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# Efficient aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran on manganese oxide catalysts

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### ABSTRACT

A cryptomelane-type manganese oxide octahedral molecular sieve with a (2 × 2, 4.6 Å × 4.6 Å) tunnel size (OMS-2) efficiently catalyzed aerobic oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-diformylfuran (DFF) with a high yield of 97.2% at 383 K and 0.5 MPa O<sub>2</sub> in N,N-dimethylformamide. OMS-2 was superior to other MnO<sub>2</sub> catalysts with different morphologies, including OMS-1, OMS-6, and OMS-7 with various tunnel sizes, amorphous MnO<sub>2</sub> and birnessite-type MnO<sub>2</sub>, apparently due to its (2 × 2) tunnel structure and consequently high reducibility and oxidizability. Kinetic and isotopic studies on OMS-2 showed near half-order dependence of the activities on HMF and O<sub>2</sub> concentrations and marked kinetic isotope effects for deuterated HMF at its methylene group. These results, together with the similar initial rates under aerobic and anaerobic conditions, suggest that HMF oxidation to DFF on OMS-2 proceeds via a redox mechanism involving kinetically-relevant steps of C–H bond cleavage in adsorbed alcoholate intermediate, derived from quasi-equilibrated dissociation of HMF, using lattice oxygen and reoxidation of Mn<sup>3+</sup> to Mn<sup>4+</sup> by dissociative chemisorption of O<sub>2</sub>.

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## 1. Introduction

5-Hydroxymethylfurfural (HMF) is an important platform molecule, which can be synthesized readily from cellulose-derived sugars or directly from cellulose [1–4] and applied to produce many value-added chemicals via different catalytic reactions [5]. One of the noteworthy examples is selective oxidation of HMF to 2,5-diformylfuran (DFF), a versatile chemical intermediate for the synthesis of pharmaceuticals [6,7], functional polymers [8–10], and other important products [5].

It is known that the presence of the more reactive  $\alpha$ , $\beta$ -unsaturated aldehyde group in HMF leads to the challenge in the aerobic oxidation of HMF to DFF with a high yield [11]. In this regard, various catalysts have been explored to date for the aerobic oxidation of HMF to DFF [11–18]. Quantitative DFF yields can be achieved by homogeneous catalysts [11,12], but they encounter difficulties, such as separation between catalysts and products. On the other hand, heterogeneous catalysts generally suffer low activity or low DFF selectivity [13–18] or require use of noble metals [19–22]. For example, an 85% DFF yield is obtained on VO<sub>x</sub>/TiO<sub>2</sub> [13], but a high catalyst/substrate ratio (2:1 wt/wt) is required. Supported Ru-based catalysts [20–22], such as  $Ru(OH)_x/HT$ , Ru/C, and  $RuCl_3/Al_2O_3$ , can afford good DFF yields (92–97%), but the Ru catalysts are expensive. Therefore, it is highly desirable to develop more practical and efficient catalysts for the synthesis of DFF.

Recently, a cryptomelane-type manganese oxide octahedral molecular sieve (KMn<sub>8</sub>O<sub>16</sub>·nH<sub>2</sub>O; OMS-2), which possesses a  $2 \times 2$  hollandite structure with one-dimensional pores [23] and also high efficacy in many oxidation reactions [24-26], has been reported to be a cheap and efficient catalyst for the HMF oxidation to DFF [27]. Similar catalytic performance was achieved by Yadav and Sharma on an OMS-2 supported Ag catalyst [28]. However, in these preliminary reports, the key fundamental issues including the relationship between the structure of OMS-2 and its performance and the reaction mechanism remain unclear, which are unequivocally important for further improving the catalyst efficiency in the DFF synthesis. Herein, we present a detailed study on the HMF oxidation to DFF on OMS-2 and other MnO<sub>2</sub> catalysts with different morphologies. Their structures and redox properties are characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET), X-ray photoelectron spectra (XPS), H<sub>2</sub>-temperature-programmed reduction  $(H_2$ -TPR), and  $O_2$ -temperature-programmed oxidation  $(O_2$ -TPO) and correlated with their HMF oxidation activities. Reaction kinetic







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and isotopic studies are also carried out to elucidate the reaction mechanism for the HMF oxidation on OMS-2.

## 2. Experimental

## 2.1. Catalyst preparation

OMS-2 was prepared by a reflux route [23]. Briefly, 30 mL aqueous solution of KMnO<sub>4</sub> (2.2 g) was added dropwise to a solution of MnSO<sub>4</sub>·H<sub>2</sub>O (3.0 g) in water (10 mL) and a concentrated HNO<sub>3</sub> solution (1.0 mL) under magnetic stirring. The resulting slurry was refluxed at 383 K for 24 h. Afterward, the obtained dark brown precipitates were filtered and washed with deionized water until the filtrate was neutral, which were then dried at 383 K overnight.

For comparison, other  $MnO_2$  catalysts including amorphous  $MnO_2$  (AMO), birnessite-type  $MnO_2$  (Na-OL-1), OMS-7,  $\gamma$ -MnO<sub>2</sub>, OMS-6, and OMS-1 were also prepared according to the methods reported in the literature [29–31].  $Mn_2O_3$  and  $Mn_3O_4$  were prepared by calcination of OMS-2 in a N<sub>2</sub> flow at 873 and 1173 K, respectively. MnO was obtained by calcination of MnCO<sub>3</sub> at 873 K in a 20%  $H_2/N_2$  flow. CrO<sub>3</sub>,  $V_2O_5$ , and MoO<sub>3</sub> were purchased (AR, Sinopharm Chemical) and used directly.

#### 2.2. Catalyst characterization

BET surface areas of the catalysts were obtained by nitrogen physisorption at 78.3 K. The measurement was taken on a Micromeritics ASAP 2010 analyzer after the samples were treated at 423 K under dynamic vacuum conditions to desorb the possible adsorbates (e.g., H<sub>2</sub>O and CO<sub>2</sub>).

The Mn contents in the reaction filtrate were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Profile Spec, Leeman Labs).

XRD patterns of the as-prepared catalysts were taken on a Rigaku D/Max-2000 diffractometer in the  $2\theta$  range of 10–80° using a Cu K $\alpha$  radiation source ( $\lambda$  = 1.5406 Å) at a scanning rate of 4°/ min. The measurement was taken at 40 kV and 100 mA.

TEM images were obtained on a Philips Tecnai F30 FEG-TEM operated at 300 kV. Before the measurement, the catalyst powders were treated ultrasonically in ethanol for 30 min and then deposited on carbon-coated Cu grids.

XPS analyses were performed on an AXIS Ultra (Kratos, UK) spectrometer using an Al anode (Al K $\alpha$ ,  $h\nu$  = 1486.6 eV). The measuring chamber was operated at ~5 × 10<sup>-9</sup> Torr. The binding energies were calibrated by referring to the C<sub>1s</sub> line at 284.6 eV.

