

*Electronic Supplementary Information (ESI) for*

## **Facile synthesis of nitriles via manganese oxide promoted oxidative dehydrosulfurization of primary thioamides**

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### **Experimental details**

**General:** GC analyses were performed on Shimadzu GC-2014 with a FID detector equipped with a TC-1 or Rxi-5 Sil capillary column. GC mass spectra were recorded on Shimadzu GCMS-QP2010 at an ionization voltage of 70 eV. Liquid-state  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on JEOL JNM-EX-270.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured at 270 and 67.8 MHz, respectively, with TMS as an internal standard ( $\delta = 0$  ppm). ICP-AES analyses were performed with Shimadzu ICPS-8100. BET surface areas were measured on micromeritics ASAP 2010 and calculated from the  $\text{N}_2$  adsorption isotherm with the BET equation. XPS measurements were carried out on JEOL JPS-90 using monochromated Al  $\text{K}\alpha$  radiation ( $h\nu = 1486.6$  eV). The X-ray anode was run at 200 W and the voltage was kept at 10 kV. The pass energy was fixed at 10.0 eV to ensure sufficient resolution to determine peak positions accurately.  $\text{KMnO}_4$  (Kanto Chemical),  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (Aldrich),  $\text{MnS}$  (Aldrich) were commercially available (reagent grade), and used as received. Solvents and substrates were obtained from Kanto Chemical, TCI, Wako, or Aldrich (reagent grade), and used as received. Manganese oxides (see below)<sup>S1-S3</sup> and  $\text{Co}_3\text{O}_4$ <sup>S4</sup> were prepared according to the literature procedures (see Table S1). Other (metal) oxides were commercially available (see Table S1).

**Manganese oxides:** Amorphous  $\text{MnO}_2$  was prepared as follows:<sup>S1</sup> An aqueous solution of  $\text{KMnO}_4$  (5.89 g, 100 mL) was added dropwise to an aqueous solution of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (8.8 g, 30 mL). The resulting mixture was stirred at room temperature for 10 min. Then, the dark brown solid formed was filtered off, washed with a large amount of deionized water (*ca.* 4 L), and dried under air at 150 °C for 12 h, affording 5.0 g of amorphous  $\text{MnO}_2$ . The content of

Mn in amorphous MnO<sub>2</sub> was 50.46 wt%.  $\alpha$ -MnO<sub>2</sub> (OMS-2) was prepared as follows:<sup>S2</sup> An aqueous solution of KMnO<sub>4</sub> (5.89 g, 100 mL) was added to an aqueous solution (30 mL) containing MnSO<sub>4</sub>·H<sub>2</sub>O (8.8 g) and concentrated HNO<sub>3</sub> (3 mL). The resulting mixture was refluxed at 100 °C for 24 h. Then, the dark brown solid formed was filtered off, washed with a large amount of water (*ca.* 3 L), and dried under air at 120 °C, affording 8.2 g of OMS-2. The content of Mn in  $\alpha$ -MnO<sub>2</sub> was 58.8 wt%.  $\beta$ -MnO<sub>2</sub> (Cat. No. 133-09681, Wako) was commercially available.  $\delta$ -MnO<sub>2</sub> (birnessite-type MnO<sub>2</sub>) was prepared according to the literature procedure.<sup>S3</sup>

**Dehydrosulfurization:** A typical procedure for dehydrosulfurization: **1a** (1.10 g, 8 mmol), amorphous MnO<sub>2</sub> (2 g), and chloroform (120 mL) were placed in a Pyrex-glass reactor with a magnetic stir bar, and the reaction was carried out at room temperature (*ca.* 25 °C) in 1 atm of air. After 30 min, MnO<sub>2</sub> was separated by filtration washed with chloroform (>95% recovery). Evaporation of chloroform gave crude mixtures containing **2a** and elemental sulfur. Then, acetone was added to the crude mixtures, followed by filtration to retrieve elemental sulfur (0.21 g, 83% yield, >99.99% purity by elemental analysis). Evaporation of acetone afforded 0.73 g of **2a** (88% yield, >95% purity by GC and NMR analyses). The retrieve MnO<sub>2</sub> was washed with deionized water and dried at 150 °C prior to being used for the reuse experiment. The products were confirmed by the comparison of their GC retention times, GC-MS spectra, and/or <sup>1</sup>H and <sup>13</sup>C NMR spectra with those of authentic data.

