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Efficient aerobic oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid over a nanofiber globule La-MnO₂ catalyst

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ABSTRACT: A La-MnO₂ catalyst exhibited excellent performance in aerobic oxidation

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of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA). Characterization of the samples revealed that the loose surface morphology and high oxygen species mobility facilitate the HMF oxidation reaction. H₂O was verified as a good solvent for the formation of FDCA due to the facilitation of aldehyde group hydration to generate carboxyl group on the HMF molecule. A 95.4% FDCA selectivity at 96.3% HMF conversion was achieved in H₂O under mild conditions.

KEYWORDS: Aerobic oxidation, 5-hydroxymethylfurfural, 2, 5-furandicarboxylic acid, Manganese oxides, Biomass

1. INTRODUCTION

Due to the ever increasing consumption of fossil fuel resources, the risk of energy crises and environmental destruction create great concerns.^{1,2} The utilization of sustainable and renewable resources as alternatives to produce petroleum derived chemicals arises widespread attention. Biomass resource relieves the dependence on fossil resources by conversion to biofuel and value-added chemicals.^{3,4} Among the biomass derived derivatives, 5-hydroxymethylfurfural (HMF) obtained from the dehydration of hexose has been deemed as a vital precursor for the generation of versatile platform chemicals and fuels.⁵⁻⁸ The downstream products of HMF, 2,5-diformylfuran (DFF), 2,5-furandicarboxylic acid (FDCA), 5-formyl-2-furancarboxylic acid (FFCA) and 5-hydroxymethyl-2-furancarboxylic acid (HMFA) have been applied in the production of pharmaceuticals, antifungal agents and functional polymers. As an ideal substitute for terephthalic acid (TPA) monomer, FDCA can be used as the monomer for the production of poly ethylenefuranoate (PEF) plastics.⁹⁻¹¹ PEF shows obvious advantages in gas containing and isolation rate of oxygen, and considers as a promising raw material in polyester chemical.^{12,13} However, the reactive α , β -unsaturated aldehyde group in HMF molecule makes byproducts prone to form during the oxidation reaction. The high yield conversion of HMF to FDCA still encounters a challenge and an efficient catalyst is called for.¹⁴⁻¹⁶

Recent advances for HMF to FDCA have been made with different catalysts.¹⁷ Cheng group developed the homogeneous Co/Mn/Br catalyst in the reaction and 92% yield of FDCA was obtained in acetic acid.¹⁸ Noble metal supported catalysts have been

extensively investigated in HMF oxidation.¹⁹⁻²¹ For example, Donoeva et al.²² reported a 75% yield of FDCA with Au/HSAG-N (a high-surface-area graphite) catalyst in H₂O solvent under a base condition. Bimetallic alloys were also employed, for instance, nearly 99% yield of FDCA was obtained in NaOH aqueous solution with a Au₈Pd₂/AC catalyst.²³ Base additives, such as NaOH, Na₂CO₃ and NaHCO₃, are often required to facilitate C-H bond activation and promote the yield of FDCA.²⁴⁻²⁶ In addition, the catalyst metal leaching can often be prevented under basic conditions.²⁷ However, the high cost and scarcity of the noble-metal catalysts impede their widespread application. Accordingly, transition metal catalysts developed as alternatives were employed.^{28,29} For example, Zhou et al. reported 96.1% yield of FDCA was achieved in H₂O with Co-Mn/N@C catalyst.²⁵

Due to the multiple valance states and abundance, manganese oxides have attracted great attention as catalytic materials in oxidation reactions.³⁰⁻³² Doping with guest ions is an effective strategy to improve the mobility of the reactive oxygen species and thus often boosting the catalytic activity. Herein, we examined the La doped MnO₂ catalyst in aerobic oxidation of HMF. The morphology, surface composition and reducibility on the catalytic performance was investigated. With the presence of NH₃·H₂O, the formation of FDCA dominates the reaction pathway in H₂O solvent.

2. EXPERIMENTAL SECTION

2.1. Reagents and instruments

Analytical grade chemicals are used as received. Mn(NO₃)₂, La(NO₃)₃, (NH₄)₂S₂O₈, (NH₄)₂SO₄, and NH₃·H₂O (25 wt%) were purchased from Aladdin Chemicals. HMF, DFF,

FDCA, FFCA and HMFCA were obtained from Alfa Aesar. The commercial MnO_2 are ordered from Tianjin Xiensi Technology Company.

