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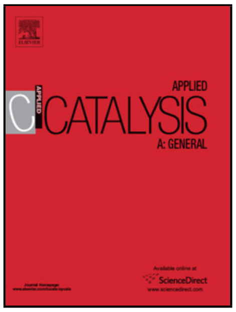

Title: Biomass derived β-Cyclodextrin-SO_3H Carbonaceous
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Highlights

- β-Cyclodextrin derived carbonaceous catalyst was synthesized for the production of 5-hydroxymethylfurfural (HMF).
- Fructose gave about 96% yield of HMF while glucose gave a 47% HMF yield in DMSO with high selectivity.
- Polysaccharides such as sucrose and inulin also gave about 85% and 92% yield of HMF.
- The catalyst can be readily recovered and reused for at least three runs without any significant impact on yields of products.

Biomass derived β-Cyclodextrin-SO_3H Carbonaceous Solid Acid Catalyst for Catalytic Conversion of Carbohydrates to 5-hydroxymethylfurfural

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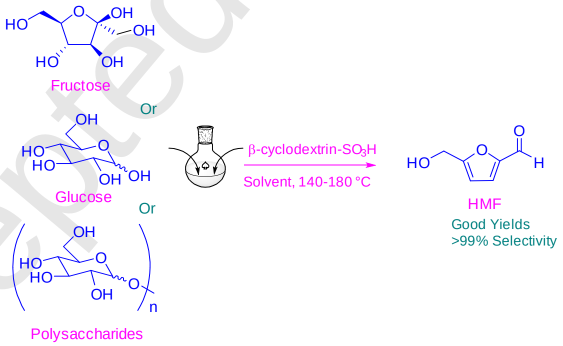
ABSTRACT

A new β-Cyclodextrin-SO_3H carbonaceous solid acid catalyst was synthesized in an ecofriendly manner and was found efficient for conversion of carbohydrates into 5-hydroxymethylfurfural. Numbers of different solvents systems were screened for efficient formation of HMF. The results showed that the β-cyclodextrin based-SO_3H catalyst resulted in 96% 5-hydroxymethylfurfural (HMF) yield from fructose while glucose gave a 47% HMF yield in DMSO in pretty good yields and high selectivity. Polysaccharides such as sucrose and inulin also gave about 85% and 92% yield of HMF. The catalyst was readily recovered and reused for atleast three runs without any significant impact on yields of products. The main advantages of this protocol include practical simplicity, high yields, recyclable catalyst, safety and cheapness of benign solvents.



Keywords: β-Cyclodextrin, carbonaceous, catalyst, 5-hydroxymethylfurfural.

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1. Introduction

Today almost whole world is dependent on fossil fuels for energy sources. With the

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increasing population there will be a concern that these fossil fuels will be used up soon. Hence there is a need to look at alternative energy sources in the biosphere. Biomass comprising of 75% carbohydrates is the only renewable source available widely, which has the potential to replace current non-renewable fossil resources. Now-a-days, most attractive and promising approach is to convert biomass derived carbohydrates to furanic aldehydes such as HMF as it is a promisable candidate and serves as a platform compound for fine chemicals, plasticizers and polymers [1-10]. As seen from the literature, dehydration of fructose into HMF is very easy and efficient [11]. However fructose is not abundant in nature and also very expensive. Hence, HMF cannot be manufactured from fructose on large scale. On the contrary, glucose is the most abundant feedstock for production of HMF. There are also some catalytic systems in which fructose is readily converted to HMF and are ineffective for conversion of glucose to HMF [12, 13] In 2007, Zhao *et al*.[14] for the first time reported dehydration of glucose to HMF in $CrCl_2$ as a catalyst. Later homogeneous catalyst systems such as $SnCl_4$, $AlCl_3$, $GeCl_4$, $MgCl_2$, $ScCl_3$, $YbCl_3$ and heterogeneous catalyst system such as SO_4^{2-}/ZrO_2, NA-p, $Ag_3PW_{12}O_{40}$, H-ZSM-5 were used for dehydration of glucose to HMF with moderate yields of 40 to 70 % [15, 16]. Heterogeneous catalytic processes have advantages over homogeneous catalysis such as straight forward catalyst separation, catalyst regeneration, relatively low cost which make them more applicative in industrial production [17-20].

