Supporting information

Metal-free hydrogenation with formic acid over N-doped carbon

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1. Experiment

1.1 Synthesis of catalysts

Dicyandiamide (0.5 g) and chitosan (2.5 g) were dispersed in 60 mL 80 vol% ethanol solution, stirred continuously for 4 h in reflux. The solution was removed by vacuum, and the obtained white solid was dried at 60 ℃ for 4 h in vacuum, then ground into powder. Finally, the precursor was pyrolyzed at 800, 900 or 1000 ℃ in argon atmosphere for 2 h then cooled to room temperature. The prepared catalysts denoted as CN-T, in which T represents pyrolysis temperatures. In addition, as a control, C-900 and G-900 catalysts were prepared using chitosan or glucose as precursors without dicyandiamide in the preparation process, and the other steps were the same as above.

1.2 Catalytic transfer hydrogenation

In a typical reaction: 0.25 mmol nitrobenzene, 0.75 mmol formic acid, 20 mg catalyst and 2.5 ml toluene were added into a 30 ml stainless steel autoclave with a Teflon liner, then filled the autoclave with N_2 to 2 MPa. The reactor was heated to 160 ℃ in an oil bath under stirring for 12 h. After reaction, the reactor was cooled to room temperature. The catalysts were recovered and the product was analyzed by gas chromatography.

1.3 Catalyst recycling experiments

For the catalyst recycling experiments, reactions were carried in a 30 ml stainless steel autoclave. 0.25 mmol nitrobenzene, 0.75 mmol formic acid, 20 mg catalyst and 2.5 ml toluene were added into a stainless-steel autoclave, then filled the autoclave with N_2 to 2 MPa. The reactor was heated to 160 ℃ in an oil bath under stirring for 10 h. The used catalyst was collected by centrifugation and washed with ethanol for 5 times, then dried under vacuum for 3 h. The collected catalyst was then used for the next run. The value of C_n/C_1 was used to measure the stability of the catalyst, where C_n represents the conversion rate of nitrobenzene when the catalyst is applied for the nth cycle, n=2,3,4,5.

2. Characterization

The X-ray diffraction (XRD) characterization of the catalyst was analyzed by Smartlab X-ray diffractometer manufactured in Japan. Main specifications and technical indicators: scanning speed 5°/min; machine reproducibility ≥0.0001°; Cu target rotation of X-ray source; maximum output power 9 kW; rated current 220 mA; rated pipe voltage 60 kV; scanning range $2\theta=5\text{-}80^\circ$. The elemental content and chemical morphology of the material surface were measured by an ESCALAB 250XI X-ray photoelectron spectrometer manufactured by Thermo Mercer Technologies. The Mg Kα source was used as the excitation source, and the binding energy (BE) was corrected according to the C 1s peak of 284.8eV. The surface morphology of the catalyst was observed by Hitachi Regulus 8100 field emission scanning electron microscope. The acceleration voltage is 50 V and the magnification is 100 K. A small amount of sample powder was first glued to the surface of conductive adhesive,

and then a gold film was sprayed under vacuum by ion sputtering instrument (Hitachi E-1045 type ion sputtering instrument, working current 15 mA, spraying time 60 s). The surface morphology and structure of catalyst materials were tested by JEM-2100F transmission electron microscope. The acceleration voltage is 200 kV and the magnification is 40 K. The defect and graphitization degree of the catalyst were measured by a DXR MicroSP-CSE Raman spectrometer produced by Thermo Fisher Technologies.
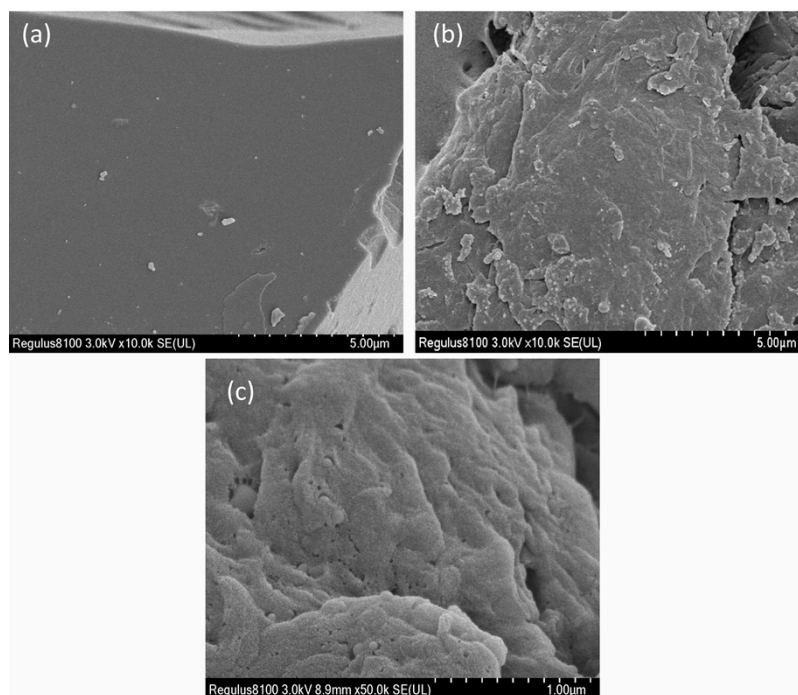

Fig.S1. SEM images of G-900(a), C-900(b), CN-900(c) catalysts.

