

Efficient and Selective Oxidation of 5-Hydroxymethylfurfural into 2, 5-Diformylfuran Catalyzed by Magnetic Vanadium-Based Catalysts with Air as Oxidant

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Abstract

In this study, a new kind of magnetic vanadium-based catalyst was successfully prepared and employed to produce 2, 5-diformylfuran (DFF) in the liquid phase through selective oxidation of biomass-derived 5-hydroxymethylfurfur (HMF) with air as oxidant. It was found that magnetic Fe₃O₄ nanoparticles supported NH₄·V₃O₈ showed excellent catalytic performance with the achievement of 95.5% HMF conversion along with 82.9% selectivity to DFF under optimal reaction conditions. More importantly, the catalyst could be readily separated from the reaction mixture by a permanent magnet, and recycled several times without the loss of its catalytic activity.

Graphic Abstract

The NH₄·V₃O₈/Fe₃O₄ catalyst showed high activity for selective oxidation of 5-hydroxymethylfurfural into 2, 5-diformylfuran.



Keywords 5-Hydroxymethylfurfural \cdot 2, 5-Diformylfuran \cdot Selective oxidation \cdot Magnetic catalyst \cdot Biomass transformation

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1 Introduction

Due to the increasing demand of petroleum-based resources for the production of chemicals and fuels, a great attention has been paid to the utilization of renewable resources as an alternative to fossil resources [1]. Biomass is the only renewable organic carbon resource in nature, whose catalytic conversion can produce important oxygenated organic compounds to partially replace and supplement traditional fossil resources [2–4]. HMF is a very important biomass-based platform compound for the comprehensive utilization of biomass resources. It can produce a wide range of widely used furan derivatives

by chemical reactions such as oxidation, hydrogenation, esterification, halogenation, and polymerization [5, 6]. Catalytic oxidation of HMF represents as one of the most important routes for the utilization of HMF (Scheme 1), as this process can generate several kinds of import chemicals such as DFF, 5-hydroxymethyl-2-furancarboxylic acid (HFCA), 5-formyl-2-furancarboxylic acid (FFCA) and 2,5-furandicarboxylic acid (FDCA). However, the selective oxidation of HMF into a special furan compound is challenging, although it has received a great deal of attention. DFF is one of the main products of HMF selective oxidation, and has been used in the synthesis of high-end drugs, pesticide antifungal agents, fluorescent materials and new polymeric materials [7, 8].

In the early research on the preparation of DFF by HMF oxidation, the focus was mainly on traditional oxidants such as pyridinium chlorochromate (PCC), NaOCl, and BaMnO₄ and 2, 2, 6, 6-tetramethylpiperidine-1-oxide (TEMPO) free radicals [9–11]. Although the traditional oxidant can successfully realize the synthesis of DFF by HMF oxidation under different reaction systems, the reaction effect is not obvious, because it consumes a large amount of oxidants due to its own defects, the low atomic utilization rate, and of the generated toxic by-products. This is not in line with the current background of green chemistry. When using H_2O_2 , air and oxygen as terminal oxidants, although the atomic utilization rate is high and environmentally friendly, the reaction process is not easy to control, and generally requires pressurization or high temperature [2, 12]. To conclude, how to achieve efficient selective oxidation of HMF under mild conditions has been an important and challenging topic.

In recent years, catalysts for HMF catalytic oxidation are mainly supported precious metals [13, 14]. Zhu et al. synthesized three novel catalysts using MnO_2 as the supporting material for the oxidation of HMF into DFF in the presence of O_2 [15]. This group further studied the bimetallic Au–Pd catalyst catalyzed HMF oxidation [16]. Srivastava et al. [17–20] also have been committed to research in this area and developed a series of catalysts with excellent catalytic activity. Precious metals have excellent catalytic properties for the preparation of DFF systems by HMF oxidation. Due to the high price of noble metal catalysts, the metallic oxides catalysts have attracted much attention, such as manganese oxide-based material [2, 21, 22] and GO-related materials [23].

