Aerobic Selective Oxidation of Biomass-derived 5-Hydroxymethylfurfural to 2,5-Diformylfuran with Active Manganese Dioxide Catalyst

Shengqiang Zhang, Weifeng Li, Xianhai Zeng,* Yong Sun, and Lu Lin*

5-hydroxymethylfurfural (HMF) is an important bio-based platform chemical, and its aerobic selective oxidation to 2,5-diformylfuran (DFF) still remains a challenge. This work dealt with active manganese dioxide (AMD) and efficiently catalyzed HMF oxidation to DFF with a yield of ~73% at 393 K and 60 bar O_2 in N,N-Dimethylformamide (DMF). Through analysis of liquid products and the catalyst characterization using X-ray diffraction (XRD), a scanning electron microscope (SEM), a transmission electron microscope (TEM), and an elemental analyzer, it can be seen that this AMD catalyst is a low-cost, efficient, and environmentally benign heterogeneous catalyst for the aerobic selective oxidation of HMF to DFF in a one-pot technique. These research results may provide guidance for the development of more efficient catalysts for the future industrial production of high-value added DFF.

Keywords: Oxidation; 5-Hydroxymethylfurfural; 2,5-Diformylfuran; Manganese Oxide; Biomass

*Contact information: School of Energy Research, College of Energy, Xiamen University, Xiamen 361102, China; *Corresponding authors: xianhai.zeng@xmu.edu.cn; lulin@xmu.edu.cn*

INTRODUCTION

Nowadays, the world has become increasingly dependent on fossil resources as its main source of chemicals and energy. Besides, driven by the drastic global population and the strong economic growth, the demand for fossil resources is ever increasing. This growth in demand, combined with the diminishing of fossil reserves, will require the R&D of new, sustainable and renewable sources for the future production of chemicals and energy. Among them, biomass is the most fascinating alternative feedstock because it is the only widely available carbon source other than coal and petroleum (van Putten *et al.* 2013). Thus, it is important for researchers worldwide to develop innovative, efficient, and sustainable pathways for the production of value-added chemicals and fuels from abundant biomass. Production of fuels and chemicals from biomass can be achieved through partially deoxygenating biomass derivatives, which are primarily obtained by methods of hydrolysis and dehydration (Alonso *et al.* 2010). For example, 5-hydroxymethylfurfural (HMF), which is a versatile bio-based platform chemical with many potential applications, can be produced by catalytic dehydration of biomass carbohydrates such as glucose, fructose, and even cellulose (van Putten *et al.* 2013). Moreover, specialty chemicals can be produced by further transformations of HMF (Antonyraj *et al.* 2013; Gallo *et al.* 2013). Among the chemicals derived from HMF, 2,5-diformylfuran (DFF) is an organic intermediate with many application prospects and has attracted much attention in recent years. It can be used not only as a monomer in the production of multifunctional materials, but also as the starting material in the synthesis of polymeric Schiff bases (Xiang *et al.* 2013), pharmaceuticals (Hopkins *et al.* 1998), antifungal agents (Del Poeta *et al.* 1998), fluorescent materials (Ma *et al.* 2011), and resins (Amarasekara *et al.* 2009). Thus, the production of DFF from biomass-derived HMF is attractive and important.

DFF can be produced through selective oxidation of the hydroxymethyl group in HMF. However, the primary challenge in this process is the existing furan and aldehyde functionalities in HMF, which makes it susceptible to side reactions such as over-oxidation, decarboxylation, and cross-polymerization (Karimi *et al.* 2014). In brief, the route for the production of DFF from HMF requires oxidation of the hydroxyl group in HMF without attacking other more reactive groups. Otherwise, unwanted products would be formed. Among the oxidation techniques described in the previous reports, only a few procedures qualify as industrially useful, economical, and environmentally acceptable green technologies; further research for efficient and selective oxidation of HMF to DFF is still necessary. The commonly used chemical catalytic oxidation methods are often carried out with various homogeneous and heterogeneous catalysts, including those aided by greener air or molecular oxygen as oxidants (Le *et al.* 2013; Ma *et al.* 2011; Sádaba *et al.* 2013; Takagaki *et al.* 2011). Although numerous homogenous catalytic systems can be applied in the production of DFF from HMF or other biomass carbohydrates, processes with heterogeneous catalysts seem to be gradually becoming more prevalent because of their likely industrial applications. The selective oxidation of HMF to DFF over heterogeneous catalysts aided by air or molecular oxygen appears as a green process with a great perspective in the future industrial production of DFF (Kazi *et al.* 2011). Also, it has been determined that the molecular oxygen has a higher activity than air in this oxidation reaction (Yang *et al.* 2012).

