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Production of 2,5-Diformylfuran from Biomass-derived Glucose via One-Pot Two-Step Process

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As a furan derivative from 5-hydroxymethylfurfural (HMF) or other biomass-based carbohydrates, 2,5-diformylfuran (DFF) is one of the most important platform molecules in the organic chemicals industry. Although it has many potential applications in the future, the production of DFF on a large scale is currently a challenge. As an alternative to the production of DFF from HMF, the target product DFF could be obtained from biomass-derived glucose with a complex catalytic system ($AlCl_3 \cdot 6H_2O$/NaBr and a vanadium compound assisted with molecular oxygen) carried out in N,N-dimethylformamide (DMF). In this research, reactions were conducted in reactors with different capacities. The results showed that DFF yields based on glucose could reach 35 to 48% with almost complete transformation of glucose. This one-pot two-step reaction is characterized by the abundance and low cost of the starting materials and by the elimination of the separation and purification of HMF. This has great potential for applications in the future production of DFF on a large scale after further advancements and optimizations.

Keywords: Glucose; Oxidation; 5-Hydroxymethylfurfural; 2,5-Diformylfuran; Biomass

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INTRODUCTION

Biomass has become an important renewable resource for the production of chemicals and fuels, and many approaches have been proposed for achieving various high-value added chemicals from biomass carbohydrates (Antonyraj *et al.* 2013). Among carbohydrates, simple sugars such as fructose and glucose can be obtained by hydrolysis of biomass. The 5-hydroxymethylfurfural (HMF), achieved from the dehydration of simple sugars (de Souza *et al*. 2012; Wang *et al*. 2011), has become an important platform molecule between biomass and specialty chemicals (Davis *et al*. 2011; Yang *et al*. 2012b). Up to this point, many approaches have been developed to produce HMF from biomass (Ding *et al*. 2012; Dutta *et al*. 2012; Simeonov *et al.* 2012; Tao *et al*. 2011). Moreover, specialty chemicals can be produced by further transformations of HMF (Alamillo *et al*. 2012; Antonyraj *et al*. 2013; Che *et al*. 2012; Gallo *et al*. 2013). Among chemicals derived from HMF, 2,5-diformylfuran (DFF) is an organic intermediate with many application prospects and has recently attracted much attention. DFF can be used not only as a monomer in the production of multifunctional materials (Amarasekara *et al*. 2009; Gandini and Belgacem 1998), but also as the starting material in the synthesis of polymeric Schiff bases (Xiang *et al*. 2013), pharmaceuticals (Hopkins *et al*. 1998), macro-cyclic ligands (Richter and Lash 1999), antifungal agents (Del Poeta *et al*. 1998), fluorescent materials (Ma *et al*. 2011), and resins (Amarasekara *et al*. 2009).

Producing DFF from HMF has been considered to be the only feasible way for the industrial production of DFF. Many efforts have been made, with a fairly high yield of DFF obtained (Ma *et al*. 2011). However, no industrially viable process has yet been developed directly from biomass to DFF. Fructose has been used in some studies, but it is not seen as competitive, partly due to its high price and low annual output (van Putten *et al*. 2013).

Glucose, as the monomer unit of cellulose in biomass, is considered as one of the most important raw materials in the development of biomass utilization for renewable fuels and chemicals. The production of DFF from glucose, adopting the process without the isolation of HMF in advance, having HMF generated *in situ* undergo selective oxidation, is not only of great economic advantage, but also conforms to the idea of green sustainable development. Some proposed reaction pathways for the production of DFF by the transformation of biomass-based carbohydrates are shown in Fig. 1 (Halliday *et al*. 2003; Karimi *et al*. 2014; Laugel *et al*. 2014; Yadav and Sharma 2014).