The X-ray diffraction (XRD) patterns were recorded with a Rigaku D/max-III A diffractometer ($\text{Cu-K}\alpha$, $\lambda = 1.54056 \text{ \AA}$), operating at 40 kV and 40 mA. The scanning was operated between 10 °C and 80 °C at rate of 10 ° min⁻¹. N_2 adsorption isotherm, BET surface area and pore volume of the catalysts were measured with a Micromeritics ASAP2020M system. The morphology of the materials was observed with a scanning electron microscope (JSM-6301F, JEOL). The surface chemical states of samples were characterized with a PHI-1600 ESCA X-ray photoelectron spectroscopy (XPS). H_2 temperature-programmed reduction experiment was carried out on a Micromeritics 2920 Autochem II Chemisorption Analyzer with a thermal conductivity detector. The sample was swept by the 5% H_2/Ar carrier gas at a flow of 25 mL min⁻¹. Subsequently, the signal was recorded as the temperature increased from ambient to 800 °C at a heating rate of 10 °C min⁻¹. The quantitative analysis of the products was done with an Agilent 1200 high performance liquid chromatograph (HPLC) equipped with UV detector operating at 280 nm. The products are separated with an Eclipse XDB-C18, 5 μm 4.6×150 mm capillary column and the column oven was set at 10 °C. The eluent was composed of acetonitrile and 0.1 wt% acetic acid solvent in a volume ratio 3:7. Besides, the qualitative analysis of the products was carried out on an Agilent 6890/5973 gas chromatograph-mass spectrometer (GC-MS). The parameters of GC-MS were set as follows: injector temperature 220 °C; detector temperature 220 °C; split ratio 50:1. The temperature program of column oven set

from 60 to 220 °C at 10 °C min⁻¹ and held at 220 °C for 2 min.

2.2. Catalysts preparation

The La-MnO₂ catalyst was prepared with a hydrothermal method. 0.01 mol of (NH₄)₂S₂O₈ and 0.04 mmol of (NH₄)₂SO₄ were successively dissolved in 60 mL deionized water. Subsequently, 0.01 mol MnSO₄·H₂O and a certain amount of La(NO₃)₃·6H₂O were added into the above mentioned solution. The mixture solution was then transferred into a teflon-lined stainless steel autoclave and heated to 140 °C for 12 h. Afterwards, a black-brown precipitate was separated by filtration and washed with deionized water until the filtrate was neutral. The filtration cake was dried in an oven at 80 °C for overnight and then calcined in a muffle furnace at 200 °C for 4 h in air. The sample is labelled as La (x mol%)-MnO₂ (x mol% refers the molar ratio of La³⁺ and MnSO₄; if x mol% = 10 mol%, x mol% can be left out). MnO₂ was prepared without La(NO₃)₃·6H₂O.

2.3. Reaction conditions

All the oxidation reactions were carried out in a 150 mL autoclave equipped with magnetic stirring and automatic temperature control. In a typical procedure, 0.126 g HMF, 0.05 g La-MnO₂ and a certain amount of base additives were added into the autoclave with 25 mL DI water. After sealing the reactor, 0.5 MPa O₂ (gauge) was pressurized into the autoclave and then the reactor was heated to 140 °C for 4 h with an on-screen rate 500 rpm stirring. Finally, the product was analyzed with HPLC and GC-MS. In addition, a reaction was also done under 0.5 MPa N₂ instead of O₂.

After the reaction, the catalyst was separated by centrifuge and washed more than six

times with anhydrous ethanol. The recovered catalyst was dried at 70 °C overnight before reused in the next run.

3. RESULTS

3.1. The reaction

The performance of MnO₂ and La-MnO₂ catalysts were evaluated and the results are listed in Table 1. Negligible conversion of HMF was detected in the absence of catalyst (entry 1). When MnO₂ catalyst was employed, an 83.4% conversion of HMF and 75.3% selectivity of FDCA were measured, with 8.2% DFF and 16.5% other by-products (entry 2). Doping with La shows positive effects, the HMF conversion of 96.3% with respective FDCA selectivity of 95.4% were achieved (entry 3). The crucial role of O₂ was confirmed by the reaction result obtained under N₂ and the conversion of HMF was given as 8.5% with almost zero selectivity of FDCA (entry 4). The commercial MnO₂ employed as catalyst exhibits poor catalytic activity and a 67.8% FDCA selectivity at 51.4% HMF conversion was detected (entry 5).