In this context, much effort has been devoted to the production of DFF from HMF or carbohydrates using various heterogeneous catalytic systems in recent years. To date, several heterogeneous metal-based catalytic systems, mostly transition metal compounds such as noble metal-based catalysts (Antonyraj *et al.* 2013; Nie *et al.* 2013a,b), vanadium-based catalysts (Grasset *et al.* 2013; Le *et al.* 2013; Navarro *et al.* 2009; Nie and Liu 2012), and manganese-based catalysts (Liu *et al.* 2014), have been utilized with varied degrees of success in the aerobic selective oxidation of HMF to DFF. However, there are still several important issues to be resolved, such as how to make the operation process easier, reduce the use of overly complex catalytic systems, and optimize the reaction conditions. As one of the largest families of transition metal oxides, heterogeneous manganese-based catalysts have received growing attention because of their unique fundamental properties, such as the lower cost of raw materials, diversity of structure, and environmentally friendly characteristics. Active manganese dioxide (AMD) is often prepared through processes of reduction, disproportionation, and densification by using natural MnO_2 of high grade as the raw material. It is actually a combination of active and chemical MnO_2 with large specific surface area. In addition to its original application in the battery industry due to its excellent electrochemical performance, it is also widely adopted in the oxidation reactions of unsaturated alcohols (Sun *et al.* 2012). The brown AMD has the highest activity among the manganese oxides obtained through different synthetic approaches, thus having a good reactivity when it is adopted as a catalyst in various conversion reactions. In particular, when it is used as catalyst in the oxidation of unsaturated alcohols, aldehydes can form selectively without the isomerization of unsaturated groups in the reactants (Pratt and Castle 1961). It is reported that a variety of unsaturated aldehydes or ketones can be produced *via* the oxidation reactions of their corresponding alcohols with manganese-based catalysts; most importantly, further oxidation reactions are usually difficult to take place, showing excellent selectivity (Taylor *et al.* 2005). The reason for this may be that manganese is a metal element with a wide distribution of valence states, from +2 to +7. Manganese oxides prepared *via* different methods will have different valences because of their different structures, thus resulting in varied reactivity. AMD shows excellent reactivity and selectivity to aldehydes in many organic reactions because the manganese elements in this compound often have intermediate valence, which means it can be oxidized and reduced simultaneously. This research presents an AMD catalyst that oxidizes HMF to DFF in a facile manner with high yields under mild conditions.

EXPERIMENTAL

Materials

HMF (>98%) was obtained from Shanghai Pu Guang Industrial Co. Ltd., China. DFF (>98%) was obtained from Tokyo Chemical Industry Co., Ltd., Japan. Manganese acetate tetra hydrate ($Mn(OAc)_2 \cdot 4H_2O$, >99%) was purchased from China National Medicine Group Shanghai Chemical Reagent Company. Manganese dioxide (MnO_2) was purchased from Xilong Chemical Co., Ltd, (Guangdong, China). All other chemicals were of analytical grade, supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), and used without further purification. Oxygen (99.5%) was purchased from Linde Gas Xiamen Ltd.

Catalyst Preparation

The preparation method for this AMD catalyst is as follows: An accurately weighed powder of $KMnO_4$ was added into a beaker, which was then completely dissolved with distilled water under mechanical agitation to obtain a homogeneous solution of $KMnO_4$. A solution containing Mn^{2+} ions was prepared with similar methods as mentioned above, in which the molar amount of manganese salt (such as manganese sulfate) was a 50% molar excess compared to $KMnO_4$. The $KMnO_4$ solution was subsequently transferred to a GCF-0.4 L reaction kettle (400-mL cylindrical Hastelloy alloy high-pressure reactor made by Dalian Controlled Plant, China). Then, the manganese sulfate solution was also added to the reaction kettle slowly, followed by the addition of an amount of distilled water to the reaction kettle to keep a constant volume of 300 mL, according to a fill rate of 80%. Then, the reaction kettle was sealed and purged thoroughly with nitrogen three times. Then, the mixture was reacted at a temperature of 150 °C and maintained for 8 h under a stirring rate of 800 rpm. After reaction, the reaction kettle was cooled down to room temperature with cold water and fully depressurized. Then, the sample from the reaction kettle was filtered 5 to 10 times with distilled water. The filtered sample was then dried at 110 °C ± 5 °C for 3 to 4 h in a drum wind-drying oven. A black powder with an average particle size of 6 mm was obtained after fully grinding (saving it in a glass desiccator).

Equipment and Experimental Procedures

HMF oxidation reactions were carried out in 50-mL or 100-mL cylindrical stainless steel high-pressure reactors made by Parr Instrument Company, USA. In each oxidation reaction, reactants and catalysts were introduced into the organic solvent in the reactor. Then, the reactor was sealed and purged thoroughly with O_2 three times. Then, the mixtures were stirred at *ca.* 800 rpm to decrease or even avoid the internal and external mass transfer limitations, which would make the obtained results more accurate.

