

Electronic Supplementary Information

Mesoporous carbon with high content of graphitic nitrogen for selective oxidation of ethylbenzene

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1. Catalyst synthesis

Mesoporous carbon (MC) and graphitic-nitrogen doped mesoporous carbon (GNMC) were synthesized through a chemical vapor deposition (CVD) method using ethanol and acetonitrile as precursor, respectively. 0.2g SBA-15 was uniformly distributed in a quartz boat and inserted into a flow-through tube furnace. Ethanol or acetonitrile liquid was placed in a separate tube furnace connected to that furnace with SBA-15. After the furnace with SBA-15 was heated to 950 °C at a ramp rate of 10 °C/min under Ar stream (50 mL/min), another furnace with ethanol or acetonitrile was heated to 90 °C, and then corresponding steam was introduced into SBA-15 area with flowing Ar. The process maintained at 950 °C for 3h. The resulting SBA-15/carbon (denoted as GNMC/SBA-15 and MC/SBA-15) composites were immersed into 10% HF acid and stirred for 24h at room temperature to remove the template. Finally the template-free carbon materials were washed with deionized water and further dried in a vacuum oven at 60 °C for 24 h.

CMK-3 was fabricated via the hard-templating method [1] using sucrose as carbon source and carbonized at 900 °C for 3 h. MCN, a mesoporous carbon nitrides, was synthesized via the hard-templating method [2] using carbon tetrachloride (CTC) and ethanediamine (EDA) as carbon and nitrogen sources and carbonized at 600 °C for 5 h. Nitrogen-doped onion-like carbon (NOLC) is prepared using NH₃ post-treatment method [3]. NCNT is fabricated via CVD method using imidazole as carbon and nitrogen source at 900 °C, and then washed with 6 mol/L HCl to remove residual metals (FeMo/Al₂O₃).

2. Characterization

X - ray diffraction (XRD) patterns were recorded on a Rigaku Ultimate IV diffractometer with a Cu K α radiation source operating at 40 kV, 40 mA. Scanning electron microscopy (SEM) images were taken using an FEI Nano450 scanning electron microscope operated at 10–15 kV. The mesostructure of the GNMC was characterized by a FEI T12 transmission electron microscopy (TEM) with an accelerating voltage of 120 kV. Nitrogen adsorption-desorption data were

measured with a Micromeritics ASAP 3020 analyser at 77 K. Prior to the measurements, the samples were degassed at 120 °C for 12 h. The specific surface areas (S_{BET}) were calculated by the Brunauer-Emmett-Teller (BET) method using adsorption data in a relative pressure range from 0.02 to 0.20. The total pore volumes (V_t) were estimated on the basis of the adsorbed amount at a relative pressure of 0.985. The pore size distributions (PSD) was calculated from adsorption data of isotherms using the Barrett-Joyner-Halenda (BJH) model. Surface chemistry of samples was investigated using an ESCALAB 250 instrument with Al $K\alpha$ X-rays (1486.6 eV). Elementary analysis was done using a Yanaco MT-5 CHN analyzer. ^{13}C NMR experiments were performed on Agilent 600 DD2 spectrometre at a resonance frequency of 150.15 MHz. ^{13}C NMR spectra were recorded with spinning rate of 15 kHz with a 4 mm probe at room temperature. The attenuated total reflectance IR (ATR-IR) experiments were performed on a Thermo Scientific Nicolet IS 10 at a resolution of 4 cm^{-1} over 128 scans. The temperature programmed oxidation (TPO) tests were carried out by a thermogravimetric analyzer (Netzsch 449 F3). About 5 mg of the sample was placed in a corundum crucible. The sample were heated from 35 to 900 °C at a rate of 10 °C $\cdot\text{min}^{-1}$ under a gas flow of 50 $\text{ml}\cdot\text{min}^{-1}$ comprising 10 vol% O_2 in Ar.

