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Selective two-step synthesis of 2,5-diformylfuran from monosaccharide, disaccharide, and polysaccharide using H-Beta and octahedral MnO₂ molecular sieves

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Keywords: 2,5-Diformylfuran 5-Hydroxymethylfurfural Biomass conversion H-Beta Octahedral MnO ₂ molecular sieve	This study deals with an economical, efficient, and sustainable catalytic process with excellent EcoScore and E- factor values for the selective, two-step synthesis of 2,5-diformylfuran (with a yield higher than 90%) from carbohydrates, especially disaccharide and polysaccharide. This catalytic process involves the abundant and low cost carbohydrate as reactant and economical and sustainable catalysts, H-Beta and octahedral MnO ₂ molecular sieve. In this two step approach, H-Beta is used in the first step for the conversion of carbohydrate to 5-hy- droxymethylfurfural (HMF). Brönsted acidity of H-Beta catalyzes the hydrolysis and dehydration reactions whereas Lewis acidity catalyzes the isomerization to produce HMF. Thus, H-Beta is suitable for the conversion of various carbohydrate molecules (starch, sucrose, glucose and fructose) to HMF. After the first step, H-Beta is withdrawn and then the reaction mixture is subjected to oxidation catalyst, octahedral MnO ₂ molecular sieve, in the presence of O ₂ atmosphere to achieve the high 2,5-diformylfuran (DFF) yield. Molecular oxygen (1 atmo- sphere, O ₂ filled balloon) is used as an eco-friendly and economical oxidant. Furthermore, no over oxidation product of DFF is observed. HMF and DFF are recovered from the reaction mixture by the extraction with methyl isobutyl ketone (MIBK) using water and brine solutions. DFF yields of 97.1%, 95.3%, 93.4% and 91.5% are obtained when the reactions are carried out using fructose, sucrose, glucose, and starch, respectively. Stepwise addition of catalysts improves DFF yield (> 90%) from fructose, glucose, sucrose, and especially starch.

Moreover, the H-Beta and octahedral MnO₂ molecular sieve are easily separable and recyclable.

1. Introduction

The sole renewable and naturally abundant source of carbon-rich compounds is biomass [1–3]. Biomass affords a better alternative to our dependence on crude oil, obtained from fossil fuels, for their applications in the transportation fuels and commodity chemicals [4–8]. Department of Energy (United States) has given emphasis on a list of most valuable chemicals produced from carbohydrate biomass useful to mankind [9]. 5-Hydroxymethylfurfural (HMF) and its oxidized derivatives are amongst the most valuable products. HMF can be prepared by the acid hydrolysis of monosaccharide, disaccharide, and polysaccharide [10–12]. Functional sites present in HMF provide an opportunity to synthesize various furan-based chemicals and fuel additives just by oxidation, reduction, and condensation reactions [13,14]. The easiest route to synthesize HMF is the triple dehydration of fructose. Mineral acids have the ability to convert fructose to HMF [15]. However, they produce side products along with the desired HMF.

Moreover, they are corrosive and non-recyclable. Sustainable production of HMF requires recyclable heterogeneous catalysts. Zeolites, silica, metal oxide, carbon-based sustainable catalysts, and ionic liquids have been developed for the catalytic conversion of monosaccharide, disaccharide, and polysaccharide to HMF [16-24]. Recent literature reports several solid acid catalysts including H-Beta and FePW₁₂O₄₀ for fructose to HMF conversion [25]. These acid catalysts produce 97% HMF yield when the reaction is carried out by evacuation at 0.97 \times 10⁵ Pa. Any pressure other than 1 atmosphere is responsible for inferior EcoScore value [26] and is, therefore, discouraged by the industries. Further, the reported study is only limited to the fructose to HMF conversion. Moreover, such catalysts are amicable for the fructose to HMF conversion, while only a limited number of reports are available for the transformation of other carbohydrates such as sucrose, glucose, or polysaccharide to HMF [27-30]. The difficulties that often arise in the transformation of carbohydrate to HMF are the simultaneous generation of formic acid (HMF degraded product), condensation products

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Scheme 1. Various possible products formed during the conversion of carbohydrate to DFF.

(polymer or humins) and levulinic acid etc.

Further, the interest lies in the conversion of HMF to 2,5-diformylfuran (DFF). During the oxidation of HMF, partial oxidized and complete oxidized furan derivative are formed in addition to the desired product DFF (Scheme 1). Therefore, selective synthesis of DFF is a challenging task. Several hazardous catalysts as well as sustainable catalysts have been explored for this selective oxidation process [31–35]. A wide range of metal oxides including various structural forms of manganese oxide have been investigated for this oxidation reaction [36]. Among different structural forms of manganese oxide, OMS-2 has produced the best activity with 97% yield of DFF at 5 bar O_2 pressure. A penalty of 3 is given to any operating pressure other than 1 atm in the EcoScore calculation [36]. Such a process is, therefore, not encouraged by industries because a huge investment is required for the installation of process equipment.