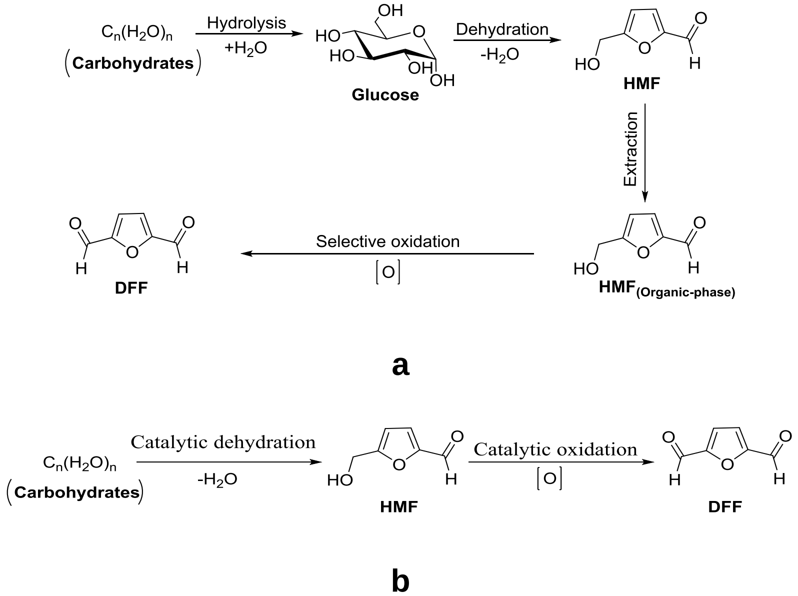

Fig. 1. Probable reaction pathways for the production of DFF by the transformation of biomass-based carbohydrates: (a) transformation route with extraction of HMF in advance, and (b) transformation pathway by reactions *in situ* (Halliday *et al*. 2003; Karimi *et al.* 2014; Laugel *et al.* 2014; Yadav and Sharma 2014)

Because of the high content of hydroxyl groups, glucose has low volatility and high reactivity; the conversion technologies of glucose to chemicals in the liquid phase should be used (Chheda *et al.* 2007). Without derivatization, glucose can be dissolved only in a few solvents, such as water, N,N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). Considering that the conversion of glucose in water is inefficient (Aida *et al.* 2007; Watanabe *et al*. 2005) and the disproportionation of DMSO might occur (Xiang et al. 2011), DMF was used as a reaction solvent in this research. Lewis acids such as $CrCl_2$ (Zhao *et al.* 2007), $SnCl_4$ (Hu *et al.* 2009), and $AlCl_3$ (Yang *et al.* 2012a), which are multifunctional catalysts that can affect the isomerization of glucose to fructose and the subsequent dehydration, can be applied in the conversion of glucose to HMF, giving a reasonable yield/selectivity of HMF. Among these catalysts, $AlCl_3$ is the cheapest metal chloride with the lowest toxicity, and it does not require the use of an expensive ionic liquid as a solvent (Yang *et al.* 2013). Catalytic oxidation processes with molecular oxygen over vanadium-based catalysts have been widely used in recent years. For example, vanadium-based catalysts have been used both in the conversion of HMF to DFF and in the direct production of DFF from biomass-derived carbohydrates (Grasset *et al.* 2013; Halliday *et al.* 2003; Le *et al.* 2013; Navarro *et al.* 2009; Nie and Liu 2012; Sádaba *et al.* 2013). Although different levels of success have been achieved, there are still many important issues that require resolution, such as how to make the process easier, reduction of the use of overly complex catalytic systems, and optimization of reaction conditions. Many reported processes were conducted in common conditions, and two-step reactions were often done in small simple devices. The possibility of improving the yield of DFF is limited with a narrow industrialization adaptation. In addition, the oxidation reaction is usually controlled by the flow rate of air/oxygen, which is time-consuming and inefficient. Herein, a one-pot two-step reaction technique applied in the production of DFF over a complex catalytic system ($AlCl_3 \cdot 6H_2O$/NaBr and a vanadium compound assisted with molecular oxygen) in DMF, without the separation and purification of HMF, was reported. The conversion of glucose to DFF in large advanced devices with different capacities was also attempted.

