Amino Acid-Aided Synthesis of a Hexagonal SrMnO₃ Nanoperovskite Catalyst for Aerobic Oxidation

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ABSTRACT: A simple and efficient synthetic method for preparing high-surface-area perovskites was investigated by focusing on the importance of the formation of an amorphous precursor. Hexagonal SrMnO₃ with high surface area was successfully synthesized by simple calcination of the amorphous precursor prepared using aspartic acid and metal acetates instead of metal nitrates, without pH adjustment. The specific surface area reached up to ca. 50 m² g⁻¹, which is much larger than that for SrMnO₃ synthesized by previously reported methods. The catalytic activity for heterogeneous liquid-phase aerobic oxidation was significantly improved in comparison with the polymerized complex method, and the present catalytic system was applicable to the oxidation of various substrates.

INTRODUCTION

Perovskite-type oxides with the general formula ABO₃ are a class of mixed oxides that exhibit compositional and structural varieties. The versatility and accessibility of perovskite-type oxides have attracted significant interest in broad fields of piezoelectric, ferroelectric, (anti)ferromagnetic, catalytic, and semiconducting materials.¹ A number of methods for the synthesis of perovskites, such as solid-state, coprecipitation, sol–gel, hydrothermal, freeze/spray drying, and microwave methods, have been developed.² In particular, an increase of surface area is important for catalytic applications, and many efforts have been made to synthesize nanoperovskites with high surface areas. The sol–gel methods represented by the Pechini method and polymerized complex (PC) method are among the most studied and frequently used techniques for the preparation of nanoperovskites because these methods can accurately control the final composition and yield pure and homogeneous perovskites.³ However, these methods have some disadvantages in that they are (i) complicated procedures that include complex and polymer gel formation, pyrolysis to an amorphous precursor, and calcination and they require (ii) the use of toxic ethylene glycol and significant amounts of organic reagents and (iii) high-temperature calcination to remove carbones formed from the carbonate precursors, which results in low specific surface area. In addition, the combustion of carbon species elevates the temperature of the material itself and further sinters the material, which decreases the surface area. Therefore, the development of simple and efficient synthesis methods to obtain highly homogeneous and dispersed perovskite nanomaterials with high surface area is still strongly required and a challenging research subject.

We have recently reported that hexagonal SrMnO₃ (SMO-PC) synthesized by the PC method with a surface area of 25 m² g⁻¹ can act as an efficient reusable heterogeneous catalyst for the selective liquid-phase oxidation of various organic substrates with O₂.⁴ The synthesis of high-surface-area SMO can improve its catalytic activity. Teraoka and co-workers reported La₈₀Sr₂₀MO₃ (M = Mn and Co) with high surface area (37 and 20 m² g⁻¹, respectively) synthesized by a hydroxyl acid-aided method combined with pH adjustment of the starting solution using nitrate salts that are commonly used as metal sources in sol–gel synthesis.⁵ However, this method could not be applied to the synthesis of high-surface-area SMO because the precursor from the metal nitrates contained only crystalline Sr(NO₃)₂ and pure SMO was not formed by calcinations, even at 1223 K (details discussed later). In this study, we focus on the importance of the formation of an amorphous precursor during nanoperovskite synthesis and investigate an alternative, simple, and efficient synthetic route to prepare high-surface-area SMO by simple calcination of the amorphous precursor.
using amino acid (aspartic acid (AA)) and metal acetates instead of metal nitrates without pH adjustment. The structures of the amorphous precursor and nanoperoxvskite and the catalytic activity for liquid-phase aerobic oxidation are investigated. This study provides the first example of amino acid-aided synthesis of a perovskite nanocatalyst for liquid-phase aerobic oxidation.

