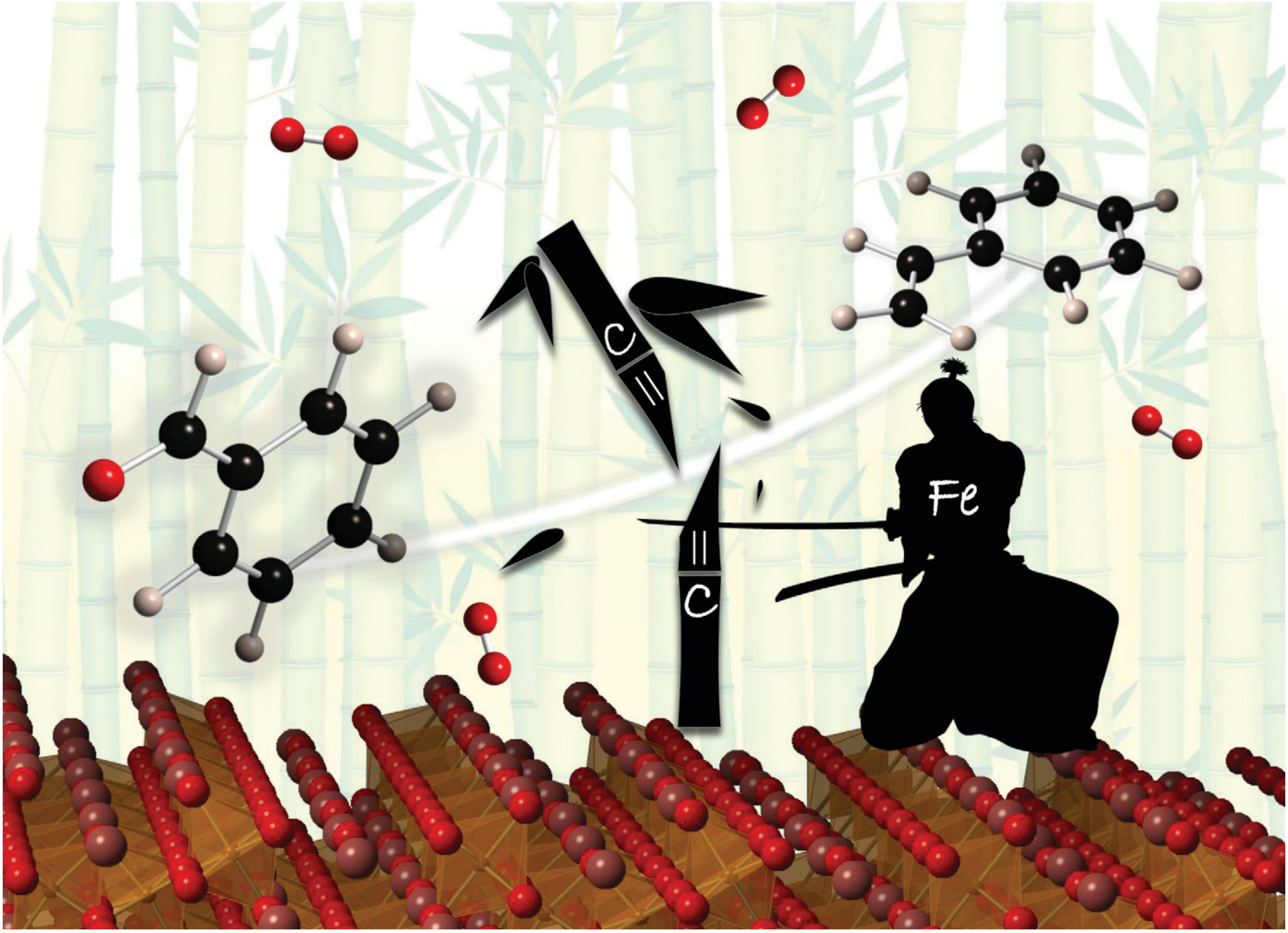

Showcasing research from Professor Keigo Kamata's laboratory, Laboratory for Materials and Structures, Tokyo Institute of Technology, Yokohama, Japan.