An amorphous carbon material consisting of small polycyclic aromatic carbon sheets with a high density of sulfonic acid (SO_3H) sites are especially attractive heterogeneous catalysts now-a-days due to their low cost, metal-free composition, and expected high stability and high reusability [21, 22]. Indeed, materials produced by this approach have shown very promising catalytic activity for many acid-catalyzed reactions than commercial catalysts like zeolites, niobic acid or Amberlyst-15 [23]. Intrigued by these studies [24, 25] and our continuing work in this field [26, 27], we choose readily available β-cyclodextrin as a carbon precursor and *p*-TSA as a sulphonating agent. Naturally occurring β-cyclodextrin can be prepared by enzymatic hydrolysis of starch which comes from biomass [28]. Cyclodextrins are cyclic oligomers of seven D-glucose units linked in a α (1-4) manner and have a pre organized structure. Hence after sulphonation of β-cyclodextrin we expected more polycyclic aromatic sheets to be formed and hence high density of sulphonated sites to be attached on the carbonaceous material ultimately showing more acidic character of the catalyst. In this study, we have prepared β-cyclodextrin-SO_3H catalyst by one step hydrothermal carbonization of β-cyclodextrin and *p*-TSA under mild reaction conditions and shown its application in the synthesis of HMF from fructose, glucose and polysaccharides. The hydrothermal carbonization promoted the structure to undergo decomposition, hydrolysis, dehydration, and a molecular rearrangement reaction to produce a polycyclic aromatic structure embedded with active –SO_3H, –COOH and -OH sites. A schematic diagram for preparation of β-cyclodextrin-SO_3H carbonaceous catalyst is shown in Figure 1

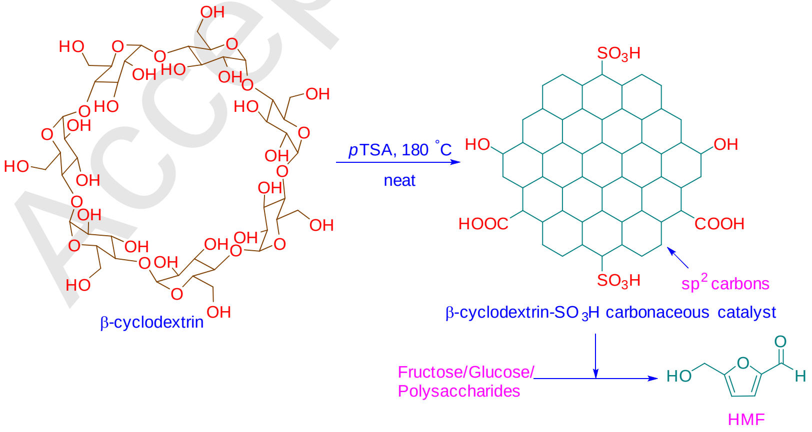


Figure 1. Preparation of β-cyclodextrin-SO_3H carbonaceous catalyst and its application in HMF synthesis.

2. Experimental

2.1. Catalyst Preparation

Typically 4 g of β-cyclodextrin powder was mixed with 18 g of *p*-TSA and was heated in an oil bath at 180 °C for 24 h under nitrogen. After 24 h, the catalyst was kept open to air and further heated for 24 h to remove all the volatile compounds adsorbed on the surface of the material. Deionised water was added to it and the catalyst was filtered and further washed several times with deionised water to remove the excess sulphate ions and then finally washed with ethanol. The black powder thus obtained was oven dried at 100 °C for 12 h. This black powder was found to be insoluble in DMSO, DMF, DMA, and all organic solvents even at boiling temperatures.