For each reaction, the reactor was heated to a desired temperature of 110 to 130 °C with a ramp rate of 5 °C $\cdot$min^{-1}. A suitable reaction temperature range of *ca*. 80 to 150 °C was selected, according to relative literature and the results obtained after practical optimization experiments, in order to have this conversion reaction be conducted under a mild reaction temperature. After the reaction, the reactor was cooled down to room temperature with cold water and fully depressurized. Then, the sample taken from the reactor was filtered and the liquid-phase products were collected for further analysis.

Catalyst Recycling and Stability Experiments

After each reaction, the AMD catalyst was separated from the reaction mixture by centrifugation, washed three times with distilled water and ethanol, and dried at 65 °C overnight in a vacuum oven. Then, the recovered AMD catalyst was used for the second cycle under the same conditions as were used the first time. These procedures were repeated several times to examine the stability of the AMD catalyst.

Catalyst Characterization

X-ray diffraction (XRD) patterns were obtained on an X-ray diffractometer (X'pert PRO, PANalytical B.V., Netherlands) using a Cu Kα radiation source operated at 40 kV and 30 mA. Data were collected from 2θ between 10° and 80° at a scanning speed of 3°/min. Scanning electron microscope (SEM) images were acquired on an SEM (Hitachi S-4800, Japan) with an accelerating voltage of either 20 kV or 30 kV. Transmission electron microscope (TEM) images were obtained on a TEM (JEOL JEM-2100, Japan) with an accelerating voltage of 200 kV. Elemental analyses were performed on an elemental analyzer (Vario EL III, Elementar Analysensysteme GmbH, Germany).

Analytical Approaches

The qualitative analysis (GC-MS) of the sample after reaction was conducted on a Shimadzu QP2010SE (Japan) instrument with Rtx-5MS column (30.0 m × 0.25 µm × 0.25 mm) and electron impact ionization (EI). The quantitative analysis (GC) of HMF and DFF in the sample were analyzed on an Agilent 7890 series (USA) equipped with a HP-5 capillary column (30.0 m × 320 µm × 0.25 µm) and a hydrogen flame ionization detector (FID) operating at 270 °C.

The carrier gas was N_2, with a flow rate of 1.0 mL$\cdot$min^{-1}. The injector temperature was 250 °C. The oven temperature was maintained at 100 °C for 2 min, rose to 250 °C with a ramp rate of 15 °C $\cdot$min^{-1}, and maintained at 250 °C for 2 min. The amounts of HMF and DFF were calculated using an external standard. The conversion of initial materials, the yield and selectivity of products on a molar basis were calculated using the following respective equations:

$$\text{HMF conversion (\%)} = \left(1 - \frac{moles\ of\ HMF\ unreacted}{moles\ of\ initial\ HMF}\right) \times 100\% \tag{1}$$

$$\text{DFF yield (\%)} = \left(\frac{moles\ of\ DFF\ produced}{moles\ of\ initial\ HMF}\right) \times 100\% \tag{2}$$

$$\text{DFF selectivity (\%)} = \left(\frac{moles\ of\ DFF\ produced}{moles\ of\ initial\ HMF - moles\ of\ HMF\ unreacted}\right) \times 100\% \tag{3}$$

RESULTS AND DISCUSSION

Catalyst Synthesis and Characterization

Because the structure types and morphologies of materials remarkably affect their physical and chemical properties, the characterization of the fresh and spent AMD catalysts was determined to provide an insight into the stability of the AMD catalytic materials. The XRD patterns of the fresh and spent AMD catalysts after calcination (Fig. 1) showed similar patterns, with two broad peaks of low intensity (amorphous form) and three narrow sharp peaks (crystalline form), indicating that no new types of phases had been formed. According to related data, the characteristic diffraction peaks of β-MnO_2 and γ-MnO_2 exist in the 2 theta positions of 29°, 37.5°, 57°, 72.5° (JCPDS Card No. 24-0735), and 21.9°, 37.2°, 42.5°, 56°, 67.3° (JCPDS Card No. 14-0644). These XRD results confirmed that the AMD catalyst is likely to be a kind of manganese oxide with properties of β-MnO_2 and γ-MnO_2 because relatively strong peaks at 2 theta =37.5°, 42.5°, 57°, and 67.3° were observed in the XRD patterns of both fresh and spent AMD catalysts.