More challenge lies in the synthesis of DFF directly from monosaccharide or disaccharide or polysaccharide [37-44]. DFF can be directly synthesized from carbohydrates with the aid of multi-functional catalysts. These multi-functional catalysts should contain acidic and oxidation capabilities. The role of a multi-functional catalyst is to convert carbohydrate molecules to HMF using acidic sites and, then, convert HMF to DFF employing its oxidation sites. Two methodologies can be adopted for the direct conversion of carbohydrate to DFF. In the first methodology, carbohydrate can be reacted with a multi-functional catalyst in O₂ atmosphere to form DFF. However, using this methodology, an inferior DFF selectivity is expected due to the degradation of carbohydrate in the presence of multi-functional catalyst. Second methodology is the tandem process. In this methodology, first carbohydrate can be reacted with multi-functional catalyst in N2 atmosphere to form HMF and then in the successive step it is reacted in O2 atmosphere to form DFF. In the recent time, a wide range of multi-functional catalysts based on metal oxides (especially magnetic nanoparticles, vanadium based systems, mixed metal oxide & heteropolyacid), mesoporous silica, zeolite, ion-exchange resins, ionic liquids, MOF, polyaniline, and carbon (C3N4 and graphene oxide) based systems have been explored [38-62]. However, these multi-functional catalysts have also provided somewhat inferior DFF selectivity. Inhibition of glucose isomerization and oxidative decomposition of carbohydrate over these catalysts are prime reasons for such inferior DFF selectivity. The details of some selected catalysts and reasons for inferior DFF selectivity are summarized in Table S1. Moreover, these reactions have been carried out using most reactive carbohydrate fructose. Only a limited efforts have been made in which difficult carbohydrates such as starch and glucose have been converted to DFF via tandem methodology. Hence, a sustainable route for the transformation of difficult carbohydrates to DFF is a challenging and important research area.

Another possibility is to carry out this reaction in a two-step process using two different catalysts. In this process, high DFF yield can be achieved. In this approach, former step is carried out using an efficient acid catalyst. After the removal of acid catalyst, the latter step is carried out with an oxidation catalyst in the presence of O_2 to achieve high DFF yield. Using this approach, oxidative decomposition of carbohydrate can be significantly minimized, and, as a result, the DFF yield can be maximized. Further, the catalyst regeneration process (if required) becomes simpler.

This study provides an economical, user-friendly and sustainable route with excellent EcoScore & E-factor for the selective production of DFF from polysaccharide starch, disaccharide sucrose and monosaccharide (fructose and glucose) at 1 atmosphere O2. Herein, two robust and economical catalysts have been employed in the two-step methodology for the selective formation of DFF from carbohydrates. In the first step, H-Beta is used as an acid catalyst whereas, in the second step, octahedral MnO₂ molecular sieve (OMS) is used as an oxidation catalyst. H-Beta possesses Lewis acidity and Brönsted acidity. Therefore, hydrolysis, dehydration, and isomerization can be accomplished using H-Beta and thus can be applicable to a wide range of carbohydrates. We have reported that OMS prepared using urea as an additive has exhibited better oxidation ability [63] than OMS-2 prepared with conventional method reported earlier for the conversion of HMF to DFF at 5 bar O_2 pressure [36]. Therefore, we anticipated that OMS prepared with urea can provide better oxidation ability and transform HMF to DFF at 1 atmosphere O2. The catalytic process demonstrated here offered greater than 90% DFF yield from various carbohydrates mentioned above at 1 atmosphere O2 (oxygen filled balloon) with higher EcoScore & lower E-factor values, hitherto reported in the literature.



Fig. 1. SEM images of (a) OMS and (b) H-Beta and HRTEM images of (c,d) H-Beta, and (e,f) OMS.



Fig. 2. High resolution XPS spectrum of Mn 2p present in OMS.

