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

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Hexagonal $BaFeO_{3-\delta}$ containing high valent iron species acted as an efficient heterogeneous catalyst for the aerobic oxidation of alkanes without the need for additives. The activity of $BaFeO_{3-\delta}$ was much higher than that of typical Fe^{3+}/Fe^{2+}-containing iron oxide-based catalysts, and the recovered catalyst could be reused without significant loss of catalytic performance.

Catalytic oxidation of the aliphatic C–H bond of alkanes to produce useful chemicals remains a significant and challenging subject of research in the chemical industry.[1] The development of effective catalysts with well-defined active sites for the oxidation of alkanes using activated oxidants such as organic peroxides/peracids and hydrogen peroxide is expected to lead to remarkable activity and selectivity.[2] In contrast to such processes, catalytic oxidation with molecular oxygen (O_2) as an oxidant offers environmental and economic advantages; however, the control of O_2 activation and selectivity remains a problem to be solved.[3] Functionalized adamantane derivatives can be biologically active compounds and functionally hybrid materials;[4] therefore, several catalytic systems for the aerobic oxidation of adamantane have been developed (Table S1, ESI).[5,6] Most of these systems are homogeneous and typically require additives (radical initiator, reductant, etc.) or photo- or microwave irradiation.[5] There are only a few examples of recoverable and reusable heterogeneous Ru- and V-based catalysts with O_2 as the sole oxidant.[6]

The versatility of perovskite oxides with formula ABO_3 has led to various applications in the fields of structural chemistry, magnetism, superconductivity, and piezoelectrics.[7a] In particular, the catalytic function of perovskite oxide-based materials has attracted much attention because their structures and physicochemical properties can be controlled by changing the composition.[7b,7c] Despite their superiority, application to perovskite-catalyzed liquid-phase organic reactions is still limited. We have very recently reported the amino acid-aided synthesis of high-surface-area perovskite catalysts that contain alkaline earth metals as A-site elements.[8] Hexagonal $SrMnO_3$ could act as an efficient heterogeneous catalyst for the aerobic oxidation of various substrates.[8] We envisaged that an iron-based perovskite containing Fe^{4+} would likely act as an efficient catalyst for alkane oxidation because high valent iron-oxo species have been postulated to be strong active oxidants under mild conditions.[9] Here, we report that hexagonal 6H-$BaFeO_{3-\delta}$, which consists of face-sharing dimeric Fe_2O_9 units linked by single corner-sharing FeO_6 units along the *c* axis (Fig. 1(a)), could act as an efficient, recyclable and heterogeneous catalyst for the oxidation of adamantane (**1a**) with 0.1 MPa of O_2 as the sole oxidant. This study provides the first example of a naturally abundant iron oxide-based heterogeneous catalyst for the aerobic oxidation of **1a** without the need for any additives.

Perovskite $BaFeO_{3-\delta}$ was prepared by the amino acid-aided method (see ESI).[8b] Fig. 1(b) shows a powder X-ray diffraction

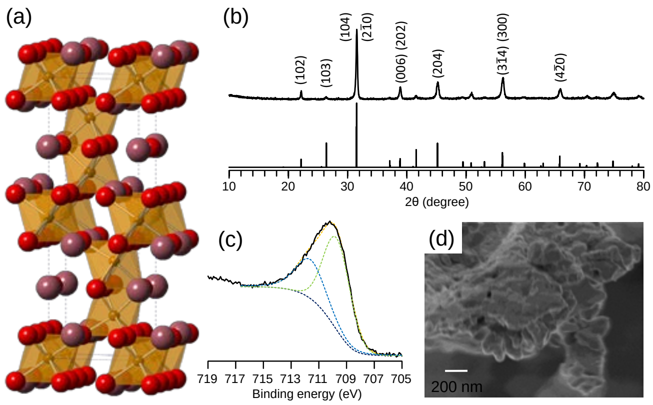

Fig. 1 (a) Structure of $BaFeO_3$. Brown, purple, and red spheres represent the Fe, Ba, and O atoms, respectively. (b) XRD patterns for $BaFeO_{3-\delta}$ (upper) and $BaFeO_3$ (lower, ICSD 50869). (c) XPS Fe $3p_{3/2}$ spectrum for $BaFeO_{3-\delta}$ and (d) SEM image.

