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Nanoscale center-hollowed hexagon  $MnCo_2O_4$  spinel catalyzed aerobic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid

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#### Abstract

A series of bimetallic Mn-Co-O catalysts were synthesized by a simple hydrothermal method, and the catalytic performance was evaluated. Among these catalysts, center-hollowed hexagon MnCo<sub>2</sub>O<sub>4</sub> exhibited excellent catalytic effect in aerobic oxidation of 5-hydroxymethylfurfural (5-HMF) to 2,5-furandicarboxylic acid (FDCA). A 99.5% 5-HMF conversion and 70.9% FDCA yield can be obtained under molecular oxygen and weak base condition. The efficient catalytic performance was attributed to the  $Mn^{3+}$  ions on the surface of  $MnCo_2O_4$  catalyst, and its high oxygen mobility and reducibility. Furthermore, this simple synthesis process of non-precious metal catalyst is beneficial to the production of FDCA.

**Keywords:** 5-hydroxymethylfurfural, 2,5-furandicarboxylic acid, non-noble metal, oxidation

#### 1. Introduction

Biomass is ubiquitously available in nature, and can replace non-renewable fossil resources for the production of renewable value-added chemicals [1]. Therefore, massive efforts has been done to the conversion of biomass into renewable chemical raw materials to reduce the overuse of fossil resources [2]. The biodegradable polyethylene furanoate (PEF) has similar chemical structure and properties with nondegradable polyethylene terephthalate (PET), which can be applied in the plastics industry for the production of films and bottles [3]. PEF has excellent performance compared with PET, such as good thermal stability, low-temperature formability and excellent gas barrier properties [4,5]. A 100% bio-based 2,5-furandicarboxylic acid (FDCA) as an crucial monomer for PEF production, could be obtained by the oxidation of bio-based 5-hydroxymethylfurfural (5-HMF) [6].

Thus, extensive research was conducted to synthesize FDCA for relieving the excessive pressure on the resources and environment [7]. Even though most of noble metal catalysts, such as Au [8], Pt [9], Pd [10], Ru [11] and their alloys [12], showed excellent performance for the oxidation of 5-HMF, the expensive prices imposed a restriction for the further industrial production. In order to reduce the cost of the catalyst, homogeneous Co/Mn/Zr/Br [13], [Co(OAc)<sub>2</sub>/Zn(OAc)<sub>2</sub>/NaBr] [14] and [Co(OAc)<sub>2</sub>/Mn(OAc)<sub>2</sub>/NaBr] [15] non-noble metal catalysts were applied for the oxidation of 5-HMF. Because homogeneous catalysts is difficult to reuse, the oxidation of 5-HMF by heterogeneous non-noble metal catalysts become an attractive green route. Recently, it was reported that 5-HMF was oxidized using Fe<sub>3</sub>O<sub>4</sub>-CoO<sub>x</sub>

catalyst or Merrifield resin-Co-Py catalyst, t-BuOOH as oxidant, DMSO or acetonitrile as solvent, the yield of FDCA could reach 68.6% and 90.4%, respectively[16,17]. Another research group [18] reported  $Mn_xFe_y$  mixed oxide as catalyst in the presence of NaOH for direct oxidation of 5-HMF, while the yield of FDCA was low. Others have showed Co-Mn modified nanospherical mesoporous silica catalyst with t-BuOOH as oxidant, 100% 5-HMF conversion could be achieved with FDCA yield of 72.4% [19]. Some improvements have been reported in the literature, for instance,  $MnO_2$  [4] and  $MnO_x$ -CeO<sub>2</sub> composite oxides [20] were also applied for the oxidation of 5-HMF, and exhibited favorable catalytic performance in the weak base condition. In addition, most heterogeneous non-noble metal catalytic systems often employ harmful oxidant, additive or solvent.