 $\rm H_2$ -TPR experiments were carried out on a TP-5000 (Tianjin Xianquan) flow unit. Typically, 20 mg samples were placed in a quartz cell and then heated in a 5%  $\rm H_2/N_2$  flow (30 mL/min). The temperature ramped from 298 to 923 K at a rate of 10 K/min. The consumption of  $\rm H_2$  was calibrated by the reduction in pure CuO powder. The initial reduction rates for the MnO<sub>2</sub> catalysts, denoted as  $\rm R_{red,497K}$ , were estimated by the reduction rates at 497 K, corresponding to the temperature at which 5% of the lattice oxygen atoms of OMS-2 were reduced by H<sub>2</sub>.

 $O_2$ -TPO experiments were performed on a TP-5080 (Tianjin Xianquan) flow unit in a way similar to the H<sub>2</sub>-TPR measurement. Before the  $O_2$ -TPO, the samples were reduced in a 5% H<sub>2</sub>/N<sub>2</sub> flow (30 mL/min) for 1 h at 497 K, a low temperature to avoid destroying the tunnel structures of the OMS materials. After the samples were cooled to 298 K, they were heated in a 5%  $O_2$ /He flow (20 mL/min) from 298 to 723 K at a rate of 10 K/min. The consumption of  $O_2$  was calibrated by the oxidation of Cu powder. The initial oxidation rates for the MnO<sub>2</sub> catalysts, denoted as  $R_{oxi,383K}$ , were estimated by the oxidation rates at 383 K, the reaction temperature typically used for HMF oxidation in this work.

#### 2.3. HMF oxidation reactions

HMF oxidation reactions were carried out in a Teflon-lined stainless steel autoclave (50 mL). Typically, 1 mmol HMF (98%, Alfa Aesar) and 50 mg catalysts were introduced to 10 mL DMF (J.T. Baker,  $\leq 0.02\%$  H<sub>2</sub>O) in the autoclave and were stirred at ca. 700 rpm. The reactants and products were analyzed by HPLC (Shimadzu LC-20A) using a UV detector and an Alltech OA-1000 organic acid column (0.005 M H<sub>2</sub>SO<sub>4</sub> mobile phase, 0.7 mL/min flow rate, and 353 K oven temperature). HMF reaction activities were reported as molar HMF conversion rates per gram (or m<sup>2</sup>) of catalysts per hour (i.e., mmol HMF/( $g_{cat}$  h)) or mmol HMF/( $m_{cat}^2$  h)) and selectivities on a carbon basis. For catalyst recycling tests, if not specially stated, the retrieved catalysts were washed thoroughly with deionized water and then dried in vacuum oven before being recycled.

#### 2.4. Kinetic isotope effects and oxygen isotope exchange

Kinetic isotope effects on the HMF oxidation were examined using  $\alpha$ -deuterated HMF (CHO-C<sub>4</sub>H<sub>2</sub>O-CH<sub>2</sub>OD) and  $\beta$ -deuterated HMF (CHO-C<sub>4</sub>H<sub>2</sub>O-CD<sub>2</sub>OH), i.e. HMF molecules deuterated at the hydroxyl (-OH) and methylene (-CH<sub>2</sub>-) groups, respectively, for comparison with undeuterated HMF. The deuterated HMF molecules were prepared according to our previous report [21].

Oxygen isotope exchange reactions between  ${}^{16}O_2$  and  ${}^{18}O_2$  were carried out under the same reaction conditions described above for the HMF oxidation, using a mixture of 0.25 MPa  ${}^{18}O_2$  (97% isotopic purity, GAISI) and 0.25 MPa  ${}^{16}O_2$ . The oxygen isotopomers  ${}^{16}O_2$ ,  ${}^{16}O^{18}O$ , and  ${}^{18}O_2$  were measured by mass spectrometry (Hiden HPR20).

## 3. Results and discussion

## 3.1. Characterization of MnO<sub>2</sub> catalysts

Fig. 1 shows the XRD patterns for the  $MnO_2$  catalysts. AMO only shows a broad peak at  $2\theta$  = 37.2°. The peaks of Na-OL-1 at  $2\theta$  = 12.5 and 25.0° are characteristic features of birnessite materials with layered structures (JCPDS 43-1456), corresponding to the (001) and (002) crystal phases, respectively [32,33]. The patterns of



Fig. 1. XRD patterns for MnO<sub>2</sub> catalysts with different morphologies.

OMS-7 and γ-MnO<sub>2</sub> are consistent with those of pyrolusite-type (JCPDS 24-0735) [29,30] and ramsdellite-type MnO<sub>2</sub> (JCPDS 14-0644) [30,34], which possess tunnel sizes of 1 × 1 (2.3 Å × 2.3 Å) and 1 × 2 (2.3 Å × 4.6 Å), respectively. The pattern of OMS-2 can be well indexed to a pure tetragonal phase of cryptomelane-type MnO<sub>2</sub> (JCPDS 44-0141) with a tunnel size of 2 × 2 (4.6 Å × 4.6 Å) [29,30]. OMS-6 shows the XRD pattern of romanechite-type (JCPDS 14-0627) MnO<sub>2</sub> with a tunnel size of 2 × 3 (4.6 Å × 6.9 Å). The peaks of OMS-1 appear at 2 $\theta$  = 9.4 (not shown here) and 18.6°, reflecting that it possesses a todorokite structure with a tunnel size of 3 × 3 (6.9 Å × 6.9 Å) [31,35]. Taken together, these results demonstrate that the MnO<sub>2</sub> catalysts with expected structures were prepared. Moreover, it can be seen that except OMS-7 and AMO, these MnO<sub>2</sub> catalysts possess similar crystallinities, consistent with the following TEM characterization.

The Mn contents of the MnO<sub>2</sub> catalysts were measured by ICP-AES. As shown in Table 1, OMS-7 and  $\gamma$ -MnO<sub>2</sub> contained 60.0–60.7 wt% Mn, while slightly lower Mn contents (53.8–56.3 wt%) were detected in the other MnO<sub>2</sub> catalysts, namely AMO, Na-OL-1, OMS-2, OMS-6, and OMS-1, mostly likely as a result of their larger sizes of pores that could accommodate other cations (e.g., K, Na, and Mg) up to ~5 wt%. These MnO<sub>2</sub> catalysts possessed BET surface areas in a narrow range of ~40–80 m<sup>2</sup>/g, except for AMO (189 m<sup>2</sup>/g) and OMS-7 (17 m<sup>2</sup>/g). The BET surface areas of these MnO<sub>2</sub> catalysts may be mainly contributed from their external surfaces as nitrogen molecule (0.36 nm) could hardly enter their pores of smaller sizes (e.g., the pore size of OMS-2 is ~0.26 nm) [24,25,36]. According to the previous reports, the accommodation of other cations, such as K, Na, and Mg, inside the pores can signif-

icantly decrease the effective pore sizes of these  $MnO_2$  catalysts [24,25,36]. It appears that the inner pores of the  $MnO_2$  catalysts are not accessible to the reactants, namely HMF (0.82 nm) and oxygen (0.35 nm), and thus, the HMF oxidation reaction mainly occurs on their external surfaces.

