

Electronic Supplementary Information (ESI) for

Liquid-phase oxidation of alkanes with molecular oxygen catalyzed by high valent iron-based perovskite

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Experimental Section

Materials

Solvents (PhCF₃ (TCI), *n*-octane (Aldrich), 1,2-dichlorobenzene (Kanto), benzonitrile (Kanto), dimethylsulfoxide (Kanto), toluene (Kanto), *o*-xylene (Kanto), and mesitylene (Kanto)) were pretreated with molecular sieves (3A) that were evacuated at 250 °C for 3 h.^{S1} Oxygen-¹⁸O₂ (97 atom%) was purchased from ISOTECH. Reagents (FeO (Aldrich), Fe₃O₄ (Aldrich), Fe₂O₃ (Aldrich), Ba(OAc)₂ (Kanto Chemical), Fe(OAc)₂ (Wako Chemical), Sr(OAc)₂·0.5H₂O (Kanto Chemical), Ca(OAc)₂ (Kanto Chemical), L-aspartic acid (Kanto Chemical), PhCF₃ (TCI), adamantane (TCI), 1-adamantanol (TCI), 2-adamantanol (TCI), 2-adamantanone (TCI), 1,3-adamantanediol (TCI), 1-ethyladamantane (TCI), 1,3-dimethyladamantane (TCI), 3,5-dimethyl-1-adamantanol (TCI), *cis*-decalin (TCI), cyclooctane (TCI), cyclooctanol (TCI), cyclooctanone (TCI), xanthene (TCI), fluorene (TCI), 9,10-dihydroanthracene (TCI), tetralin (TCI), and indan (TCI) were used as received.

Instruments

X-ray diffraction (XRD) patterns were recorded on a diffractometer (Ultima IV, Rigaku; Cu K α , λ = 1.5405 Å, 40 kV–40 mA or MiniFlex 600, Rigaku; Cu K α , λ = 1.5405 Å, 40 kV–15 mA) equipped with a high-speed one-dimensional detector (DteX Ultra, Rigaku). Diffraction data were collected in the range of 2θ = 10–80° at 0.02° steps with a scan rate

of 20° min⁻¹. Nitrogen adsorption-desorption isotherms were measured at 77 K with a surface area analyzer (Nova-4200e, Quantachrome or TriStar II 3020, Micromeritics). Prior to measurements, the samples were heated at 423 K for 1 h under vacuum to remove physisorbed water. The Brunauer-Emmett-Teller (BET) surface areas were estimated over the relative pressure (P/P_0) range of 0.05–0.30. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analyses were performed with a Shimadzu ICPS-8100 spectrometer. Iodometric titration was performed with a Mettler Toledo Easy Pro Titrator System. Approximately 50 mg of BaFeO_{3- δ} was added to 1.0 M HCl aqueous solution (20 mL) containing excess KI (1.66 g, 10 mmol), and the resulting solution was titrated with 0.05 M Na₂S₃O₃ aqueous solution.^{S2} X-ray photoelectron spectroscopy (XPS) analysis was performed with a Shimadzu ESCA-3400 spectrometer using Mg K α radiation (1253.6 eV) at 10 kV and 25 mA. Samples were pressed into pellets and fixed on double-sided carbon tape. The binding energies were calibrated using the C 1s band at 284.6 eV. The spectrum was fitted and evaluated by the XPS Peak 4.1 program, whereas the background was subtracted using Shirley function. The morphology of the samples was examined using scanning electron microscopy (SEM; S-5200, Hitachi). NMR spectra were recorded on a Bruker Biospin Avance III spectrometer (¹H, 400 MHz; ¹³C, 100 MHz) using 5 mm sample tubes. Chemical shifts (δ) were reported in parts per million downfield from SiMe₄ (solvent, CDCl₃). Liquid-phase catalytic oxidation was performed with an organic synthesizer (ALHB-80 & DTC-200HZ-3000, Techno Applications) or a liquid-phase organic synthesizer (CHEMIST PLAZA CP-1000, Sibata). Gas chromatography (GC) analyses were performed on a Shimadzu GC-18A chromatograph equipped with a DB-1 capillary column (internal diameter = 0.25 mm, length = 30 m), a Shimadzu GC-17A chromatograph equipped with a InertCap-17 capillary column (internal diameter = 0.25 mm, length = 30 m), or a Shimadzu GC-2025 chromatograph equipped with a Stabilwax capillary column (internal diameter = 0.25 mm, length = 30 m) and a flame ionization detector. Mass spectroscopy (MS) measurements were recorded on a spectrometer (GCMS-QP2010 SE, Shimadzu) equipped with an InertCap 17MS capillary column (internal diameter = 0.25 mm, length = 30 m) at an ionization voltage of 70 eV.

Synthesis of BaFeO_{3- δ}

The iron-based BaFeO_{3- δ} perovskite catalyst was synthesized by the amino-acid aided method.^{S3} The details are as follows: Ba(OAc)₂ (3.83 g, 15 mmol), Fe(OAc)₂ (2.61 g, 15 mmol), and L-aspartic acid (5.99 g, 45 mmol) were dissolved in water (100 mL). The

brown solution was evaporated to dryness at 343 K. The resulting brown powder was dried at 463 K for 2 h to give a pale brown powder (6.06 g). The precursor was calcined at 1023 K for 5 h in air to obtain BaFeO_{3-δ}. Yield: 3.12 g (86%). Elemental analysis: calcd (%) for BaFeO₃: Ba 56.94, Fe 23.16; found: Ba 57.18, Fe 22.21.

Synthesis of other mixed metal oxides

SrFeO₃ and CaFeO_{2.5} were also synthesized by the amino acid-aided method^{S3} using Sr(OAc)₂·0.5H₂O and Ca(OAc)₂ precursors, respectively. SrFeO₃ and CaFeO_{2.5} were obtained by calcination of the precursors at 923 and 873 K for 5 h, respectively. Other mixed metal oxides were synthesized by the malic acid- or aspartic acid-aided methods.^{S3}

Procedure for Catalytic Oxidation

Catalytic oxidation was conducted in a 30 mL glass vessel containing a magnetic stirring bar. A typical procedure for catalytic oxidation was as follows: BaFeO_{3-δ} (0.2 g), **1a** (1 mmol), PhCF₃ (1 mL), O₂ (0.1 MPa), and an internal standard (naphthalene) were charged into the reaction vessel. The reaction solution was heated at 363 K and periodically analyzed using GC. The products were identified by comparison of their GC retention times, MS spectra, and ¹H and ¹³C NMR signals with the commercially available authentic samples or literature data (**2b**,^{S4} 5,7-dimethyl-2-adamantanone,^{S5} **2d**,^{S6}, and decalone^{S6}). The oxidation of *cis*-decaline was carried out by using the NHPI-Co(acac)₂ system,^{S7} and the present *cis/trans* ratio of 9-decalol was determined by comparing the results of a NHPI-Co(acac)₂ system. The separated BaFeO_{3-δ} was washed with PhCF₃ (5 mL) and methanol (5 mL), and then dried under vacuum before recycling. The amounts of surface Fe species were estimated assuming that the (110) plane is a surface structure because of the abundant population of Fe species on the (110) plane. The amounts of surface Fe were estimated using this hypothesis and the BET specific surface area of BaFeO_{3-δ} (11 m² g⁻¹) to be 80 μmol g⁻¹. The turnover number (TON) was calculated according to the following equation: TON = (**2a** (mol) + **3a** (mol) + **4a** (mol) × 2 + **5a** (mol) × 2)/catalyst (mol) × 100.

