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$FeVO_4$ decorated $-SO_3H$ functionalized polyaniline for direct conversion of sucrose to 2,5-diformylfuran & 5-ethoxymethylfurfural and selective oxidation reaction

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<i>Keywords:</i> 2,5-Diformylfuran 5-hydroxymethylfurfural 5-ethoxymethylfurfural Selective oxidation Multi-functional catalyst	In this study, a multi-functional catalyst, FeVO ₄ supported –SO ₃ H functionalized polyaniline is prepared. First FeVO ₄ supported polyaniline is prepared. Then the resultant material is sulfonated using chlorosulphonic acid to obtain FeVO ₄ supported –SO ₃ H functionalized polyaniline. This multi-functional catalyst exhibits excellent activity in the synthesis of 5-hydroxymethylfurfural from sucrose and oxidation of a wide range of aromatic and aliphatic alcohols. Further, the catalyst exhibits very good activity in the one-pot direct conversion of sucrose/fructose to 2,5-diformylfuran (DFF) and 5-ethoxymethylfurfural (EMF). This catalytic process involves the economical sucrose as a reactant and economical multi-functional catalyst based on polyaniline. In this one-pot, two-step process, -SO ₃ H functionalized polyaniline is used in the first step for the conversion of sucrose to 5-hydroxymethylfurfural (HMF) followed by selective oxidation of HMF to DFF using FeVO ₄ sites present in the multi-functional catalyst. Moreover, acidic sites present in the multi-functional catalyst are suitable for the conversion of sucrose/fructose/HMF to EMF. Furthermore, molecular oxygen (1 atmosphere, 10 ml/min) is used as an eco-friendly and economical oxidant for the selective oxidation of a wide range of aromatic and aliphatic alcohols to aldehydes. The multi-functional catalyst presented here has been easily separated and recycled that make the process sustainable and economical for commercial perspectives.		

1. Introduction

In the developing nation, the price of commodities chemicals, polymers, and fuels varies with the international crude oil price. This demonstrates that the chemical industries in these nations heavily depend on the fossil fuel. Most of the commodities chemicals and polymers are produced from the raw materials obtained from the chemical transformations of fossil fuel feedstock. The carbon based chemicals derived from the fossil fuels including transportation fuels are consumed and finally converts to CO_2 . Plants utilize this abundant CO_2 from the atmosphere and convert to biomass by the photosynthesis process. Therefore, it is possible to use biomass based feedstock as an alternative to fossil fuel to produce chemicals and fuels to create socioeconomical and environmental balance in the society [1,2]. Cellulose derived disaccharide and monosaccharide are the most valuable biomass sources available to every nation. Among them, disaccharide (such as sucrose) is more interesting and economical because monosaccharide (glucose and fructose) is produced from the disaccharide sucrose. Recent literature shows that these carbohydrate biomass sources are transformed to chemicals and fuel additives by following C-C cleavage pathways [3,4]. Multi-functional acid catalysts are required for the C-C cleavage and administer the synthesis steps of desired chemicals [5]. In general, 5-hydroxymethylfurfural (HMF) and direct C-C cleavage pathways are known in the literature [4,6]. Among them, HMF mediated pathway is interesting to us because commodities chemicals and polymers can be produced from 2,5-diformylfuran (DFF) which is produced by the selective oxidation of HMF [7,8]. Moreover, ether derivative of HMF such as 5-ethoxymethylfurfural (EMF) is a very useful bio-fuel because it exhibits suitable combustion stability, high cetane number, and high energy density (~30% higher than ethanol) [9]. Therefore, the intent is to evolve a multi-functional catalyst for the one-pot conversion of disaccharide sucrose to DFF and EMF as raw materials for the production of commodities chemicals and fuel additives.

Multi-functional catalyst having acidity, basicity, and oxidation capability is required for the direct sucrose to DFF transformation [10-12]. This one-pot synthesis protocol is based on the controlled hydrolysis of sucrose to glucose and fructose, base catalyzed

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Scheme 1. Schematic representation of the synthesis of S-PANI-FeVO₄ composites.

isomerisation of glucose intermediate to fructose, acid catalyzed dehydration to HMF, followed by selective oxidation of HMF to DFF. Similarly, the functional catalyst having required acidity is required for the production of EMF [9]. Based on these requirements one can think of organic-inorganic hybrid materials for this purpose. Our group has recently reported the production of DFF from carbohydrate using Ru supported H-Beta catalyst [13]. Our aim in this work is to develop catalyst based on economical first-row transition metals. Moreover, several attempts have been made using a wide range of multi-functional catalysts based on zeolite, silica, metal oxide, and carbon materials for the conversion of carbohydrates (especially fructose) to DFF [8,10-16]. When acidity and basicity together in one catalyst is considered, polyaniline is one of the possible heterogeneous catalysts. Our group has explored the conductive nature and ion-exchange property of polyaniline for electrocatalysis [17-19]. Polyaniline has two sites which can be functionalized for required catalytic applications. It has basic -N sites (benzenoid amine (-NHC6H4-) and quinoid diimine $(-N = C_6H_4 = N)$ and aromatic sites [20]. Aromatic sites can be functionalized with -SO3H groups for acid catalysis whereas basic sites mentioned above can be used for the base catalysis [21]. This bifunctional activity has been used for the transformation of monosaccharide to HMF [20,22,23]. Moreover, basic -N sites can be further tuned by the incorporation of formyl group in the conversion of fructose to HMF [22]. However, polyaniline does not have any oxidation capability. Therefore, for the conversion of sucrose to DFF, suitable oxidation sites need to be incorporated in the polyaniline. Among the economical transition metals. Fe and V based catalysts have been shown for the conversion of HMF to DFF [24-28]. We have recently demonstrated the applicability of FeVO₄/g-C₃N₄ based catalyst for the thermal and photochemical oxidation of a wide range of aromatic compounds using H_2O_2 as the oxidant [29].