EXPERIMENTAL

Materials

The HMF (> 98%) was obtained from Shanghai Pu Guang Industrial Co. Ltd., China. The DFF (> 98%) was obtained from Tokyo Chemical Industry Co., Ltd., Japan. Sodium metavanadate ($NaVO_3$) and was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Ammonium metavanadate (NH_4VO_3) was purchased from Xilong Chemical Co., Ltd. (Guangdong, China), and potassium metavanadate (KVO_3) was purchased from Aladdin Chemistry Co. Ltd, China. Vanadium salts were used directly as oxidation catalysts. All other chemicals were all of analytical grade, supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), and used without further purification. Supported vanadium oxide (SVO) catalysts were prepared according to the principle shown in Fig. 2 (Sádaba *et al.* 2013). A molecular sieve of H-β type, purchased from Nankai University (Tianjin, China), was chosen as a support. Oxygen (99.5%) was purchased from Linde Gas Xiamen Ltd.

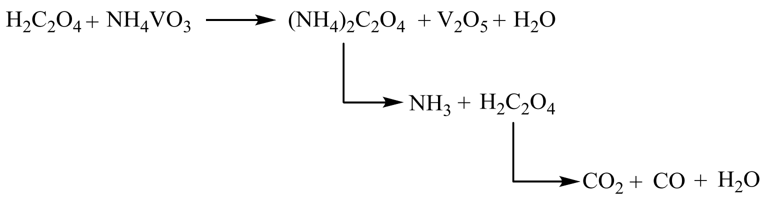

Fig. 2. The preparation process of SVO catalysts (Sádaba *et al.* 2013)

Equipment and Experimental Procedures

Glucose dehydration can be carried out in large advanced devices with different volume capacities (50- or 100-mL cylindrical stainless steel high-pressure reactors made by Parr Instrument Company, USA; or a 400-mL cylindrical Hastelloy alloy high-pressure reactor made by Dalian Controlled Plant, China.). In a typical one-pot two-step catalytic conversion of glucose to DFF, a mixture of glucose, $AlCl_3$, and NaBr in DMF was stirred at a given temperature for the desired time. After reaction, the catalyst ($AlCl_3$) and co-catalyst (NaBr) were separated from the reaction mixture by centrifugation. The recovery catalytic system $AlCl_3 \cdot 6H_2O$/NaBr can be reused in a subsequent round of the glucose dehydration for 5 or more times. Then, one of the vanadium-based catalysts ($NaVO_3$, NH_4VO_3, KVO_3, or SVO) was added to the reaction mixture. The procedures are similar for HMF oxidation. These oxidation reactions also can be conducted in one of the reactors mentioned above. In each oxidation reaction, reactants and catalysts ($NaVO_3$, NH_4VO_3, KVO_3, or SVO) were introduced to the solvent (DMF) in the reactor. Then, the reactor was sealed and purged thoroughly with oxygen three times. Then, the mixtures were stirred at *ca.* 800 rpm. For each oxidation reaction, the reactor was heated to the desired temperature. After the reaction, the reactor was taken from the oven, 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 analyses.

The conversion of glucose to DFF can also be conducted in small simple reaction devices, such as a one-mouth flask. A mixture of glucose, DMF, co-catalysts, and catalysts used in the dehydration of glucose was introduced to this small simple reactor. The reaction temperature, time, and stirring rate (*ca.* 500 rpm) were adjusted to the desired values. After the reaction, the liquid product was treated with the approaches mentioned above. The liquid solution was then transferred to a three-mouth flask and one kind of vanadium-based catalyst ($NaVO_3$, NH_4VO_3, or KVO_3) was added. The reaction was carried out under an oxygen pressure range of 1 to 10 bar, a temperature range of 80 to 150 °C, and a time range of 0.5 to 20 h. After each oxidation reaction, the liquid product was treated with similar operations mentioned above, then was analyzed by gas chromatography (GC), gas chromatography-mass spectroscopy (GC-MS), and/or high performance liquid chromatography (HPLC).