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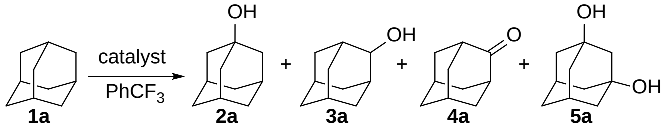
(XRD) pattern for BaFeO$_{3-\delta}$, which is in good agreement with that for hexagonal 6H-BaFeO$_{3-x}$ [space group $P6_3/mmc$ (No. 194)].[10] Impurity phases of other iron oxide species (FeO, Fe$_3$O$_4$, Fe$_2$O$_3$, and Ba$_2$FeO$_4$) were not observed. Elemental analysis of BaFeO$_{3-\delta}$ using inductively coupled plasma atomic emission spectroscopy (ICP-AES) revealed that the molar ratio of Ba:Fe was 1:1. The average oxidation state of Fe species was determined to be 3.8 by iodometry, which indicates that the δ value in BaFeO$_{3-\delta}$ is ca. 0.1. The X-ray photoelectron spectroscopy (XPS) Fe 2p spectrum of BaFeO$_{3-\delta}$ showed peaks with binding energies of 709.7 and 711.6 eV, which correspond to Fe^{3+} and Fe^{4+} species, respectively (Fig. 1(c)).[10,11] The specific surface area of BaFeO$_{3-\delta}$ was 11 m^2 g^{-1}, and this value was larger than those (0.2–6.6 m^2 g^{-1}) reported for BaFeO$_{3-\delta}$ (Table S2, ESI).[10] Fig. 1(d) shows a scanning electron microscopy (SEM) image of BaFeO$_{3-\delta}$, where the particle sizes were estimated to be 50−200 nm. Cubic SrFeO$_3$ and orthorhombic CaFeO$_{2.5}$ were also successfully synthesized by the amino acid-aided method and were characterized by XRD, N$_2$-adsorption, and elemental analyses (Table S3 and Figs. S1 and S2, ESI).

Table 1 Effects of catalysts on the oxidation of **1a** with O$_2$[a]



Entry	Catalyst	S_{BET} (m^2 g^{-1})	Yield (%)	Selectivity (%)			
				2a	3a	4a	5a
1	BaFeO$_{3-\delta}$	11	29	76	7	11	6
2[b]	BaFeO$_{3-\delta}$	11	30	82	7	6	5
3[b,c]	BaFeO$_{3-\delta}$	11	30	79	7	7	7
4[b,d]	BaFeO$_{3-\delta}$	11	31	77	8	7	7
5	SrFeO$_3$	20	27	76	8	10	6
6	CaFeO$_{2.5}$	28	<1	–	–	–	–
7	LaFeO$_3$	18	<1	–	–	–	–
8	BaFe$_2$O$_4$	14	<1	–	–	–	–
9	Fe$_2$O$_3$	39	<1	–	–	–	–
10	Fe$_3$O$_4$	12	<1	–	–	–	–
11	FeO	1	<1	–	–	–	–
12	Fe(OAc)$_2$	–	<1	–	–	–	–
13	Ba(OAc)$_2$	–	<1	–	–	–	–
14	BaCoO$_3$	19	<1	–	–	–	–
15	BaMnO$_3$	25	<1	–	–	–	–
16	SrMnO$_3$	47	<1	–	–	–	–
17	CaMnO$_3$	11	<1	–	–	–	–
18	BaRuO$_3$	25	1	>99	–	–	–
19	without	–	<1	–	–	–	–