The TEM image of the OMS-2 sample shows a nanorod morphology with typical diameters of  $\sim$ 30 nm and lengths of 100–500 nm (Fig. 2a). The fringe distances of 0.68 nm correspond to the lattice spacing of the (101) plane, growing preferentially along the direction of [001] (Fig. 2b). The other MnO<sub>2</sub> catalysts show similar nanorod morphologies, except amorphous AMO and layered Na-OL-1 (Fig. S1). These nanorods have similar lengths of several hundred nanometers, although the diameters of OMS-7 (50–100 nm) are larger than those of the other samples (20–30 nm). The larger diameters of OMS-7 reflect its higher crystallinities, as characterized by XRD (Fig. 1).

O1s XPS spectra were used to probe the surface oxygen species of the  $MnO_2$  catalysts. As shown in Fig. S2 and Scheme S1, three types of surface oxygen species can be identified from their binding energies. The peaks at low binding energies (529.3–529.7 eV), medium binding energies (530.8–531.1 eV), and high binding energies (532.6–533.6 eV) are ascribed to the lattice oxygen atoms (O<sub>1</sub>), oxygen vacancies or surface adsorbed O (OH) groups (O<sub>II</sub>), and adsorbed water (O<sub>III</sub>), respectively [24,37]. Accordingly, the relative fractions of these oxygen species were estimated and are listed in Table 2. Na-OL-1, OMS-7, and OMS-2 possess the most abundant O<sub>I</sub> species (71.5–72.8%). In contrast, lower O<sub>I</sub> species fractions (45.3– 65.2%) are observed for OMS-1 and AMO. On the other side, the fraction of the O<sub>II</sub> species is 38.1% for OMS-1, which is lower

Table 1

Mn contents and surface areas of MnO2 catalysts with different morphologies.

Entry	Catalyst	AMO	Na-OL-1	OMS-7	$\gamma$ -MnO <sub>2</sub>	OMS-2	OMS-6	OMS-1
1	Mn (%)	53.8	55.7	60.7	60.0	56.0	56.3	54.6
2	S <sub>BET</sub> (m <sup>2</sup> /g)	189	57	17	38	81	53	47



Fig. 2. TEM images of OMS-2.

#### Table 2

Relative fractions of surface oxygen species for MnO<sub>2</sub> catalysts with different morphologies.

Entry	Catalyst	OI	O <sub>1</sub>		O <sub>II</sub>		O <sub>III</sub>	
		B.E. (eV)	Fractions (%)	B.E. (eV)	Fractions (%)	B.E. (eV)	Fractions (%)	
1	AMO	529.6	65.2	531.1	26.6	533.2	8.2	
2	Na-OL-1	529.6	71.9	531.1	17.8	533.6	10.3	
3	OMS-7	529.3	71.5	530.8	21.3	532.6	7.2	
4	$\gamma$ -MnO <sub>2</sub>	529.6	66.3	531.1	27.4	533.1	6.3	
5	OMS-2	529.7	72.8	531.1	21.4	533.2	5.8	
6	OMS-6	529.6	68.3	531.1	20.2	533.4	11.5	
7	OMS-1	529.6	45.3	530.8	38.1	532.4	16.5	

(26.6–27.4%) for AMO and  $\gamma$ -MnO<sub>2</sub>, and only 17.8–21.4% for the other samples.

Mn3s XPS spectra were also collected to compare the valence of the surface Mn species for these MnO<sub>2</sub> catalysts (Fig. S3). It is known that the Mn3s multiplet splitting is sensitive to the average Mn oxidation states (AOS (XPS)) [24,38,39] and thus can be used to determine the AOS (XPS) by the following equation [24,39]: AOS (XPS) = 8.95 – 1.13 ( $\Delta$ Mn3s), where ( $\Delta$ Mn3s) represents the magnitude of the Mn3s multiplet splitting (Table S1). The results show that the AOS (XPS) is high (3.83) for OMS-7, low (3.53–3.56) for  $\gamma$ -MnO<sub>2</sub> and OMS-6, and medium (3.62–3.72) for the others. Such difference in the fractions of the lattice oxygen atoms and AOS of the Mn species for these MnO<sub>2</sub> catalysts led to the difference in their redox properties, as discussed below.

The reducibilities of the  $MnO_2$  catalysts were probed by  $H_2$ -TPR. As shown in Fig. 3a, all the MnO<sub>2</sub> catalysts exhibited two or three reduction peaks which can be ascribed to the sequential reduction steps of MnO<sub>2</sub>, i.e. MnO<sub>2</sub>( $\rightarrow$ Mn<sub>2</sub>O<sub>3</sub>)  $\rightarrow$  Mn<sub>3</sub>O<sub>4</sub>  $\rightarrow$  MnO [37,38,40]. It was reported that the initial reduction stages for many metal oxides are the chemical processes most relevant to the redox cycles required for the catalytic turnovers in selective oxidation of different hydrocarbons and alcohols [16,41-43]. Moreover, only 1.5-3.0% of the lattice oxygen atoms on OMS-2 were found to be involved in its redox cycles at 473 K, behaving as the active oxygen species in NO<sub>x</sub>-NH<sub>3</sub> selective catalytic reduction (SCR) and CO oxidation reactions [25,37]. By referring to these previous studies, in this work, the initial reduction rates at 497 K ( $R_{red,497K}$ ) were used to estimate and compare the reducibilities of the different MnO<sub>2</sub> catalysts. As shown in Table 3, AMO and Na-OL-1 are the two most reducible  $MnO_2$  catalysts, affording  $R_{red,497K}$  of 150.6 and 184.0  $\mu$ mol H<sub>2</sub>/(m<sup>2</sup><sub>cat</sub> h), respectively. OMS-7 and OMS-2 are less reducible (119.3 and 94.2  $\mu$ mol H<sub>2</sub>/(m<sup>2</sup><sub>cat</sub> h)), while  $\gamma$ -MnO<sub>2</sub>, OMS-6, and OMS-1 are the least reducible catalysts (56.8-26.9 µmol  $H_2/(m_{cat}^2 h)$ ). This reducibility that tends for the MnO<sub>2</sub> catalysts is in accordance with the change in their AOS values calculated from the H<sub>2</sub>-TPR results (AOS (TPR)). AMO, Na-OL-1, OMS-7, and OMS-2 with higher AOS values (3.76–3.92) were more reducible than  $\gamma$ -MnO<sub>2</sub>, OMS-6, and OMS-1 with lower AOS values (3.39–3.60). Such correlations between AOS and reducibility for these MnO<sub>2</sub> catalysts reflect the involvement of their lattice oxygen atoms in the HMF oxidation, as discussed in the next section. Moreover, it is apparent from Table 3 that the AOS values estimated by H<sub>2</sub>-TPR (AOS (TPR)) are in well agreement with those by XPS (AOS (XPS)), indicating no significant reconstruction on the MnO<sub>2</sub> surfaces [44].

Table 3	
H2-TPR and O2-TPO results for MnO2 catalyst	ts with different morphologies.

