

Article pubs.acs.org/JACS

## Effect of MnO<sub>2</sub> Crystal Structure on Aerobic Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid

Eri Hayashi,<sup>†</sup> Yui Yamaguchi,<sup>†</sup> Keigo Kamata,<sup>†,§</sup> Naoki Tsunoda,<sup>†</sup> Yu Kumagai,<sup>§,‡</sup> Fumiyasu Oba,<sup>†</sup> and Michikazu Hara\*,<sup>†,⊥</sup>₀

<sup>†</sup>Laboratory for Materials and Structures, Institute of Innovative Research and <sup>‡</sup>Materials Research Center for Element Strategy, Tokyo Institute of Technology, Yokohama 226-8503, Japan

<sup>§</sup>Precursory Research for Embryonic Science and Technology (PRESTO) and <sup>⊥</sup>Advanced Low Carbon Technology Research and Development Program (ALCA), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi 332-0012, Japan

Supporting Information

ABSTRACT: Aerobic oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) as a bioplastics monomer is efficiently promoted by a simple system based on a nonprecious-metal catalyst of MnO2 and NaHCO3. Kinetic studies indicate that the oxidation of 5-formyl-2-furancarboxylic acid (FFCA) to FDCA is the slowest step for the aerobic oxidation of HMF to FDCA over activated MnO2. We demonstrate through combined computational and experimental studies that HMF oxidation to FDCA is largely dependent on the MnO2 crystal structure. Density functional theory (DFT) calculations reveal that vacancy formation energies at the planar oxygen sites in  $\alpha$ - and  $\gamma$ -MnO<sub>2</sub> are higher than those at the bent oxygen sites.  $\beta$ - and  $\lambda$ -MnO<sub>2</sub> consist of only planar and bent oxygen sites, respectively,



with lower vacancy formation energies. Consequently,  $\beta$ - and  $\lambda$ -MnO<sub>2</sub> are likely to be good candidates as oxidation catalysts. On the other hand, experimental studies reveal that the reaction rates per surface area for the slowest step (FFCA oxidation to FDCA) decrease in the order of  $\beta$ -MnO<sub>2</sub> >  $\lambda$ -MnO<sub>2</sub> >  $\gamma$ -MnO<sub>2</sub> >  $\alpha$ -MnO<sub>2</sub> >  $\delta$ -MnO<sub>2</sub> >  $\varepsilon$ -MnO<sub>2</sub>; the catalytic activity of  $\beta$ - $MnO_2$  exceeds that of the previously reported activated  $MnO_2$  by three times. The order is in good agreement not only with the DFT calculation results, but also with the reduction rates per surface area determined by the H2-temperature-programmed reduction measurements for MnO<sub>2</sub> catalysts. The successful synthesis of high-surface-area  $\beta$ -MnO<sub>2</sub> significantly improves the catalytic activity for the aerobic oxidation of HMF to FDCA.

#### INTRODUCTION

Manganese oxide-based materials have received much attention in broad fields of catalysis, magnetism, chemical sensing, and electrochemistry (lithium-ion batteries, supercapacitors, etc.) because of their natural abundance, low cost, environmental friendliness, and specific chemical/physical properties including diverse crystal structures and oxidation states.<sup>1</sup> Among them, manganese dioxides (MnO<sub>2</sub>) have been extensively investigated as heterogeneous catalysts for liquidphase selective oxidation<sup>2</sup> as well as gas-phase total oxidation of hydrocarbons, alcohols, NO, and CO.<sup>3</sup> Many efforts have been made to improve the catalytic performance of MnO<sub>2</sub> through variation of the specific surface area, crystal form, oxidation state, morphology, and porosity. In particular, the crystal structure of MnO<sub>2</sub> plays a crucial role in determining the catalytic properties, and some possibly active crystal structures have been proposed depending on the target reactions. Crystalline MnO2 materials consist of MnO6 octahedral units shared by corners or edges, which result in various tunnel and layered structures (Figure 1). For the wellstudied electrochemical reactions and gas-phase reactions,  $\alpha$ - and  $\gamma$ -MnO<sub>2</sub> have been proposed as active phases based on their unique properties such as chemisorption,<sup>4</sup> electron transfer,<sup>5</sup> number of active species,<sup>5b,6</sup> and chemical bonding.<sup>4b,c,6d,7</sup> However, systematic studies on liquid-phase organic reactions with crystalline MnO<sub>2</sub> are still limited; there are only a few reports on the activity-structure relationship among  $\geq 3$  crystal structures of MnO<sub>2</sub>. In this context, the rational design and synthesis of active crystalline MnO<sub>2</sub> catalysts are attractive, yet challenging to establish the desired liquid-phase organic reaction.<sup>8</sup>

Renewable and sustainable biomass feedstocks have received significant attention as substitutes of nonrenewable fossil resources such as crude oil, coal, and natural gas for the manufacture of high value-added products. In particular, 5hydroxymethyl furfural (HMF) is a key platform compound that is synthesized from cellulose because HMF can be converted into various high value-added compounds such as 2,5-diformylfuran (DFF), dimethylfuran, levulinic acid, 2,5-

Received: September 12, 2018



**Figure 1.** Structures of (a)  $\alpha$ -MnO<sub>2</sub>, (b)  $\beta$ -MnO<sub>2</sub>, (c)  $\gamma$ -MnO<sub>2</sub>, (d)  $\delta$ -MnO<sub>2</sub>, and (e)  $\lambda$ -MnO<sub>2</sub>. Pink, green, and red spheres represent Mn, K, and O atoms, respectively.

bisaminomethylfuran, dimethylfuran, and 5-(dimethoxymethyl)-2-furanmethanol (Scheme 1).<sup>9</sup> 2,5-Furandicarboxylic acid

#### Scheme 1. Conversion of HMF into Various High Value-Added Compounds



(FDCA) is also one of the most attractive raw materials for polyethylene furanoate (PEF) because biopolyester PEF is not only a substitute for polyethylene terephthalate, but also a functional material with high gas barrier properties and excellent heat resistance that can be easily processed.<sup>10</sup> Therefore, various types of effective heterogeneous catalysts based on precious metals (Au,<sup>11</sup> Pt,<sup>12</sup> Ru,<sup>13</sup> and Pd<sup>14</sup>) have been developed for the direct oxidation of HMF to FDCA with molecular oxygen  $(O_2)$  as the sole oxidant in the presence of base additives, and several precious metal-based catalysts efficiently promote HMF oxidation, even in the absence of bases (Table S1). On the other hand, systems using nonprecious metal catalysts have disadvantages such as low yield and selectivity toward FDCA, requirement for severe reaction conditions, use of organic oxidants and solvents, and poor recyclability.<sup>15</sup> Very recently, several research groups have developed effective catalyst systems based on mixed oxides such as Ni-, Ce-, Fe-, Cu-containing manganese oxides  $^{15a-e,k}$  Zn-, Ce-, Ru-containing iron oxides,  $^{15f-h}$  and Co-containing or metal-free carbon nitrides  $^{15i,j}$  for aerobic oxidation of HMF to FDCA. We have reported for the first time that MnO<sub>2</sub> itself

could act as an efficient and reusable precious-metal-free heterogeneous catalyst for the oxidation of HMF to FDCA in the presence of NaHCO<sub>3</sub> with O<sub>2</sub> as the sole oxidant.<sup>16</sup> However, the reaction mechanism of HMF oxidation, including the structure–activity relationship of  $MnO_2$ , has not yet been clarified. In this paper, we report the synthesis and characterization of  $MnO_2$ -based materials with various crystal structures and their application as catalysts for the aerobic oxidation of HMF to FDCA. In addition, the reaction mechanism including the catalyst effect, kinetics, and experimental and computational studies on the reactivity of constituent oxygen atoms is investigated.

#### EXPERIMENTAL SECTION

Instruments. Synthesized MnO<sub>2</sub> samples were identified by X-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer with Cu K $\alpha$  radiation ( $\lambda$  = 1.5405 Å, 40 kV-40 mA) equipped with a highspeed one-dimensional detector (D/teX Ultra). Data were collected in the  $2\theta$  range  $10-80^{\circ}$  in  $0.02^{\circ}$  steps with a continuous scanning rate of 20° min<sup>-1</sup>. The Rietveld refinements were carried out using Rigaku PDXL2 software. The chemical composition was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Shimadzu ICPS-8100 spectrometer. The specific surface areas of samples were determined by nitrogen adsorption-desorption isotherms measured at 77 K using a Quantachrome Nova-4200e surface area and pre size analyzer, and the Brunauer-Emmett-Teller (BET) surface areas were estimated over the relative pressure  $(P/P_0)$ range of 0.05-0.30. Physisorbed water of the samples was removed by heating at 423 K for 1 h under vacuum prior to their measurements. The morphologies were characterized by scanning electron microscopy (SEM; S-5500, Hitachi). Transmission electron microscopy (TEM) studies were carried out using a JEOL JEM2100F transmission electron microscope operating at an accelerating voltage of 200 kV. After Cu grids were directly mixed with samples, the Cu grids were collected and mounted on a stage. Raman spectroscopic analyses were performed on a Jasco NRS-7600 spectrometer with laser excitation wavelength of  $\lambda = 532$  nm. Thermogravimetry-differential thermal analysis (TG-DTA) was performed using a Rigaku TG8120 differential thermal analyzer, and the measurements were conducted from r.t. to 1273 K at a heating rate of 10 K min<sup>-1</sup> in N<sub>2</sub> flow (200 mL min<sup>-1</sup>). X-ray photoelectron spectroscopy (XPS) data were collected on a Shimadzu ESCA-3400HSE spectrometer with a standard Mg K $\alpha$ source (1253.6 eV) working at 10 kV and 25 mA. Samples were pressed into a pellet and fixed on a piece of double-sided carbon tape. The binding energies were calibrated by assuming the biding energy of the C 1s line to be 284.6 eV. The spectrum was fitted using the XPS Peak 4.1 program after a Shirley type background subtraction. The deconvoluted Mn 2p spectrum of MnO<sub>2</sub> shows three peaks with binding energies of 640.8, 641.8, 642.8, and 644.5 eV, which ascribes to Mn<sup>II</sup>, Mn<sup>III</sup>, Mn<sup>IV</sup>, and a shakeup peak, respectively.<sup>17</sup> The average oxidation states of Mn species were determined by iodometric titration using an autotitrator (Mettler Toledo, Easy Pro Titrator System). A MnO<sub>2</sub> sample (ca. 10 mg) was added to a mixed solution of 0.5 M HCl aq. (12 mL) and 2 M KI aq. (5 mL), and the resulting solution was titrated with an aqueous solution of 0.01 M Na<sub>2</sub>S<sub>3</sub>O<sub>3</sub>.<sup>1</sup> H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) profiles were measured on a BEL Japan BELCAT-A chemisorption analyzer equipped with a thermal conductivity detector (TCD) to measure changes in the H<sub>2</sub> decrease of the gas stream. The y-axis means the TCD signal intensity and integrated area gives total H<sub>2</sub> gas consumed.<sup>19</sup> Fifty milligrams of sample was placed in a quartz cell and then heated from 323 to 923 K at a rate of 10 K min<sup>-1</sup> under 5%  $H_2/Ar$  flow (50 mL min<sup>-1</sup>). The initial reduction rates were estimated from 553 to 593 K, which correspond to the range, which is under 10% of the lattice oxygen atoms reduced by  $H_{22}$  and all the MnO<sub>2</sub> catalysts were stable in this range. High performance liquid chromatography (HPLC; LC-2000, Jasco) analyses were performed using photodiode array and refractive index detectors with a Aminex