Effect of Solvents on Aerobic Oxidation of **1a** Catalyzed by BaFeO_{3-δ}

The effect of solvents on aerobic oxidation of **1a** catalyzed by BaFeO_{3-δ} was examined (Table S4). PhCF₃ was the most effective. Non-polar *n*-octane was also effective, while polar 1,2-dichlorobenzene, benzonitrile, and dimethyl sulfoxide were poor solvents. When using alkylated benzene solvents such as toluene, *o*-xylene, and mesitylene, the side-chain oxidation of solvents occurred.

¹⁸O-Labeling experiments. ¹⁸O₂ (>97% enriched) was obtained from Isotec. Before the reaction, the catalyst was evacuated at 473 K for 2 h and PhCF₃ was degassed by freeze-pump-thaw cycling. The ¹⁸O-Labeling experiment was carried out in a schlenk flask containing a magnetic stir bar. BaFeO_{3-δ} (0.1 g), **1a** (1.0 mmol), PhCF₃ (1 mL), and an internal standard (naphthalene) were charged into the schlenk flask under Ar atmosphere, followed by the evacuation and the introduction of 97% ¹⁸O₂ (0.1 MPa). The reaction solution was heated at 363 K and periodically analyzed using GC and GC-MS. The ¹⁸O content in **2a** was determined by using the ratio of the peak intensity at *m/z* = 152 to the sum of the peak intensities at *m/z* = 152 and 154.

Data of products

1-Adamantanol (2a). ¹H NMR (400 MHz, CDCl₃, 298 K, TMS): δ = 2.14 (br, s, 3H), 1.81 (s, 1H), 1.72–1.68 (m, 6H), 1.62–1.57 (m, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 298 K, TMS): δ = 68.2, 45.4, 36.1, 30.8; MS (70 eV, EI): *m/z* (%): 152 (35) [*M*⁺], 109 (9), 96 (13), 95 (100), 94 (22), 79 (8), 77 (9), 55 (5).

2-Adamantanol (3a). ¹H NMR (400 MHz, CDCl₃, 298 K, TMS): δ = 3.87 (br, s, 1H), 2.09–2.05 (m, 2H), 1.89–1.80 (m, 6H), 1.72–1.68 (m, 5H), 1.56–1.50 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 298 K, TMS): δ = 74.7, 37.7, 36.6, 34.7, 31.1, 27.6, 27.2; MS (70 eV, EI): *m/z* (%): 152 (4) [*M*⁺], 135 (11), 134 (100), 119 (18), 106 (6), 105 (10), 93 (23), 92 (56), 91 (24), 81 (9), 80 (17), 79 (37), 78 (11), 77 (9), 67 (10), 56 (7), 55 (8), 53 (5).

2-Adamantanone (4a). ¹H NMR (400 MHz, CDCl₃, 298 K, TMS): δ = 2.54 (br, s, 2H), 2.11–1.91 (m, 12H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 298 K, TMS): δ = 218.1, 46.8, 39.1, 36.1, 27.3; MS (70 eV, EI): *m/z* (%): 151 (12), 150 (100) [*M*⁺], 132 (7), 122 (5), 117 (23), 108 (9), 107 (6), 104 (15), 94 (7), 93 (16), 91 (16), 81 (31), 80 (59), 79 (66), 78 (15), 77 (13), 72 (12), 67 (11), 66 (7), 65 (5), 55 (8), 54 (10), 53 (10).

1,3-Adamantanediol (5a). ¹H NMR (400 MHz, DMSO-*d*₆, 298 K, TMS): δ = 4.44 (s, 2H), 2.11 (br, s, 2H), 1.49–1.45 (m, 10H), 1.37–1.35 (m, 2H); ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆, 298 K, TMS): δ = 68.5, 53.4, 44.2, 34.8, 30.7; MS (70 eV, EI): *m/z* (%): 168 (18) [*M*⁺], 112 (11), 111 (100), 110 (8), 109 (5), 108 (6), 95 (20), 94 (7), 93 (7), 55 (7).

3-Ethyl-1-adamantanol (2b). MS (70 eV, EI): m/z (%): 181 (6), 180 (46) [M^+], 152 (11), 151 (99), 133 (11), 124 (10), 123 (100), 122 (16), 109 (12), 107 (22), 96 (6), 95 (78), 94 (8), 93 (621), 91 (12), 81 (13), 79 (12), 77 (11), 67 (10), 59 (7), 57 (7), 55 (13), 53 (6).

5-Ethyl-1,3-adamantanediol (3b). MS (70 eV, EI): m/z (%): 196 (14) [M^+], 167 (32), 140 (11), 139 (100), 136 (5), 123 (19), 111 (32), 110 (5), 109 (59), 107 (24), 95 (7), 81 (12).

3,5-Dimethyl-1-adamantanol (2c). ^1H NMR (400 MHz, CDCl_3 , 298 K, TMS): δ = 2.19 (sept, 1H, J = 3.2 Hz), 1.70 (s, 1H), 1.57–1.55 (m, 2H), 1.40–1.24 (m, 8H), 1.11 (s, 2H), 0.87 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 298 K, TMS): δ = 70.0, 51.6, 50.6, 43.9, 42.6, 33.9, 31.2, 30.0; MS (70 eV, EI): m/z (%): 180 (24) [M^+], 165 (8), 124 (9), 123 (100), 122 (7), 110 (7), 109 (85), 108 (7), 107 (29), 95 (6), 81 (6), 79 (5), 55 (8).

trans-9-Decalol (2d). MS (70 eV, EI): m/z (%): 154 (29) [M^+], 112 (9), 111 (100), 98 (49), 97 (22), 93 (8), 84 (5), 83 (17), 81 (5), 79 (6), 70 (6), 69 (6), 67 (9), 55 (27), 43 (8), 41 (14), 39 (5).

cis-9-Decalol (3d). MS (70 eV, EI): m/z (%): 154 (24) [M^+], 112 (9), 111 (100), 98 (52), 97 (23), 93 (9), 91 (5), 84 (6), 83 (19), 81 (5), 79 (7), 70 (7), 69 (7), 67 (10), 55 (30), 43 (10), 41 (15), 39 (6).

Cyclooctanol (2e). ^1H NMR (400 MHz, CDCl_3 , 298 K, TMS): δ = 3.82 (m, 1H), 2.49 (s, 1H), 1.85–1.44 (m, 14H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 298 K, TMS): δ = 72.0, 34.6, 27.4, 25.2, 22.7; MS (70 eV, EI): m/z (%): 128 (1) [M^+], 110 (8), 99 (7), 95 (21), 85 (11), 84 (8), 83 (5), 82 (45), 81 (41), 71 (9), 69 (15), 68 (41), 67 (42), 66 (10), 58 (9), 57 (100), 56 (22), 55 (31), 54 (19), 53 (6).

