Research article

Boron-doped sulfonated graphitic carbon nitride as a highly efficient catalyst for the production of 5-hydroxymethylfurfural from carbohydrates

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A B S T R A C T

The presence of humins during the conversion of concentrated fructose presents a major obstacle in the large-scale production of 5-hydroxymethylfurfural (HMF) from fructose. Herein, we reported a boron-doped graphitic carbon nitride sulfonated (BGCN-SO$_3$H) as an excellent catalyst for the synthesis of HMF from fructose. The BGCN-SO$_3$H catalyst structures were analyzed using various characterization techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), energy-dispersive X-ray spectroscopy (EDX), elemental mapping analysis, and Fourier-transform infrared spectroscopy (FT-IR). The BGCN-SO$_3$H catalyst was evaluated for the synthesis of HMF from fructose. We investigated the influence of catalyst performance, including solvent reactions, catalyst loading, substrates, and volume of solvent to optimize reaction conditions. As a result, the yield of HMF was obtained at 88 % within 5 h when using 30 mg of catalyst. The study of catalyst activity involved examining reactions that allowed recovery and reuse. The research findings offer a method for producing HMF with exceptional efficiency using solid catalysts.

1. Introduction

The global dependence on petroleum as the predominant supplier of chemicals and energy has experienced substantial growth [1]. However, with diminishing reserves and increasing demand, it is crucial to explore new, sustainable alternatives for both fuels and bulk chemicals [2]. Biomass emerges as the most promising substitute due to its wide availability, making it the only viable option besides oil and coal [3–5]. Within the various forms of biomass, carbohydrates play a vital role as they can be converted into valuable chemicals. 5-Hydroxymethylfurfural (HMF) and furfural are pivotal compounds in the field of organic chemistry, owing to their remarkable potential for conversion into a diverse range of valuable chemicals [6,7]. These compounds exhibit exceptional efficiency, rendering them highly desirable for various applications [8]. As an illustration, HMF has the potential to undergo conversion processes

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leading to the production of platform chemicals, namely 2,5-dimethylfuran and 2,5-diformylfuran (DFF) [9]. Furthermore, the conversion of HMF can yield ethyl levulinate, γ-valerolactone, and liquid alkanes, which possess significant potential for diverse industrial applications (Scheme 1) [10]. HMF has been widely recognized as a pivotal link connecting carbohydrates and the petroleum sector in the context of organic chemistry [11]. Hence, the pursuit of proficient synthetic methodologies to achieve optimal HMF yield from carbohydrates has garnered significant scholarly interest [12].

Hexose sugars, including fructose and glucose, have extensively been employed as substrates for the conversion of carbohydrate into HMF [13]. Hongyu Tian et al. created coprecipitation-based hafnium-aluminum bimetallic oxide (Al-HfOx) andpoly (ionic liquid) s-silica spheres (PIL@SiO$_2$) catalysts that convert glucose or fructose to HMF. The study proposes a heterogeneous bimetallic oxide and silica-based core-shell synergistic catalyst approach for carbohydrate-to-HMF conversion [14,15]. Yang *al et.* reported the transformation of biomass into HMF using solid acid catalyst, resulting in the yield of the reaction obtained about 89 % and 54 % from fructose and inulin, respectively [16]. It is significant to highlight that numerous catalytic methodologies have been devised for fructose dehydration to HMF employing diverse homogeneous and heterogeneous acid catalysts [17]. However, the specific removal of water from fructose to produce HMF is significantly influenced by different factors in the reaction, such as the catalyst employed, the medium in which the reaction takes place, and the temperature at which the reaction occurs, which made the reaction yield became low and not selectivity [18]. Notably, the solvent effects have a significant impact on various undesired side reactions, such as the formation of soluble or insoluble polymers like humin, through condensation or polymerization reactions during the reaction of fructose. Various catalysts, such as different types of acids, metal salts, and metal oxides, have been widely used in the production of HMF from fructose. These catalysts can be used in aqueous or biphasic water/organic solvent systems, as well as in ionic liquids [19]. Nevertheless, the production of HMF in an aqueous environment has been found to result in relatively low yields [20]. One possible explanation for this phenomenon is the unwanted rehydration of a compound known as HMF, which results in the formation of levulinic acid and formic acid. In contrast, polar aprotic solvents, such as dimethyl sulfoxide (DMSO), exhibit a higher propensity for dehydrating fructose by effectively mitigating side reactions and enhancing the production of HMF [21,22].

Graphitic carbon nitride (GCN) is a highly suitable material for catalytic applications. It is composed of abundant elements, namely carbon and nitrogen, and possesses excellent stability and non-toxic properties [23,24]. The GCN nanosheets are a fascinating material with a unique structure that gives it inherent basic properties. This is due to the existence of certain groups within its ring structure [25]. In a recent study, Jiang and Han presented an innovative approach to synthesizing phenol from benzene. They utilized a catalyst called vanadium-doped graphitic carbon nitride (V–g-C$_3$N$_4$) and hydrogen peroxide as the oxidant, achieving selective results [26]. In a recent study, Sanny et al. explored the functionalization of GCN nanosheets with a sulfonic group (S-GCN). This alteration rendered the nanosheets more acidic in nature. The researchers then investigated the use of S-GCN as a catalyst in an aqueous environment within a sealed tube to transform glucose into levulinic acid and fructose into HMF [27]. For example, Chen and colleagues developed the MXene/g-C$_3$N$_4$ composite (MX/CN) for photocatalytic HMF to DFF oxidation, achieving over 90 % selectivity and yield above 6 % MX/CN [28]. Wenlei Xie et al. conducted a study on the grafting copolymerization of a combination of two acidic ionic liquids onto a core-shell structured magnetic silica material, with the aim of using it for biodiesel generation [29].