### Additional references

- S1 Y. Wang, K. Yamaguchi and N. Mizuno, *Angew. Chem. Int. Ed.*, 2012, **51**, 7250.
- S2 R. N. DeGuzman, Y.-F. Shen, E. J. Neth, S. L. Suib, C.-L. O'Young, S. Levine and J. M. Newsam, *Chem. Mater.*, 1994, **6**, 815.
- S3 O. Ghodbane, J.-L. Pascal and F. Favier, *ACS Appl. Mater. Interfaces*, 2009, **1**, 1130.
- S4 D. Pope, D. S. Walker, R. L. Moss, *J. Catal.*, 1977, **47**, 33.

**Table 1.** (Metal) oxides

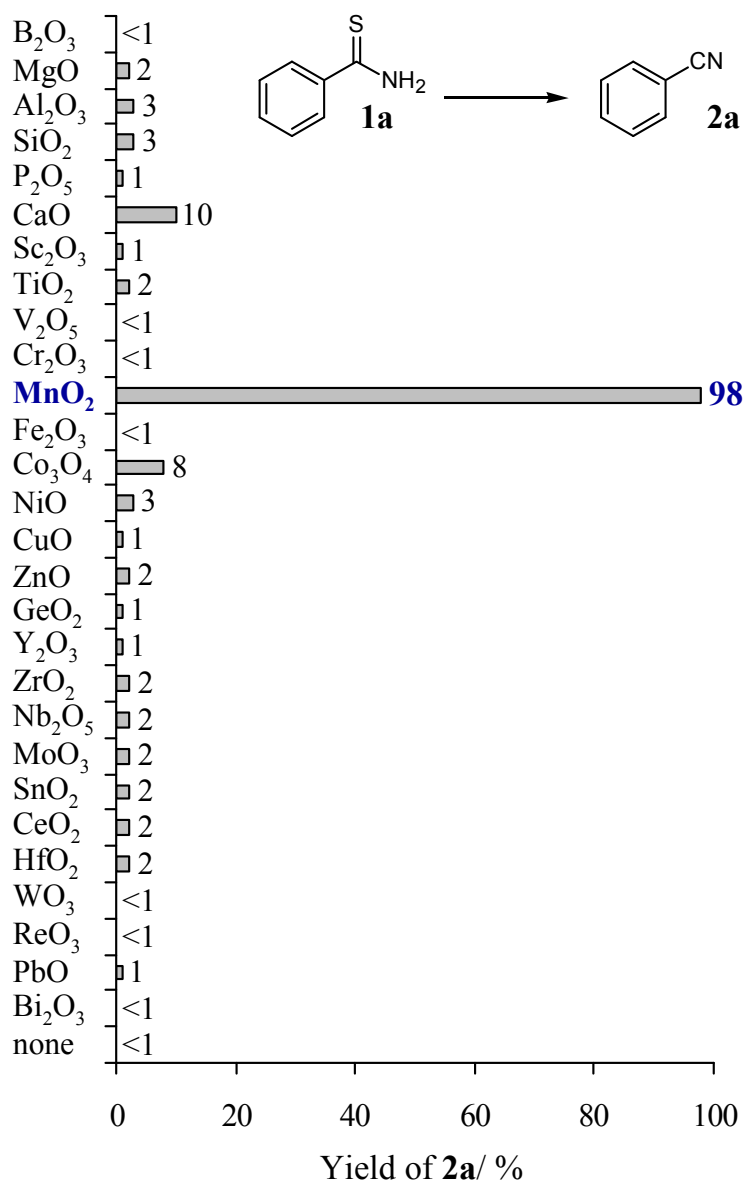
Oxide	Literature or company
Amorphous MnO <sub>2</sub>	Prepared according to Ref. S1
α-MnO <sub>2</sub>	Prepared according to Ref. S2
β-MnO <sub>2</sub>	Obtained from Wako (No. 133-09681)
δ-MnO <sub>2</sub>	Prepared according to Ref. S3
B <sub>2</sub> O <sub>3</sub>	Obtained from Aldrich (No. 221740-500G)
MgO	Obtained from Ube Industries (No. 500A)
Al <sub>2</sub> O <sub>3</sub>	Obtained from Sumitomo Chemical (No. KHS-24)
SiO <sub>2</sub>	Obtained from Fuji Silysia Chemical (No. CARiACT Q-10)
P <sub>2</sub> O <sub>5</sub>	Obtained from KANTO (No. 32196-00)
CaO	Obtained from Wako (No. 360-19655)
Sc <sub>2</sub> O <sub>3</sub>	Obtained from Aldrich (No. 307874-1G)
TiO <sub>2</sub>	Obtained from Ishihara Sangyo Kaisya (No. ST-01)
V <sub>2</sub> O <sub>5</sub>	Obtained from KANTO (No. 44017-30)
Cr <sub>2</sub> O <sub>3</sub>	Obtained from nacalai tesque (No. 08909-22)
Fe <sub>2</sub> O <sub>3</sub>	Obtained from Alfa Aesar (No. 12593)
Co <sub>3</sub> O <sub>4</sub>	Prepared according to Ref. S4
NiO	Obtained from Aldrich (No. 637130-25G)
CuO	Obtained from Wako (No. 036-09461)
ZnO	Obtained from Wako (No. 260-01261)
GeO <sub>2</sub>	Obtained from nacalai tesque (No. 1662582)
Y <sub>2</sub> O <sub>3</sub>	Obtained from KANTO (No. 47003-33)
ZrO <sub>2</sub>	Obtained from nacalai tesque (No. 3702235)
Nb <sub>2</sub> O <sub>5</sub>	Obtained from nacalai tesque (No. 2442642)
MoO <sub>3</sub>	Obtained from Wako (No. 138-03352)
SnO <sub>2</sub>	Obtained from KANTO (No. 37315-00)
CeO <sub>2</sub>	Obtained from KANTO (No. 25370-30)
HfO <sub>2</sub>	Obtained from Wako (No. 087-02171)
WO <sub>3</sub>	Obtained from Aldrich (No. 550086-5G)
ReO <sub>3</sub>	Obtained from Aldrich (No. 380997-1G)
PbO	Obtained from Koso Chemical (No. 2150204)
Bi <sub>2</sub> O <sub>3</sub>	Obtained from RARE METALLIC (No. 80624-49)

