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Highly selective oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran over an α -MnO₂ catalyst

Linhao Yu (Methodology) (Investigation) (Writing - original draft), Hong Chen (Supervision) (Conceptualization) (Writing - review and editing), Zhe Wen (Data curation), Mengmeng Jin (Software) (Visualization), Zewei Ma (Software) (Visualization), Xueli Ma (Formal analysis) (Software) (Validation), Yushuai Sang (Formal analysis) (Software) (Validation), Mengmeng Chen (Formal analysis) (Software) (Validation), Yongdan Li (Supervision) (Conceptualization) (Writing - review and editing)



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Highly selective oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran over an α -MnO₂ catalyst

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Graphical abstract



Highlights

- 1. α -MnO₂ exhibits the best performance among the catalyst tested.
- 2. Isopropanol is a good solvent for 5-hydroxymethylfurfural to 2,5-diformylfuran.
- 3. 84.3% selectivity of 2,5-diformylfuran are achieved at 93.2% conversion.

Abstract

Selective oxidation of 5-hydroxymethylfurfural (HMF) to 2, 5-diformylfuran (DFF) with molecular oxygen is realized with an α -MnO₂ catalyst under mild conditions. In this work, α -MnO₂ exhibited the best performance among the samples examined. Meanwhile, solvent shows a significant effect on the product selectivity and isopropanol is found good for improving the selectivity of DFF. 93.2% conversion of HMF was achieved at 140 °C for 4 h with 84.3% selectivity of DFF. Moreover, α -MnO₂ catalyst keeps good reusability in recycling for five times. The reaction pathway indicated that the lattice oxygen species on α -MnO₂ is involved in the selective oxidation of hydroxyl group in HMF molecule.

Keywords: Biomass, Oxidation, 5-hydroxymenthylfurfural, 2, 5-diformylfuran, Manganese oxides

1. Introduction

As a widely available energy containing material, renewable biomass becomes a very

promising alternative resource of the fossil fuels [1]. Biomass can be transformed into valuable chemicals via catalytic reactions [2-4]. 5-Hydroxymethylfurfural (HMF) belongs to furan family, which can be obtained by the dehydration of hexose. Meanwhile, HMF is considered as a vital bridge molecule between biofuel and fine chemicals [5, 6]. The selective oxidation of HMF can produce a number of valuable chemicals, for instance, 2, 5-diformylfuran (DFF). DFF has been applied as the intermediate of materials and medicines, such as in the production of antifungal agents and nematocides [7]. However, the selective oxidation of HMF to DFF encounters a challenge due to the reactive α , β -unsaturated aldehyde group in HMF molecule, which leads to occurring of many side reactions in the oxidative atmosphere [8, 9]. For example, 5-hydroxy-methyl-2-furancarboxylicacid (HMFCA), 5-formyl-2-furancarboxylic acid (FFCA), 2, 5-furandicarboxylic acid (FDCA) are prone to form in the reaction [10]. Besides, the activation energy of hydroxy group in HMF molecule is high, resulting in the low reaction rate of the oxidation process in formation of DFF. As a consequence, catalysts with high catalytic activity are still needed to realize the reaction efficiently and minimize by-products. A great effort has been devoted to the selective oxidation of HMF towards DFF with heterogeneous catalysts [11].

Recently, an ambitious prospect to use air or molecular oxygen as the green oxidant in the catalytic oxidation processes was proposed [12]. Various types of supported noble metal catalysts containing Ru, Au, Pt and Ag were examined for the selective oxidation of HMF to DFF with the existence of molecular oxygen [13-16]. Noble metal catalysts usually exhibit obvious advantages in catalytic performance with high yield toward DFF. For instance, 89.2% yield was achieved in N, N-dimethylformamide (DMF) solvent on a Ru/HT catalyst with O₂ flow at 20 mL min⁻¹ [17]. Zhu et al. [18] found K₂CO₃ exhibited significant promotion for the HMF conversion. 94.6 % yield of DFF was obtained in DMF solvent with Pd/HCN (hollow carbon nanospheres) catalyst in a O₂ balloon in the presence of K₂CO₃. On

the other hand, non-noble metal oxides such as V-, Fe- and Co-based oxide catalysts were also employed in the oxidation of HMF [19-21]. For example, nanobelt-array vanadium oxide catalyst was examined, and 89.4% yield of DFF was achieved under 3.0 MPa O₂ [22]. In this case, the authors proposed that the formation of hydrogen bond between the -CH₂OH group on HMF and the lattice oxygen of the catalytic material promote the selective formation of DFF [23].