The amount of doping La ion on catalyst sample was optimized and the corresponding experimental results were presented in Figure 1. Along with the amount of doping La ion increased from 0 mol% to 10 mol%, the catalytic activity of La(x mol%)-MnO₂ was promoted from 83.4% to 97.3% with the selectivity of HMF increased from 75.3% to 95.4%. However, when the doping amount of La ion was elevated to 12 mol%, the conversions of HMF exhibited a slightly decrease to 95.2% with 93.1% FDCA selectivity.

Consequently, the excellent catalytic performance of La(x mol%)-MnO₂ revealed the 10 mol% amount of La cation is suitable content for the catalyst sample.

As a kind of weak base and easy to separate, NH₃·H₂O was used as an additive. Different amount of NH₃·H₂O was added into H₂O solvent and the reaction results are summarized in Figure 2. The pH value of H₂O solvent, with close correlation with NH₃·H₂O concentration, exhibited significant effect on HMF conversion. Only 48.1% FDCA selectivity at 26.7% HMF conversion was measured at pH 7 in the absence of NH₃·H₂O. When the pH of the solvent was improved to 8, the conversion of HMF was greatly increased to 65.2% with 71.3% selectivity of FDCA. HMF conversion and FDCA selectivity were both improved with the increase of pH. At pH 10 the reaction gave 95.4% FDCA selectivity at 96.3% HMF conversion as the best result. Further increase the solvent pH to 12, the conversion of HMF increased to 98.7%, while the selectivity of FDCA was decreased to 87.5%. As literature presented, the catalytic performance was greatly influenced by the pH value instead of the base types.³³ Strong base conditions would cause HMF disproportionation reaction leading to low FDCA selectivity.³⁴ Here, the solvent at pH 10 is suitable and NH₃·H₂O is utilized as an efficient base additive in the aerobic oxidation of HMF to FDCA.

The effect of reaction time is examined under the same conditions. Three kinds of intermediates, HMFCa, FFCA and DFF were measured as shown in Scheme 1 and the reaction results are illustrated in Figure 3. HMF was consumed rapidly in the initial 4 h, and the conversion reached 96.3% at 4 h. The selectivity of FDCA increases monotonically

in the initial period and reached 95.4% at 4 h. After that the FDCA selectivity keeps stable and above 95.0%. The intermediates HMFCa, FFCA and DFF appear with relatively high selectivities at the first point, i.e. 0.5 h after reaching the reaction temperature 140 °C, but HMFCa selectivity showed a monotonic decrease within 4 h. The selectivity of FFCA and DFF gave highest values at 1 h, and after that, monotonic decrease of the selectivities were observed. After 4 h, the selectivities of the HMFCa, FFCA and DFF intermediates became also stabilized and the values were decreased to 0.9%, 1.3% and 1.7%, respectively.

The stability of the La-MnO₂ catalyst was measured under 0.5 MPa O₂ at 140 °C in H₂O with NH₃·H₂O and the results are plotted in Figure 4. The activity decreased slightly with the increase of cycle times and a 82.7% FDCA selectivity at 85.4% HMF conversion was still obtained in the fifth run. The intermediates HMFCa and FFCA appear with a slightly increase trend and gave 5.9% and 9.8% selectivities during the 5th cycle process. However, the catalytic activity of La-MnO₂ was completely recovered after calcining at 200 °C for 4 h in air.

3.2. Characterization

3.2.1. Texture

The isotherms of the prepared catalysts are measured with a nitrogen physisorption technique and the results are drawn in Figure 5, and all of them belong to IV type, indicating the existence of mesopore. The average value of pore diameter of the MnO₂ sample is 5.8 nm, while average pore diameters of the doped sample with La takes the values as 5.6 nm. Negligible effect of ion doping on the pore diameter was observed. The

BET surface area of MnO_2 sample was measured as $84.5 \text{ m}^2\cdot\text{g}^{-1}$, while for the La doped sample, the value is $94.1 \text{ m}^2\cdot\text{g}^{-1}$. The used La- MnO_2 sample was measured and the surface area value gave $91.2 \text{ m}^2\cdot\text{g}^{-1}$.