Catalyst Recycling Experiments

After each oxidation reaction, the SVO 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 SVO catalyst was used for the second cycle under the same conditions as were used for the first. These procedures were repeated five times to examine the stability of the SVO 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 a Hitachi S-4800 SEM (Japan) with an accelerating voltage of either 20 kV or 30 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 with a Shimadzu QP2010SE GC-MS with an Rtx-5MS column (30.0 m × 0.25 μm × 0.25 mm) with electron impact ionization (EI). The quantitative analysis (GC) of HMF and DFF in the reaction mixture were analyzed on an Agilent 7890 series GC 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 min^{-1}, and maintained at 250 °C for 2 min. The amounts of glucose, HMF, and DFF were calculated using an external standard. The analytical error was evaluated to be in the ±5% range. The HPLC analysis of HMF, DFF, and glucose was performed on a Waters 2695 separation module (USA) equipped with a refractive index detector (Waters 2414, RID), an ultraviolet detector (Waters 2998, UVD), and a Bio-Rad Aminex HPX-87H ion exclusion column (300 × 7.8 mm). The column oven temperature was 60 °C, and the mobile phase was 0.005 M H_2SO_4 at a flow rate of 0.7 $mL \cdot min^{-1}$.

The conversion of initial materials, yield, and selectivity of products on a molar base were calculated using the following equations:

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

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

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

$$\text{Glucose conversion (\%)} = \left(1 - \frac{moles\ of\ glucose\ unreacted}{moles\ of\ initial\ glucose}\right) \times 100\% \tag{4}$$

$$\text{HMF yield (\%)}_{\text{based on glucose}} = \left(\frac{moles\ of\ HMF\ produced}{moles\ of\ initial\ glucose}\right) \times 100\% \tag{5}$$

$$\begin{aligned}\text{HMF selectivity (\%)}_{\text{based on glucose}} &= \left(\frac{moles\ of\ HMF\ produced}{moles\ of\ initial\ glucose - moles\ of\ glucose\ unreacted}\right) \times 100\% \\ &= \left(\frac{HMF\ yield\ basedon\ glucose\ (\%)}{glucose\ conversion\ (\%)}\right) \times 100\%\end{aligned} \tag{6}$$

$$\text{DFF yield (\%)}_{\text{based on glucose}} = \left(\frac{moles\ of\ DFF\ produced}{moles\ of\ initial\ glucose}\right) \times 100\% \tag{7}$$

$$\begin{aligned}\text{DFF selectivity (\%)}_{\text{based on glucose}} &= \left(\frac{moles\ of\ DFF\ produced}{moles\ of\ initial\ glucose - moles\ of\ glucose\ unreacted}\right) \times 100\% \\ &= \left(\frac{DFF\ yield\ basedon\ glucose\ (\%)}{glucose\ conversion\ (\%)}\right) \times 100\%\end{aligned} \tag{8}$$

RESULTS AND DISCUSSION

Catalytic Conversion of Glucose to DFF in Small Simple Reaction Devices

The combination of $AlCl_3 \cdot 6H_2O$/NaBr and a vanadium salt exhibits relatively good catalytic performance for the conversion of glucose, as shown in Table 1, which is consistent with previous reports (Binder and Raines 2009; Hu *et al.* 2009; Xiang *et al.* 2011). The ion Al^{3+} likely enables the conversion of glucose to HMF by catalyzing the isomerization of glucose into fructose, and loosely ion-paired halide ions favor the dehydration of glucose. To reduce the influence of $AlCl_3 \cdot 6H_2O$/NaBr from the glucose dehydration on the subsequent oxidation reaction, the separation of the dehydration-step catalyst and co-catalyst ($AlCl_3 \cdot 6H_2O$/NaBr) was also conducted. Then, the mixture containing HMF was used for oxidation. The yields of DFF based on glucose can reach about 26.9% at an HMF yield of 61.4%. Thus, it is feasible to adopt the one-pot, two-step process to produce DFF from biomass-derived glucose without separation of HMF.

Table 1. Conversion of Glucose to DFF in Small Simple Reaction Devices

Entry	CAPACITY of the reactor used (mL)	MATERIAL of construction of the reactor	HMF yield (%)	DFF yield (based on HMF) (%)	DFF yield (based on glucose) (%)
1[a]	50	Glass	60.5	44.5	26.9
2[b]	50	Glass	58.3	46.0	26.8
3[c]	50	Glass	61.4	-	-
4[d]	50	Glass	58.3	43.1	25.1
5[e]	50	Glass	59.7	44.0	26.2
6[f]	50	Glass	61.8	31.9	19.7

[a] glucose 0.1690 g, DMF 5 mL, NaBr 0.2250 g, $AlCl_3 \cdot 6H_2O$ 0.0213 g, T_1 = 110 °C, t_1 = 3 h; KVO_3 0.0323 g, P_{o2} = 1 bar, T_2 = 130 °C, t_2 = 5 h;