Cyclooctanone (3e). ^1H NMR (400 MHz, CDCl_3 , 298 K, TMS): δ = 2.43–2.40 (m, 4H), 1.91–1.85 (m, 4H), 1.58–1.52 (m, 4H), 1.41–1.35 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 298 K, TMS): δ = 218.1, 41.8, 27.0, 25.5, 24.5; MS (70 eV, EI): m/z (%): 126 (18) [M^+], 111 (8), 99 (6), 98 (98), 97 (24), 93 (6), 84 (42), 83 (50), 82 (34), 71 (5), 70 (23), 69 (24), 68 (10), 67 (20), 57 (5), 56 (31), 55 (100), 54 (8), 53 (6).

9-Fluorenone (2f). ^1H NMR (400 MHz, CDCl_3 , 298 K, TMS): δ = 7.58–7.55 (m, 2H), 7.40–7.35 (m, 4H), 7.23–7.17 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 298 K, TMS): δ = 193.7, 144.3, 134.6, 134.0, 128.9, 124.1, 120.2; MS (70 eV, EI): m/z (%): 181 (29), 180 (100) [M^+], 153 (8), 152 (59), 151 (29), 150 (18), 126 (10), 76 (22), 75 (9), 74 (5), 63 (11).

Xanthone (2g). ^1H NMR (400 MHz, CDCl_3 , 298 K, TMS): δ = 8.32–8.28 (m, 2H), 7.68–7.64 (m, 2H), 7.42–7.40 (m, 2H), 7.34–7.30 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 298 K, TMS): δ = 177.1, 156.1, 134.8, 126.6, 123.9, 121.8, 118.0; MS (70 eV, EI): m/z

(%): 197 (18), 196 (100) [M^+], 195 (5), 169 (7), 168 (53), 140 (9), 139 (49), 92 (5), 84 (13), 69 (9), 64 (6), 63 (8), 50 (5).

1,2,3,4-Tetrahydro-1-naphthol (2h). ^1H NMR (400 MHz, CDCl_3 , 298 K, TMS): δ = 7.38–7.36 (m, 1H), 7.17–7.05 (m, 3H), 4.69 (t, 1H, J = 5 Hz), 2.77–2.70 (m, 2H), 2.30 (s, 1H), 1.95–1.72 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 298 K, TMS): δ = 138.9, 137.1, 129.0, 128.7, 127.5, 126.1, 68.1, 32.3, 29.3, 18.9; MS (70 eV, EI): m/z (%): 148 (30) [M^+], 147 (32), 131 (19), 130 (100), 129 (41), 128 (19), 127 (9), 121 (7), 120 (77), 119 (51), 117 (5), 116 (5), 115 (23), 105 (33), 104 (10), 103 (5), 92 (12), 91 (57), 90 (5), 89 (7), 78 (11), 77 (12), 65 (11), 64 (6), 63 (8), 51 (11).

α -Tetralone (3h). ^1H NMR (400 MHz, CDCl_3 , 298 K, TMS): δ = 8.00 (d, 1H, J = 8 Hz), 7.43 (dd, 1H, J = 8 Hz), 7.30–7.21 (m, 2H), 2.92 (t, 2H, J = 6.1 Hz), 2.63–2.60 (m, 2H), 2.13–2.06 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 298 K, TMS): δ = 198.0, 144.4, 133.3, 132.4, 128.7, 126.9, 126.5, 39.0, 29.5, 23.2; MS (70 eV, EI): m/z (%): 147 (11), 146 (90) [M^+], 145 (10), 131 (21), 119 (12), 118 (100), 117 (13), 116 (6), 115 (20), 104 (5), 91 (14), 90 (81), 89 (30), 77 (5), 65 (6), 63 (12), 58 (6), 51 (9), 50 (5).

1-Hydroxyindan (2i). ^1H NMR (400 MHz, CDCl_3 , 298 K, TMS): δ = 7.32–7.15 (m, 4H), 5.08 (t, 1H, J = 6 Hz), 3.09 (s, 1H), 2.95–2.91 (m, 1H), 2.75–2.69 (m, 1H), 2.36–2.31 (m, 1H), 1.84–1.79 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 298 K, TMS): δ = 145.0, 143.2, 128.1, 126.6, 124.7, 124.3, 76.1, 35.6, 29.7; MS (70 eV, EI): m/z (%): 135 (6), 134 (68) [M^+], 133 (100), 117 (13), 116 (17), 115 (28), 105 (26), 103 (9), 91 (20), 89 (6), 79 (11), 78 (5), 77 (15), 65 (5), 63 (6), 55 (7), 51 (10).

1-Indanone (3i). ^1H NMR (400 MHz, CDCl_3 , 298 K, TMS): δ = 7.74–7.31 (m, 4H), 3.13–3.10 (m, 2H), 2.67–2.64 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 298 K, TMS): δ = 207.0, 155.1, 137.0, 134.6, 127.2, 126.7, 123.6, 36.1, 25.7; MS (70 eV, EI): m/z (%): 133 (12), 132 (100) [M^+], 131 (32), 105 (10), 104 (89), 103 (48), 102 (10), 78 (35), 77 (24), 76 (14), 75 (5), 74 (6), 63 (8), 51 (23), 50 (12).

References

- S1 D. B. Williams and M. Lawton, *J. Org. Chem.*, 2010, **75**, 8351–8354.
S2 J. Zhu, S. Guo, Z. Chu and W. Jin, *J. Mater. Chem. A*, 2015, **3**, 22564–22573.
S3 K. Sugahara, K. Kamata, S. Muratsugu and M. Hara, *ACS Omega*, 2017, **2**, 1608–1616.