HPX-87H column (7.8 mm diameter  $\times$  300 mm, Bio-Rad Laboratories, Inc. Co. Ltd.; eluent (0.5 mM H<sub>2</sub>SO<sub>4</sub>), flow rate (0.5 mL/min), column temperature (308 K)). The retention times for FDCA, S-hydroxymethyl-2-furancarboxylic acid (HMFCA), S-formyl-2-furancarboxylic acid (FFCA), HMF, and DFF were 20.9, 27.3, 29.4, 41.7, 52.1 min, respectively. The crystal structures were drawn using the visualization for electronic and structural analysis (VESTA) program.<sup>20</sup>

**Procedure for Catalytic Oxidation.** The catalytic oxidation of various substrates was carried out in a 30 mL glass vessel or in a 13 mL autoclave reactor with a Teflon vessel containing a magnetic stirring bar. A typical procedure for the catalytic oxidation of HMF was as follows. HMF (0.2 mmol),  $MnO_2$  (0.05 g),  $NaHCO_3$  (0.6 mmol), water (5 mL), and  $O_2$  (1 MPa) were charged into the autoclave reactor. The reaction solution was heated at 373 K for 24 h. After the reaction, the catalyst was separated by filtration and the filtrate was diluted 10 times with water. The recovered catalyst was washed with water (25 mL) and then dried at 353 K.

Synthesis of High-Surface-Area  $\beta$ -MnO<sub>2</sub> ( $\beta$ -MnO<sub>2</sub>–HS).  $\beta$ -MnO<sub>2</sub>–HS was synthesized according to the following procedure. An aqueous solution (20 mL) of MnSO<sub>4</sub>·SH<sub>2</sub>O (1.45 g, 6 mmol) was added dropwise to an aqueous solution (20 mL) of NaMnO<sub>4</sub>·H<sub>2</sub>O (0.63 g, 4 mmol) with vigorous stirring, and the resulting suspension was stirred for a further 30 min. The precipitates were collected by filtration, washed with water (2 L), and dried at 353 K overnight. The product was calcined at 673 K for 5 h to give a black powder of  $\beta$ -MnO<sub>2</sub>–HS. Yield: 0.85 g (98%).

Quantum Chemical Calculations. The density functional theory (DFT) calculations of the oxygen vacancy formation were performed using the projector augmented-wave (PAW) method<sup>21</sup> as implemented in the Vienna Ab initio Simulation Package (VASP) code.<sup>22</sup> Very recently, Kitchaev et al. have reported that strongly constrained and appropriately normed (SCAN) meta generalized gradient approximation<sup>23</sup> uniquely yields accurate formation energies and properties across all  $\dot{MnO_2}$  polymorphs. Thus, we applied the SCAN functional in this study.<sup>24</sup> Plane-wave cutoff energies of 550 and 400 eV were employed for the perfect-crystal and point-defect models, respectively. Spin polarization was allowed in all of the vacancy calculations. PAW data sets with radial cutoffs of 1.22 and 0.80 Å for Mn and O, respectively, were employed, and Mn-3d and 4s and O-2s and 2p were described as valence electrons. The oxygen vacancies were modeled using 72-, 96-, 96-, and 108-atom supercells for  $\beta$ -,  $\alpha$ -,  $\lambda$ -, and  $\gamma$ -MnO<sub>2</sub>, respectively.

When calculating point defects in solids with band gaps, all relevant charge states must be considered. Therefore, 0, 1+, and 2+ charge states were considered for oxygen vacancies. Consequently,  $\beta$ -MnO<sub>2</sub> showed only 1+ and 2+ charge states, whereas 0, 1+, and 2+ charge states appeared in the other MnO<sub>2</sub> phases. Thus, neutral oxygen vacancy formation energy in  $\beta$ -MnO<sub>2</sub> was estimated with the condition that the oxygen vacancy exists in the 1+ charge state and one electron is located at the conduction band minimum. Corrections for charged defects were performed with the extended Freysoldt–Neugebauer–Van de Walle procedure.<sup>25,26</sup> See ref 25 for more details.

#### RESULTS AND DISCUSSION

**Computational Studies on Structure–Reactivity Relationship.**  $MnO_2$  has various crystallographic structures, each of which significantly influences the properties of the  $MnO_2$  as a catalyst; thus, we investigate the oxidation reactivity of  $MnO_2$ with various crystal structures. On the basis of the catalyst effect, the differences of reactivity in  $O_2$  and Ar atmospheres, and XRD, XPS, and TG-DTA results, it has been proposed that activated  $MnO_2$ -catalyzed oxidation proceeds via a Mars– van Krevelen mechanism and consists of the following two steps:<sup>16</sup> (i) oxidation of substrates with  $MnO_2$  to form a partially reduced manganese species,  $MnO_{2-\delta}$ , and (ii) rapid reoxidation of  $MnO_{2-\delta}$  by  $O_2$ . According to the total yields for the oxidation of HMF with  $MnO_2$  under Ar atmosphere, the irreversible transformation of MnO<sub>2</sub> to MnOOH likely occurred when the  $\delta$  value in MnO<sub>2- $\delta$ </sub> was more than ~0.23. Approximately three oxygen atoms per surface Mn species were estimated to be transferred to the substrate (see details given in the Supporting Information). All these results indicate that the oxygen atoms from the oxide surface layer are involved in the oxidation reaction without the reductive activation of  $O_2$ .<sup>27</sup> The role of  $O_2$  is essential for the rapid reoxidation of  $MnO_{2-\delta}$  to  $MnO_2$  without the transformation into inactive MnOOH, establishing the catalytic cycle. On the other hand, the energy for oxygen vacancy formation has been accepted as a good descriptor of the oxidizing power of an oxide; a lower vacancy formation energy indicates a better oxidant.<sup>28</sup> Therefore, the DFT calculations were conducted to estimate vacancy formation energies for MnO2 catalysts with various crystalline structures. Although the oxygen vacancies have been examined based on DFT studies correlating with experimental catalytic performance of  $\beta$ -MnO<sub>2</sub>,<sup>29</sup> the polymorph dependence on the oxygen vacancy formation energy and catalytic performance has not been investigated.

In this study,  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -,  $\varepsilon$ -, and  $\lambda$ -MnO<sub>2</sub> were synthesized by hydrothermal and sol-gel methods (see details in the Supporting Information). The crystal structures of these MnO<sub>2</sub> catalysts are shown in Figure 1. Hollandite-type  $\alpha$ -MnO<sub>2</sub> and pyrolusite-type  $\beta$ -MnO<sub>2</sub> have one-dimensional (1 × 1) and (2 × 2) tunnel structures.<sup>30</sup> Nsutite-type  $\gamma$ -MnO<sub>2</sub> and akhtenskite  $\varepsilon$ -MnO<sub>2</sub> are composed of an intergrowth of (1 × 1) tunnels (pyrolusite) and (1 × 2) tunnels (ramsdellite), while  $\varepsilon$ -MnO<sub>2</sub> exhibits more structural faults and microtwinning than  $\gamma$ -MnO<sub>2</sub>.<sup>31</sup> The removal of lithium cations from LiMn<sub>2</sub>O<sub>4</sub> spinel results in  $\lambda$ -MnO<sub>2</sub> with a cubic defective spinel structure.<sup>1b</sup> Birnessite  $\delta$ -MnO<sub>2</sub> has a layered structure containing intercalated water and cations between the MnO<sub>2</sub> octahedral sheets.<sup>32</sup>

The calculated oxygen vacancy formation energies for  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\lambda$ -MnO<sub>2</sub> are summarized in Table 1. The calculations for  $\delta$ - and  $\varepsilon$ -MnO<sub>2</sub> were omitted here because their crystal structures are not uniquely modeled. The resultant vacancy formation energies for MnO<sub>2</sub> significantly depend on the structure and type of constituent oxygen atoms (planar and bent Mn<sub>3</sub>( $\mu$ <sub>3</sub>-O)). Among the MnO<sub>2</sub> phases considered, only  $\beta$ -MnO<sub>2</sub> consists of planar  $\mu$ <sub>3</sub>-oxygen atoms with a low vacancy





• 2		2- <i>x</i> ,	2	`	л	/	`	D	
$\lambda$ -MnO <sub>2</sub>	$\rightarrow$ MnO	$x_{2-x} + x/2$	O <sub>2</sub>	3.44 (	O <sub>B</sub> aton	n)			

<sup>a</sup>O<sub>A</sub> and O<sub>B</sub> represent planar and bent oxygen atoms, respectively.

formation energy (3.25 eV).  $\lambda$ -MnO<sub>2</sub> also has only bent  $\mu_3$ oxygen atoms with a vacancy formation energy of 3.44 eV. In sharp contrast to the two MnO<sub>2</sub>-based samples,  $\alpha$ -MnO<sub>2</sub> and  $\gamma$ -MnO<sub>2</sub> consist of both types of oxygen atoms with higher and lower vacancy formation energies (bent, 3.25 and 3.15 eV; planar, 3.95 and 3.84 eV). As expected from a structural viewpoint, the vacancy formation energies at the bent oxygen sites are generally lower than those at the planar oxygen sites.  $\beta$ -MnO<sub>2</sub> is an exception, in which the planar oxygen site exhibits a lower vacancy formation energy. This could be attributed to the much smaller calculated band gap of 0.4 eV than those in the other MnO<sub>2</sub> phases ( $\alpha$ , 1.7 eV;  $\gamma$ , 1.2 eV;  $\lambda$ , 1.9 eV). Taking into account the ratio of oxygen sites with lower vacancy formation energies ( $\beta$ -MnO<sub>2</sub> (3.25 eV, 100%),  $\lambda$ -MnO<sub>2</sub> (3.44 eV, 100%),  $\alpha$ -MnO<sub>2</sub> (3.25 eV, 50%), and  $\gamma$ -MnO<sub>2</sub> (3.15 eV, 50%)), it is expected that  $\beta$ - and  $\lambda$ -MnO<sub>2</sub> would be good candidate oxidation catalysts.

