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Volume 18 | Number 7 | 7 April 2016 | Pages 1821–2242

Green Chemistry

Cutting-edge research for a greener sustainable future
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ISSN 1463-9262

ROYAL SOCIETY OF CHEMISTRY

CRITICAL REVIEW
G. Chatel *et al.*
Heterogeneous catalytic oxidation for lignin valorization into valuable chemicals: what results? What limitations? What trends?

175 YEARS

View Article Online
DOI: 10.1039/C6GC02551J

Journal Name

ARTICLE

Sustainable pathway to furanics from biomass via heterogeneous organo-catalysis

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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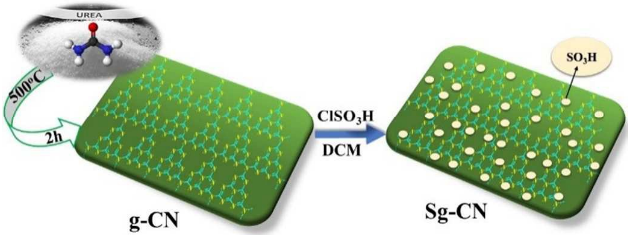
An organic sulfonated graphitic carbon nitride is synthesized and its application has been demonstrated in the conversion of carbohydrates into furanics and related value added products. The most important feature of the material is the stability and acidity which could be utilized at elevated temperatures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

Introduction

The threat of climate change is at the doorstep of our planet[1] and its symptoms are increasingly visible every passing year in terms of unpredicted weather conditions and patterns. Although technological advancements are catering to the need of increased energy demand, its environmental consequences are rampant. In the very near future, we have to substitute the petroleum-based feedstocks with bio-derived secondary sources to minimize the ongoing environmental changes and its effect 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 fuels substitutes and feedstocks for industrial applications.[3] Plants are the 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 the carbohydrates obtained from plants could be a 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 discovery and in the synthesis of polymers, among other industrial applications.[6] In general, these carbohydrates are heated with minerals acids to convert them into 5-hydroxymethylfural (HMF), levulinic acid, etc. notwithstanding some limitations in terms of product yields and experimental conditons.[7] Researchers are incessantly investigating pathways to achieve higher yields by reconnoitring a wide range of homogenous and heterogeneous catalysts;[8] using ionic liquids[9] and biphasic systems.[10] Heterogeneous and homogeneous catalysis[8] have shown limited success in terms of productivity, yield and cost-efficiency. The quest for identification of highly acidic and relatively benign material which could accomplish the conversion of carbohydrates to furanics efficiently with recyclability attributes 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 aqueous-organic solvent (70% DMSO in water) with a maximum yield of 56%. Bhaumik *et al.* used sulfonated triphenylaniline polymer as acidic organo-catalyst[14] wherein the catalyst preparation required toxic triphenylaniline, polymerization under anhydrous conditions followed by a sulfonation step. Further, the high temperature and requirement of anhydrous DMSO has limited the wider scope of this reaction. In continuation of our focus on the development of sustainable methods, [15] herein, we report the heterogeneous organo acid catalyst derived from the electron



Scheme 1. Synthesis of sulfonated graphitic carbon nitride (Sg-CN)

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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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 which is obtainable from a readily available starting material 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 ^{13}CNMR. The SEM (Figure 1), TEM (Figure 1) and XRD (Figure 2) of the graphitic carbon nitride (g-CN) and sulfonated graphitic carbon nitride (Sg-CN) show a visible difference in morphology and crystalline nature. The SO_3H immobilized Sg-CN becomes crystalline whereas before immobilization g-CN was amorphous in nature.

