Molybdenum-doped α-MnO_2 as an efficient reusable heterogeneous catalyst for aerobic sulfide oxygenation

Tsubasa Uematsu, Yumi Miyamoto, Yoshiyuki Ogasawara, Kosuke Suzuki, 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, Japan. E-mail: tmizuno@mail.ecc.u-tokyo.ac.jp

Table S1 Average oxidation states (AOSs) of manganese oxides

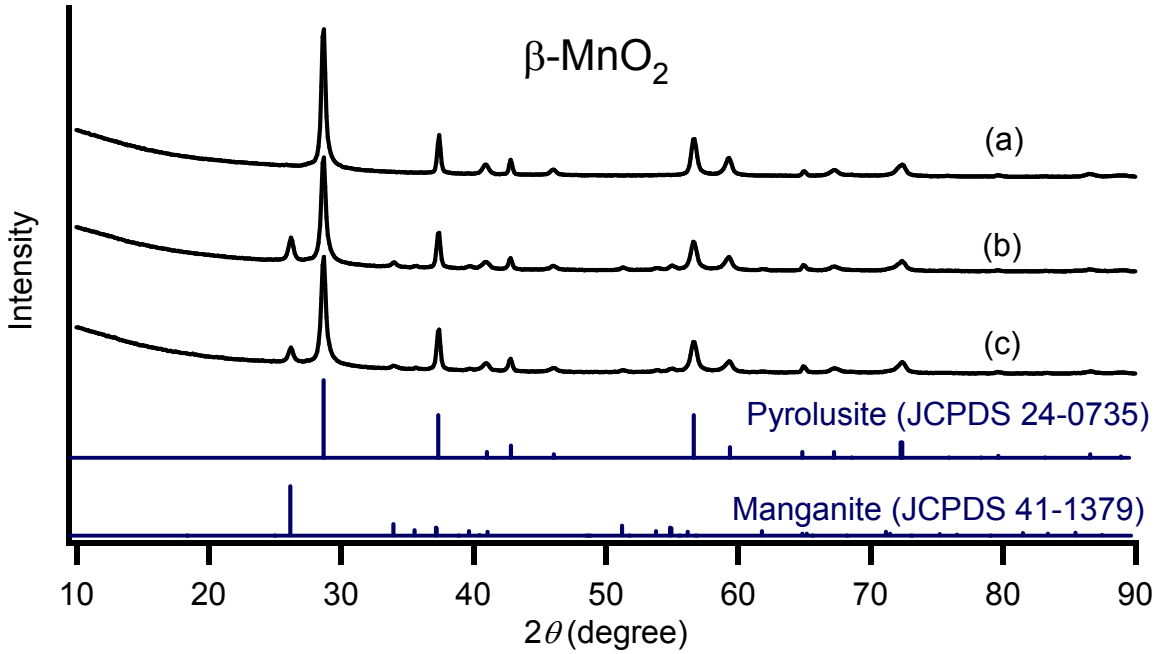
Catalyst	AOS	
	As prepared	After reaction [a]
α-MnO_2	3.77	3.52
β-MnO_2	3.90	3.60
γ-MnO_2	3.90	3.42
δ-MnO_2	3.92	3.68