[b] glucose 0.1862 g, DMF 2 mL, NaBr 0.1819 g, $AlCl_3 \cdot 6H_2O$ 0.0239 g, T_1=110 °C, t_1=3 h; NH_4VO_3 0.03648 g, P_{o2} = 1 bar, T_2=110 °C, t_2=5 h;

[c] glucose 0.1800 g, DMF 2 mL, NaBr 0.1800 g, $AlCl_3 \cdot 6H_2O$ 0.0158 g, T_1=100 °C, t_1=5 h;

[d] glucose 0.0809 g, DMF 1 mL, $AlCl_3 \cdot 6H_2O$ 0.0068 g, T_1=100 °C, t_1=5 h; $NaVO_3$ 0.005 g, P_{o2} = 1 bar, T_2=110 °C, t_2=2 h;

[e] glucose 0.1826 g, DMF 2.5 mL, NaBr 0.2009 g, $AlCl_3 \cdot 6H_2O$ 0.0239 g, T_1=100 °C, t_1=4 h; NH_4VO_3 0.0386 g, P_{o2} = 1 bar, T_2=110 °C, t_2=4 h;

[f] glucose 0.0800 g, DMF 1 mL, NaBr 0.0800 g, $AlCl_3 \cdot 6H_2O$ 0.0080 g, T_1=100 °C, t_1=6 h; $NaVO_3$ 0.0050 g, P_{o2} = 1 bar, T_2=110 °C, t_2=10 h.

Catalytic Conversion of Glucose to DFF in Large Advanced Reaction Devices

Large advanced reaction devices with different capacities, as mentioned above, were also used. The approaches were similar to those used in small simple reaction devices, and the results are shown in Table 2. The output of the target product and the conversion of reactants can be increased to some extent under certain conditions. Different from the reported processes in which the two-step reactions were often both performed in small reactors, two-step reactions during the production of DFF can be carried out in large reaction devices or conducted with combined use of small and large reaction devices according to the practical requirements. Therefore, it would be convenient and would offer increased flexibility for the experimental operation under the combined use of different reactors. This is also beneficial for wider industrial adaptations in the future. Starting from the better results under the corresponding reaction conditions, it can provide reference for the follow-up process optimization and magnification in the future industrial production of DFF.

In addition, it has to be pointed that the $AlCl_3 \cdot 6H_2O$ used in the glucose dehydration would have some unfavorable effect on the stainless steel reactor due to the presence of chloride ions. It is important to select reactors made of corrosion resistant materials such as hastelloy when chlorine ions would be introduced in aqueous solution. The activation of chloride ions play an important role on the establishment and destruction of stainless steel passivation oxide film, and have a great influence on the safety of the pressure vessels made of stainless steel.

Table 2. Conversion of Glucose to DFF in Large Advanced Reaction Devices

Entry	CAPACITY of the reactor used (mL)	MATERIAL of construction of the reactor	HMF yield (%)	DFF yield (based on HMF) (%)	DFF yield (based on glucose) (%)
1[a]	400	Hastelloy	67.9	61.5	41.7
2[b]	400	Hastelloy	57.4	-	-
3[c]	400	Hastelloy	61.4	-	-
4[d]	400	Hastelloy	69.4	46.9	32.5
5[e]	400	Hastelloy	69.7	46.7	32.5
6[f]	400	Hastelloy	67.6	-	-
7[g-1]	50	Stainless steel	67.6	45.2	30.5
8[g-2]	50	Stainless steel	67.6	42.8	28.9
9[g-3]	50	Stainless steel	67.6	44.4	30.0
10[g-4]	50	Stainless steel	67.6	47.9	32.3
11[g-5]	50	Stainless steel	67.6	46.5	31.4
12[g-6]	50	Stainless steel	67.6	40.1	27.1
13[h]	400	Hastelloy	64.0	-	-
14[i]	400	Hastelloy	67.7	-	-
15[j]	400	Hastelloy	65.8	-	-

