Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information (ESI)

Nickel Embedded in N-Doped Porous Carbon for Hydrogenation of Nitrobenzene to *p*-Aminophenol

Tao Wang,[a] Zhen Dong,[a] Teng Fu,[a] Yanchao Zhao,[b] Tian Wang,[a] Yongzheng Wang,[a] Yi Chen,[a] Baohang Han[b] , and Weiping Ding*[a]

[a]*Key Lab of Mesoscopic Chemistry, the School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China*

[b]*National Center for Nanoscience and Technology, Beijing 100190, China*

Experimental Section

Characterization

Powder XRD measurements were performed with a Philips X'Pert MPD Pro X-ray diffractometer using Cu Ka radiation (1.54 Å) at 40 kV and 40 mA. Transmission Electron Microscopy (TEM) images were recorded with a JEM-100S Electron Microscope (JEOL) at an accelerating voltage of 80 kV. HRTEM was performed with a JEOL JEM-2010 instrument at an acceleration voltage of 200 kV. Field-emission scanning electron microscopy (SEM) observations were performed on a Hitachi S-4800 microscope (Hitachi, Ltd. Japan) operating at an accelerating voltage of 6.0 kV. Elemental analysis for carbon, nitrogen and hydrogen was carried out in duplicate on a Vario EL II elemental analyzer (Elementar). X-ray fluorescence spectrometry (XRF) measurements were conducted on ARL-9800 (ARL). Inductively coupled plasma emission spectrometer (ICP) experiments were carried out on an Optima 5300DV (PE). Fourier transform infrared (FT-IR) spectra for the samples were collected on a Bruker Vertex 70 spectrophotometer using KBr pellets, recording at 64 scans with a resolution of 4 cm^{-1}. The X-ray photoelectron spectroscopy (XPS) measurements were performed in a commercial XPS system (PHI 5000 VersaProbe) equipped with a hemispherical electron analyzer and monochromatic Al Kα X-ray exciting source. Solid-state 1H–13C CP MAS NMR measurement was performed on a Bruker Avance III 400 spectrometer. Nitrogen adsorption isotherms were measured at 77 K on ASAP 2020 volumetric adsorption analyzers manufactured by Micromeritics. Before adsorption measurements, each sample was degassed under a vacuum for 12 h at 293 K °C. The specific surface area of the samples was calculated using the Brunauer−Emmett−Teller (BET) method within the relative pressure range of 0.05−0.20.

Materials

Preparation of N-containing porous polymer

The polymer is prepared from the acid-catalytic reaction between glycoluril and terephthaldehyde similar to the synthesis of cucurbit uril (cf. W.A. Freeman, W.L. Mock and N.Y. Shih, *J. Am. Chem. Soc.*, 1981, **103**, 7367.). The polymer is obtained according to the following process. 2.5 g (17.5 mmol) of glycoluril, 2.35 g (17.5 mmol) of terephthaldehyde and 20.0 g (82.0 mmol) of *p*-toluenesulfonic acid were added into a 50.0 mL PTFE-lined autoclave. After heating up to 453 K °C and kept at that temperature for 24 h in a homogeneous reactor, the resulting product was collected by filtration and washed with ethanol and deionized water several times. The final sepia-colored solid product was obtained through a further purification by Soxhlet extraction with water, ethanol, and dichloromethane for 24 h. The product was dried *in vacuo* at 393 K for more than 12 h to give the final polymer denoted as GTP. Yield: 79.8 %.

Catalyst Preparation

In a typical experiment,1.0 g $Ni(NO_3)_2{\cdot}6H_2O$ was dissolved in 10.0 mL ethanol followed by impregnating 4.0 mL as-prepared ethanol solution in GTP which had been dried *in vacuo* at 393 K for more than 12 h. Then, the mixture was kept for 24 h at room temperature and dried at 353 K, after which it was calcined at 873 K for 6 h at a heating rate of 2 K min^{-1} in argon atmosphere to give the final product, denoted as Ni/CN. As a contrast, GTP was calcined at 873 K for 6 h at a heating rate of 2 K min^{-1} in argon atmosphere to give CN. Similar to the process, catalysts with different nickel loading are prepared by adjusting the concentration of Ni impregnated into GTP.