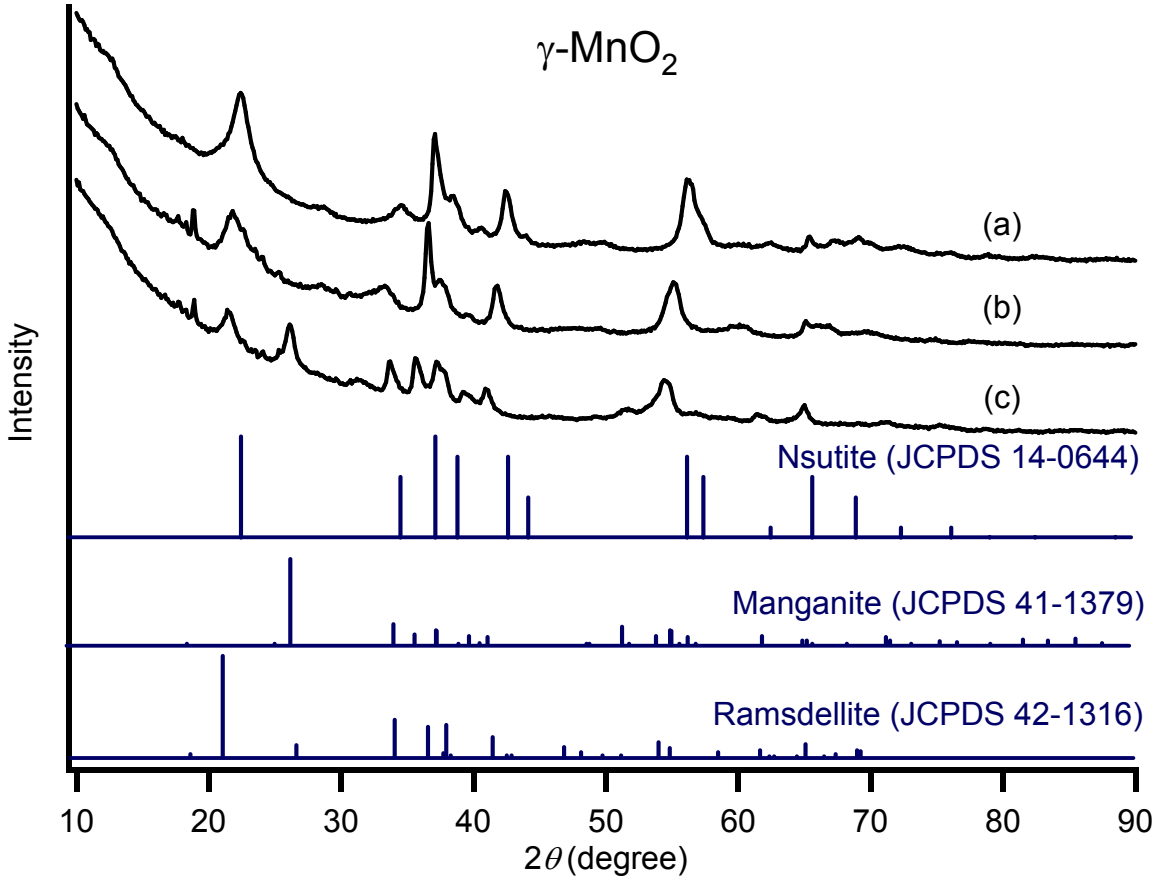
[a] The retrieved catalyst after the oxygenation of **1a** under the aerobic conditions described in Table 2.

Table S2 The binding energies and the contents of oxygen species in M-MnO_2

Catalyst	Oxygen 1s (O_{sat})		Oxygen 1s (O_{unsat})		Oxygen 1s (O_{water})	
	BE (eV)	Content (%)	BE (eV)	Content (%)	BE (eV)	Content (%)
α-MnO_2	529.9	72.2	531.3	23.2	532.2	4.5
Mo-MnO_2	530.0	76.1	531.3	17.0	532.2	6.9
V-MnO_2	529.4	72.3	531.3	23.9	532.2	3.8
Cr-MnO_2	529.9	70.2	531.3	25.8	532.2	4.0
Cu-MnO_2	529.8	66.6	531.3	30.4	532.2	3.0

O_{sat}: the coordinatively saturated lattice oxygen species. O_{unsat}: the coordinatively unsaturated oxygen species (e.g., OH and adsorbed oxygen species on the surface). O_{water}: the adsorbed H_2O molecule on the surface.


β-MnO2
(a)
(b)
(c)
Intensity
Pyrolusite (JCPDS 24-0735)
Manganite (JCPDS 41-1379)
10
20
30
40
50
60
70
80
90
2θ (degree)


γ-MnO2
(a)
(b)
(c)
Intensity
Nsutite (JCPDS 14-0644)
Manganite (JCPDS 41-1379)
Ramsdellite (JCPDS 42-1316)
10
20
30
40
50
60
70
80
90
2θ (degree)