The morphology and structure of catalysts were observed by SEM. The G-900 prepared by the direct pyrolysis of glucose had a smooth surface in Fig.S1a, while the C-900 which used chitosan as the precursor presented the lamellar structure and had a rougher surface in Fig.S1b. The dope of N atom can make the layer structure more obvious. The catalyst CN-900 prepared by chitosan and dicyandiamide had the pore structure and the rougher surface (Fig.S1c).
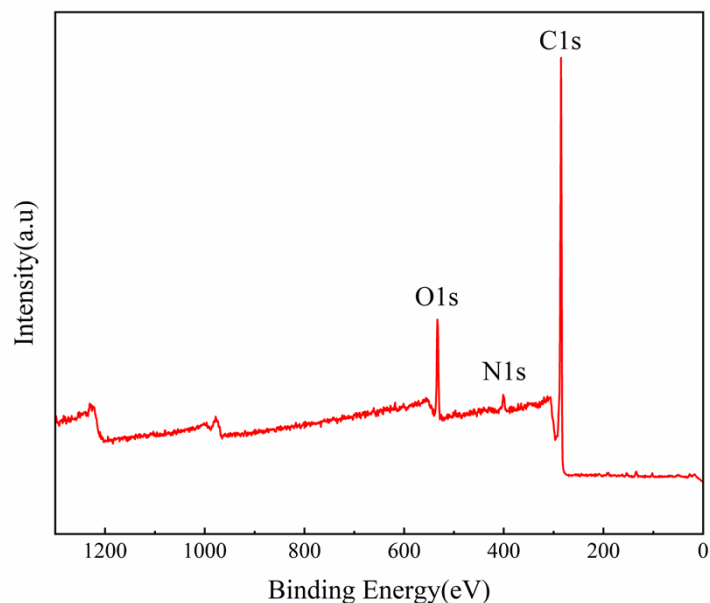
Fig S2. XPS spectra of CN-900 catalysts.

The full survey spectrum of CN-900 was shown in Fig.S2, which displayed three peaks, proving the existence of C, N, O. It proved that the nitrogen was successfully doped in the materials, which was consistent with EDX elemental maps (Fig.2c).

3. Optimization of catalytic conditions

Table S1 Influence of different solvents on catalyst activity

Entry	Solvent	Conversion（%）	Selectivity（%）
1	toluene	70.02	98.86
2	n-hexane	59.31	97.79
3	ethyl acetate	73.34	85.41
4	tetrahydrofuran	87.03	83.72
5	1,4-dioxane	80.57	69.50
6	ethanol	32.84	97.93

Reaction conditions: 0.25 mmol nitrobenzene, 2.5 mL toluene, 20 mg catalyst, 0.75 mmol formic acid in 160 ℃, 2 MPa nitrogen atmosphere for 12 h

For nonpolar solvent, such as toluene and n-hexane, both had a good aniline selectivity, but a higher nitrobenzene conversion was obtained in toluene solvent (Table S1, Entry 1-2). While in the polar aprotic solvent such as ethyl acetate, tetrahydrofuran and 1,4-dioxane, higher nitrobenzene conversion was observed, but the aniline selectivity was relatively low (Table S1, Entry 3-5). It reached higher conversion in polar solvent but better selectivity in nonpolar solvent. The interaction between nitro group and polar solvent will accelerate the polarization of N=O and N−O and weakens the bond strength, which promotes the conversion of nitrobenzene [1]. However, the polar solvent can activate the N-H bond through polarization and solvation, which is beneficial to formylation reaction [2]. This may be the reason of lower selectivity in polar solvents. Using ethanol as the solvent leads to a pretty low conversion of nitrobenzene (Table S1, Entry 6), which could be attribute to the esterification

reaction between formic acid and ethanol. The formic acid was consumed to produce ester, so it was not enough to reduce nitrobenzene (Table S1, Entry 6).