2. Experimental

2.1. Catalyst synthesis

H-Beta and H–Y (Si/Al = 2.7) were obtained from Süd-Chemie India Pvt. Ltd. Urea assisted synthesis route was adopted to prepare OMS [63]. KMnO₄ (8 mmol) was added to 20 ml of deionized water. Urea (28 mmol) was added to the above solution, followed by stirring at ambient temperature for 30 min. The resultant solution was added dropwise to a vigorously stirred mixture of $MnSO_4$.H₂O (10.5 mmol in 6 ml water) and 0.6 ml conc. HNO₃. The resulting mixture was transferred to a round-bottomed flask fitted with a condenser and refluxed for 24 h. Synthesis mixture was cooled to ambient temperature, the solid product was filtered, washed with deionized water, and dried at 393 K for 10 h to obtain OMS with 95% yield. Conventional ZSM-5 and nanocrystalline ZSM-5 were prepared by following the reported procedure [64,65]. Details of textural properties of conventional ZSM-5 and nanocrystalline ZSM-5 are provided in Table S2.

2.2. Procedure of the catalytic reactions

Procedures for the independent first step using H-Beta catalyst



Fig. 3. Influence of (a) temperature, (b) time, (c) catalyst amount, and (d) solvent in the transformation of sucrose to HMF. Reaction condition: For (a) sucrose (1 mmol) and DMSO (5 mL), H-Beta (120 mg), time (3 h), and N_2 flow rate (10 mL/min); (b) sucrose (1 mmol) and DMSO (5 mL), H-Beta (120 mg), temp. (393 K) and N_2 flow rate (10 mL/min); (c) sucrose (1 mmol) and DMSO (5 mL), H-Beta (catalyst), temp. (393 K), time (3 h), and N_2 flow rate (10 mL/min); (d) sucrose (1 mmol) and solvent (5 mL), H-Beta (catalyst), temp. (393 K), time (3 h), and N_2 flow rate (10 mL/min); (d) sucrose (1 mmol) and solvent (5 mL), H-Beta (catalyst), temp. (393 K), time (3 h), and N_2 flow rate (10 mL/min); (d) sucrose (1 mmol) and solvent (5 mL), H-Beta (catalyst), temp. (393 K), time (3 h), and N_2 flow rate (10 mL/min); (d) sucrose (1 mmol) and solvent (5 mL), H-Beta (catalyst), temp. (393 K), time (3 h), and N_2 flow rate (10 mL/min).

(HMF synthesis) & second step using OMS catalyst (DFF synthesis), and two-step catalytic process for the synthesis of DFF (from carbohydrates), and NMR data for HMF and DFF are provided in SI. Details of isolation of HMF and DFF from the reaction mixture using methyl isobutyl ketone (MIBK) are provided in SI. Analytic methods utilized for the determination of yield using ¹H NMR [66,67] and gas chromatography are also described in SI.

2.2.1. Two-step direct conversion of polysaccharide (starch) to DFF Starch (340 mg), DMSO (5 mL), and H-Beta (150 mg) (pre-activated at 393 K for 4 h) were charged into a Teflon-lined stainless steel

autoclave (23 mL) at 423 K for 12 h. Progress of the reaction was monitored using ¹H NMR spectroscopy. H-Beta catalyst was withdrawn from the reaction mixture using centrifuge machine after the reaction vessel was cooled to ambient temperature. Then the reaction mixture was transferred to a double-neck round-bottom flask fitted with a condenser, and the oxidation step was carried out using OMS (100 mg). The resulting mixture was heated at 393 K for 10 h under the O₂ environment (O₂ balloon). The OMS catalyst was withdrawn from the reaction mixture using centrifuge machine, and the reaction mixture was analyzed by ¹H NMR. DFF with an isolated yield of 91.5% was obtained using MIBK as extracting medium.



Fig. 4. The plot for lnk vs 1/T for the determination of E_a for the (a) dehydration of sucrose to HMF and (b) oxidation HMF to DFF. Reaction condition: (a) Sucrose (1 mmol) and DMSO (5 mL), H-Beta (120 mg), time (3 h), and N₂ flow rate (10 mL/min); (b) HMF (1 mmol) and DMSO (5 mL), OMS (60 mg), time (10 h), and O₂ (1 atm, balloon). Plots were constructed by taking the average values from Figs. 3 and 5.

3. Results and discussion

3.1. Physico-chemical characterization

Only a brief description of the physicochemical properties of the investigated materials is provided. The diffraction peaks and corresponding planes obtained from the powder XRD of H-Beta shown in Fig. S1 match well with the diffraction peaks of BEA framework structure [68]. OMS exhibits highly crystalline XRD pattern. The diffraction peaks and corresponding planes obtained from the powder XRD of OMS shown in Fig. S1 match well with the diffraction peaks of octahedral MnO₂ (tetragonal structure of cryptomelane-type octahedral molecular sieves) (ICDD No. 00-29-1020).