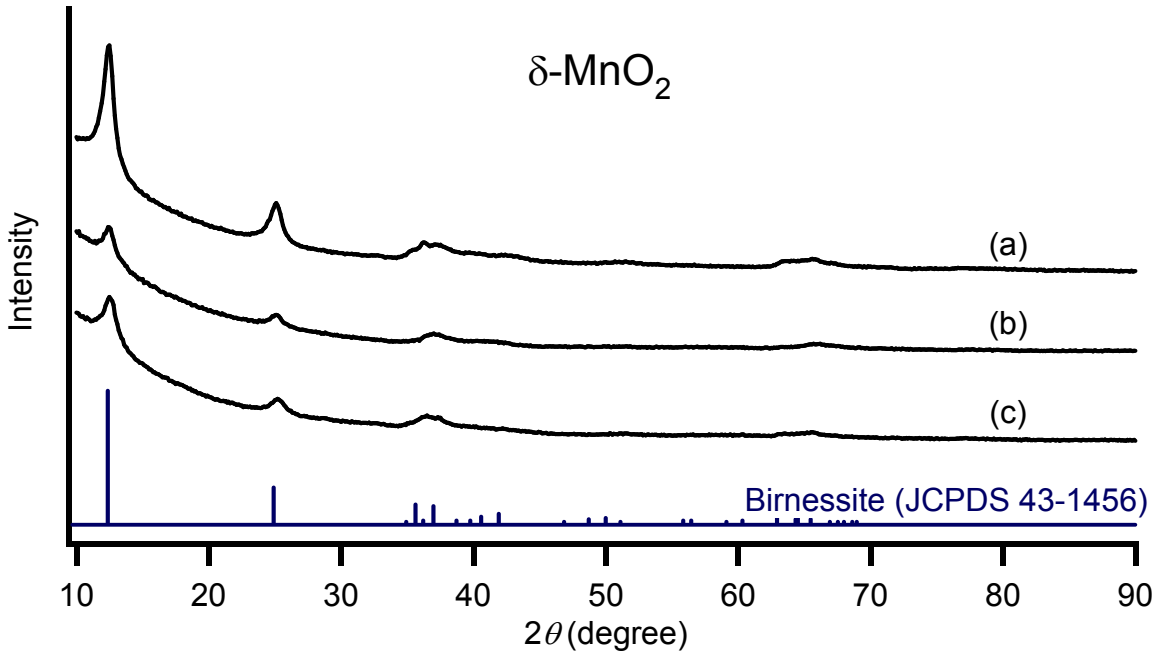


Fig. S1 The XRD patterns of β-MnO_2, γ-MnO_2, and δ-MnO_2: (a) As-prepared manganese oxides, (b) manganese oxides retrieved after the oxygenation of **1a** under aerobic conditions, and (c) manganese oxides retrieved after the oxygenation of **1a** under anaerobic conditions.