[a] glucose 11.2g, DMF 140 mL, NaBr 11.2 g, $AlCl_3·6H_2O$ 0.980 g, T_1=110 °C, t_1=3 h; $NaVO_3$ 1.7075 g, P_{o2} = 1 bar, T_2=130 °C, t_2=5 h;

[b] glucose 11.5 g, DMF 140 mL, NaBr 0 g, $AlCl_3·6H_2O$ 1.0258 g, T_1=110 °C, t_1=3 h;

[c] adding NaBr 11.2 g to the reaction solution of the entry 2 in Table 2, $NaVO_3$ 1.728 g, P_{o2} = 8 bar, T_2=150 °C, t_2=6 h;

[d] glucose 11.5 g, DMF 140 mL, NaBr 1.728 g, $AlCl_3·6H_2O$ 1.0258 g, T_1=100 °C, t_1=5 h; $NaVO_3$1.728 g, P_{o2} = 1 bar, T_2=110 °C, t_2=2 h;

[e] glucose 11.2477 g, DMF 140 mL, NaBr 11.2576 g, $AlCl_3·6H_2O$ 0.0239 g, T_1=110 °C, t_1=3 h; $NaVO_3$ 1.7161 g, P_{o2} = 1 bar, T_2=110 °C, t_2=5 h;

[f] glucose 11.2428 g, DMF 140 mL, NaBr 11.8266 g, $AlCl_3·6H_2O$ 0.9929 g, T_1=120~130 °C, t_1=3 h;

[g] the reaction conditions of entry 7~12 in Table 2 were as follows:
g-1 dehydration solution of glucose 20 mL, $NaVO_3$ 0.247 g, P_{o2} =10 bar, T_2=110 °C, t_2=3 h;
g-2 dehydration solution of glucose 20 mL, NH_4VO_3 0.244 g, P_{o2} = 10 bar, T_2=110 °C, t_2=5 h;
g-3 dehydration solution of glucose 20 mL, $NaVO_3$ 0.248 g, P_{o2} = 10 bar, T_2=110 °C, t_2=4 h;
g-4 dehydration solution of glucose 20 mL, NH_4VO_3 0.247 g, P_{o2} = 10 bar, T_2=110 °C, t_2=3 h;
g-5 dehydration solution of glucose 20 mL, $NaVO_3$ 0.247 g, P_{o2} 10 = bar, T_2=110 °C, t_2=2 h;
g-6 dehydration solution of glucose 20 mL, NH_4VO_3 0.247 g, P_{o2} =10 bar, T_2=110 °C, t_2=1 h;

[h] glucose 11.2056 g, DMF 140 mL, NaBr 11.2121 g, $AlCl_3·6H_2O$ 0.9929 g, T_1=110 °C, t_1=3 h;

[i] glucose 11.2038 g, DMF 140 mL, NaBr 11.2279 g, $AlCl_3·6H_2O$ 0.9823 g, T_1=110 °C, t_1=2 h;

[j] glucose 11.2047 g, DMF 140 mL, NaBr 11.2057 g, $AlCl_3·6H_2O$ 0.9808 g, T_1=110 °C, t_1=1 h.

Catalytic Conversion of Glucose to DFF over SVO Catalysts in Advanced Reactors with Different Capacities

In addition, SVO/H-β catalysts were prepared and applied in the catalytic conversion of glucose to DFF in advanced reactors with different capacities. To study the effect of VO_x loading, 1, 3, 10, and 20 wt% VO_x/H-β samples were synthesized and characterized. X-Ray diffraction analysis of the prepared SVO catalysts (Fig. 3) revealed that only diffraction peaks of the H-β support were observed after comparing with XRD patterns of H-β molecular sieve, indicating an amorphous structure and high dispersion of the deposited vanadium species in the SVO catalysts. A similar process for aerobic catalytic oxidation of HMF generated *in situ* from glucose to DFF over a SVO catalyst in DMF was carried out, and the results were shown in Table 3. For VO_x/H-β samples with different loadings, a better yield of DFF based on glucose (44.7%) could be achieved under the given reaction conditions. The result might be due to that 3%VO_x/H-β solid catalyst was stable and recyclable with relatively more active species under the given conditions.