A nanofiber globule morphology is observed with both the MnO_2 and La- MnO_2 samples, as shown in Figure 6. The nanofibers in the two samples have similar shape, with those in La- MnO_2 appear thinner and shorter statistically. The globules in La- MnO_2 look looser than those in the MnO_2 sample. The average nanofibers lengths of MnO_2 sample give an of $300\pm 100 \text{ nm}$ with the cross sectional diameter of $20\pm 5 \text{ nm}$, while the La- MnO_2 present $200\pm 100 \text{ nm}$ nanofibers lengths and $15\pm 10 \text{ nm}$ diameter. These observations may explain the larger BET surface area of the doped sample than the undoped sample.

3.2.2. Structure

The XRD patterns of the MnO_2 catalyst samples are depicted in Figure 7. All patterns measured were well consistent with the tetragonal manganese oxide phase of cryptomelane-type with JCPDS card No.44-0141. The peaks at $2\theta = 18.8^\circ, 23.1^\circ, 32.9^\circ, 35.6^\circ, 38.2^\circ, 40.6^\circ$ and 55.1° are corresponding to the (2 0 0), (2 1 1), (2 2 2), (3 1 2), (4 0 0), (4 1 1) and (0 4 4) crystal faces. Compared with the MnO_2 sample, the samples doped with La, gave similar structure information, but the peaks are weakened. The used La- MnO_2 exhibits similar pattern to that of the fresh one. After the reduction of MnO_2 by H_2 -TPR, MnO phase was observed with XRD measurement. The strong peaks present at $2\theta = 34.2^\circ, 39.7^\circ, 57.4^\circ, 68.6^\circ$ and 72.1° corresponding to MnO phase with JCPDS card No. 65-0641.

3.2.3. Chemical properties

The H₂-TPR curves of the MnO₂ and La-MnO₂ samples are presented in Figure 8. Two partially overlapped and one well resolved reduction peaks were observed in the temperature ranges of 270-310, 310-340 and 340-440 °C. In addition, the H₂ consumption of different reduction peaks calculated based on the H₂-TPR results are presented in Table 2. For cryptomelane-type MnO₂, the regular curve of at low temperature 120-270 °C is ascribed to remove the labile oxide species on the surface sites.³⁵ Two asymmetric shoulder peaks located between 270 and 340 °C are associated with the successive reduction of MnO₂. In these stages, the MnO₂ oxidation state was reduced, leading to the change of ionic radius and coordination number which induce new crystallographic phases appeared.^{36,37} The peak at 312 is caused by the reduction of MnO₂ to Mn₂O₃ with the maximum H₂ consumption 5.2 mmol/g, while the peak at 326 correspond to the reduction of Mn₂O₃ to Mn₃O₄ with minimum H₂ consumption 2.1 mmol/g. The last peak at high temperature 434 stands for the reduction of Mn₃O₄ to MnO with 4.3 mmol/g H₂ consumption and MnO phase formation was also confirmed by XRD pattern. Nevertheless, the peak positions of La-MnO₂ all shifts to lower ends, with values for the MnO₂ sample at 312, 326 and 434, and those at 293, 309, and 421 for the La-MnO₂ sample, respectively. The total H₂ consumption of MnO₂ sample was decreased from 11.6 to 10.2 mmol/g and the H₂ consumption ratio of the initial peak was also decreased after La doping.

The O1s spectra of the two samples are plotted in Figure 9a. The peak for the MnO₂ can be deconvoluted into two peaks with the O_I and O_{II}, while the peak of the La-MnO₂ sample

show two similar peaks after the deconvolution. The peak locating at the low binding energy of 529-530 eV is assigned to the lattice oxygen species (O_I). The peak at binding energy of 531-532 eV responds to surface adsorbed oxygen, such as O^{2-} , O_2^{2-} , and O^- (O_{II}).³⁸ The ratio values of O_{II}/O_I is increased from 0.22 to 0.35, after La doping into MnO_2 sample in Table 2. In the Mn 2p spectrum, the overlapped Mn 2p spectra can be deconvoluted into several sub-bands including Mn $2p_{1/2}$ and Mn $2p_{3/2}$. Two peaks locating at 641.5 and 653.1 eV respond to Mn^{3+} , while the major component at 642.3 and 654.1 eV are attributed to Mn^{4+} .³⁹⁻⁴¹ With doping La ion into MnO_2 material, the ratios of Mn^{3+}/Mn^{4+} is increased from 0.41 to 0.53 according to the XPS results. In addition, the binding energies of the main peak in Mn $2p_{3/2}$ shifted from 642.0 to 641.8 eV in La- MnO_2 sample.