In this work, we present the selective oxidation of HMF in the presence of molecular oxygen, with α -MnO₂ as the catalyst and isopropanol as the solvent. Isopropanol facilitates improving the selectivity of DFF and shows the best performance among various solvents.

2. Experimental

2.1. Materials and methods

KMnO₄, MnSO₄, Al₂O₃, oxalic acid, urea and HMF are of analytical grade and purchased from Aladdin Chemicals reagent company (Shanghai, China). The DFF and FDCA as the standard samples are obtained from Alfa Aesar, a Johnson Matthey Company. Methanol (MeOH), ethanol (EtOH), isopropanol (IPA), dimethylsulfoxide (DMSO), acetonitrile and N, N-dimethylformamide (DMF) are of analytical grade and purchased from Tianjin Guangfu Technology Development Co., Ltd. All the chemicals and solvents are used as received.

The X-ray powder diffraction (XRD) patterns were collected with a Rigaku D/max-IIIA diffractometer (Cu-K α , $\lambda = 1.54056$ Å). The scanning was taken from 10 ° to 80 ° at a rate of 10 ° min⁻¹. BET surface area of the materials was obtained with N₂ adsorption (77 K) measurement with a Micromeritics ASAP2020 M system. The powder sample was pretreated under vacuum at 150 °C for 4 h before measurement. The pore diameters are derived from Barrett-Joyner-Halenda (BJH) model by utilizing both the absorption and desorption data. The micrographs of catalyst materials were observed with a scanning electron microscope

(SEM: JSM-6301F, JEOL) and a transmission electron microscope (TEM: JEM-2100, JEOL). The reducibility of catalysts was measured by H₂ temperature-programmed reduction experiment with a Micromeritics 2920 Autochem II Chemisorption Analyzer. The X-ray photoelectron spectroscopy (XPS) was recorded with a PHI-1600 ESCA system. The quantitative analysis of the products was performed with an Agilent 1200 high performance liquid chromatograph (HPLC) with UV detector operating at 280 nm. The Eclipse XDB-C18, 5 µm 4.6×150 mm capillary column was used to separate the products and the column oven was set at 10 °C. Acetonitrile and 0.1 wt% acetic acid aqueous solution were mixed with a volume ratio 3:7 and used as the mobile phase at a flow rate of 0.5 mL min⁻¹. The amount of the compounds in the product molecules are identified with the Agilent 6890/5973 gas chromatograph-mass spectrometer (GC-MS). The GC-MS parameters are set as follows: injector temperature 220 °C; detector temperature 220 °C; spilt ratio 50:1. The column oven temperature program set from initial temperature 60 °C to final temperature 220 °C at 10 °C min⁻¹ and held at 220 °C for 2 min.

2.2. Catalyst preparation

0.02 mol KMnO₄ was dissolved into 30 mL distilled water. Then the solution was added dropwise to 30 mL aqueous solution of 0.03 mol MnSO₄ •H₂O under stirring. The resulting mixture was condensed with refluxing at 100 °C with vigorous stirring for 24 h in an oil bath. Afterwards, the obtained dark brown precipitate was filtrated and washed with distilled water until the filtrate was neutral. The filter cake was dried overnight and placed in an oven at 180 °C for 3 h. The sample is labelled as α -MnO₂.

Another manganese oxide catalyst was synthesized with a hydrothermal method. 1 g of KMnO4 was dissolved into 20 mL aqueous solution and then was dropped into 15 mL

aqueous solution of 0.4 g of MnSO4•H₂O under stirring. The mixed slurry was transferred into a teflon-lined stainless-steel autoclave and maintained at 140 °C for 12 h. Afterwards, the obtained product was dried overnight and calcined under open air at 300 °C for 2 h. The sample is then labelled as α -MnO₂-300. Amorphous manganese oxide catalyst (AMO), Mn₂O₃ and Mn₃O₄ catalysts were prepared according to the literature [24, 25].