3. Catalytic reaction

Typically, ethylbenzene (1.5 mmol), catalyst (0.010 g), TBHP (4.5 mmol, 65 wt% in water), anisole (110 μL) as internal standard and acetonitrile (2 mL) were added into a 70 mL glass reactor sealed with Teflon lid (Beijing Synthware Glass, Inc. Pressure Vessel, Heavy Wall). The reaction mixture was heated to 80 °C in an oil bath and stirred for 12 h. After that, the reaction vessel was took out from oil bath and cooled down. Gas chromatography (GC) analysis was performed on an Agilent GC equipped with a 30 $\text{m}\cdot 0.25\text{ mm}\cdot 0.25\text{ }\mu\text{m}$ HP-5 capillary column and a flame ionization detector.

The corresponding calculation:

$$1) \text{Con (EB)} = (n_{\text{o(EB)}} - n_{\text{t(EB)}}) / n_{\text{o(EB)}} * 100\%$$

$$2) \text{Sel (product } i) = n_{\text{t(i)}} / (n_{\text{o(EB)}} - n_{\text{t(EB)}}) * 100\%$$

$$3) \text{Yield (product } i) = n_{\text{t(i)}} / n_{\text{o(EB)}} * 100\%$$

$$4) \text{Carbon balance} = [8 * n_{\text{o(EB)}} * Y_{(\text{AcPo})} + 8 * n_{\text{o(EB)}} * Y_{(\text{PEA})} + 7 * n_{\text{o(EB)}} * Y_{(\text{BA})} + 7 * n_{\text{o(EB)}} * Y_{(\text{BZA})} + 8 * (1 - \text{Con}_{(\text{EB})}) * n_{\text{o(EB)}}] / 8 * n_{\text{o(EB)}} * 100\%$$

Note:

$n_{\text{o(EB)}}$: the mole of initial EB

$n_{\text{t(EB)}}$: the mole of EB at t (h)

$n_{\text{t(i)}}$: the mole of product i at t (h)

Table S1 Chemical composition according to elemental analysis (unit: wt%)

	C	N	O	H	C/N/H/O
MC	96.9	0.1	0.1	3.6	100/0.1/3.7/0.1
GNMC	84.3	7.3	5.8	2.9	100/8.6/3.4/6.9

Table S2 The deconvolution analysis of N1s spectra for GNMC, NOLC and NCNT.^a

	Pyridinic (398.2±0.3 eV)	Pyrrolic (399.9±0.2 eV)	Graphitic (401±0.2 eV)	N-oxides (1) (402.8±0.2 eV)	N-oxides (2) (404.9±0.1 eV)	Yield rate of AcPO (mmol • g ⁻¹ • h ⁻¹) ^b	TONs (h ⁻¹) ^c
NOLC	0.45(24)	0.73(38)	0.43(23)	0.24(13)	0.05(3)	229.7	650.5
NCNT	0.46(26)	0.16(9)	0.71(40)	0.23(13)	0.24(13)	669.9	1134. 6
GNMC	0.34(10)	-	2.98(85)	0.17(5)	-	932.6	388.2

a) the real content (unit: at%) of various nitrogen species obtained according to the deconvolution analysis and the number in parenthesis are the relative percentage (unit: %) of corresponding nitrogen species; b) Yield rate of AcPO; c) TONs is calculated assuming graphitic nitrogen is the active site.

Table S3 The selectivity of side products with GNMC as catalyst at different reaction temperature.

Reaction Scheme					Carbon Balance (%)
Entry	Reaction Temperature (°C)	Selectivity (%)			
		PEA	BA	BzA	
1	30	7.7	3.7	52.8	97.6
2	40	8.2	4.7	41.3	98.5
3	50	7.6	3.9	31.1	97.8
4	60	5.7	2.2	18	99.8
5	70	2.7	1.8	3.6	99.9
6	80	1.6	1.3	1.9	100.9
7	90	1.4	1.2	2.9	103.1

Reaction conditons: 1.5 mmol EB, 2 mL CH₃CN, 10 mg GNMC, 12h, molar ratio of EB/TBHP=1/3.

Note: carbon balance calculated according to the mole of carbon atoms for various products and unreacted EB.

Table S4 The carbon balance of the reaction on various carbon materials.

	Cat	Carbon Balance (%)
1	Blank	98.1
2	MC	95.3
3	CMK-3	86.0
4	GNMC	99.1
5	MCN	87.6
6	NOLC	84.4
7	NCNT	98.2

Reaction conditions: 1.5 mmol EB, 2 mL CH₃CN, 10 mg cat, 12h, molar ratio of EB/TBHP=1/3, T=80 °C.