- S4 Z. Liu, S. Yang, X. Jin, G. Zhang, B. Guo, H. Chen, P. Yu, Y. Sun, Z. Zhang and Y. Wang, *MedChemComm*, 2017, **8**, 135–147.
- S5 M. Kira, M. Akiyama, M. Ichinose and H. Sakurai, *J. Am. Chem. Soc.*, 1989, **111**, 8256–8262.
- S6 (a) R. Mello, M. Fiorentino, C. Fusco and R. Curci, *J. Am. Chem. Soc.*, 1989, **111**, 6749–6757; (b) K. M. Kirkwood, P. Chernik, J. M. Foght and M. R. Gray, *Biodegradation*, 2008, **19**, 785–794; (c) D. A. Clark and P. L. Fuchs, *J. Am. Chem. Soc.*, 1979, **101**, 3567–3576.
- S7 Y. Ishii, S. Kato, T. Iwahama and S. Sakaguchi, *Tetrahedron Lett.*, 1996, **37**, 4993–4996.
- S8 Y. Ishii, K. Nakayama, M. Takeno, S. Sakaguchi, T. Iwahama and Y. Nishiyama, *J. Org. Chem.*, 1995, **60**, 3934–3935.
- S9 K. Matsunaka, T. Iwahama, S. Sakaguchi and Y. Ishii, *Tetrahedron Lett.*, 1999, **40**, 2165–2168.
- S10 G. Yang, Q. Zhang, H. Miao, X. Tong and J. Xu, *Org. Lett.*, 2005, **7**, 263–266.
- S11 Y. Ishii and S. Sakaguchi, *Catal. Surv. Jpn.*, 1999, **3**, 27–35.
- S12 M. Jafarpour, A. Rezaeifard, V. Yasinzadeh and H. Kargar, *RSC Adv.*, 2015, **5**, 38460–38469.
- S13 H. Kobayashi and I. Yamanaka, *J. Mol. Catal. A*, 2008, **294**, 37–42.
- S14 H. Kobayashi and I. Yamanaka, *J. Mol. Catal. A*, 2008, **294**, 43–50.
- S15 A. S. Goldstein and R. S. Drago, *Inorg. Chem.*, 1991, **30**, 4506–4510.
- S16 M. M. T. Khan, D. Chatterjee, S. Kumar S., A. P. Rao and N. H. Khan, *J. Mol. Catal.*, 1992, **75**, L49–L51.
- S17 S. Chatterjee and T. K. Paine, *Angew. Chem. Int. Ed.*, 2015, **54**, 9338–9342.
- S18 S. Chatterjee and T. K. Paine, *Angew. Chem. Int. Ed.*, 2016, **55**, 7717–7722.
- S19 S. Shinachi, M. Matsushita, K. Yamaguchi and N. Mizuno, *J. Catal.*, 2005, **233**, 81–89.
- S20 N. Mizuno, M. Tateishi, T. Hirose and M. Iwamoto, *Chem. Lett.*, 1993, 2137–21410.
- S21 M. Bonchio, M. Carraro, A. Farinazzo, A. Sartorel, G. Scorrano and U. Kortz, *J. Mol. Catal. A*, 2007, **262**, 36–40.
- S22 R. Neumann, A. M. Khenkin and M. Dahan, *Angew. Chem. Int. Ed.*, 1995, **34**, 1587–1589.
- S23 S. Murahashi, T. Naota and N. Komiya, *Tetrahedron Lett.*, 1995, **36**, 8059–8062.

- S24 N. Theyssen, Z. Hou and W. Leitner, *Chem. Eur. J.*, 2006, **12**, 3401–3409.
- S25 R. Giannandrea, P. Mastrorilli, C. F. Nobile and G. P. Suranna, *J. Mol. Catal.*, 1994, **94**, 27–36.
- S26 P. Mastrorilli and C. F. Nobile, *Tetrahedron Lett.*, 1994, **35**, 4193–4196.
- S27 V. Rabe, W. Frey, A. Baro, S. Laschat, M. Bauer, H. Bertagnolli, S. Rajagopalan, T. Asthalter, E. Roduner, H. Dilger, T. Glaser and D. Schnieders, *Eur. J. Inorg. Chem.*, 2009, 4660–4674.
- S28 N. Kitajima, M. Ito, H. Fukui and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, 1991, 102–104.
- S29 N. Kitajima, H. Fukui and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, 1988, 485–486.
- S30 D. H. R. Barton, J. Boivin and P. L. Coupanec, *J. Chem. Soc., Chem. Commun.*, 1987, 1379–1381.
- S31 P. Battioni, J. F. Bartoli, P. Leduc, M. Fontecave and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, 1987, 791–792.
- S32 I. Yamanaka, T. Akimoto and K. Otsuka, *Chem. Lett.*, 1994, 1511–1514.
- S33 H. Jaafar, B. Vileno, A. Thibon and D. Mandon, *Dalton Trans.*, 2011, **40**, 92–106.
- S34 V. Kesavan, P. S. Sivanand, S. Chandrasekaran, Y. Koltypin and A. Gedanken, *Angew. Chem. Int. Ed.*, 1999, **38**, 3521–3523.
- S35 N. Komiya, T. Naota, Y. Oda and S. Murahashi, *J. Mol. Catal. A*, 1997, **117**, 21–37.
- S36 S. Murahashi, X.-G. Zhou and N. Komiya, *Synlett*, 2003, **3**, 321–324.
- S37 G. Balavoine, D. H.R. Barton, J. Boivin, A. Gret, N. Ozbalikae and H. Riviere, *Tetrahedron Lett.*, 1986, **27**, 2849–2852.
- S38 E. T. Farinas, C. V. Nguyen and P. K. Mascharak, *Inorg. Chim. Acta*, 1997, **263**, 17–21.
- S39 M. Haranaka, A. Hara, W. Ando and T. Akasaka, *Tetrahedron Lett.*, 2009, **50**, 3585–3587.
- S40 K. Ohkubo, A. Fujimoto and S. Fukuzumi, *Chem. Commun.*, 2011, **47**, 8515–8517.
- S41 I. Saito, M. Takayama and T. Matsuura, *Tetrahedron Lett.*, 1989, **30**, 2237–2240.
- S42 E. Baciocchi, T. D. Giacco and G. V. Sebastiani, *Tetrahedron Lett.*, 1987, **28**, 1941–1944.
- S43 K. Yamaguchi and N. Mizuno, *New J. Chem.*, 2002, **26**, 972–974.
- S44 T. Mitsudome, N. Nosaka, K. Mori, T. Mizugaki, K. Ebitani and K. Kaneda, *Chem.*

- Lett.*, 2005, **34**, 1626–1627.
- S45 I. Yamanaka, Y. Suzuki and M. Toida, *Catal. Today*, 2010, **157**, 286–290.
- S46 X.-H. Li, J.-S. Chen, X. Wang, J. Sun and M. Antonietti, *J. Am. Chem. Soc.*, 2011, **133**, 8074–8077.
- S47 L. Cermenati, D. Dondi, M. Fagnoni and A. Albini, *Tetrahedron*, 2003, **59**, 6409–6414.
- S48 K. Teramura, T. Tanaka, T. Hosokawa, T. Ohuchi, M. Kani and T. Funabiki, *Catal. Today*, 2004, **96**, 205–209.
- S49 M. Sun, Y. Jiang, F. Li, M. Xia, B. Xue and D. Liu, *Mater. Trans.*, 2010, **51**, 1981–1989.
- S50 H. Xian, X. Zhang, X. Li, H. Zou, M. Meng, Z. Zou, L. Guo and N. Tsubaki, *Catal. Today*, 2010, **158**, 215–219.
- S51 H. Xian, X. Zhang, X. Li, L. Li, H. Zou, M. Meng, Q. Li, Y. Tan and N. Tsubaki, *J. Phys. Chem. C*, 2010, **114**, 11844–11852.
- S52 X. Li, J. Chen, P. Lin, M. Meng, Y. Fu, J. Tu and Q. Li, *Catal. Commun.*, 2004, **5**, 25–28.
- S53 H. Xian, F.-L. Li, X.-G. Li, X.-W. Zhang, M. Meng, T.-Y. Zhang and N. Tsubaki, *Fuel Process. Technol.*, 2011, **92**, 1718–1724.
- S54 L. M. Córdoba, M. I. Gómez, J. A. de Morán and P. J. Aymonino, *J. Argent. Chem. Soc.*, 2008, **96** (1-2), 1–12.
- S55 L. A. Isupova, A. N. Nadeev, I. S. Yakovleva and S. V. Tsybulya, *Kinet. Catal.*, 2008, **49**, 133–137.
- S56 C. Huang, Y. Zhu, X. Wang, X. Liu, J. Wang and T. Zhang, *J. Catal.*, 2017, **347**, 9–20.
- S57 T. Masunaga, J. Izumi and N. Miura, *J. Ceram. Soc. Jpn.*, 2010, **118**, 952–954.

