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## 1. Introduction

Biomass, a renewable carbon-based resource, represents the most readily implemented, low-cost, and sustainable 'drop-in' supplement for fuel and chemicals that are currently derived from fossil fuel resources.<sup>1,2</sup> The production of value-added chemicals from biomass has thus attracted great attention. Among these chemicals, 2,5-furandicarboxylic acid (FDCA) has been identified as one of the top 10 bio-based valued-added chemicals for establishing the 'bridge' between fossil fuels and biomass resources because it is a key near-market green monomer substitute for petrochemically produced terephthalic acid that is used in a number of important biodegradable polyesters, fine chemicals, pharmaceuticals and agrochemicals.<sup>3-5</sup>

FDCA can be produced from furfural derivatives such as 5-hydroxylmethylfurfural (HMF), 5-methylfurfural, 2-furoic

# A CuMn<sub>2</sub>O<sub>4</sub> spinel oxide as a superior catalyst for the aerobic oxidation of 5-hydroxymethylfurfural toward 2,5-furandicarboxylic acid in aqueous solvent<sup>†</sup>

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A CuMn<sub>2</sub>O<sub>4</sub> spinel oxide was prepared *via* a freezing-assisted sol-gel method and used in the aerobic oxidation of 5-hydroxylmethylfurfural (HMF) toward 2,5-furandicarboxylic acid (FDCA) in aqueous solvent. A highest FDCA yield of 92.1% over the CuMn<sub>2</sub>O<sub>4</sub> spinel oxide was achieved and the catalyst could be regenerated by calcination in air after the sixth consecutive run, outperforming several other Mn-based spinel and single oxide catalysts. Kinetic studies reveal that HMF  $\rightarrow$  2,5-diformylfuran  $\rightarrow$  5-formylfuran-2-carboxylic acid (FFCA)  $\rightarrow$  FDCA is the primary reaction route of the reaction and that the oxidation of FFCA is the rate-determining step over the CuMn<sub>2</sub>O<sub>4</sub> spinel. Characterization measurements show that Mn species enrichment and proper Mn<sup>4+</sup>/Mn<sup>3+</sup>, Cu<sup>2+</sup>/Cu<sup>+</sup> and Cu/Mn ratios on the surface of the catalyst led to an appropriate O<sub>latt</sub>/O<sub>ads</sub>, ratio, which facilitated oxygen mobility between the O<sub>latt</sub>. consumption and the O<sub>latt</sub> generation *via* the refilling of oxygen vacancies. Synergistic effects between Mn and Cu in the CuMn<sub>2</sub>O<sub>4</sub> spinel inhibit the secondary reaction and accelerate the rate-determining step rate to enhance FDCA formation.

acid and its derivatives.<sup>6</sup> The primary synthesis process of FDCA is the selective oxidation of HMF, which is one of the key top 12 platform chemicals derived from C6 sugars through acid-catalyzed cellulose dehydration. Great efforts have been made over the past few decades in exploring active catalysts for the conversion of HMF into FDCA.<sup>2</sup> In early studies, stoichiometric and homogenous catalysts such as HNO<sub>3</sub>,<sup>7</sup> KMnO<sub>4</sub>,<sup>8</sup> Co/Mn/Br,<sup>9</sup> Co(OAc)<sub>2</sub>/Zn(OAc)<sub>2</sub>/Br,<sup>10</sup> and CuCl/t-BuOOH (ref. 11) were explored to transform HMF into FDCA and the maximum FDCA yield was 85%, catalyzed by KMnO<sub>4</sub>. Substantial progress has been made in attempting to produce a heterogeneous catalyst for the aerobic oxidation of HMF to FDCA using O2 as a low-cost and environmentally friendly oxidant in aqueous media. Supported noble metal nanoparticle catalysts, such as Pt,<sup>12-16</sup> Pd,<sup>13,16-20</sup> Au,<sup>21-25</sup> and Ru (ref. 26-28) and their bimetallic catalysts<sup>29-32</sup> have been reported as superior catalysts for HMF oxidation in the presence of base additives. The effect of the support, metal/ bimetal morphology and state, kinetic character and its influencing factors, reaction mechanism and so on have been investigated carefully. Our group has reported that Au-Pd alloy nanoparticles supported on carbon nanotubes (CNTs) are highly efficient and recyclable heterogeneous catalysts for the aerobic oxidation of HMF to FDCA in water under basefree conditions.<sup>31</sup> Moreover, the catalytic performances of Pt

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and Fe<sub>3</sub>O<sub>4</sub>-decorated Pt catalysts for HMF aerobic oxidation toward FDCA have also been explored in our group.<sup>16,33</sup>

In view of the high cost and insufficient supply of noble metals, non-noble catalysts with a unique ability for oxygen activation, such as transition metal oxides, have been also developed for the selective conversion of HMF toward FDCA in thermo-, electro- and photocatalytic processes over the past few years.<sup>2</sup> Oxide catalysts (MO<sub>x</sub>) have been proposed in which the oxidation proceeds via a Mars van Krevelen (MvK) mechanism consisting of two steps: (1)  $MO_x$  oxidizes substrates to form a partially reduced metal species  $(MO_{x-\delta})$ along with oxygen vacancy formation, (2)  $MO_{x-\delta}$  is rapidly oxidized by O2. Therefore, a lower vacancy formation energy has been accepted as the descriptor of the oxidizing capability of a good oxide catalyst.<sup>34</sup> Hayashi et al. studied the effect of a MnO<sub>2</sub> crystal structure on the aerobic oxidation of HMF to FDCA, and their density functional theory (DFT) calculations clarified that the vacancy formation energies of MnO<sub>2</sub> were largely dependent on the local environment around the oxygen atoms and crystal structure.35 DFT and experimental results revealed that  $\beta$ -MnO<sub>2</sub>, with a low vacancy formation energy, was a good candidate as an oxidation catalyst.35 Besides this, several mixed oxides (MnO<sub>x</sub>-CeO<sub>2</sub>, Fe-Zr-O, CuO·MnO<sub>2</sub>·CeO<sub>2</sub>, Mn-Co oxides and Mn-Fe mixed oxides)<sup>36-43</sup> have also been reported to transform HMF into FDCA, and higher FDCA yields have been obtained over mixed oxides than the corresponding mono-metal oxides. Intriguingly, Gawade et al. successfully synthesized a MnFe<sub>2</sub>O<sub>4</sub> spinel oxide for the oxidation of HMF to FDCA, and obtained an 85% yield of FDCA at 100 °C in 5 h using TBHP as the oxidant.44 Zhang et al. synthesized a series of Mn-Co-O catalysts via a simple hydrothermal method and found that a MnCo<sub>2</sub>O<sub>4</sub> spinel exhibited the highest activity for the aerobic oxidation of HMF to FDCA, affording a 70.9% yield of FDCA at 99.5% HMF conversion with 3 equivalents KHCO<sub>3</sub>, which was significantly better than the performances of single oxides (Mn<sub>3</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>) and Mn-Co oxides.<sup>45</sup>

Spinels, as one class of unique mixed oxides, appear to be a promising alternative to precious metal catalysts for oxidation reactions, owing to the abundance of their elements and superior catalytic ability.<sup>46-48</sup> Also, it is easy to improve the activity by tuning the type and compositions of the metal ions in spinel oxides.<sup>49,50</sup> In our previous work, we investigated the composition effect that ZnMn<sub>x</sub>Co<sub>2-x</sub>O<sub>4</sub> containing Mn (x = 0-2.0) spinel oxides has on an oxidation reaction.<sup>50</sup> The catalytic performance of the ZnMn<sub>x</sub>Co<sub>2-x</sub>O<sub>4</sub> spinel oxides indicated that with an increase in the amount of Mn from 0.2 to 1.8, the activity followed the variation of the nominal oxidation state of Mn instead of Co. The copresence of  $Mn^{4+}$  and  $Mn^{3+}$  with a ratio of slightly >1 ( $Mn^{4+}$ : Mn<sup>3+</sup> ratio of 1.58) resulting in moderate oxygen adsorption strength, was the key to achieving high activity. This facilitated the rate-determining step (oxygen adsorption and O vacancy refilling) during CO oxidation.<sup>50</sup> DFT calculations have been used to further verify the eg filling state of Mn and

the O p-band center relative to the Fermi level, proposed to be influential parameters for CO oxidation on  $ZnMn_xCo_{2-x}O_4$  spinel oxides.<sup>50</sup>

In the present work, four Mn-based oxide catalysts were synthesized to exclusively investigate their catalytic activity for HMF oxidation using oxygen as an oxidant in aqueous solutions. The objective is to disclose the effects that the preparation method, structural, redox and morphological properties of the Mn-based spinel catalysts have on HMF oxidation and to elucidate the synergistic effects between the Mn and Cu and the role of the oxygen mobility in the CuMn<sub>2</sub>- $O_4$  spinel catalysts in achieving high catalytic efficiency in the aerobic oxidation of HMF to FDCA. A plausible reaction mechanism is also established and discussed.