Surface area and porosity of H-Beta and OMS were calculated using N2-volumetric analyzer (Fig. S2, SI). NLDFT and BJH methods were used to determine the micropore and mesopore size distribution (intercrystalline porosity), respectively (Fig. S2, SI). H-Beta exhibits type-II isotherm and shows higher adsorption at lower P/P₀ that correlates with the micropores filling in the material. In the intermediate pressure range (P/P₀ = 0.2-0.8), a moderate growth in the adsorbed volume is perceived. This is followed by swift increase in the adsorption volume at P/P_0 higher than 0.9. This swift increase in the adsorbed volume can be correlated to the inter-particle porosity present in the material which is consistent with BJH pore size distribution in the range of 4-10 nm obtained for this material. Similarly, OMS also exhibits type-II isotherm and a moderate growth in the adsorbed volume is perceived in the intermediate pressure range ($P/P_0 = 0.2-0.85$). This is followed by the vertiginous increase in the adsorbed volume at $P/P_0 > 0.85$ (Fig. S2, SI). Micropores (approximately, 0.5 nm) is noticed during the pore size determination. Further, bimodal mesopore size distribution (first: 2-10 nm (mesopores) and second: 10-120 nm (mesoporous-macroporous overlapping domain) with a peak maximum of 33 nm) is noticed in BJH analysis. Obtained numerical values of surface area and porosity derived from N₂-adsoption studies are summarized in Table S2 (SI).

Scanning electron microscope (SEM) provides information with respect to microstructure and morphology of the synthesized materials. OMS shows highly cross-linked nanowire morphology (Fig. 1a). H-Beta shows aggregated crystal morphology (Fig. 1b). The high-resolution transmission electron microscope (HRTEM) provides information with respect to nanostructure. H-Beta exhibits highly aggregated nanocrystalline morphology with the particle sizes of 20–25 nm in the TEM images (Fig. 1c and d). Whereas the HRTEM images of OMS confirm the nanowire morphology (Fig. 1e and f). The nanowire thickness is in the range of 10–20 nm (Fig. 1f).

The presence of Lewis and Brönsted acidity is well documented in the literature for the zeolite Beta [69]. Lewis and Brönsted acid sites present in the H-Beta were evaluated from FT-IR measurement using pyridine as a probe molecule. Fig. S3a shows the pyridine FT-IR spectrum of H-Beta zeolite. The peak at 1545 cm⁻¹ corresponds to Brönsted acid site (Si–O(H)–Al groups), and the peak at 1445 cm⁻¹ corresponds to Lewis acid site (Al^{3+}) . Furthermore, the peak at 1490 cm⁻¹ can be attributed to the interaction between pyridine and both Brönsted and Lewis acidic sites. Acidity of H-Beta was determined from ammoniatemperature programmed desorption (NH₃-TPD) measurement. Desorption peak at higher temperature represents stronger acid sites. H-Beta demonstrates three types of acid sites (Fig. S3b). First desorption in 323 K-553 K range corresponds to weak acid sites, second desorption in 553 K-643 K range corresponds to medium strength acid sites, and third desorption in 643 K-823 K range corresponds to strong acid sites. In this material weak acid sites are predominant over strong acid sites. Total acidity of H-Beta is found to be 0.72 mmol/g.

Oxidation state of Mn present in OMS was confirmed from the XPS measurement. The high resolution Mn 2p XPS spectrum is shown in Fig. 2. Gaussian–Lorentzian curve fitting of XPS spectrum shows the presence of Mn $2p_{3/2}$ and Mn $2p_{1/2}$. Mn $2p_{3/2}$ can be deconvoluted into two peaks located at 641.5 and 642.8 eV, which can be assigned to Mn (III) and Mn(IV) oxidation states [70]. Similarly, Mn $2p_{1/2}$ can also be deconvoluted into two peaks located at 653.1 and 654.2 eV, which can be assigned to Mn(III) and Mn(IV) oxidation states, respectively.

3.2. Catalytic activity

A two-step methodology is reported here for the synthesis of DFF from biomass-derived carbohydrates (monosaccharide, disaccharide, and polysaccharide) *via* HMF as an intermediate. In this methodology, two catalysts were utilized in a step-wise manner to achieve DFF. The first step was realized with a solid acid catalyst H-Beta and the second step was accomplished with a solid oxidation catalyst OMS. To achieve the best DFF yield, it is important to optimize both the steps, independently, involving H-Beta and OMS as catalysts.



Scheme 2. Plausible mechanism for the two-step synthesis of DFF from sucrose involving sucrose to HMF using H-Beta catalyst, followed by HMF oxidation using OMS catalyst.