The aim of the present work was preparation of environment-friendly and simple green catalytic system to efficiently convert 5-HMF into FDCA over heterogeneous non-noble metal catalysts. In this paper, a series of novel, inexpensive and heterogeneous Mn-Co-O catalysts were prepared with different Mn/Co molar ratios by simple hydrothermal method, and applied for the production of FDCA using green molecular oxygen under weak base condition. The activity of the catalysts for the oxidation of 5-HMF were investigated. Furthermore, XRD, Raman, N<sub>2</sub> physisorption, H<sub>2</sub>-TPR, XPS and TEM were used to investigate the nature of catalysts. To the best of our knowledge, the use of Mn-Co-O bimetallic oxides as catalyst for the aerobic oxidation of 5-HMF into FDCA has not been reported previously.

#### 2. Experimental Section

#### 2.1. Catalyst preparation

A series of Mn-Co-O bimetallic oxides were prepared by hydrothermal method. First, a total of 6 mmol Manganese(II) nitrate aqueous solution and cobalt(II) nitrate hexahydrate with an appropriate Mn/Co molar ratio (Mn:Co= 1:0; 3:1; 2:1; 1:1; 1:2; 1:3; 0:1) were dissolved in 60 mL distilled water. Subsequently, the NaOH solution was slowly dropped with vigorous stirring until pH was approximate to 10. The mixed solution was vigorously stirred for 10 min at room temperature and loaded in Teflon-lined stainless steel autoclaves. After treated at 180 °C for 4 h, the samples were washed with distilled water until neutral before drying at 60 °C for 12 h. The obtained precursor was calcined in a furnace at 400 °C in air for 4 h, followed by cooling naturally to room temperature. Thus, the Mn-Co-O bimetallic oxides were prepared.

#### 2.2. 5-HMF oxidation

The oxidation of 5-HMF was studied in a stainless-steel reactor equipped with magnetic stirring and electrical heating device. In a typical experiment, 0.2 mmol 5-HMF and 0.06 g KHCO<sub>3</sub> were dissolved in 5 ml distilled water and added into the reactor together with 0.1 g catalyst and a magnetic rotor. The reactor was sealed and filled with 1 MPa O<sub>2</sub>, and heated to a desired reaction temperature. After a specific reaction time, the autoclave was naturally cooled down to room temperature, and the catalyst filtered off prior to the analysis. The reaction mixtures were analyzed by high performance liquid chromatography (HPLC, Agilent 1260 HPLC system) equipped with a UV detector and a extend-C18 column at 30 °C. The mobile phase was 0.1 wt%

formic acid solution and acetonitrile (v/v = 70.30) at a flow rate of 1.0 mL/min. The detection wavelengths of 5-HMF and FDCA were 284 and 264 nm, respectively. The retention time of 5-HMF and FDCA were 2.6 and 3.0 min, respectively.



#### 3. Results and Discussion

Fig.1. XRD patterns (a) and partial enlarged XRD patterns (b) of  $Mn_3O_4$ ,  $Co_3O_4$  and Mn-Co bimetallic oxides with different Mn/Co molar ratios.

In order to confirm the crystal structure of catalysts, XRD patterns of  $Mn_3O_4$ ,  $Co_3O_4$ , and varying proportions of Mn-Co bimetallic oxides are presented in Fig.1(a). The characteristic peaks of  $Mn_3O_4$  appears in 29.1, 31.1, 32.6, 36.2, 38.4, 44.5, 51.2, 58.6, 60.1 and 64.7°, which can be indexed to (112), (200), (103), (211), (004), (220), (105), (321), (224) and (400) lattice planes of the tetragonal  $Mn_3O_4$  (JCPDS 24-0734) [21]. And the diffraction peak of MnOOH appears in 26.6 ° indicated that  $Mn_3O_4$  sample contains a small amount of MnOOH [4]. The diffraction peaks of Mn3-Co1-O, Mn2-Co1-O and Mn1-Co1-O was similar to that of  $Mn_3O_4$ , but gradually became broader and weaker with the decrease of Mn ions [20]. The characteristic peaks of  $Co_3O_4$  appears in 31.4, 36.9, 38.8, 44.9, 55.8, 59.5 and 65.4° matched with (220),