Nevertheless, the use of heterogeneous catalysis for biomass conversion may face several constraints and problems, such as catalyst
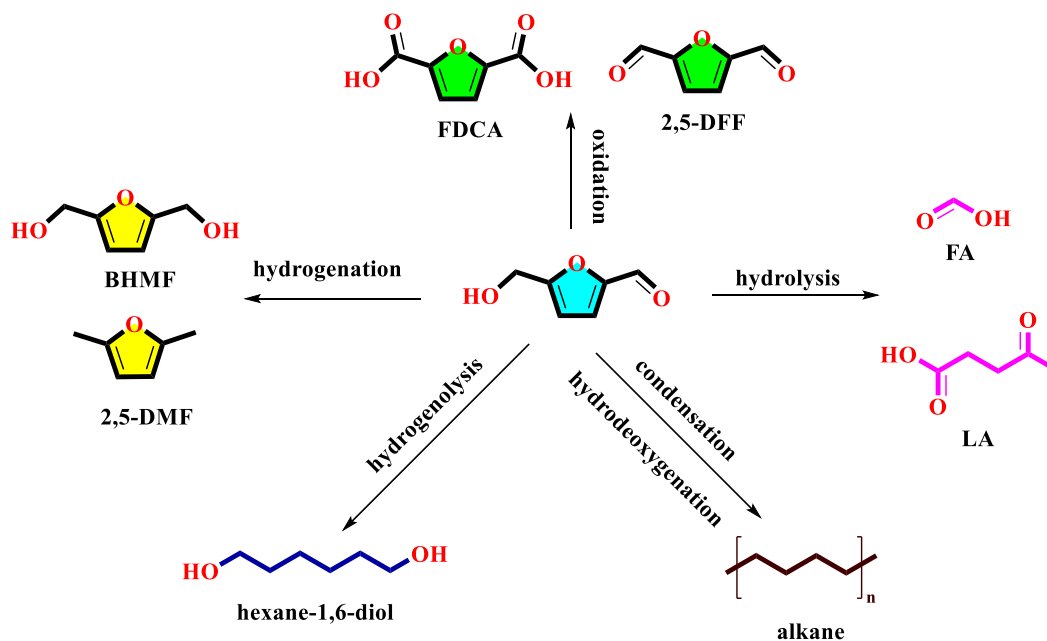
Scheme 1. Main domains of practical applications of HMF and its derivatives.

deactivation, variations in feedstock composition, reaction conditions, selectivity, and yield [30]. To achieve more efficient, sustainable, and economically feasible processes, the field of heterogeneous catalysis for biomass transformation must tackle these issues and focus on these research areas.

In this study, the BGCN-SO₃H catalysts were synthesized using a 4-step procedure. The structural analysis of the catalyst is conducted through contemporary techniques such as Fourier Transform Infrared Spectroscopy (FTIR), Energy-Dispersive X-ray Spectroscopy (EDX), and Scanning Electron Microscopy (SEM). Additionally, the thermal stability of the catalyst is assessed utilizing the Thermogravimetric Analysis (TGA) method. The catalysts synthesized in this study were subjected to a range of characterization techniques to assess their properties. These catalysts were then utilized in the dehydration of fructose to produce HMF in a solvent of dimethyl sulfoxide (DMSO). The BGCN-SO₃H catalyst has a significant impact on the acid properties and catalytic performance, as observed in our study. We also examined various reaction parameters, such as the temperature and duration of the reaction, the selection of solvent, and the potential for reusing the catalyst.

2. Experimental

2.1. Chemicals and equipment

2.1.1. Chemical
Maltose (99 %), fructose (99 %), glucose (99 %), sucrose (99 %), cellulose (99 %) was obtained from Sigmal-Aldrich. Melamine (99 %) was collected from Oxford. Boric acid (99 %), sulfuric acid (98 %, H_2SO_4), nitric acid (63 %, HNO_3), and dimethyl sulfoxide (99 %, DMSO) were obtained from Fisher. Butanol (99 %), sulfolane (99 %), ethyl acetate (99 %), and hexane (99 %) were purchased from ChemSol-Vietnam. (3-mercaptopropyl) triethoxysilane (99 %, MPTES) was obtained from Macklin. 5-Hydroxymethylfufuran (99 %, HMF), 2,5-diformylfruan (99 %, DFF) were collected from Merck.

2.2. Equipment

The FT-IR analysis was conducted using a JASCO- FT/IR-6600 instrument from 600 to 4000 cm^{-1}. An evaluation of the catalyst's thermal stability was carried out using a Toledo TGA/DSC instrument. The catalyst was subjected to calcination, with the temperature gradually increasing from ambient to 800 °C at a scanning rate of 10 Kpm. The morphologies of samples were studied using the SEM-equipped EDX on a JSM-IT200, JEOL, Japan. The crystallinities of the samples were evaluated using XRD on a Bruker D8 Advance powder X-ray diffraction machine with X-ray with wavelength $K_\alpha = 0.154178$ nm, voltage 40 kW, current intensity 40 mA, scanning angle from 3 to 30°, scanning speed 0.02°/s. Raman spectra were measured by the Horiba Xplora Plus Raman instrument, a laser source with a wavelength of 532 nm.

The quantification of HMF was conducted using an HPLC system, namely Agilent Technologies 1260 Infinity, equipped with a Diode Array Detector operating at wavelengths of 285 nm. The constituents of the reaction mixture were isolated utilizing the InertSustain C18 column (5 μm, 4.6 × 150 mm). The temperature of the column was held constant at 25–30 °C. A methanol solution containing sulfuric acid (2.5 mM) was utilized as the eluent, operating at 0.7 mL min^{-1} flow rate. The elution process followed a gradient pattern as outlined below: During the time interval of 0–2.50 min, the composition of the solution was 100 % B. From 2.50 to 2.51 min, the composition was 85 % B. This composition was maintained from 2.51 to 17.00 min. From 17.00 to 17.01 min, the composition is not specified. Finally, from 17.01 to 25.00 min, the solution consisted of 100 % B. The sample was injected with a volume of 10 μL, and the detection was performed at a wavelength of 285 nm. The equation utilized for determining HMF yield (1) is expressed as follows:

Yield of HMF (%) = (molar amount of HMF produced/ molar amount of substrate initially charged) x100   (1)

2.3. Preparation of catalyst

2.3.1. Preparation of boron-doped graphitic carbon nitride
The synthesis of boron-doped graphitic carbon nitride (BGCN) was performed according to the following our procedure [31]. First, a mixture of 4.25 g melamine and 0.75 g boric acid was added to 20 mL of deionized water. The mixture was heated at 90 °C until the water completely evaporated. Next, the dried mixture was placed into an alumina crucible and heated at 550 °C for 4 h. The heating rate during this step was set at 2.5 °C per minute. The process was carried out in a furnace with still air. After the heating process, a pale yellow powder was obtained. To eliminate any residual boric acid, the powder was rinsed with a mixture of hot water and ethanol. Finally, the powder was dried in an oven at 70 °C for 8 h to remove any remaining solvent, resulting in a dried BGCN powder.