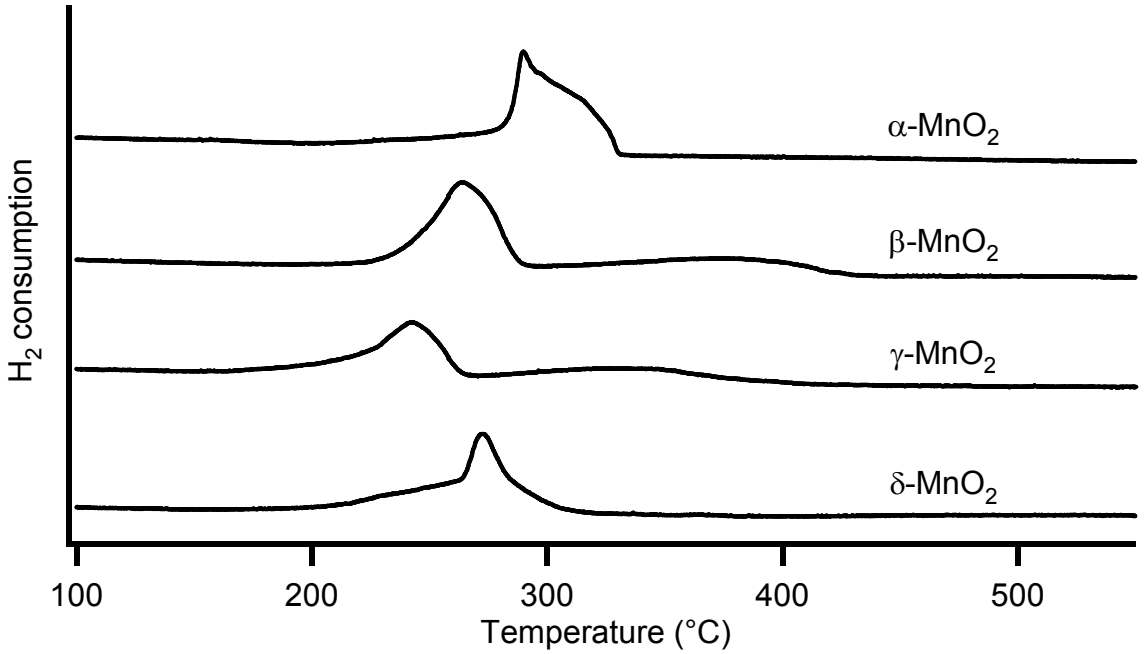


Fig. S2 H_2-TPR profiles of α-MnO_2, β-MnO_2, γ-MnO_2, and δ-MnO_2.

