**Supporting Information**

# N-, P- and B-doped Mesoporous Carbons for Direct Dehydrogenation of Propane

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## 1. Experimental Section.

### 1.1 Materials

All the chemical reagents used below were purchased from Tianjin Guangfu Fine Chemical Research Institute Co., Ltd and used without any purification further.

### 1.2 Catalyst preparation

**Preparation of oxidic NMC (NMC-o).** The prepared NMC was oxidized by nitric acid. Typically, NMC was oxided NMC in 10 mol/L nitric acid for 8 h, then washed with deionized water to neutal. After drying at 80 °C, the resulted produce was marked as NMC-o.

**Preparation of N-doped mesoporous carbon by melamine (NMC-m).** As reported by Zhao's group with some adjustment.[1] 1 g mesoporous carbon was put into a 100 ml solution with 10 g melamine at 80 °C under stirring for 8 h. After water evaporated, the precipitate was dried in oven at 100 °C and heated up to 750 °C at 2.5 °C/min and kept for 1 h in a $N_2$ atmosphere. The obtained product was denoted as NMC-m.

**Preparation of N-doped mesoporous carbon by urea (NMC-u).** The N-doped mesoporous carbon were synthesized by in-situ approach.[2] 1.41 g phenol, 0.45 g urea and 0.03 g sodium hydroxide were dissolved in 3 mL water under stirring, and then 2.5 g formaldehyde (37%) was added drop-wise. After heating up to 90 °C slowly and held 30 min, a phenol-urea-formaldehyde (PUF) resin was prepared. The obtained PUF resin was dissolved in 40 mL mixture of ethanol and water ($V_{ethanol}$: $V_{water}$ = 1:1), then 2.5 g F127 added into the above solution under stirring. When F127

dissolved completely, ~ 2 g HCl (37%) were used to adjust the pH value of the mixture to ~ 2.0. The mixture continues to be stirred at 50 °C for 12 h, then evaporating the solvent under vacuum environment at 50 °C. The obtained gel-like precipitate further aged at 100 °C for another 24 h, followed by calcination to 600 °C at 1 °C/min for 3 h under nitrogen atmosphere. The obtained product was labeled as NMC-u.