(311), (222), (400), (422), (511) and (440) crystallographic planes of the cubic phase  $Co_3O_4$  (JCPDS 74–1656) [22]. The diffraction peaks of the Mn1-Co3-O were similar to that of  $Co_3O_4$ . However, compared to  $Co_3O_4$ , the peaks of Mn1-Co2-O became broader and weaker. Partial enlarged XRD patterns clearly indicated that the crystallinity of binary oxide was lower than that of the single metal oxide. Moreover, it is noteworthy that the values of Mn1-Co2-O at 30.8, 36.4, 44.8, 59.3 and 65.2° could be indexed to (220), (311), (400), (511) and (440) lattice planes of MnCo<sub>2</sub>O<sub>4</sub> with cubic spinel structure (JCPDS 23-1237) [11]. According to JCPDS for  $(Co/Mn)^{2+}(Co/Mn)^{3+}O_4$ , manganese and cobalt ions are adopt mixed valence states of +3 and +2 in the MnCo<sub>2</sub>O<sub>4</sub> spinel structure, in which Mn<sup>3+</sup> and Co<sup>3+</sup> distributed over the octahedral sites, while Mn<sup>2+</sup> and Co<sup>2+</sup> are located at tetrahedral stacking interstices [23], which is consistent with XPS results as discussed Fig.S2.(b, c).



**Fig.2.** Raman spectra of  $Mn_3O_4$ ,  $Co_3O_4$  and Mn-Co bimetallic oxides with different Mn/Co molar ratios.

As shown in Fig.2, the Raman spectrum of  $Mn_3O_4$  indicated the characteristic diffraction peaks at 279, 341 and 631 cm<sup>-1</sup>, which were in good agreement with the

hausmannite structure of  $Mn_3O_4$  [24]. The Raman spectrum of  $Co_3O_4$  indicated the characteristic diffraction peaks at 184, 458, 504, 604 and 653 cm<sup>-1</sup>, and it can be related to cubic phase of  $Co_3O_4$  [25]. For Mn3-Co1-O, Mn2-Co1-O and Mn1-Co1-O, the main bands of  $Mn_3O_4$  become weaker and shifted to lower wavenumbers. For Mn1-Co2-O, the peaks located at 175, 447, 494, 593 and 641 cm<sup>-1</sup> are attributed to the Raman-active modes (A1<sub>g</sub>, E<sub>g</sub>, and 3F<sub>2g</sub>) of Co<sub>3</sub>O<sub>4</sub>, and the main bands of Co<sub>3</sub>O<sub>4</sub> became weaker and shifted to lower wavenumbers [23]. These phenomenon can be ascribed to the change in the surface strain or defects owing to the incorporation of Mn into the Co<sub>3</sub>O<sub>4</sub> crystal structure. Since the defects and strains in the crystal structure can result in the shifts in Raman peaks [26], which was in accordance with the XRD results that a new phase state is formed.

a	Blank <sup>[b]</sup>	Mn <sub>3</sub> O <sub>4</sub>	Mn/Co 3/1	Mn/Co 2/1	Mn/Co 1/1	Mn/Co 1/2	Mn/Co 1/3	Co <sub>3</sub> O <sub>4</sub>
Surface area $(m^2/g)$	-	24.4	55.5	60.3	51.1	62.4	79.3	30.2
Conversion (%)	19.6	88.3	95.7	98.9	99.0	99.5	95.5	18.4
FDCA Yield (%)	1.3	15.6	25.3	45.0	57.2	70.9	40.9	1.5

Table 1 The catalytic activity of different catalysts for 5-HMF oxidation.<sup>[a]</sup>

[a] 0.2 mmol 5-HMF, 0.1 g catalyst, 0.06 g KHCO<sub>3</sub>, 5 ml H<sub>2</sub>O, 1MPa O<sub>2</sub>, 100 °C, 24 h; [b] no catalyst