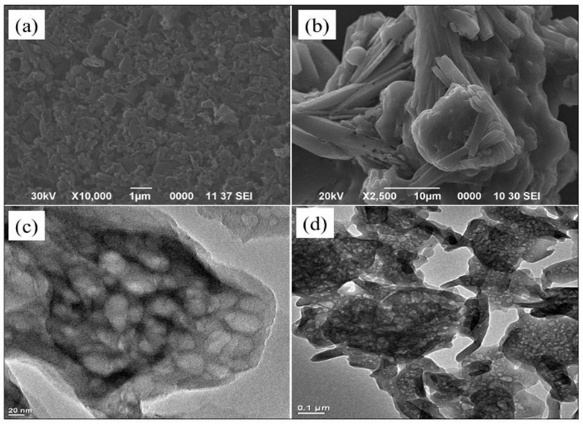

Figure 1. SEM image of a) g-CN and b) Sg-CN; TEM image of c) g-CN and d) Sg-CN

The FTIR (Figure 3), and solid state ^{13}CNMR (Figure 4) confirms the functionalization of graphitic carbon nitride surface. The presence of strong absorption between 1190- 1170 cm^{-1} and 1020-1040 cm^{-1} confirms the presence of -SO_3H moiety in the Sg-CN. The different pattern is due to a change in the electronic environment after the sulfonation. For the ^{13}CNMR 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 thermo gravimetric 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 (Figure 5). The immobilization of sulfonic group was further confirmed by B.E.T. surface analysis of sulfonated graphitic carbon nitride (10.04 m²/g, ESI) and graphitic carbon nitride (35.42 m^2/g, ESI). After the immobilization -SO_3H ion goes and sit inside the pores via ionic interaction with nitrogen lone pair. A comparison of adsorption and desorption curves for g-CN (ESI, S7 and S8) and Sg-CN (ESI, S5 and S6) clearly indicates the SO_3H 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 decrease in the total surface area although pore distribution remains uneven.

The immobilization of -SO_3H is confirmed by the presence of sulfur in energy-dispersive X-ray spectroscopy (EDX) (ESI, S9) and further supported by the X-ray photoelectron

