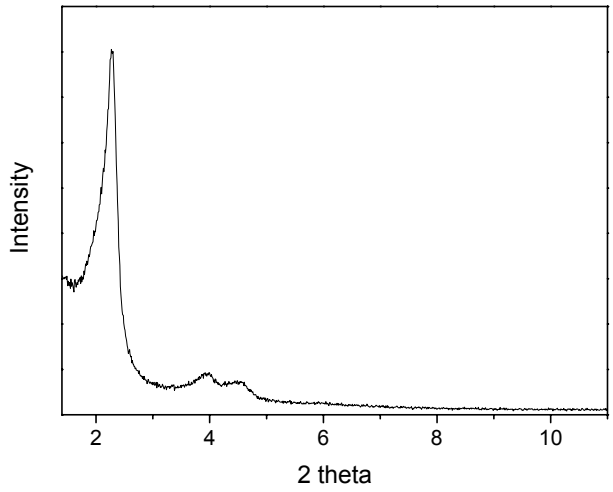
$d_{100:}$ 2.23 (2 theta); 3.96 (nm)

Al-MS



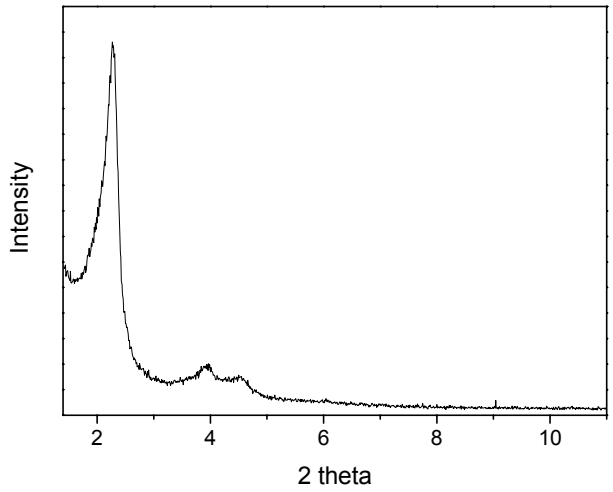
$d_{100:}$ 2.29 (2 theta); 3.86 (nm)

(SS)Al-MS



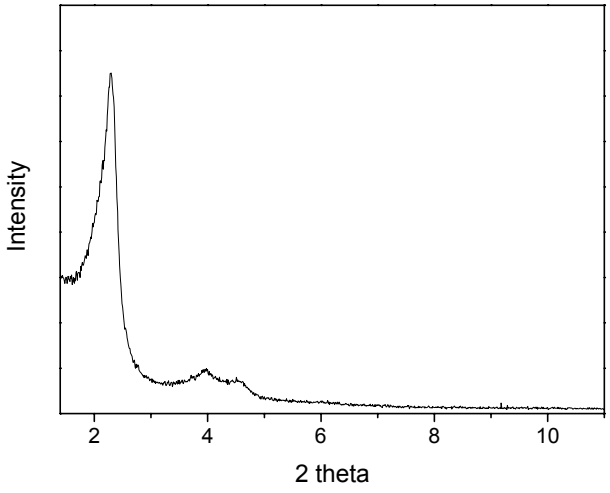
$d_{100:}$ 2.28 (2 theta); 3.87 (nm)

(SH)Al-MS



$d_{100:}$ 2.30 (2 theta); 3.84 (nm)

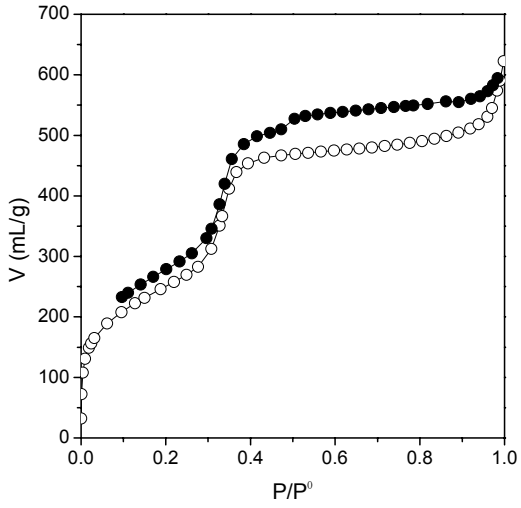
(SS)*Al-MS

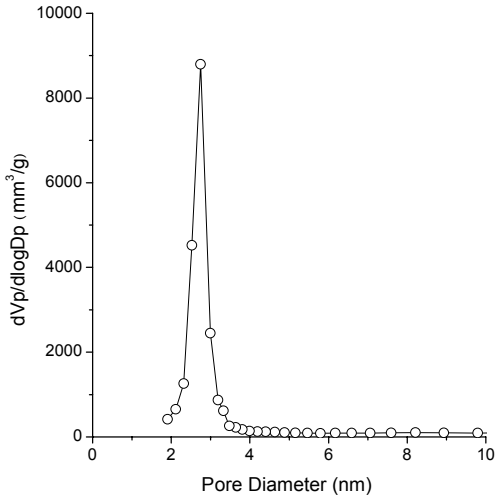


$d_{100:}$ 2.30 (2 theta); 3.84 (nm)