2.2. Catalyst Characterization

The catalyst thus obtained was characterized with FT-IR (Spectrum 400), Elemental analysis from EDAX (Quanta 200 3D, FEI), PXRD (Panalytical X'Pert Pro), NH_3TPD (Thermo Scientific TPD RO 1100), Raman (LabRAM HR 800), HRTEM (Tecnai G2 FEI), ^{13}C cross-polarization (CP) magic angle spining NMR (Jeol ECX 400, at a frequency of 100 MHz with a spinning rate of 8 KHz), BET surface area (Quantachrome Autosorb iQ), Elemental analysis C, H and O (Thermo Scientific, Flash EA 1112). The acid densities were measured by acid base titration.

2.3. HMF Synthesis

In a typical synthesis, 100 mg of carbohydrates, 100 wt% of β−cyclodextrin-SO_3H catalyst were taken in a round bottom flask under nitrogen, to which was added 10 mL of solvent. The reaction was then heated at given temperature for given time with magnetic stirring. After specified time, the reaction mass was centrifuged to separate the catalyst, and the solution was further analyzed by HPLC (Agilent 1200 Series) equipped with column

Phenomenex Gemini RP C18 5μ, (250 mm X 4.6 mm). A mixture of water and acetonitrile (93:7) was used as a mobile phase with a flow rate of 1 mL/min.

The retention times observed were as follows: solvent peaks: 3.5 to 4.5, 5-hydroxymethylfurfural: 7.5, furfuraldehyde: 10.5 (Figure S8, Supp Inf). The amounts of HMF were determined by HPLC using furfuraldehyde as an internal standard. The HMF formation was also confirmed using ^{1}H NMR (Figure S9, Supp Inf).

3. Results and Discussion

3.1. Carbonaceous material properties

The FT-IR spectrum (Figure S1, Supp Inf) showed characteristic peaks at 1008 cm^{-1} and 1032 cm^{-1} which are attributed to O=S=O stretching vibrations in -SO_3H groups and peak at 1174 cm^{-1} for SO_3H stretching. This indicates that the sulfonic acid groups have been successively incorporated on the catalyst surface. Peaks at 1610 cm^{-1} attributed for C=C stretching vibrations in aromatic carbons and peak at 1680 cm^{-1} attributed for C=O stretching. Peak at 1714 cm^{-1} attributed to presence of C=O stretching vibration of –COOH group. Bands at 2950 to 2875 cm^{-1} attributed for C-H stretching band. Bands due to O-H stretching were observed at 3421 cm^{-1}. The XRD pattern (Figure S2, Supp Inf) of a β-cyclodextrin-SO_3H catalyst exhibited broad diffraction peak at 2θ angles of 15°-30° which can be assigned to C(002) planes and a weak peak at 2θ angles of 38°-48° that are typical for amorphous carbon composed of aromatic carbon sheets oriented in a considerably random fashion [29]. The energy dispersive X-ray analysis (EDAX) analysis (Figure S3, Supp Inf) showed sulphur composition to be 2.99 %. The ammonia desorption studies (Figure S4, Supp Inf) showed the total acid density to be 2.7 mmol/g. The total acid density and the sulphonic acid density of β-cyclodextrin-SO_3H based on acid base titration was found to be 3.0 mmol/g and 1.24 mmol/g respectively. Raman spectrum (Figure S5, Supp Inf) showed two peaks, G band at around 1580 cm^{-1} due to active Raman vibration of E_{2g} symmetry and D band at around 1350 cm^{-1} due to carbon sheet stacking of the incomplete carbonized catalyst structure which explains the presence of polycyclic aromatic carbon sheets with an intensity ratio of 0.81. The broad intense D band in β-cyclodextrin-SO_3H also indicates the presence of amorphous material in the sample, consistent with the presence of the broad peak in the XRD pattern. [30]. HRTEM (Figure S6, Supp Inf) showed aggregates of particulate morphology. ^{13}C CP/MAS NMR spectrum (Figure S7, Supp Inf) showed chemical shifts at 130, 155 and 180 ppm in the NMR spectrum indicating presence of polycyclic aromatic carbon atoms, phenolic -OH and –COOH groups respectively [31, 32]. Broad peaks observed at 130 ppm and 155 ppm obscures the peak due to aromatic carbons attached to -SO_3H. BET surface areas and pore size were calculated using the standard Brunauer-Emmett-Teller (BET) equation and was found to be 1.36 m^2/g and 66.7 A ° (Table 1). Elemental analysis showed composition of C, H and O to be 70.6 %, 3.7 % and 22.6 % respectively.