Table S5 The possible other elements detected via ICP-MS (unit: %).

	Al	Ca	Na	Ni	Si	Mo	Mn	Mg	Ba	Ag	Fe	Co	Cr	Cu
MC	2.2529	17.2965	12.2093	0.0799	8.4302	0.0102	0.0131	1.4826	0.2035	0.0218	3.343	0.0073	0.2616	0.3634
GNMC	0.0077	0.014	0.0011	0.0001	0.27	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.0091	<0.0001	<0.0001	<0.0001

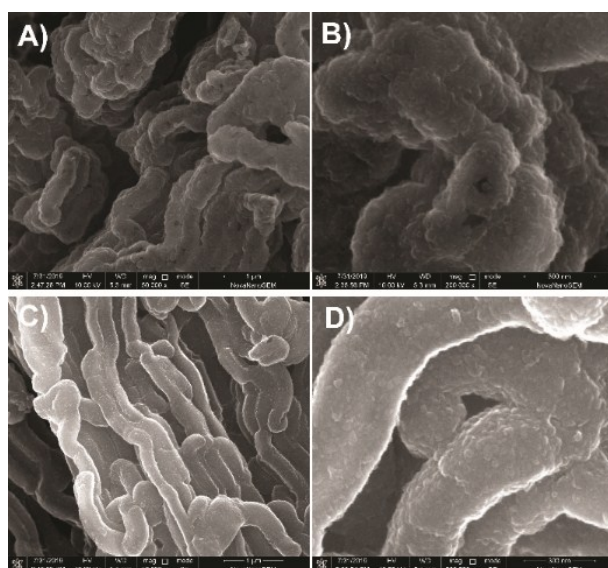


Fig. S1 SEM images of MC (A & B) and GNMC (C & D).

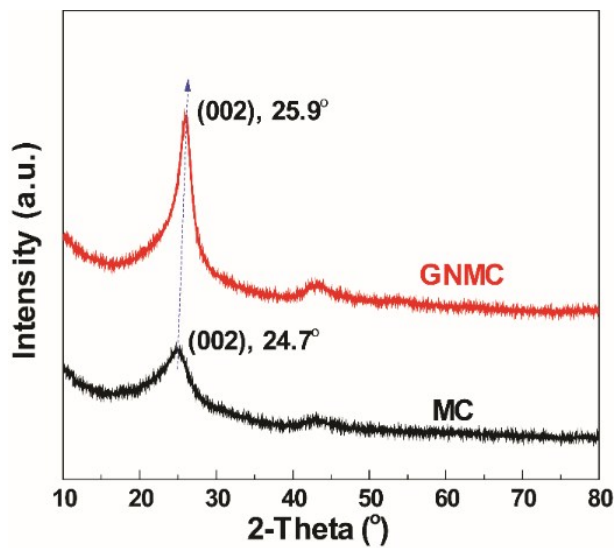


Fig. S2 XRD results of MC and GNMC.

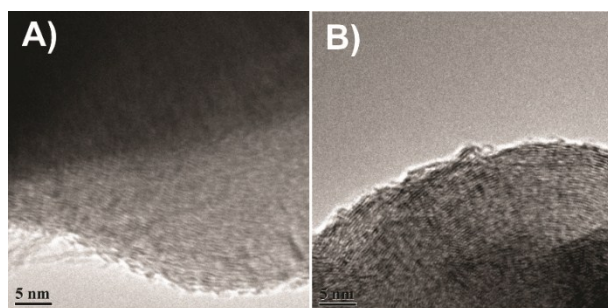


Fig. S3 HRTEM images of MC (A) and GNMC (B).