Among these catalysts, vanadium-containing catalysts are noticeable. In the past decade, some methods on the aerobic oxidation of alcohols using relative cheap V based catalysts were reported [24–26]. In this work, a new kind of magnetic Fe₃O₄ supported NH₄·V₃O₈ catalyst (NH₄·V₃O₈/Fe₃O₄) was successfully prepared and characterized. The activity of the as prepared NH₄·V₃O₈/Fe₃O₄ catalyst was evaluated by the oxidation of HMF into DFF with air as oxidant. The NH₄·V₃O₈/Fe₃O₄ catalyst was observed to have a high catalytic activity and selectivity for the selective oxidation of HMF into DFF.

2 Experimental

2.1 Materials

5-Hydroxymethylfurfural (99.5%) and 2, 5-diformylfuran were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). NH_4VO_3 , $NH_3 \cdot H_2O$ and $FeCl_2 \cdot 4H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All the chemicals were of analytical grade and used without further purification. Ultrapure water was used for the catalyst preparation and catalytic reactions.

2.2 Catalyst Preparation

The magnetic vanadium-based catalyst was prepared by using $NH_4 \cdot V_3O_8$ and $FeCl_2 \cdot 4H_2O$ as main raw materials. Typically, $NH_4 \cdot V_3O_8$ (0.458 g) was derived from the pyrolysis of NH_4VO_3 at 180 °C for 12 h, and $FeCl_2 \cdot 4H_2O$ (1.000 g) were refluxed in ultrapure water (20 mL) at 80 °C for 30 min, and slowly dropped $NH_3 \cdot H_2O$ (2.5%, 10 mL) under high speed agitation. The black $NH_4 \cdot V_3O_8/Fe_3O_4$ nanoparticles were thoroughly washed with ultrapure water, separated by external magnet, and dried at 80 °C for 2 h.

2.3 Characterizations

Fourier transform infrared spectra (FT-IR) of the samples were collected by the KBr pellet technique on a Nicolet 370

Scheme 1 General routes for the oxidation of HMF into furan compounds



infrared spectrophotometer in the range 400–4000 cm⁻¹. The crystal structure of the samples were determined by X-ray diffraction (XRD) spectroscopy using Bruker diffractometer with Cu K α wavelength (λ =1.5418 Å) and diffraction angle (2 θ) ranging from 10° to 70°. Thermogravimetric and derivative thermogravimetric (TG-DTG, Germany) curves were recorded in N₂ flow on a Netzsch Model STA 409PC instrument with a heating rate of 20 °C/min from room temperature to 600 °C using α -Al₂O₃ as the standard material. The morphologies of the samples were investigated by using transmission scanning microscopy (TEM) with FEI Tecnai G2 F20. The magnetic of the samples was also investigated using vibrating sample magnetometry (VSM, LakeShore7404).

2.4 Catalytic Oxidation of HMF

The oxidation of HMF in the air under atmospheric pressure was performed in a 10 mL round bottom flask, which was coupled with a reflux condenser using the following general procedure. Typically, HMF (0.1 mmol, 12.6 mg) was firstly dissolved into DMSO (5 mL) in the flask with a magnetic stirrer. Then, 10 mg catalysts were added into the reaction mixture. The mixture was heated to the desired temperature while stirring under an air atmosphere. After reaction, the reaction solution was quantitatively analyzed by Agilent 1100 HPLC system equipped with Agela Technologies Venusil XBP C18(L) (4.6×250 mm) and a UV-Vis (280 nm) detector. The mobile phase was constituted of acetonitrile and 0.1 wt% acetic acid aqueous solution (V:V = 15: 85), and the samples was eluted at a rate of 0.5 mL/min at 30 °C. The amount of each compound was quantified by external standard calibration curve method. According to the test results, the oxidation of HMF mainly leads to DFF, HFCA, FFCA and FDCA.