Aerobic oxidative C=C bond cleavage of aromatic alkenes by a high valency iron-containing perovskite catalyst

High valency iron-containing perovskite BaFeO$_{3-\delta}$ could efficiently promote the oxidative C=C bond cleavage of various aromatic alkenes to carbonyl compounds using only O$_2$, without the need for any additives. The activation of C=C bond to a radical species by BaFeO$_{3-\delta}$ is a key step for the reaction.

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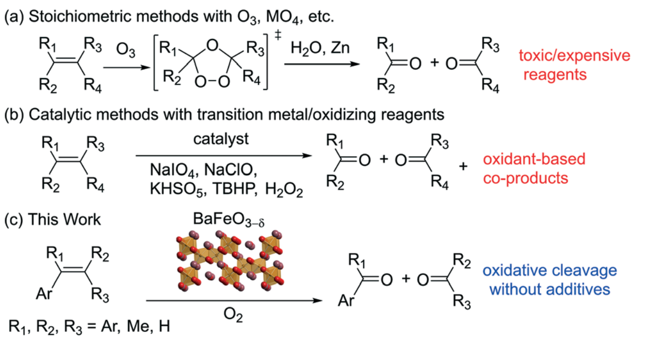
Aerobic oxidative C=C bond cleavage of aromatic alkenes by a high valency iron-containing perovskite catalyst†

Satomi Shibata, Keigo Kamata * and Michikazu Hara *

High valency iron-containing perovskite catalyst $BaFeO_{3-\delta}$ could efficiently promote the additive-free oxidative C=C bond cleavage of various aromatic alkenes to the corresponding aldehydes or ketones using O_2 as the sole oxidant. This system was applicable to the gram-scale oxidation of 1,1-diphenylethylene, in which 2.71 g (75% yield) of the analytically pure ketone could be isolated.

The oxidative C=C bond cleavage of alkenes into the corresponding carbonyl compounds is an important reaction in both laboratories and chemical industry because aldehydes and ketones are useful synthetic intermediates for the production of perfumes, dyes, and pharmaceuticals.[1–3] Stoichiometric oxidants such as O_3, *m*-chloroperbenzoic acid, $KMnO_4$, CrO_2Cl_2, RuO_2, and OsO_4 are typically utilized to accomplish efficient oxidative C=C bond cleavage (Scheme 1(a)),[2,4] although these methods have disadvantages such as a requirement for specific equipment due to the instability of O_3 and the use of excess toxic and expensive reagents and/or solvents. To address these issues, research has been conducted on catalytic oxidative C=C bond cleavage reactions based on second- or third-row transition metal salts and complexes (Ru, W, Os, In, Pd, Mo, Re, *etc.*) with $NaIO_4$, NaClO, $KHSO_5$, *tert*-butyl hydroperoxide (TBHP), and H_2O_2 as oxidants and/or radical initiators (Scheme 1(b)); (ref. 2, 5, 6) however, most of these reactions are homogeneous, and have some problems in the separation and recyclability of expensive catalysts from reaction mixtures that include co-products of the oxidants. In contrast, the development of effective heterogeneous catalysts based on naturally abundant and easily available first-row transition metals with molecular oxygen (O_2) is a strongly desired and challenging research subject. Although heterogeneous catalyst systems based on first-row transition metals such as Cu, Ti, Mn, Co, Fe, and V have been reported for aerobic C=C bond cleavage, there is plenty of room for improvement with respect to the activity, selectivity, substrate scope, and need for additives (Table S1, ESI†).