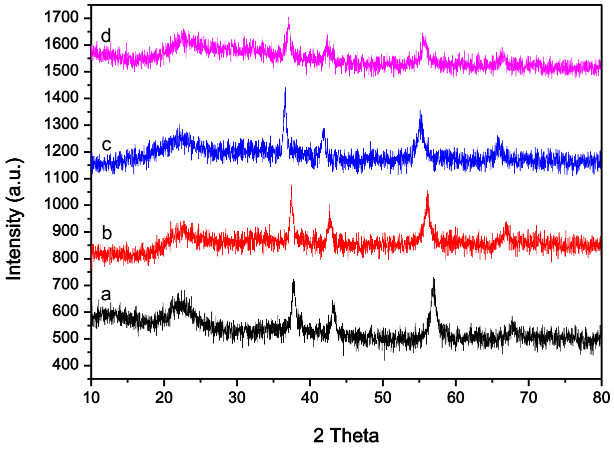


Fig. 1. XRD patterns of the fresh and spent AMD catalysts. (a): fresh AMD catalyst; recycle times of (b): 1 cycle; (c): 3 cycles; (d): 5 cycles

The AMD catalyst exhibited little to no morphological changes, as evidenced by the comparison of TEM images of the fresh and spent AMD catalyst after 5 cycles (Fig. 2).

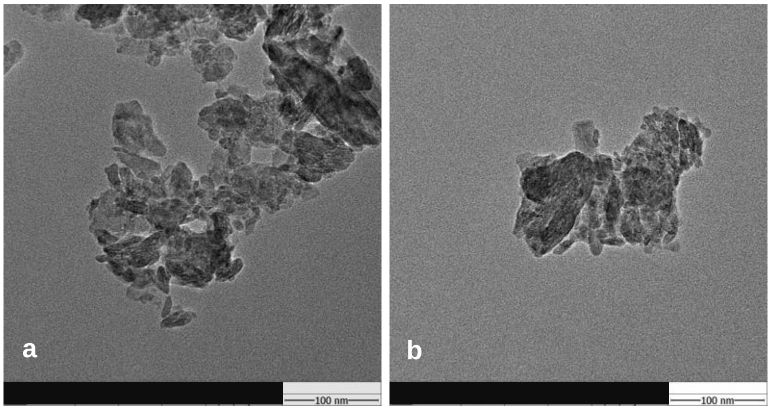


Fig. 2. TEM micrographs of (a) fresh and (b) spent AMD catalyst after 5 cycles (scale bar 100 nm)

In addition, an SEM was used to observe the surface morphology of the AMD catalyst. The SEM images showed that both the fresh and spent AMD catalysts were composed of aggregations of small irregularly shaped particles (Fig. 3). There was no remarkable change in surface morphology of the catalysts before and after recycling experiments. These results indicated that the AMD catalyst has outstanding stability under the given reaction conditions, which is consistent with the catalytic activity results of the subsequent catalyst recycling experiments.

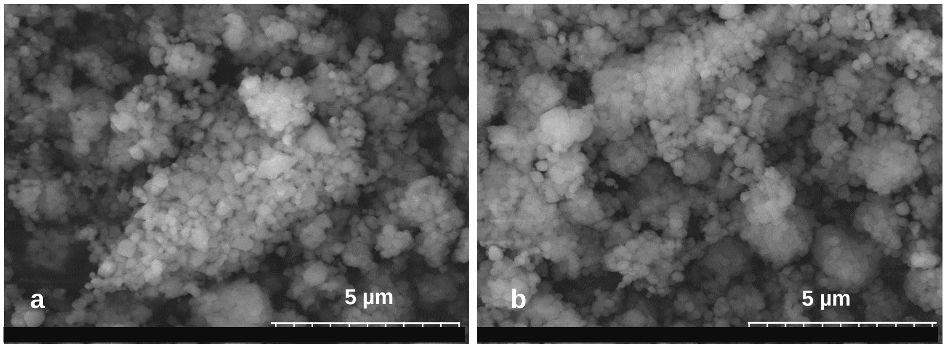


Fig. 3. SEM images of (a) fresh and (b) spent AMD catalyst after 5 cycles

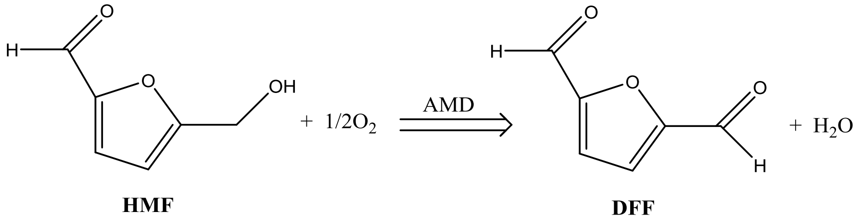
Furthermore, the results of the elemental analysis of the fresh and spent AMD catalysts after different cycle times are listed in Table 1. Carbon residues of 1.2 to 1.4% (based on the mass ratio of carbon on the surface of the solid AMD catalyst) on the catalyst resulted in a slight deactivation of the catalyst, which led to a slight drop in the yields of DFF. No excessive carbon deposits increased with the recycling of the catalyst, which was the probable reason for the cycling stability of AMD, even though the carbon content was the highest value among the analyzed elements of the spent AMD catalysts after different times of catalyst recycling experiments. The total amount of C and H elements in the spent AMD catalysts (2.2% to 2.6%) was generally higher than that in the fresh AMD catalyst (0.8%); this may be due to the adsorption of a small amount of DFF and other oxidation byproducts. In addition, the N content might be derived from the used solvent DMF, the mass percentage of which was 0.1% to 0.2%, which indicated that the solvent DMF had a good stability in the oxidation reaction under the given conditions.