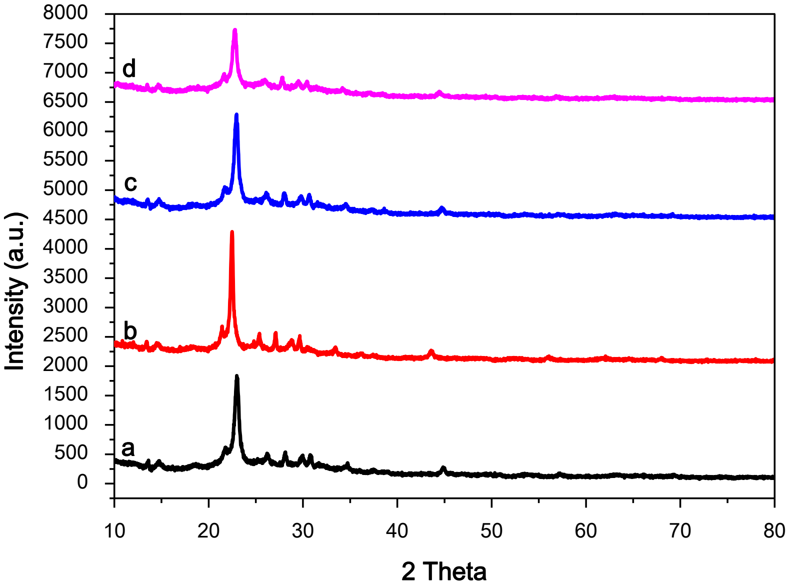

Fig. 3. XRD patterns of the SVO catalysts: (a) 1% VO_x; (b) 3% VO_x; (c) 10% VO_x; and (d) 20% VO_x

Table 3. Aerobic Catalytic Oxidation of HMF Generated in situ from Glucose to DFF over SVO Catalysts in DMF

Entry	Catalysts	HMF yield (%)	DFF yield (based on HMF) (%)	DFF yield (based on glucose) (%)
1[a]	$AlCl_3$/NaBr	67.6	-	-
2[b]	1%VO_X	67.6	53.7	33.5
3[c]	3%VO_X	67.6	65.6	44.7
4[d]	10%VO_X	67.6	58.3	35.4
5[e]	20%VO_X	67.6	54.8	33.3
6[f]	H-β support	67.6	-	-

[a] glucose 11.2428g, DMF 140mL, NaBr 11.8266g, $AlCl_3·6H_2O$ 0.9929g, T_1=120~130 °C, t_1=3h; The reaction conditions of entry 2~5 in Table 3 were as follows:

[b] dehydration solution of glucose 20 mL, 1% VO_X 0.252 g, P_{o2} = 10 bar, T_2=110 °C, t_2=3 h;

[c] dehydration solution of glucose 20 mL, 3% VO_X 0.246 g, P_{o2} = 10 bar, T_2=110 °C, t_2=3 h;

[d] dehydration solution of glucose 20 mL, 10% VO_X 0.249 g, P_{o2} = 10 bar, T_2=110 °C, t_2=3 h;

[e] dehydration solution of glucose 20 mL, 20% VO_X 0.255 g, P_{o2} = 10 bar, T_2=110 °C, t_2=3 h;

[f] dehydration solution of glucose 20 mL, H-β support in the absence of VO_X 0.253g, P_{o2} = 10 bar, T_2=110 °C, t_2=3 h.

The active species in 1%VO_x/H-β solid catalyst was perhaps lower than that of 3%VO_x/H-β solid catalyst; other catalysts with higher loading than 3%VO_x are possibly unstable due to the leaching of a certain amount of active sites in the surface of H-β support. In addition, the surface area of the supported catalysts often decreases with increase of active species, which would also lead to the decrease of the yield of DFF. Moreover, when a blank experiment in the absence of VO_x (with only H-β support) was conducted (Table 3, Entry 6), only a negligible yield of DFF was detected, which confirmed that the catalytic activity of this catalyst was basically provided by the active species of vanadium metal loaded on the H-β support.