Herein we report the synthesis of a multi-functional catalyst, FeVO₄ decorated $-SO_3H$ functionalized polyaniline, for the one-pot tandem, sucrose to DFF transformation. Moreover, FeVO₄ decorated $-SO_3H$ functionalized polyaniline has also been found successful in the synthesis of EMF directly from sucrose. The catalyst exhibits excellent activity with more reactive substrate fructose in the production of DFF and EMF. Moreover, the developed catalyst demonstrates excellent activity in the oxidation of a wide range of alcohols to aldehydes/ketones using O₂ at 1 atm (10 mL/min).

2. Experimental section

2.1. Materials and methods

AR grade chemicals were procured. HMF, HCl (35%), cinnamyl alcohol, cyclohexanol, benzyl alcohol, and Fe(NO₃)₃·9H₂O were obtained from Sigma-Aldrich. DMSO, Na₂SO₄, octanol, and NaCl were purchased from Merck Chemicals, India. Sucrose, fructose, glucose, aniline, ammonium persulphate (APS), and NH₄VO₃ were purchased from Loba Chemie Pvt. Ltd., India. Sd Fine Chemicals Pvt. Ltd supplied 1,2-Dichloro-ethane (DCE). Chlorosulphonic acid and allyl alcohol were received from Spectrochem. Methyl isobutyl ketone (MIBK) was purchased from Alfa-aesar, Pvt. Ltd., India.

2.2. Catalyst preparation

Polyaniline (PANI) was synthesized using a molar composition of 2.0 aniline/2.0 HCl/4.0 (APS) by following a well-established procedure [19]. Further, the $-SO_3H$ group was introduced in the PANI framework structure using chlorosulphonic acid by following the reported procedure to prepare sulfonated polyaniline (S-PANI) [21]. The details of the synthesis of PANI and S-PANI are provided in the supporting infromation section. FeVO₄ was hydrothermally synthesized by following the reported procedure [29].

The required amount of the calcined FeVO₄ was added to the dispersed aqueous HCl solution of aniline and polymerization was carried out by following the procedure described above for the PANI synthesis. Three composites with PANI:FeVO₄ weight ratio of 3:7, 1:1, and 7:3 were synthesized and the samples are designated as PANI-FeVO₄(37), PANI-FeVO₄(11), and PANI-FeVO₄(73), respectively. All the three materials were sulfonated as described above for the synthesis of S-PANI to obtain S-PANI-FeVO₄(37), S-PANI-FeVO₄(11), and S-PANI-FeVO₄(73). The schematic representation for the synthesis of S-PANI-FeVO₄ is depicted in Scheme 1.

2.3. Procedure of catalytic reaction

Details of the HMF synthesis from sucrose/fructose, aerobic oxidation of HMF to DFF and alcohols to aldehydes, synthesis of EMF from HMF and carbohydrates, and one-pot two-step production of DFF from carbohydrates are provided in the supporting information section.



Fig. 1. XRD patterns of (a) PANI, FeVO₄, and PANI-FeVO₄(11), (b) S-PANI and S-PANI-FeVO₄(11).

3. Results and discussion

3.1. Physicochemical characterization

The formation of multi-functional catalyst was first confirmed from the XRD investigation. XRD pattern of FeVO₄ and designated planes are shown in Fig. 1a that match well with the literature report and confirms the successful formation of FeVO₄ crystalline phase [29]. The phases present in FeVO₄ XRD pattern are confirmed using X'Pert High Score Plus software which correspond to monoclinic Fe₂V₄O₁₃ (JCPDS Card no. 01-087-1845) and triclinic FeVO₄ (JCPDS Card no. 01-071-1592) phases (Fig. S1, SI). A broad and less crystalline phase is observed for PANI in the XRD pattern. The designated crystal planes for PANI correspond to the emeraldine polyaniline salt (Fig. 1) [30]. PANI-FeVO₄(11) shows overlapping and broad reflections corresponding to PANI and FeVO₄ phases and confirms the formation of PANI-FeVO₄ composite. However, the heat treatment has changed the phase composition of FeVO₄ and in this case, FeVO₄ exists in triclinic $Fe_{6.5}V_{11.5}O_{35}$ (JCPDS Card no. 01-074-0766) and triclinic $FeVO_4$ (JCPDS Card no. 01-071-1592) phases (Fig. S2, SI). Upon sulfonation, the crystallinity of PANI is further reduced which is confirmed from the very broad XRD pattern of S-PANI (Fig. 1b). Such broad XRD pattern is consistent with the previous report [31]. The S-PANI-FeVO₄(11) exhibits XRD pattern corresponding to S-PANI and FeVO₄ phases and confirm the formation of a multi-functional catalyst (Fig. 1b). However, in this case, FeVO₄ exists in triclinic Fe_{6.5}V_{11.5}O₃₅ (JCPDS Card no. 01-074-0766) and triclinic FeVO₄ (JCPDS Card no. 01-071-1592) phases. Such FeVO₄ phases are also observed when FeVO₄ was treated with chlorosulfonic acid in the absence of PANI (Fig. S1, SI).