## 2. Supplementary Figures and Tables

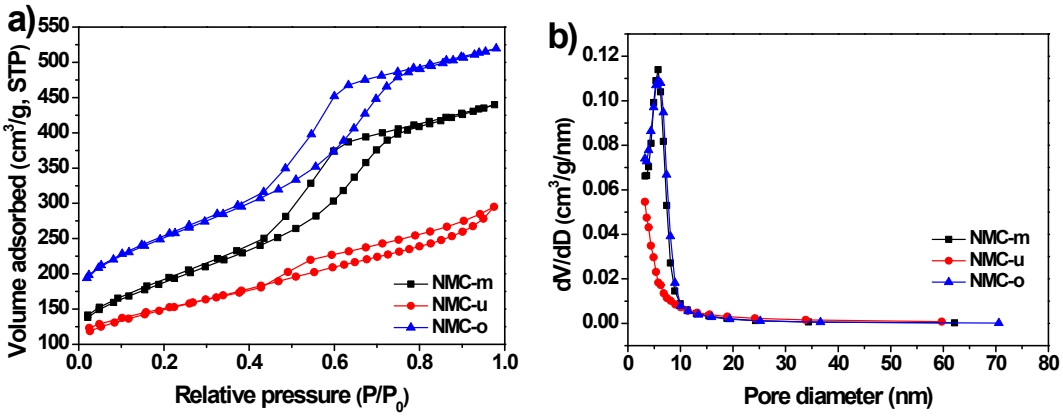


**Fig. S1** $N_2$ sorption isotherms (a) and the corresponding pore size distribution curves (b) of the N-doped carbons.

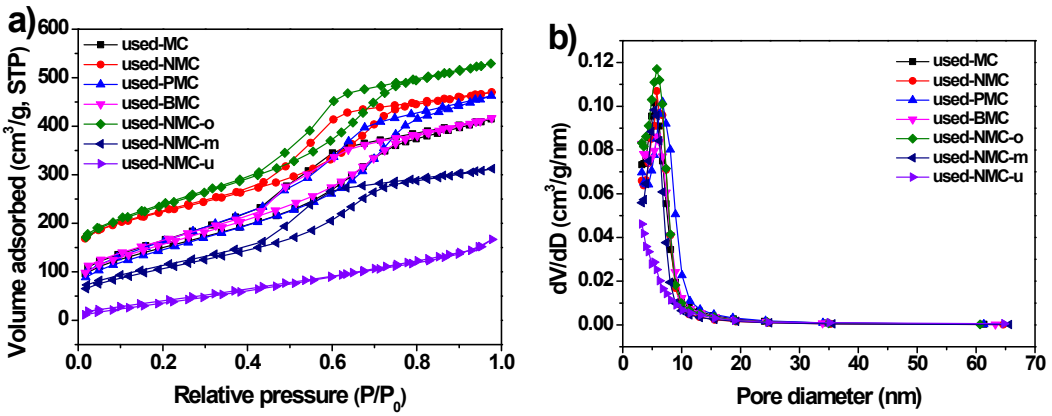


**Fig. S2** $N_2$ sorption isotherms (a) and the corresponding pore size distribution curves (b) of all the used carbon catalysts.

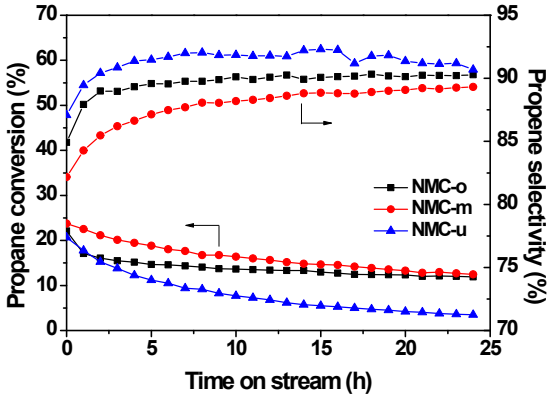


**Fig. S3** Propane conversion and propene selectivity in propane dehydrogenation over N-doped mesoporous carbons.

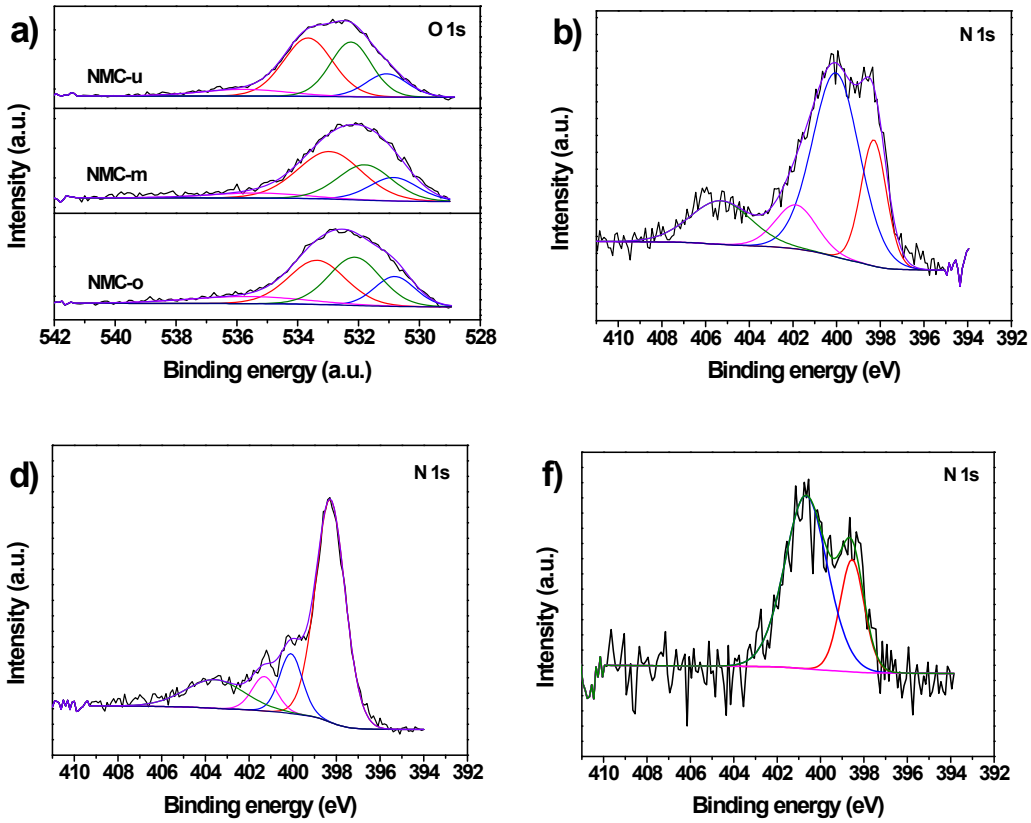


**Fig. S4** High-resolution XPS O 1s spectra of N-doped carbons (a), and N 1s spectra of NMC-o (b), NMC-m (d) and NMC-u (f).