Perovskite oxides with the general formula ABO_3 are being actively explored for industrial applications, such as piezoelectric, (multi)ferroelectric, magnetic, and superconducting materials.[7,8] Moreover, perovskite oxides and related materials have received significant attention as substitutes for noble metal catalysts because of their unique stability, compositional and structural varieties, and controllable physicochemical properties.[9,10] However, catalysis over multicomponent perovskites with corner-sharing BO_6 octahedra has mainly been investigated for gas-phase reactions ($CO/CH_4/NO$ oxidation),[10,11] and reports on liquid-phase organic reactions are limited. Therefore, we have focused on the liquid-phase catalysis of hexagonal perovskites with unique face-sharing octahedral units based on high valency metal species. During the course of our investigation on crystalline first-row metal oxide catalysts,[12–17] we have successfully synthesized various hexagonal perovskite nanoparticle catalysts for the liquid phase selective oxidation of various organic substrates with O_2 as the sole oxidant.[15–17] In particular, high valency iron-



Scheme 1 Various oxidants for the oxidative C=C bond cleavage of alkenes.

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containing $BaFeO_{3-\delta}$ was found to act as an efficient heterogeneous catalyst for the aerobic oxidation of alkanes to the corresponding alcohols and ketones, in sharp contrast to Fe^{3+}/Fe^{2+} oxides.[17] Herein, we apply the superior oxidizing ability of a $BaFeO_{3-\delta}$ perovskite catalyst to aerobic oxidative C=C bond cleavage. In the presence of $BaFeO_{3-\delta}$ various types of aromatic alkenes are converted to the corresponding carbonyl compounds using only O_2, without the need for any additives. This study provides the first demonstration of an effective and reusable perovskite oxide catalyst for the oxidative C=C bond cleavage of alkenes.‡

Perovskite oxides including $BaFeO_{3-\delta}$ were synthesized by the sol–gel method using aspartic acid and/or malic acid and characterized by elemental analysis, powder X-ray diffraction (XRD), N_2 sorption, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) (Fig. S1, ESI†).[17] First, the oxidative cleavage of styrene (**1a**) in benzotrifluoride ($PhCF_3$) using O_2 (0.1 MPa) as the sole oxidant in the presence of various types of perovskite oxide and simple oxide catalysts was examined (Fig. 1). Three main products, namely, benzaldehyde (**2a**), styrene oxide (**3a**), and benzoic acid (**4a**), were formed. The reaction did not proceed in the absence of a catalyst under the reaction conditions employed. Among the catalysts tested, $BaFeO_{3-\delta}$ exhibited the highest catalytic activity and gave **2a** with 68% selectivity in 34% total yield. Another high valency iron-containing $SrFeO_3$ also efficiently catalyzed the oxidation of **1a**; however, the intrinsic activity per surface area of $SrFeO_3$ (20 $m^2\ g^{-1}$) was lower than that of $BaFeO_{3-\delta}$ (11 $m^2\ g^{-1}$). In addition, other Fe^{3+}/Fe^{2+}-containing perovskite and simple oxides such as $CaFeO_{2.5}$, $LaFeO_3$, Fe_2O_3, and Fe_3O_4 were much less effective for the present oxidation than $BaFeO_{3-\delta}$. These trends were also observed in the aerobic oxidation of adamantane with iron-containing oxides,[17] which indicates the high intrinsic oxidation activity of high valency iron-containing perovskite oxides. Other Mn-, Co-, Ni-, Cu-, and Ru-containing oxides ($SrMnO_3$, $BaMnO_3$, activated MnO_2, $BaCoO_3$, $LaCoO_3$, Co_3O_4, $LaNiO_3$, NiO, CuO, and $BaRuO_3$) were also inactive. In the presence of commercially-available Fe_3O_4 nanoparticles and montmorillonite K10, which have been reported to be active for the oxidative cleavage of **1a** to **2a**,[18,19] no formation of **2a** was observed under the reaction conditions employed.

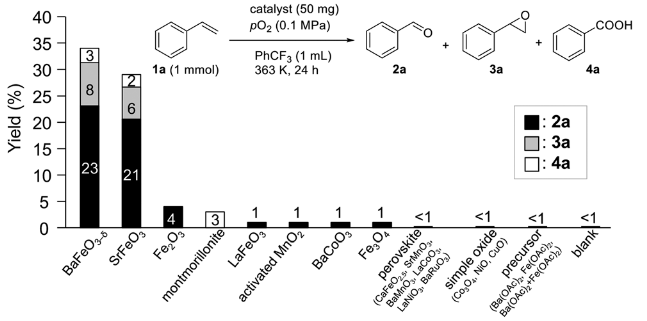


Fig. 1 Effect of catalysts on the C=C bond cleavage reaction of **1a** with O_2.