2.3. The oxidation reaction

The oxidation reaction was carried out in a 150 mL stainless steel autoclave equipped with a magnetic stirrer and a temperature controller made by Xi 'an Taikang Biotechnology Co., Ltd. In a typical experiment, HMF (1 mmol, 0.126 g) was dissolved in (25 mL) isopropanol solvent. Then (0.05 g) as-prepared catalyst was added into the autoclave. After the reactor is sealed, pure oxygen was switched in to replace the atmosphere inside at room temperature. Under 0.5 MPa O₂, the reactor was preheated to 140 °C with magnetic stirring at an on-screen rate of 500 rpm and kept for 4 h. In addition, to explore the role of experimental atmosphere, the reaction is performed under same conditions in the presence of 0.5 MPa N₂.

After reaction, the used catalyst was separated from the reaction solution by centrifugation and the mixed solution was analyzed by HPLC and GC-MS. The used catalyst was washed with distilled water and ethanol more than six times through the Buchner funnel and then was oven-dried at 70 °C overnight before reuse.

3. Results

3.1. The reaction

As shown in Scheme 1, three kinds of products were mainly detected in the HMF oxidation reaction. At approximate 80% HMF conversion, the catalytic performance of prepared catalysts was compared by DFF selectivity and results were summarized in Table 1. When α -MnO₂ catalyst was employed, a 79.4% conversion of HMF and 93.7% selectivity of DFF

was obtained. Besides, 3.2% selectivity of 5-(diethoxymethyl) furan-2-propionaldehyde (DFP) and 1.1% selectivity of FDCA were detected as the by-products (entry 1). As comparison, a serious of manganese oxide samples was employed in the reaction. With α -MnO₂-300 used as catalyst, 80.5% conversion of HMF and the selectivity of DFF was decreased to 86.4% (entry 2). Furthermore, a 79.7% conversion of HMF and 78.9% selectivity of DFF were achieved with the amorphous AMO catalyst (entry 3). Two low valence Mn₂O₃ and Mn₃O₄ catalyst samples exhibited only moderate activity, while 77.2% and 72.8% conversions of HMF with 71.5% and 63.5% selectivities of DFF were measured (entries 4 and 5), respectively. When the commercial KMnO₄ was employed directly, the conversion of HMF was 76.9% and the selectivity of DFF was 80.7% (entry 6). In addition, the reaction atmosphere of oxygen was replaced by nitrogen to test the role of the molecular oxygen under same conditions, and only 13.1% conversion of HMF was detected (entry 7). To summarize the comparation of catalytic performance, α -MnO₂ exhibited the highest DFF selectivity under approximately same HMF conversion level in isopropanol solvent.

The data in Table 2 show that the solvents have crucial effects on the selective oxidation of HMF to DFF under same conditions. According to previous report, good HMF conversion was measured in polar organic solvents [26]. However, the strong polar solvents, H₂O and CH₃CN only facilitate moderate activities of α -MnO₂ catalyst with conversions as 60.9% and 81.2%, and selectivities of DFF as 78.2% and 76.8% (entries1 and 2), respectively. Actually, low boiling point solvents simplify the separation process and make the DFF easy to isolate. Thus, four kinds of low carbon alcohols were employed as solvents in the reaction. With methanol, ethanol and n-propanol as solvents, the conversions of HMF were 67.8%, 79.3% and 86.4%, while the selectivities of DFF were 35.4%, 65.3% and 67.8% (entries 3, 4 and 5), respectively. HMF was converted to DFF with a selectivity of 84.3% at a conversion of 93.2% in isopropanol indicating isopropanol is the most effective solvent. Isopropanol was

selected as the optimal solvent for the further HMF oxidation investigation. Acetal accounts for the major by-product and FDCA as the secondary by-product in low carbon alcohols during the reaction. Only 7.8% selectivity of DFP and 4.6% selectivity of FDCA were detected, indicating the least by-products were measured in isopropanol solvent.