■ RESULTS AND DISCUSSION

The synthesis of SMO with high surface area was attempted according to the hydroxy acid-aided method; however, this was unsuccessful (Figure 1). The powder X-ray diffraction (XRD) pattern for the precursor synthesized with metal nitrates and malic acid (HA precursor) exhibited only peaks assignable to Sr(NO₃)₂ (Figure 2a). Complex mixtures, including SMO, Sr₇Mn₄O₁₅, and unidentified phases, were formed by the calcination of HA precursor at 823−1223 K (Figure S1). The pH adjustment during precursor preparation has been reported to play an important role in the synthesis of pure La₀.₈Sr₀.₂MO₃ (M = Mn and Co); therefore, HA precursors were also synthesized by adjustment of the starting solution pH in the range of 3.0−9.0 with aqueous NH₃. However, pH adjustment was not effective for reducing the formation of Sr(NO₃)₂ in precursors and did not improve the purity of SMO (Figure 3). These results indicate that the presence of NO₃⁻ in the starting materials likely prevents (i) the formation of the amorphous precursor on the basis of metal malate species, which would be required to obtain single SMO nanomaterials and (ii) fast ligand exchange reaction between the metal nitrates and malic acid. Therefore, the metal sources were changed from nitrates to acetates due to the weaker acidity of acetic acid ($pK_a = 4.76$) than that of malic acid ($pK_{a1} = 3.4$), which is expected to accelerate the ligand exchange reactions. The aqueous solution containing acetates (Sr(OAc)₂·0.5H₂O and Mn(OAc)₂·4H₂O) and malic acid (1.5 equiv with respect to the total metal amount) was evaporated to dryness, and the resultant pale pink powder was dried at 463 K for 1 h to give the MA precursor. The precursor is completely amorphous, as confirmed by the lack of XRD peaks that would suggest a crystalline material (Figure 2b). The IR absorption spectrum of the MA precursor is shown in Figure 4c. Although the spectrum of precursor MA has carboxylate bands similar to that of the acetate starting materials (Sr(OAc)₂ and Mn(OAc)₂) (Figure S2), the observed bands are assignable to metal carboxylate salts because of the following results: (i) The carboxylate stretching band positions in the IR spectra of precursor MA (1401/1578 cm⁻¹) were different from those (1429/1563 and 1415/1560 cm⁻¹ for Sr(OAc)₂ and Mn(OAc)₂, respectively) of the starting materials. (ii) Other IR bands of MA were hardly observed in the IR spectra of precursor MA. (iii) The XRD patterns of the precursors did not show the peaks of the acetate starting materials. (iv) The electrospray ionization time-of-flight mass
spectroscopy (ESI-TOF-MS) spectrum of precursor MA in MeOH/H₂O (1/1, v/v) showed several peaks assignable to strontium and/or manganese malate salts (e.g., \( m/z = 489, 522, \) and 555 assignable to \([\text{Mn}_2(C_6H_5O_7)_2(C_4H_4O_6)]^-\), \([\text{SrMn}(C_6H_5O_7)_2(C_4H_4O_6)]^-\), and \([\text{Sr}_2(C_6H_5O_7)_2(C_4H_4O_6)]^-\), respectively) without the observation of the peaks of the acetate starting materials (Figures 4d and S3). These results suggest that the anion exchange reaction between acetate salts and carboxylic acid likely proceed. The bands at 1401 and 1578 cm⁻¹ are assignable to the symmetric and asymmetric stretching vibrations of carboxylate groups, respectively, and the \( \Delta (\nu_{\text{asym}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-)) \) value was 177 cm⁻¹, which suggests bridging bidentate bonding. These results suggest that precursor MA is an amorphous malate salt with the metal cations linked by malate anions, as shown in Figure 1. Next, the effect of various carboxylic acid additives (MA, AA, tartaric acid, oxalic acid, lactic acid, alanine, and glutamic acid (Figure 5)) on the precursor formation was investigated (3 equiv of total carboxylic group with respect to the total metal amount). XRD measurements indicated that only the AA, MA, and glutamic acid precursors are completely amorphous (Figure 6). Although small XRD peaks were observed for the precursors from citric acid, which is the most frequently used

![Figure 3. XRD patterns for the (a) HA precursor with pH adjustment to 9, (b) sample obtained by the calcination of the HA precursor (pH 9) at 823 K for 5 h, (c) HA precursor with pH adjustment to 7, (d) sample obtained by the calcination of the HA precursor (pH 7) at 823 K for 5 h, (e) HA precursor with pH adjustment to 4, (f) sample obtained by the calcination of the HA precursor (pH 4) at 823 K for 5 h, (g) HA precursor with pH adjustment to 3, (h) sample obtained by calcination of the HA precursor (pH 3) at 823 K for 5 h, (i) Sr(NO₃)₂ (JCPDS 01-087-0557), (j) SrMnO₃ (JCPDS 01-084-1612), and (k) SrCO₃ (JCPDS 01-078-4340).](image)

