# Wheat flour derived N-doped mesoporous carbons extrudate as superior

## metal-free catalysts for acetylene hydrochlorination

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### 1. Experimental

#### 1.1 Materials

Wheat starch was purchased from Zhengzhou Boda Wheat Flour Co., Ltd. and commercialized nano-silica with a particle size of  $15 \pm 5$  nm and surface area of  $250 \pm 30 \text{ m}^2\text{g}^{-1}$  provided by Hangzhou Wanjing New Material Co., Ltd. was used as a hard template. The reagents including HCl gas (99.999%, Shuanglin Reagent Co., Ltd., China), and acetylene gas (99.99%) were used. All materials except wheat starch were analytical grade and used without further purication. Commercial Coal-based

carbon was also used. The commercial activated carbon were crushed and screened to 40-80 mesh followed by washing with deionized water to remove powder and drying in oven at 110 °C for 8 h. Other reagents were obtained from Shanghai Chemical Reagent Inc. of Chinese Medicine Group. All materials were analytical grade and used without any further purification.

#### 1.2 Preparation of the materials

Preparation of nitrogen doped mesoporous carbon (N-MC-W): In a typical procedure: 50 g of wheat flour were added into a mortar and ground for 30 min followed by adding 12 g of SiO<sub>2</sub> and grinding for another 30 min until the solid powders were mixed well. Then 25 mL deionized water was added into the mortar. The mixture was rubbed into dough as shown in the scheme 1 and keep at room temperature for more than 0.5 hours. After that, an extrusion of a cylinder shaped particles with size of  $\phi 2.5 \times 30$  mm were made by using a home-made noodle machine (see methods section in the supporting information) and dry at room temperature in air for 10 h. Following that, the composite was dried at 110 °C for 8 h. Finally, the precursor was carbonized at 850 °C for 3 h under N<sub>2</sub> flow. The N-carbon-silica composite was then dissolved with 5 wt% hydrofluoric acid, filtrated and washed several times with hot water, and dried at 110 °C for 10 h. Finally, ca. 12.5 gram dried carbon materials can be obtained. The final size of the cylindrical particles is about ( $\phi 2.0 \times 30$  mm) due to the dehydrogenation of wheat flour makes the particles shrinkage. The obtained particles were crushed into 40-80 mesh for catalytic test.

Preparation of MC-Su via a wet impregnation method: Typical procedures as the followings: 2.0 g of SiO<sub>2</sub> was impregnated with 7 mL of aqueous solution containing sucrose (4.18 g), 0.33 g oxalic acid, which was divided into two equal solutions and the first part of the solution was allowed to infiltrate the mesopores of the SiO<sub>2</sub>. The composite dried at 100 °C for 6 h and at 160 °C for 6 h. The infiltration and drying were repeated once more with additional precursor solution. Then the composite was

carbonized at 850 °C for 3 h under  $N_2$  flow. The carbon-silica composite was then dissolved with 5 wt% hydrofluoric acid, filtrated and washed several times with hot water, and dried at 110 °C for 10 h. The template-free product thus obtained (donated as MC-Su).

Preparation of MCN: 4 g calcined SBA-15 together with 6.8 g ethylenediamine and 24 g carbon tetrachloride were added into a 100 mL round-bottom flask, the resultant mixture was refluxed and stirred at 90 °C for 6 h. Then the obtained dark orchid mixture was carbonized at 600 °C in a nitrogen flow of 30 mL/min with a heating rate of 3.0 °C/min and kept under these conditions for 5 h. The samples were recovered after dissolution of the silica framework in 5 wt % hydrofluoric acid (HF), treated by filtration, washed several times with ethanol and deionized water, and dried at 100 °C in air. The template-free product thus obtained (donated as MCN).

#### 1.3 Measurement of catalytic activities

The catalytic performance was investigated using a fix-bed glass reactor (i.d. of 20 mm). Acetylene (99.9% purity) was passed through concentraed sulfuric acid solution to remove the trace impurities, and hydrogen chloride gas (99.9% purity) was dried using 5A molecular sieves. Acetylene (2.0 mL·min<sup>-1</sup>) and hydrogen chloride (2.4 mL min<sup>-1</sup>) were introduced into a heated reactor containing catalyst (4.0 mL) through a mixing vessel via calibrated mass flow controllers, giving a  $C_2H_2$  gas hourly space velocity (GHSV) of 30 h<sup>-1</sup> at 220 °C. The pressure for  $C_2H_2$  and HCl is 0.06 MPa and the feed volume ratio of  $V_{HCl}/V_{C2H2}$  is 1.2. The microreactor was purged with nitrogen to remove water and air before the reaction. The reactor effluent was passed through an absorption bottle containing a sodium hydroxide solution to remove the unreacted hydrogen chloride. The gas mixture was analyzed using a GC-1690F gas chromatograph (GC) equipped with FID detector.

#### **1.4 Characterizations**

Nitrogen adsorption isotherms were determined at -196 °C on a Quantachrome Autosorb-IQ apparatus. The samples were outgassed at 300 °C for 8 hour before adsorption measurement. The specific surface area was obtained using the Brunauer-Emmett-Teller (BET) model for adsorption data in a relative pressure ranging from 0.05 to 0.30. The total pore volume was determined from the aggregation of  $N_2$  vapor adsorbed at a relative pressure of 0.99. The pore size distribution was acquired from the desorption branches of the isotherms using the Barrett-Joyner-Halenda method.