Entry	Catalyst	$\begin{array}{l} R_{red,497K}{}^{a} \\ (\mu mol \; H_2/(m_{cat}^2 \; h)) \end{array}$	$\begin{array}{l} R_{\text{oxi,383K}}{}^a \\ (\mu mol \ O_2/(m_{cat}^2 \ h)) \end{array}$	AOS <sup>b</sup> (TPR)	AOS <sup>b</sup> (XPS)
1	AMO	150.6	8.2	3.76	3.72
2	Na-OL-1	184.0	24.6	3.76	3.62
3	OMS-7	119.3	20.1	3.92	3.83
4	$\gamma$ -MnO <sub>2</sub>	56.8	12.4	3.60	3.56
5	OMS-2	94.2	17.0	3.91	3.71
6	OMS-6	46.4	24.5	3.39	3.53
7	OMS-1	26.9	19.5	3.42	3.64

 $^a$   $R_{red,497K}$  and  $R_{oxi,383K}$  represent the rates of reduction/oxidation at 497 and 383 K, respectively.

<sup>b</sup> AOS represents average oxidation state.

The oxidizabilities of the MnO<sub>2</sub> catalysts were probed by O<sub>2</sub>-TPO. Before the O<sub>2</sub>-TPO measurements, the samples were first reduced in H<sub>2</sub> at 497 K for 1 h. As shown in Fig. 3b, most of the MnO<sub>2</sub> catalysts exhibited oxidation peaks in a narrow temperature range of ca. 450–620 K. Similar to the aforementioned definition of  $R_{red,497K}$  in the H<sub>2</sub>-TPR profiles, the initial oxidation rates ( $R_{oxi,383K}$ ) at 383 K can be used to compare the oxidizabilities of the MnO<sub>2</sub> catalysts and their oxidation rates at the HMF oxidation temperature (383 K). As shown in Table 3, the R<sub>oxi,383K</sub> were as high as 24.5–24.6  $\mu$ mol O<sub>2</sub>/(m<sup>2</sup><sub>cat</sub> h) for Na-OL-1 and OMS-6, while only 8.2 and 12.4  $\mu$ mol O<sub>2</sub>/(m<sup>2</sup><sub>cat</sub> h) for AMO and  $\gamma$ -MnO<sub>2</sub>, and 17.0–20.1  $\mu$ mol  $O_2/(m_{cat}^2 h)$  for OMS-7, OMS-2, and OMS-1. Combined with the R<sub>red.497K</sub> results, it can be found that the R<sub>red.497K</sub> of AMO is very high, but it possesses the lowest Roxi,383K among the MnO2 catalysts. In contrast, OMS-6 and OMS-1 possess low Rred,497K, but high Roxi,383K.  $\gamma$ -MnO<sub>2</sub> exhibits both low R<sub>red,497K</sub> and R<sub>oxi,383K</sub>, which are, however, high for Na-OL-1, OMS-7 and OMS-2. The origin of this difference in the redox properties for these MnO<sub>2</sub> catalysts, although remained unclear, might be related to the discrepancy of their Mn-O bond lengths and exposed planes [45,46]. These results suggest that the structure of the MnO<sub>2</sub> catalysts strongly influence their redox properties, which should subsequently determine their reaction activities, as indeed observed in the next section.

## 3.2. HMF oxidation activity and DFF selectivity on MnO<sub>2</sub> catalysts

Table 4 shows the HMF conversions and DFF selectivities in N,N-dimethylformamide (DMF) at 383 K and 0.5 MPa  $O_2$  on



Fig. 3. H<sub>2</sub>-TPR (a) and O<sub>2</sub>-TPO (b) profiles for MnO<sub>2</sub> catalysts with different morphologies.

#### Table 4

Conversions and product selectivities in aerobic oxidation of HMF on MnO<sub>2</sub> catalysts, and for comparison on other metal oxide catalysts.<sup>a</sup>

Entry	Catalyst	Conversion (%)	Selectivi	ty (%)
			DFF	FFCA
1	OMS-2	100	97.2	1.7
2	AMO	59.0	94.7	2.6
3	KMnO <sub>4</sub> <sup>b</sup>	93.4	37.6	33.4 (9.1) <sup>c</sup>
4	MnSO4 <sup>b</sup>	12.1	21.4	9.8
5	$Mn_2O_3^{b}$	37.8	88.7	5.2
6	Mn <sub>3</sub> O <sub>4</sub> <sup>b</sup>	8.2	67.3	10.8
7	MnO <sup>b</sup>	<1	<1	-
8	CrO <sub>3</sub>	77.6	60.3	13.7
9	V <sub>2</sub> O <sub>5</sub>	60.8	49.5	4.8
10	MoO <sub>3</sub>	6.0	69.1	2.3
11	Blank	No reaction	-	-

<sup>a</sup> 383 K, 0.5 MPa O<sub>2</sub>, 1.0 mmol HMF, 50 mg catalyst, 10 mL DMF, 1 h.

<sup>b</sup> The same amount of Mn was used as compared with OMS-2.

<sup>c</sup> The value in the parenthesis is the selectivity to FDCA.

different MnO<sub>2</sub> catalysts. DMF was chosen as solvent because it was superior, in terms of both the catalytic activity and DFF selectivity, to the other polar and non-polar solvents, such as dimethylsulfoxide (DMSO), H<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub>, in the HMF oxidation (Table S2). As shown in Table 4, HMF was completely transformed in 1 h on OMS-2, and the selectivity to DFF was as high as 97.2%, corresponding to a 97.2% DFF yield. Only 1.7% FFCA was detected, which indicates that DFF is stable on OMS-2 in DMF under the reaction conditions employed in this work, as further verified by the separate reaction of DFF under the identical conditions. AMO shows a similar DFF selectivity (94.7%), but with a much lower HMF conversion (59.0%). The precursors used for the preparation of OMS-2, KMnO<sub>4</sub>, and MnSO<sub>4</sub> were also tested. KMnO<sub>4</sub> was efficient for the HMF oxidation (93.4% conversion), but the DFF selectivity was only 37.6%, as a result of the further oxidation of HMF or DFF to FFCA (33.4%) and FDCA (9.1%). In contrast, MnSO<sub>4</sub> shows much lower HMF conversion (12.1%) and DFF selectivity (21.4%). On other manganese oxides with lower valences, the oxidation rates decreased dramatically. Mn<sub>2</sub>O<sub>3</sub> exhibited only a moderate HMF conversion (37.8%) with a DFF selectivity of 88.7%, while Mn<sub>3</sub>O<sub>4</sub> was much less active and MnO was almost inactive for the HMF oxidation. Similar effect of oxidation state of manganese oxides on their activities was also reported for SCR of NO<sub>x</sub> using NH<sub>3</sub> [47]. For comparison with OMS-2, other metal oxides were examined (Table 4). CrO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> were also active for the HMF oxidation, but showing lower HMF conversions (77.6% and 60.8%) and DFF selectivities (60.3% and 49.5%). MoO<sub>3</sub> was, however, not effective under the identical reaction conditions (6.0% HMF conversion and 69.1% DFF selectivity). These results show that only the Mn(IV) dioxide with tunnel structures is efficient for the aerobic oxidation of HMF to DFF.