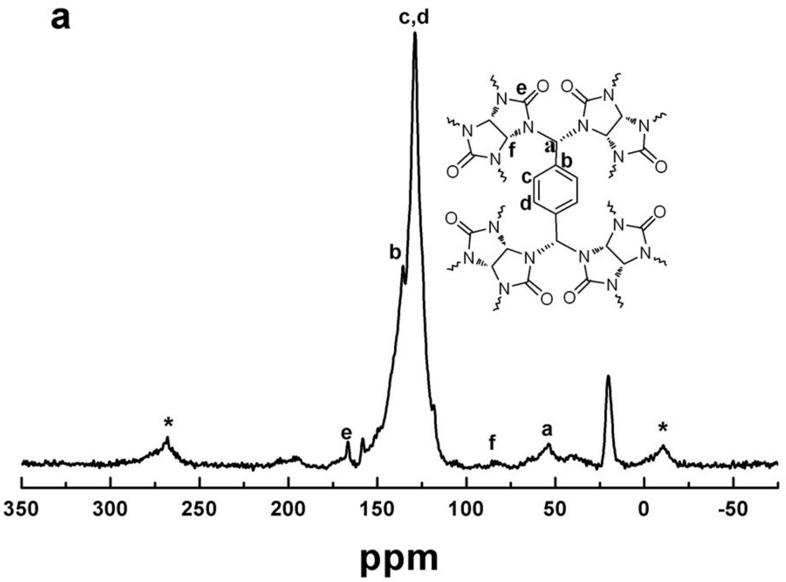
D/H exchange

The catalyst sample (200 mg) was reduced in 5 vol % H_2/N_2 (30 $mL{\cdot}min^{-1}$) at a heating rate of 10 K min^{-1} to 873 K and kept at this temperature for 1 h. Then the sample was cooled in the same atmosphere to room temperature, for adsorption of H_2, and switched to Ar (35 $mL{\cdot}min^{-1}$) to remove the physically adsorbed H_2. Deuterium exchanged with protonium presented in the sample was measured by increasing the temperature to 873 K at a heating rate of 10 $K{\cdot}min^{-1}$.

The signal of HD was monitored by mass spectrometry.

Catalytic test

The catalytic hydrogenation of NB to PAP was conducted in a bath-type autoclave reactor equipped with magnetic stirring. In a representative hydrogenation, nitrobenzene (100.0 mg), Ni/CN (20.0 mg), and 15 wt % aqueous sulphuric acid solution (30.0 mL) were introduced into the autoclave. After replacing the air in the reactor with hydrogen for several times, the reactor was filled with hydrogen to 1.0 MPa at room temperature. The agitation was started and maintained at 300 rpm/min, and the autoclave was heated to 393 K and kept for a 1 h. After that, the reactor was cooled to room temperature naturally, and the catalyst was filtered. The resulting solution was analyzed by HPLC equipped with a 4.6 mm × 25 mm C18 column and a UV detector (254 nm). The column temperature was kept at 293 K and the eluent was methanol/water (40/60).