Table 1. The structure and surface properties of β-cyclodextrin-SO_3H catalyst

Catalyst	Surface area (m^2/g)	Pore size (A^0)	Acid density (mmol/g)	SO_3H amount (mmol/g)
β-cyclodextrin- SO_3H	1.36	66.7	3.0	1.24

3.2 Optimization of reaction conditions in HMF formation

The performance of β-cyclodextrin-SO_3H as an acid catalyst was tested for the conversion of carbohydrates to HMF. Initially we started to investigate the catalytic activity for this new catalyst for the dehydration of fructose to HMF in DMSO, as DMSO is versatily known to give good yields of HMF from fructose. In an optimized reaction, 100 mg of fructose and 100 wt% catalyst was placed in a round bottom flask, to it was added 10 mL of

DMSO and the reaction mixture was heated at 140 °C for 2 h. HMF was seen to be formed with 100% selectivity from HPLC analysis. The same reaction was then repeated on glucose as an substrate. In this case also HPLC analysis showed formation of HMF. These results indicate that the sulphonic acid groups on the β-cyclodextrin-SO_3H played a vital role in HMF formation from fructose as well as glucose. The same reaction was carried out on glucose without addition of catalyst in DMSO as a solvent, and in this case no HMF formation was observed.

We further studied the effect of reaction temperature, reaction time and catalyst concentration on the performance of β-cyclodextrin-SO_3H in DMSO. For this, fructose and glucose were reacted with β-cyclodextrin-SO_3H at different temperatures i.e 100 °C, 140 °C and 180 °C. Aliquots at intervals were taken out and studied for formation of HMF using HPLC. It was observed that reaction time and reaction temperature had an significant influence on HMF yields. In case of fructose, the reaction was slower at 100 °C and much faster at 140 °C and reached a maximum HMF formation at 140 °C in 2 h, while at 180 °C HMF formation was not so efficient (Figure 2). While, in the case of glucose, HMF was formed in traces at 100 °C and 140 °C (Figure 3). At higher temperature of 180 °C glucose reached a maximum HMF formation in 5 h. It was found that heating for longer time and higher temperature had an negative impact on HMF yields due to formation of side products. The catalyst concentration was also studied to get maximum HMF formation. Catalyst concentration of 10 wt%, 50 wt% and 100 wt% was studied in DMSO as shown in Figure 4. It was found that 100 wt% of metal catalyst gave maximum HMF formation in fructose as well as glucose.

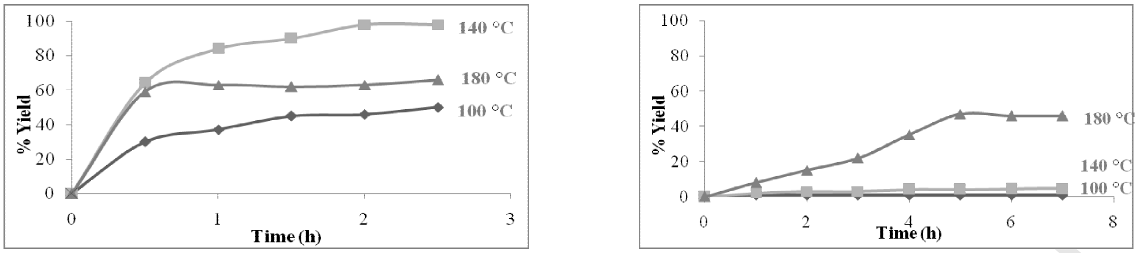


Figure 2 and 3. Study of formation of HMF **1** from D- fructose and D-glucose using β-cyclodextrin-SO_3H catalyst at different temperature in DMSO.

