## **Supporting Information**

# Sustainable pathway to furanics from biomass via heterogeneous organo-catalysis

Sanny Verma<sup>a†</sup>, R. B. Nasir Baig<sup>a†</sup>, Mallikarjuna N. Nadagouda,<sup>b</sup> Christophe Len<sup>c</sup> and Rajender

S. Varma<sup>a\*</sup>

<sup>a</sup>Sustainable Technology Division, National Risk Management Research Laboratory, U. S. Environmental Protection Agency, MS 443, Cincinnati, Ohio 45268, USA. Fax: 513- 569-7677; Tel: 513-487-2701. E-mail: <u>varma.rajender@epa.gov</u>

<sup>b</sup>WQMB, WSWRD, National Risk Management Research Laboratory, U. S. Environmental Protection Agency, Cincinnati, Ohio 45268, USA

°Sorbonne Universités, Université de Technologie de Compiègne, Compiègne, France

- 1. Synthesis of g-CN and Sg-CN
  - (a) Synthesis of g-CN
  - (b) Synthesis of Sg-CN
- 2. General procedure for the synthesis of carbohydrates to value added chemicals
- 3. General procedure for the synthesis of levulinic acid from glucose
- 4. Recycling of Sg-CN catalyst (S1)
- 5. Higher magnification SEM image of Sg-CN catalyst (S2)
- 6. TEM image (different view) of Sg-CN catalyst (S3)
- 7. XRD of Sg-CN catalyst (S4)
- 8.  $N_2$  sorption isotherms of Sg-CN (S5)
- 9. Distribution of pore diameter of Sg-CN (S6)
- 10. N<sub>2</sub> sorption isotherms of g-CN (S7)
- 11. Distribution of pore diameter of g-CN (S8)
- 12. EDX of Sg-CN catalyst (S9)
- 13. GC-MS data of the product
- 14. <sup>1</sup>H and <sup>13</sup>C NMR of the product

#### 1. Synthesis of g-CN and Sg-CN catalyst

#### a) Synthesis of g-CN

The pure urea obtained from Aldrich was calcinated at 500 °C for 2 hours in a closed furnace. A pale-yellow solid of pure graphitic carbon nitride (g-CN) was obtained and used without any purification.

#### b) Synthesis of Sg-CN catalyst

Graphitic carbon nitride, g-CN (1.0 g) and dichloromethane (50 mL) were taken in a round bottom flask. Chlorosulfonic acid (0.5 mL) was added to the reaction mixture over the period of 10 min under continuous stirring and then stirring was continued for 3 hours. The ensuing white solid was filtered off, washed with water, methanol and dried under vacuum at 50 °C. The Sg-CN catalyst was characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA).

#### 2. General procedure for the synthesis of carbohydrates to value added chemicals

A reaction tube equipped with a stir bar was charged with the desired amount of carbohydrate (2 mmol), catalyst (25 mg of Sg-CN and 5.0 mg of KBr, if required) and water (2 mL). The glass tube was then heated in oil bath at 100 °C. After the completion of the reaction, the reaction temperature was brought down to room temperature, the catalyst was recovered *via* filtration/centrifugation and the product was isolated using solvent extraction using ethyl acetate, dried over sodium sulfate, concentered, and characterized.

#### 3. General procedure for the synthesis of levulinic acid from glucose

A reaction tube equipped with a stir bar was charged with the desired amount of glucose (2 mmol), catalyst (25 mg), and water (2 mL). The glass tube was sealed and placed in an oil bath and heated at 150 °C over a period of 8 hours. After completion of the reaction, the reaction temperature was allowed to come at room temperature. The catalyst was recovered using a centrifuge and the product was isolated using solvent extraction.

## 4. Recycling of the catalyst

After the completion of each reaction, the Sg-CN catalyst was recovered using a centrifuge,



**S1.** Recycling of the catalyst

washed with water followed by acetone, and dried under vacuum and used for the fresh set

of reactants. It was observed that the catalyst remains active even 3<sup>rd</sup> cycle of the reaction.

5. Higher magnification SEM image of Sg-CN catalyst



**S2.** Higher magnification SEM image of Sg-CN catalyst



6. TEM image (different view) of Sg-CN catalyst.

**S3.** TEM image (different view) of Sg-CN catalyst.

# 7. XRD of Sg-CN catalyst



**S4.** XRD of Sg-CN catalyst

## 8. N<sub>2</sub> sorption isotherms of Sg-CN



**S5**.  $N_2$  sorption isotherms of Sg-CN

## 9. Distribution of pore diameter of Sg-CN



**S6**. Distribution of pore diameter of Sg-CN

# 10. $N_2$ sorption isotherms of g-CN



**S7.**  $N_2$  sorption isotherms of g-CN

## 11. Distribution of pore diameter of g-CN



Pore diameter (nm)

S8. Distribution of pore diameter of g-CN

# 12. EDX of Sg-CN catalyst



**S9.** EDX of Sg-CN catalyst

#### 13. GC-MASS data of the product

```
File :C:\Sanny\Data\NS 125 GH.D
Operator : kt
Acquired : 20 Oct 2015 12:43 pm using AcqMethod SAMPLES- 20 MIN_20151015_A.M
Instrument : Instrument #1
Sample Name: NS 125 GH
Misc Info :
Vial Number: 12
```





```
File :C:\Sanny\Data\NS 128.D
Operator : kt
Acquired : 26 Oct 2015 3:53 pm using AcqMethod SAMPLES- 20 MIN_20151015_A.M
Instrument : Instrument #1
Sample Name: NS 128
Misc Info :
Vial Number: 15
```

```
File :C:\Sanny\Data\ns 128 gyt.D
Operator : kt
Acquired : 3 Nov 2015 3:31 pm using AcqMethod SAMPLES- 20 MIN_20151015_A.M
Instrument : Instrument #1
Sample Name: ns 128 gyt
Misc Info :
Vial Number: 6
```



```
File :C:\Sanny\Data\NS 135.D
Operator : kt
Acquired : 25 Nov 2015 4:13 pm using AcqMethod SAMPLES- 20 MIN_20151015_A.M
Instrument : Instrument #1
Sample Name: NS 135
Misc Info :
Vial Number: 13
```



```
File :C:\Sanny\Data\NS 164 (35).D
Operator : kt
Acquired : 25 Jan 2016 11:20 am using AcqMethod SAMPLES- 20 MIN_20151015_A.M
Instrument : Instrument #1
Sample Name: NS 164 (35)
Misc Info :
Vial Number: 100
```



# 14. <sup>1</sup>H and <sup>13</sup>C NMR of the product





#### 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm





| Ninist Norther |
|----------------|

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm