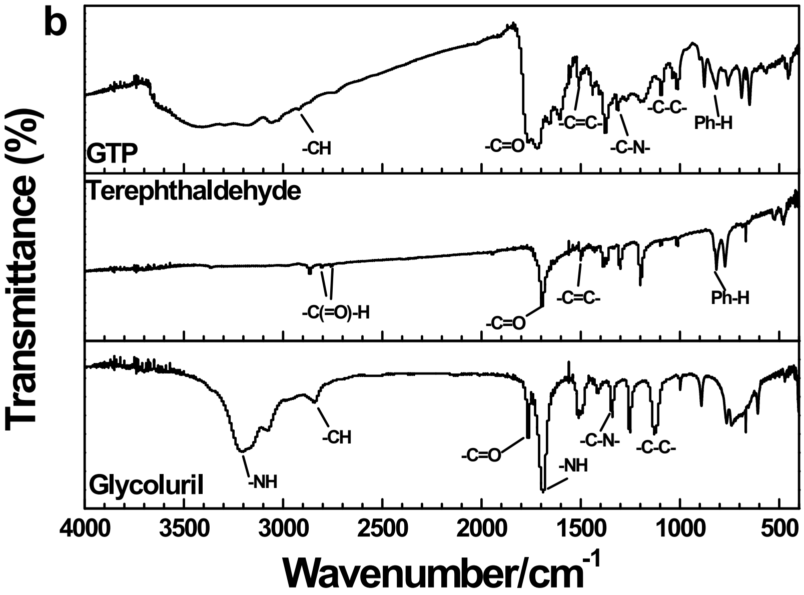
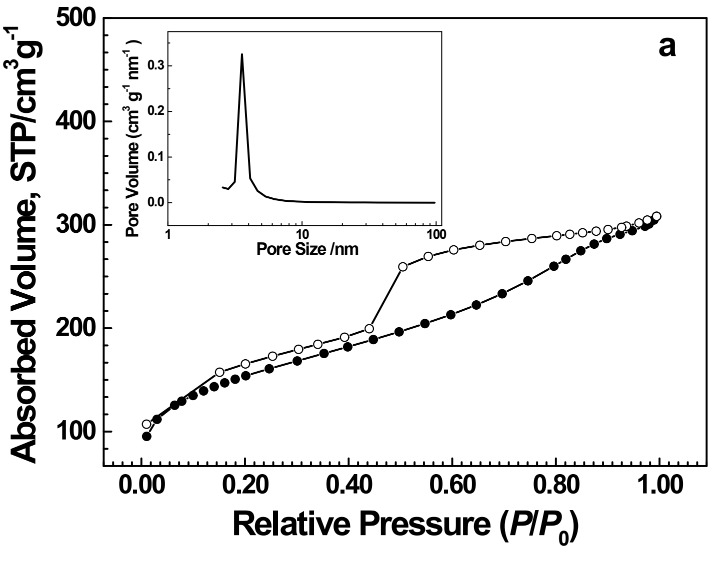


Fig. S1. (a) Solid-state 1H–13C CP MAS NMR spectra of GTP, asterisks (*) indicate peaks arising from spinning side bands and (b) FT-IR spectra of GTP, glycoluril and terephthaldehyde.



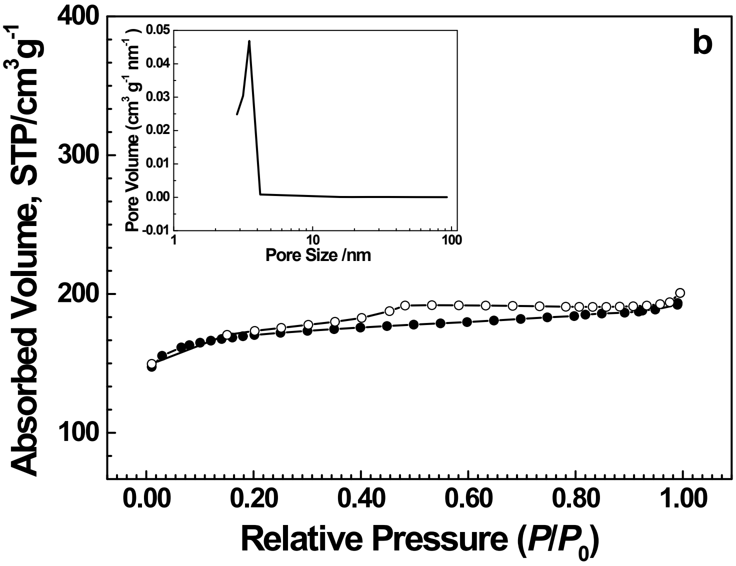


Fig. S2. N_2-physisorption isotherms and BJH desorption pore size distributions of (a) GTP and (b) Ni/CN.