3 Results and Discussion

3.1 Catalyst Characterization

The functional groups of these samples were identified by FT-IR analysis, and the corresponding FT-IR spectra were depicted in Fig. 1. The FT-IR spectra of different $NH_4 \cdot V_3O_8$ illustrated the typical $NH_4 \cdot V_3O_8$ crystal structure. The peak at 583 cm⁻¹ was the characteristic peak of Fe₃O₄, which was the vibration of Fe–O bond [27]. The FT-IR results also indicated that $NH_4 \cdot V_3O_8$ was successfully supported on the magnetic Fe₃O₄ nanoparticles.

The XRD pattern in Fig. 2 illustrated the typical Fe_3O_4 crystal structure with JCPDS card 88-0315 for the magnetic Fe_3O_4 nanoparticles, suggesting that this phase has been successfully synthesized. It is seen that the Fe_3O_4 showed the



Fig.1 FT-IR spectra of (a) Fe_3O_4, (b) $NH_4{\cdot}V_3O_8,$ and (c) $NH_4{\cdot}V_3O_8/$ Fe_3O_4



Fig. 2 XRD patterns of (a) Fe_3O_4, (b) $NH_4 \cdot V_3O_8,$ and (c) $NH_4 \cdot V_3O_8/$ Fe_3O_4

largely enhance (311) facet signal at $2\theta = 35.5^{\circ}$ than other facet signals of the Fe₃O₄ sample. The XRD spectra of the pyrolysis product of NH₄VO₃ revealed that solid NH₄·V₃O₈ is formed according JCPDS card 88-1473. The XRD pattern of NH₄·V₃O₈/Fe₃O₄ was also collected showing a strong peak at $2\theta = 35.6^{\circ}$, in which is different from those of Fe₃O₄ at $2\theta = 35.5^{\circ}$ and NH₄·V₃O₈ at $2\theta = 27.7^{\circ}$. In addition, some peaks with low intensity also appeared in NH₄·V₃O₈/Fe₃O₄, and all the peaks could be assigned to the corresponding peaks rather in Fe₃O₄ or NH₄·V₃O₈. These XRD results confirmed that the catalyst NH₄·V₃O₈/Fe₃O₄ was composed of Fe₃O₄ and NH₄·V₃O₈.

The TEM images of $NH_4 \cdot V_3O_8/Fe_3O_4$ were shown in Fig. 3. Figure 3b shows that the magnetic Fe_3O_4 nanoparticles were deposited on the surface $NH_4 \cdot V_3O_8$, and the



100

98

96

94

92

90

Mass (%)

a



Fig. 4 TG-DTG curves of (a) Fe_3O_4 and (b) $NH_4 \cdot V_3O_8/Fe_3O_4$

nanoparticles have a serious agglomeration phenomenon. The (111) facet signal at 18.3° corresponded to the 1.5 nm of facet spacing according to the Fig. 3c.

The thermogravimetric analysis results of $NH_4 \cdot V_3O_8/Fe_3O_4$ and Fe_3O_4 samples were compared as shown in Fig. 4. The weight loss lower than 5% at about 237 °C was observed for Fe_3O_4 , corresponding to the loss of the physically adsorbed water. In contrast, the $NH_4 \cdot V_3O_8/Fe_3O_4$ catalyst has three weight loss stages appearing at 200–300 °C, 300–370 °C and 370–440 °C, respectively. The first loss stage at temperatures lower than 300 °C is due to the loss of absorbed water. In the second stage, the decomposition into V_2O_5 begins with the loss of around 5% of mass at temperatures higher than 300 °C. These results indicate that $NH_4 \cdot V_3O_8$ was successfully supported on the magnetic Fe_3O_4 nanoparticles.

The magnetic performance of $NH_4 \cdot V_3O_8/Fe_3O_4$ catalyst was also investigated using vibrating sample magnetometry (VSM). The obtained curves are depicted in Fig. 5. The Hcb of $NH_4 \cdot V_3O_8/Fe_3O_4$ is 120.0 G/s, and the saturation magnetization (Ms) is 18.8 emu/g. It shows that the sample behaves good magnetic properties at room temperature.