The effect of reaction time and temperature on the reaction were examined with α -MnO₂ catalyst in isopropanol under 0.5 MPa O₂. Fig. 1 (a) shows the effect of reaction time at 140 °C. The conversion of HMF increases to 95.3% along with the prolonging of the reaction time to 6 h. Nevertheless, the selectivity of DFF was slightly decreased with the extension of time after 4 h. The selectivity of FDCA as a by-product increases monotonically along with the reaction time. At 4 h, the selective of FDCA is 4.6%. Thus, the optimal reaction time is 4 h.

The effect of the reaction temperature on the reaction results at 4 h is presented in Fig. 1 (b). The HMF conversion increased from 58.1 to 93.2% while the reaction temperature increased from 120 to 140 °C. Further increase the temperature to 160 °C, the conversion remained almost the same. The selectivity of DFF was slightly decreased from 95.2 to 84.3% with the increase of the temperature from 120 to 140 °C and then remained unchanged with the temperature further increased to 160 °C. The selectivity of FDCA increased gradually from 0.6 to 7.8% as the reaction temperature increased from 120 to 160 °C. 140 °C is thus regarded as the optimum reaction temperature.

Fig. 2 depicts the result of the stability test of the α -MnO₂ catalyst in isopropanol at 140 °C for 4 h under 0.5 MPa O₂. The performance of the catalyst decreased monotonically along with the increase of the reuse cycles, but the conversion of HMF still remained above 65% while the selectivity of DFF was retained above 75.0 % in the 5th run.

3.2. Catalyst characterization

3.2.1. Texture of the catalyst

In Fig. 3, the SEM micrographs of the α -MnO₂ and α -MnO₂-300 samples both show nano-stick-like morphology. Nevertheless, the surface of α -MnO₂ exhibits more regular and looser, while that of α -MnO₂-300 is disordered and aggregated. The α -MnO₂ sample presents a typical tubular texture, with the internal diameter of 4 ± 2 nm , an average overall diameter of 25 ± 5 nm and length of 300 ± 100 nm, in the TEM micrograph (Fig. 3 c). α -MnO₂-300 gives a similar tubular texture as that of the α -MnO₂ sample (Fig. 3 d). However, the lengths of α -MnO₂-300 tubes are shorter with an average of 200 ± 100 nm.

The isotherms of α -MnO₂ and α -MnO₂-300 samples obtained from nitrogen physisorption are illustrated in Fig. 4. The α -MnO₂ sample has a larger specific surface area (79 m²·g⁻¹) than that of the α -MnO₂-300 sample (68 m²·g⁻¹). Both of the isotherms belong to IV type. However, α -MnO₂-300 has more mesopores. The average mesopore diameters of α -MnO₂ and α -MnO₂-300 samples are 5.2 and 4.8 nm, respectively. In addition, the surface area of used α -MnO₂ was decreased to 75 m²·g⁻¹ compared to the fresh one, which suggest the absorption of impurity species. The decrease of surface area of used catalyst may cause the deactivation of activity.

3.2.2. Structure

The XRD patterns of the catalyst samples are presented in Fig. 5. The diffraction peaks of α -MnO₂ appeared at 2 θ = 12.8 °, 18.1 °, 28.8 °, 37.5 °, 49.8 °, 60.3 °, 69.7 ° and 72.7 ° can be assigned to the diffractions of (1 1 0), (2 0 0), (3 1 0), (2 1 1), (4 1 1), (5 2 1), (5 4 0) and (3 1 2) crystal faces of tetragonal asymmetry in consistency with JCPDS card No. 44-0141. Sample α -MnO₂-300 exhibits relatively weaker diffraction peaks than those of sample α -MnO₂. The pattern of Mn₂O₃ displays also a high crystallinity, with peaks at 2 θ =18.8 °,

23.1 °, 32.9 °, 35.6 °, 38.2 °, 40.6 °, 55.1 ° and 67.3 °, corresponding to the (2 0 0), (2 1 1), (2 2 2), (3 1 2), (4 0 0), (4 1 1), (0 4 4) and (6 3 1) crystal faces of tetragonal asymmetry in consistency with JCPDS card No. 24-0508.