Effect of MnO<sub>2</sub> Crystal Structure on the Oxidation of HMF to FDCA. To confirm the possible superiority of the  $\beta$ and  $\lambda$ -MnO<sub>2</sub> catalysts, MnO<sub>2</sub> with various crystal structures were synthesized, characterized, and the oxidation catalysis was investigated.  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -,  $\varepsilon$ - and  $\lambda$ -MnO<sub>2</sub> were synthesized according to previously reported procedures (see details in the Supporting Information). <sup>6f,32,33</sup> The structure of each sample was characterized by powder XRD analysis. The XRD patterns are shown in Figures 2 and S1–S6 and are in good agreement with those reported for tetragonal  $\alpha$ -MnO<sub>2</sub> (JCPDS 00–044– 0141), tetragonal  $\beta$ -MnO<sub>2</sub> (JCPDS 00–024–0735), orthorhombic  $\gamma$ -MnO<sub>2</sub> (JCPDS 00–014–0644), trigonal  $\delta$ -MnO<sub>2</sub> (JCPDS 01–073–7867), hexagonal  $\varepsilon$ -MnO<sub>2</sub> (JCPDS 00– 030–0820), and cubic  $\lambda$ -MnO<sub>2</sub> (JCPDS 00–044–0992). For



Figure 2. XRD patterns for (a)  $\alpha$ -MnO<sub>2</sub>, (b)  $\beta$ -MnO<sub>2</sub>, (c)  $\gamma$ -MnO<sub>2</sub>, (d)  $\delta$ -MnO<sub>2</sub>, (e)  $\varepsilon$ -MnO<sub>2</sub>, and (f)  $\lambda$ -MnO<sub>2</sub>.

example, the following lattice parameters (tetragonal, a = 4.40 Å, c = 2.87 Å) were obtained by the Rietveld refinements for XRD data of  $\beta$ -MnO<sub>2</sub> (Figure S7), and these values well agree with the previously reported ones.<sup>34</sup> The TEM image for  $\beta$ -MnO<sub>2</sub> showed that the clear lattice fringes were observed through the particle, indicating the high crystallinity of  $\beta$ -MnO<sub>2</sub> particles (Figure S8). The distances between two fringes are 0.31 and 0.24 nm, which are close to the *d*-spacings of the (110) and (101) planes of  $\beta$ -MnO<sub>2</sub>, respectively.<sup>34</sup> The Raman spectrum of fresh  $\beta$ -MnO<sub>2</sub> showed the bands around 650 and 530 cm<sup>-1</sup> assignable to  $A_{1g}$  and  $E_g$  modes characteristic of  $\beta$ -MnO<sub>2</sub>, respectively.<sup>35</sup>

The metal contents, amounts of physisorbed water, and average oxidation states (AOSs) of the manganese species in the synthesized MnO<sub>2</sub> were determined using ICP-AES, TG-DTA,<sup>36</sup> and iodometry, respectively. The results are summarized in Table 2. The Mn contents of all MnO<sub>2</sub> catalysts were in the range of 47.86–62.39 wt %.<sup>33</sup>  $\alpha$ - and  $\delta$ -MnO<sub>2</sub> have some cations or water inside the tunnels or between the layers to stabilize the structures; thus, the Mn contents of  $\alpha$ - and  $\delta$ -MnO<sub>2</sub> were lower than those of  $\beta$ -,  $\gamma$ -, and  $\lambda$ -MnO<sub>2</sub>.<sup>30,32</sup> Since  $\epsilon$ -MnO<sub>2</sub> was synthesized in the presence of Fe species, low Mn content (47.46 wt %) was observed due to small amounts of residual Fe species (6.10 wt %). The AOS for  $\beta$ -,  $\gamma$ , and  $\varepsilon$ -MnO<sub>2</sub> was approximately 4, while the AOSs for  $\alpha$ -,  $\delta$ -, and  $\lambda$ -MnO<sub>2</sub> were lower (3.70–3.81), which is in good agreement with the charge compensation by the presence of K<sup>+</sup> ions as previously reported (Table S2).<sup>37</sup>

SEM images of the synthesized MnO<sub>2</sub> samples are shown in Figure 3. The morphology and average particle size are summarized in Table 2.  $\alpha$ -,  $\beta$ -, and  $\gamma$ -MnO<sub>2</sub> have rod-like particle morphology (Figure 3a–c), and the particle size was dependent on the sample.  $\delta$ - and  $\lambda$ -MnO<sub>2</sub> have spherical-like particle morphology (Figures 3d,f).  $\varepsilon$ -MnO<sub>2</sub> has flower-like spherical particles composed of nanoplates (Figure 3e). The specific surface areas of the synthesized MnO<sub>2</sub> samples were calculated from Brunauer–Emmett–Teller (BET) plots of the N<sub>2</sub> adsorption isotherms (77 K). The specific surface area of  $\varepsilon$ -MnO<sub>2</sub> (181 m<sup>2</sup> g<sup>-1</sup>) was significantly large, while those of  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\lambda$ -MnO<sub>2</sub> were relatively low to moderate (14–67 m<sup>2</sup> g<sup>-1</sup>). These results are in good agreement with the average particle sizes determined from SEM observations.

The oxidation of HMF with  $O_2$  (1 MPa) in the presence of  $NaHCO_3$  (3 equiv with respect to HMF) was investigated using MnO<sub>2</sub> catalysts with various crystal structures, and the results are shown in Table 3. In the absence of catalysts, the reaction did not proceed.<sup>16</sup> In all cases, the HMF conversion was in the range of 93-99%. Among the catalysts tested, activated MnO<sub>2</sub>,  $\alpha$ -MnO<sub>2</sub>, and  $\varepsilon$ -MnO<sub>2</sub> exhibited moderate activities to afford FDCA in 59–74% yield. Although  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\lambda$ -MnO<sub>2</sub> also exhibited high HMF conversion, FFCA was obtained as the main product in 60-69% yield with low FDCA yields (5-28%). To confirm the stability of the catalysts after the oxidation of HMF, XRD patterns of the recovered MnO<sub>2</sub> catalysts were measured, and the amounts of metal species leached into the reaction solution were determined by ICP-AES analysis. In all catalysts except for  $\varepsilon$ -MnO<sub>2</sub>, the leaching of Mn species into the reaction solution was negligible (Table S3). There was no significant difference in the XRD peak positions of  $\alpha$ -,  $\beta$ -, and  $\varepsilon$ -MnO<sub>2</sub> between the fresh and recovered catalysts, while the peak intensities of recovered  $\alpha$ and  $\beta$ -MnO<sub>2</sub> were slightly increased. The SEM measurement for the recovered  $\varepsilon$ -MnO<sub>2</sub> shows that the morphology changed

Table 2. Bulk Contents, Surface Area, Particle N	phology, and Particle Size of MnO <sub>2</sub> Catalysts
--	--

catalyst	bulk contents (wt %)	specific surface area $(m^2 g^{-1})$	particle morphology	particle size <sup>d</sup> (nm)
$\alpha$ -MnO <sub>2</sub>	Mn, 56.75; K, 7.12; water, 0.82	$30 \pm 1$	nanorod <sup>a</sup>	30–60 wide, 60–1000 long
$\beta$ -MnO <sub>2</sub>	Mn, 60.81; water, 0.46	$14 \pm 1$	nanorod <sup>a</sup>	50-70 wide, 150-1000 long
$\gamma$ -MnO <sub>2</sub>	Mn, 62.03; water, 2.45	$39 \pm 1$	nanorod <sup>a</sup>	10–60 wide, 40–800 long
$\delta$ -MnO <sub>2</sub>	Mn, 52.43; K, 8.67; water, 6.86	$35 \pm 1$	nanosphere <sup>b</sup>	50-150
$\epsilon$ -MnO <sub>2</sub>	Mn, 47.86; Fe, 6.1; water, 4.84	$181 \pm 1$	flower-like nanosphere <sup>c</sup> (composed of nanoplates)	60–200 wide, 10–20 thick
$\lambda$ -MnO <sub>2</sub>	Mn, 62.39; water, 3.76	$67 \pm 4$	nanosphere <sup>b</sup>	40-70
<i>a</i> .				<i>d</i>

<sup>a</sup>Particle size of nanorod is a diameter and length. <sup>b</sup>Average particle diameter. <sup>c</sup>Thickness and length of nanoplate. <sup>d</sup>Particle size from SEM observations.



**Figure 3.** SEM images of (a) α-MnO<sub>2</sub>, (b) β-MnO<sub>2</sub>, (c) γ-MnO<sub>2</sub>, (d)  $\delta$ -MnO<sub>2</sub>, (e) ε-MnO<sub>2</sub>, and (f)  $\lambda$ -MnO<sub>2</sub>.

# Table 3. Effect of $MnO_2$ Catalysts on Oxidation of HMF to FDCA<sup>*a*</sup>

о́ О́ О́ О́Н HMF	MnO <sub>2</sub> NaHCO <sub>3</sub> O <sub>2</sub> water	HO HMFCA HO O FFCA	ОН	O DFF HO O FDC/	OH OH
			yield	ł (%)	
catalyst	conv. (%)	HMFCA	DFF	FFCA	FDCA
activated MnO <sub>2</sub>	>99	_b	_b	15	74
$\alpha$ -MnO <sub>2</sub>	>99	1	_b	36	59
$\beta$ -MnO <sub>2</sub>	>99	1	_ <sup>b</sup>	66	28
$\gamma$ -MnO <sub>2</sub>	93	2	3	60	5
$\delta$ -MnO <sub>2</sub>	96	_b	1	69	10
$\varepsilon$ -MnO <sub>2</sub>	>99	1	b	27	63
$\lambda$ -MnO <sub>2</sub>	>99	_b	_b	66	12
Reaction condition	ns: catalyst (	(0.05 g), HN	AF (0.2	mmol), N	VaHCO <sub>3</sub>

(0.6 mmol), water (5 mL), pO<sub>2</sub> (1 MPa), 373 K, 24 h. <sup>b</sup>Not detected.

from flower-like spherical particles composed of nanoplates to rod-like particle (Figure S9). The catalytic activity and selectivity did not much change for the oxidation of HMF using recovered  $\varepsilon$ -MnO<sub>2</sub> (Table S4); thus, the morphology of  $\varepsilon$ -MnO<sub>2</sub> does not significantly affect the catalytic activity, while the effect of morphologies of other MnO<sub>2</sub> on their catalytic activity could not be ruled out.

There was no significant difference in XPS and Raman spectra and morphology observed by SEM images between fresh and recovered  $\beta$ -MnO<sub>2</sub> catalysts, which also supports the stability of  $\beta$ -MnO<sub>2</sub> (Figures S10–S12). Some XRD peaks (e.g., (110), (310), and (221) peaks) for recovered  $\gamma$ -MnO<sub>2</sub> were shifted to lower angles after the reaction, which was likely due to expansion of the unit cell caused by H-insertion into the material.<sup>38</sup> On the other hand, the peak intensities assignable to the layered structure of  $\delta$ -MnO<sub>2</sub> ((003) and (006) peaks) were decreased, and the significant leaching of K<sup>+</sup> ions (55% relative to the fresh sample) was confirmed by ICP-AES analysis. In addition, the XRD peaks observed for fresh  $\lambda$ - $MnO_2$  almost disappeared after the oxidation reaction. These results indicate that the structures of  $\delta$ - and  $\lambda$ -MnO<sub>2</sub> would not be completely maintained under the reaction conditions employed in contrast to other MnO2. The SEM images of  $\delta$ and  $\lambda$ -MnO<sub>2</sub> after the oxidation of HMF showed that both morphologies changed spherical-like particles to rod-shaped particles (Figure S13). Despite the highest reaction rate per Mn of  $\lambda$ -MnO<sub>2</sub> for oxidation of FFCA, the catalytic activity of  $\lambda$ -MnO<sub>2</sub> for oxidation of HMF was low, which likely indicates the poor stability of  $\lambda$ -MnO<sub>2</sub> during the oxidation of HMF. On the other hand, the recovered  $\delta$ -MnO<sub>2</sub> catalyst showed higher FDCA yield than fresh one in the reuse experiments (Table S5). The structure changes including the cation exchange or morphology effect possibly affect the reactivity, while the mechanism of increase in yield is unclear.