The N₂-volumetric analyzer was used to determine the textural properties of the materials. A very low increase in the adsorption in the range of 0-0.8 (P/P₀) is observed for FeVO₄, which is followed by a steep increase in the adsorption above 0.85 (P/P₀) demonstrating mesoporous-macroporous void space present in the material (Fig. S3, SI). PANI also exhibits similar adsorption behaviour to that of FeVO₄ but it shows comparatively low adsorption above 0.85 (P/P₀) when compared to FeVO₄. Both these materials exhibit non-uniform multi-modal pore size distribution (Fig. S3, Inset, SI). S-PANI-FeVO₄(11) exhibits similar adsorption isotherm to that of S-PANI. The details of the surface area and pore volume are provided in Table 1.

The size, morphology, and microstructures of the synthesized

materials were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. S4 (SI) shows the aggregated morphology of FeVO₄ and PANI. The aggregated rod like morphology is seen to be manufactured of FeVO₄ nanocrystals whereas PANI morphology is manufactured of wheat-like nanocrystals. Highly aggregated crystal morphology is obtained for PANI-FeVO₄(11) (Fig. S5, SI). During the -SO₃H treatment, S-PANI crystals are aggregated and produced micrometer size large S-PANI material (Fig. S5, SI). S-PANI-FeVO₄(11) exhibits similar morphology to that of S-PANI (Fig. S5, ESI). The energy dispersive X-ray (EDX) profile was recorded for S-PANI-FeVO₄(11) to evaluate the elemental composition (Fig. S6 indicates the presence of C, N, O, S, Fe, and V in S-PANI-FeVO₄(11), which confirms the successful formation of a composite of S-PANI and FeVO₄. FE-SEM images recorded for S-PANI-FeVO₄(11) confirms that the large crystal shown in SEM investigation is built with small nanocrystals of FeVO₄ grown over S-PANI (Fig. 2). The TEM images of S-PANI-FeVO₄(11) confirm the presence of light PANI domains and black dispersed domains of FeVO₄ in the nanocomposites (Fig. 2). HR-TEM images clearly show the lattice fringes corresponding to FeVO₄ phase. The d-spacing of 0.22 nm corresponds to (111) plane of FeVO4 as identified from IMAGE J software [32].

The successful incorporation of -SO3H group in PANI (S-PANI) and nanocomposite (S-PANI-FeVO₄(11)) were confirmed by FT-IR spectroscopy. Fig. S7 (SI) shows the FT-IR spectra of FeVO₄, PANI, S-PANI, and S-PANI-FeVO₄(11). PANI exhibits characteristic bands in the range of 600-1600 cm⁻¹ [21]. Vibration frequencies observed for PANI are following: 1584 cm^{-1} and 1500 cm^{-1} (C=C stretching of quinoid and benzenoid rings), 1304 cm⁻¹ (C–N stretching), 1150 cm⁻¹ (protonated $(=NH^+-)$ emeraldine polyaniline salt), 853 cm⁻¹ (C-H out of plane bending of the 1,4-disubstituted benzene ring). The absorption bands at 1203 cm⁻¹, 1070 cm⁻¹, 1020 cm⁻¹, 697 cm⁻¹, 619 cm⁻¹ are observed in S-PANI that correspond to the asymmetric and symmetric O-S-O stretching, S=O stretching, S-O stretching, and -S stretching modes of vibrations, respectively [21]. The absence of these characteristic bands in pristine PANI confirms that the -SO3H groups are successfully bonded to the aromatic rings in the polymeric chain of PANI after the treatment of PANI with chlorosulfonic acid. Vibration frequencies observed for FeVO₄ are the following: 960 cm^{-1} and 905 cm^{-1} (terminal V–O stretching vibration), 840 cm^{-1} and 737 cm^{-1} (stretching of V–O \equiv Fe bridge), 694 cm⁻¹ and 666 cm⁻¹ (mixed bridging of V–O=Fe and V=O=Fe stretching), and 504 cm^{-1} (V–O–V

Table 1

Physico-chemical properties of various materials synthesized in this study.

Catalyst	Surface area $(m^2 g^{-1})^a$	External surface area $(m^2 g^{-1})$	Total pore volume (cc g^{-1})	Elemental contents ^b
FeVO ₄	38	34	0.470	Fe (21.6%), V (27.3%)
PANI	26	26	0.148	-
S-PANI	15	15	0.046	-
S-PANI-FeVO ₄ (11)	11	11	0.031	Fe (3.0 %), V (1.5%)
PANI-FeVO ₄ (11)	23	20	0.145	Fe (12.8 %), V (6.1%)
^c S-PANI-FeVO ₄ (11)	12	12	0.034	Fe (2.9 %), V (1.6%)

^a S_{BET} was calculated from the adsorption branch in the relative pressure range $0.05 < P/P0 \le 0.3$.

^b Determined using MP-AES.

^c Recycled catalyst.

deformations mixed with Fe—O stretching modes) [33]. FT-IR bands corresponding to S-PANI and FeVO₄ are observed in the S-PANI-FeVO₄(11), confirming the incorporation of S-PANI and FeVO₄ in the multi-functional catalyst. Moreover, FT-IR measurement was also carried out using pyridine as a probe molecule to investigate the presence of Brönsted acid sites due to the incorporation of $-SO_3H$ group in S-PANI and S-PANI-FeVO₄(11) (Fig. S8, SI). The peak at 1545 cm⁻¹ corresponds to Brönsted acid site (Py–(H)–O₃S groups). Furthermore, the peak at 1490 cm⁻¹ can be attributed to the interaction between pyridine with Brönsted acidic sites of $-SO_3H$ group present in the catalyst [35].

The presence of various elements and their oxidation state were confirmed from X-ray photoelectron spectroscopy (XPS). Fig. 3 demonstrates the full surface survey of S-PANI-FeVO₄(11) and high resolution spectra of Fe 2p, V 2p, O 1s, S 2p, C 1s, and N 1s elements present in the nanocomposite. The high resolution spectrum of Fe 2p exhibits two peaks at 710.8 eV and 724.6 eV corresponding to Fe 2p_{3/2} and Fe $2p_{1/2}$ electronic configurations, respectively [29]. These peaks confirm the presence of Fe^{+3} in FeVO₄ (Fig. 3b). Two spin-orbit peaks with binding energies 524 eV and 516.2 eV in the high resolution spectrum of V 2p can be assigned to V $2p_{1/2}$, and V $2p_{3/2}$ electronic configurations, respectively, of V^{+5} in FeVO₄ (Fig. 3c) [29]. The high resolution spectrum of C 1s exhibits a broad peak that can be deconvoluted into four peaks at 284.4 eV, 285.5 eV, 286.4 eV, and 287.8 eV corresponding to C-C/C=C, C-N, C-O, and C=O, respectively (Fig. 3d). Furthermore, a less resolved peak is deconvoluted to two well resolved spin-orbit peaks at 167.7 eV and 168.5 eV that can be assigned to S $2p_{3/2}$ and S $2p_{1/2}$ electronic configurations, respectively (Fig. 3e) [34]. The broad peak in N 1s high resolution XPS spectrum can be deconvoluted into three peaks for quinonoid amine (-N=), benzenoid amine (-NH-), and protonated amine (-NH⁺) with binding energies of 399.2 eV, 400 eV, and 401.1 eV, respectively (Fig. 3f). In the high resolution XPS spectrum of O 1s, the broad peak can be deconvoluted into four peaks at 528.4 eV, 530.1 eV, 530.6 eV, and 531.5 eV. The peaks with binding energies 528.4 eV and 530.1 eV are corresponding to the O 1s and hydroxylated oxygen atom present in FeVO₄ [29]. The peaks at 530.6 eV and 531.5 eV are ascribed to different oxygen atoms in -SO₃H group (i.e., S=O/S-O-H) [36]. These results confirm the presence of C, N, O, S, Fe, and V elements in the multi-functional catalyst and also support the results obtained from XRD and FT-IR investigations for the successful formation of a composite of -SO₃H functionalized PANI and FeVO₄.

Since the amount of FeVO₄ plays a decisive role in the selective oxidation step, therefore, its content was determined from elemental analysis and the data is provided in Table 1. Based on the content, it can be concluded that only 3% FeVO₄ was incorporated in S-PANI-FeVO₄(11) whereas it was around 13% in the case of PANI-FeVO₄(11). These results confirm that chlorosulphonic acid and heat treatment significantly reduced the amount of FeVO₄ loading in the nano-composite. Weak signals observed for Fe and V in XPS analysis further confirms the incorporation of low loading of FeVO₄ in the

nanocomposite.

3.2. Catalytic investigation

The aim of present research is to demonstrate the oxidation and acid property of the developed bi-functional catalyst. The application of this catalyst is demonstrated in the conversion of carbohydrate to HMF and EMF which are catalyzed by the acid sites present in the catalyst. The final aim is to develop one-pot, two-step transformation of carbohydrate to DFF which also requires oxidation functionality that can catalyze the selective oxidation of HMF to DFF without forming any other oxidized products. Therefore, the reaction condition for the selective oxidation of HMF and other aromatic and aliphatic alcohols to aldehydes was optimized. To optimize the selective oxidation, HMF was chosen as the model compound.