3.2.1. Optimization of the first step (HMF synthesis)

The first step was optimized using sucrose as a model substrate. The reaction was carried out in N₂ atmosphere (10 mL/min) with H-Beta catalyst in DMSO solvent medium. ¹H NMR was used as an analytical tool to determine the yield of the product in the optimization reactions. Parameters influencing the dehydration of sucrose to HMF were investigated. Temperature played significant role to enhance the product (HMF) yield. The influence of temperature was investigated in 363 K–403 K (Fig. 3a). With an increase in the temperature from 363 K to 393 K, the HMF yield was increased from 45% to 99% (MIBK extracted yield 95.4%). Considering the highest yield at 393 K, this temperature was optimized for rest of the studies. Rate of reaction, calculated at different temperature, was used to determine the activation energy (E_a) (Fig. 4a). E_a (67.6 kJ/mol) was calculated from lnK *vs* 1/T plot for this reaction using H-Beta catalyst. Catalytic path having lower activation energy (Ea) is suitable for a reaction. E_a of 99 kJ/mol and

103.4 kJ/mol for the dehydration of fructose has been reported using 3 M H₂SO₄ and ion-exchanged resin as catalysts, respectively [71,72]. However, the present study using H-Beta, E_a of 67.6 kJ/mol was calculated for difficult substrate sucrose when compared to fructose reported above, signifying the better activity of H-Beta at the optimum condition. During the initial period, the reaction rate was high (Yield of HMF after 1 h = 51%; product selectivity: HMF (52%), fructose (22%), and glucose (26%)) (Fig. S4, SI). Almost quantitative yield of HMF was obtained after 3 h of reaction (Fig. 3b). ¹H NMR recorded at 0 h, 1 h, 2 h, and 3 h for the reaction using sucrose as substrate is shown in Fig. S4. Influence of catalyst amount was investigated for the reactions carried out for 3 h (Fig. 3c). Based on the results obtained, an optimum amount of 120 mg H-Beta was optimized to get the maximum yield of HMF. The influence of solvents having different polarity was investigated in the dehydration of sucrose to HMF (Fig. 3d). Result shows that aprotic polar solvent DMSO was excellent to achieve the highest



Fig. 5. Influence of (a) temperature, (b) catalyst amount, and (c) reaction time, in the transformation of HMF to DFF. Reaction condition: for (a) HMF (1 mmol), DMSO (5 mL), OMS (60 mg), time (10 h), and O_2 (1 atm, balloon); (b) HMF (1 mmol), DMSO (5 mL), time (10 h), temperature (393 K), and O_2 (1 atm, balloon); and (c) HMF (1 mmol), DMSO (5 mL), temperature (393 K), OMS (60 mg), and O_2 (1 atm, balloon); (a) HMF (1 mmol), DMSO (5 mL), temperature (393 K), OMS (60 mg), and O_2 (1 atm, balloon); (b) HMF (1 mmol), DMSO (5 mL), temperature (393 K), OMS (60 mg), and O_2 (1 atm, balloon); (b) HMF (1 mmol), DMSO (5 mL), temperature (393 K), OMS (60 mg), and O_2 (1 atm, balloon).

yield of HMF. DMSO plays an important role in the dehydration of carbohydrates (discussed below in Scheme 2). In a strong polar aprotic solvent, especially DMSO, the electronic pair of O, N, or S can attract and disperse the positive charge of DMSO, and accelerates the dehydration of carbohydrate to HMF. DMSO is known to form sulfuric and methanesulfonic acids at high temperature which are suitable for the dehydration of carbohydrate (fructose) [73,74]. Moreover, DMSO has the ability to suppress the formation of undesired side product such as humus due to the degradation of HMF [75–77]. In another study, Caroline Laugel et al. [73] reported that HMF could degrade in organic solvents other than DMSO. Furthermore, a wide range of carbohydrates are soluble in DMSO when compared to other solvents makes DMSO an excellent solvent for this study. After the successful transformation of

sucrose to HMF, fructose and glucose were converted to HMF.

An excellent HMF yield (MIBK extracted yield 96.2%) was obtained in the absence of catalyst with fructose as a reactant in just 1 h. ¹H NMR spectra recorded at 0 h, 0.5 h, and 1 h for the dehydration of fructose using H-Beta catalyst is shown in Fig. S5. Lone pairs of oxygen present in DMSO helps in the step-wise dehydration to form HMF (Scheme 2). Result shows that glucose required more time for the conversion to HMF using H-Beta catalyst. HMF and fructose are observed in the ¹H NMR spectrum recorded after 2 h in addition to the un-reacted glucose (Fig. S6, SI). In this case, more than 98% HMF (MIBK extracted yield 93.2%) was observed in the time-dependent ¹H NMR spectrum obtained after 5 h (Fig. S6, SI).