## 2. Experimental

#### 2.1. Materials and reagents

Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (>99%) from Aladdin, Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (>98%) from Energy Chemical, and citric acid and ethanol from Sinopharm Chemical Co. Ltd. were used for synthesizing spinel oxide  $(CuMn_2O_4)$ . the Mn–Cu 5-Hydroxymethylfurfural (HMF, 98%) from Sigma-Aldrich, 2,5-diformylfuran (DFF, 98%) from Energy Chemical, and acid (HMFCA, 98%), 5-hydroxymethyl-2-furancarboxylic 5-formylfuran-2-carboxylic acid (FFCA, 98%) and 2,5-furandicarboxylic acid (FDCA, 98%) from J&K Chemicals were used for the catalytic reactions and related quantification. All the purchased chemicals were used as received without further purification or treatment.

#### 2.2. Catalysts preparation

2.2.1 Freezing-assisted sol-gel method (CuMn<sub>2</sub>O<sub>4</sub>). CuMn<sub>2</sub>O<sub>4</sub> spinel oxides were synthesized *via* a sol-gel method using citric acid as the chelating agent. Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O and citric acid mixed in a 1:2:2 molar ratio were dissolved in an ethanol and water mixed solution by stirring. The resulting solution was continuously stirred for a further 3 h. The solution was then placed in a freeze dryer overnight until the sample temperature was below -20 °C and a blue colored solid was formed. The sample was vacuum dried for three days, and then ground into a powder. The powder was calcined in air at 500 °C for 3 h (heating rate: 4 °C min<sup>-1</sup>) to afford the spinel CuMn<sub>2</sub>O<sub>4</sub> powder sample. NiMn<sub>2</sub>O<sub>4</sub>, MnCu<sub>2</sub>O<sub>4</sub> and CuMn<sub>2</sub>O<sub>4</sub> spinels were synthesized using this method.

**2.2.2** Conventional sol-gel method (CuMn<sub>2</sub>O<sub>4</sub>\_CSM). The mixed solution obtained according to the above method was dried at 60 °C for 5 h under magnetic stirring. Programmed heating was carried out in an air atmosphere, and the temperature ramping rate was 4 °C min<sup>-1</sup>. When the temperature reached 500 °C, the sample was calcined at this temperature for 3 h, and finally the spinel structure was obtained. CuMn<sub>2</sub>O<sub>4</sub>\_CSM and LiMn<sub>2</sub>O<sub>4</sub> spinels were synthesized using this method.

2.2.3 Coprecipitation method (CuMn<sub>2</sub>O<sub>4</sub>\_CM). Cu  $(NO_3)_2 \cdot 3H_2O$  (10 mmol) and  $Mn(NO_3)_2$  (20 mmol) were dissolved in 100 mL of deionized water to prepare solution I. Anhydrous Na<sub>2</sub>CO<sub>3</sub> (20 mmol) and NaOH (20 mmol) were dissolved in 60 mL of deionized water to prepare solution II. Solution I was then added dropwise to solution II under vigorous stirring. The resulting suspension was stirred and crystallized at 65 °C for 18 h, cooled to room temperature, and filtered to obtain a white powder. The sample was thoroughly washed with deionized water, and dried at 120 °C overnight, and calcined at 500 °C in air for 4 h. Finally, CuMn<sub>2</sub>O<sub>4</sub>\_CM spinel was obtained.

#### 2.3. Catalytic reaction

The aerobic oxidation of HMF was carried out in a Teflonlined stainless-steel autoclave (NS-50-C276, Anhui Kemi Machinery Technology Co., Ltd. 50 mL). HMF (0.5 mmol) and a certain amount of catalyst and sodium bicarbonate were added to the reactor using deionized water (10 mL) as the solvent. The reaction kettle was installed, purged with oxygen several times and pressurized with 1 MPa of  $O_2$ , the reaction temperature was 120 °C, and stirring was achieved using a magnetic stirrer operated at 600 rpm for 18 h. After the reaction, the autoclave was quickly transferred to ice water. The reaction solution was filtered and stored in a sample vial.

The oxidation of HMF in the absence of oxygen was also conducted: (1) a certain amount of HMF,  $H_2O$  and  $CuMn_2O_4$  catalyst were added to the batch reactor; (2), the reactor was installed and purged with  $N_2$ ; (3) stirred for 10 min then stirring was stopped and the  $N_2$  vented; (4) the procedure of purging with  $N_2 \rightarrow$  stirring  $\rightarrow$  stop stirring  $\rightarrow$  venting with  $N_2$  was carried out three times to ensure the absence of air in the mixture; (5) the reactor was pressurized with  $N_2$  at 1 MPa, and then heated to 120 °C for 3 or 4 h.

The liquid products were analyzed by high performance liquid chromatography (HPLC, Shimazu LC-20 A) using a diode-array detector (DAD) and a Shodex SH-1011 sugar column (8 mm × 300 mm × 6  $\mu$ m), and the mobile phase was 5 mM dilute sulfuric acid solution. At specific wavelengths, various products and reactants were calibrated using standard solutions, 260 nm for HMFCA and FDCA, 285 nm for HMF, and 290 nm for DFF and FFCA. The conversion of HMF, the selectivity and yield of the product were calculated using the following formula.

Conv. (%) = 
$$\frac{n_{\text{HMF},0} - n_{\text{HMF},t}}{n_{\text{HMF},0}}$$
  
Yield (%) =  $\frac{n_{\text{product}} \times N_{\text{carbon number of product}}}{n_{\text{HMF},0} \times 6}$ 

#### 2.4. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained on a Bruker AXS D8 Advanced Focus diffractometer using  $CuK\alpha$  radiation

 $(\lambda = 1.5418 \text{ Å})$ , operated at 40 kV and 40 mA. Scanning electron microscopy (SEM) morphology characterization was conducted using a Quanta FEG 450 microscope operated in high vacuum mode. Transmission electron microscopy (TEM) measurements were carried out on a JEOL JEM 2100F microscope at an acceleration voltage of 300 kV. The molar ratio of Cu/Mn was determined by ICP-OES using ICAP7400.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a US Thermo Fisher ESCALAB 250XI spectrometer. The analysis chamber vacuum was  $8 \times 10^{-10}$ Pa, the excitation source was Al K $\alpha$  ( $h\nu$  = 1486.6 eV), the working voltage was 12.5 kV, the filament current was 16 mA, and the constant energy of the analyzer was 20 eV. Charge correction was performed using the C 1s 284.80 eV combined energy as the energy standard. Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) measurements were performed on a Lambda 950 spectrometer (PerkinElmer) equipped with a 150 mm integrating sphere diffuse reflection accessory at room temperature in the 200-800 nm wavelength range. Fourier-transform infrared (FTIR) spectroscopy analysis was carried out on a Thermo Fisher Scientific spectrometer using the KBr and sample mixed tableting method, in the recording wavelength range of 400-4000 cm<sup>-1</sup>.

