

Electronic Supplementary Information (ESI) for

Manganese oxide-catalyzed transformation of primary amines to primary amides through the sequence of oxidative dehydrogenation and successive hydration

Ye Wang, Hiroaki Kobayashi, Kazuya Yamaguchi and Noritaka Mizuno*

Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656
E-mail: tmizuno@mail.ecc.u-tokyo.ac.jp

Full Experimental Section

General: GC analyses were performed on Shimadzu GC-2014 or GC-17A with a FID detector equipped with a TC-5, InertCap 5, or Rxi-5 Sil capillary column. The GC mass spectra were recorded on Shimadzu GCMS-QP2010 at an ionization voltage of 70 eV. The liquid-state ^1H and ^{13}C NMR spectra were recorded on JEOL JNM-EX-270. The ^1H and ^{13}C NMR spectra were measured at 270 and 67.8 MHz, respectively, with TMS as an internal standard ($\delta = 0$ ppm). The ICP-AES analyses were performed with Shimadzu ICPS-8100.

Catalysts and reagents: $\beta\text{-MnO}_2$ (Cat. No. 133-09681, Wako), activated MnO_2 (Cat. No. 217646-5G, for organic oxidations, Aldrich), RuHAP (Cat. No. 182-01851, for organic synthesis, Wako) were commercially available. $\beta\text{-MnOOH}$,^{S1} birnessite-type MnO_2 ,^{S2} and $\text{Ru}(\text{OH})_x/\text{Al}_2\text{O}_3$ ^{S11} were prepared according to the literature procedures. KMnO_4 and $\text{MnSO}_4\cdot\text{H}_2\text{O}$ were obtained from Kanto Chemical and Aldrich (reagent grade), respectively. Solvents and substrates (mainly amines) were obtained from Kanto Chemical, TCI, Wako, or Aldrich (reagent grade), and purified prior to the use.^{S3} In particular, amines were carefully purified just before the use for catalytic reactions.

Preparation of OMS-2: OMS-2 was prepared according to the literature procedure (see below).^{7a} KMnO_4 (5.89 g) in water (100 mL) was added to a solution of $\text{MnSO}_4\cdot\text{H}_2\text{O}$ (8.8 g) in water (30 mL) and conc. HNO_3 (3 mL). The solution was refluxed at 100°C for 24 h. Then, the dark brown solid was filtered off, washed with a large amount of water (ca. 3 L), and dried at 120°C to afford 8.2 g of OMS-2. The contents of Mn and K in OMS-2 were 58.8 wt% and 6.98 wt%, respectively. The BET surface area of OMS-2 was $97\text{ m}^2\text{ g}^{-1}$.

Additional References

- S1 M. Oba, Y. Oaki, H. Imai, *Adv. Funct. Mater.*, 2010, **20**, 4279.
- S2 O. Ghodbane, J.-L. Pascal, F. Favier, *ACS Appl. Mater. Interfaces*, 2009, **1**, 1130.
- S3 *Purification of Laboratory Chemicals*, 3rd ed., eds. by D. D. Perrin, W. L. F. Armarego, Pergamon Press, Oxford, U.K., 1988.

Table S1 Scope of the OMS-2 catalyzed transformation of primary amines to primary amides (details of Table 2)^a

Entry	Substrate	Time (h)	Conv. (%)	Yield (%)			
				amide	nitrile	alkylimine	aldehyde
1	1a	3	97	87	4	2	<1
2 ^b	1a	3	96	82	6	3	<1
3	1b	3	>99	98	1	<1	<1
4 ^b	1b	3	98	90	7	<1	<1
5	1c	3	93	92	<1	<1	<1
6	1d	3	99	89	5	<1	<1
7	1e	3	96	96	<1	<1	<1
8	1f	3	96	82	4	3	<1
9	1g	3	>99	93	2	2	2
10	1h	3	>99	65	2	<1	<1
11	1i	3	>99	91	4	<1	<1
12 ^b	1i	3	98	84	7	<1	<1
13	1j	3	>99	90	4	<1	<1
14 ^c	1k	8	74	66	3	<1	<1

^a Reaction conditions: catalyst (100 mg), substrate (0.5 mmol), aqueous ammonia (28 wt%, 100 μ L), 1,4-dioxane (1 mL), 130°C (bath temperature), air (6 atm). Yields were determined by GC using diphenyl or naphthalene as an internal standard. ^b Reuse experiment. ^c OMS-2 (200 mg), aqueous ammonia (28 wt%, 200 μ L), 160°C.