2.3.2. Preparation of boron-doped graphitic carbon nitride sulfonated (O-BGCN)
The next step in the synthesis process involved adding the synthesized BGCN powder (1.0 g) to a mixed solution of concentrated H_2SO_4 (98 %) and HNO_3 (69 %) in a 1:1 ratio (20 mL). The resulting mixture was heated at 40 °C while being sonicated for 2 h. Afterward, a 6 % H_2O_2 solution (5 mL) was added dropwise, and the reaction mixture was sonicated for an additional 3 h.

The resulting product was an opaque white substance. To further process it, ice-cold deionized water (100 mL) was added to the

reaction mixture. A dilute suspension of oxidized graphitic carbon nitride (O-BGCN) was then obtained by filtering the mixture and washing it alternately with deionized water and acetone. The material was finally dried in a furnace at 80 °C for 12 h, resulting in a white O-BGCN catalyst.

2.3.3. Synthesis of BGCN-SH using (3-mercaptopropyl) triethoxysilane

BGCN was activated with (3-mercaptopropyl) triethoxysilane (MPTES) to form BGCN-SH. In a 100 mL flask, O-BGCN (1.0 g) was dispersed in toluene (50 mL) by ultrasound for 15 min, and at the same time, MPTES (1 mL) was dissolved separately in toluene (10 mL). Next, the MPTES solution was slowly introduced to O-BGCN under ultrasonic conditions. The reaction mixture was carried out under reflux conditions with N_2 atmosphere for 24 h. After reflux, the catalyst was filtered, washed with ethanol, and dried at room temperature.

2.3.4. Synthesis of BGCN-SO$_3$H

To synthesize BGCN-SO$_3$H, BGCN-SH (1.0 g) was dispersed in 30 % H_2O_2 solution (30 g) and stirred at room temperature for 24 h. The material was then filtered, washed three times with deionized water, and dried in a vacuum oven at 80 °C for 12 h (Scheme 2).

2.4. General procedure of synthesis of HMF using BGCN-SO$_3$H

A mixture of fructose (1 mmol, 180 mg), BGCN-SO$_3$H (30 mg), DMSO (3 mL) were heated with a magnetic field. An extensive experimental study was conducted to assess the various factors affecting the conversion of carbohydrates into HMF. The study involved investigating the influence of reaction time, reaction temperature, choice of solvent, catalyst dosage, substrate type, and volume of solvent. The reaction times tested ranged from 0.5 to 7 h, while the reaction temperatures varied from 80 °C to 140 °C. Different solvents, including butanol, DMSO, sulfolane, DMF, and water, were examined for their impact on the reaction. Catalyst dosages of 5 mg, 10 mg, 30 mg, 50 mg, and 100 mg were tested to determine their effect on the conversion process. Additionally, different carbohydrate substrates such as glucose, fructose, cellulose, maltose, and sucrose were also investigated. The volume of solvent used in the reaction was also varied, with quantities of 1, 3, 5, and 10 mL being tested. This comprehensive study aimed to evaluate the influence of these reaction conditions on the conversion of carbohydrates into HMF. After the reaction, the sample was weighed at different times and diluted with deionized water (10 mL) and filtered with 0.45 μm nylon. The HMF yield was determined by HPLC with a DAD detector.