First, the reaction condition was optimized for the conversion of carbohydrate to HMF. For this reaction, sucrose was chosen as the model substrate. Our previous investigation has shown that this conversion step is facilitated using DMSO as a solvent [13]. The role of catalysts was investigated. An immensly low yield of HMF was obtained when no catalyst was used (Table 2, Entry 1). Further, using PANI, a very low yield of HMF was obtained (Table 2, Entry 2). Using S-PANI, a very high yield of HMF was obtained (Table 2, Entry 3). ¹H NMR investigation confirmed that in this case 95% sucrose conversion and 84% HMF selectivity were obtained. In this case, in addition to HMF; formic acid, glucose, and DFF with the selectivity of 3%, 8%, and 5%, were obtained (Fig. S9, SI). This clearly shows that the incorporation of -SO₃H in PANI matrix facilitated the hydrolysis and hydration reactions leading to HMF as the major product with very high selectivity. Moreover, the catalyst did not follow the C-C cleave pathway leading to formic acid as a product. Then finally nanocomposites were investigated to catalyze the sucrose to HMF conversion. With all the S-PANI-FeVO₄ nanocomposites, complete sucrose conversion was obtained. However, product selectivity varies by varying the S-PANI content in the nanocomposite. Using S-PANI-FeVO₄(11), 87% HMF selectivity was obtained. In all the cases, HMF, formic acid, fructose, and DFF were also obtained in small quantity as shown in Table 2. For illustration, ¹H NMR spectrum is provided indicating various products identified from NMR study during the conversion of sucrose to HMF (Fig. S10, SI). In this case, fructose was obtained as one of the minor products in contrast to S-PANI mediated synthesis in which glucose was obtained as one of the minor product. This shows that Fe/V sites present in the catalyst convert glucose to fructose during the reaction. Based on this study, it can be confirmed that S-PANI-FeVO₄(11) has ability to provide high yield and selectivity for HMF. Having optimized S-PANI-FeVO₄(11) as the best nanocomposite, the detailed investigation was carried out to optimize the reaction parameters. Sucrose to HMF conversion was carried out at different temperature in the range of 353 K to 413 K (Fig. 4a). With increase in the reaction temperature, sucrose conversion was increased and reached to 100% at all temperature higher than 373 K. However, the highest HMF selectivity was



Fig. 2. (a,b) FE-SEM micrographs and (c–d) HR-TEM images of S-PANI-FeVO₄(11).



Fig. 3. XPS surface survey of (a) S-PANI-FeVO₄(11), and high resolution XPS spectra of (b) Fe 2p, (c) V 2p, (d) C 1s, (e) S 2p, (f) N 1s, and (g) O 1s.

obtained at 393 K. Therefore, 393 K was set as the best temperature. Then, the influence of catalyst amount in the range of 70–130 mg was optimized (Fig. 4b). The study shows that with an increase in the catalyst amount from 70 mg to 110 mg, sucrose conversion was also increased. Maximum sucrose conversion and maximum selectivity for HMF were obtained using 110 mg of catalyst. Finally, the influence of reaction time was optimized (Fig. 4c). During the initial period, the reaction rate was high and with an increase in the reaction time, sucrose conversion was increased and the maximum sucrose conversion and the highest HMF selectivity were obtained for the reaction occurring after 6 h. Therefore, 6 h reaction time was optimized for the sucrose. It is important to note that under optimized reaction condition,

Table 2			
Transformation of sucrose to	HMF using various	catalysts investigated	in this study.

S. No.	Catalyst	Sucrose conv. (%) ^a	Product select. (%) ^a
1	None	3.3	HMF (95.2 %), FA (4.8%)
2	PANI	3.9	HMF (94.8 %), FA (5.2%)
3	S-PANI	95	HMF (84 %), FA (3 %), Glucose (8%), and DFF (5 %)
4	S-PANI-FeVO ₄ (37)	100	HMF (86 %), FA (2.8 %), Fructose (6.4 %), and DFF (4.8 %)
5	S-PANI-FeVO ₄ (11)	100	HMF (87 %), FA (0.9 %), Fructose (7 %), and DFF (5.1 %). (Isolated HMF yield 82 %) ^b
6	S-PANI-FeVO ₄ (73)	100	HMF (86 %), FA (0.7 %), Fructose (6 %), and DFF (7.3 %)
7	None ^c	100 ^c	HMF (100 %) ^c (Isolated HMF yield = 95 %) ^b

Reaction condition: Sucrose (1 mmol), catalyst (110 mg), DMSO (5 mL), temperature (393 K), time (6 h). ^aDetermined from ¹H NMR. ^bIsolated using MIBK as extracting solvent. ^cFructose was reacted for 1 h.



Fig. 4. Optimization of reaction parameters (a) temperature, (b) catalyst amount, and (c) reaction time for sucrose to HMF transformation over S-PANI-FeVO₄(11).

temperature (393 K), DMSO (5 mL), carbohydrate (1 mmol), fructose was completely and selectively converted to HMF in just 1 h without using a catalyst (Fig. S10, SI). Furthermore, HMF was isolated using MIBK as extracting medium and the isolated yields of HMF obtained from sucrose and fructose were 82% and 95% respectively. The activity of the present catalyst was also investigated for glucose but only a poor glucose conversion (32.4%) and HMF yield (23.7%) were obtained. In addition small amount of DFF and formic acid were also formed.