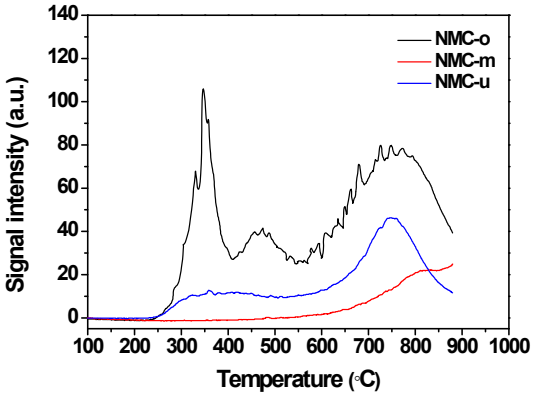


**Fig. S5** TPD profiles of N-doped carbons.

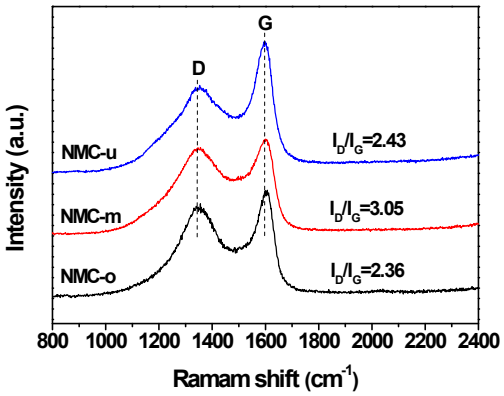


**Fig. S6** Raman spectra of N-doped carbons.

**Table S1** Textural properties and specific catalytic activities of N-doped carbons.

| Samples | $S_{BET}$ ($m^2/g$) | $V_{total}$ ($cm^3/g$) | $D_{pore}$ (nm) | TOF (mmol/g/h) | Initial conversion (%) | Initial selectivity (%) |
|---|---|---|---|---|---|---|
| NMC-o | 844 (813)[a] | 0.80 | 5.8 | 38.3 | 22.1 | 84.9 |
| NMC-m | 649 (395) | 0.68 | 5.7 | 48.4 | 23.7 | 82.2 |
| NMC-u | 502 (171) | 0.46 | – | 34.2 | 20.7 | 87.1 |

[a] Data in the parentheses are corresponding to the used catalysts after 24 h of propane dehydrogenation reaction.

**Table S2** Relative integrated intensity of deconvoluted O 1s, N 1s, P 2p and B 1s XPS spectra for all mesoporous carbons.

| | O | | | | | N | | | | | P | | | B | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| catalysts | Total (at%) | C=O (at%) | O=C-O (at%) | C-OH (at%) | Water | Total (at%) | Pyridinic N (at%) | Pyrrolic N (at%) | Graphitic N (at%) | oxidized N (at%) | Total (at%) | P-C bond (at%) | $PO_4$ tetrahedra (at%) | Total (at%) | C-$(BO_3)_n$ bond (at%) | graphitic-B (at%) |
| MC | 10.33 | 0.95 | 2.86 | 6.21 | 0.31 | – | – | – | – | – | – | – | – | – | – | – |
| BMC | 9.89 | 1.29 | 3.46 | 4.70 | 0.44 | – | – | – | – | – | – | – | – | 0.20 | 0.11 | 0.09 |
| PMC | 7.19 | 1.68 | 1.50 | 3.34 | 0.66 | – | – | – | – | – | 0.31 | 0.18 | 0.13 | – | – | – |
| NMC | 4.92 | 0.48 | 2.99 | 1.11 | 0.34 | 5.98 | 2.23 | 1.87 | 1.25 | 0.61 | – | – | – | – | – | – |
| NMC-o | 7.07 | 1.22 | 2.51 | 2.52 | 0.83 | 6.98 | 1.37 | 3.70 | 0.77 | 1.13 | – | – | – | – | – | – |
| NMC-m | 4.90 | 0.85 | 1.43 | 2.27 | 0.35 | 7.00 | 4.41 | 0.91 | 0.56 | 1.12 | – | – | – | – | – | – |
| NMC-u | 8.98 | 1.30 | 3.03 | 3.86 | 0.78 | 2.35 | 0.64 | 1.71 | – | – | – | – | – | – | – | – |

## Reference

[1] Z. Zhao, Y. Dai, G. Ge, X. Guo, G. Wang, Phys. Chem. Chem. Phy., 2015, **17**, 18895-18899.

[2] M. Xie, Y. Xia, J. Liang, L. Chen, X. Guo, Micropor. Mesopor., 2014, **197**, 237-243.