3.2.3. Chemical properties

In Fig. 6, two well resolved reduction peaks was presented on H₂-TPR curves. In the reduction process of α -MnO₂ sample, the peaks located at 298 and 406 are assigned to the reduction of Mn⁴⁺ to Mn³⁺ and then to Mn²⁺, respectively [27]. The two reduction peak positions of α -MnO₂-300 sample shift to higher temperature as 321 and 442. As previous reported [28], the low reduction temperature is related to the easy reducibility of sample, which is in favor of the redox process. The reducibility of α -MnO₂ catalysts agrees well with the high catalytic activity.

As shown in Fig. 7 (a), the O1s spectrum of the fresh α -MnO₂ sample can be deconvoluted into three peaks. The components at binding energies of 529-530, 531-532 and 532-533 eV correspond to surface lattice O²⁻ (denoted as O₁), reactive oxygen species such as O²⁻, O₂²⁻, and O⁻ (denoted as O₁₁) and hydrated oxide species (denoted as O₁₁₁), respectively [29]. Compared to the fresh α -MnO₂ catalyst, the used catalyst shows lower ratio of O₁/O₁₁. Furthermore, when the reaction was performed in the nitrogen atmosphere, the ratio of O₁/O₁₁ decreased obviously further after the reaction. In Fig. 7 (b), The Mn 2p XPS spectra can be decomposed into four peaks. The components at binding energies of 642.1 and 653.8 eV correspond to Mn⁴⁺, while the components at binding energies of 641.3 and 653.0 eV is assigned to Mn³⁺ [30]. Compared to that of the fresh α -MnO₂ catalyst, the proportion of Mn³⁺ is increased on the surface of the used α -MnO₂ catalyst. Similarly, the highest ratio of Mn³⁺/Mn⁴⁺ is obtained after the reaction performed in the presence of nitrogen.

4. Discussion

The data reported in table 1 exhibit that α -MnO₂ and α -MnO₂-300 perform quite well in the selective oxidation of HMF to DFF. Compared to α -MnO₂-300 sample, α -MnO₂ shows better crystallinity and exposes more crystal faces. α -MnO₂ exhibits a more regular and looser morphology than α -MnO₂-300, which is consistent with the comparative values of their BET surface area data. Since the sizes of the HMF molecule (0.82 nm) and oxygen molecule (0.35 nm), the oxidation of the HMF occurs on both the external surface and inner surface inside the pores of α -MnO₂ tubes [25]. The larger surface area of α -MnO₂ (79 m²·g⁻¹) increases the frequency of contact between HMF and active sites during the reaction. In addition, the easy reducibility of α -MnO₂ sample indicating the high mobility of oxygen species is also facilitate the catalytic activity in HMF oxidation.

Six different solvents were employed in the selective oxidation of HMF at 140 °C for 4 h and the catalytic activity of α -MnO₂ increases in line with the order, H₂O < MeOH < EtOH < CH₃CN < n-propanol < isopropanol. It has been reported that H₂O is not a good solvent due to the strong coordination of water to the active sites on metal oxides [31]. With the organic solvents used, the catalytic performance of α -MnO₂ was promoted. The conversion of HMF is higher in CH₃CN than in EtOH under the same conditions, which may explain by the polar solvent assisted. In the alcoholic solvents, the catalytic activity of α -MnO₂ and the selectivity of DFF increased with the carbon chain elongated. However, lone pair electrons on alcohol hydroxyl are possible to attack DFF molecule via a nucleophilic addition step and form acetal as the by-product. In isopropanol solvent, DFP was formed as a kind of acetal via the above process. However, DFP only accounts for 7.8% selectivity of the total product, indicating that isopropanol is quite good as a solvent.

