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Sustainable pathway to furanics from biomass via heterogeneous organo-catalysis

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Abstract

An organic sulfonated graphitic carbon nitride is synthesized and its application has been demonstrated in the conversion of carbohydrates into furanics and related value-added products. The most important feature of the material is the stability and acidity, which could be utilized at elevated temperatures for cleaving carbohydrates and converting them into biologically important scaffolds and platform chemicals.

Introduction

The threat of climate change lies at the doorstep of our planet¹ and its symptoms are increasingly visible every passing year in terms of unpredicted weather conditions. Although technological advancements are catering to the need of increased energy demand, their environmental consequences are rampant. In near future, we have to substitute petroleum-based feedstocks with bio-derived secondary sources to minimize the ongoing environmental changes and their effects on living species.² The scientific community has started seeking sustainable solutions for the conversion of biomass to value-added platform chemicals, which can be used as fuel substitutes and feedstocks for industrial applications.³ Plants are a bio-renewable source of energy, which ultimately can generate most of the chemicals while maintaining an ecological balance. The popular and general consensus is that carbohydrates obtained from plants could be benign substitutes, which can meet the requirements of human beings without compromising the environment.⁴

Glucose and fructose are among the most abundant plant-derived carbohydrates.⁵ They have been converted into building blocks for the synthesis of value-added chemicals used in drug

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discovery and in the synthesis of polymers among other industrial applications.⁶ In general, these carbohydrates are heated with mineral acids to convert them into 5-hydroxymethylfurfural (HMF) and levulinic acid notwithstanding some limitations in terms of product yields and experimental conditions.⁷ Researchers are incessantly investigating pathways to achieve higher yields by reconnoitring a wide range of homogenous and heterogeneous catalysts⁸ using ionic liquids⁹ and biphasic systems.¹⁰ Heterogeneous and homogeneous catalysis⁸ have shown limited success in terms of productivity, yield and cost-efficiency. The quest for identification of a highly acidic and relatively benign material that could efficiently accomplish the conversion of carbohydrates to furanics with a recyclability attribute has been a challenge.¹¹ Heterogeneous organo-catalysis is probably an ideal choice as it does not involve the use of any metals.¹² Cao *et al.* reported the use of ammonium resin to convert glucose in to HMF.¹³ However, this reaction required high temperature (140 °C) along with an aqueous–organic solvent (70% DMSO in water) with a maximum yield of 56%. Bhaumik *et al.* used sulfonated triphenylamine polymer as an acidic organo-catalyst¹⁴ wherein the catalyst preparation required the use of toxic triphenylamine, polymerization under anhydrous conditions followed by a sulfonation step. Furthermore, the high temperature and requirement of anhydrous DMSO have limited the wider scope of this reaction. In continuation of our focus on the development of sustainable methods,¹⁵ herein, we report a heterogeneous organo-acid catalyst derived from the electron-rich graphitic carbon nitride for the conversion of carbohydrates into value-added platform chemicals (Scheme 1).

Synthesis and characterization

Invariably, carbohydrates can be converted into furanics under acidic conditions.¹⁶ The scarcity of an active heterogeneous acidic organic framework obtainable from readily available starting materials enthused us to design and develop an inexpensive solid acid organo-catalyst. Accordingly, we designed and synthesized sulfonated graphitic carbon nitride (Scheme 1). Synthesis of the catalyst involves calcination of urea at 500 °C for 2 hours,¹⁷ followed by stirring with chlorosulfonic acid leading to the formation of sulfonated graphitic carbon nitride (Sg-CN).

The synthesized catalyst was characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and solid state ¹³C NMR. The SEM (Fig. 1a and b), TEM (Fig. 1c and d) and XRD (Fig. 2) of graphitic carbon nitride (g-CN) and sulfonated graphitic carbon nitride (Sg-CN) show a visible difference in morphology and crystalline nature. The SO₃H-immobilized Sg-CN becomes crystalline, whereas before immobilization, g-CN was amorphous in nature.