Considering the broad variety of the tunnel structures of MnO<sub>2</sub>, several other MnO<sub>2</sub> catalysts including Na-OL-1, OMS-7,  $\gamma$ -MnO<sub>2</sub>, OMS-6, and OMS-1 were also examined for comparison with OMS-2 and AMO, as shown in Table 5. These catalysts possess morphologies varying from amorphous (AMO), layered-type (Na-OL-1) to one-dimensional tunnel structures (the other MnO<sub>2</sub> samples) with tunnel sizes ranging from  $(1 \times 1)$  to  $(3 \times 3)$ , as discussed above (Figs. 2 and S1). When compared at similar HMF conversions  $(\sim 30\%)$  in the kinetic regime, OMS-2 and Na-OL-1 exhibited much superior mass activities (77.6 and 95.7 mmol HMF/( $g_{cat}$  h), respectively) than the other MnO<sub>2</sub> catalysts (6.4-24.1 mmol  $HMF/(g_{cat} h)$ ). After normalized by their surface areas, the most active catalysts turned to be Na-OL-1, OMS-7 and OMS-2 (1.68, 1.11, and 0.96 mmol HMF/ $(m_{cat}^2 h)$ , respectively). AMO and OMS-1 were the least active ones  $(0.13-0.14 \text{ mmol HMF}/(m_{cat}^2 \text{ h}))$ , while  $\gamma$ -MnO<sub>2</sub> and OMS-6 showed the moderate activities

#### Table 5

Activities and product selectivities in aerobic oxidation of HMF on MnO<sub>2</sub> catalysts with different morphologies.<sup>a</sup>

Entry	Catalyst	Activity (mmol HMF/(g <sub>cat</sub> h))	Activity (mmol HMF/(m <sup>2</sup> <sub>cat</sub> h))	Selectivity (%)	
				DFF	FFCA
1	AMO	24.1	0.13	95.3	1.3
2	Na-OL-1	95.7	1.68	92.0	1.2
3	OMS-7	12.2	1.11	81.5	1.4
4	$\gamma$ -MnO <sub>2</sub>	14.5	0.38	90.1	1.3
5	OMS-2	77.6	0.96	97.6	1.4
6	OMS-6	17.7	0.34	82.7	1.1
7	OMS-1	6.4	0.14	92.3	1.3

 $^a$  383 K, 0.5 MPa  $O_2,$  1.0 mmol HMF,  ${\sim}1.8~m^2$  catalyst, 10 mL DMF,  ${\sim}30\%$  HMF conversion.

(0.34–0.38 mmol HMF/( $m_{cat}^2$  h)). The DFF selectivities, however, were superior on OMS-2 (97.6%) and AMO (95.3%), and slightly lower on  $\gamma$ -MnO<sub>2</sub>, Na-OL-1, and OMS-1 (90.1–92.3%), while only 81.5–82.7% on OMS-7 and OMS-6. These results clearly demonstrate the strong effect of the structures of the MnO<sub>2</sub> catalysts on their activities, among which OMS-2 is the most efficient catalyst for the synthesis of DFF in term of its highest DFF selectivity and good activity.

The stability and recyclability of the OMS-2 catalyst were examined for six successive cycles in the HMF oxidation at 383 K and 0.5 MPa O<sub>2</sub>. OMS-2 was characterized by XRD (Fig. S4), showing that its crystalline structure remained unaltered after the sixth cycle in the HMF oxidation. The ICP-AES analysis of the filtrate after each reaction cycle showed negligible leaching of the manganese species (<0.1%). Using such filtrates, no further HMF oxidation was detected after the removal of OMS-2, consistent with the ICP-AES result and also confirming the heterogeneous catalysis nature of OMS-2 in the HMF oxidation. Accordingly, as shown in Fig. S5, after recycling the OMS-2 catalyst for six times, the HMF conversion only decreased slightly to 84.2%, while the DFF selectivity remained constant (97.0%). Such slight activity loss most likely arose from the blockage of the active sites by carbonaceous byproducts on OMS-2, as implied by Mizuno et al. in the synthesis of amides [48]. Consistent with such proposition, the activity of the OMS-2 catalyst after the six cycles can be largely regenerated (93.1% HMF conversion) upon calcination at 573 K for 1 h to remove the adsorbed by-products (Fig. S5).

#### 3.3. Effects of reaction parameters on HMF oxidation to DFF

Fig. 4 shows the effect of HMF concentrations on the activities and selectivities for HMF oxidation on OMS-2 at 383 K and 0.5 MPa O<sub>2</sub>. At similar HMF conversions (~30%), the activities increased almost linearly from 0.33 to 0.50 mmol HMF/( $m_{cat}^2$  h) with increasing HMF concentrations from 10 to 25 mmol/L, which then increased gradually to reach a constant value of ~0.60 mmol HMF/( $m_{cat}^2$  h) at above 100 mmol/L. Such effect indicates the saturated adsorption of HMF-derived intermediates (e.g., alcoholate) on the active OMS-2 surfaces, as also observed on Ru/C and other catalysts in the HMF oxidation [13,16,21,49]. The reaction order was estimated to be 0.44 ± 0.06 with respect to HMF concentrations from the linear range. The DFF selectivities decreased slightly from 98.3% to 96.8% with increasing the HMF concentrations from 10 to 150 mmol/L, while the FFCA selectivities were almost unchanged (~1.0%).

Similarly, the product selectivities are not sensitive to the  $O_2$  pressures. As shown in Fig. 5, the DFF (~97%) and FFCA (~1.0%) selectivities remained almost unchanged at similar HMF conversions (~30%) when  $O_2$  pressures increased from 0.1 to 2.0 MPa. However, the effect of  $O_2$  pressures on the activities strongly



Fig. 4. Dependence of activities and selectivities to DFF and FFCA on HMF concentrations for aerobic oxidation of HMF on OMS-2 at ca. 30% HMF conversion (383 K, 0.5 MPa O<sub>2</sub>, 0.1–1.5 mmol HMF, 1–15 mg OMS-2, 10 mL DMF).

depends on the HMF concentrations employed. At a low HMF concentration (10 mmol/L, Fig. 5a), the activities increased slightly from 0.24 to 0.33 mmol HMF/( $m_{cat}^2$  h) with increasing O<sub>2</sub> pressures from 0.1 to 0.5 MPa and then reached a constant value of ~0.35 mmol HMF/( $m_{cat}^2$  h) up to 4.0 MPa. Such phenomenon is similar to that observed on supported  $VO_x$  catalysts [13,16]. Differently, at a high HMF concentration (100 mmol/L, Fig. 5b), the activities increased almost linearly from 0.36 to 0.70 mmol HMF/ $(m_{cat}^2 h)$  with increasing O<sub>2</sub> pressures from 0.1 to 1.0 MPa and then increased more gradually to 1.17 mmol HMF/ $(m_{cat}^2 h)$  at 4.0 MPa. Such different behavior indicates that at high HMF concentrations, the active surfaces of OMS-2 are saturated by the HMF-derived alcoholate species, which hinder the adsorption of  $O_2$  and thus require higher  $O_2$  pressures to improve the surface coverage of oxygen species and HMF oxidation activities. Fu and coworkers [27] also found that the change of oxidant from air to oxygen increased the HMF conversion dramatically from 39% to 99% on OMS-2. Similar phenomenon was reported in oxidation of volatile and phenol compounds on OMS-2

[50,51]. Such requirement for  $O_2$  adsorption is consistent with the Mars–van Krevelen redox mechanism involving the lattice oxygen atoms on OMS-2, as discussed in the next section. The reaction order was estimated to be  $0.47 \pm 0.01$  with respect to  $O_2$  pressures in the linear range (<1.0 MPa), similar to the order in the HMF concentrations, indicating the dissociative chemisorption of  $O_2$  and HMF on the OMS-2 surface, as observed on Ru/C [21].