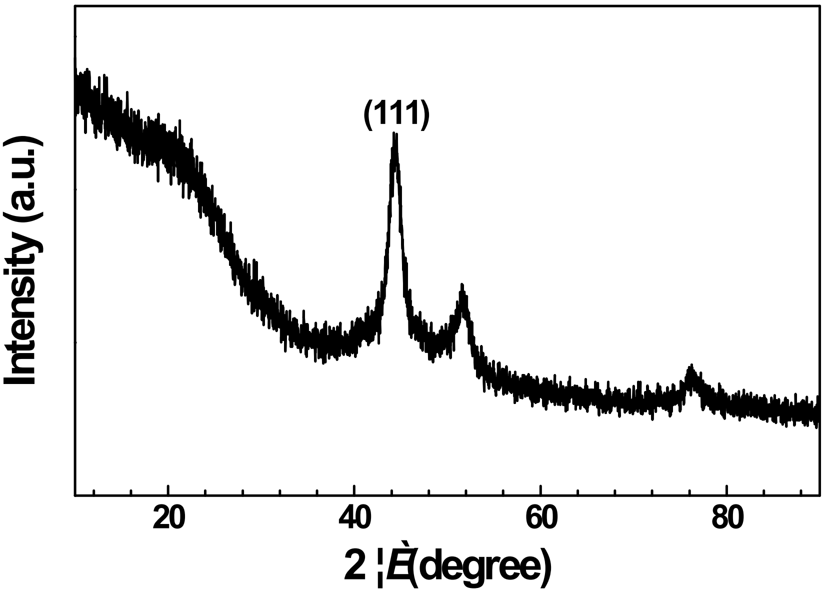


Fig. S3. XRD pattern of Ni/CN.

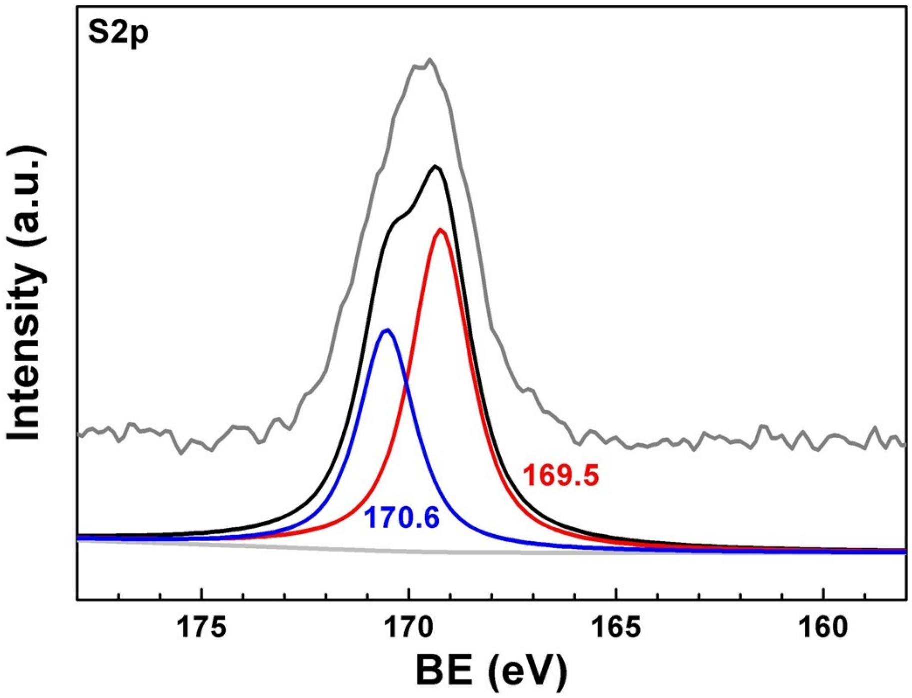


Fig. S4. XPS spectrum of S 2p for Ni/CN. (The gray line in the spectrum give the original data).

Table S1. Reported catalyst performance of hydrogenation of nitrobenzene to *p*-aminophenol

Catalyst	NB Conversion (%)	PAP Selectivity (%)
4.4 % PVP-$PdCl_2$[1]	100	18.1
5.0 % Pt/C[2]	88	89.8
1 % Pt-S/C[3]	97	14.3
3 % Pt/C[4]	100	75
3 % Pt/C[5]	100	88
10 % Ni/C[6]	14	14
10 % Ni-1 % Pd/ZSM-5[6]	99	20
10 % Ni-3 % Pt/ZSM-5[6]	99	65
1.5 % Pt/C[7]	100	84.3
5 % Pd/C[8]	90	61.1
4 % CN/Ni/Al_2O_3[9]	80	100

