

Dioxygen Activation by a Hexagonal SrMnO₃ Perovskite Catalyst for Aerobic Liquid-Phase Oxidation

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Heterogeneous catalysts, which allow a reductive activation of dioxygen (O_2) under mild reaction conditions, are promising candidates for highly efficient aerobic oxidation. An effective hexagonal SrMnO₃ (SMO) perovskite catalyst for liquid-phase selective oxidation with O_2 was successfully synthesized by the polymerized complex method. The activity of SMO for the aerobic oxidation of alcohols was higher than those of typical manganese oxide-based catalysts and was heterogeneous, so

Introduction

Selective oxidation of petroleum-based feedstocks into useful oxygenated products is an important reaction because these products are widely used as platform commodity and specialty chemicals.^[1] In contrast to traditional oxidation that uses superstoichiometric amounts of toxic organic/inorganic reagents, catalytic oxidation with environmentally friendly oxidants such as hydrogen peroxide (H₂O₂), and molecular oxygen (O₂) has received much attention because of the high content of active oxygen species with often only water as a by-product.^[1] Despite the advantages of using O₂ as the sole oxidant, it remains a challenge to effectively activate O₂ for selective liquid-phase oxidation. Active oxygen species bound on mono- and polynuclear metal species (M_n-O₂⁻, M_n-O₂²⁻, M_n-O²⁻) are formed by reductive activation of O2 with well-defined metal complexes and enzymes can oxygenate various substrates (e.g., alkanes, alkenes, arenes, alcohols, amines, and sulfides).^[2] However, heterogeneous systems that not only efficiently activate O₂ under mild conditions, but are also applicable to a wide range of substrates are scarcely known.^[3]

Manganese oxides have attracted growing interest because of their unique fundamental properties and wide applications in the fields of catalysis, magnetism, supercapacitors, and

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that the recovered catalyst could be reused without heat treatment under oxidative conditions while keeping its high catalytic performance. The reversible reaction on the surface Mn species on SMO with O_2 leads to the formation of Mn-superoxo species, which catalyze the selective oxidative transformation of various types of organic substrates into the desired oxygenated or dehydrogenated products.

batteries.^[4] Although various types of Mn-based solid catalysts have been developed as alternatives to the stoichiometric oxidant of MnO₂, these systems have disadvantages such as applicability only to limited substrates and deactivation during the recycling process (see the Supporting Information, Table S1).^[5,6] These problems have prompted us to examine the hexagonal Mn-based perovskite-type oxide SrMnO₃ (Figure 1 a) as a potential catalyst because Mn^{IV} species are thermodynamically favorable owing to the low enthalpy of oxidation of Mn^{III} to Mn^{IV} for hexagonal $SrMnO_{3-\delta}$ (-590 kJ per mole O₂) compared with those for the cubic structure (-293 kJ) and MnO₂ (from Mn₂O₃, -158 kJ).^[7] In addition, the face-sharing octahedra give rise to Mn₂O₉ dimers with a Mn-Mn distance close to that in metallic Mn and effective dinuclear oxidation catalysts including $[(tmtacn)_2 Mn_2(\mu-O)_3]^{2+}$ (tmtacn = (N, N', N''-trimethyl-1,4,7-triazacyclononane) and complexes relevant to biocatalysis.^[2,8] However, hexagonal SrMnO₃ catalysts have been investigated only for the gas-phase combustion of hydrocarbons and CO, and their low surface area $(2-10 \text{ m}^2\text{g}^{-1})$ often leads to a problem that limits the overall performance of the bulk catalyst.^[9] In this communication, we report that hexagonal SrMnO₃ (SMO) synthesized by the polymerized complex method can act as an effective heterogeneous catalyst for the aerobic oxidation of various types of substrates, including alcohols, amines, phenols, arenes, sulfides, and alkenes The SMO catalyst can be recovered by simple filtration and recycled without reactivation of the catalyst. This study provides the first example of O₂ activation by SMO and its catalytic application to liquid-phase selective oxidation.

Results and Discussion

The SMO catalyst was synthesized by the polymerized complex method (see details given in the Experimental Section).^[10] The powder X-ray diffraction (XRD) pattern for SMO is shown in





Figure 1. (a) Structure of hexagonal SrMnO₃. Pink, yellowish green, and red spheres represent the Mn, Sr, and O atoms, respectively. (b) XRD patterns for SMO (upper) and SrMnO₃ (lower, JCPDS 084 1612). (c) Raman spectrum and (d) SEM image of SMO.