Fig. 5 VSM magnetization curve of NH₄·V₃O₈/Fe₃O₄

3.2 Effects of the Solvents on the Oxidation of HMF

5.0k

10.0k

The oxidation HMF was further carried out in a variety of solvents. As shown in Table 1, the solvents were found to play a crucial role in the conversion of HMF and the selectivity of DFF. DMSO showed the lowest conversion of 59.6% with the highest 31.3% DFF selectivity (Table 1, Entry 2), suggesting that DMSO was a reliable solvent for the selective oxidation of HMF into DFF. On the other hand, high conversion of 98.9% albeit with 7.5% DFF selectivity was obtained in MIBK (Table 1, Entry 4). The reactions carried in K₂CO₃ solution and acetonitrile also showed high HMF conversion but with almost no detectable DFF after oxidation reaction (Table 1, Entry 1 and 2). Therefore, DMSO was supposed to be a superior solvent for the selective oxidation of HMF into DFF and will be used in the next step.

3.3 Catalytic Oxidation of HMF Using Various Oxidants

The prepared $NH_4 \cdot V_3O_8$ catalyst was used for the selective oxidation of HMF into DFF using various oxidants in DMSO and the results are given in Table 2. It is found that

Table 1Effects of differentsolvents on the oxidation ofHMF

Entry	Solvent	Conversion/(%)	Selectivi	Yield				
			FDCA	HFCA	FFCA	DFF	Others ^a	of DFF/ (%)
1	$K_2CO^b_{3(aq)}$	73.1	0.9	2.5	0.8	_	95.7	0
2	DMSO	59.6	13.6	1.2	31.3	51.8	30.6	13.9
3	Acetonitrile	77.9	0	7.5	7.2	0.6	84.7	0.4
4	MIBK	98.9	2.9	0.5	11.0	7.5	78.1	7.4

Reaction conditions: 0.1 mmol HMF, 20 mg $NH_4 \cdot V_3O_8$, 5 mL solvent, 120 °C, 6 h, 0.5 mmol TBHP ^aOthers are mainly acetalized products and ring-opening products, e.g. ethyl levulinate and ethyl formate ^b0.05 g/5 mL

Table 2 Effects of different
oxidants on the oxidation of
HMF

Entry	Oxidant	Conversion/(%)	Selectivi	Yield of				
			FDCA	FFCA	HFCA	DFF	Others ^a	DFF/(%)
1	Air	74.9	14.7	6.0	_	64.8	14.5	48.5
2	$TBHP^{b}$	76.6	13.2	6.3	-	68.5	11.9	52.5
3	$H_2O_2^b$	75.4	13.0	8.0	_	78.0	1.0	58.8
4	O ₂	91.4	11.6	7.7	-	57.6	23.2	52.6

Reaction conditions: 0.1 mmol HMF, 10 mg NH₄·V₃O₈, 5 mL DMSO, 120 °C, 6 h

^aOthers are mainly acetalized products and ring-opening products, e.g. ethyl levulinate and ethyl formate ^b0.5 mmol

molecular oxygen showed the highest conversion of 91.4% with 57.6% DFF selectivity (Table 2, Entry 4). This was consistent with our previous conclusion that O_2 was a reliable oxidant for the oxidant of HMF into DFF. On the other hand, high conversion of 75.4% with high DFF selectivity of 78.0% was obtained in the presence of TBHP and H_2O_2 (Table 2, Entry 2 and 3). Interestingly, air afforded 74.9% conversion of HMF with 64.8% selectivity (Table 2, Entry 1), which is close to the results of other oxidants. Therefore, in terms of the economic and green viewpoint, the use of air as an oxidant for the selective oxidation of HMF into DFF should be advantageous and will be used in the next step (Table 2).