Table 1. Elemental Analyses of the Fresh and Spent AMD Catalysts

Recycle times	N Content (%)	C Content (%)	H Content (%)
Fresh	0. 085	0. 065	0.697
1	0. 139	1.194	0.998
2	0.086	1.362	0.923
3	0. 203	1.412	1.166
5	0. 108	1.215	0.974

Catalytic Oxidation of HMF to DFF with Different Manganese Oxides

The reaction pathway for the conversion of HMF to DFF using AMD catalyst is shown in Scheme 1. The stability of HMF was studied first. HMF was stable in DMF without catalyst and oxygen pressure. The conversion of HMF in DMF for 3 h at 110 °C with an oxygen pressure of 45 bar was almost negligible (Table 2, Entry 1). This indicated that HMF could remain stable in DMF under neutral conditions, which was consistent with previous reports (Vuyyuru and Strasser 2012). According to related reports, acid-catalyzed side reactions such as aldol addition and condensation could take place under acidic conditions, and some side reactions, such as condensation and the Cannizarro reaction, could occur under alkaline conditions (Kang *et al.* 2012; Patil and Lund 2011). Thus, a neutral condition is important for the formation reaction of DFF to achieve high yield and selectivity of DFF. AMD catalyst showed relatively good catalytic activity on the aerobic selective oxidation of HMF to DFF, with a 65.8% yield of DFF at an 86.8% conversion of HMF (Table 2, Entry 2). In addition, this conversion reaction using other common manganese oxides was also investigated. Unlike the prepared AMD powders, commercially available manganese oxides such as MnO_2, Mn_2O_3, and Mn_3O_4 gave poor catalytic performance (Table 2, Entries 3 to 5). This is probably due to the different structure of these manganese compounds and the different forms of Mn in them. The higher catalytic activity of the prepared AMD catalyst was mostly due to the fact that the manganese elements in this compound often have intermediate valence, which means it can be oxidized and reduced simultaneously. In addition, it was found that some homogenous manganese salts such as $Mn(OAc)_2 \cdot 4H_2O$ and $MnCl_2 \cdot 4H_2O$ also didn't have a high catalytic activity for the reaction of HMF to DFF (Table 2, Entries 6 and 7).



Scheme 1. Reaction pathway for the conversion of HMF to DFF using AMD catalyst

Table 2. Effect of Different Manganese Oxides on the Aerobic Selective Oxidation of HMF to DFF[a]

Entry	Catalyst	Catalyst amount (g)	Time (h)	HMF conversion (%)	DFF yield (%)
1[b]	-	-	3	4.6	-
2	AMD	1.16	3	86.8	65.8
3[c]	MnO_2	1.27	8	7.8	0.4
4[c]	Mn_2O_3	1.25	8	7.6	2.3
5[c]	Mn_3O_4	1.24	8	21.2	16.3
6	$Mn(OAc)_2 \cdot 4H_2O$	4.18	8	12.3	7.2
7	$MnCl_2 \cdot 4H_2O$	3.35	8	8.4	3.9

[a] Reaction conditions: HMF (10 mmol) and a set amount of catalyst were added to DMF (65 mL), and the reaction was carried out at 110 °C with an oxygen pressure of 45 bar
[b] The reaction was conducted without catalyst or oxygen
[c] Commercial catalyst