Figure 1b, which is in good agreement with that for the reported hexagonal SrMnO₃ phase [space group P63/mmc].^[11] Impurity phases of other manganese oxides and SrCO₃ were not observed (Figure S1). The Raman spectrum of SMO showed bands at 634 and 433 cm⁻¹, assignable to the A_{1a} and E_{1a} modes, respectively, which are characteristic of a Mn₂O₉ moiety. The band positions are similar to those for the previously reported hexagonal SrMnO₃ (Figure 1 c).^[11] Elemental analysis of SMO using inductively coupled plasma atomic emission spectroscopy (ICP-AES) revealed that the molar ratio of Sr/Mn is approximately 1/1. The average oxidation state of Mn species in SMO was determined to be 3.9 ± 0.1 by iodometry. The specific surface area of SMO calculated from a Brunauer-Emmett-Teller (BET) plot of the N₂ adsorption isotherm (77 K) was up to $25 \text{ m}^2\text{g}^{-1}$, which was much larger than that of $SrMnO_3$ (2 m²g⁻¹) synthesized by the solid-phase method. A scanning electron microscopy (SEM) image of SMO is shown in Figure 1 d. The nanoparticles have a spherical-like morphology and the particle size was estimated to be 20-50 nm, which is in reasonable agreement with that calculated from the (110) diffraction lines using Scherrer's equation (d = 27 nm), and that calculated from the BET surface area (25 m^2g^{-1}) and density (5.4 g cm⁻³) assuming that the particles are spherical (d = 44 nm).

First, the oxidation of 1-phenylethanol (**1 a**) to acetophenone (**2 a**) under atmospheric pressure of O₂ (1 atm) at 323 K for 6 h was examined in the presence of various manganese catalysts (Table 1). The reaction did not proceed in the absence of a catalyst (Table 1, entry 15). Among the catalysts tested, SMO gave the highest yield of **2a** at 83% (entry 1). The oxidation proceeded quantitatively if the reaction time was prolonged to 8 h or if the reaction temperature was increased to 353 K (entries 2 and 3). The reaction proceeded even at room temperature without an induction period caused by the formation of other active oxygen species (entry 4). The catalytic activity of SMO was higher than those of activated $MnO_2^{[12]}$ and the

cryptomelane-type octahedral molecular sieve material (OMS-2),^[5a] whereas the surface area of SMO was much lower than those of activated MnO_2 ($122 m^2 g^{-1}$) and OMS-2 ($96 m^2 g^{-1}$) (entries 6 and 7). Other Mn^{2+} - and Mn^{3+} -containing manganese oxides (Mn_2O_3 , Mn_3O_4 , and MnO) and complexes ($Mn(acac)_3$, $Mn(NO_3)_2$ ·6H₂O, and $Mn_{12}O_{12}(OAc)_{16}(H_2O)_4$) were almost inactive under the present reaction conditions (entries 8–10 and 12–14). La $MnO_{3+\delta}$ showed much lower catalytic



[a] Reaction conditions: catalyst (0.1 g), **1a** (1 mmol), toluene (2 mL), O₂ (1 atm), 323 K, 6 h. Yield was determined by GC analysis. Yield of **2a** (%) calculated as **2a** (mol) per initial **1a** (mol) times 100. [b] 8 h. [c] 353 K, 1.5 h. [d] Room temperature (\approx 293 K), 96 h. [e] SrMnO₃ was synthesized by the solid-phase method. [f] Mn₂O₃ was synthesized by the polymerized complex method in a similar way to that of SMO without the addition of Sr(NO₃)₂. [g] Mn (525 µmol, i.e., equivalent to the Mn content in SMO (0.1 g)).



activity than that of SMO, which indicates that the Mn valence plays an important role in this oxidation system (entry 11).^[13]

Next, the scope of the SMO-catalyzed system for the oxidation of various alcohols with O_2 was investigated (Table 2).



[a] Reaction conditions: SMO (0.1 g), **1** (1 mmol), solvent (1 mL), O₂ (1 atm), 353 K, 1 h. Yield was determined by GC analysis. Values in parentheses are isolated yields. Yield of **2** (%) calculated as **2** (mol) per initial **1** (mol) times 100. [b] Toluene (8 mL). [c] SMO (0.2 g). [d] SMO (0.3 g).