We also studied the effect of water, an inevitable by-product, on the HMF oxidation on OMS-2 at 383 K and 0.5 MPa  $O_2$ . Water was externally introduced into the reaction solutions by controlling its concentrations in the range of 20–100 mmol/L, corresponding to the amount of water produced in the HMF oxidation with ~20– 100% conversion. As shown in Fig. 6, both the activities (~0.60 mmol HMF/( $m_{cat}^2$  h)) and the selectivities to DFF (~97.5%) and FFCA (~0.7%) remained essentially constant with variation in the H<sub>2</sub>O concentrations between 20 and 100 mmol/L, indicating the lack of inhibition by water for the HMF oxidation on OMS-2, as also observed on the Ru/C catalyst [21]. This result is consistent with



**Fig. 6.** Dependence of activities and selectivities to DFF and FFCA on  $H_2O$  concentrations for aerobic oxidation of HMF on OMS-2 at ca. 30% HMF conversion (383 K, 0.5 MPa  $O_2$ , 1.0 mmol HMF, 0.2–1.0 mmol  $H_2O$ , 10 mg OMS-2, 10 mL DMF).



**Fig. 5.** Dependence of activities and selectivities to DFF and FFCA on O<sub>2</sub> pressures for aerobic oxidation of HMF on OMS-2 at a low HMF concentration ((a) 0.1 mmol HMF, 0.1–2.0 MPa O<sub>2</sub>) and high HMF concentration ((b) 1.0 mmol HMF, 0.1–4.0 MPa O<sub>2</sub>) at ca. 30% HMF conversion (383 K, 10 mg OMS-2, 10 mL DMF).

the aforementioned dominant adsorption of the HMF-derived alcoholate species on the OMS-2 surface, which thus suppresses the adsorption of water. Such difference in adsorption of HMF and water reflects the hydrophobic nature of the OMS-2 surfaces with stronger affinity for organic species than for water, as reported by Suib and coworkers [25], which can account for the observed low fraction of the surface  $O_{III}$  species (from the adsorbed H<sub>2</sub>O molecules) on OMS-2 by XPS (Table 2).

Fig. 7 shows the effect of the reaction temperature on the activities and selectivities in the HMF oxidation on OMS-2. At similar HMF conversions (~30%), the activities increased dramatically from 0.07 to 1.20 mmol HMF/( $m_{cat}^2$  h) with increasing the temperature from 353 to 393 K. The apparent activation energy ( $E_a$ ) was estimated to be 81 kJ/mol, which is comparable with that of VO<sub>x</sub>/TiO<sub>2</sub> catalyst (67–77 kJ/mol) [13,16]. The DFF selectivities decreased slightly from 98.9% to 96.2% when reaction temperature increased from 353 to 393 K while the FFCA selectivities were always below 1% in this temperature range. These results show that OMS-2 is



**Fig. 7.** Dependence of activities and selectivities to DFF and FFCA on reaction temperatures for aerobic oxidation of HMF on OMS-2 at ca. 30% HMF conversion (353–393 K, 0.5 MPa O<sub>2</sub>, 1.0 mmol HMF, 10 mg OMS-2, 10 mL DMF).

advantageous for the aerobic oxidation of HMF, and its activity can be increased at higher temperatures without detriment to its high DFF selectivity.

#### 3.4. Reaction kinetics and mechanism of HMF oxidation

As discussed above, the activities of the MnO<sub>2</sub> catalysts strongly depend on their tunnel structures (Table 5). Such dependence is found to be related to the structural effects on their redox properties as probed by H<sub>2</sub>-TPR and O<sub>2</sub>-TPO (Table 3). The activities (normalized per surface area) of the MnO<sub>2</sub> catalysts, except for AMO, show a good correlation with their reducibilities (Fig. 8a). The more reducible Na-OL-1, OMS-2, and OMS-7 (94.2-184.0 µmol  $H_2/(m_{cat}^2 h))$  exhibited higher activities (0.96–1.68 mmol HMF/  $(m_{cat}^2 h))$  while the less reducible OMS-1, OMS-6, and  $\gamma$ -MnO<sub>2</sub>  $(26.9-56.8 \mu mol H_2/(m_{cat}^2 h))$  led to lower activities (0.14-0.38 mmol HMF/ $(m_{cat}^2 h)$ ). It is noted that AMO had a high reducibility  $(150.6 \,\mu\text{mol}\,\text{H}_2/(\text{m}_{cat}^2 \,\text{h}))$ , but it was the least active MnO<sub>2</sub> catalyst  $(0.13 \text{ mmol HMF}/(m_{cat}^2 \text{ h}))$ , most likely as a result of its low oxidizability, as discussed below, and thus, the limitation of its redox cycle required for the HMF oxidation. Similarly, the activities of the MnO<sub>2</sub> catalysts, except for OMS-6 and OMS-1, increased linearly with their oxidizabilities (Fig. 8b). OMS-6 and OMS-1 had very high oxidizabilities  $(19.5-24.5 \,\mu\text{mol} \, O_2/(m_{cat}^2 \,h))$  but very low reducibilities  $(26.9-46.4 \,\mu\text{mol} \, \text{H}_2/(m_{cat}^2 \, \text{h}))$ , which may account for their low activities. These results show that the efficient HMF oxidation on the MnO<sub>2</sub> catalysts requires their both high reducibilities and high oxidizabilities, as exhibited by Na-OL-1, OMS-2, and OMS-7.

Such requirement indicates the involvement of the lattice oxygen atoms on the MnO<sub>2</sub> catalysts in the HMF oxidation, as indeed confirmed by comparison of the anaerobic and aerobic experiments on OMS-2 under N<sub>2</sub> and O<sub>2</sub> atmospheres, respectively. Fig. 9 shows the DFF yields in the HMF oxidation as a function of reaction time (within 35 min) on OMS-2 at 383 K, and the initial reaction rates were extracted by using a first-order exponential decay function to fit the reaction profiles for the first 2 min. The initial rates were essentially the same (1.18 vs. 1.21 mmol HMF/ ( $m_{cat}^2$  h)) under N<sub>2</sub> and O<sub>2</sub>, reflecting the reactivity of the lattice oxygen atoms on OMS-2 for the HMF oxidation to DFF by the Mars-van Krevelen redox mechanism (Scheme 1), which is consistent with the weak kinetic consequences of O<sub>2</sub> pressures on the HMF oxidation observed at low HMF concentrations (Fig. 5a).



Fig. 8. Relationship between activities and reducibilities (a) and oxidizabilities (b) of MnO<sub>2</sub> catalysts with different morphologies.



Fig. 9. Initial reaction rates on OMS-2 for HMF oxidation under  $O_2$  and  $N_2$  atmospheres, respectively (383 K, 0.5 MPa  $O_2$ , 1.0 mmol HMF, 5 mg OMS-2, 10 mL DMF).