Hydrogen temperature-programmed reduction  $(H_2$ -TPR) measurements were carried out on a Micromeritics AutoChem II 2920 analyzer equipped with a mass spectrometry (MS) detector (QGA, Hiden Analytical Ltd.). Sample (50 mg) contained in a quartz reactor was pretreated with argon at 300 °C for 1 h. After cooling the sample to 50 °C, the argon gas was switched to a 10%  $H_2$ -90% Ar (in vol) gas mixture for hydrogen reduction at a flow rate of 30 mL min<sup>-1</sup>. The temperature was increased from 50 to 900 °C at a heating rate of 10 °C min<sup>-1</sup>. O<sub>2</sub> temperature-programmed desorption (O2-TPD) measurements were performed using the same apparatus. Sample (50 mg) contained in a quartz reactor was pretreated with argon at 300 °C for 1 h. After cooling the sample to 50 °C, the argon gas was switched to a 10% O<sub>2</sub>-90% He (in vol) mixed gas for O<sub>2</sub> adsorption at a flow rate of 30 mL min<sup>-1</sup>, and then purged with argon at this temperature. The temperature was then raised to 900 °C at a rate of 10 °C min<sup>-1</sup>, and the data was recorded in an argon stream.

### 3. Results and discussion

#### 3.1. Catalytic performances

**3.1.1 Effect of preparation method.** Various  $CuMn_2O_4$  spinel catalysts prepared using different methods, including  $CuMn_2O_4$  (freezing-assisted sol-gel method),  $CuMn_2O_4\_CSM$  (conventional sol-gel method), and  $CuMn_2O_4\_CM$  (coprecipitation method), were used in the aqueous-phase aerobic oxidation of HMF. The performances of these three catalysts are summarized in Table 1 (entries 1–3). Although HMF was almost completely converted over these three  $CuMn_2O_4$  spinel catalysts (conversions >99.0%), only the

Table 1 Catalytic behavior of different oxide catalysts in the aerobic oxidation of HMF<sup>a</sup>

Entry		Conv.	Yield <sup>b</sup> (%)				
	Catalyst	(%)	DFF	HMFCA	FFCA	FDCA	Others <sup>c</sup>
1	CuMn <sub>2</sub> O <sub>4</sub> _CSM	99.1	0.0	0.0	6.2	13.4	79.5
2	CuMn <sub>2</sub> O <sub>4</sub> _CM	100.0	0.0	0.0	2.5	16.7	80.8
3	CuMn <sub>2</sub> O <sub>4</sub>	100.0	0.0	0.0	1.4	90.1	8.5
4	$LiMn_2O_4$	92.4	1.3	0.0	5.9	35.1	50.1
5	$NiMn_2O_4$	77.1	0.0	0.0	7.1	21.0	49
6	$MnCu_2O_4$	92.1	0.6	3.8	34.3	25.7	27.7
7	CuO-Mn <sub>2</sub> O <sub>3</sub>	88.7	1.0	1.0	38.5	15.3	32.9
8	CuO	66.6	2.5	0.0	9.3	6.4	48.4
9	$Mn_2O_3$	98.7	0.0	0.0	5.8	34.1	58.8
10	$Mn_3O_4$	62.0	0.9	0.0	11.9	5.9	43.3
11	$MnO_2$	100.0	0.0	0.0	3.4	41.4	55.2

<sup>*a*</sup> Reaction conditions: 0.5 mmol of HMF, 0.84 mmol of Cu-based catalyst or 1.68 mmol of Mn-based catalyst, 10 mL of  $H_2O$ , NaHCO<sub>3</sub>/HMF = 2, 1.0 MPa of O<sub>2</sub>, 120 °C, and 18 h. <sup>*b*</sup> DFF, HMFCA, FFCA, and FDCA denotes 2,5-diformylfuran, 5-hydroxymethyl-2-furancarboxylic acid, 5-formyl-2-furan-carboxylicacid, and 2,5-furandicarboxylic acid, respectively. <sup>*c*</sup> Others denote succinic acid, glycolic acid, formic acid, 2,5-furandimethanol (DHMF) and humin, *etc.* General situation, humin is the main by-product.

 $CuMn_2O_4$  catalyst afforded  $\geq 90\%$  FDCA yield. Unsatisfactory FDCA yields were observed over the CuMn<sub>2</sub>O<sub>4</sub>\_CSM and CuMn<sub>2</sub>O<sub>4</sub>CM catalysts, indicating that side reactions occurred to a great extent over these two catalysts. The XRD patterns in Fig. S1<sup>†</sup> show that CuMn<sub>2</sub>O<sub>4</sub> possesses a pure cubic CuMn<sub>2</sub>O<sub>4</sub> spinel phase (JCPDS #84-0543), whereas CuMn<sub>2</sub>O<sub>4</sub>\_CSM and CuMn<sub>2</sub>O<sub>4</sub>\_CM consist of CuMn<sub>2</sub>O<sub>4</sub> spinel and Mn<sub>2</sub>O<sub>3</sub> (ICPDS #89-4836). The preparation of the pure spinel phase benefits from the sol-gel method using citric acid as a chelating agent, which has been widely used to prepare multicomponent oxides such as  $CoAl_2O_4$ , <sup>51</sup> AMn<sub>2</sub>O<sub>4</sub> (A = Cu, Ni and Zn),<sup>52</sup> copper-manganese oxides, and<sup>53</sup> Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>.<sup>54</sup> Zhao et al. first prepared OM-Ti<sup>3+</sup>-Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> via a modificative solgel method and reported the stoichiometric cationic coordination assembly process of Ti4+/Li+-citrate chelate and PEO (polyethylene oxide) segments in Pluronic F127.<sup>54</sup> In this work, we believe that citric acid coordinates with Mn<sup>2+</sup> and Cu<sup>2+</sup> to form a three-dimensional Mn/Cu-citrate chelate gel; after the vacuum freeze-drying, the pyrolysis of this gel then results in a homogeneous mixed CuMn<sub>2</sub>O<sub>4</sub> spinel oxide that has a pure cubic CuMn<sub>2</sub>O<sub>4</sub> spinel phase (JCPDS #84-0543).

**3.1.2 Effect of composition on Mn-based spinel oxides and single oxides.**  $LiMn_2O_4$  and  $NiMn_2O_4$  oxides with a pure cubic spinel phase were also prepared, and their structures were confirmed by XRD characterization (JCPDS #35-0782 for  $LiMn_2O_4$  and JCPDS #71-0852 for  $NiMn_2O_4$ ), as shown in Fig. S2.† Catalytic performances of the  $LiMn_2O_4$  and  $NiMn_2O_4$ oxides are shown in Table 1 (entries 4–5). The FDCA yields over the  $LiMn_2O_4$  and  $NiMn_2O_4$  spinel oxides are only 35.1% and 21%, respectively.  $CuMn_2O_4$  displays a superior catalytic performance in comparison with  $LiMn_2O_4$  and  $NiMn_2O_4$ , even though they possess the same cubic spinel structure (entries 3–5, Table 1).

Considering that composition is a critical factor with respect to the catalytic performances of spinel oxides,  $MnCu_2$ - $O_4$  was also prepared *via* a freezing-assisted sol-gel method. The XRD pattern of  $MnCu_2O_4$  shows diffraction peaks corresponding to mixed phases of  $Cu_{1.5}Mn_{1.5}O_4$  (JCPDS #70-0262) and CuO (JCPDS #44-0706) (Fig. S3†). The FDCA yield over MnCu<sub>2</sub>O<sub>4</sub> (entry 6, Table 1) is 25.7%, remarkably lower than that over CuMn<sub>2</sub>O<sub>4</sub>. Furthermore, single oxide catalysts such as CuO, Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, and MnO<sub>2</sub> exhibit <42% FDCA yield (entries 8–11, Table 1). A mechanical mixture of CuO and Mn<sub>2</sub>O<sub>3</sub> (CuO–Mn<sub>2</sub>O<sub>3</sub>) shows 15.3% FDCA yield (entry 7, Table 1). These results demonstrate that the CuMn<sub>2</sub>O<sub>4</sub> spinel oxide efficiently catalyzes the aerobic oxidation of HMF in comparison to other Mn-based spinel oxides and single metal oxides (entries 3–11, Table 1), affording a high FDCA yield (90.1%, entry 3 in Table 1).