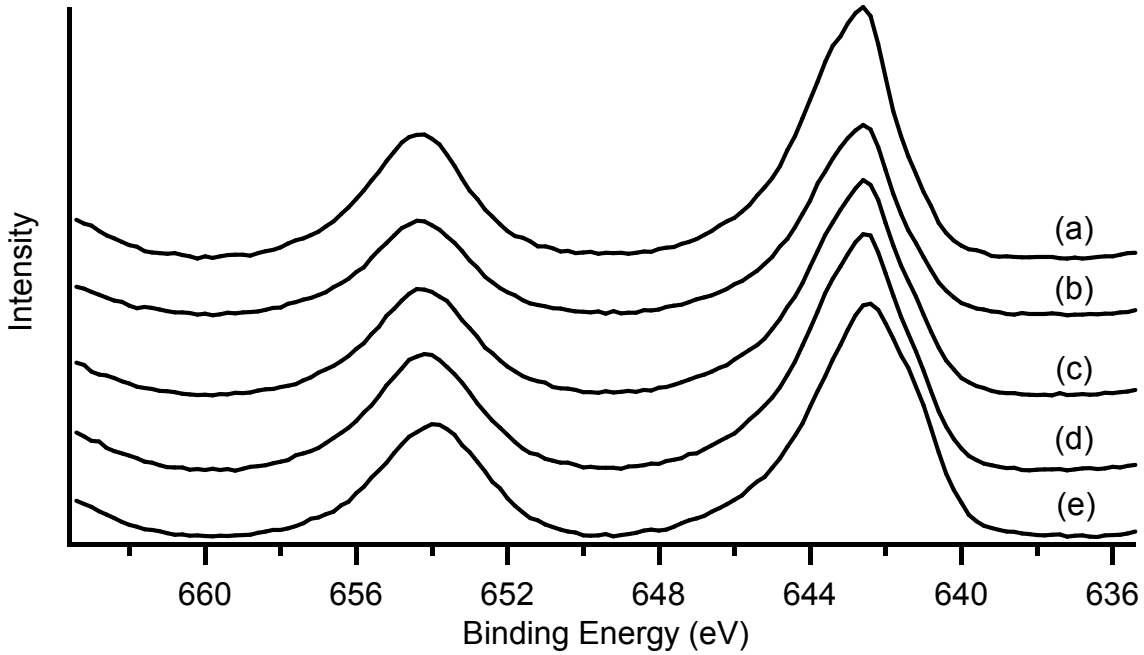
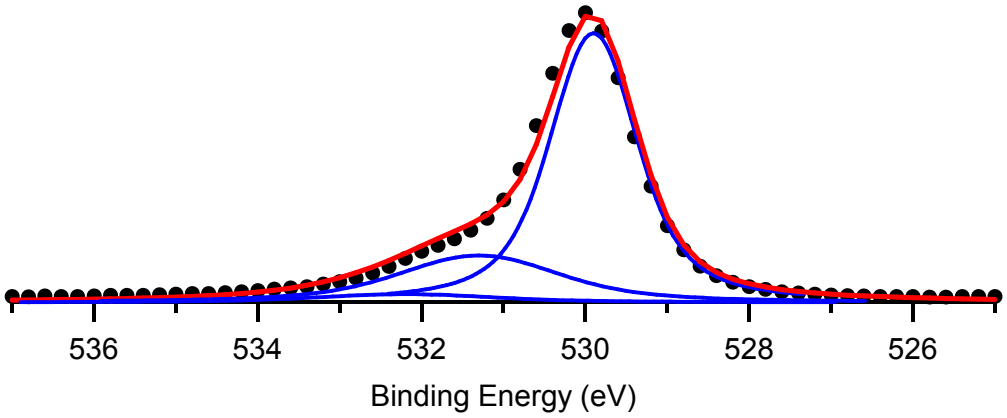
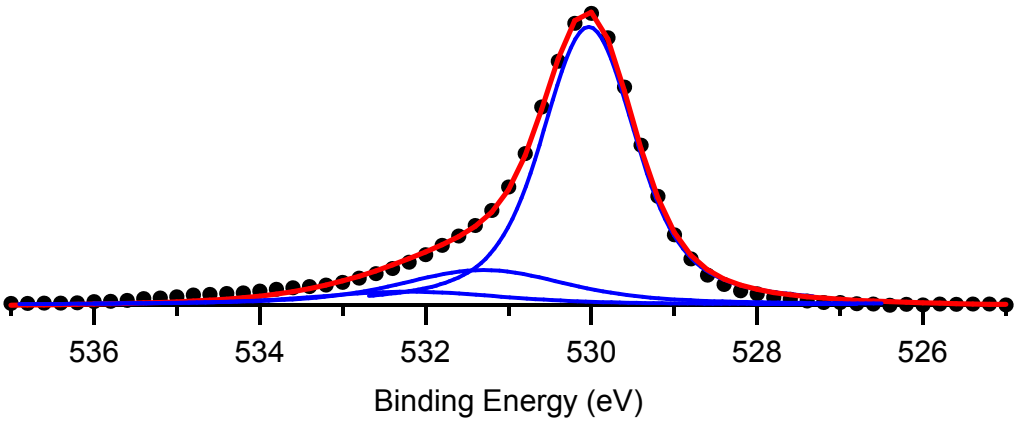