Second, the reaction condition was optimized for the conversion of HMF to EMF. The previous study has shown that this conversion step is facilitated in the presence of a large excess of ethanol in the absence of any other solvent [37]. The role of catalysts was investigated. An immensly low yield of EMF was obtained when no catalyst was used (Table 3, Entry 1). Using PANI, a very low yield of EMF was obtained (Table 3, Entry 2). When S-PANI was used as a catalyst, a very high yield of EMF was obtained (Table 3, Entry 2). When S-PANI was used as a catalyst, a very high yield of EMF was obtained (Table 3, Entry 3). ¹H NMR investigation confirmed that in this case 96% HMF conversion and 87% EMF selectivity were obtained. Only formic acid was obtained as a minor

product in this case. This clearly shows that the incorporation of -SO₃H in PANI matrix facilitated the esterification reaction leading to EMF as the major selective product. Then finally nanocomposites were investigated to catalyze the HMF to EMF conversion. With all the S-PANI-FeVO₄ nanocomposites, > 90% HMF conversion was obtained. However, selectivity varies by varying the S-PANI content in the nanocomposite. Using S-PANI-FeVO₄(11), 85% EMF selectivity was obtained. In all these cases, formic acid was obtained in small quantity as shown in Table 3. For illustration, ¹H NMR spectrum is provided indicating various products identified from NMR study during the conversion of HMF to EMF over S-PANI-FeVO₄(11) (Fig. S12, SI). Based on this study, it can be confirmed that S-PANI and S-PANI-FeVO₄(11) have the ability to provide high yield and high selectivity for EMF. Then onepot conversion of sucrose to EMF was carried out using S-PANI-FeVO₄(11). In this case, after 24 h of the reaction, 75% sucrose conversion and 76% EMF selectivity were obtained. In this case, a relatively large amount of formic acid (24% selectivity) was observed (Table 3, Entry 5). Under the similar condition, after 24 h of the

Table 3

Transformation of HMF and carbohydrates to EMF using various catalysts investigated in this study.

S. No.	Catalyst	Reactant Conv. (%)	Product select. (%)
1 2 3 4 5 6	None ^a PANI ^a S-PANI ^a S-PANI-FeVO ₄ (11) ^a S-PANI-FeVO ₄ (11) ^b S-PANI-FeVO ₄ (11) ^b	HMF conv. < 1 % HMF conv. < 1 % HMF conv. 96.3% HMF conv. 94.1 % Sucrose conv. 75.2 % Fructose conv. 86.3 %	EMF (100) EMF (100) EMF (87), FA (3) EMF (85), FA (15) EMF (76), FA (24) EMF (84), FA (16)

^a **Reaction condition**: Reactant (1 mmol), catalyst (50 mg), ethanol (5 mL), temperature (363 K), time (6 h).

^b time = 24 h.

reaction, 86% fructose conversion and 84% EMF selectivity were obtained (Table 3, Entry 6).

Third, the reaction condition was optimized for HMF to DFF transformation. Since the final aim of this study is to convert sucrose to DFF via HMF as an intermediate, therefore, this study was conducted in DMSO as a solvent which exhibited the best activity in the conversion of sucrose to HMF. The role of catalysts was investigated. In the absence of catalyst, a minute amount of DFF was obtained (Table 4, Entry 1). Using PANI and S-PANI as catalysts, very low yields of DFF were obtained (Table 4, Entries 2, 3). When FeVO₄ was used as a catalyst, a very high vield of DFF was obtained in O₂ flow condition (Table 4, Entry 3), GC analysis showed that in this case 84% HMF conversion and 100% DFF selectivity were obtained. This clearly shows that FeVO₄ facilitated the selective oxidation reaction leading to DFF. When the similar reaction was carried out using O₂ (1 atm, balloon) then in that case also DFF was selectively obtained but in this case, low HMF conversion was obtained when compared with O_2 in flow condition (10 mL/min) (Table 4, compare entries 4,5). Therefore, remaining of the reaction was conducted in O₂ flow condition. Finally, nanocomposites were investigated to catalyze the selective oxidation of HMF to DFF conversion. By varying the S-PANI-FeVO₄ nanocomposites, HMF conversion varies but in all the cases, DFF was obtained in exceptionally high selectivity. HMF conversion varies by varying the S-PANI content in the nanocomposite. Using S-PANI-FeVO₄(11), 100% HMF conversion with > 99% DFF selectivity were obtained. Based on this study, it can be confirmed that S-PANI-FeVO₄(11) has the ability to provide high yield and selectivity for DFF. Very small loading of FeVO₄ in the catalyst confirmed that finely dispersed small size FeVO4 is more suitable for the oxidation reaction when compared to bulk FeVO₄. Having optimized S-PANI-FeVO₄(11) as the best nanocomposite, the detailed investigation was carried out to optimize the reaction parameters (Fig. 5). HMF to DFF conversion was carried out at different temperatures in the range of 353 to 423 K (Fig. 5a). Increasing temperature of the reaction, HMF conversion was

Table 4

Selective oxidation of HMF to DFF using various catalysts investigated in this study.