Reactions of 1-phenyethanols with electron-donating and electron-withdrawing para-substituents (1b and 1c) proceeded to afford the corresponding ketones (2b and 2c) in high yields (Table 2, entries 2 and 3). Activated alcohols such as diphenylmethanol (1 d) and fluorenol (1 e) were also guantitatively oxidized to benzophenone (2d) and fluorenone (2e), respectively (entries 4 and 5). The oxidation of α -cyclopropylbenzyl alcohol (1 f) proceeded selectively without opening of the cyclopropyl ring (Table 2, entry 6). Not only secondary benzylic alcohols, but also primary benzylic and allylic alcohols gave good yields of the corresponding aldehydes (entries 7 and 8). The oxidation of cinnamyl alcohol (1 h) proceeded smoothly without influence on the C=C double bond (entry 8). Furthermore, the present system effectively catalyzed the oxidation of alcohols containing heteroatoms such as (2-hydroxymethyl)thiophene (1 i) and 2-pyridinemethanol (1 j) to the corresponding aldehydes in high yields (entries 9 and 10). The present system showed low catalytic activity for the oxidation of aliphatic alcohols such as 2- and 1-octanol (**1k** and **1l**, entries 11 and 12), and the present substrate scope of SMO was determined to be

similar to that of stoichiometric Mn reagents such as activated MnO₂.^[12]

To verify whether the observed catalysis is derived from solid SMO or leached manganese and strontium species, the oxidation of 1a was conducted under the conditions described in entry 1 of Table 1, and SMO was removed from the reaction mixture by hot filtration at approximately 40% conversion of 1 a (at t=3 h). The filtrate was then heated again at 323 K. In this case, no further production of 2a was observed, as shown in Figure 2. No leaching of manganese or strontium species in the filtrate was found by ICP-AES. In addition, a first-order dependence of the reaction rate on the amount of SMO was observed (Figure 3a). These results rule out any contribution to the observed catalysis from manganese or strontium species leached into the reaction solution, and the nature of the observed catalysis was confirmed as truly heterogeneous.^[14]

The used SMO catalyst could readily be recovered from the reaction mixture by simple filtration (>98% recovery). The recovered SMO catalyst could then be reused at least three times without any heat treatment under oxidative conditions while maintaining high catalytic performance for the same reaction: yield of 2a: \geq 99% (fresh), 99% (1st reuse), (2nd reuse), 99% and >99% (3rd reuse) (Figure 4).^[15, 16] On the other hand, the catalytic activity of activated MnO₂ gradually decreased as the recycle number increased (Supporting Information, Figure S2). There was no significant difference in XRD pattern, average oxidation state, and Raman spectrum between the fresh and three-times-reused SMO catalysts, which indicates the high durability of SMO (Figure S1 and S3).



Figure 2. Effect of SMO removal on the oxidation of **1 a** with O₂. Without removal of SMO (\blacklozenge), and where the arrow indicates the point of SMO removal of (\triangle). Reaction conditions: SMO (0.1 g), **1 a** (1 mmol), toluene (2 mL), O₂ (1 atm), 323 K.



Figure 3. Dependence of reaction rate on the concentration of (a) SMO, (b) **1 a**, and (c) pO_2 for epoxidation of **1 a** with O_2 catalyzed by SMO. Conditions: (a) SMO (0.025–0.10 g), **1 a** (0.47 M), toluene (1.0 mL), pO_2 (1.0 atm), 323 K; (b) SMO (0.050 g), **1 a** (0.12–1.27 M), toluene (1.0 mL), pO_2 (1.0 atm), 323 K; (c) SMO (0.05 g), **1 a** (0.47 M), toluene (1.0 mL), pO_2 (0.2–1.0 atm), 323 K.



Figure 4. Reaction profiles for the oxidation of 1 a with O₂ over fresh SMO and recovered SMO. Reaction conditions: catalyst (0.1 g), 1 a (1 mmol), toluene (2 mL), O₂ (1 atm), 323 K.

Notably, the reactivity of SMO under O_2 and Ar atmospheres is distinct from those of activated MnO_2 and OMS-2. The reaction profile for each catalyst for the oxidation of **1a** under O_2 (1 atm) and Ar (1 atm) atmospheres is shown in Figure 5a.



Figure 5. (a) Reaction profiles for the oxidation of **1 a** under O_2 or Ar atmosphere catalyzed by Mn oxides. Reaction conditions: catalyst (0.1 g), **1 a** (1 mmol), toluene (2 mL), O_2 or Ar (1 atm), 323 K. (b) Differential IR spectra of ¹⁶ O_2 - and ¹⁸ O_2 -adsorbed SMO.