Table S1 Representative catalytic systems for the aerobic oxidation of adamantane (**1a**)

Entry	Catalyst	1a /C/A ^a	Solvent	O ₂ /MPa	Temp. (K)	Time (h)	Yield (%)				Ref.
							2a	3a	4a	5a	
<i>Homogeneous systems</i>											
1	NHPI ^b	10/1	PhCN	0.1	373	6	12	–	–	–	S8
2	NHPI ^b / <i>n</i> -Bu ₄ NBr	10/1/0.2	PhCF ₃ /H ₂ O (6/0.03, v/v)	0.1	353	6	44	–	9	17	S9
3	NHPI ^b /1,4-diamino-2,3-dichloro-anthraquinone	80/1/4	CH ₃ CN	0.3	353	7	(55)	–	–	(18)	S10
4	NHPI ^b /Co(acac) ₂	10/1/0.5	AcOH	0.1	348	15	10	–	5	53	S7
5	NHPI ^b /Co(acac) ₂	10/1/0.05	AcOH	0.1	348	6	43	–	8	40	S11
6	NHPI ^b /CoL ₂ @SMNP ^c	6.7/1/0.03	CH ₃ CN	flow	343	9	87	7	13	–	S12
7	VO(acac) ₂	1000/1	AcOH	0.1	393	6	24 ^d	3 ^d	4	3 ^d	S13
8	VO(acac) ₂	1000/1	EtCOOH	0.1	373	6	16 ^d	2 ^d	2	1 ^d	S14
9	[Co(NCCH ₃) ₄](PF ₆) ₂	1000/1	CH ₃ CN	air (0.3)	348	12	65 ^e	25 ^e	10 ^e	–	S15
10	K[Ru ^{III} (saloph)Cl ₂]	100/1	0.2 M KCl (pH 3.0)	0.1	–	7	8	3.7	1.6	–	S16
11	[(Tp ^{Ph2})Fe ^{II} (benzilate)]/Sc(OTf) ₃	–	benzene	flow	rt	0.42	47	12	0	–	S17
	[(Tp ^{Ph2})Fe ^{II} (benzilate)]/PyNHClO ₄ ^g /TBACl	50/1/2/2	benzene	flow	rt	0.42	45 ^h	0	–	–	S18
12	H ₅ PV ₂ Mo ₁₀ O ₄₀	500/1	butyronitrile	0.1	356	288	36	9	17	20	S19
13	[(<i>n</i> -C ₄ H ₉) ₄ N] ₄ H ₆ [PW ₉ O ₃₇ {Fe ₂ Ni(OAc) ₃ }]	103/1	benzene	0.1	355	48	22	3	3	–	S20
14	THA ₆ [β-Fe ₄ (H ₂ O) ₁₀ (AsW ₉ O ₃₃) ₂]	300/1	1,2-DCE	0.1	348	300	37	–	8 ⁱ	–	S21
15	TCM _{11-x} Na _x [WZnRu ^{III} ₂ (OH)(H ₂ O)(ZnW ₉ O ₃₄) ₂] ^j	1000/1	1,2-DCE	0.1	353	24	12	trace	trace	–	S22
16	Co(TPFPP)/acetaldehyde	400/1/400	EtOAc	0.1	343	24	50	1	24	17	S23

Table S1 (Continued)

Entry	Catalyst	1a/C/A ^a	Solvent	O ₂ /MPa	Temp. (K)	Time (h)	Yield (%)				Ref.
							2a	3a	4a	5a	
17	–/acetaldehyde	0.5/1/1/7.6 ^k	scCO ₂	total (3)	325	27	1.5	–	0.3	1.3	S24
18	Fe(AAEMA) ₃ /isovaleraldehyde	125/1/750	1,2-DCE	air (0.1)	rt	36	24	–	–	–	S25
19	Fe(AAEMA) ₃ /isovaleraldehyde	125/1/1875	1,2-DCE	air (0.1)	rt	60	59	–	–	–	S26
20	[Fe ₄ (μ ₃ -O) ₂ (5aH) ₂ Cl ₂ (H ₂ O) ₈] (NO ₃) ₄ ·3H ₂ O/Zn	286/1/2861	pyridine/AcOH (27/2.3, v/v)	1	rt	18	2	1	6	–	S27
21	[{Fe(HBpz ₃)(hfacac)} ₂ O]/Hhfacac/Zn	1107/1/287/333/5098	CH ₂ Cl ₂	0.1	298	30	42	2	trace	–	S28
22	μ-oxo binuclear iron complex/Zn	1147/1/225	CH ₂ Cl ₂ /AcOH	0.1	rt	30	2	<1	1	–	S29
23	[Fe ₃ O(OAc) ₆ py _{3,5}]/(PhSe) ₂ /Zn/AcOH	286/1/44/5714	pyridine/H ₂ O	air (0.1)	293	–	1 ^m	2	12	–	S30
24	Mn(TPP)Cl/1-Me-Im/Zn/AcOH	579/1/76/227/132	CH ₃ CN/CH ₂ Cl ₂	flow	293	0.5	2	<1	<1	–	S31
25	EuCl ₃ ·6H ₂ O/Zn	11/1/467	AcOH/1,2-DCE	0.1	313	1	33	24	10	–	S32
26	TPAFeCl ₂ /Zn-amalgam/AcOH	1100/1/2	CH ₃ CN	0.1	–	5	0.2	<0.1	<0.1	–	S33
27	Fe/isobutyraldehyde/AcOH	–/1/111/11	–	4	301	10-15	45	3	8	–	S34
28	Cu(OCH ₃) ₂ /acetaldehyde	33/1/100	dichloromethane	0.1	rt	17	24	1	1	–	S35
29	chlorinated phthalocyanine Fe(II) complex/acetaldehyde	4000/1/400	dichloromethane	0.1	rt	–	39	4	4	–	S36
30	Fe ₃ (OAc) ₆ Pyr _{3,5} /2,2'-dipyridyl/CF ₃ COOH/e [–]	80/1/40/1044	pyridine	flow	293		1.9		16.1		S37
31	[Co(BPI)(OAc)(OO ^t Bu)] ⁿ /photoirradiation	140/1	benzene	0.1	303	3	1.8	0.4	0.4	–	S38
32	diazofluorene/Mn(TPP)Cl ^o /photoirradiation	17/1/0.03	benzene	flow			35	6.4	–	–	S39
33	[Acr ⁺ –Mes]ClO ₄ ^p /HCl/photoirradiation	10/1/2	CH ₃ CN	0.1	298	4	8	7	3	–	S40