The FTIR (Fig. 3) and solid state ¹³C NMR (Fig. 4) confirm the functionalization of graphitic carbon nitride surface. The presence of strong absorption between 1190 and 1170 cm⁻¹ and 1020 and 1040 cm⁻¹ confirms the presence of the –SO₃H moiety in Sg-CN. The different pattern is due to a change in the electronic environment after sulfonation. For the ¹³C NMR spectra of graphitic carbon nitride and sulfonated graphitic carbon nitride, the peak at 140 ppm is the characteristic signal for sulfonated graphitic carbon nitride (Sg-CN),

which is affirmed by FTIR of g-CN and Sg-CN. The stability of Sg-CN was examined using thermogravimetric analysis (TGA). The TGA analysis curve of sulfonated graphitic carbon nitride (Sg-CN) confirmed that the catalyst is stable up to ~250 °C as negligible weight loss (<3%) was observed in the TGA (Fig. 5). The immobilization of the sulfonic group was further confirmed by BET surface analysis of the sulfonated graphitic carbon nitride (10.04 m² g⁻¹, ESI[†]) and graphitic carbon nitride (35.42 m² g⁻¹, ESI[†]). After the immobilization, –SO₃H ion goes and sits inside the pores *via* ionic interaction with the nitrogen lone pairs. A comparison of adsorption and desorption curves for g-CN (ESI, Fig. S7 and S8[†]) and Sg-CN (ESI, Fig. S5 and S6[†]) clearly indicates that the SO₃H ions are sitting in the pores and binding with the nitrogen in Sg-CN. Due to this, the nature of g-CN changes from amorphous to crystalline in Sg-CN, which results in better packing and consequently a decrease in the total surface area although the pore distribution remains uneven.

The immobilization of –SO₃H is confirmed by the presence of sulfur in the energy-dispersive X-ray (EDX) spectrum (ESI, Fig. S9[†]) and further supported by the X-ray photoelectron spectrum (XPS) of Sg-CN (Fig. 6). The exact concentration of sulfur was determined using elemental analysis and found to be 5.47 mmol g⁻¹. The higher acidity strength of the Sg-CN catalyst was anticipated due to the positive charge developed on the nitrogenous framework after the –SO₃H immobilization.

Results and discussion

After synthesizing the sulfonated graphitic carbon nitride (Sg-CN), it was imperative to find ideal conditions for the conversion of carbohydrates into furanics. Accordingly, xylose was treated with Sg-CN in DMSO under ambient conditions and the reaction was monitored at regular time intervals. DMSO was chosen as a solvent as it was the most effective media known for the reaction.¹⁴ Apparently, ~3% formation of furfural was isolated after 24 hours stirring at room temperature (Table 1, entry 1). Increasing the reaction temperature to 50 °C to accelerate the rate of reaction resulted in a 60% yield of furfural after 8 hours (Table 1, entry 2). Increasing the reaction temperature to 100 °C afforded a quantitative yield of the desired aldehyde within 25 min (Table 1, entry 3). After finding the ideal conditions, we screened low-boiling solvents to accomplish the transformation. Consequently, the reaction was run in dimethylformamide (DMF), dioxane, acetonitrile, ethanol, methanol and water (Table 1, entries 4–11). We observed selective conversion of xylose into furfural in pure water, which was not demonstrated earlier. Other solvents were not as effective as water and DMSO (Table 1). The appropriate weight percentage of the catalyst requirement was evaluated to accomplish the speedy conversion of xylose to furfural. With this goal in mind, the reactions were performed using 50 mg, 25 mg and 12.5 mg of the catalyst for 2.0 mmol of the substrate (Table 1, entries 9–11). The reactions with 50 mg and 25 mg of the Sg-CN were completed within 30 min, whereas the reaction with 12.5 mg of Sg-CN required a longer reaction time of 4 hours. Finally, studies were conducted with 25 mg of the catalyst to maintain the expeditious conversion of carbohydrates to the corresponding furan derivatives.

After optimizing the reaction conditions, we embarked on the applications of sulfonated graphitic carbon nitride (Sg-CN). In order to make broader use of this methodology, we

added 1,2-phenylenediamine to the reaction mixture, which directly gave the pharmaceutically important benzimidazole derivative in 84% yield (Scheme 2).