4. DISCUSSION

The data reported in Table 1 exhibit that catalytic activity of MnO_2 was improved after incorporation of La ions in aerobic oxidation of HMF to FDCA. HMF oxidation occurs at both the external and inner surface of the catalysts, as the smaller sizes of HMF (0.82 nm) and molecular oxygen (0.35 nm) in comparison with the 5.6 nm average pore diameter of La- MnO_2 .³⁹ Therefore, much available active sites can be provided and the frequency of contact between catalyst and HMF are increased to facilitate the oxidation reaction by the large surface areas of La- MnO_2 .

The catalytic performance of metal oxides was greatly influenced by the mobility of lattice oxygen species on catalyst.⁴² As a matter of facts, lattice oxygen was migrated to the interface between reactant and catalyst to involve in reaction by transferring through

oxygen vacancies.³⁸ Hence, the mobility of oxygen species can be improved by oxygen vacancies and then promote the lattice oxygen reactivity to accelerate the oxidation reaction. The mobility of oxygen species of La-MnO₂ were increased based on the facts. (1) According to XPS results, the increased ratio of O_{II}/O_I was observed after La doping, demonstrating that the content of surface absorbed oxygen species was increased on the MnO₂ catalyst. It was reported that the formation of surface absorbed oxygen species is related to the surface oxygen vacancies.^{43,44} (2) The electrostatic balance of catalyst sample was maintained by the existence of Mn³⁺ when oxygen vacancies appear.^{45,46} Thus the amount of Mn³⁺ is a parameter to exhibit the content of oxygen vacancies. The amount of oxygen vacancies was increased by the improving of the ratio of Mn³⁺/Mn⁴⁺ on the La-MnO₂ catalyst. (3) The lower reduction temperatures measured by H₂-TPR technique manifest easier reduction of La-MnO₂. Apparently, the easy reduction is closely related to the high mobility of oxygen species on metal oxides.^{47,48} On the other hand, the lower Mn 2p_{3/2} binding energy of La-MnO₂ implies the electron transfer from catalyst to doped La ion, suggesting the surface properties of manganese oxide influenced by La species. These results indicate that La doping in MnO₂ is conducive to activate the oxygen species or change the valance state of manganese ions and thus enhance the catalytic activity of La-MnO₂.⁴⁹

In the step of FDCA formation, the reversible hydration of aldehyde group on HMF to form the geminal diol intermediate in H₂O is a crucial step.⁵⁰ In neutral pH H₂O, an equilibrium will be established between HMF molecular and the geminal diol

intermediate.¹² Under base conditions, the equilibrium is influenced by the pH value of the solutions and hydroxide ions can accelerate the reversible hydration process. Then HMFCa was produced from dehydrogenation of the geminal diol assisted by hydroxide ions adsorbed on La-MnO₂ interface.²⁵ These facts make H₂O a good solvent in conversion of HMF to HMFCa instead of DFF because the transformation of hydroxyl group in H₂O is not favored. Moreover, the activation of C-H and O-H bonds on HMF is facilitated via proton transfer in base solutions which further decreases the barrier for the formation of FDCA.⁵¹ On the other hand, H-metal species appear with β -hydride elimination of HMF during the production of FDCA, while the deprotonation step of H-metal species to regenerate catalyst can be accelerated with base.^{52,53} Consequently, the FDCA is prone to form in H₂O under base conditions.

Based on our experimental results and previous literatures, the reaction pathway of the FDCA formation is proposed as Scheme 2.^{54,55} First, the hydroxide ions release from NH₃·H₂O and then catalyze the reversible hydration step between H₂O and HMF to form the geminal diol intermediates. Then the oxidative dehydrogenation of geminal diols to generate HMFCa is occurred on the La-MnO₂ interface and the deprotonation of the H-metal species is facilitated in the assistance of hydroxide ions. Afterwards, the hydroxyl group on HMFCa is oxidized by La-MnO₂ to form FFCA intermediates. Finally, the aldehyde group on FFCA undergoes a similar geminal diols intermediate process to further generate FDCA.