3. Results and discussion

3.1. Characterization of catalyst

The FTIR spectrum seen in Fig. 1a attested evidence of the successful surface alteration of BGCN-SO$_3$H. Tri-s-triazine units are represented by the absorption peak at 795 cm^{-1}, and the peaks in the range of 1200–1700 cm^{-1} confirm the production of C-N bonds in graphitic carbon nitride [32]. However, because of the overlapping signals, it is difficult to distinguish between peaks in the 1200–1700 cm^{-1} range, namely B-N and C-N bonds [33]. The N-H vibration modes and the adsorbed water molecules are responsible for the broad absorption signal observed in the 2900-3400 cm^{-1} region. A structural difference between BGCN and O-BGCN is
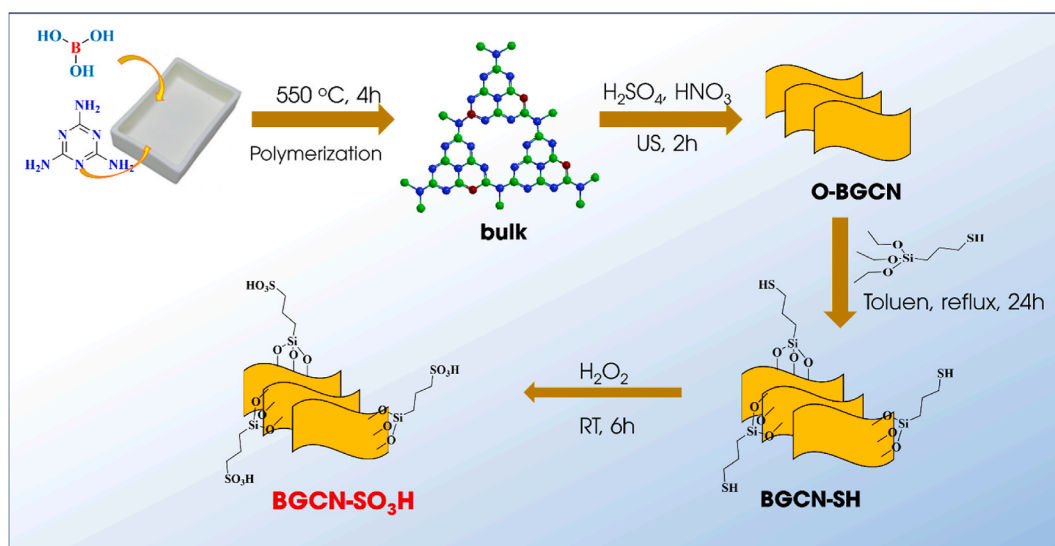
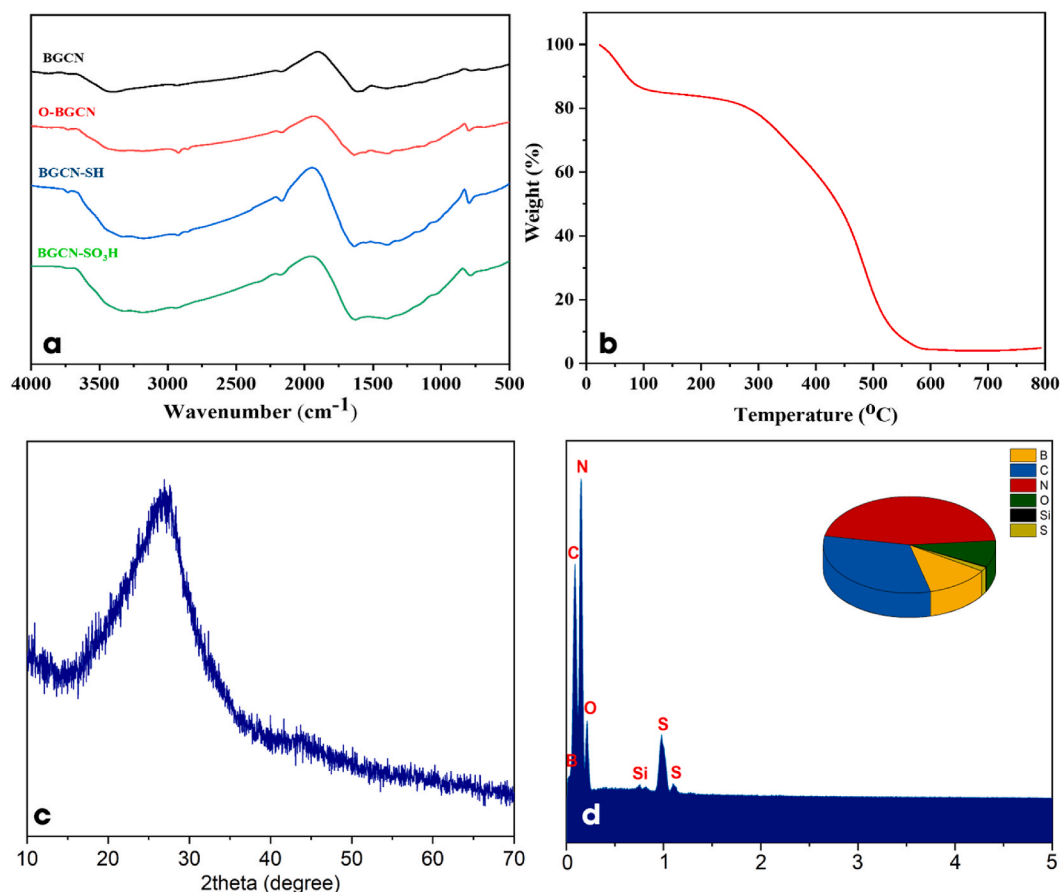**Scheme 2.** The procedure of synthesis of BGCN-SO$_3$H.

Fig. 1. FTIR spectra (a), TGA curve (b), Raman spectroscopy (c), EDX analysis of BGCN-SO₃H (d).

indicated by the tiny absorption peak at 2170 cm^{-1}, and this difference is present in both BGCN-SH and BGCN-SO₃H. The -OH of -SO₃H group forms a unique signal range between 2500 and 3500 cm^{-1}. The stretching vibration of the Si-O bond is observed at 1090 and the nearby region around 795 cm^{-1} shows absorption changes compared to BGCN with a typical tri-s-triazine structure. The butyl groups of the salivating agent's C-H bond stretching vibrations are responsible for the absorption peaks at 2850 and 2930 cm^{-1}. Furthermore, the successful grafting of propylsulfonic acid groups onto BGCN through the salinization process of the O-H surface groups is shown by a large absorption range of -OH (3300 cm^{-1}). Because the C-N and Si-O-Si bonds produce overlapping absorption bands in the 1000-1200 cm^{-1} region, it is difficult to distinguish the distinctive signals of sulfonic acid [34]. Fig. 1b illustrated the thermogravimetric analysis that was conducted on BGCN-SO₃H within the temperature range of 50–800 °C. BGCN-SO₃H undergoes a relatively early thermal degradation process, with a decrease of 5.7 % at 100 °C, mostly because of water molecules breaking down. In the following range, the breakdown of water molecules that form hydro bonds with -SO₃H causes BGCN-SO₃H to lose weight by about 3.92 % as the temperature rises from 100 to 200 °C. On the TGA curve of BGCN-SO₃H, weight loss in the 200–500 °C region is ascribed to the breakdown of sulfonic groups connected to the silica surface, which accounts for 14.83 % of the mass loss. A further mass loss was noted because of the tri-s-triazine structure breaking down when the temperature was increased above 500 °C. This may be explained by the strong thermal stability that is produced when amine groups combine to form hydrogen bonds.

The structural characterizations of BGCN-SO₃H were conducted using powder X-ray diffraction (XRD) analysis, with the pattern displayed in Fig. 1c. The highest peak is observed at 2θ = 27°, indicating an interplanar spacing of 002. This indicates an arrangement of the aromatic system that resembles a structure similar to graphite [35]. There is a less prominent peak at 2θ = 13°, indicating a slight tilt in the cyclic structure of the tri-s-triazine framework. The observed low intensity peak is indicative of the structural pattern within the sample [36].