Reaction Mechanism for Oxidation of HMF to FDCA Catalyzed by Activated MnO<sub>2</sub>. It is difficult to estimate the intrinsic reactivity of MnO2 from the oxidation of HMF to FDCA because of the complicated sequential reactions involved. Thus, kinetic analysis was conducted to determine the key step for the aerobic oxidation of HMF with activated MnO<sub>2</sub>. Scheme 2 shows the possible reaction pathways from HMF to FDCA. The hydroxyl and formyl groups of HMF are oxidized to give DFF and HMFCA, respectively. The successive oxidation of DFF and HMFCA gives FFCA, and FFCA is finally oxidized to FDCA. The reaction pathway from HMF to FFCA is dependent on the catalytic system. While the pathway through HMFCA has been proposed for Au-,<sup>11</sup> Pt-,<sup>1</sup> Ru-,<sup>13</sup> and Pd-supported<sup>14</sup> catalyst/NaOH/O<sub>2</sub> systems, a comparable pathway through DFF and HMFCA has been reported for the Pt/C catalyst/NaHCO<sub>3</sub>/O<sub>2</sub> system.<sup>12c</sup> On the other hand, the possible reaction pathway and the most important step in this MnO2-based catalysis has not yet been examined.

Scheme 2. Reaction Pathways for Oxidation of HMF to FDCA, and Rate Constants for the Aerobic Oxidation of HMF with Activated  $MnO_2^{\ a}$ 



<sup>a</sup>Reaction conditions are shown in Figure S14.

Therefore, the rate-constants  $(k_1 - k_5 \text{ in Scheme 2})$  were estimated from the time course for each product (Figure S14), assuming first-order reactions with respect to organic molecules for all steps. The kinetic simulation gave solid lines with  $k_1 = 2.4 \times 10^{-3}$ ,  $k_2 = 2.0 \times 10^{-4}$ ,  $k_3 = 4.2 \times 10^{-2}$ ,  $k_4 = 1.2 \times 10^{-3}$ , and  $k_5 = 4.6 \times 10^{-4} \text{ s}^{-1}$ , and good fits were observed.  $k_2$  was approximately 10-times smaller than  $k_1$ , which indicated that the conversion of HMF into FFCA through DFF was the main pathway over activated MnO<sub>2</sub>. It has been widely accepted that MnO<sub>2</sub> oxidizes benzylic and allylic alcohols to the corresponding carbonyl compounds not only stoichiometrically, but also catalytically without significant formation of carboxylic acids.<sup>39</sup> Therefore, the oxidation of alcohols with MnO<sub>2</sub> proceeds much faster than that of aldehydes, which is in good agreement with the proposed pathway through DFF.<sup>2</sup> The significantly lower value for  $k_5$  than  $k_1$ ,  $k_3$ , and  $k_4$  supports the oxidation of FFCA to FDCA as the rate-determining step based on the dependence of the reaction rate on the O2 pressure.<sup>16</sup>

Effect of MnO<sub>2</sub> Crystal Structure on Oxidation of FFCA to FDCA. On the basis of the kinetic results, the structure-reactivity relationship for the MnO2-catalyzed oxidation was examined by comparison of the reaction rates  $(R_0)$  for the oxidation of FFCA to FDCA, which is the slowest step for the aerobic oxidation of HMF to FDCA (Table 4). To investigate the effect of surface areas of  $MnO_2$ , the  $\alpha$ -MnO<sub>2</sub> catalysts, which were most frequently studied, were synthesized by the solid-state and precipitation methods with the surface areas of 215 and 96 m<sup>2</sup>  $g^{-1}$ , respectively.<sup>40</sup> The catalytic activity of  $\alpha$ -MnO<sub>2</sub> for the oxidation of HMF increased as the surface area increased (Table S6), which indicates that surface areas of MnO<sub>2</sub> are important. Therefore, we should compare the catalytic performance per surface area to investigate the intrinsic activity of oxygen atoms depending on the crystal structures. The initial reaction rates per surface area decreased in the order of  $\beta$ -MnO<sub>2</sub> (16.4  $\mu$ mol h<sup>-1</sup> m<sup>-2</sup>) >  $\lambda$ -MnO<sub>2</sub> (12.2  $\mu$ mol h<sup>-1</sup> m<sup>-2</sup>) >  $\alpha$ -MnO<sub>2</sub> (7.6  $\mu$ mol h<sup>-1</sup> m<sup>-2</sup>)  $\approx \gamma$ -MnO<sub>2</sub> (7.4  $\mu$ mol h<sup>-1</sup> m<sup>-2</sup>) >  $\delta$ -MnO<sub>2</sub> (5.3  $\mu$ mol h<sup>-1</sup> m<sup>-2</sup>) >  $\epsilon$ -MnO<sub>2</sub> (2.3  $\mu$ mol h<sup>-1</sup> m<sup>-2</sup>) >  $\epsilon$ -MnO<sub>2</sub> (2.3  $\mu$ mol h<sup>-1</sup> m<sup>-2</sup>) =  $\epsilon$ -MnO<sub>2</sub> (2 expected from computational results.

XPS analysis was performed to clarify the superior FFCAoxidation ability of  $\beta$ -MnO<sub>2</sub> over those of other MnO<sub>2</sub> crystal

Table 4. Effect of Synthesized	MnO <sub>2</sub> Cataly	sts on Oxida	tion
of FFCA to FDCA <sup>a</sup>			

HO O FFCA	MnO <sub>2</sub>	NaHCO <sub>3</sub> , O <sub>2</sub>	HO OH O OH FDCA
catalyst	conv. (%)	FDCA yield (%)	$R_0 \ (\mu \text{mol } h^{-1} \ \text{m}^{-2})$
activated MnO <sub>2</sub>	30	34	5.6
$\alpha$ -MnO <sub>2</sub>	8	12	7.6
$\beta$ -MnO <sub>2</sub>	7	12	16.4
$\gamma$ -MnO <sub>2</sub>	10	14	7.4
$\delta$ -MnO <sub>2</sub>	6	9	5.3
$\epsilon$ -MnO <sub>2</sub>	16	21	2.3
$\lambda$ -MnO <sub>2</sub>	47	50	12.2
Reaction condition	ns: catalyst	(0.05 g), FFCA (0	.2 mmol), NaHCO <sub>3</sub>

(0.6 mmol), water (5 mL),  $pO_2$  (1 MPa), 373 K, 2 h.

structures. The Mn 2p and O 1s XPS spectra for the MnO<sub>2</sub> catalysts are shown in Figures S15 and S16. The deconvolution results are summarized in Table 5. Surface Mn<sup>4+</sup>, Mn<sup>3+</sup>, and Mn<sup>2+</sup> species were observed in the Mn 2p XPS spectra, and the surface Mn valent states were estimated to be 3.00-3.57 by deconvolution of the Mn 2p spectra. The broad O 1s peaks can be deconvoluted into the peaks around 529.2, 531.2, and 533.0 eV, which correspond to lattice oxygen, adsorbed oxygen, and adsorbed molecular water, respectively.<sup>42</sup> It has been reported that the states of metal or adsorbed oxygen species (rather than lattice oxygen species) likely play an important role in aerobic oxidation over metal oxide catalysts.<sup>55,6</sup> However, no good agreement between the reactivity and the surface as well as bulk average Mn valences or amounts of adsorbed oxygen was observed (Figure S17), which indicates that the reactivity order cannot be simply explained by the two factors and that the intrinsic reactivity of oxygen atoms likely due to the crystal structure would be crucial for this oxidation.

H2-TPR analysis was performed next, and the H2-TPR profiles for MnO<sub>2</sub> are shown in Figure 4. All MnO<sub>2</sub> catalysts were reduced, starting from 410-470 K, and showed two main reduction peaks attributed to transitions of (i) MnO<sub>2</sub> to  $Mn_3O_4$  (through  $Mn_2O_3$ ) and (ii)  $Mn_3O_4$  to MnO. The peak top temperature was different for each crystal phase, and there was no significant relation between the peak top temperature and the reactivity for HMF oxidation. A decrease in the surface area of the catalyst has been reported to cause a shift of the reduction peaks toward higher temperatures due to the increased diffusion resistance, 43 and that the reaction rate (e.g., the oxidation of alcohol and oxidative dehydration of carbohydrate) is dependent on the initial reduction rate.<sup>44</sup> Thus, the reactivity was not compared with the reduction peak tops, but with the initial reduction rates estimated from the H<sub>2</sub>-TPR profiles. The reduction rates per surface area decreased in the order of  $\beta$ -MnO<sub>2</sub> (174 H<sub>2</sub>  $\mu$ mol h<sup>-1</sup> m<sup>-2</sup>) >  $\delta$ -MnO<sub>2</sub> (161  $H_2 \ \mu mol \ h^{-1} \ m^{-2}) > \lambda - MnO_2 \ (95 \ H_2 \ \mu mol \ h^{-1} \ m^{-2}) > \alpha$  $MnO_2$  (89 H<sub>2</sub> µmol h<sup>-1</sup> m<sup>-2</sup>) > γ-MnO<sub>2</sub> (69 H<sub>2</sub> µmol h<sup>-1</sup>  $m^{-2}$ ) >  $\varepsilon$ -MnO<sub>2</sub> (23 H<sub>2</sub>  $\mu$ mol h<sup>-1</sup> m<sup>-2</sup>). Plots of the reduction rates against the FFCA oxidation rates are shown in Figure 5. An almost linear correlation was observed for the various MnO<sub>2</sub> catalysts, except for unstable  $\delta$ - and  $\lambda$ -MnO<sub>2</sub>, which supports the present reaction mechanism in which oxidation of the substrate likely proceeds with oxygen supplied from MnO<sub>2</sub>.