Table S1 (Continued)

Entry	Catalyst	1a /C/A ^a	Solvent	O ₂	Temp. (K)	Time (h)	Yield (%)				Ref.
							2a	3a	4a	5a	
34	Fe(NO ₃) ₃ /MDAP ²⁺ (BF ₄ ⁻) ₂ /oxalic acid/photoirradiation ^q	49/1/0.06/493	CH ₃ CN/H ₂ O (9/1, v/v)	flow		7	7.6	3.1	3.5	–	S41
35	CAN ^r /HNO ₃ /photoirradiation	50/1/10	CH ₃ CN	flow	rt	5	85	5	5	–	S42
Heterogeneous systems											
36	[(<i>n</i> -C ₄ H ₉) ₄ N] ₄ H [SiW ₁₁ Ru ^{III} (H ₂ O)O ₃₉]·2H ₂ O	2000/1	isobutyl acetate	0.1	373	72	38	1	9	16	S43
37	vanadium cation-exchanged montmorillonite	167/1	<i>t</i> -BuOAc	0.1	373	96	38	–	14	41	S44
38	Pt/Eu ₂ O ₃ /TiO ₂ /SiO ₂	1 mmol/0.1 g	AcOH	flow ^s	313	10	13	10	2	–	S45
39	graphene sheet/polymeric carbon nitride nanocomposite	0.1 g/50 mg	CH ₃ CN	1	423	4	29	–	15	7	S46
40	TiO ₂ /photoirradiation	0.4 mmol/140 mg	MeCN	slow flux	–	3	6	0.6	5	–	S47
41	V ₂ O ₅ /Al ₂ O ₃ /photoirradiation	0.15/2.5 wt%	CH ₃ CN	flow	323	24	4	0.2	1	–	S48

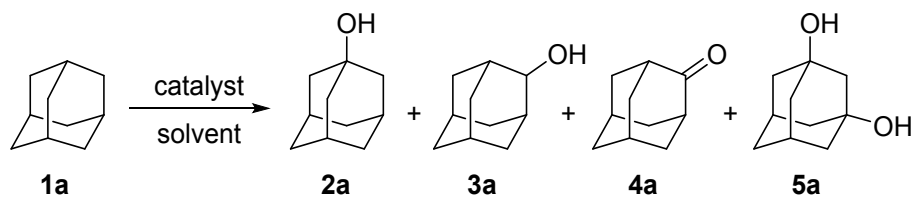
^a **1a**/C/A = molar ratio of **1a**/catalyst/additives. ^b NHPI = *N*-hydroxyphthalimide. ^c CoL₂@SMNP = immobilized cobalt Schiff base complex on the starch coated γ -Fe₂O₃ nanoparticles. ^d Sum of adamantanol and its esters. ^e Selectivity. ^f Tp^{Ph2} = hydrotris(3,5-diphenyl-pyrazol-1-yl)borate. ^g PyNHClO₄ = pyridinium perchlorate. ^h 1-Chloroadamantane (12% yield). ⁱ Including 2-Cl. ^j TCM = tricaprilmethylammonium. ^k **1a**/O₂/acetaldehyde/CO₂. ^l AAEMA = deprotonated form of the β -ketoester 2-(acetoacetoxy)ethyl methacrylate. ^m Tertiary phenyl selenide (2% yield). ⁿ BPI = 1,3-bis(2'-pyridylimino) isoindoline. ^o Tetraphenylporphin. ^p Acr⁺-Mes = 9-mesityl-10-methylacridinium. ^q MDAP²⁺ = *N,N'*-dimethyl-2,7-diazapyrenium dication, hv > 320 nm. ^r CAN = Cerium(IV) ammonium nitrate. ^s H₂/O₂ = 96/5.

Table S2 Synthetic methods and specific surface areas of BaFeO₃-based materials

Entry	Method	Metal source		S_{BET} (m ² g ⁻¹)	Calcination temp. (K)	Notes	Ref
		Ba	Fe				
1	amino acid-aided method	acetate	acetate	11	1023		This work
2	sol-gel method	nitrate	nitrate	6.6	973	Impurities were observed in XRD pattern.	S49
3	sol-gel method	nitrate	nitrate	6.0	1023	BaFe ₂ O ₄ was observed in XRD pattern.	S50
4	sol-gel method	nitrate	nitrate	5.9	1123	Impurities were observed in XRD pattern.	S51
5	sol-gel method	nitrate	nitrate	4.7	1023	Impurities were observed in XRD pattern.	S52
6	sol-gel method	nitrate	nitrate	4.0	1123		S53
7	thermal decomposition	BaNH ₄ [Fe(CN) ₆]		2.8	1173	BaCO ₃ was observed in XRD pattern.	S54
8	mechanochemical	BaCO ₃	Fe ₂ O ₃	1.0	1373	Mixture of perovskite and brownmillerite	S55
9	sol-gel method	acetate	nitrate	0.9	1473	Rhombohedral BaFeO _{2.67} (JCPDS 20-0129)	S56
10	nitrate decomposition method	nitrate	nitrate	0.18	1474	Hexagonal perovskite (JCPDS 23-1024)	S57

Table S3 Characterization results for iron-based perovskites

Entry	Perovskite	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Elemental analysis
1	$\text{BaFeO}_{3-\delta}$	11	calcd (%) for BaFeO_3 : Ba 56.94, Fe 23.16 found: Ba 57.18, Fe 22.21.
2	SrFeO_3	20	calcd (%) for SrFeO_3 : Sr 45.76, Fe 29.17 found: Sr 48.53, Fe 31.48,
3	$\text{CaFeO}_{2.5}$	28	calcd (%) for $\text{CaFeO}_{2.5}$: Ca 29.49, Fe 41.09 found: Ca 31.67, Fe 40.77.

Table S4 Effects of solvents on the oxidation of **1a** catalyzed by BaFeO_{3-δ} with O₂^a

Entry	Solvent	Yield (%)	Selectivity (%)			
			2a	3a	4a	5a
1	PhCF ₃	29	76	7	11	6
2	<i>n</i> -Octane	20	76	10	9	5
3	1,2-Dichlorobenzene	7	77	11	9	2
4	Benzonitrile	5	95	0	0	5
5	Dimethylsulfoxide	0	–	–	–	–

^a Reaction conditions: BaFeO_{3-δ} (0.1 g), **1a** (0.5 mmol), solvent (1 mL), *p*O₂ (0.1 MPa), 363 K, 48 h. Yield and selectivity were determined by GC analysis. Yield (%) = (**2a**+**3a**+**4a**+**5a**) (mol)/initial **1a** (mol)×100. Selectivity (%) = product (mol)/(**2a**+**3a**+**4a**+**5a**) (mol)×100.