Using EDX, the elemental composition of the catalyst was confirmed (Fig. 1d). The results indicate that the catalyst contains C, N, O, S, Si, and B, indicating that surface modification on a catalyst was effective; the presence of Si indicates that surface silane wiring has been completed. Additionally, the following elemental weight percentages were confirmed: C (11.89 ± 0.09), N (45.61 ± 0.19), B (11.89 ± 0.04), O (8.90 ± 0.11), Si (0.24 ± 0.03), and S (1.43 ± 0.04). The C (34.87 ± 0.10), N (42.71 % 18.), B (14.432 ± 0.05), O (7.30 ± 0.09), Si (0.11 ± 0.01), and S (0.58 ± 0.02) comprise the elemental percentages. The SEM mapping image demonstrates the uniform distribution of elements across the surface of the catalyst. Additionally, it captures the layer structure, which exhibits an uneven surface (Fig. 2).

3.2. Carbohydrate conversion

3.2.1. Effect of solvent

In this part, the effect of solvent reaction was investigated to evaluate the yield of HMF. The experiment was conducted with the combination of fructose (180 mg), BGCN-SO$_3$H (30 mg), 5 h at 120 °C with various solvents (butanol, DMSO, sulfolane, DMF, water). Fig. 3 presented the results of the findings. The reaction efficiency reached about 5 % HMF when using butanol as solvent, meanwhile, with sulfolane solvents, the efficiency was improved, reaching about 12 % HMF within 5 h at 120 °C. In previous studies, butanol and sulfolane solvents were often unfavorable for the preparation of HMF [37]. In addition, we also investigated the effects of the solvent dimethylformamide (DMF) and water. However, the reaction efficiency was not as high as expected, reaching about 8 % HMF and 4 % HMF when used DMF and water as a solvent, respectively. Interestingly, the yield of the desired product was dramatically increased when using DMSO solvent and obtained at about 55 % HMF within 5 h. In prior research, it was shown that the DMSO solvent is the
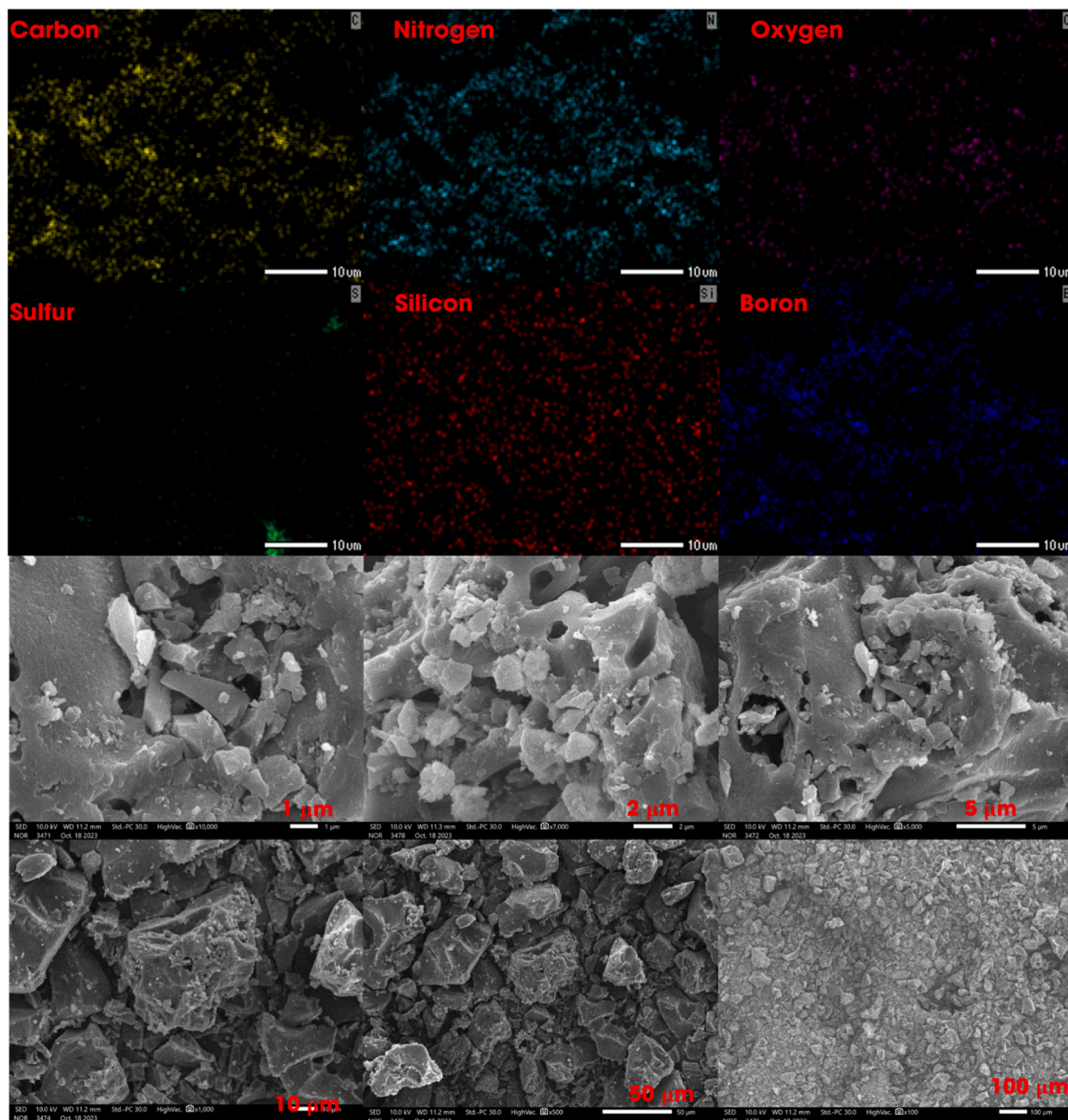