Although synthesis for  $\beta$ -MnO<sub>2</sub> using hydrothermal method has been reported, their specific surface areas are generally low

Fable 5.	Binding	Energy, F	raction and	Average	Oxidation	State of	Synthesized	MnO <sub>2</sub>	Catalysts	
----------	---------	-----------	-------------	---------	-----------	----------	-------------	------------------	-----------	--

	binding energy	of Mn 2p (eV)	binding energy of O 1s (eV)		
catalyst	Mn (IV)	Mn (III)	lattice oxygen	adsorbed oxygen species	adsorbed molecular water
$\alpha$ -MnO <sub>2</sub>	642.4 (54%)	641.4 (46%)	529.5 (77%)	531.2 (19%)	533.0 (4%)
$\beta$ -MnO <sub>2</sub>	642.2 (44%)	641.2 (56%)	529.2 (74%)	531.2 (23%)	533.0 (3%)
$\gamma$ -MnO <sub>2</sub>	642.2 (54%)	641.2 (46%)	529.4 (71%)	531.2 (25%)	533.0 (4%)
$\delta$ -MnO <sub>2</sub>	642.5 (36%)	641.5 (64%)	529.7 (73%)	531.4 (21%)	533.0 (6%)
$\varepsilon$ -MnO <sub>2</sub> <sup>b</sup>	642.4 (32%)	641.4 (38%)	529.5 (69%)	531.4 (27%)	533.0 (4%)
$\lambda$ -MnO <sub>2</sub>	642.2 (53%)	641.2 (47%)	529.6 (71%)	531.4 (25%)	533.0 (4%)
d		$h_{-} = 2 + 1$			

<sup>*a*</sup>Values in parentheses are peak percentages. <sup>*b*</sup>Mn<sup>2+</sup> species were observed on the surface of  $\varepsilon$ -MnO<sub>2</sub>.



Figure 4. H<sub>2</sub>-TPR profiles for (a) α-MnO<sub>2</sub>, (b) β-MnO<sub>2</sub>, (c) γ-MnO<sub>2</sub>, (d) δ-MnO<sub>2</sub>, (e) ε-MnO<sub>2</sub>, and (f) λ-MnO<sub>2</sub>.

(Table S8), leading to a problem that often limits the catalytic performance.  $^{4a,6a,7a,d}$  We successfully developed a simple synthetic method for  $\beta$ -MnO<sub>2</sub> to improve the specific surface area from 14  $m^2/g$  (by the hydrothermal method in this work) to 82  $m^2/g$  (see experimental section). The calcination of amorphous precursor prepared by Na[MnO<sub>4</sub>] and Mn(SO<sub>4</sub>) with the molar ratio of 2:3 gave analytically pure  $\beta$ -MnO<sub>2</sub> ( $\beta$ -MnO<sub>2</sub>-HS). The XRD pattern for  $\beta$ -MnO<sub>2</sub>-HS well agreed with that for tetragonal  $\beta$ -MnO<sub>2</sub> (JCPDS 00-024-0735, Figure 6a), and the SEM image showed the formation of flower-like spherical particles composed of small nanoplates (ca. 40-80 wide, 10-20 thick, Figure 6b). The grain sizes estimated from (110) and (101) diffraction lines using Scherrer's equation were 11 and 15 nm, respectively, in agreement with the SEM measurements. The catalytic performance of  $\beta$ -MnO<sub>2</sub>-HS was significantly improved in comparison with  $\beta$ -MnO<sub>2</sub> synthesized by hydrothermal method to give FDCA in 86% yield for 24 h (Scheme 3). The TG-DTA curve of the recovered catalysts had exothermic peaks with small weight losses at around rt-657 K, which



**Figure 5.** Relationship between FFCA oxidation rate ( $R_0$ ) and reduction rate estimated from H<sub>2</sub>-TPR ( $\blacksquare$ ,  $\alpha$ -MnO<sub>2</sub>;  $\blacktriangle$ ,  $\beta$ -MnO<sub>2</sub>;  $\blacklozenge$ ,  $\beta$ -MnO<sub>2</sub>).



**Figure 6.** (a) XRD patterns for  $\beta$ -MnO<sub>2</sub>–HS (upper) and  $\beta$ -MnO<sub>2</sub> (lower, JCPDS 00–024–0735) and (b) SEM image of  $\beta$ -MnO<sub>2</sub>–HS.

Scheme 3.	Comparison	of Catalytic A	ctivities bet	ween β-
MnO <sub>2</sub> and	$\beta$ -MnO <sub>2</sub> -HS	for Oxidation	of HMF to	o FDCA



suggests that adsorbed organic compounds would be removed. The weight loss (4.6 wt %) of  $\beta$ -MnO<sub>2</sub>–HS was much larger than that (0.5 wt %) of  $\beta$ -MnO<sub>2</sub>; thus, the adsorption amounts of reactants and intermediates would be increased in the case of  $\beta$ -MnO<sub>2</sub>–HS.

Figure 7 shows the time course for aerobic oxidation of HMF to FDCA with  $\beta$ -MnO<sub>2</sub>-HS. The formation rate of



**Figure 7.** Time courses for the oxidation of HMF to FDCA with O<sub>2</sub> over  $\beta$ -MnO<sub>2</sub>-HS and activated MnO<sub>2</sub> ( $\blacksquare$ ,  $\beta$ -MnO<sub>2</sub>-HS; O, activated MnO<sub>2</sub>). Reaction conditions: catalyst (0.05 g), HMF (0.2 mmol), NaHCO<sub>3</sub> (0.4 mmol), water (5 mL), *p*O<sub>2</sub> (1 MPa), 373 K. Experimental errors of FDCA yield were estimated to be ±2%.

FDCA with  $\beta$ -MnO<sub>2</sub>-HS was much higher than that with activated MnO<sub>2</sub> in spite of the lower specific surface area (83  $m^2/g$ ) of  $\beta$ -MnO<sub>2</sub>-HS than activated MnO<sub>2</sub> (122 m<sup>2</sup>/g). The time courses of all products for the oxidation of HMF to FDCA are shown in Figure S18. There was no significant difference in the reaction profiles of HMF, DFF, and HMFCA between activated  $MnO_2$  and  $\beta$ -MnO<sub>2</sub>-HS. On the other hand, both the decrease in FFCA yield and increase in FDCA yield with  $\beta$ -MnO<sub>2</sub>-HS were much faster than that with activated MnO<sub>2</sub>, which suggests that  $\beta$ -MnO<sub>2</sub>-HS more efficiently catalyzed the oxidation of FFCA to FDCA than activated  $MnO_2$ .<sup>16</sup> All these results indicate that the synthesis of high-surface-area  $\beta$ -MnO<sub>2</sub> is a promising strategy for the development of highly efficient oxidation of HMF with MnO<sub>2</sub> catalysts and that planar oxygen site or related adsorbed oxygen species in  $\beta$ -MnO<sub>2</sub> likely play an important role in the present oxidation reaction (Figure S19). However, the reaction rate per surface area of  $\beta$ -MnO<sub>2</sub>-HS (6.2  $\mu$ mol h<sup>-1</sup> m<sup>-2</sup>) for the oxidation of FFCA to FDCA was lower than that (16.4  $\mu$ mol h<sup>-1</sup> m<sup>-2</sup>) of  $\beta$ -MnO<sub>2</sub> probably due to the low crystallinity or different morphology. On the other hand, the effect of  $\varepsilon$ -MnO<sub>2</sub> morphology on its catalytic activity was hardly observed, while the effect of morphologies of other MnO<sub>2</sub> on their catalytic activity could not be ruled out (see the details in the Supporting Information). Since the physicochemical properties of materials (e.g., oxidation state of Mn species, amount of oxygen vacancy, crystallinity, morphology, surface structures, etc.) would be affected by the synthesis methods,<sup>3</sup> calcination temperatures, and constituent elements, thus, further characterization of high-surface-area  $\beta$ -MnO<sub>2</sub> synthesized under various conditions is under investigation.

#### CONCLUSIONS

In summary, a simple nonprecious metal-based system of  $MnO_2/NaHCO_3$  could act as a reusable heterogeneous catalyst for the oxidation of HMF to FDCA with  $O_2$  as the sole oxidant. DFT calculations revealed that the vacancy formation energies of  $MnO_2$  were largely dependent on the crystal structure and the local environment around oxygen atoms. Furthermore,  $\beta$ -MnO<sub>2</sub> exceptionally consists of planar oxygen atoms with lower vacancy formation energy than the other types of crystalline  $MnO_2$ . On the basis of the kinetic, mechanistic, and spectroscopic results, oxidation of the substrate most likely proceeds via oxygen atoms from  $MnO_2$ ,

where the oxidation of FFCA to FDCA is the slowest step. Investigation of the structure-activity relationship for six types of crystalline MnO<sub>2</sub> ( $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -,  $\varepsilon$ -, and  $\lambda$ -MnO<sub>2</sub>) indicated the highest intrinsic reactivity per surface area for  $\beta$ -MnO<sub>2</sub>. Furthermore, the intrinsic reactivity was well correlated with the calculated oxygen vacancy formation energy as well as the experimental reduction rates. The combined computational and experimental approaches can thus lead to the rational design and synthesis of highly effective MnO<sub>2</sub> catalysts for aerobic oxidation. Actually, the potential of  $\beta$ -MnO<sub>2</sub> as a highly active oxidation catalyst for liquid phase aerobic oxidation was evidenced by the successful synthesis of high-surface-area  $\beta$ -MnO<sub>2</sub>. Further functionalization of  $\beta$ -MnO<sub>2</sub> will open up a new avenue for the development of highly efficient heterogeneous catalysts for the oxidation of various types of substrates including biomass-derived compounds.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b09917.

Experimental details, tables, figures (PDF)

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*hara.m.ae@m.titech.ac.jp

#### ORCID 🔍

Keigo Kamata: 0000-0002-0624-8483 Fumiyasu Oba: 0000-0001-7178-5333 Michikazu Hara: 0000-0003-3450-5704

### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

The authors thank M. Yumoto (JASCO Corporation) for the measurement of Raman spectra. This work was supported in part by the ALCA (JPMJAL1205) and PRESTO (JPMJPR15S3 and JPMJPR16N4) programs of the Japan Science and Technology Agency (JST) and Grants-in-Aid for Japan Society for the Promotion of Science (JSPS) Fellows and for Scientific Research from the Ministry of Education, Culture, Science, Sports, and Technology (MEXT) of Japan.

#### REFERENCES

(1) (a) Ciotonea, C.; Averlant, R.; Rochard, G.; Mamede, A.-S.; Giraudon, J.-M.; Alamdari, H.; Lamonier, J.-F.; Royer, S. A Simple and Green Procedure to Prepare Efficient Manganese Oxide Nanopowder for the Low Temperature Removal of Formaldehyde. *ChemCatChem* **2017**, *9*, 2366–2376. (b) Robinson, D. M.; Go, Y. B.; Greenblatt, M.; Dismukes, G. C. Water Oxidation by  $\lambda$ -MnO<sub>2</sub>: Catalysis by the Cubical Mn<sub>4</sub>O<sub>4</sub> Subcluster Obtained by Delithiation of Spinel LiMn<sub>2</sub>O<sub>4</sub>. *J. Am. Chem. Soc.* **2010**, *132*, 11467–11469. (c) Deng, Y.; Wan, L.; Xie, Y.; Qin, X.; Chen, G. Recent Advances in Mn-Based Oxides as Anode Materials for Lithium Ion Batteries. *RSC Adv.* **2014**, *4*, 23914–23935. (d) Zhang, K.; Han, X.; Hu, Z.; Zhang, X.; Tao, Z.; Chen, J. Nanostructured Mn-based Oxides for Electrochemical Energy Storage and Conversion. *Chem. Soc. Rev.* **2015**, *44*, 699–728.