Aerobic Selective Oxidation of HMF to DFF in Various Solvents

It is known that the solvent plays a critical role in the reaction efficiency. The aerobic selective oxidation of HMF to DFF was thus further conducted with a variety of common solvents. The effect of solvent on this conversion reaction is summarized in Table 3. The solvent showed a remarkable effect on both the conversion of HMF and the yield of DFF. DMF and dimethyl sulfoxide (DMSO), which are organic solvents with strong polarities and high boiling points, were favorable for the examined reaction. The conversion of HMF reached 84.6% and 85.5% in DMF and DMSO, respectively (Table 3, Entries 1 and 2). The selectivity of DFF in DMF was slightly higher than that in DMSO, due to the fact that the generated DFF would be further oxidized into 2,5-furandicarboxylic acid (FDCA) in DMSO. Moderate HMF conversion (44.7%) and DFF yield (34.6%) were obtained in toluene. The conversion of HMF was low during the reactions carried out in other solvents, such as methyl isobutyl ketone (MIBK), N, N-Dimethylacetamide (DMAC), acetonitrile (MeCN), and N-methyl-2-pyrrolidone (NMP) (Table 3, Entries 4 to 7); the reactions in these three solvents gave poor DFF yields of 10.6%, 6.5%, and 13.2%, respectively. A control experiment was also carried out in the absence of AMD catalyst; the conversion of HMF was only 3.6% after 8 h in DMF, with no oxidation products. These results indicated that DMF was a superior solvent for the conversion of HMF to DFF. According to the previous results and the general acceptable mechanism on the oxidation of alcohols (Biswal *et al.* 2011), it can be speculated that Mn^{3+} was the active site for the oxidation of HMF, which would be reduced to Mn^{2+} by the abstraction of one hydrogen atom connected with a carbon atom in the hydroxymethyl group; simultaneously, carbon cations were produced, and then they released H^+ to give rise to DFF. Then, the Mn^{2+} was deoxidized to Mn^{3+}, which generated a catalytic cycle. Based on general knowledge of the solvent effect, a polarity solvent usually contains hydroxyl or carbonyl groups in its molecule structure, which results in a very strong polarity. Moreover, polar solvents also have electronic properties of having opposite charges attract each other; the positive charge of the cations can be stabilized in strong polar solvents such as DMSO and DMF. Thus, a high yield of DFF was obtained when this conversion catalyzed by AMD catalyst was carried out in DMF.

Table 3. Effect of Solvents on the Aerobic Selective Oxidation of HMF to DFF

Entry	Solvent	AMD amount (g)	Time (h)	HMF conversion (%)	DFF yield (%)
1	DMF	2.23	3	84.6	69.8
2	DMSO	2.23	3	85.5	59.7
3	Toluene	2.22	3	44.7	34.6
4	MIBK	2.24	3	16.7	10.6
5	DMAC	2.21	3	82.3	66.4
6	MeCN	2.26	3	12.6	6.5
7	NMP	2.25	3	28.5	13.2
8	DMF	-	8	3.6	-

[a] Reaction conditions: HMF(10 mmol) and AMD catalyst were added to DMF (65 mL), and the reaction was carried out at 130 °C with an oxygen pressure of 45 bar

Effect of Catalyst Amount on Aerobic Selective Oxidation of HMF to DFF

The aerobic selective oxidation of HMF to DFF was also carried out with different amounts of AMD catalyst to investigate the effect of catalyst loading. As shown in Table 4, the loading of AMD catalyst had a remarkable effect on the aerobic selective oxidation of HMF to DFF. The conversions of HMF were 38.4% and 45.7% after 8 h with 1.5 and 2.9 g of AMD catalyst, respectively, and the corresponding yields of DFF were 32.5% and 39% (Table 4, Entries 1 and 2). The conversions of HMF reached 82.4% and 85.8% after 4 and 6 h, respectively, when 3.3 g of AMD was used (Table 4, Entries 3 and 4). Increasing the amount of AMD to 4.5 g, this conversion reaction proceeded faster (Table 4, Entries 5 and 6). Only 3 h were required to achieve the maximum yield of DFF (73.3%) with a high conversion of HMF (87.5%). Thus, as for the effect of the AMD catalyst amount on the aerobic selective oxidation of HMF to DFF, a general rule can be concluded that the conversion of HMF and the yield of DFF would be increased with the increasing of the catalyst amount to some extent at a given reaction time. This can be attributed to an increase in the availability and the number of catalytically active sites, leading to a high oxidation rate under otherwise identical reaction conditions; a similar phenomenon was also found for the oxidation of alcohols (Davis *et al.* 2013). However, the selectivity of DFF between 64.8% and 73.3% was almost the same with different amounts of catalyst loadings. It seems that the selectivity of DFF may not have a direct relationship with the catalyst loading, as the examined reactions were conducted under otherwise identical conditions. Moreover, the active sites of the AMD catalyst might not be the only factor for the HMF conversion and the yield/selectivity of the desired DFF. Considering that the mass transfer limitations do play a key role in this system, the turnover frequency (TOF) of the reactant over the active sites of the AMD catalyst should be taken into account at the same time.

Table 4. Effect of Different Catalyst Loadings on the Aerobic Selective Oxidation of HMF to DFF

Entry	Catalyst amount (g)	Time (h)	HMF conversion (%)	DFF yield (%)
1	1.5	8	38.4	32.5
2	2.9	8	45.7	39.0
3	3.3	4	82.4	69.3
4	3.3	6	85.8	71.2
5	4.5	1	78.6	64.8
6	4.5	3	87.5	73.3

[a] Reaction conditions: HMF (10 mmol) and an amount of AMD catalyst were added to DMF (65 mL), and the reaction was carried out at 120 °C with an oxygen pressure of 60 bar.