![Figure 4. FTIR spectra for the (a) AA and (c) MA precursors. ESI-TOF-MS spectra for the (b) AA precursor (upper, \( m/z = 530–545; \) solvent: MeOH/H₂O = 1/1, v/v) and calculated patterns for \([\text{SrMn}(C_6H_5NO_3)_2(C_4H_6NO_4)]^-\) (lower, \( m/z = 537\)), and for the (d) MA precursor (upper, \( m/z = 515–530; \) solvent: MeOH/H₂O = 1/1, v/v) and calculated patterns for \([\text{SrMn}(C_6H_5O_7)_2(C_6H_4O_4)]^-\) (lower, \( m/z = 522\)).](image)

![Figure 5. Various carboxylic acids used in this study.](image)
hydroxyl acid additive, the precursors prepared with tartaric, oxalic acids, and alanine or without carboxylic acids were not amorphous (Figure 6). Thermogravimetry-differential thermal analysis (TG-DTA) curves of the AA and MA precursors had exothermic peaks with weight loss at around 573–823 K, which suggests that both precursors decompose below 823 K (Figure 7). Therefore, the formation of single-phase SMO was confirmed by calcination of these precursors at 823 K for 5 h. Among the precursors tested, only AA and MA gave single-phase SMO (SMO-AA and SMO-MA, respectively) without the formation of SrCO₃ and manganese oxides (Figures 2 and 6). Although the precursor prepared from glutamic acid was amorphous, the XRD measurement revealed the formation of a mixture of SrMnO₃ and SrCO₃ after the calcination likely due to the higher carbon content in glutamic acid than AA. The calcination temperature of precursors AA and MA to obtain pure SMO was 823 K and lower than that (923 K) of precursor PC. The measurements of TG-DTA for the decomposition of amorphous precursors AA, MA, and PC revealed that a significant weight loss of each precursor was observed at 473–873 K (Figures 7 and S5). However, the percent weight losses of precursors AA and MA in the temperature range of 300–1073 K (70 and 66%, respectively) were smaller than that (75%) of precursor PC. The difference is likely due to the lower carbon contents of precursors AA and MA (28.36 and 28.00 wt %, respectively) than that of precursor PC (37.76 wt %). In separate experiments, it was confirmed by IR spectroscopy that SMO-AA and SMO-MA showed lower band intensities of surface carbonates than that of SMO-PC (Figure S6). All of these results suggest that the formation of an amorphous precursor by using dicarboxylic acid with a lower carbon content would be important to obtain pure SMO at a low calcination temperature. The specific surface areas of SMO-AA and SMO-MA calculated from a Brunauer–Emmett–Teller (BET) plot of the N₂ adsorption isotherm (77 K) were up to 47 and 42 m² g⁻¹, respectively. It should be noted that these
specific surface areas for SMO-AA and SMO-MA are much larger than those (2–25 m² g⁻¹) for SMOs synthesized by conventional methods such as the PC, acetate, sol–gel combustion, cellulose templating, and citrate methods (Table S1). In addition, synthesis using the AA and MA precursors yield pure SMO at lower calcination temperatures (by 100–400 K), possibly because the amorphous precursors with relatively low carbon contents are readily decomposed. The pH of the starting solution for the AA precursor (pH 4.23) was higher than those for the HA and MA precursors (pHs 1.64 and 3.70, respectively), which indicates that the use of metal acetates and AA containing NH₂ amino groups significantly accelerates the ligand exchange reaction without pH adjustment. Such a difference of the precursor formation processes is considered to influence the purity of SMO and the resultant surface areas. Scanning electron microscopy (SEM) images of SMO-AA and SMO-MA obtained at 823 K and SMO-PC obtained at 923 K are shown in Figure 8. The nanoparticles have spherical-like morphology and are estimated to be 10–40 nm. On the other hand, a sintering of SMO nanoparticles was observed in the case of SMO-PC. In addition, the size and morphology of SMO-AA and SMO-MA were quite different from those of the amorphous AA and MA precursors (Figure 8). Therefore, these nanostructures are constructed during low-temperature decomposition of the amorphous precursors with micrometer-order plate-like morphologies. The Raman spectra of SMO-AA and SMO-MA showed bands at 635/434 and 635/434 cm⁻¹, respectively (Figure S7). The band positions are similar to those for the previously reported SMO. These bands are assignable to the A₁g and E₁g modes, respectively, which are characteristic of the Mn₂O₉ moiety. The transmission electron microscopy (TEM) image of SMO-AA is shown in Figure 9. A particle size distribution of ca. 10–40 nm was observed, in reasonable agreement with that observed for the SEM measurement, that calculated from the (110) diffraction lines using Scherrer’s equation (d = 27 nm), and that calculated from the BET surface area and density, assuming the particles are spherical (d = 24 nm). The clear lattice fringes throughout the particles indicate crystallinity of the SMO particles. The distance between two fringes is ca. 0.28 nm, which is close to the d-spacing of (110) the plane of hexagonal SMO. These Raman and TEM results also support the formation of SMO-AA and SMO-MA nanoperovskites. The surface Mn valent state was investigated by X-ray photoelectron spectroscopy (XPS). There was no significant difference in the relative intensities of the Mn(III) and Mn(IV) species between SMO-AA (55/45) and SMO-MA (52/48) (Figure S8a). XPS spectra of O1s for SMO-AA and SMO-MA were also measured (Figure S8b). The broad peaks can be deconvoluted into four components (lattice oxygen, surface OH group, defective oxygen, and adsorbed H₂O). Quantitative analysis showed that the amount of defective oxygen, which is possibly related to the site for O₂ activation, in SMO-AA (18%) was larger than that in SMO-MA (13%). H₂ temperature-programmed reduction (H₂-TPR) and TG-DTA analyses were carried out to examine the reducibilities of SMO-AA and SMO-MA (Figures S9 and S10). The H₂-TPR profile of SMO-AA and SMO-MA showed that the catalysts were reduced starting from ca. 423 K and two broad peaks at 683/719 and 686/716 K were observed, respectively. These peaks are likely ascribed to the reduction of SrMnO₃ to SrMnO₂, Figure S10 shows the TG-DTA curves of SMO-AA and SMO-MA under H₂/N₂ and N₂ atmospheres. The significant weight losses were observed in the temperature range between 473 and 723 K under reductive conditions (H₂/N₂ = 1/9), whereas the TG curves under N₂ atmosphere remained almost unchanged. These results support that the reduction of SMO occurs due to the reaction with H₂ and that SMO is more thermally stable in N₂ atmosphere than typical
On the other hand, the reduction peak temperatures of SMO-PC were 720 and 758 K and higher than those of SMO-AA and SMO-MA.