The yield of 2a was up to 39% and 20% with activated MnO₂ and OMS-2, respectively, for 6 h under an Ar atmosphere. Such phenomena are also observed for manganese oxide based catalysts and are explained by substrate oxidation with oxygen supplied from the solid (Mars-van Krevelen mechanism).^[5a,d] On the other hand, the SMO-catalyzed oxidation of 1 a was significantly accelerated by the presence of O₂, and oxidation did not readily proceed under an Ar atmosphere, which indicates that O2 activation is most likely involved for the present SMOcatalyzed oxidation. Differential infrared (IR) spectra for O2-adsorbed SMO were measured to investigate the surface oxygen species (Figure 5b). Upon exposure of SMO powder (dehydrated at 573 K) to an ¹⁶O₂ atmosphere (55 Torr) at room temperature, a new band appeared at 1152 cm^{-1} and the band position is in the range of v(O-O) for typical metal-superoxo species (1200–1100 cm⁻¹).^[17] If the O₂-adsorbed SMO was evacuated at room temperature, the band completely disappeared. The IR spectrum of ¹⁸O₂-adsorbed SMO showed a new band at 1086 cm⁻¹, and the shift of 66 cm⁻¹ was consistent with the theoretical shift (66 cm⁻¹). However, the formation of such a superoxo species was not observed for activated MnO₂ and OMS-2 under the same conditions. These results suggest the reversible formation of a Mn-superoxo species, which likely

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Scheme 1. Proposed reaction mechanism for the oxidation of alcohols with O₂ catalyzed by SMO.

plays an important role in the present oxidation. The isolation of Mn–superoxo molecular complexes^[18] and computational studies on O₂ reduction over La_{1-x}Sr_xMnO₃^[19] have been reported; however, the detection of O₂ reduction over SMO and its catalytic application have never been reported.^[20]

We propose a possible mechanism for the SMO-catalyzed oxidation of alcohols in Scheme 1. The reversible reaction of surface Mn species on SMO with O_2 initially proceeds to form a Mn-superoxo species. The active oxygen species then reacts with an adsorbed alcohol to form the corresponding

ketone. Furthermore, the kinetics for the oxidation of 1 a with O₂ catalyzed by SMO were investigated. A first-order dependence of the reaction rate on the amount of SMO was observed (see Figure 3 a), and the reaction rate was almost independent of the concentration of 1a (Figure 3b). The dependence of the reaction rate on the O₂ pressure showed saturation kinetics (Figure 3 c). This dependence is explained by the Langmuir-Hinshelwood mechanism through the non-dissociative adsorption of O₂ and alcohol without mutual displacement. A kinetic isotope effect $(k_{\rm H}/k_{\rm D})$ of 3.7 ± 0.1 for the SMO-catalyzed oxidation of 1a and 1-phenylethan-1- d_1 -ol (1a-d) at 323 K indicates that C-H bond cleavage is the ratelimiting step. All of these results support the proposed mechanism.[5b]

The SMO-catalyzed aerobic oxidation of various substrates was investigated to evaluate the effectiveness of the present O_2 -activation system (Table 3). Oxidative homocoupling reactions of amines and phenols also proceeded efficiently. Benzylamine (**3 a**) was selectively converted into *N*-benzylidenebenzylamine (**4a**) in 87% yield (Table 3, entry 1). On the other hand, activated MnO₂ gave **4 a** and benzonitrile in 33% and 51% yields, respectively, under the same conditions.^[21] The coupling reaction of 2,6-di-*tert*-bu-tylphenol (**3 b**) proceeded quantitatively under mild reaction conditions (entry 2). Aerobic oxygenation or oxidative dehydrogenation of alkylarenes such as fluorene (**3 c**), xanthene (**3 d**), and 9,10-dihydroanthracene (**3 e**) also proceeded efficiently to give the corresponding oxygenated or dehydrogenated products (entries 3–5). Thioanisole (**3 f**) and cyclooctene (**3 g**) were selectively converted into the corresponding sulfoxide (**4 f**) and epoxide (**4 g**) in the presence of isobutyraldehyde at ambient temperature in a similar manner to that for a Mn–superoxo complex,^[18b] whereas electrophilic oxidation did not proceed without the additive.



[a] Reaction conditions: SMO (0.02 g for entry 2 0.1 g for entries 1, 6, and 7, and 0.2 g for entries 3–5); **3** (1 mmol); solvent (toluene, 2 mL, for entries 1, 2, 6, and 7, toluene, 4 mL, for entry 5, and *n*-octane, 4 mL, for entries 3 and 4); O_2 (1 atm); reaction temperature (300 K for entries 6 and 7, 353 K for entries 1–4, and 383 K for entry 5). Yield was determined by GC analysis. [b] Anthraquinone (12% yield). [c] Isobutyraldehyde (3 mmol).