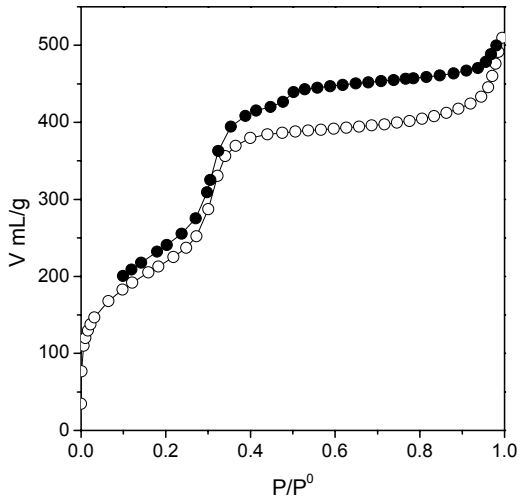
Nitrogen adsorption-desorption isotherms and BJH pore size distribution estimated by the adsorption branches of the isotherms

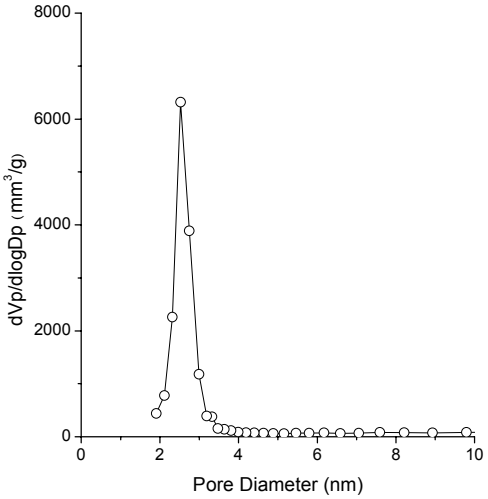
Sample: MS



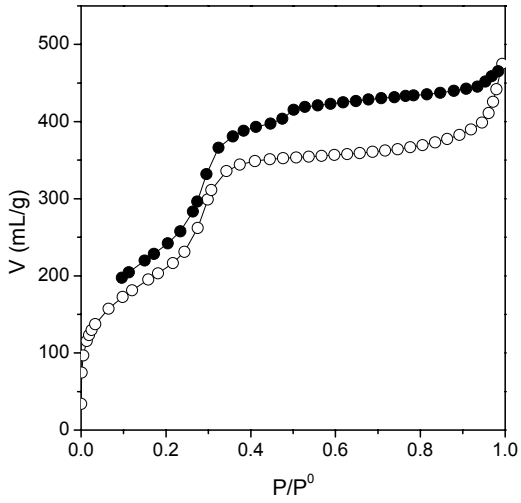


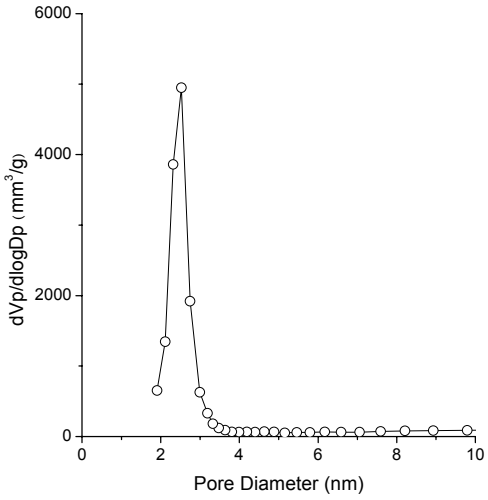
Sample: Al-MS



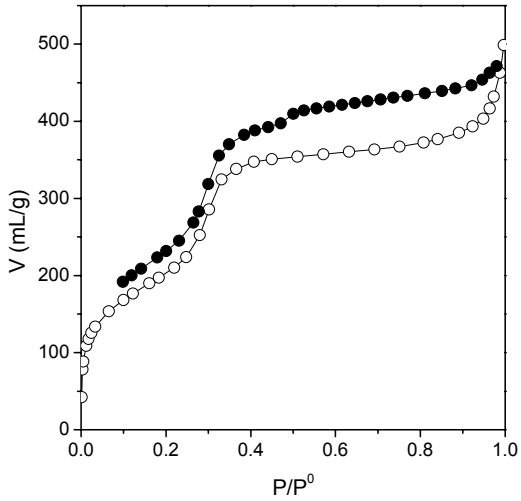


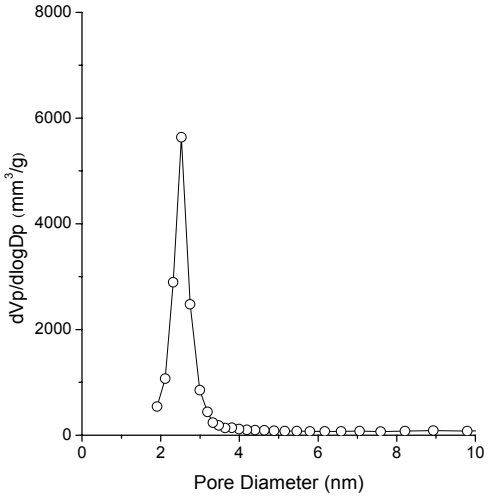