The optimum condition required for monosaccharide and



Fig. 6. Time-dependent ¹H NMR spectra recorded during two-step conversion of sucrose to DFF.

disaccharide was not suitable for the conversion of polysaccharide starch to HMF. Therefore, the reaction was carried out at 423 K for 12 h using H-Beta catalyst (150 mg) to obtain the quantitative yield of HMF. ¹H NMR spectra recorded at 0 h, 5 h, and 12 h of the reaction are presented in Fig. S7 (SI). After 5 h, ¹H NMR spectrum shows 99% starch conversion to its hydrolyzed products: HMF (50%), glucose (24%), and fructose (26%). Whereas, after 12 h, no by-product was observed and 98% yield (MIBK extracted yield 92.1%) of HMF was obtained (Fig. S7, SI).

ZSM-5, H-Y, nanocrystalline ZSM-5, and OMS were investigated for the sucrose to HMF transformation (Table S3, SI). Conventional ZSM-5 and OMS were found to be inactive whereas H-Y and nanocrystalline ZSM-5 were active but required longer time to produce lower yield of HMF. Since OMS contains only Fe and V sites, therefore OMS was inactive during the conversion of sucrose to HMF. Acid sites are located in the micropores of conventional ZSM-5 with 0.55 nm pore size therefore conventional ZSM-5 was found to be inactive to catalyze this reaction. Nanocrystalline ZSM-5 has large external surface area and only the acid sites present on the pore mouth are accessible to sucrose molecules therefore nanocrystalline ZSM-5 exhibited inferior activity. H-Y zeolite with lower Si/Al ratio and inferior Brönsted acidity produced lower yield of HMF. In this case, an additional side product, dimer of HMF [5,5-oxy-(bismethylene)-2-furaldehyde] was obtained. H-Beta with pore size of 0.65 nm and significant defect sites makes H-Beta suitable for this reaction. Products selectivity obtained using H-Beta at different time interval during the conversion of sucrose to HMF is provided in Table S3 (SI).

3.2.2. Selective oxidation of HMF to DFF

Since the aim was to develop two-step reaction protocol, therefore one has to optimize the oxidation of HMF to DFF in the same solvent as it was optimized in the first step (carbohydrate to HMF). Considering the high yield of HMF in DMSO, reactions were carried out in DMSO solvent using OMS as a catalyst. In this step, the product yield was easily determined using GC. Reaction parameters were optimized using oxygen filled balloon (at 1 atm). HMF oxidation was carried out in DMSO under the optimized reaction condition without any catalyst. Only 1.9% DFF yield was obtained as product in the absence of catalyst. Only a negligible amount of DFF (2.1% DFF) was formed when H-Beta was used as a catalyst. These control experiments suggest that DMSO did assist in the oxidation reaction but without suitable catalyst its activity was negligible. With increase in the temperature in the range of 353 K - 393 K using OMS catalyst, the DFF yield (or HMF conversion) was increased from 40% to 99% (since DFF was observed as the only product) (Fig. 5a). From the plot of lnk vs 1/T, E_a was determined (Fig. 4b). The E_a for this reaction using OMS was determined to be 61.5 kJ/mol (Reaction condition: HMF (1 mmol), OMS (60 mg), DMSO (5 mL), time (10 h), and temperature (353-393 K). Furthermore, the activation energy calculated for HMF to DFF conversion is lower (61.5 kJ/mol) using OMS catalyst when compared to other catalysts (VOx/TiO₂ (67 kJ/mol) [78] and multilayered V₂O₅/TiO₂ (77 kJ/mol) [79]) suggesting the superiority of the present catalyst at the optimum reaction condition. With an increase in the catalyst amount, from 20 mg to 60 mg, the DFF yield was increased and the highest DFF yield was obtained using 60 mg of catalyst (Fig. 5b). With the increase in reaction time from 2 h to 10 h, DFF yield was increased gradually from 29% to



Fig. 7. Time-dependent ¹H NMR spectra recorded during two-step conversion of fructose to DFF.

99% (Fig. 5c). Therefore, the optimum condition for the oxidation of HMF to DFF was chosen as: Reaction time -10 h; temperature -393 K; and the catalyst amount -60 mg.

The aim of this study was to maximize the yield in both steps so that the separation can be avoided, especially after the first step of the process (carbohydrate to HMF). Further, any lower yield has penalty points during the determination of EcoScore of the process [26]. Therefore, the reaction parameters were optimized to maximize the HMF and DFF yields.

3.3. Two-step conversion of carbohydrate to DFF

Having optimized the reaction condition independently for the first and second steps, the stage was set to perform reactions for the transformation of carbohydrates to DFF in the two-step process.