Conclusions

Hexagonal SrMnO₃ (SMO) could activate O₂ to form a superoxo species, which resulted in an efficient heterogeneous catalyst for the selective liquid-phase oxidation of various types of organic substrates. This study shows the importance of developing heterogeneous catalysts that can activate O₂ under mild conditions, and further elucidation of the catalytic mechanism is now in progress.

Experimental Section

Materials

Toluene (Kanto Chemical) was pretreated with molecular sieves (3 A) that were evacuated at 250 °C for 3 h.^[22] Substrates and products (TCI, Kanto Chemical, and Aldrich) were used as-received, and **2g** and **3a** were purified according to reported procedures.^[23] Oxygen-¹⁸O₂ (97 atom %) was purchased from ISOTEC. Reagents such as Sr(NO₃)₂ (Kanto Chemical), Mn(NO₃)₂·6H₂O (Kanto Chemical), citric acid (Kanto Chemical), ethylene glycol (Kanto Chemical), NaBD₄ (ACROS), and CDCl₃ (ACROS) were used as-received. OMS-2 and Mn₁₂O₁₂(OAc)₁₆(H₂O)₄ were synthesized and characterized according to procedures given in the literature.^[24] 1-Deutero-1-phenylethanol was synthesized by the reaction of acetophenone with NaBD₄.^[25]

Instruments

XRD patterns were recorded on a diffractometer (Ultima IV, Rigaku; Cu_{Kar} $\lambda = 1.5405$ Å, 40 kV-40 mA) equipped with a high-speed 1-dimensional detector (D/teX Ultra, Rigaku). Diffraction data were collected in the range of $2\theta = 10-80^{\circ}$ 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). 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. FTIR spectra were obtained at a resolution of 4 cm⁻¹ by using a spectrometer (FT/IR-6100, Jasco) equipped with an extended KBr beam splitting device and a mercury cadmium telluride (MCT) detector. A total of 256 scans were averaged for each spectrum. Raman spectra were recorded on a spectrometer (NRS-3200, Jasco) with excitation at 532 nm using a green laser. ICP-AES analyses were performed with a Shimadzu ICPS-8100 spectrometer. Differential thermal analysis (DTA) and thermogravimetric (TG) measurements were performed with a differential thermal analyzer (TG8120, Rigaku). Iodometric titration was performed with a Mettler Toledo Easy Pro Titrator System. SMO (\approx 10 mg) was added to a mixture of 0.5 M HCl aq. (12 mL) and 2 M KI ag. (5 mL), and the resulting solution was titrated with 0.01 M Na₂S₃O₃ aq.^[26] X-ray photoelectron spectroscopy (XPS) analysis was performed with JEOL JPC-9010 MC using Mg_{Ka} radiation (1253.6 eV) at 10 kV and 25 mA. Samples were pressed into pellet and fixed on a double-stick carbon tape. The binding energies were calibrated using the C1s 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 deconvoluted Mn2p spectrum of SMO shows three peaks with binding energies of 641.9, 642.9, and 644.6 eV, which corresponds to Mn^{III}, Mn^{IV}, and shakeup peak, respectively.^[27] The morphology of the samples was examined using SEM (S-5200, Hitachi). 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). Distillation of substrates or drying of samples were performed with a glass oven (B-585 Kugelrohr, BUCHI). The isolation of products was performed with a single channel automated flash chromatography system (Smart Flash EPCLC AI-580S, Yamazen). 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 ppm downfield from SiMe₄ (solvent, CDCI₃). GC analyses were performed on Shimadzu GC-2025 equipped with a Stabilwax capillary column (internal diameter = 0.25 mm, length = 30 m) and with a flame ionization detector, or on a Shimadzu GC-17 A with an InertCap 17 capillary column (internal diameter = 0.25 mm, length = 30 m). Mass spectra were recorded on a spectrometer (GCMS-QP2010 SE, Shimadzu) equipped with an InertCap 17 MS capillary column (internal diameter = 0.25 mm, length = 30 m) at an ionization voltage of 70 eV.