S. No.	Catalyst	Oxidant	HMF Conv. (%)	DFF select. (%)
1	None	O ₂ flow	1.3	100
2	PANI	O ₂ flow	1.6	100
3	S-PANI	O ₂ flow	1.5	100
4	FeVO ₄	O ₂ flow	84.3	100
5	FeVO ₄	O ₂ (1 atm, balloon)	46.2	100
6	FeVO ₄ treated with Chlorosulfonic acid	O ₂ (1 atm, balloon)	100	88
7	S-PANI-FeVO ₄ (37)	O ₂ flow	94.4	> 99
8	S-PANI-FeVO ₄ (11)	O ₂ flow	100	> 99
9	S-PANI-FeVO ₄ (73)	O ₂ flow	100	> 99

Reaction condition: HMF (1 mmol), catalyst (120 mg), DMSO (5 mL), temperature (413 K), time (24 h).

increased and it was reached to 100% at 413 K. However, beyond 413 K, the selectivity of DFF dropped down. Therefore, 413 K was chosen as the best temperature. Then, the role of catalyst amount in the range of 50-130 mg was investigated (Fig. 5b). Increasing the catalyst amount from 50 mg to 110 mg, HMF conversion was increased and maximum HMF conversion and maximum selectivity for DFF were obtained using 110 mg catalyst. Finally, the influence of reaction time was optimized (Fig. 5c). During the initial duration, the rate was high and by increasing the reaction time, HMF conversion was increased and the maximum HMF conversion and the highest DFF selectivity were obtained for the reaction occurring after 24 h. Therefore, 24 h reaction time was optimized for the selective conversion of HMF to DFF. Having optimized the reaction condition for the selective oxidation of HMF to DFF, various aromatic and aliphatic alcohols were converted to aldehyde products, selectively. Benzyl alcohol was converted to benzaldyde exclusively in just 5 h under the optimum reaction condition (Table 5). Even cinnamyl alcohol was converted to cinnamaldehyde in 5 h with 98% yield (Table 5). However, aliphatic alcohols such as hexanol and allyl alcohols required 6 h to get the quantitative amount of the product (Table 5). Moreover, cyclohexanol was converted to cyclohexanone in just 5 h with > 99% yield. Under the optimum condition, furfural alcohol was also converted selectively to furfural but with low yield as shown in Table 5.

Finally, one-pot two-step tandem reaction was carried out using the highly active catalyst S-PANI-FeVO₄(11). In the first step of the one-pot tandem reaction, sucrose (1 mmol), DMSO (5 mL), and catalyst (120 mg) were heated at 393 K under N₂ flow (10 mL min⁻¹) for 6 h to achieve the maximum conversion of sucrose to HMF. The HMF formation was monitored by ¹H NMR after a regular time interval. After the first-step, N₂ flow was stopped and the temperature was rose to 413 K. Then O₂ flow was started and the reaction mixture was recorded after 24 of the reaction. Fig. 6 shows the ¹H NMR spectra recorded during one-pot synthesis of DFF from sucrose. Moreover, DFF was isolated with 80% yield from the reaction medium using MIBK as extraction medium as described in the experimental section. Using fructose as reactant, one-pot two step conversion led to give an isolated yield of 91% DFF.

In order to explain the catalytic role of S-PANI-FeVO₄(11) in the dehydration and oxidation steps in the one-pot reaction, a potential pathway is proposed for the direct transformation of sucrose to DFF via HMF as the intermediate (Scheme 2). The first step of one-pot reaction is the hydrolysis of sucrose to monosaccharide (glucose and fructose) catalyzed by the acid sites of the catalyst. Then glucose isomerisation into fructose takes place using FeVO₄. In the next step, the most basic hydroxyl group in fructose attached to the anomeric carbon is hydrolysed by the Brönsted acid sites (-SO₃H group) of the S-PANI. This results into enol form which immediately tautomerizes into most stable keto form by the loss of water molecule. This is followed by three successive dehydration steps assisted by S-PANI and DMSO leading to the formation of HMF as an intermediate. Finally, the selective oxidation of HMF to DFF is catalyzed by FeVO₄ present in the nanocomposite. The HMF is adsorbed on the catalyst surface through the interaction between the hydroxyl group of HMF and oxidation sites, i.e., Fe, and V, on the catalyst surface. This interaction results in the formation of intermediate (I), which after β -elimination affords DFF as the selective product. In the final step, the catalyst is regenerated by the dissolved oxygen present in the reaction medium with the elimination of a water molecule. The catalyst S-PANI-FeVO₄(11) is more effective for the selective production of DFF and this is the reason that some amount of DFF was also formed in the first step of one-pot reaction even under N_2 atmosphere as confirmed from ¹H NMR (Fig. 6). This may be due to the oxidation of HMF by lattice oxygen $(V^{+5}-O-Fe^{+3})$, in the presence of a minute amount of molecular oxygen (O₂) present in the reaction vessel according to the Mars-van Krevelen mechanism [38,39].