3.4 Effects of Catalyst Dosage on the Oxidation of HMF

The effects of catalyst dosage was also studied. As shown in Fig. 6, the conversion of HMF keeps increasing with the amount of catalyst, while the selectivity of DFF is almost constant. The results indicate that the dosage of $NH_4 \cdot V_3O_8$ showed a remarkable effect on the selective oxidation of HMF into DFF due to an increase in the availability and number of catalytically active sites. The results also suggested that the selectivity of DFF had no relationship with the catalyst loading when the reaction was carried out in the



Fig. 6 Effects of catalyst dosage on the oxidation of HMF. Reaction conditions: 0.1 mmol HMF, 5 mL DMSO, 120 $^\circ$ C 6 h, in the air

same conditions, such as reaction time and reaction temperature. The yield of DFF is up to 54.4% with the equal amount of catalyst, however, the DFF selectivity begins to decline due the generation of a new by-product as detected by HPLC.

3.5 Time Course of the Oxidation of HMF

The catalytic performances of $NH_4 \cdot V_3O_8$ were investigated in different reaction time, and the results are shown in Fig. 7. The reaction products, DFF, FDCA, FFCA, and FMF, were detected by HPLC. It is found that the conversion of HMF increased with the reaction time and reached 76.2% conversion with DFF selectivity of 72.7% by 6 h. In the initial stage, the fast reaction rate should be due to the high concentration of HMF. FDCA showed a highest selectivity of 17.0% at 3 h, while the yield of FFCA and FMF keeps increasing with the reaction time.

3.6 Effects of Reaction Temperature on the Oxidation of HMF

The effects of the reaction temperature was also studied and the results are shown in Fig. 8. It is seen that both the HMF conversion and the DFF yield were greatly affected by the reaction temperature. At the reaction temperature of 110 °C, the HMF conversion obtained was 49.2%, while it increased to 99.5% when further elevating the temperature to 150 °C. The yield of DFF also increased with the reaction temperature. The highest yield of DFF obtained was 67.5% at 140 °C and it slightly decreased to 65.0% at 150 °C. These results indicated that high reaction temperature promoted the selective oxidation of HMF into DFF, allowing the achievement of quantitative HMF conversion when the reaction was carried out at 140 °C and 150 °C.



Fig.8 Effects of reaction temperature on the oxidation of HMF. Reaction conditions: 0.1 mmol HMF, 12.6 mg NH_4 · V_3O_8 , 5 mL DMSO, 6 h, in the air



Fig. 7 Effects of reaction time on the oxidation of HMF. Reaction conditions: 0.1 mmol HMF, 12.6 mg NH_4 · V_3O_8 , 5 mL DMSO, 120 °C, in the air

3.7 Catalytic Activities of NH₄·V₃O₈/Fe₃O₄ Catalyst with Different V/Fe Molar Ratios

The catalytic performance of NH₄·V₃O₈/Fe₃O₄ catalysts with different V/Fe molar ratios was tested under atmospheric air and the results are listed in Fig. 9. As expected, no catalytic activity is observed in the presence of only Fe₃O₄. In the presence of NH₄·V₃O₈/Fe₃O₄ which the V/Fe molar ratio was 0.2, 25.8% of HMF conversion and 11.8% of DFF yield implies that the selective oxidation of HMF into DFF takes place. As the V/Fe ratio of NH₄·V₃O₈/Fe₃O₄ increases to



Fig. 9 Effects of V/Fe molar ratios of NH_4 · V_3O_8 / Fe_3O_4 on the oxidation of HMF. Reaction conditions: 0.1 mmol HMF, 10 mg NH_4 · V_3O_8 / Fe_3O_4 , 5 mL DMSO, 120 °C, 6 h, in the air

0.4, the HMF conversion and DFF yield increase to 35.1% and 15.3%, respectively. However, increasing the V/Fe ratio to 0.8 and 1.0, only slightly improved catalytic activities are observed, suggesting that further increase of the V/Fe ratio couldn't provide quantitative active sites. These observations reveal that an appropriate V/Fe ratio of $NH_4 \cdot V_3O_8/Fe_3O_4$ is essential to achieving an optimized catalytic performance for the oxidization of HMF into DFF. Amount of loading have determined using ICP, the results showed that the V/Fe ratio of $NH_4 \cdot V_3O_8/Fe_3O_4$ catalysts were 0.20, 0.36, 0.60, 0.80 and 0.87, respectively.