(2) (a) Sarmah, B.; Srivastava, R.; Manjunathan, P.; Shanbhag, G. V. Green and Sustainable Tandem Catalytic Approach for Fine-Chemicals Synthesis Using Octahedral  $MnO_2$  Molecular Sieve: Catalytic Activity versus Method of Catalyst Synthesis. ACS Sustainable Chem. Eng. 2015, 3, 2933–2943. (b) Kona, J. R.;

#### Journal of the American Chemical Society

King'ondu, C. K.; Howell, A. R.; Suib, S. L. OMS-2 for Aerobic, Catalytic, One-pot Alcohol Oxidation-Wittig Reactions: Efficient Access to  $\alpha,\beta$ -Unsaturated Esters. *ChemCatChem* **2014**, *6*, 749–752. (c) Son, Y.-C.; Makwana, V. D.; Howell, A. R.; Suib, S. L. Efficient, Catalytic, Aerobic Oxidation of Alcohols with Octahedral Molecular Sieves. *Angew. Chem., Int. Ed.* **2001**, *40*, 4280–4283. (d) Wang, Y.; Yamaguchi, K.; Mizuno, N. Manganese Oxide Promoted Liquid-Phase Aerobic Oxidative Amidation of Methylarenes to Monoamides Using Ammonia Surrogates. *Angew. Chem., Int. Ed.* **2012**, *51*, 7250–7253.

(3) (a) Hou, J.; Li, Y.; Liu, L.; Ren, L.; Zhao, X. Effect of Giant Oxygen Vacancy Defects on the Catalytic Oxidation of OMS-2 Nanorods. J. Mater. Chem. A **2013**, 1, 6736–6741. (b) Opembe, N. N.; Guild, C.; Kingondu, C.; Nelson, N. C.; Slowing, I. I.; Suib, S. L. Vapor-Phase Oxidation of Benzyl Alcohol Using Manganese Oxide Octahedral Molecular Sieves (OMS-2). Ind. Eng. Chem. Res. **2014**, 53, 19044–19051. (c) Hamaguchi, T.; Tanaka, T.; Takahashi, N.; Tsukamoto, Y.; Takagi, N.; Shinjoh, H. Low-temperature NO-Adsorption Properties of Manganese Oxide Octahedral Molecular Sieves with Different Potassium Content. Appl. Catal., B **2016**, 193, 234–239. (d) Li, K.; Chen, J.; Peng, Y.; Lin, W.; Yan, T.; Li, J. The Relationship between Surface Open Cells of  $\alpha$ -MnO<sub>2</sub> and CO Oxidation Ability from a Surface Point of View. J. Mater. Chem. A **2017**, 5, 20911–20921.

(4) (a) Liang, S.; Teng, F.; Bulgan, G.; Zong, R.; Zhu, Y. Effect of Phase Structure of MnO<sub>2</sub> Nanorod Catalyst on the Activity for CO Oxidation. J. Phys. Chem. C 2008, 112, 5307–5315. (b) Xiao, W.; Wang, D.; Lou, X. W. Shape-Controlled Synthesis of MnO<sub>2</sub> Nanostructures with Enhanced Electrocatalytic Activity for Oxygen Reduction. J. Phys. Chem. C 2010, 114, 1694–1700. (c) Meng, Y.; Song, W.; Huang, H.; Ren, Z.; Chen, S.-Y.; Suib, S. L. Structure– Property Relationship of Bifunctional MnO<sub>2</sub> Nanostructures: Highly Efficient, Ultra-Stable Electrochemical Water Oxidation and Oxygen Reduction Reaction Catalysts Identified in Alkaline Media. J. Am. Chem. Soc. 2014, 136, 11452–11464. (d) Xie, Y.; Yu, Y.; Gong, X.; Guo, Y.; Guo, Y.; Wang, Y.; Lu, G. Effect of the Crystal Plane Figure on the Catalytic Performance of MnO<sub>2</sub> for the Total Oxidation of Propane. CrystEngComm 2015, 17, 3005–3014.

(5) (a) Devaraj, S.; Munichandraiah, N. Effect of Crystallographic Structure of MnO<sub>2</sub> on Its Electrochemical Capacitance Properties. J. Phys. Chem. C 2008, 112, 4406–4417. (b) Cheng, G.; Xie, S.; Lan, B.; Zheng, X.; Ye, F.; Sun, M.; Lu, X.; Yu, L. Phase controllable synthesis of three-dimensional star-like MnO<sub>2</sub> hierarchical architectures as highly efficient and stable oxygen reduction electrocatalysts. J. Mater. Chem. A 2016, 4, 16462–16468. (c) Revathi, C.; Kumar, R. T. R. Electro Catalytic Properties of  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\varepsilon$ -MnO<sub>2</sub> and  $\gamma$ -MnOOH Nanoparticles: Role of Polymorphs on Enzyme Free H<sub>2</sub>O<sub>2</sub> Sensing. Electroanalysis 2017, 29, 1481–1489.

(6) (a) Chen, H.; Wang, Y.; Lv, Y.-K. Catalytic Oxidation of NO over MnO2 with Different Crystal Structures. RSC Adv. 2016, 6, 54032-54040. (b) Gao, F.; Tang, X.; Yi, H.; Chu, C.; Li, N.; Li, J.; Zhao, S. In-situ DRIFTS for the Mechanistic Studies of NO Oxidation over  $\alpha$ -MnO<sub>2</sub>,  $\beta$ -MnO<sub>2</sub> and  $\gamma$ -MnO<sub>2</sub> Catalysts. Chem. Eng. J. 2017, 322, 525-537. (c) Zhao, B.; Ran, R.; Wu, X.; Weng, D. Phase Structures, Morphologies, and NO Catalytic Oxidation Activities of Single-phase MnO2 Catalysts. Appl. Catal., A 2016, 514, 24-34. (d) Zhang, J.; Li, Y.; Wang, L.; Zhang, C.; He, H. Catalytic Oxidation of Formaldehyde over Manganese Oxides with Different Crystal Structures. Catal. Sci. Technol. 2015, 5, 2305-2313. (e) Sun, M.; Lan, B.; Lin, T.; Cheng, G.; Ye, F.; Yu, L.; Cheng, X.; Zheng, X. Controlled Synthesis of Nanostructured Manganese Oxide: Crystalline Evolution and Catalytic Activities. CrystEngComm 2013, 15, 7010-7018. (f) Shi, F.; Wang, F.; Dai, H.; Dai, J.; Deng, J.; Liu, Y.; Bai, G.; Ji, K.; Au, C. T. Rod-, Flower-, and Dumbbell-like MnO2: Highly Active Catalysts for the Combustion of Toluene. Appl. Catal., A 2012, 433-434, 206-213. (g) Jia, J.; Zhang, P.; Chen, L. Catalytic Decomposition of Gaseous Ozone over Manganese Dioxides with Different Crystal Structures. Appl. Catal., B 2016, 189, 210-218.

(7) (a) Smith, P. F.; Deibert, B. J.; Kaushik, S.; Gardner, G.; Hwang, S.; Wang, H.; Al-Sharab, J. F.; Garfunkel, E.; Fabris, L.; Li, J.;

Dismukes, G. C. Coordination Geometry and Oxidation State Requirements of Corner-Sharing  $MnO_6$  Octahedra for Water Oxidation Catalysis: An Investigation of Manganite ( $\gamma$ -MnOOH). ACS Catal. 2016, 6, 2089–2099. (b) Robinson, D. M.; Go, Y. B.; Mui, M.; Gardner, G.; Zhang, Z.; Mastrogiovanni, D.; Garfunkel, E.; Li, J.; Greenblatt, M.; Dismukes, G. C. Photochemical Water Oxidation by Crystalline Polymorphs of Manganese Oxides: Structural Requirements for Catalysis. J. Am. Chem. Soc. 2013, 135, 3494–3501. (c) Zaharieva, I.; Chernev, P.; Risch, M.; Klingan, K.; Kohlhoff, M.; Fischer, A.; Dau, H. Electrosynthesis, Functional, and Structural Characterization of a Water-oxidizing Manganese Oxide. Energy Environ. Sci. 2012, 5, 7081–7089. (d) Dong, Y.; Li, K.; Jiang, P.; Wang, G.; Miao, H.; Zhang, J.; Zhang, C. Simple Hydrothermal Preparation of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -MnO<sub>2</sub> and Phase Sensitivity in Catalytic Ozonation. RSC Adv. 2014, 4, 39167–39173.

(8) (a) Nie, J.; Liu, H. Efficient Aerobic Oxidation of 5-Hydroxymethylfurfural to 2,5-Diformylfuran on Manganese Oxide Catalysts. J. Catal. 2014, 316, 57–66. (b) Fu, X.; Feng, J.; Wang, H.; Ng, K. M. Manganese Oxide Hollow Structures with Different Phases: Synthesis, Characterization and Catalytic Application. Catal. Commun. 2009, 10, 1844–1848. (c) Nawaz, F.; Cao, H.; Xie, Y.; Xiao, J.; Chen, Y.; Ghazi, Z. A. Selection of Active Phase of MnO<sub>2</sub> for Catalytic Ozonation of 4-Nitrophenol. Chemosphere 2017, 168, 1457–1466.

(9) (a) van Putten, R. J.; van der Waal, J. C.; de Jong, E.; Rasrendra, C. B.; Heeres, H. J.; de Vries, J. G. Hydroxymethylfurfural, A Versatile Platform Chemical Made from Renewable Resources. Chem. Rev. 2013, 113, 1499-1597. (b) Hara, M.; Nakajima, K.; Kamata, K. Recent Progress in the Development of Solid Catalysts for Biomass Conversion into High Value-added Chemicals. Sci. Technol. Adv. Mater. 2015, 16, No. 034903. (c) Komanoya, T.; Kinemura, T.; Kita, Y.; Kamata, K.; Hara, M. Electronic Effect of Ruthenium Nanoparticles on Efficient Reductive Amination of Carbonyl Compounds. J. Am. Chem. Soc. 2017, 139, 11493-11499. (d) Kanai, S.; Nagahara, I.; Kita, Y.; Kamata, K.; Hara, M. A Bifunctional Cerium Phosphate Catalyst for Chemoselective Acetalization. Chem. Sci. 2017, 8, 3146-3153. (e) Kong, X.; Zhu, Y.; Fang, Z.; Kozinski, J. A.; Butler, I. S.; Xu, L.; Song, H.; Wei, X. Catalytic Conversion of 5-Hydroxymethylfurfural to Some Value-added Derivatives. Green Chem. 2018, 20, 3657-3682

(10) (a) Bozell, J. J.; Petersen, G. R. Technology Development for the Production of Biobased Products from Biorefinery Carbohydrates—the US Department of Energy's "Top 10" Revisited. *Green Chem.* **2010**, *12*, 539–554. (b) Peelman, N.; Ragaert, P.; Ragaert, K.; De Meulenaer, B.; Devlieghere, F.; Cardon, L. Heat Resistance of New Biobased Polymeric Materials, Focusing on Starch, Cellulose, PLA, and PHA. *J. Appl. Polym. Sci.* **2015**, *132*, 42305. (c) Eerhart, A. J. J. E.; Faaij, A. P. C.; Patel, M. K. Replacing Fossil Based PET with Biobased PEF; Process Analysis, Energy and GHG Balance. *Energy Environ. Sci.* **2012**, *5*, 6407–6422. (d) *Avantium PEF bottles*; Avantium, 2018. http://avantium.com/yxy/products-applications/ fdca/PEF-bottles.html.