5. CONCLUSIONS

A nanofiber globule La-MnO₂ catalyst was examined in aerobic oxidation of HMF to FDCA. The texture becomes loose leading to a large BET surface area with La doping into the MnO₂ phase. The incorporation of La ion increases the mobility of oxygen species and thus improves the catalytic activity of La-MnO₂. H₂O is utilized as a good solvent and the reversible hydration process was enhanced by the increase of the pH value of the solution with addition of NH₃·H₂O. Under 0.5 MPa O₂, a 96.3% conversion of HMF with 95.4% selectivity of FDCA is achieved in H₂O with NH₃·H₂O at 140 °C for 4 h. The La-MnO₂ keeps good activity after being used for five times. This work will provide an effective strategy for the production of value-added chemicals from biomass derived compounds.

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Notes

The authors declare no competing financial interest.

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Figures and table captions

Table 1. The aerobic oxidation of HMF to FDCA with different catalysts.

Figure 1. Effect of the La doping amount on HMF oxidation.

Figure 2. Effect of the pH on HMF oxidation.

Scheme 1. The aerobic oxidation of HMF to FDCA with molecular oxygen.

Figure 3. The reaction time for aerobic oxidation of HMF to FDCA.

Figure 4. The recycling of the La-MnO₂ catalyst.

Figure 5. N₂-physisorption of different catalysts.

Figure 6. The SEM micrographs of the catalytic materials (a), (c) SEM of MnO₂; (b), (d) SEM of La-MnO₂.

Figure 7. XRD patterns of different catalysts.

Figure 8. H₂-TPR curves of MnO₂ and La-MnO₂.

Table 2. H₂ consumption and XPS result of catalysts.

Figure 9. XPS spectra of MnO₂ and La-MnO₂ samples (a) O1s, (b) Mn2p.

Scheme. 2 Proposed reaction pathways for aerobic oxidation of HMF to FDCA.

Table 1. The aerobic oxidation of HMF to FDCA with different catalysts^a.

Entry	Catalyst	Conv. (%)	Product selectivity (%)		
			FDCA	DFF	Others
1	Blank	6.2	--	--	6.2
2	MnO ₂	83.4	75.3	8.2	16.5
3	La-MnO ₂	96.3	95.4	2.6	2.0
4 ^b	La-MnO ₂	8.5	--	--	8.5
5	MnO ₂ (commercial)	51.4	67.8	3.5	28.7

^a Reaction conditions: 0.126 g HMF, 0.05 g catalyst, 25 mL H₂O, 0.05g NH₃·H₂O, 0.5 MPa O₂, reaction time 4 h, temperature 140 °C.

^b The reaction is performed in nitrogen atmosphere.

Figure 1. Effect of the La doping amount on HMF oxidation.

Reaction conditions: 0.126 g HMF, 0.05 g catalyst, 0.05 g $\text{NH}_3 \cdot \text{H}_2\text{O}$, 25 mL H_2O , 0.5 MPa O_2 , 4 h, temperature 140 °C.

Figure 2. Effect of the pH on HMF oxidation.

Reaction conditions: 0.126 g HMF, 0.05 g La-MnO₂ catalyst, different amounts of NH₃·H₂O, 25 mL H₂O, 0.5 MPa O₂, 4 h, temperature 140 °C.

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Table 2. H₂ consumption and XPS results of catalysts.

Cat.	H ₂ -TPR peaks (°C)	H ₂ consumption (mmol/g)	Total H ₂ consumption (mmol/g)	XPS analysis	
				Mn ³⁺ /Mn ⁴⁺ (mol)	O _{II} /O _I (mol)
MnO ₂	312/326/434	5.2/2.1/4.3	11.6	0.22	0.41
La-MnO ₂	293/309/421	3.7/2.3/4.2	10.2	0.35	0.53

Figure 9. XPS spectra of MnO₂ and La-MnO₂ samples (a) O1s, (b) Mn2p.

Scheme. 2 Proposed reaction pathways for aerobic oxidation of HMF to FDCA.