The success of Sg-CN-catalyzed conversions of xylose into value-added platform chemicals motivated us to expand further the prospects and applications of this catalyst. Consequently, we treated fructose with sulfonated graphitic carbon nitride under similar conditions, leading to the formation of the corresponding 5-hydroxymethylfurfural (HMF) in very good yield (Scheme 3). Utilizing a one-pot protocol, KBr, Sg-CN catalyst and fructose afford a 94% yield of 2,5-diformylfuran (DFF) *via in situ* oxidation of HMF (Scheme 4). KBr serves as an internal oxidant that oxidizes HMF *in situ*, leading to the selective formation of DFF. Replacement of KBr oxidant with DMSO, which may also serve as an oxidant,¹³ resulted in no formation of desired product. Interestingly, the use of KBr in conjunction with DMSO afforded predominantly 5-methylsulfanylmethyl-furan-2-carbaldehyde with a minor amount of DFF (95 : 5 ratio; Scheme 3), the thiolated compound being the major product. In most of the documented results under similar conditions, DFF was the sole product described with occasional traces of 5-methylsulfanylmethyl-furan-2-carbaldehyde.^{13,18} However, herein, the reaction of fructose with Sg-CN afforded the selective formation of 5-methylsulfanylmethyl-furan-2-carbaldehyde with insertion of methylsulfide (CH₃S-) in very high yields (Scheme 3). This unprecedented formation of 5-methylsulfanylmethyl-furan-2-carbaldehyde is an important finding, missing in earlier explorations. Interestingly, heating the aqueous solution of fructose/glucose with Sg-CN in a sealed tube over a longer period of time (8 h) at 150 °C provided levulinic acid (Scheme 4). Levulinic acid is an important intermediate of use in the synthesis of basic building blocks such as γ -valerolactone and many natural products.¹⁹

The plausible mechanisms for the dehydration of xylose and fructose have been proposed in Schemes 5 and 6, respectively. The dehydration of xylose to furfural takes place *via* the formation of 2,5-anhydroxylose furanose cyclic intermediate **I**²⁰ and dehydration of fructose to HMF *via* an enol tautomerization intermediate.²¹

It was imperative to evaluate the stability of the catalyst in recycling experiments using fructose as the model substrate. The reaction of fructose in water at 100 °C gave the formation of HMF. After the reaction, the catalyst was separated by filtration/centrifugation, washed with acetone and re-used for the next cycle with the fresh reactants. The catalyst was found to be active even after three cycles, clearly indicating that it does not lose its activity during the course of reaction (ESI, Fig. S1†). The SEM, TEM and XRD of the recycled catalyst showed that it retained its morphology and crystalline nature (ESI†), which is in corroboration with the outcome of the recycling experiments.

Conclusions

Heterogenized sulfonated graphitic carbon nitride (Sg-CN) has been synthesized, which showed its ability as a highly acidic solid organo-catalyst. Several applications have been demonstrated in the conversion of carbohydrates to value-added furan derivatives. The generated furanics could be used as starting materials in the syntheses of natural products and polymers. We have also shown that the furan derivatives could be used *in situ* for the

synthesis of biological important heterocycles in cascade reactions. The most important feature of the catalyst is its accessibility from benign material, recyclability and stability.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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Fig. 1. SEM images of (a) g-CN and (b) Sg-CN; TEM images of (c) g-CN and (d) Sg-CN.

Fig. 2.
XRD spectra of g-CN and Sg-CN.

Fig. 3.
FTIR spectra of g-CN and Sg-CN.

Fig. 4.
Solid state ^{13}C NMR spectra of g-CN and Sg-CN.

Fig. 5.
TGA trace of Sg-CN.

Fig. 6.
XPS analysis of Sg-CN.

Scheme 1.

Synthesis of sulfonated graphitic carbon nitride (Sg-CN).

Scheme 2.
Conversion of xylose to benzimidazoles.

Scheme 3.

Sg-CN catalysed conversion of fructose to HMF, DFF and thiolated furfural derivatives.

Scheme 4.

Sg-CN catalysed conversion of glucose to levulinic acid.

Scheme 5.

Xylose dehydration mechanism *via* cyclic intermediates.

Scheme 6.

Fructose dehydration mechanism *via* enol tautomerization intermediate.

Table 1Reaction optimization for the conversion to furfural from xylose^a

$\text{Xylose} \xrightarrow[\text{Solvent, 100 } ^\circ\text{C}]{\text{Sg-CN}} \text{Furfural}$				
Entry	Solvent	Temperature (°C)	Time	Yield ^b
1	DMSO	25	24 h	<3%
2	DMSO	50	8 h	60%
3	DMSO	100	25 min	95%
4	DMF	100	1 h	30%
5	Dioxane	100	1 h	10%
6	Acetonitrile	82	1 h	trace
7	Ethanol	78	1 h	9%
8	Methanol	65	1 h	10%
9	Water	100	30 min	95%
10 ^c	Water	100	30 min	96%
11 ^d	Water	100	4 h	86%

Reaction conditions:

^aXylose (2 mmol), Sg-CN (50 mg).^bIsolated yield.^c25 mg of Sg-CN used.^d12.5 mg of Sg-CN used.