(11) (a) Cai, J.; Ma, H.; Zhang, J.; Song, Q.; Du, Z.; Huang, Y.; Xu, J. Gold Nanoclusters Confined in a Supercage of Y Zeolite for Aerobic Oxidation of HMF under Mild Conditions. Chem. - Eur. J. 2013, 19, 14215-14223. (b) Casanova, O.; Iborra, S.; Corma, A. Biomass into Chemicals: Aerobic Oxidation of 5-Hydroxymethyl-2-furfural into 2,5-Furandicarboxylic Acid with Gold Nanoparticle Catalysts. ChemSusChem 2009, 2, 1138-1144. (c) Gupta, N. K.; Nishimura, S.; Takagaki, A.; Ebitani, K. Hydrotalcite-supported Gold-nanoparticle-catalyzed Highly Efficient Base-free Aqueous Oxidation of 5-Hydroxymethylfurfural into 2,5-Furandicarboxylic Acid under Atmospheric Oxygen Pressure. Green Chem. 2011, 13, 824-827. (d) Davis, S. E.; Zope, B. N.; Davis, R. J. On the Mechanism of Selective Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid over Supported Pt and Au Catalysts. Green Chem. 2012, 14, 143-147. (e) Kim, M.; Su, Y.; Fukuoka, A.; Hensen, E. J. M.; Nakajima, K. Aerobic Oxidation of 5-(Hydroxymethyl)furfural Cyclic Acetal Enables Selective Furan-2,5-dicarboxylic Acid Formation with

#### Journal of the American Chemical Society

CeO<sub>2</sub>-Supported Gold Catalyst. Angew. Chem., Int. Ed. 2018, 57, 8235–8239.

(12) (a) Zhou, C.; Deng, W.; Wan, X.; Zhang, Q.; Yang, Y.; Wang, Y. Functionalized Carbon Nanotubes for Biomass Conversion: The Base-Free Aerobic Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid over Platinum Supported on a Carbon Nanotube Catalyst. ChemCatChem 2015, 7, 2853-2863. (b) Han, X.; Geng, L.; Guo, Y.; Jia, R.; Liu, X.; Zhang, Y.; Wang, Y. Base-free Aerobic Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid over a Pt/C-O-Mg Catalyst. Green Chem. 2016, 18, 1597-1604. (c) Ait Rass, H.; Essayem, N.; Besson, M. Selective Aqueous Phase Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid over Pt/C Catalysts: Influence of the Base and Effect of Bismuth Promotion. Green Chem. 2013, 15, 2240-2251. (d) Shen, J.; Chen, H.; Chen, K.; Qin, Y.; Lu, X.; Ouyang, P.; Fu, J. Atomic Layer Deposition of a Pt-Skin Catalyst for Base-Free Aerobic Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid. Ind. Eng. Chem. Res. 2018, 57, 2811-2818.

(13) (a) Artz, J.; Palkovits, R. Base-Free Aqueous-Phase Oxidation of 5-Hydroxymethylfurfural over Ruthenium Catalysts Supported on Covalent Triazine Frameworks. *ChemSusChem* 2015, *8*, 3832–3838.
(b) Yi, G.; Teong, S. P.; Zhang, Y. Base-free Conversion of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid over a Ru/C Catalyst. *Green Chem.* 2016, *18*, 979–983. (c) Mishra, D. K.; Lee, H. J.; Kim, J.; Lee, H.-S.; Cho, J. K.; Suh, Y.-W.; Yi, Y.; Kim, Y. J. MnCo<sub>2</sub>O<sub>4</sub> Spinel Supported Ruthenium Catalyst for Air-oxidation of HMF to FDCA under Aqueous Phase and Base-free Conditions. *Green Chem.* 2017, *19*, 1619–1623. (d) Chen, C.-T.; Nguyen, C. V.; Wang, Z.-Y.; Bando, Y.; Yamauchi, Y.; Bazziz, M. T. S.; Fatehmulla, A.; Farooq, W. A.; Yoshikawa, T.; Masuda, T.; Wu, K. C.-W. Hydrogen Peroxide Assisted Selective Oxidation of 5-Hydroxymethylfurfural in Water under Mild Conditions. *ChemCatChem* 2018, *10*, 361–365.

(14) (a) Liu, B.; Ren, Y.; Zhang, Z. Aerobic Oxidation of 5-Hydroxymethylfurfural into 2,5-Furandicarboxylic Acid in Water under Mild Conditions. *Green Chem.* 2015, *17*, 1610–1617.
(b) Zhang, Z.; Zhen, J.; Liu, B.; Lv, K.; Deng, K. Selective Aerobic Oxidation of the Biomass-derived Precursor 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid under Mild Conditions over a Magnetic Palladium Nanocatalyst. *Green Chem.* 2015, *17*, 1308–1317.
(c) Chen, C.; Li, X.; Wang, L.; Liang, T.; Wang, L.; Zhang, Y.; Zhang, J. Highly Porous Nitrogen- and Phosphorus-Codoped Graphene: An Outstanding Support for Pd Catalysts to Oxidize 5-Hydroxymethylfurfural into 2,5-Furandicarboxylic Acid. ACS Sustainable Chem. Eng. 2017, *5*, 11300–11306.

(15) (a) Ventura, M.; Nocito, F.; de Giglio, E.; Cometa, S.; Altomare, A.; Dibenedetto, A. Tunable Mixed Oxides Based on CeO2 for the Selective Aerobic Oxidation of 5-(Hydroxymethyl)furfural to FDCA in Water. Green Chem. 2018, 20, 3921-3926. (b) Yu, K.; Liu, Y.; Lei, D.; Jiang, Y.; Wang, Y.; Feng, Y.; Lou, L.-L.; Liu, S.; Zhou, W. M<sup>3+</sup>O(-Mn<sup>4+</sup>)<sub>2</sub> Clusters in Doped MnO<sub>x</sub> Catalysts as Promoted Active Sites for the Aerobic Oxidation of 5-Hydroxymethylfurfural. Catal. Sci. Technol. 2018, 8, 2299-2303. (c) Gawade, A. B.; Nakhate, A. V.; Yadav, G. D. Selective Synthesis of 2,5-Furandicarboxylic Acid by Oxidation of 5-Hydroxymethylfurfural over MnFe<sub>2</sub>O<sub>4</sub> Catalyst. Catal. Today 2018, 309, 119-125. (d) Han, X.; Li, C.; Liu, X.; Xia, Q.; Wang, Y. Selective Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid over MnO<sub>x</sub>-CeO<sub>2</sub> Composite Catalysts. Green Chem. 2017, 19, 996-1004. (e) Neatu, F.; Marin, R. S.; Florea, M.; Petrea, N.; Pavel, O. D.; Pârvulescu, V. I. Selective Oxidation of 5-Hydroxymethyl Furfural over Non-precious Metal Heterogeneous Catalysts. Appl. Catal., B 2016, 180, 751-757. (f) Yan, D.; Xin, J.; Zhao, Q.; Gao, K.; Lu, X.; Wang, G.; Zhang, S. Fe-Zr-O Catalyzed Base-free Aerobic Oxidation of 5-HMF to 2,5-FDCA as a Bio-based Polyester Monomer. Catal. Sci. Technol. 2018, 8, 164-175. (g) Yang, Z.; Qi, W.; Su, R.; He, Z. Selective Synthesis of 2,5-Diformylfuran and 2,5-Furandicarboxylic Acid from 5-Hydroxymethylfurfural and Fructose Catalyzed by Magnetically Separable Catalysts. Energy Fuels 2017, 31, 533-541. (h) Yan, Do.; Xin, J.; Shi,

C.; Lu, X.; Ni, L.; Wang, G.; Zhang, S. Base-free Conversion of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid in Ionic Liquids. Chem. Eng. J. 2017, 323, 473-482. (i) Nguyen, C. V.; Liao, Y.-T.; Kang, T.-C.; Chen, J. E.; Yoshikawa, T.; Nakasaka, Y.; Masuda, T.; Wu, K. C.-W. A Metal-free, High Nitrogen-doped Nanoporous Graphitic Carbon Catalyst for an Effective Aerobic HMF-to-FDCA Conversion. Green Chem. 2016, 18, 5957-5961. (j) Xu, S.; Zhou, P.; Zhang, Z.; Yang, C.; Zhang, B.; Deng, K.; Bottle, S.; Zhu, H. Selective Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid Using O<sub>2</sub> and a Photocatalyst of Co-thioporphyrazine Bonded to g-C<sub>3</sub>N<sub>4</sub>. J. Am. Chem. Soc. 2017, 139, 14775-14782. (k) Jain, A.; Jonnalagadda, S. C.; Ramanujachary, K. V.; Mugweru, A. Selective Oxidation of 5-Hydroxymethyl-2-furfural to Furan-2,5-dicarboxylic Acid over Spinel Mixed Metal Oxide Catalyst. Catal. Commun. 2015, 58, 179-182. (1) Saha, B.; Gupta, D.; Abu-Omar, M. M.; Modak, A.; Bhaumik, A. Porphyrin-based Porous Organic Polymer-supported Iron(III) Catalyst for Efficient Aerobic Oxidation of 5-Hydroxymethyl-furfural into 2,5-Furandicarboxylic Acid. J. Catal. 2013, 299, 316-320. (m) Aellig, C.; Scholz, D.; Conrad, S.; Hermans, I. Intensification of TEMPO-Mediated Aerobic Alcohol Oxidations under Three-phase Flow Conditions. Green Chem. 2013, 15, 1975-1980.

(16) Hayashi, E.; Komanoya, T.; Kamata, K.; Hara, M. Heterogeneously-Catalyzed Aerobic Oxidation of 5-Hydroxymethyl-furfural to 2,5-Furandicarboxylic Acid with  $MnO_2$ . *ChemSusChem* **2017**, *10*, 654–658.