Synthesis and characterization of SMO

Hexagonal SrMnO₃ was synthesized by the polymerized complex method. Citric acid (15.4 g, 80 mmol) and ethylene glycol (25.1 mL, 450 mmol) were added to an aqueous solution (50 mL) containing Sr(NO₃)₂ (2.11 g, 10 mmol) and Mn(NO₃)₂·6H₂O (2.87 g, 10 mmol). After complete dissolution was achieved, the resulting solution was evaporated at 333 K to reduce the water content. The transparent solution was heated at 463 K with continuous stirring to accelerate polymerization, whereby it finally gelled into a transparent brown resin. The resultant resin was heated at 523 K for 20 min and 573 K for an additional 20 min to give a black powder, which is hereafter referred to as the precursor. The precursor was calcined at 923 K for 5 h on an Al₂O₃ plate in air. After cooling to room temperature, the samples were collected and washed with water (\approx 2 L) followed by evacuation at room temperature for 3.5 h to give the hexagonal SrMnO₃ catalyst. Yield: 1.70 g (89%). Elemental analysis calcd (%) for SrMnO₃: Sr 45.98, Mn 28.83; found: Sr 45.25, Mn 27.65.

Procedure for catalytic oxidation

The catalytic oxidation of various substrates was conducted in a 30 mL glass vessel containing a magnetic stirring bar. All products were identified by comparison of the GC retention time, mass spectra, and NMR spectra with those of authentic samples. A typical procedure for catalytic oxidation was as follows: SMO (0.1 g), alcohol (1 mmol), toluene (2 mL), O₂ (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. After the reaction was completed, the catalyst was separated by filtration. The analytically pure product was then isolated using a flash chromatography separation system with silica gel (pore size 60 Å, particle size 30 µm) and *n*-hexane/ethyl acetate as an eluent. The products are known and were identified by comparison of their ¹H and ¹³C NMR signals with the literature data. The separated SMO was washed with acetone (40 mL) and water (500 mL), and then dried under vacuum before recycling. The amounts of surface Mn species were estimated assuming that the (110) plane is a surface structure because of the abundant population of Mn species on the (110) plane. The amounts of surface Mn were estimated using this hypothesis and the BET surface area of SMO (25 m²g⁻¹) to be 193 μ mol·g⁻¹.

Procedure for IR measurements

Samples were pressed into self-supporting disks (20 mm diameter, 0.1 g), placed in an IR cell attached to a closed glass-circulation

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system, and FTIR measurements were performed before (evacuation at 573 K for 1 h) and after O₂ adsorption onto the samples. Two IR bands at 3800–2600 and 1700–1500 cm⁻¹, which were assignable to the OH stretching and bending modes of physisorbed H₂O, respectively, were absent after evacuation. The IR spectrum of the sample at room temperature before O₂ adsorption was used as the background for differential spectra obtained by subtracting the background from the spectra measured for O₂-adsorbed samples. After the exposure to O₂ atmosphere (55 Torr) at room temperature for 1 min, differential IR spectra were measured. The band at 1152 cm⁻¹, assignable to the Mn–superoxo species, appeared after O₂ adsorption and the intensity did not change after 5 min. In addition, the 1152 cm⁻¹ band completely disappeared after the sample was evacuated at room temperature for 1 min. These results indicate that the reaction of SMO with O₂ is reversible.

Acknowledgements

The authors thank the Material Analysis Suzukake-dai Center, Technical Department, Tokyo Institute of Technology, for conducting the ICP-AES and NMR analyses. We would like to express our sincere appreciation to Prof. Takashi Tatsumi and Assist. Prof. Toshiyuki Yokoi (Tokyo Institute of Technology) for the use of the FE–SEM instrument and to Prof. Junko K. Nomura (Tokyo Institute of Technology) for helpful discussion regarding IR measurements This work was supported by a Kakenhi Grant-in-Aid (No. 15H04184) from the Japan Society for the Promotion of Science (JSPS).

Keywords: heterogeneous catalysis • manganese • oxidation • oxygen • surface chemistry