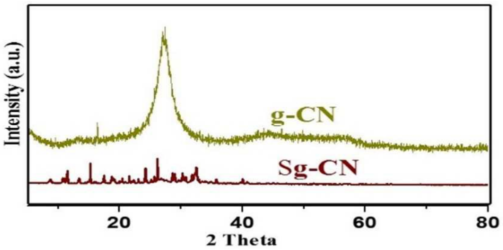

Figure 2. XRD spectra of g-CN and Sg-CN

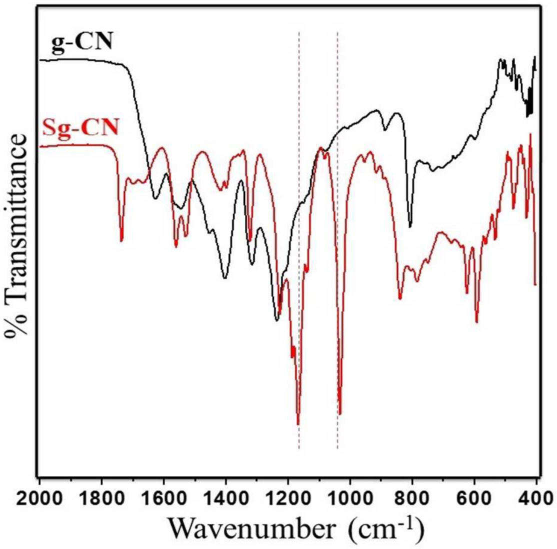

Figure 3. FTIR spectra of g-CN and Sg-CN

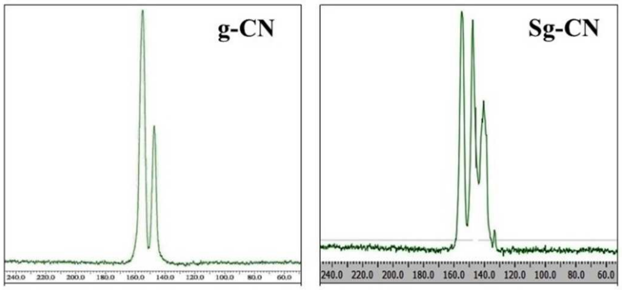

Figure 4. Solid state ^{13}CNMR of g-CN and Sg-CN

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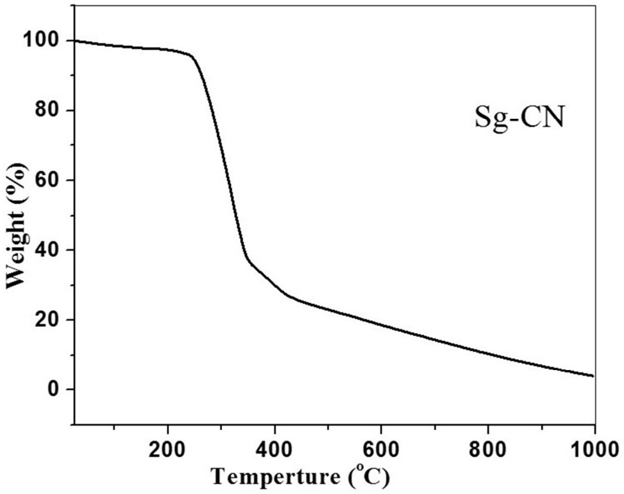


Figure 5. TGA analysis of Sg-CN

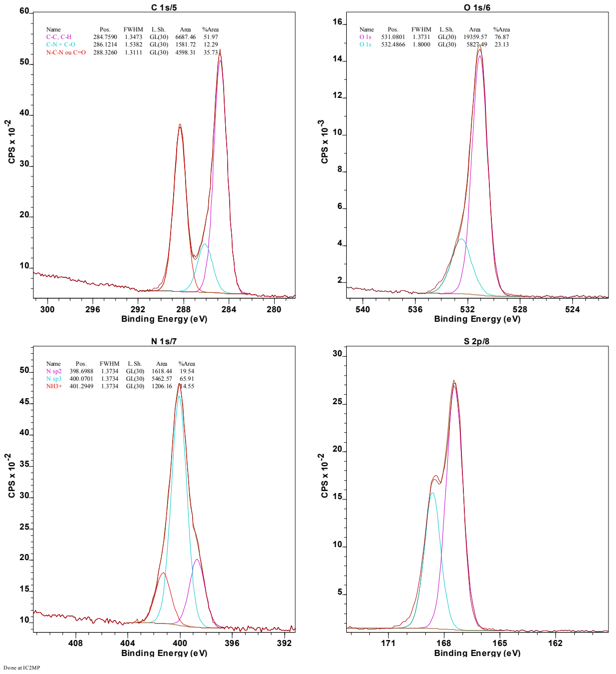


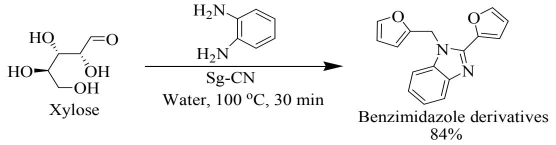
Figure 6. XPS analysis of Sg-CN

spectroscopy (XPS) of Sg-CN (Figure 6). The exact concentration of sulfur was determined using elemental analysis and it was found to be 5.47 mmol/g. The higher acidity strength of Sg-CN catalyst was anticipated due to positive charge developed on the nitrogenous framework after the -SO_3H immobilization.

Result and discussion

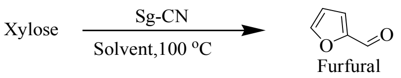
After synthesizing the sulfonated graphitic carbon nitride (Sg-CN), it was imperative to find ideal conditions for the conversion of carbohydrates into furanics. Accordingly, xylose was treated with Sg-CN in DMSO under ambient conditions and reaction was monitored at regular time intervals. DMSO was 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. Raising the reaction temperature to 50 °C to accelerate the rate of reaction was resulted in a 60% yield of furfural after 8 hours. Increasing the reaction temperature to 100 °C, afforded a quantitative yield of desired aldehyde within 25 min. After finding the ideal conditions, we screened low boiling solvents to accomplish the transformation. Consequently, the reaction was run in dimethyl formamide (DMF), dioxane, acetonitrile, ethanol, methanol and water. 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 reactions were performed using 50 mg, 25 mg and 12.5 mg of the catalyst for 2.0 mmol of the substrate. The reaction with 50 mg and 25 mg of the Sg-CN were complete within 30 min, whereas, the reaction with 12.5 mg of Sg-CN required 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).