Fig. 2. EDX mapping and SEM with different magnification of BGCN-SO$_3$H.
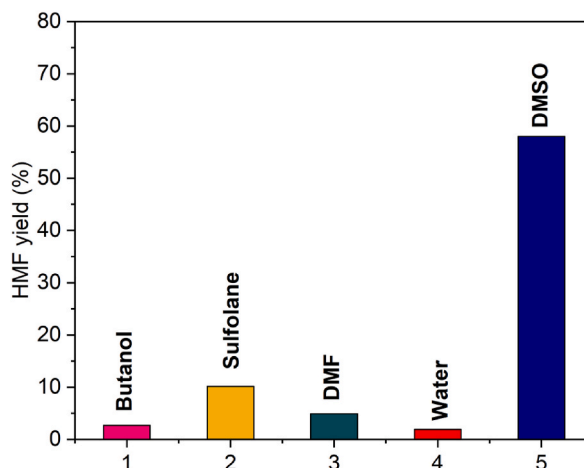
Fig. 3. Effect of solvent on the yield of HMF. Experiment set: An experiment was conducted using specific quantities of fructose, a catalyst, and DMSO at elevated temperature and for a specific duration.

most effective solvent for biomass conversion [38].

DMSO is ideal for synthesizing HMF from fructose due to its high polarity, intermediate stabilization, heat stability, and side re-action inhibition. It often outperforms water, alcohol, and ionic liquids [39]. Based on the findings of our academic research on the impact of solvents, it can be inferred that DMSO is a widely used and appropriate solvent for the reaction involved in the production of HMF from carbohydrates.

3.2.2. Effect of temperature

The reaction kinetics, yield, selectivity, and by-products of HMF synthesis from fructose depend on the temperature (Fig. 4). The experiment commenced at a temperature of 80 °C, and as time progressed, the yield showed a slight increase. The maximum yield achieved was approximately 20 % HMF after 7 h. By raising the temperature from 80 °C to 100 °C, the HMF production reached approximately 30 % in a mere 7 h. The most compelling evidence is raised reaction temperature led to an increase in the production of HMF; the yield was 0 % HMF, 11 % HMF, 15.3 % HMF, 51 % HMF, and 68 % HMF within 0.5, 1, 3, 5, and 7 h, respectively, at 120 °C. However, the yield of HMF declined with a long-time reaction. Without any doubt, the reason for increasing HMF has formed humins and created by-products [40]. The reaction was obtained at about 7.1 % HMF, 16.9 % HMF, 64.9 % HMF, 88.7 % HMF, 95.4 % HMF from 0.5 h to 7 h. In this work, we successfully synthesized HMF form fructose using BGCN-SO$_3$H as a catalyst, the yield of the reaction was obtained about 88.7 % HMF within 5 h at 140 °C.

3.2.3. Effect of catalyst loading

Our study focused on examining the effects of catalyst loading and time on the production of HMF from fructose (Fig. 5). In an
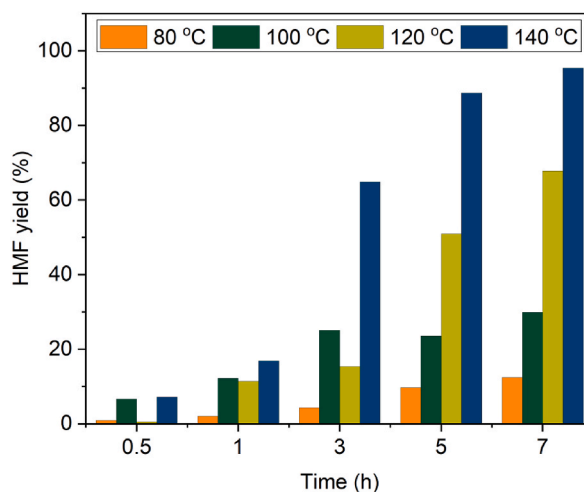

Fig. 4. The impact of temperature on the production of HMF. Experiment set: 1 mmol of fructose (180 mg), BGCN-SO$_3$H (30 mg), solvents (DMSO, 3 mL) with different temperatures from 80 °C to 140 °C.

academic context, it is observed that a higher catalyst loading has the potential to enhance the dehydration of fructose. However, it is essential to note that this can also increase side reactions. These side reactions involve the polymerization of HMF with sugars, resulting in the formation of humins. Additionally, the rehydration of HMF can occur, leading to levulinic and formic acid formation [41]. As shown in Fig. 5, at 5 mg of catalyst, the yield of HMF was 19.5 % HMF, 44.4 % HMF, 70.0 % HMF, 71.8 % HMF, and 69.2 % HMF with increasing time reaction (0.5, 1, 3, 5, and 7 h). When the catalyst loading increased to 10 mg, the yield of HMF increased to 72 % in 5 h. When the catalyst loading was further evaluated to 30 mg, the yield of HMF increased quickly to 88 % at the initial 5 h. Besides, the reaction was increased time led to decrease the yield of the reaction, because of formation by-products. At 140 °C, when highly using weight of catalyst (100 mg), the HMF yield was slowly obtained about 30 % in 7 h. Thus, 30 mg of catalyst was chosen for the next investigation.

At 140 °C, the formation of HMF and its conversion to HMF *versus* time with six loadings of BGCN-SO$_3$H were depicted in Fig. 6. The yield of the reaction was obtained about 37 % without catalyst at 5 h. By increasing the amount of catalyst, the yield of HMF reached approximately 71 % and 73 % when using 5 mg and 10 mg of catalyst, respectively. Interestingly, the yield of the reaction was dramatically increased, resulting in about 88 % HMF within 5 h. The high catalyst loading led to a decline in the yield of the reaction, which accounted for about 43 % HMF. Besides, using 100 mg of catalyst, the HMF was slightly increased when compared to 50 mg of catalyst, reaching at about 20 % HMF.