**Table S2.** Effect of solvents on the dehydrosulfurization of benzthioamide (**1a**)<sup>a</sup>

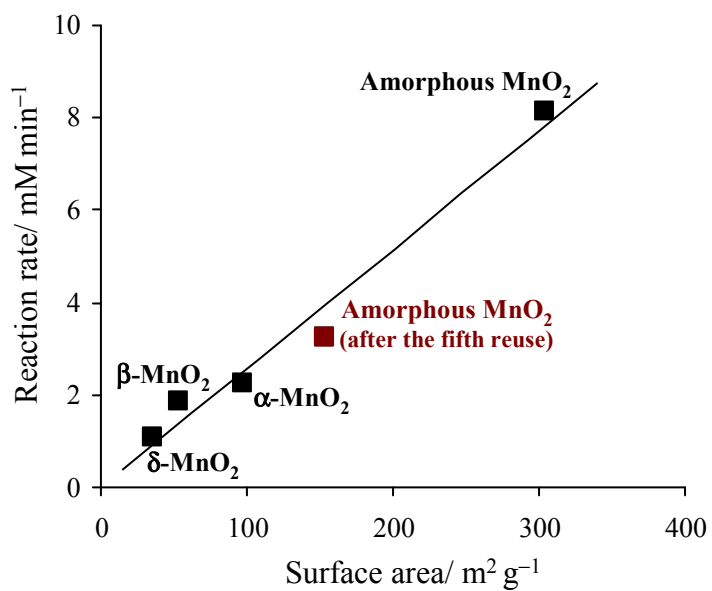


Entry	Solvent	Yield [%]
1	Chloroform	98
2	Toluene	95
3	Acetonitrile	78
4	Acetone	65
5	1,4-Dioxane	21
6	DMF	20