CONCLUSIONS

1. An inexpensive, efficient, selective, easily recyclable, and environmentally benign heterogeneous AMD catalyst was adopted in the aerobic selective oxidation of HMF to DFF with a relatively good yield of ~73% at 393 K and 60 bar O_2 in DMF.
2. The research results might provide guidance for the development of more efficient catalysts for the further industrial production of high-value added DFF.
3. It is of great importance to carry out surveys on the carbon balance analysis, so as to obtain the desired DFF more efficiently in the future.
4. The process optimization and the detailed catalytic mechanism of this approach require further study.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from the Key Research Program of Cooperation between Universities and Industry (2013N5011) from the Department of Science and Technology of Fujian Province of China, the National Key Basic Research Program (2010CB732201) from the Ministry of Science and Technology of China, the Key Research Platform Program (3502Z20131016) from Xiamen Municipal Bureau of Science and Technology, the Natural Science Foundation of China (21106121), and the Fundamental Research Funds for the Xiamen University (201312G009).

REFERENCES CITED

Alonso, D. M., Bond, J. Q., and Dumesic, J. A. (2010). "Catalytic conversion of biomass to biofuels," *Green Chem.* 12(9), 1493-1513.

Amarasekara, A. S., Green, D., and Williams, L. D. (2009). "Renewable resources based polymers: Synthesis and characterization of 2,5-diformylfuran–urea resin," *Eur. Polym. J.* 45(2), 595-598.

Antonyraj, C. A., Jeong, J., Kim, B., Shin, S., Kim, S., Lee, K. Y., and Cho, J. K. (2013). "Selective oxidation of HMF to DFF using Ru/γ-alumina catalyst in moderate boiling solvents toward industrial production," *J. Ind. Eng. Chem.* 19(3), 1056-1059.

Biswal, M., Dhas, V. V., Mate, V. R., Banerjee, A., Pachfule, P., Agrawal, K. L., Ogale, S. B., and Rode, C. V. (2011). "Selectivity tailoring in liquid phase oxidation over MWNT-Mn_3O_4 nanocomposite catalysts," *J. Phys. Chem. C* 115(31), 15440-15448.

Davis, S. E., Ide, M. S., and Davis, R. J. (2013). "Selective oxidation of alcohols and aldehydes over supported metal nanoparticles," *Green Chem.* 15(1), 17-45.

Del Poeta, M., Schell, W. A., Dykstra, C. C., Jones, S. K., Tidwell, R. R., Kumar, A., Boykin, D. W., and Perfect, J. R. (1998). "In vitro antifungal activities of a series of dication-substituted carbazoles, furans, and benzimidazoles," *Antimicrob. Agents Ch.* 42(10), 2503-2510.

Gallo, J. M. R., Alonso, D. M., Mellmer, M. A., and Dumesic, J. A. (2013). "Production and upgrading of 5-hydroxymethylfurfural using heterogeneous catalysts and biomass-derived solvents," *Green Chem.* 15(1), 85-89.

Grasset, F. L., Katryniok, B., Paul, S., Nardello-Ratajade, V., Pera-Titusf, M., Clacens, J.-M., Campo, F. D., and Dumeignil, F. (2013). "Selective oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran over intercalated vanadium phosphate oxides," *Rsc. Adv.* 3(25), 9942-9948.

Hopkins, K. T., Wilson, W. D., Bender, B. C., McCurdy, D. R., Hall, J. E., Tidwell, R. R., Kumar, A., Bajic, M., and Boykin, D. W. (1998). "Extended aromatic furan amidino derivatives as anti-*Pneumocystis carinii* agents," *J. Med. Chem.* 41(20), 3872-3878.

Kang, E.-S., Chae, D. W., Kim, B., and Kim, Y. G. (2012). "Efficient preparation of DHMF and HMFA from biomass-derived HMF via a Cannizzaro reaction in ionic liquids," *J. Ind. Eng. Chem.* 18(1), 174-177.

Karimi, B., Mirzaei, H. M., and Farhangi, E. (2014). "Fe_3O_4@ SiO_2–TEMPO as a magnetically recyclable catalyst for highly selective aerobic oxidation of 5-hydroxymethylfurfural into 2, 5-diformylfuran under metal-and halogen-free conditions," *ChemCatChem* 6(3), 758-762.

Kazi, F. K., Patel, A. D., Serrano-Ruiz, J. C., Dumesic, J. A., and Anex, R. P. (2011). "Techno-economic analysis of dimethylfuran (DMF) and hydroxymethylfurfural (HMF) production from pure fructose in catalytic processes," *Chem. Eng. J.* 169(1), 329-338.