To investigate the effectiveness of the present synthesis methods, the catalytic activities of SMO-AA, SMO-MA, and SMO-PC were compared for the oxygenation of fluorene (1a) to fluorenone (2a) at 333 K with molecular oxygen as the sole oxidant. The time course for each catalyst is shown in Figure 10. Oxidation did not proceed at all in the absence of a catalyst.

Catalytic oxidation with SMO proceeded sufficiently without an induction period caused by the formation of other active species. Among the catalysts tested, SMO-AA had the highest catalytic activity to afford 2a in 96% yield for 24 h. The reaction rate decreased in the order of SMO-AA (2.4 mM min⁻¹) > SMO-MA (1.1 mM min⁻¹) > SMO-PC (0.50 mM min⁻¹). There was no significant difference in the XPS of Mn 2p, H₂-TPR, and TG-DTA results between SMO-AA and SMO-MA, whereas the surface area and the amount of defective oxygen in SMO-AA were larger than those in SMO-MA. These results suggest that the activity differences between SMO-AA and SMO-MA are possibly due to the surface area and/or the number of active sites. Although several effective heterogeneous catalyst systems including Mn-based catalysts for the aerobic oxidation of 1a have been reported, they typically require high reaction temperatures, high O₂ pressures, or additives (radical initiator, strong base, etc.) to obtain 2a in high yield. Thus, the present system catalyzes the oxidation under mild reaction conditions; the reaction temperature (333 K) was much lower than that (368—443 K) for previously reported systems at 1 atm of O₂ without any additives (Table S2). The oxygenation of 1a was completed within 8 h by increasing the reaction temperature to 353 K (Figure 10e). To verify whether the observed catalysis is derived from solid SMO-AA or leached manganese and strontium species, the oxidation of 1a was performed under the condition described in Figure 10e. The catalyst, SMO-AA, was removed from the reaction mixture by hot filtration at approximately 50% conversion of 1a (at t = 30 min), and then the filtrate was heated again at 353 K. In this case, no further production of 2a was observed, suggesting that the observed catalysis for the present oxidation is truly heterogeneous (Figure 11). The used SMO-AA could be recovered from the reaction mixture by simple filtration.