3.1.3 Effect of base additives. The nature and concentration of base additives have a great impact on the catalytic HMF oxidation performance.<sup>36-40</sup> Fig. 1a shows the effect that added base has on the aerobic oxidation of HMF over the CuMn<sub>2</sub>O<sub>4</sub> spinel catalyst. Potassium/sodium bicarbonate/carbonate/hydroxide show noticeable differences. The HMF conversions reach nearly 100% in the presence of different bases, significantly higher than under base-free conditions. The addition of weak bases (NaHCO<sub>3</sub> or KHCO<sub>3</sub>, 2 equiv.) leads to higher FDCA yield. However, less than 50% FDCA yield was observed using medium and strong bases such as Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, NaOH, and KOH. These results are in good agreement with the experimental observations made by Li et al. on the promotion effect of NaHCO<sub>3</sub> and KHCO<sub>3</sub>, suggesting that base additives might facilitate the activation of HMF.36-40 Relatively stronger bases could lead to the degradation of HMF into undetectable humin or other intermediates in side reactions. In this work, NaHCO<sub>3</sub> was found to be more effective at promoting the catalytic performances in comparison with KHCO<sub>3</sub>.

We further explored the optimal amount of NaHCO<sub>3</sub> for the aerobic oxidation of HMF over  $CuMn_2O_4$  spinel oxides. Identical reaction conditions were used, except that the amount of NaHCO<sub>3</sub> was altered from 0 to 3 equivalents. As shown in Fig. 1b, the base amount has a remarkable effect



**Fig. 1** Effect of (a) the base type and (b) the NaHCO<sub>3</sub> equivalent on the aerobic oxidation of HMF over the CuMn<sub>2</sub>O<sub>4</sub> spinel catalyst. Reaction conditions: 0.5 mmol of HMF; 0.84 mmol of CuMn<sub>2</sub>O<sub>4</sub> catalyst; O<sub>2</sub>, 1 MPa; H<sub>2</sub>O, 10 ml; temperature, 120 °C; reaction time, 18 h; n(base)/n(HMF) = 2.

on the selective oxidation of HMF to FDCA. The HMF conversion and FDCA yield were 36.3% and 10.9% in the absence of NaHCO<sub>3</sub>, respectively. In the presence of 1 equivalent of NaHCO<sub>3</sub>, both increased significantly to 81.8% and 35.1%, respectively. Notably, the FDCA yield reached 90.1% when the NaHCO<sub>3</sub>/HMF ratio was increased to 2:1. Further increasing the NaHCO<sub>3</sub> equivalents to 3, the FDCA yield slightly decreased to 88.9%. Therefore, 2 equivalents of NaHCO<sub>3</sub> was adopted in the following studies.

3.1.4 Effect of reaction temperature,  $O_2$  pressure, and catalyst dosage. Fig. 2a shows the influence that temperature

has on the catalytic behavior of  $\text{CuMn}_2\text{O}_4$  in the aerobic oxidation of HMF. Upon increasing the reaction temperature from 90 to 100 °C, the main product was FFCA while the FDCA yield was slowly increased from 5.4 to 11.5%. Intriguingly, both the activity and FDCA yield were significantly increased to 98.2 and 60.0%, respectively, when the reaction temperature was increased to 110 °C. Increasing the reaction temperature to 120 °C, the FDCA yield reached 90.1% at ~100% HMF conversion. However, at a higher temperature of 130 °C, the FDCA yield decreased to 59.2%, suggesting that the high reaction temperature resulted in



**Fig. 2** Effect of the (a) temperature, (b)  $O_2$  pressure, and (c and d) time course on the aerobic oxidation of HMF over the CuMn<sub>2</sub>O<sub>4</sub> spinel catalyst. Reaction conditions: 0.5 mmol of HMF; 0.84 mmol of the CuMn<sub>2</sub>O<sub>4</sub> catalyst; H<sub>2</sub>O, 10 ml; *n*(NaHCO<sub>3</sub>)/*n*(HMF) = 2. Note that for a clear visual display, the changing trends of DFF, HMFCA, FFCA yield with reaction time are shown in (d), respectively.

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HMF decomposition and the occurrence of other side reactions. Although full conversion of HMF could be accomplished at 110 °C, the transformation of FFCA to FDCA was still incomplete and required higher temperatures.

The dependency of aerobic oxidation of HMF on the  $O_2$  pressure was also tested, as shown in Fig. 2b. When the  $O_2$  pressure was 0.5 MPa, HMF conversion was 82.8% and the main product was FFCA. When the  $O_2$  pressure was 1.0 MPa, FDCA was produced as the main product, and its yield reached 90.1%. Further increasing the  $O_2$  pressure to 1.5 MPa slightly boosted the FDCA yield. These results suggest that the catalytic performance of the CuMn<sub>2</sub>O<sub>4</sub> spinel catalyst is sensitive to  $O_2$  pressure over a certain range (0.5–1.0 MPa), and that an excessively high pressure (1.5 MPa) was redundant in terms of promoting the conversion of HMF and the yield of FDCA.

The effect of CuMn<sub>2</sub>O<sub>4</sub> spinel catalyst dosage on the aerobic oxidation of HMF is shown in Fig. S4.† In a reference test, 65.4% of HMF conversion was observed in the absence of catalyst (Table S1<sup>†</sup>). A remarkably low carbon balance was obtained at 44.8%, and the yield of FDCA was only 3.3%. Furthermore, the total yields of DFF, FFCA, and HMFCA were 10.6%, while the yields of byproducts (e.g., formic acid, levulinic acid, 2,5-furandimethanol (DHMF), humin, etc.) were 20%. The color of the liquid after reaction turned to dark-brown from transparent yellow (Fig. S5a†). In sharp contrast, the liquid mixture remained unchanged (light vellow color) during the CuMn<sub>2</sub>O<sub>4</sub>-catalyzed reaction (Fig. S5b<sup>†</sup>). The color change in the HMF oxidation reaction without catalyst was attributed to the significant degradation of HMF, e.g., disproportionation via the Cannizzaro reaction into undetectable by-products and a small quantity of oxidation products.<sup>40</sup> As shown in Fig. S4,† when the catalyst dosage was 0.42 mmol, HMF conversion reached 76.6%, FFCA was the primary product and the FDCA yield was 26.9%. When the amount of catalyst was doubled, the HMF was completely converted, FDCA became the main product and the FDCA yield was 90.1%. Further increasing the catalyst dosage maintained the HMF conversion at 100%, and the FDCA yield slightly improved to 92.1%.

**3.1.5 Time course and reaction pathways.** Fig. 2c shows the catalytic performances of  $\text{CuMn}_2\text{O}_4$  on HMF oxidation as a function of the reaction time. The conversion of HMF presents a linear increase up until nearly complete transformation at 12 h. Similarly, the FDCA yield increased

linearly within 12 h, then it further increased slowly from 12 to 18 h. For the intermediate products, such as DFF, HMFCA, and FFCA, their yields revealed volcano-like curves with an increase in the reaction time, and their maximum values reached 2.1% (at 3 h), 9.2% (at 6 h), and 32.2% (at 6 h), respectively, as shown in Fig. 2d. FFCA served as the main product in the initial 8 h, and the aerobic oxidation of HMF to FDCA over the CuMn<sub>2</sub>O<sub>4</sub> spinel catalyst was a series-parallel reaction. As illustrated in Scheme 1, two pathways exist in the reaction, HMF  $\rightarrow$  DFF  $\rightarrow$  FFCA  $\rightarrow$  FDCA and HMF  $\rightarrow$  HMFCA  $\rightarrow$  FFCA  $\rightarrow$  FDCA. In particular, the aerobic oxidation of FFCA to FDCA. The latter acts as the rate-limiting step, which is further discussed in detail in section 3.1.7.