In the two-step process, sucrose (1 mmol) was dissolved in DMSO (5 mL) and then heated at 393 K under N_2 flow (10 mL/min) in the presence of H-Beta (120 mg). The transformation of sucrose to HMF was evaluated using ¹H NMR (Fig. 6). After achieved the maximum HMF yield in 3 h, the N_2 -flow was stopped, and the reaction vessel was cooled to room temperature. The catalyst was withdrawn from the reaction mixture with the help of centrifuge machine. Then oxidation catalyst OMS (60 mg) was added and the reaction mixture was heated to 393 K. The reaction was continued for another 10 h using O_2 filled balloon (1 atm). After 13 h of the reaction, the catalyst was withdrawn and reaction mixture was analyzed using ¹H NMR. Time-dependent ¹H NMR spectra for the two-step transformation of sucrose to DFF using H-Beta and OMS catalysts are shown in Fig. 6. After 13 h of the reaction, 100% sucrose conversion and 99% DFF yield were obtained. DFF was

isolated from the reaction mixture by extracting with MIBK using water and brine solutions and DFF was isolated with 95.3% yield. The Eco-Score and E-factor were calculated to be 85 and 0, respectively (SI).

The bi-functional catalyst, OMS(30%)/H-Beta, was also prepared by following the reported procedure [80]. This bi-functional catalyst was investigated in the two-step reaction. Sucrose (1 mmol) was dissolved in DMSO (5 mL) and then heated to 393 K in the presence of OMS (30%)/H-Beta (120 mg). The first reaction was performed for 3 h in N₂ flow (10 mL/min) and then next step was carried out in the presence of O₂ balloon. In this two-step reaction, sucrose conversion (72%) and DFF yield (37%) were obtained.

The mechanism for the formation of HMF from sucrose is presented in Scheme 2. The first step of this conversion process involves hydrolysis of disaccharide sucrose to monosaccharide, fructose and glucose. Small amount (0.5 wt %) of water present in the DMSO facilitates this step. Mild Brönsted acidity accelerates the hydrolysis step by the cleavage of glycosidic bond present in the sucrose to form equimolar fructose and cyclic oxonium ion (Scheme 2). Then water reacts with the cyclic oxonium ion and forms the glucose. Later Lewis acid sites present in H-Beta facilitate the isomerization of glucose to fructose. Brönsted acid sites present in H-Beta protonate the hydroxyl group (most basic) attached to the anomeric carbon of the fructose and facilitate the dehydration process via enol-keto tautomerization to form HMF. The oxidation step is favored in the presence of OMS. Initially, the lattice oxygen present in OMS oxidizes HMF to DFF and simultaneously Mn⁴⁺ reduces to Mn³⁺ [36]. Then the refilling of oxygen vacancies (i.e. consumed lattice oxygen atom) by molecular O2 and re-oxidation of Mn^{3+} to Mn^{4+} [36] takes place.

The catalysts were easily withdrawn and reused for multiple cycles.



Fig. 8. ¹H NMR spectra recorded during two-step conversion of glucose to DFF at different time.

H-Beta and OMS were recovered from the reaction mixture using centrifuge machine after each step. The catalysts were washed with DMSO and deionized water, and, then, dried in an oven at 373 K for 10 h. H-Beta was activated at 773 K for 4 h in a furnace whereas OMS was activated at 473 K in an oven for 10 h before next cycle. Catalytic activity data obtained after each cycle confirmed that no significant decrease in the DFF yield was observed after five cycles (Fig. S8, SI). XRD (Fig. S9, SI) and N2-adsorption investigations (Table S2, SI) of the recycled catalysts confirm that the catalyst was stable after recycle. Mn, Al, and Si species were not detected in the reaction mixture which confirmed that these elements were not leached into the reaction mixture, and H-Beta & OMS catalyzed the reaction as heterogeneous catalysts to produce DFF. Recyclability study of H-Beta zeolite was carried out at lower conversion. Therefore, H-Beta was recycled for three times after performing the reaction for 0.5 h for the conversion of sucrose to HMF. After each cycle, H-Beta was withdrawn from the reaction mixture using centrifuge machine. The catalyst was washed with DMSO and deionized water, and, then, dried in an oven at 373 K for 10 h and activated at 773 K for 4 h before next cycle. Table S3 (SI) shows that H-Beta was successfully recycled with no considerable loss in the activity after three recycles.