3.2.4. Effect of substrates

During this phase, the impact of different substrates on the overall reaction yield was carried out. The experiment was conducted with carbohydrates (1 mmol), BGCN-SO$_3$H (30 mg), DMSO (3 mL), 5 h, 140 °C (Fig. 7). With fructose as substrates, the yield was reached at about 89 % within 5 h. Fructose dehydrated with the help of Brønsted acid on the catalyst to form HMF. Next, when we investigated the glucose substrate, the reaction efficiency was not as expected, less than 10 % HMF was formed. When using sucrose as substrate, the reaction efficiency reached about 68 % HMF in 5 h. Sucrose is made up of glucose and fructose, so in the presence of a catalyst, the reaction is carried out easily on a sucrose substrate. For cellulose, the reaction does not occur, no HMF was obtained. Because cellulose required a catalyst with a strong acid center to perform the hydrolysis process and break the bond chains [42].

3.2.5. Effect of volume of solvent

Following an in-depth analysis of the variables impacting reaction efficiency, our study delved into the correlation between solvent volume and the effectiveness of HMF formation. Various quantities of solvent were used in the experiment, ranging from 1 mL to 7 mL of DMSO (Fig. 8). Upon analysis of 1 mL of DMSO solvent, the reaction efficiency was found to be approximately 83 %. However, when using larger volume in DMSO solvent (3 mL), the reaction efficiency slightly increased to around 89 %. The reaction efficiency reached about 60 % of HMF when increasing the volume of DMSO to 5 mL and reached about 43 % when using 7 mL of DMSO. From there it can be seen that the effect of solvent volume plays a critical role and directly affects the efficiency of forming HMF.

3.2.6. Reusability test

The recovery ability of BGCN-SO$_3$H was investigated and is illustrated in Fig. 9. After optimizing the reaction conditions, the reusability of catalyst test was investigated with fructose (1 mmol), BGCN-SO$_3$H (30 mg) in DMSO (3 mL) at 140 °C for 5 h. The ratio of ethyl acetate to diethyl ether used to extract the reaction mixture was 95:5 (5 × 5 mL). Then, diethyl ether was used to wash the catalyst several times and dried under a vacuum for the next run. The HPLC-DAD method was used to determine the yield of HMF. After the initial trial, there was a small decline in the DFF yield, going from 88 % to 76 % HMF. The lack of efficiency in converting fructose
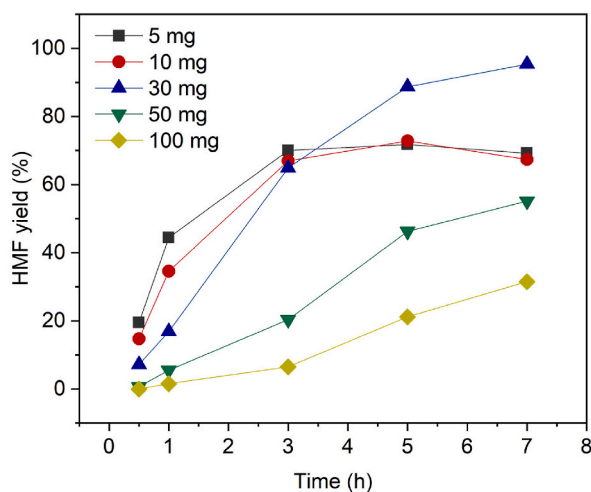

Fig. 5. Exploring the influence of catalyst loading on HMF production. Experiment set: 1 mmol of fructose (180 mg), BGCN-SO$_3$H, solvent (DMSO, 3 mL) with different catalyst's weight.
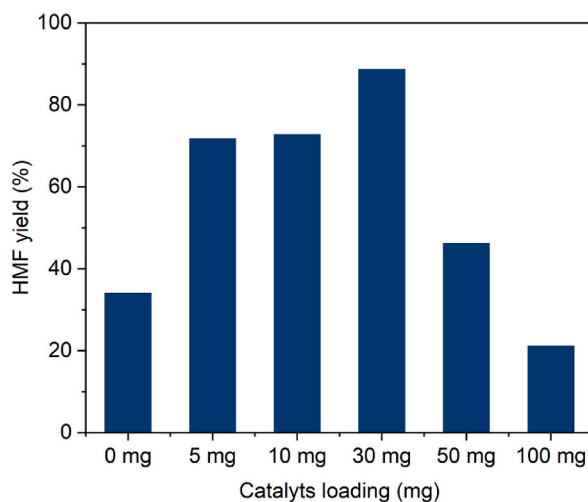
Fig. 6. The impact of catalyst loading on the production of HMF at 5 h. Experiment set: 1 mmol of Fructose (180 mg), BGCN-SO$_3$H, solvent (DMSO, 3 mL) with different catalyst's weight, 140 °C.
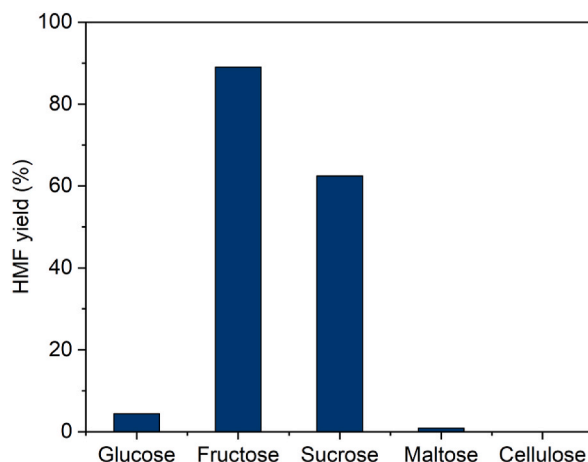

Fig. 7. The impact of substrates on the production of HMF at 5 h. Experiment set: 1 mmol of carbohydrates (glucose, fructose, sucrose, maltose, and cellulose), BGCN-SO$_3$H (30 mg), solvents (DMSO, 3 mL), 140 °C.

into HMF resulted from the depletion of active sites on the catalyst surface after each run, particularly the -SO$_3$H group. Despite a decline in HMF yields after four reuses, the efficiency of the desired product remained consistently above 60 %.