To examine the activity and stability of SVO catalysts, recycling experiments with the 3% VO_x/H-β sample were conducted with 5 cycles. SEM images showed that both the fresh and spent 3% VO_x/H-β catalysts after 5 cycles were composed of aggregations of primary crystallites (Fig. 4). The surface morphology of the catalysts was apparently unchanged before and after the recycling experiments. These results indicated that the SVO catalyst has outstanding stability under the given reaction conditions, which is in line with the catalytic activity results of the catalyst recycling experiments. The results of the elemental analysis for the spent 3% VO_x/H-β catalyst after 5 cycles are listed in Table 4. Carbon residues of 0.1 to 0.2% (based on the mass ratio of carbon on the surface of the solid 3% VO_x/H-β catalyst) on the catalyst had no significant effect on the deactivation of the catalyst and did not lead to a large decrease in the yields of DFF. A low carbon deposit with the recycling of the catalyst was the probable reason for the good catalytic performance of the catalyst after the catalyst recycling experiments. In addition, the N content may be derived from the used solvent DMF, the mass percentage of which was approximately 0.1%, which indicated that the solvent DMF has a good stability in the oxidation reaction under the given conditions.

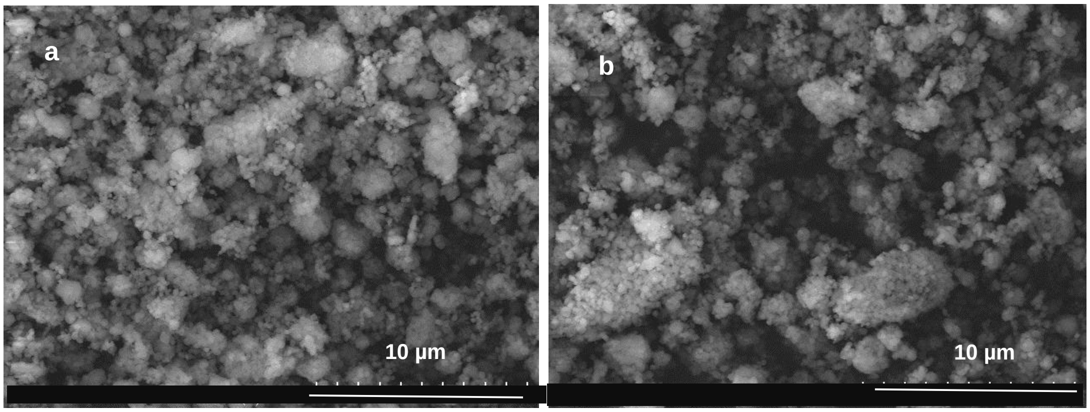

Fig. 4. SEM images of the (a) fresh and (b) spent 3% VO_x/H-β catalyst after 5 cycles

Table 4. Elemental Analyses of the Fresh and Spent 3% VO_x/H-β Catalyst after 5 Cycles

Recycle times	N Content (%)	C Content (%)	H Content (%)
Fresh	0. 115	0. 096	1.587
1	0. 135	0.162	1.581
3	0. 138	0.075	1.580
5	0. 099	0.078	1.519

CONCLUSIONS

1. An approach was proposed for the production of DFF from biomass-derived glucose *via* a one-pot, two-step process. This could provide a route for future research on the production of DFF in an economical and sustainable way, especially the direct production of DFF from HMF generated in situ from biomass-based carbohydrates.
2. Reactions were conducted in different reactors according to the practical requirements. The combined utilization of different reactors makes the reaction procedures flexible and feasible and open to wider adaptations.
3. Problems such as preventing the contamination of the dehydration-step catalysts for the subsequent oxidation reaction still need to be solved, and further studies will be essential.
4. In view of the moderate yield and selectivity of DFF, it is of great importance to carry out some research on the carbon balance analysis, so as to obtain DFF more efficiently in the future.
5. The key to realizing the production of HMF from cellulose system is the dissolution and depolymerization of the raw biomass materials. Obtaining DFF by the conversion of cellulose and even raw biomass materials with glucose structure units will be the future research and developmental goals. The conversion of sugars from cellulose compounds and even biomass raw materials to DFF by the catalytic dehydration of sugar and the subsequent molecular selective oxidation of HMF generated *in situ* will be an effective way to realize the goal of the rational utilization of biomass. Also, it is a major challenge in this field and many problems have yet to be further studied.

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