Fig. S3 XPS spectra of (a) α-MnO_2, (b) Mo-MnO_2, (c) V-MnO_2, (d) Cr-MnO_2, and (e) Cu-MnO_2 in the Mn 2p regions.

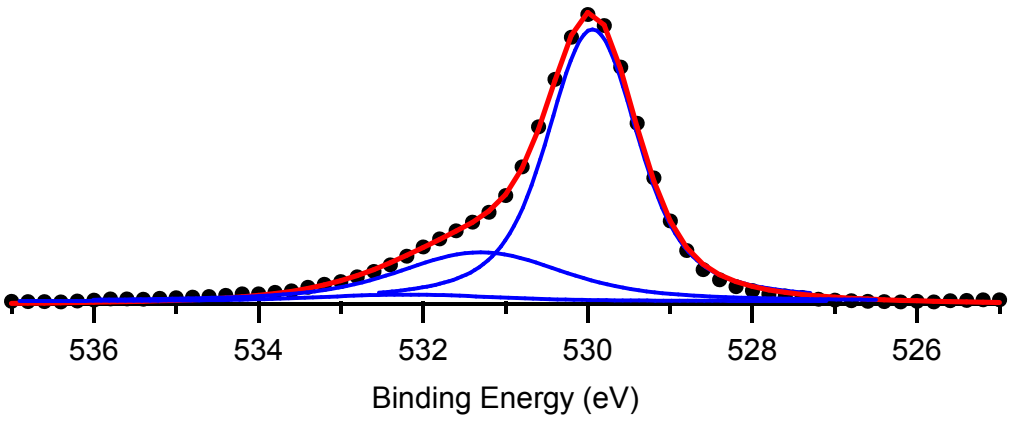
α-MnO_2



Mo-MnO_2



V-MnO_2



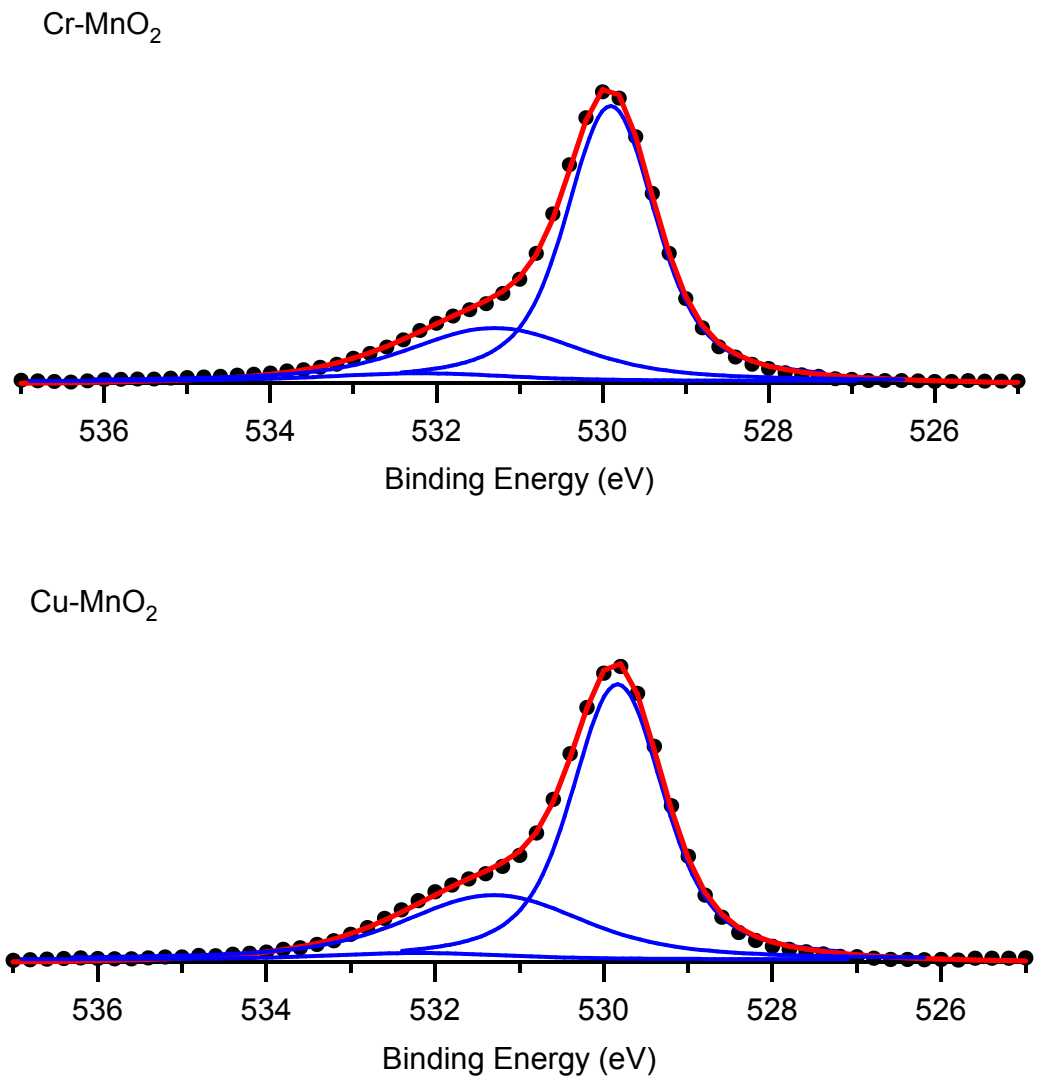


Fig. S4 XPS spectra of α-MnO_2 and M-MnO_2 in the O 1s regions. The red and blue lines represent the sum of the deconvolution and the deconvolution of the spectra, respectively. The low (around 530 eV), medium (around 531 eV), and high binding energy peaks (around 532 eV) show the coordinatively saturated lattice oxygen species, the coordinatively unsaturated oxygen species (e.g., OH and adsorbed oxygen species), and adsorbed molecular H_2O, respectively.