Fig. S1 shows N<sub>2</sub> adsorption/desorption isotherm curve of Mn<sub>3</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub> and Mn-Co bimetallic oxides with different Mn/Co molar ratios. It can be seen that all the catalysts belong to type-IV isotherm and typical H<sub>2</sub>-hysteresis loop appears in relative pressure ( $P/P_0$ ) range of 0.83-1.0. And the specific surface area of samples calculated by BET method is the range of 24.4-79.3 m<sup>2</sup>/g (Table 1). The specific surface area of

bimetallic oxide was larger than that of the single metal oxide. It may be due to the lower crystallinity of binary oxide [20]. The specific surface area of 1Mn-3Co-O (79.3  $\text{m}^2/\text{g}$ ) was larger than that of MnCo<sub>2</sub>O<sub>4</sub> (62.4  $\text{m}^2/\text{g}$ ), but the FDCA yield of 1Mn-3Co-O was less than that of MnCo<sub>2</sub>O<sub>4</sub>. Thus, the specific surface area of catalysts was not the main factor affecting the catalytic activity.

To determine the optimum catalyst for the oxidation of 5-HMF to FDCA, a series of tests were carried out over Mn<sub>3</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub> and Mn-Co bimetallic oxides with different Mn/Co molar ratios, and results are listed in Table 1. It was observed from the Table 1, only 19.6% 5-HMF conversion and 1.3% FDCA yield can be obtained without catalyst. When Mn<sub>3</sub>O<sub>4</sub> was used as catalyst, the conversion of 5-HMF was 88.3% and the yield of FDCA was 15.6%. When Co<sub>3</sub>O<sub>4</sub> was used as catalyst, the conversion of 5-HMF was 18.4% and the yield of FDCA was only 1.5%. However, it can be found that 5-HMF conversion and FDCA yield for binary oxide was higher than that of single metal oxide, Among bimetallic oxides, MnCo<sub>2</sub>O<sub>4</sub> showed optimal catalytic activity on the selective oxidation of 5-HMF into FDCA, 99.5% 5-HMF conversion and 70.9% FDCA yield were obtained. Furthermore, the catalytic activity of MnCo<sub>2</sub>O<sub>4</sub> was compared with other heterogeneous non-noble metal catalysts, and the results are shown in Table S1.



Fig.3. H<sub>2</sub>-TPR of Mn<sub>3</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub> and Mn-Co bimetallic oxides with different Mn/Co molar ratios.

The relative reducibility of Mn<sub>3</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub> and Mn-Co bimetallic oxides with different Mn/Co molar ratios were investigated by H2-TPR as shown in Fig. 3. The H<sub>2</sub>-TPR profiles of Mn<sub>3</sub>O<sub>4</sub> shows that two significant reduction peaks at 300 °C and 420 °C, respectively. The first peak can be attributed to the reduction of MnOOH to  $Mn_3O_4$ , and the second peak can be attributed to the further reduction of  $Mn_3O_4$  to MnO [27]. The H<sub>2</sub>-TPR profile of Co<sub>3</sub>O<sub>4</sub> possessed two adjacent reduction peaks at 296 °C and 372 °C. The first reduction peak was assigned to the reduction of Co<sub>3</sub>O<sub>4</sub> to CoO, whereas the high temperature peak represents the further reduction of CoO to Co [28]. Furthermore, the reduction peaks in bimetallic oxides are shifted to a lower temperature compared with  $Mn_3O_4$  and  $Co_3O_4$ , implying higher oxygen mobility in the Mn-Co bimetallic oxides [29]. Importantly, MnCo<sub>2</sub>O<sub>4</sub> can be obtained the lowest reduction peaks (231°C) among these catalysts, which reveals it have highest oxygen mobility and reducibility. Therefore, the oxygen mobility and reducibility are the important factor on catalytic activity of Mn-Co bimetallic oxides.