[a] Reaction conditions: catalyst (0.1 g), **1a** (0.5 mmol), PhCF$_3$ (1 mL), pO$_2$ (0.1 MPa), 363 K, 48 h. Yield and selectivity were determined by gas chromatography (GC) analysis. Yield (%) = (**2a**+**3a**+**4a**+**5a**) (mol)/initial **1a** (mol)×100. Selectivity (%) = product (mol)/(**2a**+**3a**+**4a**+**5a**) (mol)×100. [b] **1a** (1 mmol). [c] Reuse (1st). [d] Reuse (2nd).

The aerobic oxidation of **1a** in benzotrifluoride (PhCF$_3$) at 0.1 MPa of O$_2$ without any additives was performed using various perovskites and iron oxides (Tables 1 and S4, ESI). Four products, 1-adamantanol (**2a**), 2-adamantanol (**3a**), 2-adamantanone (**4a**), and 1,3-adamantanediol (**5a**), were mainly formed. The reaction did not proceed in the absence of a catalyst (entry 19). Among the catalysts tested, Fe^{4+}-containing BaFeO$_{3-\delta}$ and SrFeO$_3$ exhibited high catalytic activity (entries 1 and 5), and the intrinsic activity of BaFeO$_{3-\delta}$ (with face-sharing octahedra) per surface was approximately two times higher than that of SrFeO$_3$ (with the corner-sharing octahedra). Other Fe^{3+}/Fe^{2+}-containing oxides such as CaFeO$_{2.5}$, LaFeO$_3$, BaFe$_2$O$_4$, and simple iron oxides (FeO, Fe$_3$O$_4$, and Fe$_2$O$_3$) and catalyst precursors of Fe(OAc)$_2$ and Ba(OAc) were almost inactive (entries 6–13). In the presence of Ba- and Mn-based perovskites (BaBO$_3$ (B = Mn, Co, and Ru) and AMnO$_3$ (A = Ca and Sr)), oxidation did not proceed (entries 14–18). The total yield of **2a**–**5a** reached 67% for the oxidation of **1a** under optimum conditions (entry 1 in Table 2), and the value was the second highest among the heterogeneous systems without additives (Table S1, ESI). In this case, the selectivity ratio of tertiary/secondary (3°/2°) C–H activation normalized to the number of C–H bonds was 29. This value is comparable to those of metal-catalyzed radical-mediated oxidation catalysts with O$_2$.[5,6,9c] Although BaFeO$_3$-based materials have been investigated for the catalytic combustion of CH$_4$ and CO, NO$_X$ decomposition, and electrochemical reaction,[10] their application to liquid-phase organic reactions has not been reported.

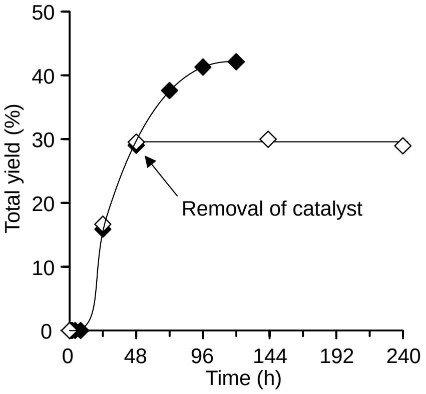
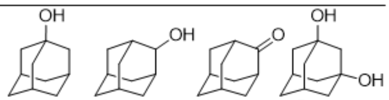
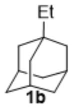
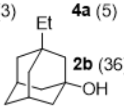
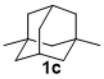
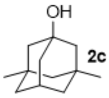
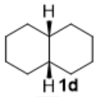
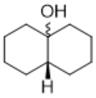
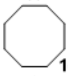
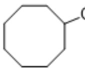
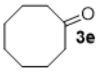
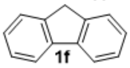
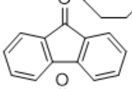
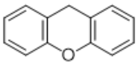
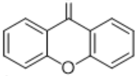
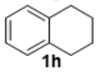
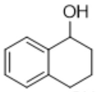
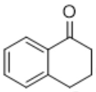
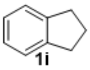
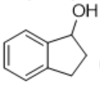
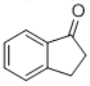