Scheme 2. Conversion of xylose to benzimidazoles

Table 1. Reaction optimization for the conversion to furfurl from xylose[a]



Entry	Solvent	Temperture (°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: a) Xylose (2 mmol), Sg-CN (50 mg); b) Isolated yield; c) 25 mg of Sg-CN used; d) 12.5 mg of Sg-CN used

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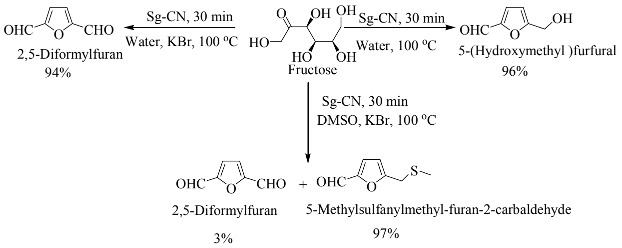
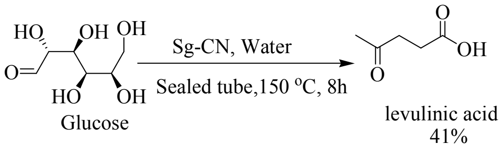
The success of Sg-CN catalyzed conversions of xylose into value added platform chemicals motivated us to expand further the prospects and applications of this catalyst. Consequently, we treated fructose with sulfonated graphitic carbon nitride under similar condition which led to the formation of corresponding 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 HMF (Scheme 4). KBr serves as an internal oxidant which 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 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, here the reaction of fructose with Sg-CN afforded the selective formation of 5-methylsulfanylmethyl-furan-2-carbaldehyde with insertion of methylsulfide (CH_3S-) in very high yield (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 sealed tube over a longer period of time (8h) at 150 °C provided levulinic acid (Scheme 4). Levulinic acid is an important intermediate use in the synthesis of basic building blocks such as γ-valerolactone and many natural products.[19]

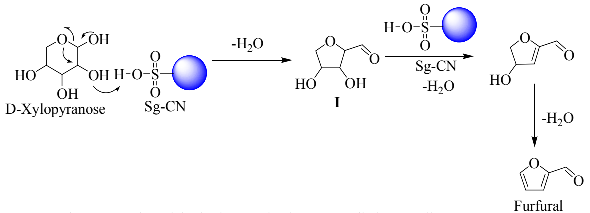


Scheme 3. Sg-CN catalyzed conversion of fructose to HMF, DFF and thiolated furfural derivatives

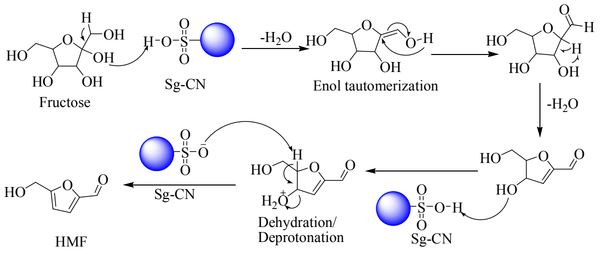


Scheme 4. Sg-CN catalyzed conversion of glucose to levulinic acid

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



Scheme 5. Xylose dehydration mechanism *via* cyclic intermediates



Scheme 6. Fructose dehydration mechanism *via* enol tautomerization intermediate

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 reused 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, 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

A 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 a starting material in the synthesis 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.

Acknowledgements

S. V. and N. B. R. B. were supported by the Postgraduate Research Program at the National Risk Management Research Laboratory administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the U.S. Department of Energy and the U. S. Environmental Protection Agency.

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View Article Online
DOI: 10.1039/C6GC02551J

Sustainable pathway to furanics from biomass via heterogeneous organo-catalysis

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Organic sulfonated graphitic carbon nitride (Sg-CN) is synthesized and deployed in the conversion of carbohydrates to furanics; enhanced acidity and stability of Sg-CN is exploited for cleaving and converting carbohydrates to biologically important scaffolds and platform chemicals.