For the $BaFeO_{3-\delta}$-catalyzed oxidation of **1a**, the O_2 pressure had a strong effect on the selectivity to **2a** and **3a**, although the total yield remained unchanged (Fig. 2(a)). The selectivity to **2a** increased from 68% to 87% with an increase in the O_2 pressure from 0.1 MPa to 1.0 MPa (Fig. S2, ESI†), which indicates the concentration of O_2 is critical to the selective C=C bond cleavage of **1a** to **2a**. The $BaFeO_{3-\delta}$-catalyzed oxidation systems could be applied to the solvent-free oxidative cleavage of **1a** to give **2a** in 29% yield (Fig. 2(a)). In this case, the reaction rate per surface area was 1.2×10^{-3} μmol $h^{-1}\ m^{-2}$ and much higher than those (2.0×10^{-4}–4.8×10^{-6} μmol $h^{-1}\ m^{-2}$) of previously reported catalysts (Table S1†). The total yield could also be increased to 71% by using *tert*-amyl alcohol (*t*-AmOH) as a solvent (Fig. 2(a)).

After the oxidation of **1a** was completed under the conditions shown in Fig. 1, the used $BaFeO_{3-\delta}$ catalyst could be easily recovered from the reaction mixture by simple filtration. No significant leaching of Fe and Ba species into the filtrate was confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis (Fe 0.04% and Ba 0.2% with respect to the fresh $BaFeO_{3-\delta}$). In addition, catalyst precursors ($Fe(OAc)_2$, $Ba(OAc)_2$, and a mixture of $Fe(OAc)_2$ and $Ba(OAc)_2$) were almost inactive for the oxidative C=C bond cleavage of **1a** to **2a** (Fig. 1), which suggests that there was no contribution to the observed catalysis from iron

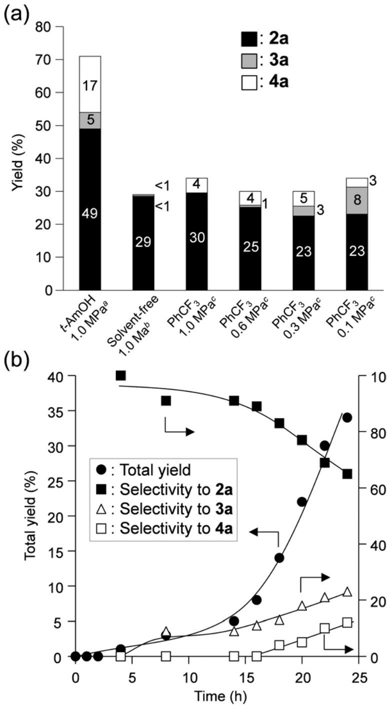
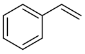
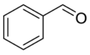
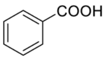
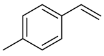
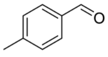
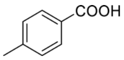
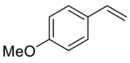
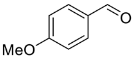
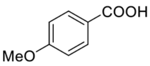
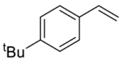
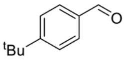
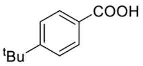
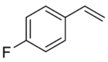
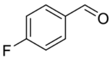
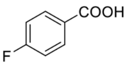
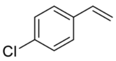
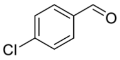
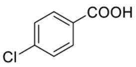
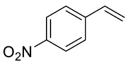
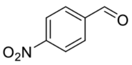
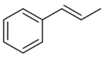
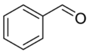
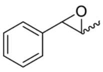
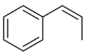
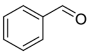
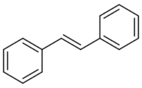
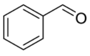
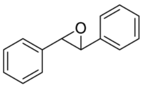
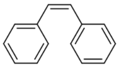
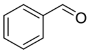
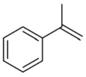
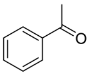
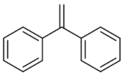
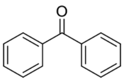