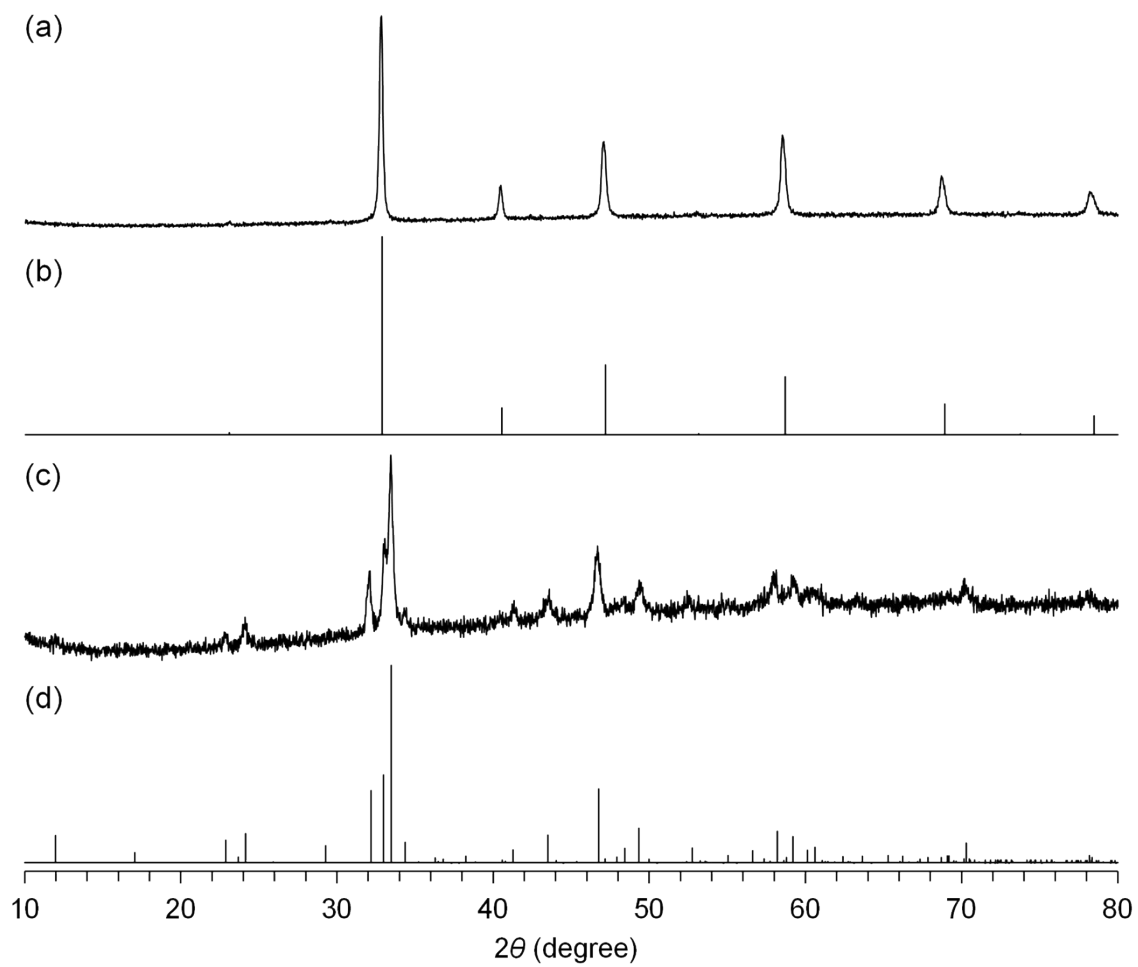


Fig. S1 XRD patterns for (a) SrFeO_3 , (b) cubic SrFeO_3 (ICSD 92335), (c) $\text{CaFeO}_{2.5}$, and (d) orthorhombic $\text{CaFeO}_{2.5}$ (ICSD 14296).

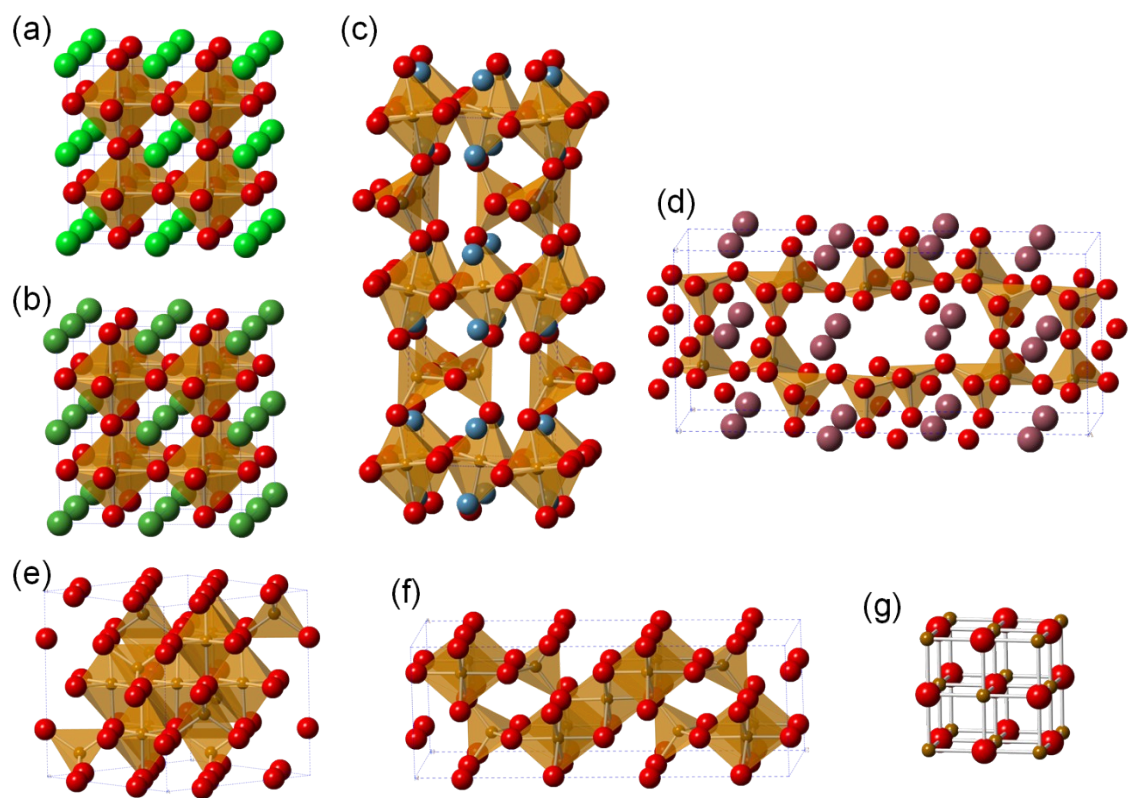


Fig. S2 Structures of (a) cubic SrFeO_3 , (b) cubic LaFeO_3 , (c) orthorhombic $\text{CaFeO}_{2.5}$, (d) orthorhombic BaFe_2O_4 , (e) cubic Fe_2O_3 , (f) monoclinic Fe_3O_4 , and (g) cubic FeO .