Similarly, two-step transformation of fructose to DFF was accomplished. In this case, the first step was carried out in the absence of H-Beta for 1 h to achieve the quantitative yield of HMF (Fig. 7). The second step was carried out in the presence of OMS (60 mg) for 10 h in O₂ (balloon). Time-dependent ¹H NMR study shows the 100% DFF yield after 11 h of the reaction in two-step process (Fig. 7). DFF (yield 97.1%) was recovered from the reaction mixture by extracting with MIBK using

water and brine solutions. The EcoScore and E-factor were calculated to be 86 and 0, respectively (SI).

Next, two-step transformation of glucose to DFF was carried out. In the case of glucose, after 2 h, only 60% glucose conversion and 70% HMF yield were obtained. ¹H NMR spectrum shows that after 5 h, 99% glucose conversion with quantitative yield for HMF was obtained (Fig. 8). After 5 h, H-Beta was removed and the next step was carried out in the presence of OMS (60 mg) in O₂ balloon for 10 h. ¹H NMR (Fig. 8) shows the quantitative yield for DFF (98%) after 15 h of the reaction. DFF was recovered from the reaction mixture by extracting with MIBK using water and brine solutions and DFF was isolated with 93.4% yield. The EcoScore and E-factor were calculated to be 84 and 0.016, respectively (SI).

Finally, the reaction with polysaccharide starch was carried out. For starch, the first step was carried out at 423 K for 12 h using H-Beta catalyst (150 mg). ¹H NMR spectra recorded after 5 h and 12 h are shown in Fig. 9. After 12 h of reaction, a quantitative yield of HMF was obtained (Fig. 9). Subsequently, the second step was performed using OMS catalyst (100 mg) for 10 h using an O_2 balloon. After, 17 h of the reaction, approximately 50% DFF yield was obtained. ¹H NMR investigation shows the 98% yield of DFF was obtained after 22 h of total reaction time (Fig. 9). DFF was recovered from the reaction mixture by extracting with MIBK using water and brine solutions and DFF was isolated with 91.5% yield. The EcoScore and E-factor were calculated to be 83 and 0.016, respectively (SI).

The comparative catalytic efficiency of this catalyst system (H-Beta & OMS) in the carbohydrates to DFF conversion with other reported catalysts are summarized in Table S4-S7 (SI). Literature shows that only



Fig. 9. Time-dependent ¹H NMR spectra recorded during two-step conversion of starch to DFF.

a limited success has been obtained in the transformation of glucose to DFF [37–43]. Reported heterogeneous catalysts could able to produce a maximum of 51% DFF yield from glucose (Table S5, SI). However, the present catalytic process is able to afford 93.4% DFF yield from glucose. Literature also shows that only a meager success has been made using sucrose and starch as reactants. Only a few reports are available for the conversion of starch to DFF and the reported catalysts have afforded DFF yield < 40% (Table S6, SI) [39,42]. However, the present catalytic process is able to afford 95.3% and 91.5% yields of DFF from sucrose and starch, respectively, under mild reaction condition. EcoScore and Efactor values are superior to various reported catalysts (Table S8-S11).

4. Conclusion

In summary, a facile, economical, and sustainable two-step transformation of carbohydrates (including monosaccharide, disaccharide, and polysaccharide) to DFF was demonstrated under mild reaction condition. Each step was independently optimized to maximize the carbohydrate conversion and to achieve the excellent yield of DFF. Moreover, the activation energy for each step, sucrose to HMF over H-Beta catalyst was determined to be 67.5 kJ/mol and HMF to DFF over OMS catalyst was determined to be 61.5 kJ/mol. The activation energies were lower than various reported catalysts demonstrating the effectiveness of the present catalytic process. Brönsted acid sites and Lewis acid sites (Al-centre) present in H-Beta facilitated the hydrolysis, isomerization, and dehydration steps. Furthermore, the oxidation catalyst, OMS which contains the redox Mn^{4+}/Mn^{3+} sites facilitated the oxidation of the HMF to DFF. Having received the maximum yields of HMF from carbohydrates and DFF from HMF oxidation, a two-step transformation of carbohydrates (fructose, glucose, sucrose, and especially starch) to DFF was investigated using O₂ (1 atm, O₂ filled balloon). After the two-step process, DFF was recovered by the solvent extraction process and the DFF yields of 97.1%, 95.3%, 93.4% and 91.5% were obtained for the reactions carried out using fructose, sucrose, glucose, and starch. The Beta and OMS catalysts demonstrated no loss in the activity in the sucrose to DFF conversion even after five cycles. Isolated yield, EcoScore, and E-factors were better than hitherto reported catalysts in literature. Such an eco-friendly two-step transformation of carbohydrates to DFF with economical reusable heterogeneous catalysts will be suitable for commercial execution.

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