- a) Modern Oxidation Methods (Ed. J.-E. Bäckvall), Wiley-VCH, Weinheim, 2004; b) T. Punniyamurthy, S. Velusamy, J. Iqbal, Chem. Rev. 2005, 105, 2329–2363; c) F. Cavani, J. H. Teles, ChemSusChem 2009, 2, 508–534; d) Modern Heterogeneous Oxidation Catalysis (Ed.: N. Mizuno), Wiley-VCH, Weinheim, 2009.
- [2] a) E. I. Solomon, P. Chen, M. Metz, S.-K. Lee, A. E. Palmer, Angew. Chem. Int. Ed. 2001, 40, 4570-4590; Angew. Chem. 2001, 113, 4702-4724; b) L. Que, Jr., W. B. Tolman, Nature 2008, 455, 333-343; c) S. Friedle, E. Reisner, S. J. Lippard, Chem. Soc. Rev. 2010, 39, 2768-2779; d) J. P. Mahy, J. D. Marechal, R. Ricoux, Chem. Commun. 2015, 51, 2476-2494.
- [3] a) P. J. Smeets, J. S. Woertink, B. F. Sels, E. I. Solomon, R. A. Schoonheydt, Inorg. Chem. 2010, 49, 3573–3583; b) Q. Gao, C. Giordano, M. Antonietti, Angew. Chem. Int. Ed. 2012, 51, 11740–11744; Angew. Chem. 2012, 124, 11910–11914; c) E. Roduner, W. Kaim, B. Sarkar, V. B. Urlacher, J. Pleiss, R. Glaeser, W.-D. Einicke, G. A. Sprenger, U. Beifuss, E. Klemm, C. Liebner, H. Hieronymus, S.-F. Hsu, B. Plietker, S. Laschat, ChemCatChem 2013, 5, 82–112.
- [4] a) S. L. Suib, J. Mater. Chem. 2008, 18, 1623–1631; b) A. J. J. Jebaraj,
 D. A. Scherson, Acc. Chem. Res. 2013, 46, 1192–1205; c) K. Zhang, X.
 Han, Z. Hu, X. Zhang, Z. Tao, J. Chen, Chem. Soc. Rev. 2015, 44, 699–728.
- [5] a) Y.-C. Son, V. D. Makwana, A. R. Howell, S. L. Suib, Angew. Chem. Int. Ed. 2001, 40, 4280-4283; Angew. Chem. 2001, 113, 4410-4413; b) V. D. Makwana, Y. C. Son, A. R. Howell, S. L. Suib, J. Catal. 2002, 210, 46-52; c) G. Yang, W. Zhu, P. Zhang, H. Xue, W. Wang, J. Tian, M. Song, Adv. Synth. Catal. 2008, 350, 542-546; d) F. Schurz, J. M. Bauchert, T. Merker, T. Schleid, H. Hasse, R. Gläser, Appl. Catal. A 2009, 355, 42-49; e) K. Nagashima, T. Mitsudome, T. Mizugaki, K. Jitsukawa, K. Kaneda, Green Chem. 2010, 12, 2142-2144; f) Q. Tang, C. Wu, R. Qiao, Y. Chen, Y. Yang, Appl. Catal. A 2011, 403, 136-141.
- [6] It has been reported that the deactivation during recycling is probably a result of strongly bonded catalyst poisons (water, organic products) and/or insufficient reoxidation of the reduced catalyst by O_2 .^[5]