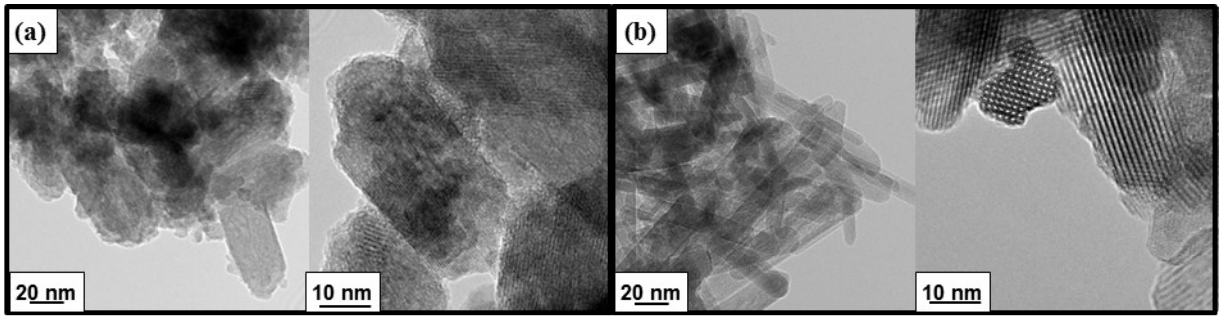


Fig. S5 TEM images of (a) Mo-MnO_2 (molybdenum content = 2.5 mol%), (b) V-MnO_2 (vanadium content = 2.5 mol%).

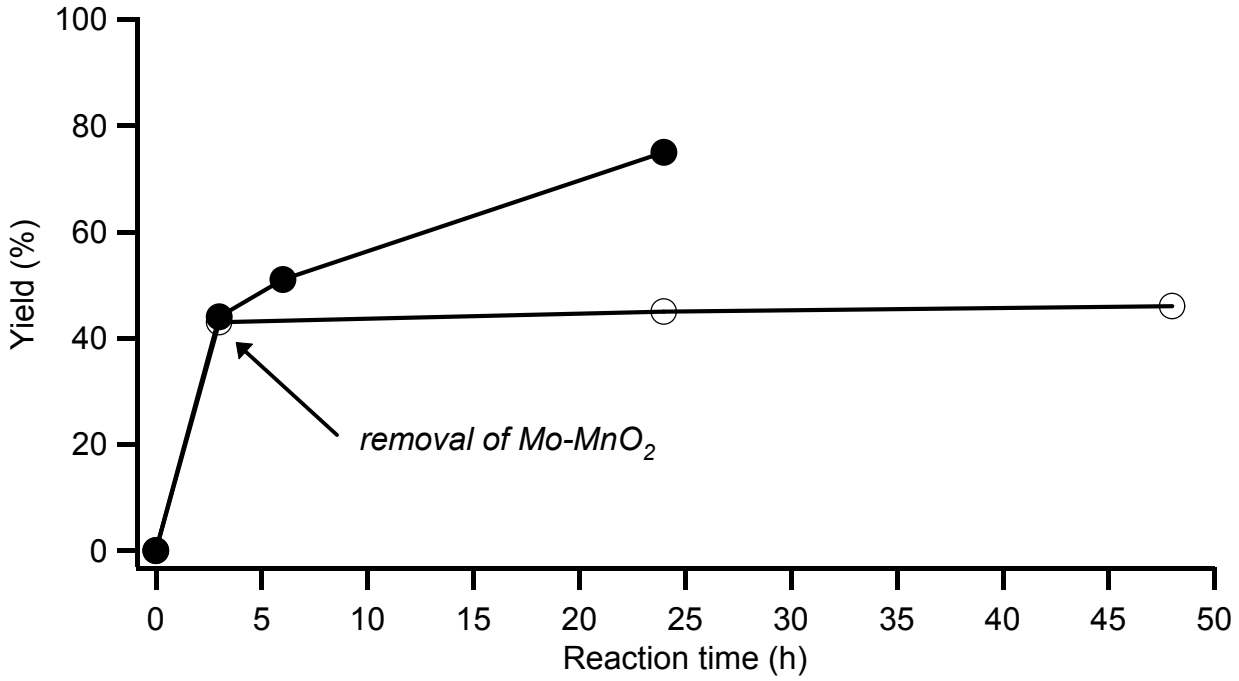


Fig. S6 Effect of removal of Mo-MnO_2 on the oxidation of **1a**; without (●) or with removal of Mo-MnO_2 (○). The arrow indicates the removal of Mo-MnO_2. Reaction conditions: Mo-MnO_2 (25 mg), **1a** (0.5 mmol), *o*-dichlorobenzene (1 mL), 150 ºC (bath temp.), O_2 (5 atm). Yields were determined by GC analysis using naphthalene as an internal standard.