3.1.6 Reusability of the CuMn<sub>2</sub>O<sub>4</sub> catalyst. Recycling reactions were performed to reveal the stability of the CuMn<sub>2</sub>-O4 spinel catalyst. After each reaction, the catalyst was posttreated by centrifuging it, washing it with deionized water and drying it in an oven at 100 °C. Satisfactory recyclability of the catalyst was observed over six successive runs, as shown in Fig. 3. The HMF conversion was maintained at ~100%. The FDCA yield remained stable in the initial three cycles, and then slightly decreased in the next three cycles. The XRD characterization of the spent catalyst after six reaction runs exhibited the diffraction peaks of carbon species, which originated from the deposition of the reaction mixture. After the regeneration of the spent catalyst by calcination in air at 500 °C for 3 h, the catalyst was still made up of nano-sized particles (30-200 nm, Fig. S6<sup>†</sup>) and possessed a pure cubic spinel phase (JCPDS #84-0543, Fig. S7†), and its catalytic activity could be successfully recovered to the original level at 90% FDCA yield.

**3.1.7 Initial reaction rates and rate-limiting step.** The key steps of HMF oxidation were further evaluated. The oxidation reactions of HMF → DFF, DFF → FFCA, HMF → HMFCA, HMFCA → FFCA, and FFCA → FDCA were carried out under <30% conversions to measure the initial reaction rates. As shown in Table 2, the initial oxidation reaction rates of HMF, DFF, HMFCA, and FFCA over the CuMn<sub>2</sub>O<sub>4</sub> catalyst were 649, 19 820, 299, and 192 µmol g<sup>-1</sup> h<sup>-1</sup>, respectively. The rate of DFF → FFCA oxidation was 66 times that of HMFCA → FFCA oxidation, while the rate of HMF → DFF was 4 times that of HMF → HMFCA oxidation. In view of the nature of HMF oxidation as a series-parallel reaction, HMF → DFF → FFCA



**Scheme 1** Reaction pathway for the selective aerobic reaction of HMF to FDCA over the  $CuMn_2O_4$  spinel catalyst. Reaction conditions: 0.5 mmol of HMF; 0.84 mmol of the  $CuMn_2O_4$  catalyst;  $H_2O$ , 10 ml;  $n(NaHCO_3)/n(HMF) = 2$ .



Fig. 3 The recyclability experiments of the CuMn<sub>2</sub>O<sub>4</sub> spinel catalyst in the oxidation of HMF. Reaction conditions: HMF (0.5 mmol), catalyst (0.84 mmol), O<sub>2</sub>, 1.0 MPa; H<sub>2</sub>O, 10 ml; temperature, 120 °C; reaction time, 18 h;  $n(NaHCO_3)/n(HMF) = 2$ .

→ FDCA was the primary pathway of HMF oxidation with higher reaction rates, whereas HMF → HMFCA → FFCA → FDCA was the secondary pathway with relatively lower reaction rates. It should be noted that the rate of FFCA → FDCA transformation was 0.37 and 0.0097 times those of the HMF → DFF and DFF → FFCA steps, respectively, clearly suggesting that FFCA → FDCA is the rate-limiting step in the primary pathway. The rate-determining step in the secondary pathway (HMF → HMFCA → FFCA → FDCA) is HMF → HMFCA oxidation. Therefore, the transformation of FFCA → FDCA serves as the rate-determining step in the overall HMF oxidation reaction catalyzed by CuMn<sub>2</sub>O<sub>4</sub> spinel oxides.

The initial oxidation reaction rates over the  $MnCu_2O_4$ catalyst were also studied, as shown in Table 2. Although the initial oxidation rate of HMF oxidation over  $MnCu_2O_4$  was slightly faster than that over  $CuMn_2O_4$ , the rates of DFF and FFCA oxidations over the  $MnCu_2O_4$  catalyst were 1/2 and 2/3 of the rates over the  $CuMn_2O_4$  catalyst, respectively. Note that the yield of by-products such as HCOOH, levulinic acid (LA) and humin reached 15% over  $MnCu_2O_4$ .

#### 3.2. Catalyst characterization

In view of the presence of two Jahn-Teller ions ( $Mn^{3+}$  and  $Cu^{2+}$ ) in the  $Cu_xMn_{3-x}O_4$  spinel materials, different Cu/Mn

ratios played significant roles in the catalytic performances.<sup>47,55,56</sup> In this study, when the Cu/Mn ratio was 1:2, 100% HMF conversion and 90.1% FDCA yield were achieved, while when the Cu/Mn ratio was 2:1, only 25.7% FDCA yield was obtained with 92.1% HMF conversion. Hence, the physical and chemical properties of the CuMn<sub>2</sub>O<sub>4</sub> and MnCu<sub>2</sub>O<sub>4</sub> catalysts were benchmarked using various characterization techniques.

3.2.1 Bulk compositions and structures of the CuMn<sub>2</sub>O<sub>4</sub> and MnCu<sub>2</sub>O<sub>4</sub> catalysts. The crystal structures of the CuMn<sub>2</sub>-O4 and MnCu2O4 oxide catalysts were confirmed by XRD (Fig. S1 and S3<sup>†</sup>). As mentioned in section 3.1.1, the XRD pattern of CuMn<sub>2</sub>O<sub>4</sub> oxide shows sharp crystalline peaks corresponding to pure cubic CuMn<sub>2</sub>O<sub>4</sub> spinel phase. The pattern of MnCu<sub>2</sub>O<sub>4</sub> oxide includes Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and CuO phases. CuMn<sub>2</sub>O<sub>4</sub> and MnCu<sub>2</sub>O<sub>4</sub> oxide catalysts were measured by inductively coupled plasma mass spectrometry (ICP-MS) to calculate the Mn/Cu ratios, as shown in Table S5.<sup>†</sup> The results indicate that the ICP-MS experimentally measured Cu/Mn ratios in the stoichiometry of the final oxides matched the theoretical values, which were also the Cu/Mn ratios used in preparing these oxides. The surface areas of CuMn<sub>2</sub>O<sub>4</sub> and MnCu<sub>2</sub>O<sub>4</sub> were measured as 18.8 and 19.5 m<sup>2</sup> g<sup>-1</sup>, respectively. The SEM analyses (Fig. S8<sup>+</sup>) indicate that both CuMn<sub>2</sub>O<sub>4</sub> and MnCu<sub>2</sub>O<sub>4</sub> comprise nano-sized particles that range in size from 30 to 200 nm.

The TEM, high-resolution TEM (HRTEM), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of the CuMn<sub>2</sub>O<sub>4</sub> and MnCu<sub>2</sub>O<sub>4</sub> catalysts are presented in Fig. 4 and S5.<sup>†</sup> The lattice spacings of 0.25, 0.29 and 0.48 nm can be observed clearly from the HRTEM image (Fig. 4b), corresponding well to the (311), (220), and (111) standard planes of the CuMn<sub>2</sub>O<sub>4</sub> spinel. For the MnCu<sub>2</sub>O<sub>4</sub> oxides, cubic lattices with distances between the planes of 0.21, 0.25, 0.29, and 0.48 nm can be identified, as shown in Fig. S9b.† These values are identical to the distances of the (400), (311), (220), and (111) standard planes of the Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> spinel. 0.25 nm corresponds to the (002) planes of CuO. Energy-dispersive X-ray spectroscopy (EDS mapping) was used to directly observe the distribution characteristics of the spinel target elements. Cu, Mn, and O elements were found to be evenly distributed and highly dispersed in CuMn<sub>2</sub>O<sub>4</sub> (Fig. 4d–f). For MnCu<sub>2</sub>O<sub>4</sub>, the Cu, Mn,

Table 2	Initial reaction rates of	f HMF,	DFF, HMFCA	and FFCA	oxidation	over various catal	ysts <sup>a</sup>
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	Initial reaction rate ( $\mu$ mol g <sup>-1</sup> h <sup>-1</sup> )												
Catalyst	HMF oxidation <sup>b</sup>	Step 1 HMF $\rightarrow$ DFF	Step 1' HMF $\rightarrow$ HMFCA	Step 2 DFF $\rightarrow$ FFCA	Step 2' HMFCA $\rightarrow$ FFCA	Step 3 FFCA $\rightarrow$ FDCA							
CuMn <sub>2</sub> O <sub>4</sub>	649	519	130	19 820	299	192							
MnCu <sub>2</sub> O <sub>4</sub>	604	604	_	9870	_	127							
CuO	475	475	_	30 543	_	9							
$Mn_2O_3$	1309	1309	_	51 988	_	1250							
MnO <sub>2</sub>	3317	3317	_	32 168	_	705							

<sup>*a*</sup> Reaction conditions: 84 mg of NaHCO<sub>3</sub>, 10 mL of H<sub>2</sub>O, 1 MPa of O<sub>2</sub>, 120 °C. The details are referred to in Tables S2–S4.† <sup>*b*</sup> The initial reaction rate of HMF oxidation is equal to the rate of step 1 plus the rate of step 1'.