Fig. 2 Effect of BaFeO$_{3-\delta}$ removal on the oxidation of **1a**. ◆, with BaFeO$_{3-\delta}$; ◇, without BaFeO$_{3-\delta}$ as indicated by the arrow. Reaction conditions: BaFeO$_{3-\delta}$ (0.1 g), **1a** (0.5 mmol), PhCF$_3$ (1 mL), pO$_2$ (0.1 MPa), 363 K.

To verify whether the observed oxidation catalysis is due to solid BaFeO$_{3-\delta}$ or leached Fe or Ba species, the oxidation of **1a** was performed under the conditions described in Fig. 2. When BaFeO$_{3-\delta}$ was removed by hot filtration after 48 h, no further oxidation proceeded (Fig. 2). In addition, no leaching of Fe or Ba species in the filtrate was determined by ICP-AES analysis. These results suggest that the observed catalysis is heterogeneous. The BaFeO$_{3-\delta}$ used could readily be recovered from the reaction mixture by simple filtration. There was no significant difference in the XRD patterns of the fresh and recovered BaFeO$_3$ catalyst (Fig. S3, ESI).‡ The recovered catalyst could be reused twice without significant change in the total yield or the selectivity: e.g., 82% selectivity to **2a** at 30% total yield (fresh), 79% selectivity to **2a** at 30% total yield (reuse 1st), and 77% selectivity to **2a** at 31% total yield (reuse 2nd) (entries 2–4 in Table 1),§ which indicates the durability of $BaFeO_{3-\delta}$.

Table 2 Oxidation of various substrates catalyzed by $BaFeO_{3-\delta}$ with O_2[a]

Entry	Substrate	Time (h)	Product (Yield (%))
1	 **1a**	96	 **2a** (48) **3a** (3) **4a** (5) **5a** (11)
2[b]	 **1b**	72	 **2b** (36)
3[c]	 **1c**	96	 **2c** (36)
4[c]	 **1d**	96	 **2d** (14) *cis*/*trans* = 26/74
5	 **1e**	72	 **2e** (3)  **3e** (11)
6[d]	 **1f**	96	 **2f** (59)
7	 **1g**	96	 **2g** (95)
8	 **1h**	30	 **2h** (12)  **3h** (39)
9	 **1i**	30	 **2i** (6)  **3i** (37)

[a] Reaction conditions: $BaFeO_{3-\delta}$ (0.2 g), **1** (1.0 mmol), $PhCF_3$ (1 mL), pO_2 (0.1 MPa), 363 K. [b] Ketones (6% yield). [c] Ketones (5% yield). [d] *n*-Octane (1 mL), 353 K.

The present system could be applied to the oxidation of various hydrocarbon substrates with O_2 as the sole oxidant (Table 2). The tertiary C–H bonds of **1a**, as well as its derivatives (1-ethyladamantane (**1b**) and 1,3-dimethyladamantane (**1c**)), were mainly oxidized, and the yields of the corresponding alcohols were 42% and 31%, respectively (entries 2 and 3). In the case of *cis*-decalin (**1d**), the stereoisomeric mixture of 9-decalol (**2e**, *cis*/*trans* = 26/74) was obtained (entry 4), which indicates the formation and the substantial inversion of the 9-decalyl radical intermediate in this reaction.[2b,3a,9c,13] The secondary C–H bonds of cyclooctane (**1e**) was also oxidized to the corresponding alcohol and ketone (**2e** and **3e**), while the yields were low (entry 5). This catalyst system also efficiently catalyzed the oxidation of alkylarenes. Fluorene (**1f**) and xanthene (**1g**) with two benzene rings were oxidized to the corresponding ketones in 59% and 95% yields, respectively (entries 6 and 7). In the case of tetralin (**1h**) and indan (**1i**) with one benzene ring, the corresponding oxygenated products (alcohols and ketones) were obtained (entries 8 and 9).