Elemental contents were measured with an element analyzer (VARIO EL, GERMANY). Thermo gravimetric analysis (TGA) of samples was conducted on the TG-DSC simultaneous thermal analyzer. About 15 mg of sample was used and heated to 800 °C under the air atmosphere, flow rate of 30 ml min<sup>-1</sup>, and heating rate of 10 °C•min<sup>-1</sup>.

High resolution Transmission electron microscopy (HRTEM) was performed on a Philips-FEI Tecnai G2 F30 S-Twin electron microscope with a field emission gun as the source of electrons operated at 300 kV. The samples were mounted and ultrasonically dispersed in ethanol, and then a few droplets of the suspension were deposited on a copper grid coated by a holey carbon film, followed by drying at ambient conditions.

X-ray photoelectron measurements were conducted on a Kratos AXIS Ultra DLD instruments using 300W Al Ka. The binding energies were calibrated by the contaminant carbon (C 1s 284.6 eV).



Figure S1 The home made instruments for the extrusion of the nitrogen doped mesoporous carbon

materials.



Figure S2 The extrudate of wheat flour with silica composite before and after carbonization.



Figure S3 N<sub>2</sub> adsorption-desorption isotherms (a) and pore distribution (b) of N-MC-W, N-MC-G,

MC-Su, MC-St and MCN.



Figure S4. HRTEM (a-b) and STEM (c) and C (d), N (e), and O (f) element mapping for N-MC-G.



Figure S5 the TPD-MS profiles CO: m/e = 28 and CO<sub>2</sub>: m/e = 44 of MC-Su, MC-St, N-MC-W and N-MC-G.



Figure S6 XRD paten (a) and Raman spectra (b) of of N-MC-G and MCN.



Figure S7 (a) The N species distribution derived from XPS spectra for N-MC-W, N-MC-G, MCN N-MC-G-used and MCN-used; (b) N1s XPS spectra of N-MC-G-used and MCN-used.



Figure S8 N<sub>2</sub> adsorption-desorption isotherms (a) and pore distribution (b) for N-MC-G and N-MC-G-

used.



Table S1 The relative contents and binding energies of nitrogen species of catalysts determined by XPS.

| Samples     | N<br>(wt %) | Area%, Binding Energy (eV) |               |               |               |  |  |
|-------------|-------------|----------------------------|---------------|---------------|---------------|--|--|
|             |             | Oxidized N                 | Quaternary N  | Pyrrolic N    | Pyridinic N   |  |  |
|             |             | (403.0 eV)                 | (401.1±0.2eV) | (400.0±0.2eV) | (398.3±0.2eV) |  |  |
| N-MC-W      | 2.24        | 13.93                      | 59.39         | 13.77         | 12.92         |  |  |
| N-MC-G      | 5.67        | 3.37                       | 59.77         | 17.66         | 19.02         |  |  |
| N-MC-G-used | 4.48        | 14.37                      | 62.89         | 8.71          | 13.67         |  |  |
| MCN         | 20.99       | 2.38                       | 23.16         | 33.60         | 40.86         |  |  |
| MCN-used    | 16.67       | 0.90                       | 30.31         | 31.47         | 37.32         |  |  |

| Catalysts | Notes/precursors       | Au    | Bulk    | Temp. | $C_2H_2$           | $C_2H_2$ | VCM                         | References         |
|-----------|------------------------|-------|---------|-------|--------------------|----------|-----------------------------|--------------------|
|           |                        | (wt%) | density | (°C)  | GHSV               | Conver   | Productivity                |                    |
|           |                        |       | (g/mL)  |       | (h <sup>-1</sup> ) | sion     | (mol kg <sub>cat</sub> -1h- |                    |
|           |                        |       |         |       |                    | (%)      | 1)                          |                    |
| MC        | -                      | -     | 0.17    | 180   | 600                | ~2.1     | ~3.5                        | This work          |
| N-MC-W    | -                      | -     | 0.24    | 180   | 600                | ~7.2     | ~8.5                        | This work          |
| Au/MC     | HAuCl <sub>4</sub>     | 0.1   | 0.17    | 180   | 600                | ~9.7     | ~16.8                       | This work          |
| Au/N-MC-W | HAuCl <sub>4</sub>     | 0.1   | 0.24    | 180   | 600                | ~27      | ~27                         | This work          |
| Au/C      | $(NH_4)_3Au(S_2O_3)_2$ | 0.3   | 0.4     | 180   | 227                | ~97      | ~24.7                       | Ref <sup>[1]</sup> |
| Au/C      | $(NH_4)_3Au(S_2O_3)_2$ | 0.15  | 0.4     | 180   | 227                | ~90      | ~22.9                       | Ref <sup>[1]</sup> |
| Au-Cu/C   | SCN:Au = 20 : 1        | 0.25  | 0.44    | 180   | 360                | ~90      | ~32.9                       | Ref <sup>[2]</sup> |

Table S2 The Catalyst performance of metal-free carbon and Au/C Catalysts.

References

1. P. Johnston, N. Carthey, G. J. Hutchings, J. Am. Chem. Soc. 2015, 137, 14548-14557.

2. K. Zhou, J. Jia, C. Li, H. Xu, J. Zhou, G. Luo, F. Wei, Green Chem. 2015, 17, 356-364.