Fig. 4 (a) TEM, (b) HRTEM, (c) HAADF-STEM images and corresponding EDS mappings of (d) Cu, (e) Mn and (f) O elements, respectively, of the  $CuMn_2O_4$  catalysts.

O elements were found to be evenly distributed and Cu was densely distributed in some areas (Fig. S9d-f†), confirming the presence of copper oxide in the  $MnCu_2O_4$  spinel.

3.2.2 Bulk redox properties of the  $CuMn_2O_4$  and  $MnCu_2O_4$  catalysts. H<sub>2</sub>-TPR experiments were performed to determine the reducibility of the  $CuMn_2O_4$  and  $MnCu_2O_4$  samples



Fig. 5  $H_2$ -TPR profiles of the CuMn<sub>2</sub>O<sub>4</sub>, MnCu<sub>2</sub>O<sub>4</sub>, CuO, and Mn<sub>2</sub>O<sub>3</sub> catalysts.

(Fig. 5). The H<sub>2</sub>-TPR profile of CuMn<sub>2</sub>O<sub>4</sub> shows one main peak at 252 °C and one shoulder peak at 187 °C. There is one broad peak at 217 °C in the MnCu<sub>2</sub>O<sub>4</sub> H<sub>2</sub>-TPR profile. Note that the reduction profile of pure CuO is characterized by a main peak at 268 °C, and a two-step reduction profile was observed for Mn<sub>2</sub>O<sub>3</sub> at 370 and 500 °C, attributed to the reduction of Mn<sub>2</sub>O<sub>3</sub> to Mn<sub>3</sub>O<sub>4</sub> and Mn<sub>3</sub>O<sub>4</sub> to MnO.<sup>46,47,55</sup> Hence, the reduction temperatures of the CuMn<sub>2</sub>O<sub>4</sub> and MnCu<sub>2</sub>O<sub>4</sub> spinel samples were lower than those of pure CuO and Mn<sub>2</sub>O<sub>3</sub>, implying enhanced reducibility and oxygen mobility owing to the Jahn–Teller effect on Cu–Mn spinel oxide and the synergistic interaction between Mn<sup>δ+</sup> and Cu<sup>δ+</sup> ions.

O2-TPD profiles of the CuMn2O4 and MnCu2O4 catalysts were analyzed to determine the oxygen species, as presented in Fig. 6. The desorption of reactive surface oxygen species and lattice oxygen species occurred at moderate temperatures from 300 to 600 °C and relatively higher temperatures above 600 °C, respectively.<sup>28</sup> The desorption temperature of the surface oxygen species of CuMn<sub>2</sub>O<sub>4</sub> was 416.1 °C, ~35 °C lower than that of the MnCu<sub>2</sub>O<sub>4</sub> oxide, indicating the higher oxygen mobility of the CuMn<sub>2</sub>O<sub>4</sub> in comparison with that of MnCu<sub>2</sub>O<sub>4</sub>. The desorption of the lattice oxygen species at above 600 °C included two peaks, at 710.6 and 844.6 °C, for MnCu<sub>2</sub>O<sub>4</sub> and 719.4 and 772.7 °C for CuMn<sub>2</sub>O<sub>4</sub>. The distinct desorption behavior of the lattice oxygen species (e.g., easier desorption from CuMn<sub>2</sub>O<sub>4</sub>) reflects the different degrees of the Jahn Teller effect of the  $Cu^{\delta+}$  and  $Mn^{\delta+}$  ions and Cu-O-Mn interaction strengths due to the various location and ratio of these two ions in the catalysts.

3.2.3 Surface properties of the CuMn<sub>2</sub>O<sub>4</sub> and MnCu<sub>2</sub>O<sub>4</sub> catalysts. The FTIR spectra of the CuMn<sub>2</sub>O<sub>4</sub> and MnCu<sub>2</sub>O<sub>4</sub> samples display peaks from 800 to 400 cm<sup>-1</sup> in low-frequency mode, assigned to M–O lattice vibrations. The bands above 580 cm<sup>-1</sup> can be readily indexed to the vibration of atoms in tetrahedral oxygen environment corresponding to A–O of the AMn<sub>2</sub>O<sub>4</sub> in the spinels.<sup>56–60</sup> The bands between 500 and 570 cm<sup>-1</sup> correspond to the vibration of atoms in the octahedral oxygen environment mainly as a result of the manganese in the Mn-base spinel (Fig. S10†). The bands at 439.0 cm<sup>-1</sup> belong to the vibration mode of Cu–O–Mn in the Cu–Mn spinel.<sup>56–60</sup>



Fig. 6  $O_2$ -TPD profiles of the CuMn<sub>2</sub>O<sub>4</sub> and MnCu<sub>2</sub>O<sub>4</sub> catalysts.

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The deconvoluted XPS spectra of the Cu 2p, Mn 2p and O 1s electronic energy levels in the CuMn<sub>2</sub>O<sub>4</sub> and MnCu<sub>2</sub>O<sub>4</sub> samples are displayed in Fig. 7 and S11,† respectively, and their corresponding surface atomic ratios of Cu:Mn:O are also reported in Table 3. It is shown that the Mn<sup>3+</sup>, Mn<sup>4+</sup>, Cu<sup>2+</sup>, Cu<sup>+</sup>, lattice oxygen (O<sup>2-</sup>, O<sub>latt.</sub>) and reactive surface oxygen (O<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>2-</sup> and/or O<sup>-</sup>, O<sub>ads.</sub>) all coexist on the surface of the CuMn<sub>2</sub>O<sub>4</sub> sample, while there is also Mn<sup>2+</sup> on the surface of the MnCu<sub>2</sub>O<sub>4</sub> sample.

The binding energies (BEs) of  $Mn^{2+}$ ,  $Mn^{3+}$  and  $Mn^{4+}$ (2p<sub>3/2</sub>) of the CuMn<sub>2</sub>O<sub>4</sub> and MnCu<sub>2</sub>O<sub>4</sub> samples are approximately 640.5, 642.1 and 644.0 eV, respectively.<sup>55,60-64</sup> Clearly signal differences can be observed in the Mn 2p region, and each signal has two different components. Under the condition that the peak area ratio of 2p<sub>3/2</sub> and 2p<sub>1/2</sub> is 2: 1, and the half-peak widths are nearly identical, the two sets of peaks were well fitted by a Mn 2p electron curve. The Mn compositions on the surface of the CuMn<sub>2</sub>O<sub>4</sub> sample were  $Mn^{3+}$  and  $Mn^{4+}$ , and the ratio of  $Mn^{3+}:Mn^{4+}$  was 59.3:40.7 (Table 3). However, there were three compositions on the MnCu<sub>2</sub>O<sub>4</sub> surface,  $Mn^{2+}$ ,  $Mn^{3+}$ , and  $Mn^{4+}$ , and the ratio of  $Mn^{2+}:Mn^{3+}:Mn^{4+}$  was 25.9:36.6:37.5 (Table 3).