Fig. 2 (a) Effect of O_2 pressure and solvent on the C=C bond cleavage reaction of **1a** with O_2 catalyzed by $BaFeO_{3-\delta}$. [a]Catalyst (25 mg), **1a** (1 mmol), *t*-AmOH (1 mL), pO_2 (1.0 MPa), 363 K, 12 h. [b]Catalyst (50 mg), **1a** (8.8 mmol), pO_2 (1.0 MPa), 363 K, 4 h. [c]Catalyst (50 mg), **1a** (1 mmol), $PhCF_3$ (1 mL), pO_2 (0.1–1.0 MPa), 363 K, 24 h. (b) Time course for the C=C bond cleavage reaction of **1a** with O_2 catalyzed by $BaFeO_{3-\delta}$. The reaction conditions are the same as those of Fig. 1.

or barium species leached into the reaction solution. There was no significant difference in the XRD patterns and XPS spectra between the fresh and recovered catalysts, although the XRD peaks were slightly shifted, possibly due to the formation of oxygen-deficient $BaFeO_{3-\delta}$ (Fig. S3, ESI†). The recovered $BaFeO_{3-\delta}$ catalyst could then be reused without a significant change in the total yield or selectivity to each product: selectivity (**1a**/**2a**/**3a** = 68%/24%/8%) at 34% total yield (fresh), selectivity (**1a**/**2a**/**3a** = 65%/25%/10%) at 37% total yield (reused).

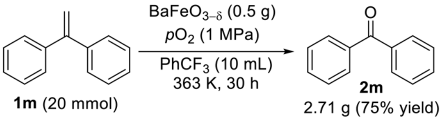
Furthermore, the $BaFeO_{3-\delta}$-catalyzed system was applicable to oxidative C=C bond cleavage reactions of various types of alkenes with O_2 (1.0 MPa) as the sole oxidant (Table 1). Styrenes with electron-donating *p*-substituents (**1b**–**1d**) were converted into the corresponding aldehydes (**2b**–**2d**) as main products, and the formation of their

Table 1 C=C bond cleavage reaction of various aromatic alkenes with O_2 catalyzed by $BaFeO_{3-\delta}$[a]

Entry	Substrate	Time (h)	Product (yield (%))	
1	 **1a**	24	 **2a** (30)	 **4a** (4)
2	 **1b**	12	 **2b** (26)	 **4b** (14)
3[b]	 **1c**	6	 **2c** (30)	 **4c** (1)
4[c]	 **1d**	24	 **2d** (27)	 **4d** (10)
5	 **1e**	24	 **2e** (34)	 **4e** (17)
6	 **1f**	24	 **2f** (47)	 **4f** (6)
7[d]	 **1g**	96	 **2g** (32)	
8	 **1h**	12	 **2a** (30)	 **3h** (4)
9	 **1i**	24	 **2a** (4)	
10	 **1j**	24	 **2a** (12)	 **3j** (4)
11	 **1k**	24	 **2a** (1)	
12	 **1l**	24	 **2l** (75)	
13[e]	 **1m**	30	 **2m** (70)	

[a] Reaction conditions: catalyst (50 mg), substrate (0.5 mmol), solvent (1 mL), pO_2 (1 MPa), 363 K, 24 h. [b] Epoxide (1% yield). [c] Epoxide (2% yield). [d] 373 K. [e] Catalyst (25 mg).

