

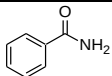
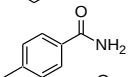
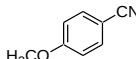
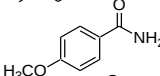
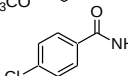
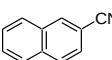
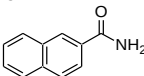
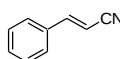
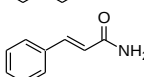
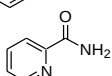
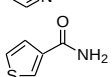
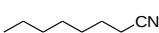
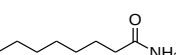
Electronic Supplementary Information (ESI) for

Green oxidative synthesis of primary amides from primary alcohols or aldehydes catalyzed by a cryptomelane-type manganese oxide-based octahedral molecular sieve, OMS-2

Kazuya Yamaguchi, Hiroaki Kobayashi, Ye Wang, Takamichi Oishi, Yoshiyuki Ogasawara 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

Table S1 OMS-2-catalyzed nitrile hydration with aqueous ammonia^a

Entry	Substrate	Product	Time (h)	Yield (%)
1			3	91
2			3	98
3			3	94
4			3	97
5			3	97
6			3	93
7			1	96
8			3	88
9 ^b			24	98

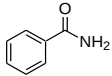
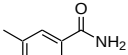
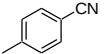
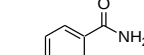
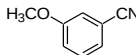
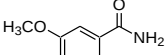
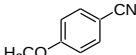
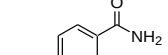
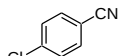
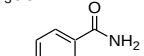
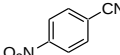
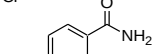
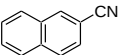
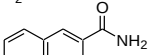
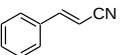
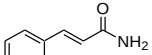
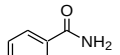
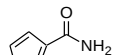
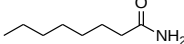
^a Conditions: OMS-2 (100 mg), nitrile (0.5 mmol), 28% aq. ammonia (100 μ L, ca. 2.6 equiv. with respect to substrate), 1,4-dioxane (2 mL), Ar (3 atm), 130 $^{\circ}$ C (bath temp.). Yields were determined by GC using naphthalene or biphenyl as an internal standard. ^b OMS-2 (200 mg).

Table S2 Aerobic oxidation of 1-phenylethanol in the presence of aqueous ammonia^a

Entry	Catalyst	Yield of acetophenone (%)
1	OMS-2	68
2	Amorphous MnO ₂	95
3	Birnessite-type MnO ₂	10
4	β-MnO ₂	79

^a Conditions: Catalyst (100 mg), alcohol (0.5 mmol), 28% aq. ammonia (100 μL, ca. 2.6 equiv. with respect to substrate), 1,4-dioxane (2 mL), O₂ (3 atm), 130 °C (bath temp.), 1 h. Yields were determined by GC using naphthalene as an internal standard.

Table S3 Amorphous MnO₂-catalyzed nitrile hydration with 2 equiv. of water (without aqueous ammonia)^a

Entry	Substrate	Product	Time (h)	Yield (%)
1			1	87
2			1	82
3			1	80
4			1	94
5			1	86
6			1	97
7			1	99
8			3	96
9			2	93
10			1	>99
11			1	96
12 ^b			12	54

^a Conditions: Amorphous MnO₂ (50 mg), nitrile (0.5 mmol), water (18 μL, *ca.* 2 equiv. with respect to substrate), 1,4-dioxane (2 mL), Ar (3 atm), 140 °C (bath temp.). Yields were determined by GC using naphthalene or biphenyl as an internal standard. ^b Amorphous MnO₂ (100 mg), 150 °C (bath temp.).

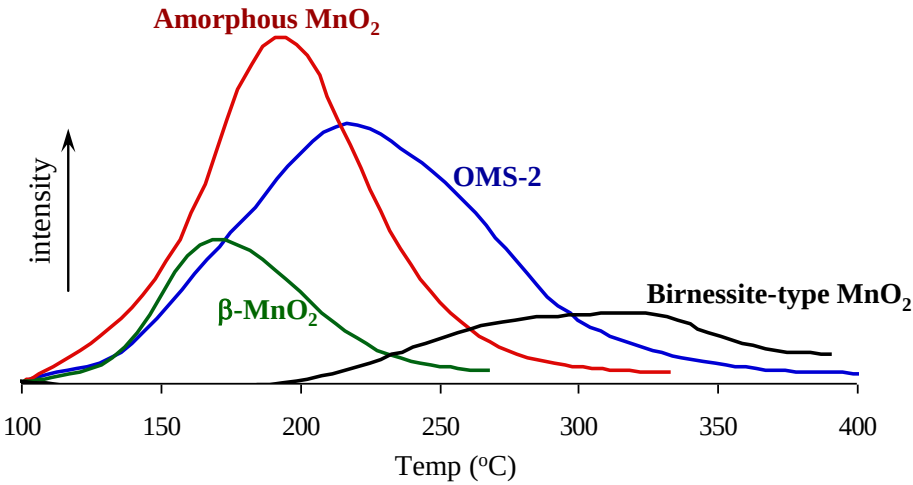


Fig. S1 NH₃-TPD profiles of OMS-2, amorphous MnO₂, birnessite-type MnO₂, and β-MnO₂.