The $BaFeO_{3-\delta}$-catalyzed oxidation of **1a** under the conditions of entry 1 in Table 1 proceeded with an induction period and was completely suppressed by the presence of a radical scavenger (2,6-di-*tert*-butyl-4-methylphenol, 1 equiv. with respect to **1a**). The oxidation of **1a** did not proceed under an Ar atmosphere (Fig. S4, ESI), which indicates that $BaFeO_{3-\delta}$ did not act as a stoichiometric oxidant but as a catalyst. A good correlation between the logarithm of the reaction rate normalized on a per hydrogen basis ($\log R_0'$) for the oxidation of alkylarenes and C–H bond dissociation energy (BDE) was observed (Fig. 3).[14] A kinetic isotope effect (k_H/k_D) value of 5.0 was observed for the oxidation of **1f** and **1f**-d_{10} at 363 K. All these data including the catalyst effect, 3°/2° value for **1a**, and the stereospecificity for **2d** indicate that the present oxidation proceeds via a radical-mediated oxidation mechanism and that H-abstraction (likely by high valent iron oxo species in $BaFeO_{3-\delta}$) is the rate-determining step (Fig. S5). The high ^{18}O content (96–97 %) in **2a** (^{18}O-labeled **2a**/total **2a**) was observed from the initial stage of the $BaFeO_{3-\delta}$-catalyzed oxidation of **1a** at 0.1 MPa of $^{18}O_2$ (97 atom%, Fig. S6),§§ supporting the reaction mechanism.

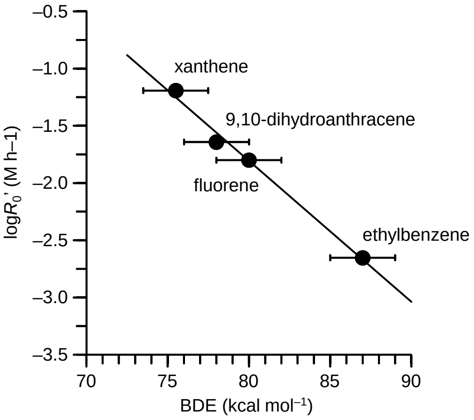


Fig. 3 Plot of $\log R_0'$ versus BDE for the oxidation of alkylarenes. Reaction conditions: $BaFeO_{3-\delta}$ (0.1 g), substrate (1 mmol), $PhCF_3$ (1 mL), pO_2 (0.1 MPa), 363 K.

In conclusion, hexagonal iron-based perovskite $BaFeO_{3-\delta}$ synthesized by the amino acid-aided method could heterogeneously catalyze the aerobic oxidation of various alkanes and alkylarenes without the need for any additives. This work was supported by the PRESTO program (No. JPMJPR15S3) of the Japan Science and Technology Agency (JST).

Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ The slight peak shifts due to the increase of oxygen vacancies were observed.

§ The total turnover number (TON) was estimated to be 124 based on surface Fe (see details in ESI). For oxygenation of **1a** using 0.1 MPa of O_2 without any additives, the value is higher than or comparable to those (25–162) of homogeneous iron-based catalysts,[12] but lower than those (247–3300) of Ru- and V-based homogeneous and heterogeneous catalysts.[5,6]

§§ The gradual decrease of the ^{18}O contents in **4a** is probably caused by the different reaction mechanism for oxidation of **3a** into **4a** and/or exchange with ^{16}O oxygen (lattice, water, etc.).

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