The reaction time and temperature were optimized in HMF oxidation. As a kind of byproduct, FDCA formed by the conversion of DFF are facilitated along with the elevation of reaction time and temperature. The conversion of HMF was increased slightly and the DFF

selectivity was decreased after 4 h. Meanwhile, when the reaction temperature was elevated above 140 °C, the HMF conversion was nearly stable and FDCA byproduct was slightly increased. To ensure high DFF selectivity and efficient catalytic performance, the 4 h and 140 °C were selected as the suitable reaction time and temperature in HMF oxidation.

On the other hand, β -hydride elimination step is proposed as the rate-determining step in the oxidation of alcohol to aldehyde with heterogeneous catalysts [11]. For the metal oxide catalysts in this work, the oxygen species is conducive to combine hydroxy group and then leads to eliminating β -hydride in HMF molecule. In Fig. 6 (a), the O1s XPS spectrum reflects the surface oxygen species of the α -MnO₂ catalyst. Under molecular oxygen atmosphere, the ratio of O_I/O_{II} was slightly decreased in O1s spectra, indicating that lattice O²⁻ was consumed after the reaction. When the oxidation reaction was performed in the nitrogen atmosphere, the content of lattice O²⁻ decreased more obviously. These results illustrate that the consumed active lattice O^{2-} species (O_I) on the surface of α -MnO₂ can be replenished in the presence of molecular oxygen. The recovery rate of active lattice O²⁻ species is slower than the consumption of them as the amount of lattice O^{2-} on the surface of used α -MnO₂ is decreased. The increased content of oxygen species (OII) are related to the appearance of surface oxygen vacancies, which is also an indirect proof of the increased content of oxygen vacancies [32-34]. Moreover, the Mn^{3+} is relevant to the creation of oxygen vacancies [35]. In Mn 2p XPS spectra (Fig. 6b), the ratio of Mn^{3+}/Mn^{4+} increased after the oxidation reaction indicating that more oxygen vacancies appear on used α -MnO₂. This result further identifies that the active lattice O^{2-} species is closely associated with the redox potential of α -MnO₂ [25]. According to the XPS analysis results, the lattice O²⁻ serves as the active sites in the selective oxidation reaction. The reaction undergoes likely the following pathways according to the Mars-van-Krevelen mechanism. In Scheme 2, the hydroxymethyl species of HMF were firstly adsorbed on the surface of α -MnO₂ and then the active lattice O²⁻ species was

consumed to form DFF along with the reduction of Mn^{4+} to Mn^{3+} . Finally, the Mn^{3+} was reoxidized by the chemisorbed molecular oxygen, which continuously supplied the active lattice O^{2-} species via the cyclic redox couple of Mn^{4+} and Mn^{3+} ions.

5. Conclusions

The nano-stick-like α -MnO₂ is utilized as an efficient catalyst in selective oxidation of HMF to DFF. The characterizations of α -MnO₂ reveal large BET surface area is related to the loose and regular tubular texture. The average diameter of inside pores on α -MnO₂ are larger than the diameter of HMF molecule, which makes the reaction occur on both the external surface and inner surface inside the pores of α -MnO₂. Acetal and FDCA are found to be by-products in alcoholic solvents. Isopropanol is good solvent for selective oxidation of HMF to DFF. Molecular oxygen is crucial for regeneration of α -MnO₂ catalyst to finish the redox cycle. Under 0.5 MPa O₂, 93.2% conversion of HMF and 84.3% selectivity of DFF were measured in isopropanol solvent at 140 °C for 4 h. α -MnO₂ keeps good reusability after being used for 5 times.

The reaction proceeds via the Mars-van-Krevelen mechanism. The lattice O^{2-} on α -MnO₂ serves as the active sites to realize the oxidation of hydroxy group in HMF. The consumption of the lattice O^{2-} on α -MnO₂ is replenished by the chemisorbed molecular oxygen during the reaction and then α -MnO₂ is involved in next catalytic cycle process.

Credit author statement

Linhao Yu: Methodology, Investigation and Writing-Original draft preparation.

Hong Chen and Yongdan Li: Supervision, Conceptualization and Writing-Review & Editing.

Zhe Wen: Data curation.

Mengmeng Jin and Zewei Ma: Software and Visualization.