Sample: (SS)Al-MS



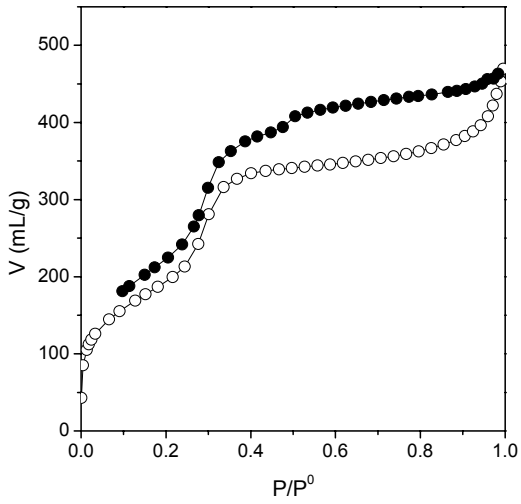


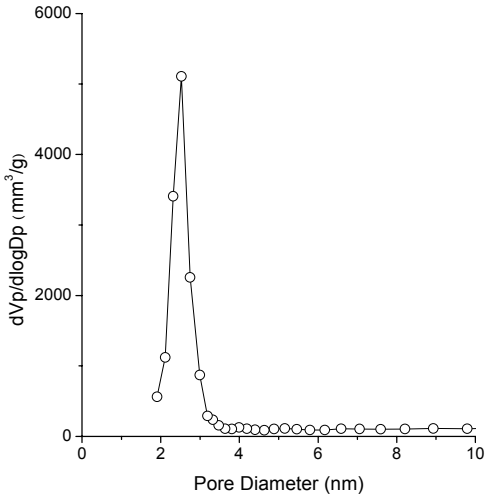
Sample: (SH)Al-MS





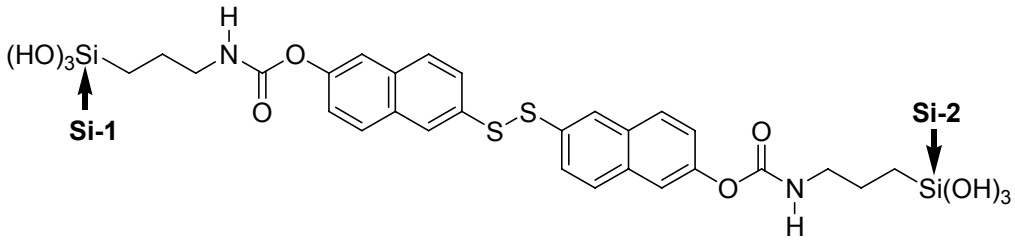
Sample: (SS)*Al-MS

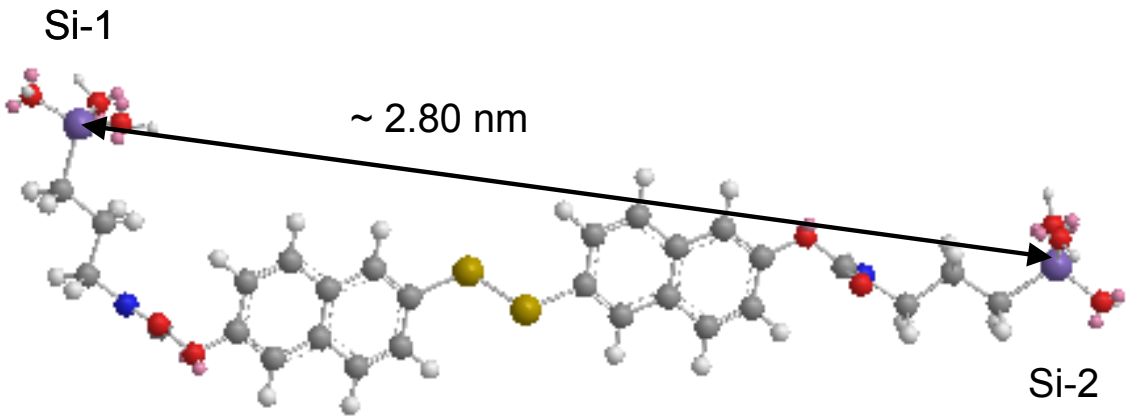




TGA measurement

Chem 3D figure of disulfide substituent





Distance of two silicon atom is estimated to be about 2.80 nm from Chem3D (Ultra 9.0) simulation.