Figure 10. Time courses for the oxidation of fluorene (1a) under O₂ atmosphere catalyzed by (a, e) SMO-AA, (b) SMO-MA, (c) SMO-PC, and (d) without catalyst. Reaction conditions: SMO (0.1 g), 1a (0.5 mmol), n-octane (2 mL), pO₂ (1 atm), reaction temperature (333 K for (a−d), 353 K for (e)).

Figure 11. Effect of removal of SMO-AA on the oxidation of 1a. ◆, without removal of SMO-AA; ◇, removal of SMO-AA as indicated by the arrow. Reaction conditions: SMO-AA (0.1 g), 1a (0.5 mmol), n-octane (2 mL), pO₂ (1 atm), 353 K.

To investigate the reaction mechanism, the oxidation of 1a with activated MnO₂ and SMO-AA was carried out under Ar atmosphere (Figure 12a). In the case of activated MnO₂, the yields of 2a were 64 and 41% for 8 h under O₂ and Ar atmospheres, respectively. These phenomena have been observed for MnO₂-catalyzed oxidation with O₂ and are explained by oxidation with oxygen supplied from the solid (Mars-van Krevelen Mechanism). On the other hand, the reactivity of SMO-AA under O₂ and Ar atmospheres was significantly different from that of activated MnO₂. The SMO-AA-catalyzed oxidation of 1a to 2a efficiently proceeded in the presence of O₂, whereas 2a was not obtained under Ar atmosphere and a small amount of only 9,9′-difluorene was formed for 27 h. Such a reactivity difference has been reported for the catalytic oxidation of alcohols with O₂ over SMO-PC, and the reaction mechanism involving O₂ activation (e.g., the formation of Mn-superoxo species confirmed by IR spectroscopy) has been proposed. Such a species would also play an important role in the present oxidation. The origin of the oxygen atoms incorporated in 2a was investigated with ¹⁸O-labeling experiments (Figure 12b). For the MnO₂-catalyzed oxidation of 1a, the ¹⁸O content in 2a (¹⁸O-labeled 2a/total 2a) increased with the reaction progress and was below 60% throughout the oxidation. The ¹⁸O content extrapolated at 2a yield = 0% was estimated to be almost zero, indicating the oxidation with ¹⁸O supplied from the solid in the initial stage and re-oxidation of the catalyst with ¹⁸O₂. On the other hand, high ¹⁸O contents (73—87%) were observed from the initial stage of the SMO-AA-catalyzed oxidation, suggesting that the oxygen in 2a mainly originates from gaseous O₂. These results support that the SMO-catalyzed oxidation of 1a likely involves the hydrogen atom abstraction by O₂-activated SMO.

The SMO-AA-catalyzed system was applicable to other substrates (see eq 1). The oxidation of xanthene (1b)
proceeded efficiently with SMO-AA (81% yield for 12 h) to afford the corresponding ketone (2b) in higher yield than the SMO-PC-catalyzed system (42% yield for 24 h). In the case of diphenylmethane (1c), the oxidation product (2c) could be obtained in 81% yield. The SMO-AA perovskite also efficiently catalyzed the oxidative dehydrogenation reaction of 1,2,3,4-tetrahydroisoquinoline (1d) to give 3,4-dihydroisoquinoline (2d) in 94% yield.