(17) (a) Tang, Q.; Jiang, L.; Liu, J.; Wang, S.; Sun, G. Effect of Surface Manganese Valence of Manganese Oxides on the Activity of the Oxygen Reduction Reaction in Alkaline Media. ACS Catal. 2014, 4, 457–463. (b) Kang, M.; Park, E. D.; Kim, J. M.; Yie, J. E. Manganese Oxide Catalysts for NO<sub>x</sub> Reduction with NH<sub>3</sub> at Low Temperatures. Appl. Catal., A 2007, 327, 261–269. (c) Iwanowski, R. J.; Heinonen, M. H.; Paszkowicz, W.; Minikaev, R.; Story, T.; Witkowska, B. X-ray Photoelectron Study of Sn<sub>1-x</sub>Mn<sub>x</sub>Te Semimagnetic Semiconductors. Appl. Surf. Sci. 2006, 252, 3632–3641. (d) Nesbitt, H. W.; Banerjee, D. Interpretation of XPS Mn(2p) Spectra of Mn Oxyhydroxides and Constraints on the Mechanism of MnO<sub>2</sub> Precipitation. Am. Mineral. 1998, 83, 305–315.

(18) Rormark, L.; Wiik, K.; Stolen, S.; Grande, T. Oxygen Stoichiometry and Structural Properties of  $La_{1-x}A_xMnO_{3\pm\delta}(A = Ca$  or Sr and  $0 \le x \le 1$ ). J. Mater. Chem. **2002**, 12, 1058–1067.

(19) Hurst, N. W.; Gentry, S. J.; Jones, A.; McNicol, B. D. Temperature Programmed Reduction. *Catal. Rev.: Sci. Eng.* **1982**, *24*, 233–309.

(20) Momma, K.; Izumi, F. VESTA 3 for Three-dimensional Visualization of Crystal, Volumetric and Morphology Data. *J. Appl. Crystallogr.* **2011**, *44*, 1272–1276.

(21) Blöchl, P. E. Projector Augmented-wave Method. Phys. Rev. B: Condens. Matter Mater. Phys. 1994, 50, 17953-17979.

(22) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, 47, 558–561. (23) Sun, J.; Ruzsinszky, A.; Perdew, J. P. Strongly Constrained and

Appropriately Normed Semilocal Density Functional. *Phys. Rev. Lett.* 2015, 115, 036402–036407.

(24) Kitchaev, D. A.; Peng, H.; Liu, Y.; Sun, J.; Perdew, J. P.; Ceder, G. Entanglement Properties of Correlated Random Spin Chains and Similarities with Conformally Invariant Systems. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *93*, 045132–045136.

(25) (a) Freysoldt, C.; Neugebauer, J.; van de Walle, C. G. Fully Ab Initio Finite-Size Corrections for Charged-Defect Supercell Calculations. *Phys. Rev. Lett.* **2009**, *102*, 016402–016405. (b) Kumagai, Y.; Oba, F. Electrostatics-based Finite-size Corrections for First-principles Point Defect Calculations. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *89*, 195205–195219.

(26) Kumagai, Y.; Choi, M.; Nose, Y.; Oba, F. First-principles Study of Point Defects in Chalcopyrite ZnSnP<sub>2</sub>. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *90*, 125202–125213.

(27) (a) Sugahara, K.; Kamata, K.; Muratsugu, S.; Hara, M. Amino Acid-aided Synthesis of a Hexagonal SrMnO<sub>3</sub> Nanoperovskite Catalyst for Aerobic Oxidation. ACS Omega **2017**, *2*, 1608–1616.

#### Journal of the American Chemical Society

(b) Kawasaki, S.; Kamata, K.; Hara, M. Dioxygen Activation by a Hexagonal SrMnO<sub>3</sub> Perovskite Catalyst for Aerobic Liquid-Phase Oxidation. *ChemCatChem* **2016**, *8*, 3247–3253.

(28) (a) McFarland, E. W.; Metiu, H. Catalysis by Doped Oxides. *Chem. Rev.* **2013**, *113*, 4391–4427. (b) Agarwal, V.; Metiu, H. Energy of Oxygen-Vacancy Formation on Oxide Surfaces: Role of the Spatial Distribution. *J. Phys. Chem. C* **2016**, *120*, 2320–2323. (c) Kamata, K.; Sugahara, K.; Kato, Y.; Muratsugu, S.; Kumagai, Y.; Oba, F.; Hara, M. Heterogeneously Catalyzed Aerobic Oxidation of Sulfides with a BaRuO3 Nanoperovskite. *ACS Appl. Mater. Interfaces* **2018**, *10*, 23792–23801.

(29) (a) Li, L.; Feng, X.; Nie, Y.; Chen, S.; Shi, F.; Xiong, K.; Ding, W.; Qi, X.; Hu, J.; Wei, Z.; Wan, L.-J.; Xia, M. Insight into the Effect of Oxygen Vacancy Concentration on the Catalytic Performance of  $MnO_2$ . ACS Catal. **2015**, 5, 4825–4832. (b) Dawson, J. A.; Tanaka, I. Oxygen Vacancy Formation and Reduction Properties of  $\beta$ -MnO<sub>2</sub> Grain Boundaries and the Potential for High Electrochemical Performance. ACS Appl. Mater. Interfaces **2014**, 6, 17776–17784. (c) Tompsett, D. A.; Parker, S. C.; Islam, M. S. Rutile ( $\beta$ -)MnO<sub>2</sub> Surfaces and Vacancy Formation for High Electrochemical and Catalytic Performance. J. Am. Chem. Soc. **2014**, 136, 1418–1426.

(30) (a) Wang, C.; Ma, J.; Liu, F.; He, H.; Zhang, R. The Effects of  $Mn^{2+}$  Precursors on the Structure and Ozone Decomposition Activity of Cryptomelane-Type Manganese Oxide (OMS-2) Catalysts. *J. Phys. Chem. C* **2015**, *119*, 23119–23126. (b) Luo, J.; Zhang, Q.; Garcia-Martinez, J.; Suib, S. L. Adsorptive and Acidic Properties, Reversible Lattice Oxygen Evolution, and Catalytic Mechanism of Cryptomelane-Type Manganese Oxides as Oxidation Catalysts. *J. Am. Chem. Soc.* **2008**, *130*, 3198–3207. (c) Oxford, G. A. E.; Chaka, A. M. Structure and Stability of Hydrated  $\beta$ -MnO<sub>2</sub> Surfaces. *J. Phys. Chem. C* **2012**, *116*, 11589–11605.

(31) (a) Hill, L. I.; Verbaere, A. On the Structural Defects in Synthetic  $\gamma$ -MnO<sub>2</sub>s. J. Solid State Chem. 2004, 177, 4706–4723. (b) Simon, D. E.; Morton, R. W.; Gislason, J. J. Advances in X-ray Analysis; International Centre for Diffraction Data, 2004; Vol. 47, pp 267–280.

(32) Ching, S.; Landrigan, J. A.; Jorgensen, M. L. Sol-gel Synthesis of Birnessite from  $KMnO_4$  and Simple Sugars. *Chem. Mater.* **1995**, *7*, 1604–1606.

(33) Li, D.; Du, G.; Wang, J.; Guo, Z.; Chen, Z.; Liu, H. Microwaveassisted Synthesis of Flower-like Structure  $\varepsilon$ -MnO<sub>2</sub> as Cathode for Lithium Ion Batteries. *J. Chin. Chem. Soc.* **2012**, *59*, 1211–1215.33.

(34) Baur, W. H. Rutile-type Compounds. V. Refinement of  $MnO_2$  and  $MgF_2$ . Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 1976, B32, 2200–2204.

(35) Gao, T.; Fjellvag, H.; Norby, P. A Comparison Study on Raman Scattering Properties of  $\alpha$ - and  $\beta$ -MnO<sub>2</sub>. *Anal. Chim. Acta* **2009**, *648*, 235–239.

(36) Qiu, G.; Huang, H.; Dharmarathna, S.; Benbow, E.; Stafford, L.; Suib, S. L. Hydrothermal Synthesis of Manganese Oxide Nanomaterials and Their Catalytic and Electrochemical Properties. *Chem. Mater.* **2011**, *23*, 3892–3901.

(37) Kim, N. I.; Sa, Y. J.; Yoo, T. S.; Choi, S. R.; Afzal, R. A.; Choi, T.; Seo, Y. S.; Lee, K. S.; Hwang, J. Y.; Choi, W. S.; Joo, S. H.; Park, J. Y. Oxygen-deficient Triple Perovskites as Highly Active and Durable Bifunctional Electrocatalysts for Oxygen Electrode Reactions. *Sci. Adv.* **2018**, *4*, eaap9360.

(38) MacLean, L. A. H.; Tye, F. L. The Structure of Fully H-Inserted  $\gamma$ -Manganese Dioxide Compounds. J. Solid State Chem. 1996, 123, 150–160.

(39) Fatiadi, A. J. Active Manganese Dioxide Oxidation in Organic Chemistry - Part II. *Synthesis* **1976**, *65*, 133–167.

(40) (a) Si, W.; Wang, Y.; Peng, Y.; Li, X.; Li, K.; Li, J. A Highefficiency  $\gamma$ -MnO<sub>2</sub>-like Catalyst in Toluene Combustion. *Chem. Commun.* **2015**, *51*, 14977–14980. (b) Makwana, V. D.; Son, Y. C.; Howell, A. R.; Suib, S. L. The Role of Lattice Oxygen in Selective Benzyl Alcohol Oxidation Using OMS-2 Catalyst: A Kinetic and Isotope-Labeling Study. *J. Catal.* **2002**, *210*, 46–52. (41) The initial reaction rates per amount of Mn appear in Table S7. The reactivity order was almost consistent with that of HMF oxidation except for unstable  $\lambda$ -MnO<sub>2</sub>.

(42) Kang, M.; Park, E. D.; Kim, J. M.; Yie, J. E. Manganese oxide catalysts for  $NO_x$  reduction with  $NH_3$  at low temperatures. *Appl. Catal.*, A 2007, 327, 261–269.

(43) Irusta, S.; Pina, M. P.; Menéndez, M.; Santamaría, J. Catalytic Combustion of Volatile Organic Compounds over La-Based Perovskites. J. Catal. 1998, 179, 400-412.

(44) (a) Nie, J.; Liu, H. Aerobic Oxidation of 5-Hydroxymethylfurfural to 2,5-Diformylfuran on Supported Vanadium Oxide Catalysts: Structural Effect and Reaction Mechanism. *Pure Appl. Chem.* **2011**, *84*, 765–777. (b) Liu, H.; Cheung, P.; Iglesia, E. Structure and Support Effects on the Selective Oxidation of Dimethyl ether to Formaldehyde Catalyzed by MoO<sub>x</sub> Domains. *J. Catal.* **2003**, *217*, 222–232. (c) Liu, H.; Iglesia, E. Selective Oxidation of Methanol and Ethanol on Supported Ruthenium Oxide Clusters at Low Temperatures. *J. Phys. Chem. B* **2005**, *109*, 2155–2163. (d) Chen, K.; Xie, S.; Bell, A. T.; Iglesia, E. Structure and Properties of Oxidative Dehydrogenation Catalysts Based on MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>. *J. Catal.* **2001**, *198*, 232–242.

(45) The total turnover number for recycling experiments using activated  $MnO_2$  based on bulk and surface Mn species reached up to 1.9 and 12.6, respectively, indicating that  $MnO_2$  could act as a catalyst (see the details in the Supporting Information).