carboxylic acids (**4b** and **4d**) was observed in alkyl substituent-containing styrenes (entries 2–4). Oxidative cleavage of *para*-halogenated 4-fluorostyrene (**1e**) and 4-chlorostyrene (**1f**) also proceeded to afford the corresponding aldehydes (**2e** and **2f**) and carboxylic acids (**4e** and **4f**) (entries 5 and 6). On the other hand, *p*-nitrostyrene (**1g**) with a strong electron-withdrawing group was also oxidized to the corresponding aldehyde, although a longer reaction time was required (entry 7). It has been reported for Pt@Fe_2O_3 and $Pd(OAc)_2$ systems that substrates with electron-withdrawing substituents are less active for the oxidative cleavage of styrene derivatives than those with electron-donating substituents.[20,21] Not only monosubstituted styrenes, but also disubstituted styrenes were also oxidized to the corresponding aldehydes and ketones. In the case of 1,2-disubstituted β-methylstyrenes, the *trans*-isomer (**1h**) was more reactive than the *cis*-isomer (**1i**), and the yields of **2a** were 30% and 4% from **1h** and **1i**, respectively (entries 8 and 9). Similar stereospecificity for more electron-rich but sterically-hindered *trans*-stilbene (**1j**) and *cis*-stilbene (**1k**) was observed; however, the yields of **2a** were low in comparison with **1h** and **1i** (entries 10 and 11). It has also been reported that *trans*-isomers are more active than *cis*-isomers in radical-mediated reactions.[22] 1,1-Disubstited α-methylstyrene (**1l**) and 1,1-diphenylethylene (**1m**) were efficiently converted to acetophenone (**2l** and benzophenone (**2m**) in 75% and 70% yields, respectively (entries 12 and 13). In addition, the present system was applicable to the gram-scale reaction of **1m** and 2.71 g of analytically pure **2m** could be isolated (eqn (1)). The present system was not effective for the oxidative cleavage of aliphatic alkenes (1-octene, 2-octene, and allylbenzene), and such a limitation of scope is similar to previously reported systems based on first-row transition metals (Table S1†).[2]



(1)

H_2 temperature-programmed reduction (H_2-TPR) analysis was conducted to compare the intrinsic oxidation ability of $BaFeO_{3-\delta}$ to those of other iron-based perovskite oxides (Fig. S4, ESI†). The H_2 consumption per surface area below 573 K decreased in the order of $BaFeO_{3-\delta}$ (3.1×10^{-2} mmol m^{-2}) > $SrFeO_3$ (8.3×10^{-3} mmol m^{-2}) > $LaFeO_3$ (1.3×10^{-3} mmol m^{-2}) > $CaFeO_{2.5}$ (6.2×10^{-4} mmol m^{-2}), which is reasonable given the high reactivity of $BaFeO_{3-\delta}$. The time course for the oxidative cleavage of **1a** to **2a** with 0.1 MPa of O_2 catalyzed by $BaFeO_{3-\delta}$ is shown in Fig. 2(b). The reaction proceeded with an induction period, and only **2a** was observed at the initial stage of the reaction. The selectivity to **2a** then gradually decreased with an increase in the selectivity to **3a** and **4a**. This induction period completely disappeared upon the addition of a radical initiator (TBHP; 0.3 equiv. relative to **1a**, Fig. S5(a), ESI†), and the addition of a radical scavenger (2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) or 2,6-di-*tert*-butyl-*p*-cresol (BHT); 1 equiv. relative to **1a**) from the begging and in the middle of the reaction completely suppressed the progress of the reaction (Fig. S6, ESI†). A similar effect of a radical initiator and scavenger have been observed in the KSF montmorillonite systems, for which a radical-type mechanism has been proposed.[19] When $BaFeO_{3-\delta}$ was removed by hot filtration after 16 h, the reaction did not stop and proceeded in a similar way to that without the filtration step (Fig. S3, ESI†). Such phenomena were also reported for the aerobic oxidation of sulfides with MIL-101 catalysts *via* a radical-chain mechanism.[23] The reaction did not proceed at all under an Ar atmosphere (Fig. S5(b), ESI†), which suggests that $BaFeO_{3-\delta}$ does not act as a stochiometric oxidant, but as a catalyst for the present oxidation.