**CONCLUSIONS**

In conclusion, SMO with high surface area was successfully synthesized by the amino acid-aided method, which involves the formation of a completely amorphous precursor from AA and metal acetates instead of metal nitrates. The specific surface area of SMO-AA reached up to 47 m² g⁻¹, which is the highest value among the previously reported SMO samples. The catalytic activity of SMO for heterogeneous liquid-phase oxidation with O₂ was significantly improved and the SMO-AA-catalyzed system was applicable to the oxidation of various substrates. This method does not require complicated operations such as polymer gel formation and transformation processes. The simplicity and versatility of the amino acid-aided method, by which metal oxide nanomaterials including perovskites with various combinations of constituent metals can be easily synthesized, are expected to contribute to the development of efficient catalytic systems.

**EXPERIMENTAL SECTION**

**Materials.** Reagents such as Sr(OCOCH₃)₂·0.5H₂O (Kanto Chemical), Mn(OCOCH₃)₂·4H₂O (Kanto Chemical), d-, l-malic acid (Kanto Chemical), d- and l-aa (Kanto Chemical), S-lactic acid (Kanto Chemical), oxalic acid (Kanto Chemical), citric acid (Kanto Chemical), fluorene (TCI), 9-fluorenone (TCI), diphenylmethane (TCI), benzophenone (TCI), xanthene (TCI), xanthone (TCI), and 1,2,3,4-tetrahydroisoquinoline (TCI) were used as-received.

**Instruments.** XRD patterns were recorded on a diffractometer (Ultima IV, Rigaku; Cu Kα, λ = 1.5405 Å, 40 kV to 40 mA) equipped with a high-speed one-dimensional detector (D/teX Ultra, Rigaku). Diffraction data were collected in the range of 2θ = 10°–80° at 0.02° steps with a scan rate of 20°/min. Nitrogen adsorption–desorption isotherms were measured at 77 K with a surface area analyzer (Nova-4200e, Quantachrome). Prior to measurement, the samples were heated at 423 K for 1 h under vacuum to remove physisorbed water. The BET surface areas were estimated over the relative pressure (P/P₀) range of 0.05–0.30. IR spectra were obtained at a resolution of 4 cm⁻¹ using a spectrometer (FT/IR-6100, Jasco) equipped with an extended KBr beam splitting device and a triglycerine sulfate (TGS) detector. A total of 64 scans were averaged for each spectrum. The IR spectra of SMO were measured by KBr pellets containing ca. 0.5 wt % of SMO.
Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analyses were performed with a Shimadzu ICPS-8100 spectrometer. DTA and thermogravimetric (TG) measurements were performed with a differential thermal analyzer (TG8120; Rigaku). The morphology of the samples was examined using FE-SEM (S-5500; Hitachi). Raman spectra were recorded on a spectrometer (NRS-3200; Jasco) with excitation at 532 nm using a green laser. TEM images were taken on a JEOL JEM2100F-HK transmission electron microscope using an accelerating voltage of 200 kV. Cu grids were directly mixed with samples, and the Cu grids were collected and mounted on a stage. XPS analysis was performed with a JEOL JPCA-9010 MC using Mg Kα radiation (1253.6 eV) at 10 kV and 25 mA. Samples were pressed into the pellet and fixed on a double-stick 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 the Shirley function. The deconvoluted Mn 2p spectrum of SMO shows three peaks with binding energies of 641.8, 642.8, and 644.5 eV, which correspond to Mn(II), Mn(III), Mn(IV), and the shakeup peak, respectively. The deconvoluted O 1s spectrum of SMO shows four peaks with binding energies of 529.2, 530.8, 531.8, and 533.3 eV, which correspond to lattice oxygen, surface OH group, defective oxygen, and adsorbed H2O, respectively. The temperature-programmed reduction (H2-TPR) profiles were measured on BEL Japan BELCAT-A at a heating rate of 10 K min\(^{-1}\) from 303 to 1073 K under 5% H2/Ar flow (30 mL min\(^{-1}\)). Liquid-phase catalytic oxidation was performed with an organic synthesizer (ALHB-80 and DTC-200HZ-3000; Techno Applications) or a liquid phase organic synthesizer (CHEMIST PLAZA CP-1000; Shibata). NMR spectra were recorded on a Bruker Biospin Avance III spectrometer (1H, 400 MHz; 13C, 100 MHz) using 5 mm tubes. Chemical shifts (δ) were reported in parts per million downfield from SiMe4 (solvent, CDC\(_3\)). Gas chromatography (GC) analyses were performed on a Shimadzu GC-2025 equipped with a Stabilwax capillary column (internal diameter = 0.25 mm, length = 30 m) and a flame ionization detector. Mass spectra 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 SMO by Amino Acid-Aided Method.** Hexagonal SMO was synthesized as follows: Sr(OOCCH\(_3\))\(_2\)-0.5H\(_2\)O (5.64 g, 26.25 mmol), Mn(OOCCH\(_3\))\(_2\)-4H\(_2\)O (6.44 g, 26.25 mmol), and L-ALA (10.48 g, 78.75 mmol) were dissolved in water (250 mL). The colorless solution was evaporated to dryness at 343 K. The resulting pale pink powder was dried at 343 K in air to give a pale yellow powder (14.75 g), which is the MA precursor. Based on the elemental analysis and TG-DTA results, the formula for the MA precursor was estimated to be SrMn(C\(_4\)H\(_4\)O\(_8\))\(_2\)(C\(_4\)H\(_4\)O\(_4\))(CH\(_3\)COOH)\(_{0.5}\) on the basis of the elemental analysis and TG-DTA results. Elemental analysis: calcd (%) for SrMnO\(_3\): Sr 45.98, Mn 28.83; found: Sr 48.33, Mn 28.82.