- [7] a) S. Stølen, T, Grande, in *Chemical Thermodynamics of Materials: Macroscopic and Microscopic Aspects*, Wiley, Chichester, **2003**, pp. 197–227;
 b) L. Rørmark, A. B. Mørch, K. Wiik, S. Stølen, T. Grande, *Chem. Mater.* **2001**, *13*, 4005–4013.
- [8] P. Saisaha, J. W. de Boer, W. R. Browne, Chem. Soc. Rev. 2013, 42, 2059– 2074.
- [9] a) G. Parravano, J. Am. Chem. Soc. 1953, 75, 1497–1498; b) H. M. Zhang, Y. Teraoka, N. Yamazoe, Hyomen Kagaku 1987, 8, 23–29; c) N. Rezlescu, E. Rezlescu, P. D. Popa, C. Doroftei, M. Ignat, Composites Part B 2014, 60, 515–522; d) K. Langfeld, R. Marschner, B. Frank, R. Schomaecker, Chem-CatChem 2011, 3, 1354–1358; e) A. I. Bostan, Y. I. Pyatnitskii, L. N. Raevskaya, V. G. Pryanikova, S. A. Nedil'ko, A. G. Dzyaz'ko, E. G. Zen'kovich, Theor. Exp. Chem. 2005, 41, 32–36.
- [10] M. Kakihana, J. Sol-Gel Sci. Technol. 1996, 6, 7-55.
- [11] A. Sacchetti, M. Baldini, P. Postorino, C. Martin, A. Maignan, J. Raman Spectrosc. 2006, 37, 591–596.
- [12] A. J. Fatiadi, Synthesis 1976, 133-167.
- [13] In the absence of $Sr(NO_3)_2$ during the synthesis of SMO, the XRD pattern for the resulting manganese oxide showed only signals from Mn_2O_3 .
- [14] R. A. Sheldon, M. Wallau, I. W. C. E. Arends, U. Schuchardt, Acc. Chem. Res. 1998, 31, 485–493.
- [15] In separate experiments, the heterogeneous nature of SMO for oxidation of 1a was also confirmed even at 353 K.
- [16] The total turnover number (TON) was up to 7.6, based on the bulk Mn, and was estimated to be 207 based on surface Mn (see details in the Experimental Section).
- [17] a) K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th ed., 2006, Wiley, New York; b) C. Descorme, Y. Madier, D. Duprez, J. Catal. 2000, 196, 167–173.
- [18] a) E. Gallo, E. Solari, C. Floriani, N. Re, A. Chiesi-Villa, C. Rizzoli, Angew. Chem. Int. Ed. Engl. 1996, 35, 1981–1983; Angew. Chem. 1996, 108, 2113–2115; b) L.-L. Liu, H.-X. Li, L.-M. Wan, Z.-G. Ren, H.-F. Wang, J.-P. Lang, Chem. Commun. 2011, 47, 11146–11148.
- [19] a) Y. Choi, M. C. Lin, M. Liu, Angew. Chem. Int. Ed. 2007, 46, 7214–7219; Angew. Chem. 2007, 119, 7352–7357; b) Y. Choi, D. S. Mebane, M. C. Lin, M. Liu, Chem. Mater. 2007, 19, 1690–1699; c) W. Cen, Y. Liu, Z. Wu, H. Wang, X. Weng, Phys. Chem. Chem. Phys. 2012, 14, 5769–5777.
- [20] The surface Mn valent state was investigated by X-ray photoelectron spectroscopy (XPS). In contrast to bulk oxidation state, the Mn^{IV} and Mn^{III} species were observed with the relative intensities of 34% and 66%, respectively (Figure S4). Thus, such a reduced Mn^{III} species likely reacts with O₂ to form a Mn^{IV}-superoxo species.
- [21] The reactivity of alkylarenes for SMO decreased in the order of **3e** $(1.6) \sim$ **3d** (1.5) > **3c** (1.0) and is different from that (**3d** (4.2) > **3e** (1.8) > **3c** (1.0)) for activated MnO₂. Such differences of selectivity and reactivity between SMO and activated MnO₂ would be caused by the different properties of active oxygen species: J. M. Mayer, *Acc. Chem. Res.* **1998**, *31*, 441–450.
- [22] D. B. G. Williams, M. Lawton, J. Org. Chem. 2010, 75, 8351-8354.
- [23] W. L. F. Armarego, C. L. L. Chai, Purification of Laboratory Chemicals, 6th ed., Elsevier, Oxford, 2009.
- [24] a) R. N. DeGuzman, Y.-F. Shen, E. J. Neth, S. L. Suib, C.-L. O'Young, S. Levine, J. M. Newsam, *Chem. Mater.* **1994**, *6*, 815–821; b) E. Nicolas-Tolentino, Z.-R. Tian, H. Zhou, G. Xia, S. L. Suib, *Chem. Mater.* **1999**, *11*, 1733–1741; c) E. Terazzi, C. Bourgogne, R. Welter, J. L. Gallani, D. Guillon, G. Rogez, B. Donnio, *Angew. Chem. Int. Ed.* **2008**, *47*, 490–495; *Angew. Chem.* **2008**, *120*, 500–505.
- [25] T. Delgado-Abad, J. Martinez-Ferrer, A. Caballero, A. Olmos, R. Mello, M. E. Gonzalez-Nunez, P. J. Perez, G. Asensio, *Angew. Chem. Int. Ed.* 2013, *52*, 13298–13301; *Angew. Chem.* 2013, *125*, 13540–13543.
- [26] L. Rørmark, K. Wiik, S. Stolen, T. Grande, J. Mater. Chem. 2002, 12, 1058– 1067.
- [27] a) Q. Tang, L. Jiang, J. Liu, S. Wang, G. Sun, ACS Catal. 2014, 4, 457–463;
 b) M. Kang, E. D. Park, J. M. Kim, J. E. Yie, Appl. Catal. A 2007, 327, 261–269;
 c) R. J. Iwanowski, M. H. Heinonen, W. Paszkowicz, R. Minikaev, T. Story, B. Witkowska, Appl. Surf. Sci. 2006, 252, 3632–3641.

Received: May 20, 2016 Published online on

FULL PAPERS

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Dioxygen Activation by a Hexagonal SrMnO₃ Perovskite Catalyst for Aerobic Liquid-Phase Oxidation



Manganese hex: The reversible reaction of surface manganese species on hexagonal $SrMnO_3$ with O_2 leads to the formation of manganese–superoxo species, which likely catalyze the selective oxidative transformation of various types of organic substrates into the desired oxygenated or dehydrogenated products.