Table S2. Surface composition of the catalyst measured by XPS

C at%	O at%	N at%	Ni at%	S at%
64.69	26.48	1.85	3.57	3.41

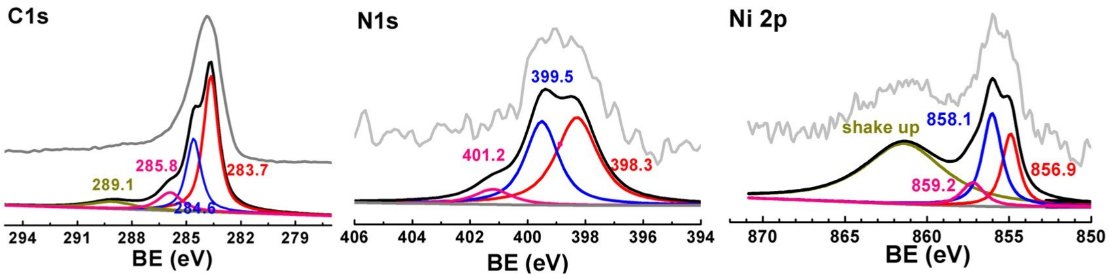


Fig. S5. XPS spectra of C 1s, N 1s and Ni 2p for Ni/CN. (The gray lines in the spectra give the original data).

Table S3. Surface composition of the spent catalyst measured by XPS

C at%	O at%	N at%	Ni at%	S at%
76.59	16.42	2.99	3.2	0.8

Table S4. Elemental analysis data for carbon, nitrogen and hydrogen of Ni/CN before and after reaction.

	C wt. %	N wt. %	H wt. %
Fresh catalyst	69.74	2.94	2.61
Spent catalyst	71.15	3.05	2.65

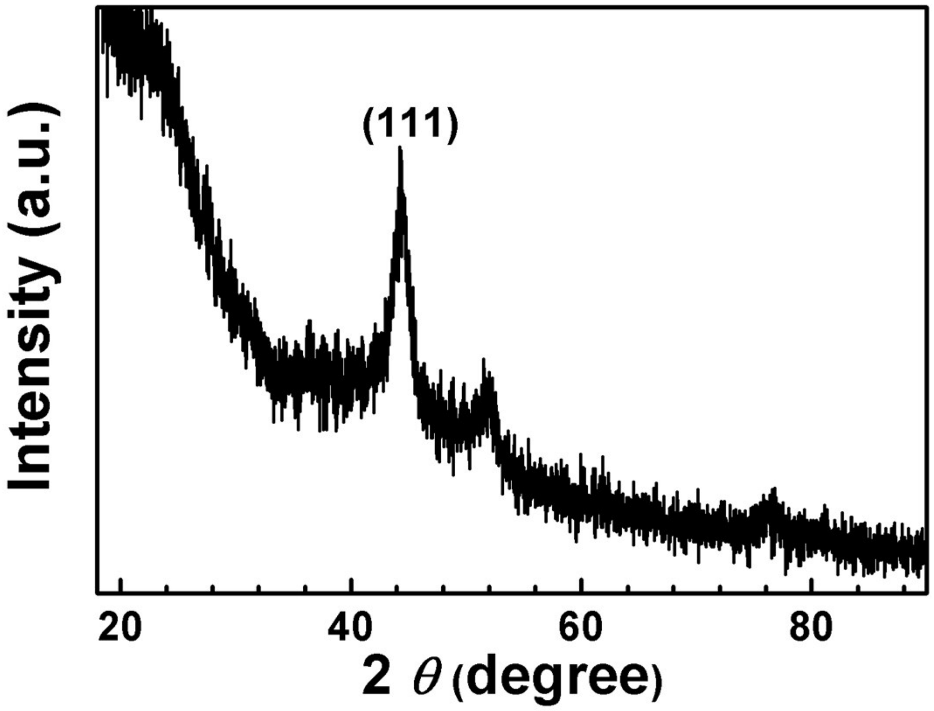


Fig. S6. XRD pattern of spent Ni/CN.