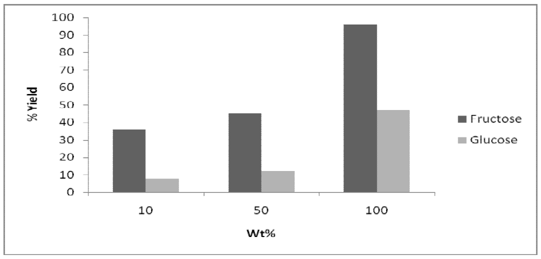


Figure 4. Study of formation of HMF from fructose and glucose using different concentrations of β-cyclodextrin-SO_3H catalyst in DMSO.

3.3 HMF formation from carbohydrates

After setting the optimum conditions for HMF formation from fructose and glucose, we further tried to explore the β-cyclodextrin-SO_3H catalyst in various solvents so as to obtain higher yields and the results are summarized in Table 2 and 3. Fructose gave excellent yields of HMF in DMSO, DMF, NMP and DMA as shown in Table 2. Highest yield of about 96% was obtained in DMSO. Polar solvents like GVL, nitromethane, sulpholane, isopropanol, ethylene glycol, CH_3CN and [BMIM]Cl gave moderate to good yields of HMF from fructose. It can be seen that water is not a suitable solvent for HMF formation as water is not favourable for dehydration reactions and hence promotes side reactions. The β-cyclodextrin-SO_3H was also effective in converting glucose to HMF in good yields. In case of glucose, an maximum yield of HMF formation of about 47% was observed in DMSO as seen in Table 3. Solvents like DMF, NMP, DMA, sulpholane, and [BMIM]Cl gave moderate yields of HMF in the range of 24 to 37%. All the reactions proceeded with almost > 99% selectivity.

Table 2. Fructose to HMF using β-cyclodextrin-SO_3H catalyst.

Entry	Substrate	Solvent	Temp (°C)	Time (h)	Yield (%)[a]
1	Fructose	DMSO	140	2	96
2	Fructose	DMF	140	2	92
3	Fructose	NMP	140	2	84
4	Fructose	GVL	140	2	79
5	Fructose	Nitromethane	100	2	74
6	Fructose	Sulpholane	140	2	72
7	Fructose	DMA	140	2	85
8	Fructose	Isopropanol	100	2	63
9	Fructose	Ethylene glycol	140	2	25
10	Fructose	Water	140	2	-
11	Fructose	[BMIM]Cl	140	2	76
12	Fructose	CH_3CN	100	2	45

[a] Yields are based on HPLC analysis.

Table 3. Glucose to HMF using β-cyclodextrin-SO_3H catalyst.

Entry	Substrate	Solvent	Temp (°C)	Time (h)	Yield (%)[a]
1	Glucose	DMSO	180	5	47
2	Glucose	DMF	180	5	37
3	Glucose	NMP	180	5	24
4	Glucose	DMA	180	5	29
5	Glucose	Sulpholane	180	5	28
6	Glucose	[BMIM]Cl	180	5	32

[a] Yields are based on HPLC analysis.

No rehydration by-products such as levulinic acid and formic acids were detected in any of the samples. The catalyst was found to efficiently convert less expensive and easily available polysaccharides (sucrose, inulin and starch) to HMF as shown in Table 4. 85% yield of HMF was obtained from sucrose, whereas inulin gave about 92% yield of HMF. Starch gave about 10% yield of HMF.

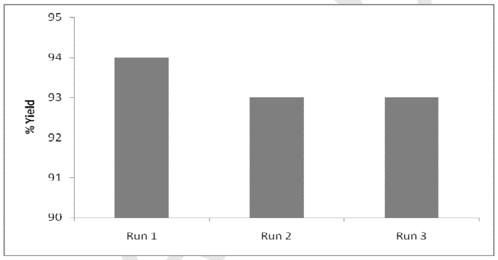
Table 4. Polysaccarides to HMF using β-cyclodextrin-SO_3H catalyst.