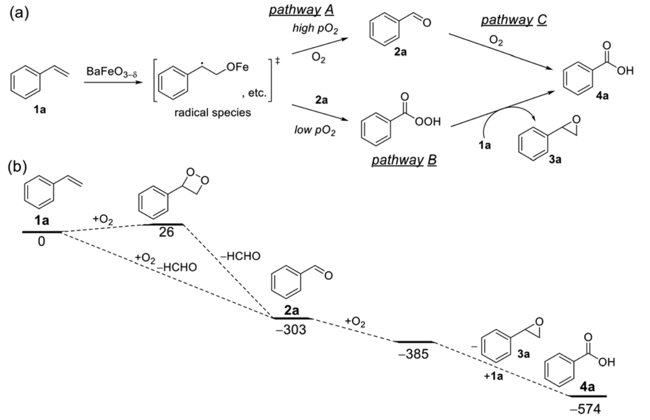


Fig. 3 (a) Proposed reaction pathways and (b) computational free energy diagrams of the aerobic oxidative cleavage reaction of **1a** and related reactions. Energies are shown in kJ mol^{-1}.

These results indicate the $BaFeO_{3-\delta}$-catalyzed oxidation of **1a** to **2a** likely involves a radical mechanism where $BaFeO_{3-\delta}$ would activate **1a** to form an active radical species such as a benzyl radical, which has been often suggested for Fe and Mn catalysts (Fig. 3(a)).[2] The selectivity to **3a** decreased with an increase in the O_2 pressure and the selectivity to **3a** and **4a** increased with a decrease in the selectivity to **2a**; therefore, **3a** would be formed by the aerobic epoxidation of **1a** with **2a** as a co-reductant.[24] At high O_2 pressure, radical species likely react with O_2 to form peroxy intermediates followed by rearrangement to **2a** (Fig. 3(a), pathway A). On the other hand, at low O_2 pressure radical species would attack hydrogen atom of **2a** followed by reaction with O_2 to form a peracid, which can promote the epoxidation of **1a** to **3a** with the co-production of **4a** (Fig. 3(a), pathway B). **4a** is also formed by the aerobic oxidation of **2a** (Fig. 3(a), pathway C). Density functional theory (DFT) calculations were performed to confirm the possible reaction pathways for the formation of **2a**, **3a**, and **4a** from **1a** and O_2 (Fig. 3(b)). The reaction of **1a** with O_2 to form an intermediate with a four-membered dioxyethane moiety was calculated to be endothermic by 26 kJ mol^{-1}; therefore, the pathway *via* this intermediate proposed for Co, Cu, and Cr catalysts would be thermodynamically unfavorable.[2,25,26] On the other hand, not only the C═C bond cleavage oxidation of **1a** with O_2 to **2a** and HCHO (exothermic by −303 kJ mol^{-1}), but also the epoxidation of **1a** to **3a** with peroxybenzoic acid from **2a** and O_2 (exothermic by −271 kJ mol^{-1}) were thermodynamically favourable, which is in good agreement with the proposed reaction pathways.

In conclusion, the high valency iron-based $BaFeO_{3-\delta}$ perovskite oxide could act as a heterogeneous catalyst for the aerobic oxidative C═C bond cleavage of various aromatic alkenes to the corresponding carbonyl compounds with O_2 as the sole oxidant.

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Author contributions

S. S. performed the experimental investigation and the data analysis with the help of K. K. S. S. and K. K. wrote the paper. The draft was reviewed by S. S., K. K., and M. H.

Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ While oxidative cleavage of styrene with O_2 has been reported for some heterogeneous iron-based catalytic systems, there are only two examples of all-inorganic heterogeneous catalysts such as KSF[19] montmorillonite and hollow Fe_3O_4 nanoshells.[18]