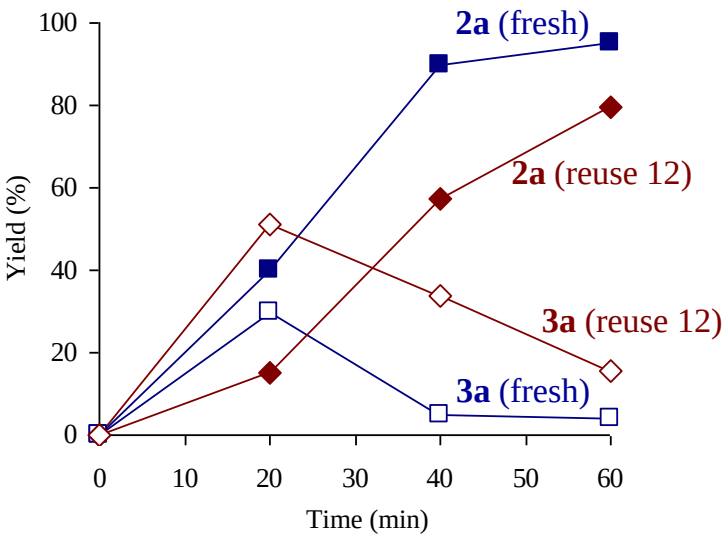


Fig. S2 Reaction profiles for the amidation of **1o** with fresh and used OMS-2.

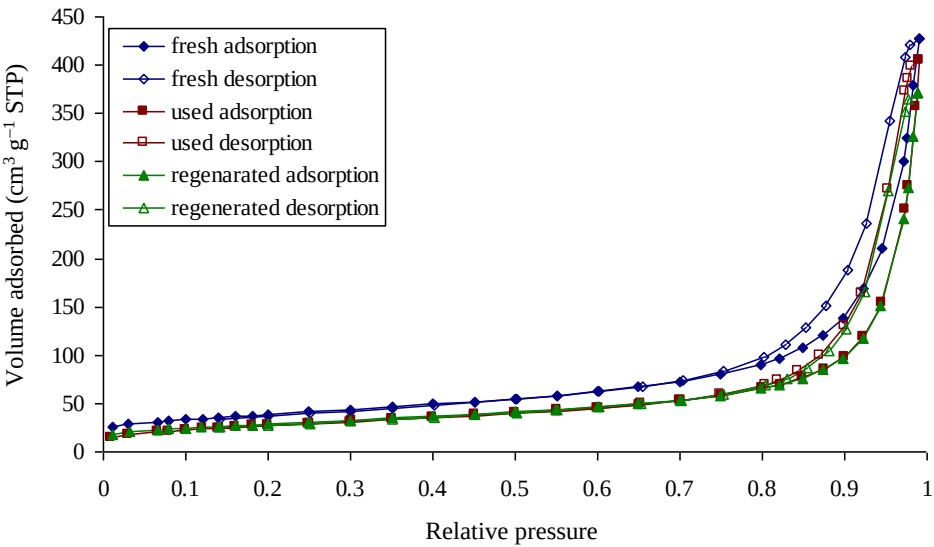


Fig. S3 N₂ adsorption-desorption isotherms of fresh, used, and regenerated OMS-2.

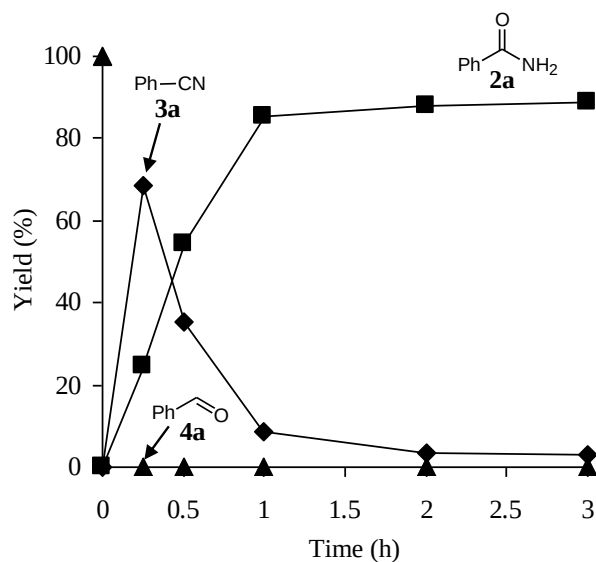


Fig. S4 Reaction profile for the amidation of benzaldehyde (**4a**). The reaction was carried out under the conditions in Table 7.