The Cu 2p XPS spectra of the CuMn<sub>2</sub>O<sub>4</sub> and MnCu<sub>2</sub>O<sub>4</sub> samples are shown in Fig. 7 and S8,<sup>†</sup> respectively. The Cu 2p spectrum of both samples can be resolved into Cu  $2p_{1/2}$  and Cu  $2p_{3/2}$ . The signal with low binding energy (930.7 eV) was attributed to Cu<sup>+</sup>  $2p_{3/2}$ , and the signal at high binding energy (933.7 eV) was indicative of Cu<sup>2+</sup>  $2p_{3/2}$  along with its satellite from 938.0 to 948.0 eV.<sup>55,60–64</sup> Even though the presence of Cu<sup>+</sup> was clearly distinguishable in the CuMn<sub>2</sub>O<sub>4</sub> and MnCu<sub>2</sub>O<sub>4</sub> samples, this Cu<sup>+</sup> phase was not observed in the XRD pattern of the sample due to the detection limit of the XRD technique.

The ratio of  $Cu^+: Cu^{2+}$  on the surface of  $CuMn_2O_4$  and  $MnCu_2-O_4$  was 38.3:61.7 and 14.2:85.8, respectively (Table 3).

The corresponding O 1s XPS spectra of the CuMn<sub>2</sub>O<sub>4</sub> and MnCu<sub>2</sub>O<sub>4</sub> samples are shown in Fig. 7 and S8,† respectively. The deconvolution of the O 1s spectrum clearly shows two surface oxygen species at 529.6 and 530.9 eV, attributed to  $O_{latt.}$  and  $O_{ads.}$ .<sup>64–68</sup> The O quantitative analysis of the XPS is listed in Table 3. On the surface of the CuMn<sub>2</sub>O<sub>4</sub> sample, the  $O_{latt.}$  amount was nearly equal to that of  $O_{ads.}$ , in a ratio of 50.7:49.3. However, on the MnCu<sub>2</sub>O<sub>4</sub> surface, the  $O_{latt.}$  content (44.7%) was slightly lower than the  $O_{ads.}$  content (55.3%).

To better understand the surface properties together with the bulk properties, quantitative XPS analysis was carried out, as shown in Table 3. Comparing the surface Mn molar fraction determined by XPS to the bulk Mn molar fraction measured by ICP, the Mn molar fraction on the CuMn<sub>2</sub>O<sub>4</sub> surface (Cu:Mn, 1:3) was higher than the bulk (1:2), indicating the surface enrichment of the Mn species. The Mn surface enrichment phenomenon was also exhibited on the MnCu<sub>2</sub>O<sub>4</sub> catalyst. In comparison with the Cu:Mn:O ratio of bulk CuMn<sub>2</sub>O<sub>4</sub> (1:2:4), O species also enriched the surface (Cu:Mn:O, 1:3:6). While the Cu:Mn:O ratio of MnCu<sub>2</sub>O<sub>4</sub> surface (1:1:3) was close to the ratio of bulk Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> (1:1:2.7), one of the compositions of MnCu<sub>2</sub>O<sub>4</sub>, this also implied that the composition on the surface of MnCu<sub>2</sub>O<sub>4</sub> is mainly Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>.

#### 3.3. Discussion

3.3.1 Synergy promotion effect of the  $CuMn_2O_4$  spinel on HMF oxidation. The mechanical mixture of  $Mn_2O_3$  and CuO

Table 3	Summary of the XPS	spectral results ov	er the CuMn <sub>2</sub> O <sub>4</sub>	and MnCu <sub>2</sub> O <sub>4</sub> c	atalysts
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	Binding energy (eV)															
	Mn 2p <sub>3/2</sub>		Cu 2p <sub>3</sub>	/2	O 1s		Area fraction (%)						Cu:Mn:O ratio			
Catalyst	Mn <sup>2+</sup>	Mn <sup>3+</sup>	$Mn^{4+}$	$Cu^+$	Cu <sup>2+</sup>	O <sub>ads.</sub>	O <sub>latt.</sub>	Mn <sup>2+</sup>	Mn <sup>3+</sup>	$Mn^{4+}$	$\mathrm{Cu}^+$	$\mathrm{Cu}^{2^+}$	O <sub>ads.</sub>	O <sub>latt.</sub>	Bulk <sup>a</sup>	Surface
CuMn <sub>2</sub> O <sub>4</sub>		641.3	644.0	930.8	933.6	530.9	529.6	0	59.3	40.7	38.3	61.7	49.3	50.7	1:2:4	1:3:6
$MnCu_2O_4$	640.6	641.6	644.3	930.7	933./	530.9	529.5	25.9	36.6	37.5	14.2	85.8	55.3	44./	2:1:4	1:1:3

<sup>a</sup> Calculated based on the ICP-OES results.

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showed a higher FDCA yield than the mono oxide (Mn<sub>2</sub>O<sub>3</sub> or CuO). When Mn- and Cu-based oxides formed a spinel, a higher FDCA yield was obtained. Hence, in comparison with the mono oxide and CuO-Mn<sub>2</sub>O<sub>3</sub> the CuMn<sub>2</sub>O<sub>4</sub> spinel exhibited a synergy promotion effect for HMF oxidation to FDCA. To better understand the synergy promotion effect of the CuMn<sub>2</sub>O<sub>4</sub> spinel, the initial oxidation reaction rates of HMF/DFF/FFCA (Table 2) and the catalytic behavior with reaction time over mono oxides (Mn<sub>2</sub>O<sub>3</sub>) were investigated (Fig. S12<sup>†</sup>). As shown in Table 2, the initial rates of HMF, DFF, and FFCA conversions over the CuMn<sub>2</sub>O<sub>4</sub> spinel, Mn<sub>2</sub>O<sub>3</sub> and CuO catalysts were evaluated from the results of the oxidation of the substrates at the initial stage. The initial rates over CuMn<sub>2</sub>O<sub>4</sub> spinel or Mn<sub>2</sub>O<sub>3</sub> or CuO catalysts were in the order of  $r_{\text{step3}} < r_{\text{step1}} \ll r_{\text{step2}}$ , which indicates that the limiting step of HMF oxidation over the three catalyst is step 3 (the oxidation of -CHO in FFCA), and the next is step 1 (the oxidation of -CHO or -CH<sub>2</sub>OH in HMF). The  $r_{\text{step3}}$  and  $r_{\text{step1}}$ steps over the CuMn<sub>2</sub>O<sub>4</sub> spinel were 21 and 1.4 times faster than over CuO, respectively. Therefore, in comparison with CuO, the  $CuMn_2O_4$  spinel improves the rate of the limiting step.

Intriguingly, the initial rates of steps 1, 2 and 3 over Mn<sub>2</sub>O<sub>3</sub> were higher than the rates over the CuMn<sub>2</sub>O<sub>4</sub> spinel (Table 2), while the FDCA yield over Mn<sub>2</sub>O<sub>3</sub> was 34.1% with 98.7% HMF conversion (Table 1). Hence, the time course for HMF conversion and the corresponding products over the Mn<sub>2</sub>O<sub>3</sub> mono oxide was investigated. As summarized in Fig. S12,† DFF, FFCA, and FDCA were detected as the products, while no HMFCA was produced in the first step for HMF oxidation over Mn<sub>2</sub>O<sub>3</sub>. Fig. S12<sup>†</sup> shows that byproducts including HCOOH, LA, and DHMF were observed in the initial stage of the Mn<sub>2</sub>O<sub>3</sub>-catalyzed HMF oxidation reaction, implying that in addition to the oxidation, HMF could also be catalyzed by Mn<sub>2</sub>O<sub>3</sub> through Cannizzaro disproportionation or degradation to byproducts. This could explain why the reaction color became darker as the reaction time was prolonged. Therefore, in spite of the high catalytic ability to activate HMF molecules over the Mn<sub>2</sub>O<sub>3</sub> catalyst, the CuMn<sub>2</sub>O<sub>4</sub> spinel catalyst can suppress the side reactions to produce byproducts and enhance the production of FDCA.