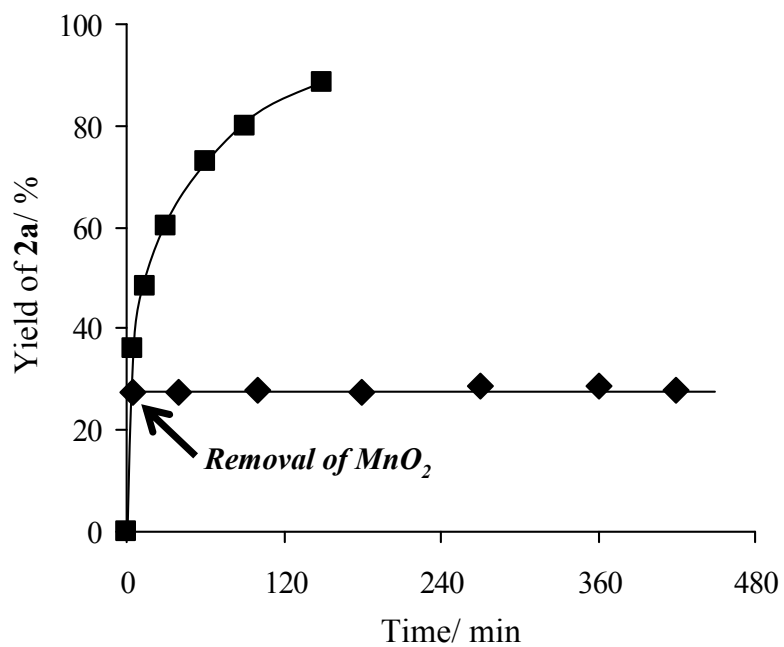
<sup>a</sup> Reaction conditions: **1a** (0.2 mmol), amorphous MnO<sub>2</sub> (50 mg), chloroform (3 mL), air (1 atm), 30 °C, 15 min. Yields were determined by GC using naphthalene as an internal standard.



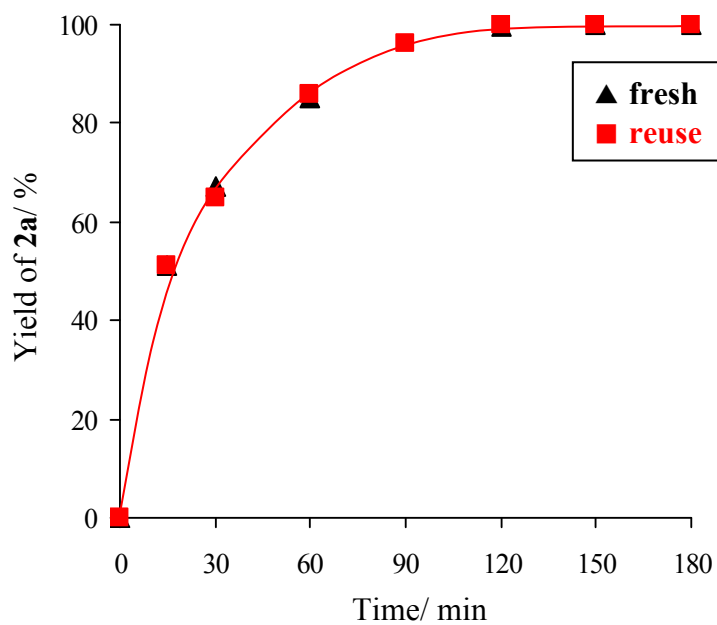
**Fig. S1.** Dehydrosulfurization of benzthioamide (**1a**) to benzonitrile (**2a**) by various oxides. Reaction conditions: **1a** (0.2 mmol), oxide (50 mg), chloroform (3 mL), air (1 atm), 30 °C, 15 min. MnO<sub>2</sub> = amorphous MnO<sub>2</sub>.



**Fig. S2.** Dehydrosulfurization of benzthioamide (**1a**) to benzonitrile (**2a**) by various manganese oxides (Reaction rates vs surface areas plots). Reaction conditions: **1a** (0.2 mmol), manganese oxide (50 mg), chloroform (3 mL), air (1 atm), 30 °C.



**Fig. S3** Effect of removal of amorphous MnO<sub>2</sub>. An arrow indicates the removal of MnO<sub>2</sub>. Reaction conditions: **1a** (0.2 mmol), amorphous MnO<sub>2</sub> (20 mg), chloroform (3 mL), air (1 atm), 30 °C.



**Fig. S4.** Reaction profiles for the dehydrosulfurization of benzthioamide (**1a**) to benzonitrile (**2a**) with fresh and reuse  $\alpha$ -MnO<sub>2</sub>. Reaction conditions: **1a** (0.2 mmol),  $\alpha$ -MnO<sub>2</sub> (50 mg), chloroform (3 mL), air (1 atm), 30 °C.