Entry	Substrate	Solvent	Temp (°C)	Time (h)	Yield (%)[a]
1	Sucrose	DMSO	140	2	85
2	Inulin	DMSO	140	2	92
3	Starch	DMSO	140	5	10

[a] Yields are based on HPLC analysis.

3.4 Catalyst reusability

The stability of the catalyst is of great importance for practical use, so the cycle usage test of β-cyclodextrin-SO_3H was conducted and the results are listed in Figure 5. After the reaction, the catalyst was separated by centrifugation, washed with water and ethanol, dried at 100 °C for 2 h to remove the adsorbed by-products prior to reuse in the next run. The catalytic activity of the catalyst for the conversion of fructose to HMF in DMSO showed constant activity when reused 3 times. 1st run showed 94% yield of HMF while 2nd and 3rd run both showed 93% yield of HMF from D-fructose indicating good stability of the catalyst.



[a] Yields are based on HPLC analysis.

Figure 5. Yields of HMF when β-cyclodextrin-SO_3H catalyst was reused

4. Conclusion

In summary, we have developed a novel sulphonated carbonaceous material having -SO_3H, -COOH and -OH groups by one step hydrothermal carbonization of β-cyclodextrin and *p*-toulene sulphonic acid under mild and ecofriendly conditions. Such carbonaceous catalyst having high acid strength was found effective for conversion of carbohydrates to HMF in DMSO with pretty good yields and high selectivity. The catalyst showed good reusability too. The catalyst can also be used industrially due to its green preparation, high activity, selectivity and reusability.

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Graphical Abstract

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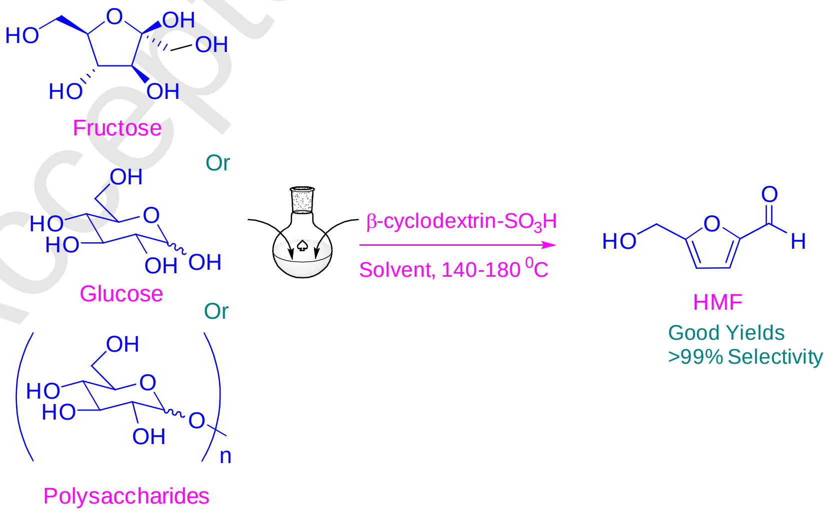
A new β-Cyclodextrin-SO_3H carbonaceous solid acid catalyst was synthesized in an ecofriendly manner and was found efficient for conversion of carbohydrates into 5-hydroxymethylfurfural. Numbers of different solvents systems were screened for efficient formation of HMF. The results showed that the β-cyclodextrin based-SO_3H catalyst resulted in 96% 5-hydroxymethylfurfural (HMF) yield from fructose while glucose gave a 47% HMF yield in DMSO which are pretty good yields with high selectivity. Polysaccharides such as sucrose and inulin also gave about 85% and 92% yield of HMF. The catalyst can be readily recovered and reused for atleast three runs without any significant impact on yields of products. The main advantage of this protocol includes clean reactions, practical simplicity, high yields, recyclable catalyst, safety and cost effective starting materials.



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