The XPS spectra of  $MnCo_2O_4$  is shown in Fig. S2. The survey spectra is shown in Fig. S2 (a), it gives signals mainly associated with Co 3p, O 1s, Mn2p and Co 2p species, indicating that MnCo<sub>2</sub>O<sub>4</sub> was composed of Co, O and Mn elements. As shown in Fig. S2 (b), the binding energy of Co 2p3/2 and Co 2p1/2 are located at 780.1 eV and 796.1 eV, respectively, which are attributed to the coexistence of Co(II) and Co(III) [11]. In addition, two peaks of Mn 2p3/2 and Mn 2p1/2 are located at 641.9 eV and 653.7 eV in Fig. S2 (c) are responsible for the Mn(II) and Mn(III) [11]. In order to further determine the oxidation states of Mn ions, we can deconvolute the Mn 2p peak into four peaks by refined fitting. The peaks at 641.7 eV and 653.2 eV can be assigned to the presence of Mn(II), while the other two peaks at 643.5 and 654.9 eV are characteristic of the Mn(III) [30]. According to literature [26], surface oxygen species have high mobility, and easier to be activated. So, the types of surface oxygen species of MnCo<sub>2</sub>O<sub>4</sub> were also identified by the O 1s XPS spectra as displayed in Fig. S2 (d). The O 1s curves of  $MnCo_2O_4$  can be fitted into three peaks at 530.2 eV, 531.3 eV and 532.4 eV, denoted as O<sub>I</sub>, O<sub>II</sub> and O<sub>III</sub> respectively. The main peak  $O_I$  was associated with lattice oxygen ( $O^{2-}$ ); a shoulder peak  $O_{II}$  was assigned to oxygen defects or surface adsorbed oxygen ( $O_2^{2-}$  and  $O^{-}$ ), another shoulder peak  $O_{III}$ was likely to be ascribed to adsorbed molecular water. The 5-HMF oxidation to FDCA may be proceed via the  $Mn^{3+}/Mn^{2+}$  redox cycles of  $MnCo_2O_4$  catalyst. Firstly,  $Mn^{2+}$  was oxidized by O<sub>2</sub> to  $Mn^{3+}$  forming  $Mn^{3+}O^{2-}$  species, and the  $Mn^{3+}O^{2-}$  could oxidize 5-HMF to FDCA while reduced to  $Mn^{2+}$ , which could be reoxidized by O<sub>2</sub>. Thus,  $Mn^{3+}$  is the active site of  $MnCo_2O_4$  catalyst.

TEM images of  $Mn_3O_4$ ,  $Co_3O_4$  and Mn-Co bimetallic oxides are shown in Fig S3. In addition to the irregular  $Mn_3O_4$  and Mn3-Co1-O,  $Co_3O_4$  and Mn2-Co1-O are close rectangle, Mn1-Co1-O forms a solid hexagonal structure of about 100 nm. When Mn/Co molar ratios is 1/2, it was observed that  $MnCo_2O_4$  is about 100 nm hexagon with a hole at the centre. And this structure was broken along with the reduction of manganese content. It can be seen the morphology of catalyst can be changed by controlling the molar ratio of manganese and cobalt.

#### 4. Conclusions

Mn-Co bimetallic oxides with different Mn/Co molar ratios have been synthesized via simple hydrothermal method, and a nanoscale hexagon MnCo<sub>2</sub>O<sub>4</sub> with a hole at the centre was formed when Mn/Co molar ratios was 1/2. MnCo<sub>2</sub>O<sub>4</sub> was proved to have high activity for the aerobic oxidation of 5-HMF to FDCA, and can be obtained 99.5% the conversion of 5-HMF and 70.9% the yield of FDCA under optimal reaction conditions, which was significantly better than Mn<sub>3</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub> and other bimetallic oxides. XPS analysis identified that Mn<sup>3+</sup> is the active site of MnCo<sub>2</sub>O<sub>4</sub> catalyst. MnCo<sub>2</sub>O<sub>4</sub> has the lowest reduction peaks illustrated by the H<sub>2</sub>-TPR, which can improve oxygen mobility of catalyst and benefit the oxidation of 5-HMF. This work provided a green and facile method for developing the aerobic oxidation of 5-HMF to FDCA using non-precious metal catalysts.

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#### **Graphical abstract**



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#### Highlights

- Nanoscale center-hollowed hexagon MnCo<sub>2</sub>O<sub>4</sub> was synthesized by a simple hydrothermal method.
- An 70.9% yield of FDCA was obtained under mild conditions.
- This work provides a green and economical route for FDCA production.

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