Xueli Ma, Yushuai Sang and Mengmeng Chen: Formal analysis, Software and Validation.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. Acknowledgments

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Figures and table captions

Scheme 1. The selective oxidation of HMF with molecular oxygen.

Table 1. The selective oxidation of HMF with different catalysts.

Table 2. The oxidation of 5-hydroxymethylfurfural (HMF) in different solvents.

Fig. 1. The effect of the (a) reaction time and (b) temperature.

Fig. 2. The recycling experiment for HMF oxidation.

Fig. 3. The SEM and TEM miscrographs of the catalytic materials (a) SEM of α -MnO₂; (b)

SEM of α -MnO₂-300; (c) TEM image of α -MnO₂; (d) TEM image of α -MnO₂-300.

Fig. 4. The adsorption isotherms of manganese oxide samples.

Fig. 5. The XRD patterns of catalyst samples.

Fig. 6. The H₂-TPR curves of catalyst samples.

Fig. 7. (a) O1s and (b) Mn2p XPS spectra of the α -MnO₂.

Scheme 2. The reaction pathways of selective oxidation of HMF to DFF with α -MnO₂.



Scheme 1. The selective oxidation of HMF with molecular oxygen.

| Entry | Catalyst | Solvent | Conv.(%) | Product selectivity (%) | | | |
|-------------|--------------------------------|---------|----------|-------------------------|------|------|--------|
| | | | | DFF | DFP | FDCA | Others |
| 1 | α -MnO ₂ | IPA | 79.4 | 93.7 | 3.2 | 1.1 | 2.0 |
| 2 | α-MnO2-300 | IPA | 81.7 | 86.4 | 7.5 | 4.2 | 1.9 |
| 3 | AMO | IPA | 79.7 | 78.9 | 6.8 | 6.3 | 8.0 |
| 4 | Mn ₂ O ₃ | IPA | 77.2 | 71.5 | 11.6 | 7.4 | 9.5 |
| 5 | Mn ₃ O ₄ | IPA | 72.8 | 63.5 | 17.3 | 8.5 | 10.7 |
| 6 | KMnO ₄ | IPA | 76.9 | 80.7 | 10.1 | 6.6 | 2.6 |
| $7^{\rm b}$ | α-MnO ₂ | IPA | 13.1 | 69.2 | 13.6 | 6.8 | 10.4 |

Table 1. The selective oxidation of HMF with different catalysts^{*a*}.

^{*a*} Reaction conditions: HMF 0.126 g (1mmol), 0.05 g catalyst, 25 mL isopropanol, 500 rpm, 0.5 MPa O₂.

^b The reaction was performed in nitrogen atmosphere.

| Entry | Solvent | Conv.(%) ^b | Product selectivity $(\%)^b$ | | | |
|-------|---------|-----------------------|------------------------------|------|--------|--------|
| | | | DFF | FDCA | Others | |
| | 1 | H ₂ O | 60.9 | 78.2 | 13.5 | 8.3 |
| | 2 | CH ₃ CN | 81.2 | 76.8 | 8.3 | 14.9 |
| | 3 | MeOH | 67.8 | 35.4 | 12.3 | acetal |
| | 4 | EtOH | 79.3 | 65.3 | 9.2 | acetal |
| | 5 | n-propanol | 86.4 | 67.8 | 10.6 | acetal |
| | 6 | isopropanol | 93.2 | 84.3 | 4.6 | 11.1 |

Table 2. The oxidation of 5-hydroxymethylfurfural (HMF) in different solvents^{*a*}.

^{*a*} Reaction conditions: HMF 0.126 g (1mmol), catalyst 0.05 g α-MnO₂ catalyst, 25 mL isopropanol, 500 rpm, 0.5 MPa O₂, reaction time 4 h, temperature 140 °C. ^{*b*} The results are obtained by HPLC with the external standard technique and GC-MS

^b The results are obtained by HPLC with the external standard technique and GC-MS instrument.



Fig. 1. The effect of the reaction time (a) and temperature (b).



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Fig. 7. (a) O1s and (b) Mn2p XPS spectra of the α -MnO₂.



Scheme 2. The reaction pathway of selective oxidation of HMF to DFF with α -MnO₂.