Scheme 1. Proposed reaction mechanism involving Mn<sup>4+</sup>/Mn<sup>3+</sup> redox cycles.

As depicted in Scheme 1, the HMF oxidation to DFF is proposed to proceed via the Mn<sup>4+</sup>/Mn<sup>3+</sup> redox cycles including the HMF oxidation with the lattice oxygen atoms on OMS-2 and the reduction of Mn<sup>4+</sup> to Mn<sup>3+</sup> (Step 1), followed by the replenishment of the consumed lattice oxygen atoms (i.e., oxygen vacancies) by gaseous  $O_2$ and the reoxidation of Mn<sup>3+</sup> to Mn<sup>4+</sup> (Step 2). Characterization of OMS-2 before and after the HMF oxidation at a high HMF concentration (1.0 mmol HMF, 383 K and 0.5 MPa O<sub>2</sub>) by XPS showed the fraction of the surface lattice oxygen atoms decreased from 72.8% to 65.0%, while the fraction of the oxygen vacancies increased from 21.4% to 27.8% after the reaction (Fig. S6). The XPS result indicates that the reoxidation of  $Mn^{3+}$  to  $Mn^{4+}$  by O<sub>2</sub> is a slower step relative to the Mn<sup>4+</sup> reduction step in the redox cycles at high HMF concentrations, which may limit the overall rate of the HMF oxidation and also account for the strong effect of O2 pressures on the activities of OMS-2 observed at high HMF concentrations (Fig. 5b).

The observed near half-order dependence of the HMF oxidation activities on HMF and  $O_2$  concentrations (Figs. 4 and 5) suggests that HMF and  $O_2$  adsorb dissociatively on OMS-2, similar to the finding on Ru/C [21], to form the corresponding adsorbed alcoholate (R-CH<sub>2</sub>O\*, where R hereinafter denotes the furfural CHO-C<sub>4</sub>H<sub>2</sub>O- part of HMF) and hydroxyl (OH\*) species and the adsorbed atomic oxygen (O\*) species, respectively. It has been reported that alcohol oxidation generally involves the C-H bond cleavage of the adsorbed alcoholate species as a kinetically-relevant step [16,26,43]. To understand the kinetic relevance of the C-H bond cleavage in the HMF oxidation on OMS-2, kinetic isotope effects

(KIE) were studied with HMF molecules deuterated at the hydroxyl group (R-CH<sub>2</sub>OD) and at the methylene group (R-CD<sub>2</sub>OH). Table 6 shows the KIE  $(k_{\rm H}/k_{\rm D})$ , defined as the ratio of the HMF oxidation rates for undeuterated and deuterated HMF at 383 K and 0.5 MPa O<sub>2</sub> in the kinetic regime. R-CH<sub>2</sub>OD gave a KIE value of 1.03, close to unity, which indicates that the dissociative adsorption of HMF to form the adsorbed R-CH<sub>2</sub>O\* species is quasi-equilibrated and kinetically inconsequential during the HMF oxidation on OMS-2. However, the use of R-CD<sub>2</sub>OH led to a significant KIE value of 4.19 at a low HMF concentration (0.1 mmol HMF). This value is similar to those observed in the HMF oxidation on Ru/C (3.73) [21] and in oxidation of other alcohols (e.g., p-methylbenzyl alcohol) on  $Ru(OH)_x/Al_2O_3$  (5.0-4.2) at 333-373 K in liquid phases [49]. At a high HMF concentration (1.0 mmol HMF), a smaller KIE value of 1.71, but still greater than unity, was found. Notwithstanding such discrepancy at low and high HMF concentrations. these normal KIE reveal that the C-H bond cleavage of the adsorbed R-CH<sub>2</sub>O\* species is kinetically-relevant in the HMF oxidation on OMS-2. For the dissociative chemisorption of  $O_2$  to  $O^*$ , its irreversible nature was confirmed by oxygen isotope exchange between <sup>16</sup>O<sub>2</sub> and <sup>18</sup>O<sub>2</sub>, showing no detectable formation of the mixed <sup>18</sup>O<sup>16</sup>O isotopomer under the identical reaction conditions. The O<sub>2</sub> dissociation also appears to be kinetically-relevant in the HMF oxidation, as reflected by the combined results at high HMF concentrations including the observed strong effect of O<sub>2</sub> pressures on the HMF oxidation activities (Fig. 5b), the increased fraction of the oxygen vacancies on the used OMS-2 surface characterized by XPS (Fig. S6), and the smaller KIE value (Table 6).

Moreover, the effect of a radical scavenger, e.g. 2,6-di-tertbutyl-p-cresol, on the HMF oxidation was also examined on OMS-2. The scavenger was introduced to the reaction solution, and the DFF yield was 52.1% after reaction for 6 min at 383 K and 0.5 MPa  $O_2$  with 50 mg OMS-2, which was close to the value of 53.7% in the absence of the scavenger. This result suggests that radical intermediates, even present, did not involve in the kinetic relevant steps of the HMF oxidation.

Based on these kinetic and isotopic results, a sequence of elementary steps for the HMF oxidation on OMS-2 is proposed in Scheme 2. In this sequence, the reaction is preceded by the dissociative chemisorption of HMF on a reduced Mn center or oxygen vacancy (denoted as \*) of the OMS-2 surface via interaction with its neighboring lattice oxygen O\* to form the adsorbed R–CH<sub>2</sub>O\* and OH\* species (Step 1). R–CH<sub>2</sub>O\* then undergoes irreversible and kinetically-relevant  $\beta$ -H elimination by its reaction with O\* to form the adsorbed DFF (R–CHO\*) and OH\* species (Step 2). The subsequent recombination of these OH\* groups forms the adsorbed water (H<sub>2</sub>O\*) and O\* species (Step 3), which is assumed to be fast and irreversible on the basis of the observed lack of inhibition by H<sub>2</sub>O (Fig. 6). Afterward, both H<sub>2</sub>O\* and R–CHO\* species readily desorb from the OMS-2 surface to liberate the reduced Mn centers (\*) (Steps 4 and 5). Finally, the reduced Mn centers are reoxidized by

Table	6
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Activities, selectivities, and kinetic isotopic effects (KIE) for a erobic oxidation of HMF on OMS-2.  $^{\rm a}$ 

Entry	Reactant	Activity (mmol HMF/(g <sub>cat</sub> h))	Selectivity (%)		KIE $(k_{\rm H}/k_{\rm D})$	
			DFF	FFCA		
1	R-CH <sub>2</sub> OH	48.3	97.5	1.3	-	
2	R-CH <sub>2</sub> OD	46.9	94.8	1.4	1.03	
3	R-CD <sub>2</sub> OH	28.2	85.2	2.6	1.71	
4	R-CH <sub>2</sub> OH <sup>b</sup>	26.8	98.3	1.1	-	
5	R-CD <sub>2</sub> OH <sup>b</sup>	6.4	86.0	2.3	4.19	

 $^a$  383 K, 0.5 MPa  $O_2,\ 1.0\ mmol\ HMF,\ 10\ mg\ OMS-2,\ 10\ mL\ DMF,\ {\sim}30\%\ HMF$  conversion.

<sup>b</sup> 0.1 mmol HMF.