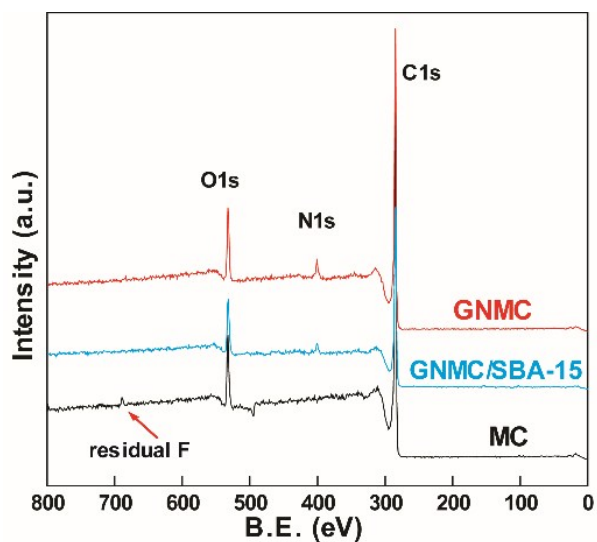


Fig. S4 XPS spectra of MC, GNMC and GNMC/SBA-15.

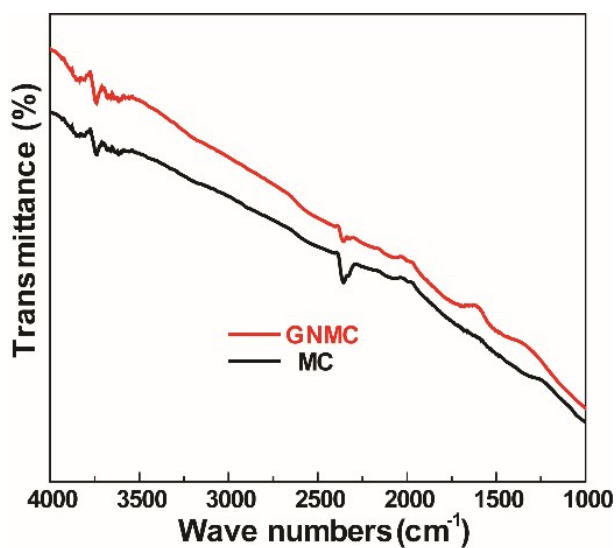


Fig. S5 ATR-IR spectra of MC and GNMC

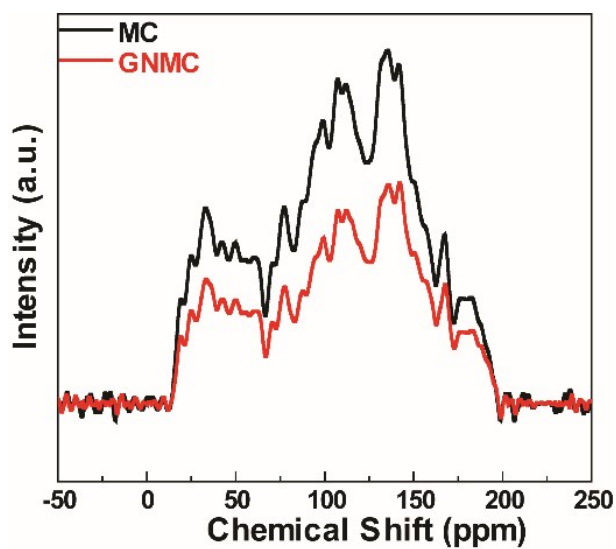


Fig. S6 ¹³C NMR spectra of MC and GNMC.

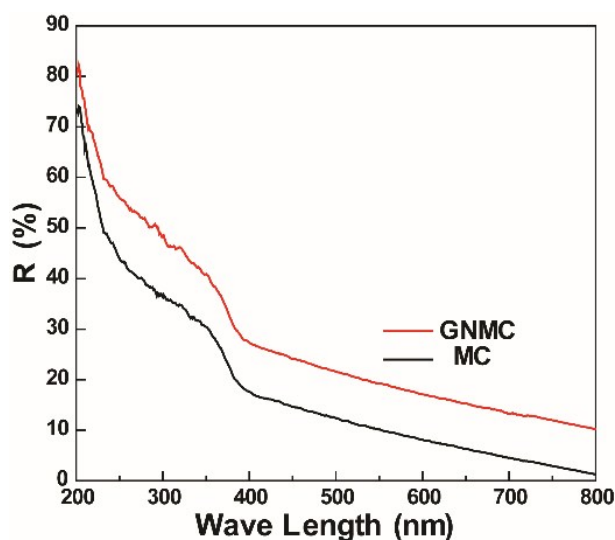


Fig. S7 UV-vis DRS results of MC and GNMC.