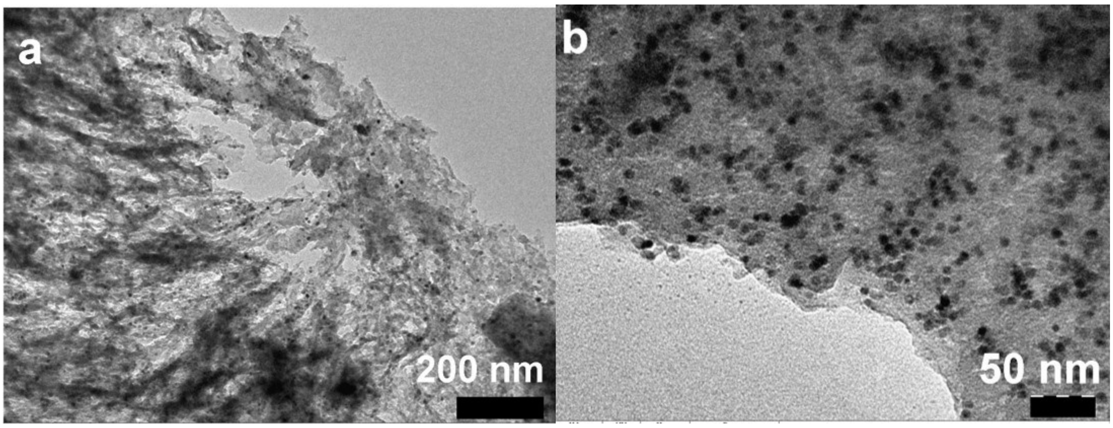


Fig. S7. TEM images of catalyst after a long-term reaction.

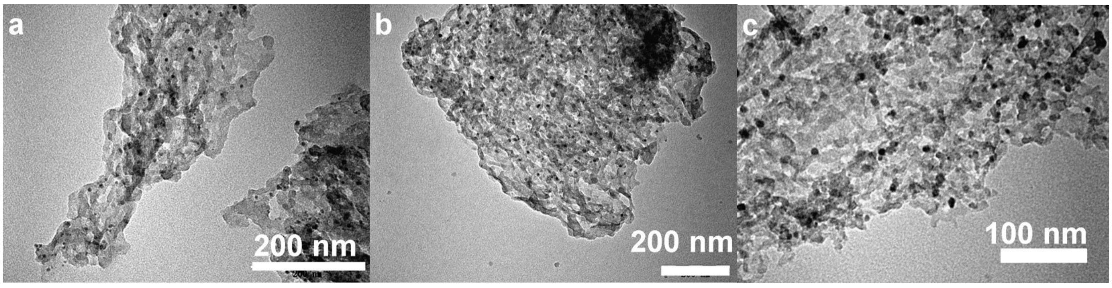


Fig. S8. TEM images of catalysts with different Ni loading (a) 2 wt. %; (b) 5 wt. % and (c) 9 wt. %.

Table S5. Catalytic performance of catalysts with various Ni loading

Catalyst	NB Conversion (%)	PAP Selectivity (%)
2 %	28.7	100
5 %	36.5	100
9 %	38.3	100

References

1. Y. Gao, F.D. Wang, S.J. Liao and D.R. Yu, *React. Kinet. Catal. Lett.*, 1998, **64**, 351.
2. R.G. Bennern, US Patent, 1968, 3383416.
3. R.V. Chaudhari, S.S. Divekar, M.J. Vaidya and C.V. Rode, US Patent, 2000, 6028227.
4. C.V. Rode, M.J. Vaidya and R.V. Chaudhari, *Org. Process Res. Dev.*, 1999, **3**, 465.
5. C.V. Rode, M.J. Vaidya, R. Jaganathan and R.V. Chaudhari, *Chem. Eng. Sci.*, 2001, **56**, 1299
6. C.V. Rode, M.J. Vaidya and R.V. Chaudhari, Europe Patent, 2002, 1229018.
7. S.K. Tanielyan, J.J. Nair, N. Martin, G. Alvez, R.J. McNair, D.J. Wang and R.L. Augustine, *Org. Process Res. Dev.*, 2007, **11**, 681
8. A. Zoran, O. Khodzhaev and Y. Sasson, *J. Chem. Soc. Chem. Commun.*, 1994, 2239

9. T. Fu, M. Wang, W.M. Cai, Y.M. Cui, F. Gao, L.M. Peng, W. Chen and W.P. Ding, *ACS Catal.*, 2014, **4**, 2536