Le, N.-T., Lakshmanan, P., Cho, K., Han, Y., and Kim, H. (2013). "Selective oxidation of 5-hydroxymethyl-2-furfural into 2,5-diformylfuran over VO^{2+} and Cu^{2+} ions immobilized on sulfonated carbon catalysts," *Appl. Catal. A* 464-465, 305-312.

Liu, B., Zhang, Z. H, Lv, K., Deng, K. J, and Duan, H. M. (2014). "Efficient aerobic oxidation of biomass-derived 5-hydroxymethylfurfural to 2,5-diformylfuran catalyzed by magnetic nanoparticle supported manganese oxide," *Appl. Catal. A* 472, 64-71.

Ma, J. P, Du, Z. T, Xu, J., Chu, Q. H, and Pang, Y. (2011). "Efficient aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran, and synthesis of a fluorescent material," *ChemSusChem* 4(1), 51-54.

Navarro, O., Canós, A., and Chornet, S. (2009). "Chemicals from biomass: Aerobic oxidation of 5-hydroxymethyl-2-furaldehyde into diformylfurane catalyzed by immobilized vanadyl-pyridine complexes on polymeric and organofunctionalized mesoporous supports," *Top. Catal.* 52(3), 304-314.

Nie, J. F, and Liu, H. C (2012). "Aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran on supported vanadium oxide catalysts: Structural effect and reaction mechanism," *Pure Appl. Chem.* 84(3), 765-777.

Nie, J. F, Xie, J. H, and Liu, H. C (2013a). "Activated carbon-supported ruthenium as an efficient catalyst for selective aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran," *Chinese J. Catal.* 34(5), 871-875.

Nie, J. F, Xie, J. H, and Liu, H. C (2013b). "Efficient aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran on supported Ru catalysts," *J. Catal.* 301, 83-91.

Patil, S. K. R., and Lund, C. R. F. (2011). "Formation and growth of humins via aldol addition and condensation during acid-catalyzed conversion of 5-hydroxymethylfurfural," *Energ. Fuel* 25(10), 4745-4755.

Pratt, E. F., and Castle, J. F. V. D. (1961). "Oxidation by solids. I. Oxidation of selected alcohols by manganese dioxide," *J. Org. Chem.* 26(8), 2973-2975.

Sádaba, I., Gorbanev, Y. Y., Kegnæs, S., Putluru, S. S. R., Berg, R. W., and Riisager, A. (2013). "Catalytic performance of zeolite-supported vanadia in the aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran," *ChemCatChem* 5(1), 284-293.

Sun, H. Y., Hua, Q., Guo, F. F., Wang, Z.Y., and Huang, W. X. (2012). "Selective aerobic oxidation of alcohols by using manganese oxide nanoparticles as an efficient heterogeneous catalyst," *Adv. Synth. Catal*. 354(4), 569-573.

Takagaki, A., Takahashi, M., Nishimura, S., and Ebitani, K. (2011). "One-pot synthesis of 2,5-diformylfuran from carbohydrate derivatives by sulfonated resin and hydrotalcite-supported ruthenium catalysts," *ACS Catal.* 1(11), 1562-1565.

Taylor, R. J. K., Reid, M., Foot, J., and Raw, S. A. (2005). "Tandem oxidation processes using manganese dioxide: Discovery, applications, and current studies," *Accounts Chem. Res.* 38(11), 851-869.

van Putten, R.-J., van der Waal, J. C., de Jong, E., Rasrendra, C. B., Heeres, H. J., and de Vries, J. G. (2013). " Hydroxymethylfurfural, a versatile platform chemical made from renewable resources," *Chem. Rev.* 113(3), 1499-1597.

Vuyyuru, K. R., and Strasser, P. (2012). "Oxidation of biomass derived 5-hydroxymethylfurfural using heterogeneous and electrochemical catalysis," *Catal. Today* 195(1), 144-154.

Xiang, T. F., Liu, X. M., Yi, P., Guo, M. M., Chen, Y. S., Wesdemiotis, C., Xu, J., and Pang, Y. (2013). "Schiff base polymers derived from 2,5-diformylfuran," *Polym. Int.* 62(10), 1517-1523.

Yang, Z. Z., Deng, J., Pan, T., Guo, Q. X., and Fu, Y. (2012). "A one-pot approach for conversion of fructose to 2,5-diformylfuran by combination of Fe_3O_4-SBA-SO_3H and K-OMS-2," *Green Chem.* 14(11), 2986-2989.

Article submitted: April 9, 2014; Peer review completed: June 7, 2014; Revised version received and accepted: June 17, 2014; Published: June 20, 2014.