The catalyst was separated from the reaction mixture using



Fig. 5. Optimization of reaction parameters (a) temperature, (b) catalyst amount, and (c) reaction time for HMF to DFF transformation over S-PANI-FeVO₄(11).

Table 5Selective oxidation of alcohol to aldehyde over S-PANI-FeVO4(11).



Reaction condition: Substrate (1 mmol), S-PANI-FeVO₄(11) (120 mg), DMSO (5 mL), and reaction temperature (413 K).



Fig. 6. Time-dependent ¹H NMR spectra recorded for the one-pot production of DFF from sucrose.

centrifuge machine, washed with MIBK, and then dried in an oven at 393 K for 4 h before it was used in the next cycle. The catalyst was recycled five times and no significant reduction in the isolated DFF yield was observed confirming the efficient reusability of the multifunctional catalyst (Fig. 7). XRD investigation of the recycled catalyst confirmed the stability of the catalyst after the recycling experiments (Fig. S13, SI). The leaching of the active group, especially –SO₃H group in the reused catalyst was studied by XPS and FT-IR spectroscopy. Fresh and recycled catalysts exhibited similar spectral profiles confirming that no significant leaching of the -SO₂H groups was observed (Fig. S14-15, SI). Furthermore, SEM, N2-sorption study and elemental analysis of the recovered catalyst confirmed that no appreciable change in the textural properties was observed (Table 1, Fig. S16). The comparative catalytic efficiency of this catalyst in the sucrose to DFF and sucrose to HMF conversion is found to better or comparable to other reported catalysts (Table S1 shows that a formyl-modified polyaniline exhibited low HMF yield (42.9% in 4 h) in DMSO solvent at 413 K from sucrose [22]. This literature report also revealed that only sulfonated polyaniline (S-PANI) can catalyze the fructose dehydration with 44.9% HMF yield, which is in good agreement with our results [22]. However in our case, a higher (80% HMF) yield is obtained using S-PANI-

FeVO₄(11) catalyst after 6 h at 393 K in DMSO solvent. Moreover polyaniline-GO nanocomposite exhibited inferior activity and produced only 38% HMF yield in NMP solvent in 5 h at 433 K (Table S1, entry 2) [23]. Even -SO₃H functionalized polystyrene-PEG based heterogeneous catalyst exhibited inferior activity (Table S1) suggest that the activity of various catalysts follow the order of fructose > sucrose > > glucose. This activity difference is based on the difficulty of aldose sugar dehydration when compared to the ketose sugar. The sucrose conversion to HMF is difficult when compared to fructose because sucrose hydrolysis produces one aldose (glucose) and one ketose (fructose) sugars. Since ketose sugar can be easily converted to HMF than aldose, therefore the lower activity of sucrose is because of the lower dehydration of aldose formed by the hydrolysis of sucrose. The activity of the present catalyst was also investigated for glucose (an aldose sugar) dehydration into HMF but only a poor glucose conversion and HMF yield (23.7%) were obtained.

4. Conclusion

In summary, a sustainable $FeVO_4$ supported $-SO_3H$ functionalized polyaniline multi-functional catalyst was prepared. FT-IR and XPS



Scheme 2. Proposed mechanism for the one-pot production of DFF from sucrose.



Fig. 7. Catalyst reusability test for sucrose to DFF transformation.

analysis confirmed the successful incorporation of -SO₃H and FeVO₄ in the nanocomposites. Further HR-TEM analysis showed the FeVO4 dark domains and S-PANI light domains in the multi-functional catalyst. Using this multi-functional catalyst, isolated HMF yields of 82% and 95% from sucrose and fructose, respectively, were obtained. Further, EMF with the selectivity of 76% and 84% were obtained from sucrose and fructose, respectively, in one-step conversion process using this catalyst. Moreover, oxidation of HMF and other aromatic and aliphatic alcohols led to produce quantitative yields of DFF and other aldehydes. Finally, one-pot, two-step conversion of sucrose and fructose led to give isolated yields of 80% and 91% DFF, respectively. Brönsted acid sites (-SO₃H) and Fe/V active centres of FeVO₄ present in the multi-functional catalyst facilitated the hydrolysis, isomerization, and dehydration steps. Furthermore, the oxidation sites, FeVO₄, which contains the redox $\overline{Fe^{3+}}/V^{5+}$ sites facilitated the oxidation of the HMF to DFF. The multi-functional catalyst exhibited no loss in the activity in the sucrose to DFF conversion even after five cycles. Isolated yields for DFF, HMF, and EMF are better than hitherto reported catalysts in literature. Such an economical and sustainable two-step transformation of carbohydrates to DFF and EMF with the polyaniline based reusable heterogeneous catalyst will be interesting to catalysis researchers and industrial chemists.

Electronic supporting information (ESI)

Supplementary information includes details of catalyst synthesis and characterization, procedure of catalytic reactions. XRD, N₂ adsorption-desorption isotherm, time-dependent ¹H NMR spectra of carbohydrates to HMF and EMF conversion are provided. XRD, XPS, FT-IR, SEM, N₂-sorption and elemental contents of the recycled catalyst, comparative catalytic activity data reported in the literature for the oxidation of carbohydrates to DFF and HMF are also provided.

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