3.3.2 Reaction mechanism of the CuMn<sub>2</sub>O<sub>4</sub>-catalyzed HMF oxidation. The MvK mechanism is generally accepted in the catalytic oxidation of organic compounds over spinel oxides. The MvK mechanism involves surface oxygen mobility as follows: (1) the O<sub>latt</sub>. depletion to form oxygen vacancies ([]<sub>vacan</sub>.) during the organic molecule being oxidized, O<sub>latt</sub>. (O<sub>latt</sub>.  $\rightarrow$  []<sub>vacan</sub>.), (2) the O<sub>latt</sub>. regeneration O'<sub>latt</sub> from O<sub>ads</sub>. resulting in corresponding O vacancy generation (O<sub>ads</sub>. + []<sub>vacan</sub>.  $\rightarrow$  O'<sub>latt</sub>. + []'<sub>vacan</sub>.), along with O<sub>ads</sub>. regeneration through the []'<sub>vacan</sub>. adsorption and dissociation of O<sub>2</sub> molecules. At the same time, the oxygen mobility was accompanied by the oxidation and re-oxidation of metal with different oxidation states.<sup>50,65-68</sup>

To further clarify the MvK mechanism of the Olatt, over CuMn<sub>2</sub>O<sub>4</sub> in the HMF oxidation reaction, anaerobic HMF oxidation reactions were carried out with N2 under base-free reaction conditions (O<sub>2</sub> free conditions, experimental details are given in the ESI<sup>†</sup>). The results indicate that even though there was no oxygen in the reactor, HMF could be transformed into HMFCA, FFCA and FDCA through oxygen insertion (Oins) processes, where the HMF conversion was 8.4% and the amount of  $O_{ins}$  was 34.3 µmol within 3 h (entry 1 in Table S6†). These inserted  $O_{\rm ins}$  species came from the lattice oxygen of the CuMn<sub>2</sub>O<sub>4</sub> catalyst. Upon increasing the reaction time to 4 h, the HMF conversion and Oins amount slightly increased to 9.4% and 36.2 µmol (entry 2 in Table S6<sup>†</sup>), implying that most of the lattice oxygen on the catalyst surfaces was consumed within 3 h for a slow reaction rate in the Oins process. The autoclave of the 4 h O2-free reaction was cooled to room temperature,  $O_2$  gas was charged into the reactor, stirring was carried out at room temperature for 2 h, and then the O2 was released. Then, the anaerobic HMF oxidation reaction was performed again under N2 for 4 h. The HMF conversion and amount of Oins were almost regained to the original levels (entry 3 in Table S6<sup>†</sup>). All these results demonstrate that the lattice oxygen of the CuMn<sub>2</sub>O<sub>4</sub> catalyst was catalytically active in HMF oxidation in the way of a consuming-resupplying cycle.

Taking full account of the materials characterization and catalytic results, a plausible reaction mechanism for the



Scheme 2 Plausible reaction mechanism of the aerobic oxidation of HMF to FDCA over the CuMn<sub>2</sub>O<sub>4</sub> catalyst.

aerobic oxidation of HMF to FDCA over the CuMn<sub>2</sub>O<sub>4</sub> catalyst is proposed in Scheme 2A. Based on the above-mentioned (3.3.2 Reaction mechanism of CuMn<sub>2</sub>O<sub>4</sub>-catalyzed HMF oxidation) MvK mechanism, the lattice oxygen species on the CuMn<sub>2</sub>O<sub>4</sub> surface ([O<sup>2-</sup>]) were clarified as being catalytically active sites. The key reaction progresses include (1) the oxidation of the -CH<sub>2</sub>OH group in HMF or HMFCA to a -CHO group and (2) the oxidation of the -CHO group in HMF, DFF or FFCA to a -COOH group (Scheme 1). As shown in Scheme 2A, the R-CH<sub>2</sub>OH was adsorbed by  $[O^{2-}]$  to form a pentacyclic compound and further converted to R-CHO through a dehvdrogenation oxidation. The R-CHO could be generated as a hemiacetal or gem-diol intermediate by OHions, which was then was dehydrogenated by  $[O^{2-}]$  to form R-COOH. In this context, [O<sup>2-</sup>] was critical in driving the aerobic oxidation of HMF toward FDCA over the CuMn<sub>2</sub>O<sub>4</sub> catalyst, suggesting that the formation of [O2-] was also crucial in this oxidation reaction.

The generation of  $[O^{2-}]$  through oxygen mobility on the CuMn<sub>2</sub>O<sub>4</sub> surface could be determined by these factors (Scheme 2B): (1) the amount of high-valent metal ions  $(Mn^{4+},$  $Cu^{2+}$ ) available to directly form  $[O^{2-}]$ , (2) the amount of lowvalent metal ions (Mn3+, Cu+) along with oxygen vacancies, (3) the coexistence of  $Cu^{2+}$ ,  $Mn^{3+}$ ,  $Cu^{+}$  and  $Mn^{4+}$  in the balance of  $Cu^{2+} + Mn^{3+} \Rightarrow Cu^+ + Mn^{4+}$ , (4) the reaction gas including O2. Only when these four factors are met simultaneously, can  $[O^{2-}]$  be continuously generated. In this work, the Mn<sup>4+</sup>/Mn<sup>3+</sup> ratio (40.7:59.3), Cu<sup>2+</sup>/Cu<sup>+</sup> ratio (61.7: 38.3), Cu/Mn ratio (1:3) on the surface enable oxygen species enrichment and an the appropriate Olatt./Oads. ratio (50.7: 49.3), further ensuring oxygen mobility balance between the Olatt, consumption which facilitates the oxidation and the Olatt. generated by refilling of the oxygen vacancies, enabling acceleration of the oxidation reaction.

# 4. Conclusions

In this work, several Mn-based spinel oxides were synthesized by the preparation method detailed and applied in the aerobic oxidation of HMF to FDCA using O2 as an oxidant in water, with the CuMn<sub>2</sub>O<sub>4</sub> spinel catalyst showing the best performance. The CuMn<sub>2</sub>O<sub>4</sub> spinel was reported for the first time as a highly efficient catalyst for the HMF aerobic oxidation. Moreover, the CuMn2O4 spinel catalyst also exhibited a remarkable FDCA yield in the aerobic oxidation of HMF, compared with the MnCu<sub>2</sub>O<sub>4</sub> spinel catalyst and single oxides such as MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, CuO and Mn<sub>2</sub>O<sub>3</sub>-CuO. The CuMn<sub>2</sub>O<sub>4</sub> spinel catalyst could be regenerated by calcination in air to remove organic substances. In addition, a higher FDCA yield (92.1%) was obtained. Kinetic studies clearly reveal that the aerobic oxidation of HMF towards FDCA over the CuMn<sub>2</sub>O<sub>4</sub> spinel catalyst is a series-parallel reaction, where HMF  $\rightarrow$  DFF  $\rightarrow$  FFCA  $\rightarrow$  FDCA is the main reaction route and FFCA  $\rightarrow$  FDCA is the rate-determining step. Furthermore, structure analysis using characterization measurements revealed that Mn species enrichment and

proper  $Mn^{4+}/Mn^{3+}$  (40.7:59.3),  $Cu^{2+}/Cu^{+}$  (61.7:38.3), and Cu/Mn (1:3) ratios on the surface enhance the selective catalytic behavior of  $CuMn_2O_4$ . All these conditions provide the appropriate  $O_{latt.}/O_{ads.}$  ratio (50.7:49.3), which facilitates oxygen mobility between the  $O_{latt.}$  consumption and the  $O_{latt.}$  generation *via* refilling of the oxygen vacancies, accelerating the oxidation reaction. Finally, significant synergistic effects between Mn and Cu in the  $CuMn_2O_4$  spinel oxide inhibit the secondary reaction and improve the rate of the limiting step to enhance FDCA production.

## Conflicts of interest

There are no conflicts to declare.

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