**Synthesis of SMO by Malic Acid-Aided Method.** Perovskite SMO-AA was synthesized according to the procedure for SMO-AA and modified using malic acid instead of AA. The formula for the MA precursor was estimated to be SrMn(C\(_4\)H\(_4\)O\(_8\))(C\(_4\)H\(_4\)O\(_2\))(CH\(_3\)COOH)\(_{0.5}\) on the basis of the elemental analysis and TG-DTA results. Elemental analysis: calcd (%) for SrMnO\(_3\): Sr 45.98, Mn 28.83; found: Sr 48.33, Mn 28.82.

**Synthesis of SMO with Other Carboxylic Acids.** Various SMO samples with other carboxylic acids (S-lactic acid, oxalic acid, and citric acid) were synthesized using the procedure for SMO-AA modified by using carboxylic acid (3 equiv of the total carboxylic group with respect to the total metal amount) instead of AA.

**Procedure for Catalytic Oxidation.** The catalytic oxidation of alkylarenes was conducted in a 30 mL glass vessel containing a magnetic stirring bar. A typical procedure for catalytic oxidation was as follows: SMO (0.1 g), fluorene (0.5 mmol), n-octane (2 mL), O\(_2\) (1 atm), and an internal standard (naphthalene) were charged into the reaction vessel. The reaction solution was heated at 353 K and periodically analyzed using GC. The products are known and were identified by comparison of their \(^1\)H and \(^13\)C NMR signals with the literature data. After the reaction was completed, the catalyst was recovered by filtration. The recovered SMO-AA was washed with acetone (250 mL) and water (250 mL) and then calcined at 723 K for 2 h before recycling.

\(^{18}\)O-Labeling Experiments. \(^{18}\)O\(_2\) (>97% enriched) was obtained from Isotec. Before the reaction, the catalyst was evacuated at 423 K for 1 h and n-octane was degassed by freeze–pump–thaw cycling. The \(^{18}\)O-labeling experiment was carried out in a Schlenk flask containing a magnetic stir bar. Catalyst (0.1 g), fluorene (0.5 mmol), n-octane (2 mL), and an internal standard (naphthalene) were charged into the Schlenk flask under Ar atmosphere, followed by the evacuation and the introduction of 97% of \(^{18}\)O\(_2\) (1 atm). The reaction solution was heated at 333 K and periodically analyzed using GC and GC–MS. The \(^{18}\)O content in 2a was determined by using the ratio of the peak intensity at m/z = 182 to the sum of the peak intensities at m/z = 180 and 182.

### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00146.

Experimental details and analytical data (PDF)

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Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

A part of this work was supported by the Nagoya University Advanced Characterization Platform as a program of “Nano-technology Platform” and “Creation of Life Innovative Materials for Interdisciplinary and International Researcher Development” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. This work was supported by the PRESTO program of the Japan Science and Technology Agency (JST) and by a Kakenhi Grant-in-Aid (No. 15H04184) from the Japan Society for the Promotion of Science (JSPS).
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