3.2.7. The comparison of this study to previous studies

In recent years, there has been extensive research conducted on the synthesis of HMF from fructose using a variety of catalyst systems (Table 1). Besides investigation of activity of many types of catalyst, the effect of temperature, time reaction, solvent, or method was also tested. Zhao et al. performed the efficiency of transformation of fructose to HMF using heating method with NH$_4$Cl as Brønsted acid catalyst in isopropanol at 100 °C (Table 1, entry 1). The yield of desired product was obtained at 56 % after 12 h. The other studies of Hu and Liu et al. were also carried out at 100 °C, employing CrCl$_2$ as catalyst in [Emim]Cl and SnCl$_4$ in [Emim]BF$_4$, respectively. However, the yield performance of HMF attained higher at shorter reaction time (3 h) (entries 2 and 3). In addition, the use of continuous flow can increase the yield of HMF in a short time. Sonsiam et al. got 61 % yield in 13 min at lower temperature (80 °C) using HCl/MIBK – [ChCl] [3 EG] (3:1) catalyst system (entry 4). Ruan and co-workers developed another catalyst system (HCl/MIBK and 2–butanol) to enhance the performance of converting fructose into HMF, gaining the yield of 80 % in 3 min but the higher temperature (180 °C) was required (Table 1, entry 5). Overall, the catalyst system of this study has higher yield compared with others. Although utilizing this catalyst obtained insignificantly higher yield of HMF than HCl/MIBK and 2–butanol catalyst system, our catalyst has high reusability.
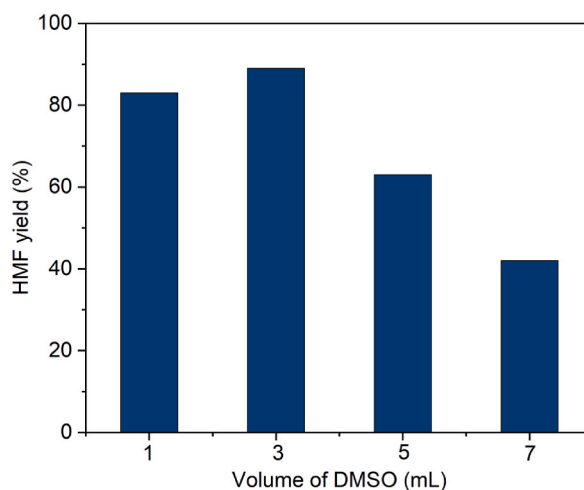
Fig. 8. The impact of volume of solvent on the production of HMF at 5 h. Experiment set:1 mmol of fructose (180 mg), BGCN-SO$_3$H (30 mg), DMSO (3 mL) with different volume DMSO (1, 3, 5, and 7 mL), 140 °C.
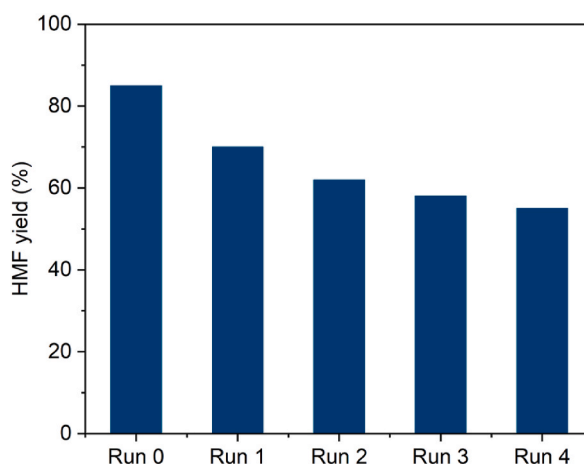

Fig. 9. Reusability test of BGCN-SO$_3$H. Experiment set: 1 mmol of Fructose (180 mg), BGCN-SO$_3$H (30 mg), solvent (DMSO, 3 mL), 5 h, 140 °C.

Table 1
The comparison of this work to previous work for conversion of fructose into HMF.

Entry	Catalyst systems	Reaction condition	HMF (%)	Method
1	NH$_4$Cl/Isopropanol [43]	12 h/100 °C	56	Heating
2	CrCl$_2$/[Emim]Cl [44]	3 h/100 °C	68	Heating
3	SnCl$_4$/[Emim]BF$_4$ [44]	3 h/100 °C	60	Heating
4	HCl/MIBK-[ChCl][3 EG] (3:1) [45]	13 min/80 °C	61	Continuous flow
5	HCl/MIBK and 2-butanol [46]	3 min/180 °C	80	Continuous flow
6	**BGCN-SO$_3$H/DMSO (this work)**	**5 h/140 °C**	**88**	**Heating**

4. Conclusion

In conclusion, we presented a BGCN-SO$_3$H catalyst as a highly effective catalyst for converting fructose into HMF. The structures of the BGCN-SO$_3$H catalyst were analyzed using a range of characterization techniques. This included X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), energy-dispersive X-ray spectroscopy (EDX), elemental mapping analysis, and Fourier-transform infrared spectroscopy (FTIR). An evaluation was conducted on the performance of the BGCN-SO$_3$H catalysts in converting fructose into HMF. We explored the impact of catalyst performance, such as solvent reactions, catalyst loading, substrates, and volume of solvent, to determine the most favorable reaction conditions. Consequently, an impressive 88 % yield of HMF was achieved in just 5 h by employing a mere 30 mg of catalyst. Investigating catalyst activity required analyzing reactions that

enabled the recovery and subsequent reuse of materials. This process offers numerous advantages, including its user-friendly operation, efficient recovery, and impressive catalytic efficiency even after recovery. Additionally, it boasts a high yield of HMF. Our next objective is to enhance the durability and reliability of the catalyst.

Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

Diep Dinh Le: Writing – original draft, Resources, Methodology, Investigation, Formal analysis, Data curation. **Trinh Hao Nguyen:** Writing – original draft, Resources, Methodology, Investigation, Formal analysis, Data curation. **Luc Tan Nguyen:** Methodology, Investigation, Data curation. **Dao Anh Le Nguyen:** Methodology, Investigation, Data curation. **Mai Ngoc Thi Le:** Methodology, Investigation, Data curation. **Khoa Dang Nguyen:** Methodology, Investigation, Data curation. **Ha Bich Phan:** Formal analysis. **Phuong Hoang Tran:** Writing – review & editing, Supervision, Resources, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e37812.

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