- (1)  $R CH_2OH + O^* + \stackrel{fast}{\Leftrightarrow} R CH_2O^* + OH^*$
- (2)  $R CH_2O^* + O^* \xrightarrow{slow} R CHO^* + OH^*$
- (3)  $OH^* + OH^* \xrightarrow{fast} H_2O^* + O^*$
- (4)  $H_2O^* \stackrel{fast}{\Leftrightarrow} H_2O + *$
- (5)  $R CHO^* \Leftrightarrow^{fast} R CHO + *$
- (6)  $O_2 + 2 \stackrel{slow}{\ast} 2O^{\ast}$

Scheme 2. Proposed reaction pathways for aerobic oxidation of HMF to DFF on OMS-2.

dissociative chemisorption of  $O_2$  to complete the catalytic cycle (Step 6), which, as mentioned above, is irreversible and assumed to be a kinetically-relevant step.

These proposed elementary steps in Scheme 2, together with pseudo-steady state assumptions for all chemisorbed species and quasi-equilibrium assumptions for Steps 1, 4, and 5, led to the derivation of the HMF oxidation rate equation (Eq. (1)) by referring to the method reported in the literature [21,52,53]. The derivation details of this equation are included in the Supplementary Content.



Fig. 10. Parity plot for measured HMF oxidation activities (reaction conditions: 383 K, 0.1–4.0 MPa  $O_2$ , 0.10–1.5 mmol HMF, 10 mg OMS-2, 10 mL DMF, ~30% HMF conversion) and calculated activities from Eq. (6).

In Eq. (1), each term in the denominator represents the surface coverage of the indicated adsorbed species relative to that of the free sites on the OMS-2 surfaces.  $k_6$  is the rate coefficient for Step 6 while  $K_{-4}$  and  $K_{-5}$  represent the equilibrium constants for DFF and H2O adsorption, respectively.  $M_1$ ,  $M_2$  and  $M_3$  are given by the combination of the rate and equilibrium constants for the elementary steps, as shown below (Eqs. (2)–(4)).

$$M_1 = (2k_6 \cdot k_3)^{1/4} \cdot (K_1 \cdot k_2^{-1})^{1/2}$$
<sup>(2)</sup>

$$M_2 = \left(2k_6 \cdot k_3^{-1}\right)^{1/2} \tag{3}$$

$$M_3 = (K_1 \cdot k_2)^{-1/2} \cdot k_3^{-1/4} \cdot (2k_6)^{3/4}$$
(4)

The surface coverages of the OH<sup>\*</sup>, R–CHO<sup>\*</sup> and H<sub>2</sub>O<sup>\*</sup> species are likely much smaller than those of R–CH<sub>2</sub>O<sup>\*</sup>, O<sup>\*</sup> and free Mn surface sites (<sup>\*</sup>) under our reaction conditions, according to the observed

Table 7Kinetic parameters in HMF oxidation obtained from nonlinear regression analysis ofEq. (5) with kinetic data measured on OMS-2 at 383 K.

Entry	$M_1$ ((mol/L) <sup>-1/2</sup> atm <sup>-1/4</sup> )	$M_3$ ((mol/L) <sup>1/2</sup> atm <sup>-3/4</sup> )	k <sub>6</sub> (h <sup>-1</sup> atm <sup>-1</sup> )	$k_2 \ (h^{-1})$
1	1.49	$\textbf{5.08}\times \textbf{10}^{-2}$	$\textbf{2.95}\times \textbf{10}^{-1}$	7.76

kinetic dependence on HMF,  $O_2$  and  $H_2O$  concentrations and the isotopic data. Therefore, Eq. (1) can be further simplified to Eq. (5).

$$r = \frac{2k_6 \cdot [O_2]}{\left(1 + M_1 \cdot ([O_2])^{1/4} \cdot ([R - CH_2OH])^{1/2} + M_3 \cdot ([O_2])^{3/4} \cdot ([R - CH_2OH])^{-1/2}\right)^2}$$
(5)

The parameters in Eq. (5) were derived from the nonlinear regression analysis of the measured HMF oxidation activities (Figs. 4 and 5), as shown in Eq. (6) and Table 7.

$$r = \frac{0.590 \cdot [O_2]}{\left(1 + 1.49 \cdot [O_2]^{1/4} \cdot [R - CH_2OH]^{1/2} + 0.0508 \cdot [O_2]^{3/4} \cdot [R - CH_2OH]^{-1/2}\right)^2}$$
(6)

As shown in Fig. 10, the predicted HMF oxidation rates from Eq. (6) are found to agree well with the measured rates (Figs. 4 and 5) in a wide range of HMF concentrations (10–150 mmol/L) and  $O_2$  pressures (0.1–4.0 MPa), demonstrating that Eq. (6) can accurately describe the experimental kinetic results. Alternate elementary steps of the HMF oxidation were also considered; for example, the recombination of OH<sup>\*</sup> (Step 3) or the dissociative chemisorption of  $O_2$  (Step 6) was assumed to be reversible. But they did not lead to rate expressions in agreement with the experimental activities or led to discrepancy with the isotopic data. The excellent agreement between these data in Fig. 10 indicates that the proposed ele-

mentary steps in Scheme 2 reflect the reaction mechanism of the aerobic HMF oxidation to DFF on OMS-2.

4. Conclusions

OMS-2 is an efficient and stable catalyst in the selective aerobic oxidation of HMF to DFF, affording a DFF yield of as high as 97.2% at 383 K and 0.5 MPa O<sub>2</sub> in DMF. It exhibits both high activity and DFF selectivity, compared to other MnO<sub>2</sub> catalysts with different structures, including amorphous MnO<sub>2</sub>, Na-OL-1, OMS-7,  $\gamma$ -MnO<sub>2</sub>, OMS-6, and OMS-1, most likely as a result of its  $(2 \times 2)$  tunnel structure and consequently its high reducibility and oxidizability. The correlation between the structures and redox properties of the MnO<sub>2</sub> catalysts and their HMF oxidation activities, combined with the similar initial rates of anaerobic and aerobic HMF oxidation on OMS-2, suggests that the HMF oxidation to DFF proceeds via a Mars-van Krevelen redox mechanism involving Mn<sup>4+</sup>/Mn<sup>3+</sup> redox cycles, and the high oxidation activity requires for both high reducibility and oxidizability of the MnO<sub>2</sub> catalysts. The near half-order dependence of the HMF oxidation activity on the HMF and O<sub>2</sub> concentrations, together with the measured kinetic isotopic data, indicates that the C-H cleavage of the adsorbed alcoholate intermediate using lattice oxygen and the reoxidation of Mn<sup>3+</sup> to Mn<sup>4+</sup> by dissociative chemisorption of O<sub>2</sub> are kinetically-relevant steps in the HMF oxidation on OMS-2. This mechanism is well confirmed by the excellent agreement between the measured HMF oxidation activities and predicted results by this mechanismderived kinetic rate expression in a wide range of HMF and O<sub>2</sub> concentrations. Such insights into the structural requirements and reaction mechanism provide a rationale for the design of more efficient MnO<sub>2</sub> catalysts for the HMF oxidation to DFF and other valuable products.

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#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2014.05.003.

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