1 F. E. Kühn, R. W. Fischer, W. A. Herrmann and T. Weskamp, in *Transition Metals for Organic Synthesis*, ed. M. Beller and C. Bolm, Wiley-VCH, Weinheim, 2004, vol. 2, p. 427.
2 P. Spannring, P. C. A. Bruijnincx, B. M. Weckhuysen and R. J. M. Klein Gebbink, *Catal. Sci. Technol.*, 2014, **4**, 2182–2209.
3 G. Urgoitia, R. SanMartin, M. T. Herrero and E. Domínguez, *ACS Catal.*, 2017, **7**, 3050–3060.
4 R. Willand-Charnley, T. J. Fisher, B. M. Johnson and P. H. Dussault, *Org. Lett.*, 2012, **14**, 2242–2245.
5 P. Daw, R. Petakamsetty, A. Sarbajna, S. Laha, R. Ramapanicker and J. K. Bera, *J. Am. Chem. Soc.*, 2014, **136**, 13987–13990.
6 R. Noyori, M. Aoki and K. Sato, *Chem. Commun.*, 2003, 1977–1986.
7 Y. Zhu, W. Zhou and Z. Shao, *Small*, 2017, **13**, 1603793.
8 A. S. Bhalla, R. Guo and R. Roy, *Mater. Res. Innovations*, 2000, **4**, 3–26.
9 S. Royer, D. Duprez, F. Can, X. Courtois, C. Batiot-Dupeyrat, S. Laassiri and H. Alamdari, *Chem. Rev.*, 2014, **114**, 10292–10368.
10 K. Kamata, *Bull. Chem. Soc. Jpn.*, 2019, **92**, 133–151.
11 X. Zhang, C. Pei, X. Chang, S. Chen, R. Liu, Z.-J. Zhao, R. Mu and J. Gong, *J. Am. Chem. Soc.*, 2020, **142**, 11540–11549.
12 Y. Yamaguchi, R. Aono, E. Hayashi, K. Kamata and M. Hara, *ACS Appl. Mater. Interfaces*, 2020, **12**, 36004–36013.
13 E. Hayashi, Y. Yamaguchi, Y. Kita, K. Kamata and M. Hara, *Chem. Commun.*, 2020, **56**, 2095–2098.
14 E. Hayashi, Y. Yamaguchi, K. Kamata, N. Tsunoda, Y. Kumagai, F. Oba and M. Hara, *J. Am. Chem. Soc.*, 2019, **141**, 890–900.
15 K. Sugahara, K. Kamata, S. Muratsugu and M. Hara, *ACS Omega*, 2017, **2**, 1608–1616.
16 K. Kamata, K. Sugahara, Y. Kato, S. Muratsugu, Y. Kumagai, F. Oba and M. Hara, *ACS Appl. Mater. Interfaces*, 2018, **10**, 23792–23801.
17 S. Shibata, K. Sugahara, K. Kamata and M. Hara, *Chem. Commun.*, 2018, **54**, 6772–6775.
18 M. J. Rak, M. Lerro and A. Moores, *Chem. Commun.*, 2014, **50**, 12482–12485.
19 C. Schäfer, C. J. Ellstrom and B. Török, *Top. Catal.*, 2018, **61**, 643–651.
20 H. Hong, L. Hu, M. Li, J. Zheng, X. Sun, X. Lu, X. Cao, J. Lu and H. Gu, *Chem. – Eur. J.*, 2011, **17**, 8726–8730.
21 C. A. Hone, A. O'Kearney-McMullan, R. Munday and C. O. Kappe, *ChemCatChem*, 2017, **9**, 3298–3302.
22 P. E. Correa, G. Hardy and D. P. Riley, *J. Org. Chem.*, 1988, **53**, 1695–1702.
23 A. Gómez-Paricio, A. Santiago-Portillo, S. Navalón, P. Concepción, M. Alvaro and H. Garcia, *Green Chem.*, 2016, **18**, 508–515.
24 K. Kaneda, S. Haruna, T. Imanaka, M. Hamamoto, Y. Nishiyama and Y. Ishii, *Tetrahedron Lett.*, 1992, **33**, 6827–6830.
25 S. Rahman, C. Santra, R. Kumar, J. Bahadur, A. Sultana, R. Schweins, D. Sen, S. Maity, S. Mazumdar and B. Chowdhury, *Appl. Catal., A*, 2014, **482**, 61–68.
26 A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *ACS Catal.*, 2011, **1**, 836–840.