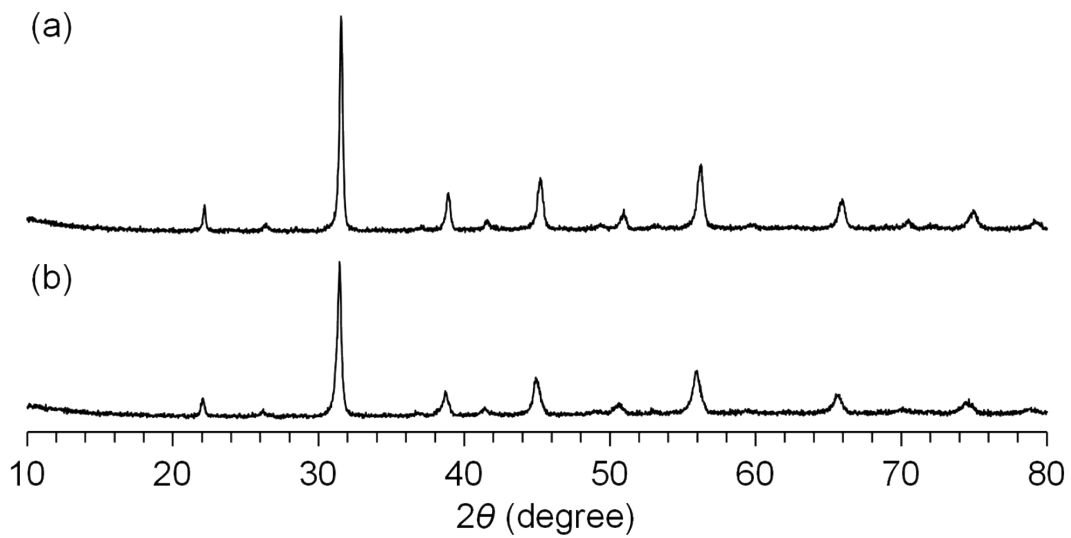


Fig. S3 XRD patterns for (a) fresh $\text{BaFeO}_{3-\delta}$ and (b) recovered $\text{BaFeO}_{3-\delta}$.

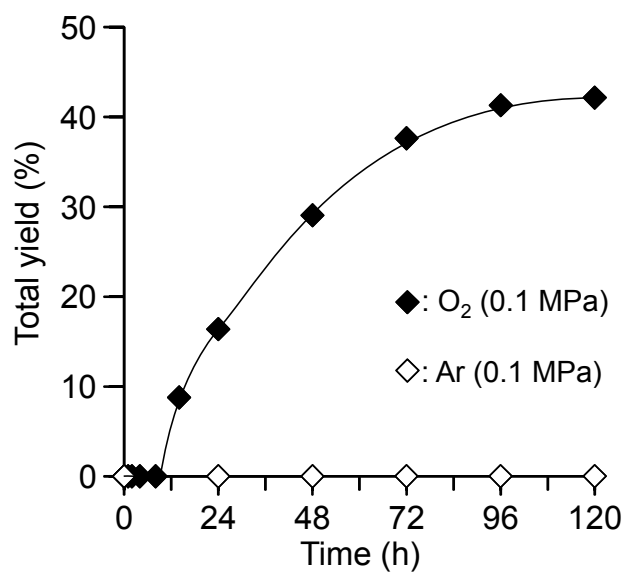
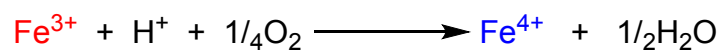
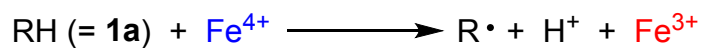
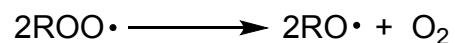
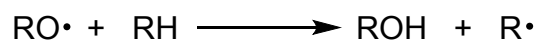
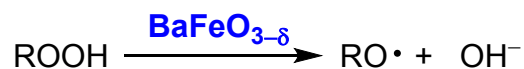
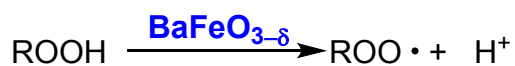
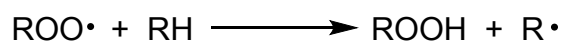
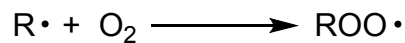


Fig. S4 Time courses for the oxidation of **1a** under Ar or O₂ atmospheres catalyzed by BaFeO_{3- δ} . Reaction conditions: BaFeO_{3- δ} (0.1 g), **1a** (0.5 mmol), PhCF₃ (1 mL), *p*Ar or *p*O₂ (0.1 Ma), 363 K.

Initiation and reoxidation



Propagation



Termination

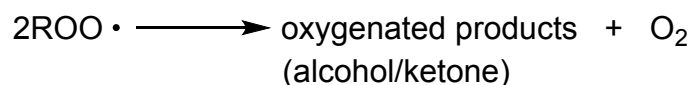


Fig. S5 Possible reaction mechanism for the BaFeO_{3-δ}-catalyzed oxidation of adamantine with O₂ as the sole oxidant. BaFeO_{3-δ} would play important roles in the initial formation of R• and decomposition of ROOH species into radical species.

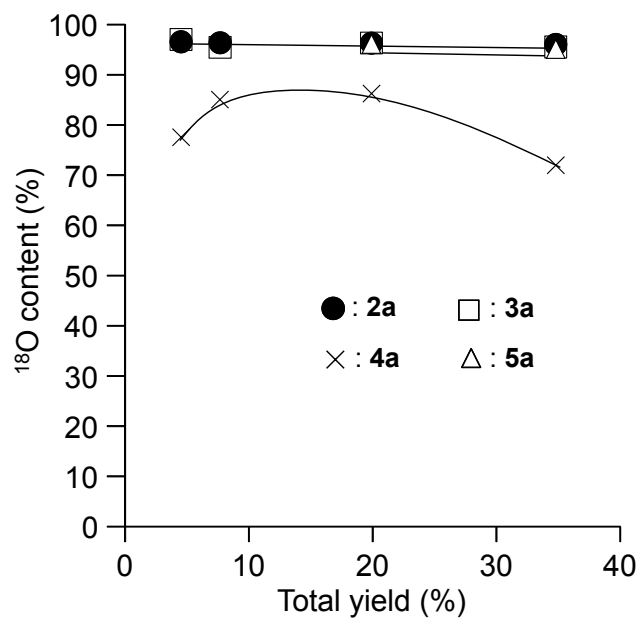


Fig. S6 Plots of the ratio of ^{18}O contents in **2a**, **3a**, and **4a** against the total yield for the oxidation of **1a** with 97 atom% $^{18}\text{O}_2$. Reaction conditions: $\text{BaFeO}_{3-\delta}$ (0.1 g), **1a** (1.0 mmol), PhCF_3 (1 mL), $p\text{O}_2$ (0.1 MPa), 363 K.