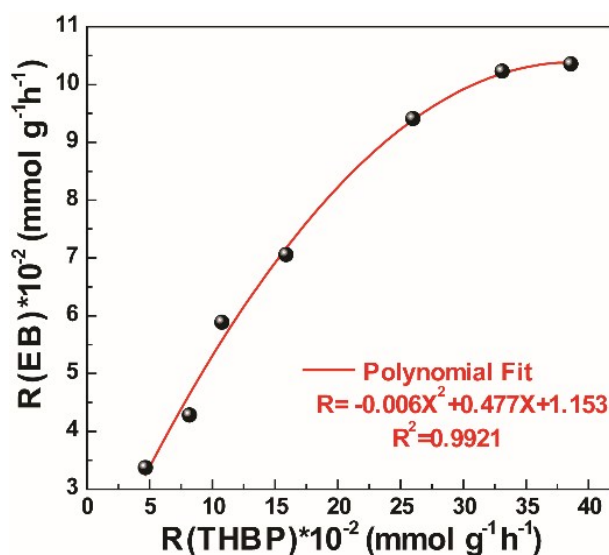


Fig. S8 EB consumption rate vs TBHP consumption rate.

In the selective oxidation of EB with GNMC as a catalyst, TBHP is an oxidant. The incorporated nitrogen (graphitic-type nitrogen) is pivotal for the C-H bond oxidation. As the results of various characterizations, such as the *electronic partial density of states* (PDOS), the charge of N and C, and the X-ray absorption spectroscopy (XAS) [4], the nitrogen dopant do not participant in the reaction process, but it changes the electronic structure of the adjacent carbon atoms and promotes their reactivity. The real active site is the peroxide group generated on carbon atom adjacent to graphitic nitrogen. Therefore, only carbon atoms adjacent to graphitic nitrogen could effectively activate TBHP to form the active oxygen groups which convert EB to AcPO. With the decomposition of TBHP, the conversion of EB also increase. However, if the decomposition rate of TBHP is too high, no enough EB adsorbed on the surface of GNMC will result in slow increase of EB conversion rate. Besides, we also observe that the decomposition rate of TBHP on NCNT catalyst is higher than that on GNMC catalyst (3986 vs 3311 $\text{mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), however, the conversion rate of EB on NCNT is lower than that on GNMC (759 vs 1022 $\text{mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), which also suggests that adequate TBHP decomposition rate is necessary to efficiently

convert EB to AcPO.

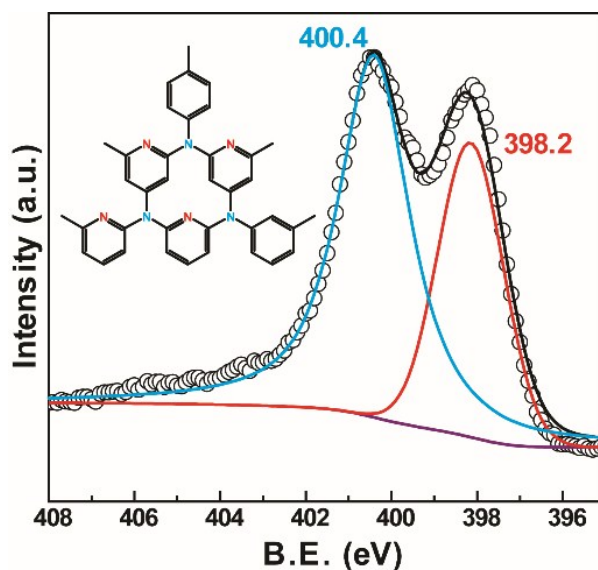


Fig. S9 N1s spectrum of MCN catalyst and its scheme of nitrogen species (Red: nitrogen atoms bonded with the graphitic carbon atoms or pyridinic nitrogen; Cran: nitrogen atoms trigonally bonded to all sp² carbons or pyrrolic nitrogen)

The lowest energy (398.2 eV) contribution of the N1s spectrum is attributed to nitrogen atoms bonded with the graphitic carbon atoms which is similar with pyridinic nitrogen, while the highest energy contribution at 400.4 eV is assigned to N atoms trigonally bonded to all sp² carbons [5, 6].

References

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