The possible reaction mechanism of HMF to DFF catalyzed by the catalyst was illustrated in Scheme 2. The reduction of V^{5+} to V^{4+} by HMF, and the further reoxidation of V^{4+} to V^{5+} by oxygen in the air through a Mars-Van Krevelen mechanism.

3.8 Recycle Experiments of the Catalyst

Developing a convenient and economical method to reuse the catalyst and the solvent is very crucial in terms of the green chemistry. The main advantage of magnetic catalysts is that they can be readily separated from the reaction mixture by an external magnet. For this purpose, the used catalyst was washed by ethanol to remove the adsorbed products and dried under vacuum at 80 °C overnight. Then the catalyst was reused for the next cycle under otherwise identical reaction conditions. As shown in Fig. 10, the conversion of HMF and the selectivity of DFF were quite stable, indicating that the catalyst could be reused without significant decrease of the catalytic activity. To confirm the stability of the catalysts after the oxidation of HMF, ICP of the recovered $NH_4 \cdot V_3O_8/Fe_3O_4$ was measured. The result confirmed that the V/Fe ratio of NH₄·V₃O₈/Fe₃O₄ catalysts was no obvious change around 0.85, suggesting that the $NH_4 \cdot V_3O_8$ groups were essentially preserved. Although nonmagnetic heterogeneous catalysts could also be reused, some heterogeneous catalysts lost their catalytic activity due to the inevitable loss of catalyst mass in the recycling experiments by the conventional filtration method. In comparison, the recovery of the catalyst by a permanent magnet obviously avoids the catalyst loss during the recycling experiments, and thereby is



Fig. 10 Recycle experiments of the catalyst $NH_4 \cdot V_3 O_8/Fe_3 O_4$ on the oxidation of HMF. Reaction conditions: 0.1 mmol HMF, 50 mg catalyst (V/Fe ratio: 0.87), 5 mL DMSO, 120 °C, 6 h, in the air

promising for practical applications comparison with some others latest catalysts (Table 3).

4 Conclusions

In summary, a new method was developed for the synthesis of DFF from the selective oxidation of HMF. The magnetic $NH_4 \cdot V_3O_8/Fe_3O_4$ was prepared by NH_4VO_3 , $NH_3 \cdot H_2O$ and $FeCl_2 \cdot 4H_2O$, and showed an excellent catalyst performance with the achievement of 95.5% HMF conversion as well as 82.9% DFF selectivity in a 6-h reaction time at 140 °C. The catalyst could be easily separated from the reaction mixture, and could be reused multiple times without losing catalytic activity. Such high activity, stability and magnetic recovery, combined with the simple preparation of catalysts, make it a promising application in conversion of biomass-derived platform chemicals into valuable bulk chemicals.

Scheme 2 Possible mechanism for the formation of DFF on the $NH_4 \cdot V_3O_8$



Table 3Catalytic oxidationof HMF into DFFover different catalysts

Entry	Catalyst	Oxidation	Solvent	HMF conver- sion/%	DFF selec- tivity/%	Ref.
1	MnOx/P25	Air	Ethanol	33.2	97.0	[2]
2	VOx-ms	O_2	H_2O	93.7	95.4	[5]
3	Au-Pd/MnO ₂	O_2	H_2O	76.0	98.0	[16]
4	SBA-NH2-VO2+	O_2	Toluene	98.8	29.3	[26]
5	$NH_4 \cdot V_3O_8/Fe_3O_4$	Air	DMSO	95.5	82.9	This work

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