Table S2 Influence of reaction temperature on catalytic performance of catalyst

Entry	Temperature (℃)	Conversion (%)	Selectivity (%)
1	140	38.61	98.37
2	160	70.02	98.86
3	180	77.88	94.81
4	200	99.89	64.25

Reaction conditions: 0.25 mmol nitrobenzene, 2.5 mL toluene, 20 mg catalyst, 0.75 mmol formic acid in 160 ℃, 2 MPa nitrogen atmosphere for 12 h

Temperature is an important parameter for this reaction, so the influence of temperature was shown in Table S2. The increase of temperature from 140 to 200 ℃ led to an obvious rise in the nitrobenzene conversion from 38.61% to 99.89%. While the aniline selectivity descended with the growth of temperature. The nitrobenzene conversion can raise up to 99.89% at 200 ℃, but the selectivity of aniline was only 64.25% (Table S2, Entry 4). The reason of declined selectivity probably is that formic acid tends to dehydrate into CO and H_2O at higher temperature and more CO promote the occurrence of formylation.[3] The higher temperature is conductive to the aniline further react with formic acid to produce formyl aniline and lead a lower selectivity of aniline.
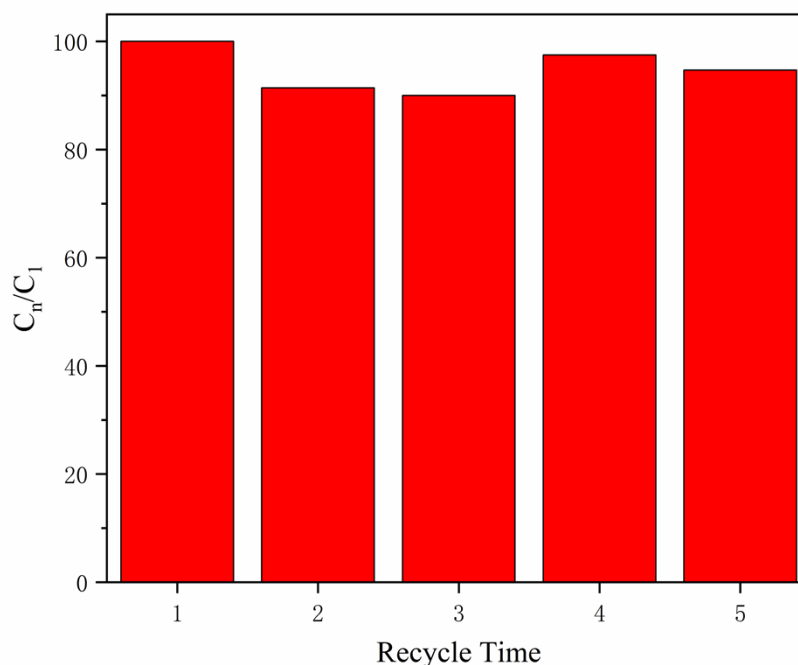
4. the recycle of catalyst

Fig. S3. Stability of CN-900.
Reaction condition: 0.25 mmol of nitrobenzene, 2.5 mL toluene, 20 mg catalyst, and 0.75 mmol formic acid under 160 ℃, 2 MPa nitrogen atmosphere for 10 h

Catalyst stability is an important characteristic in practical application. The catalytic reusability of CN-900 catalyst was investigated and shown in Fig.S3. The catalyst still exhibited excellent performance after 5 cycles, indicating the good stability of CN-900.
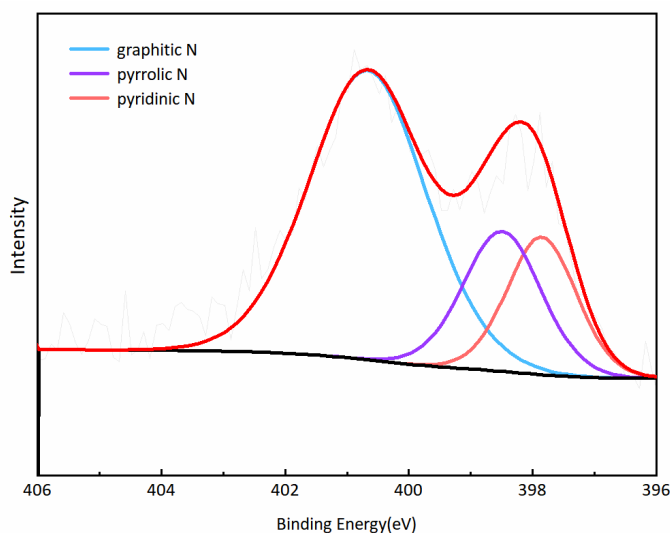

Fig S4. N 1s spectra of CN-900 after reaction

Table S3 the composition of nitrogen species in CN-900 before and after reaction

Catalysts	Pyridinic N (at. %)	Pyrrolic N (at. %)	Graphitic N (at. %)
CN-900	16.95	16.54	66.51
CN-900 after reaction	17.31	20.05	62.42

The excellent catalytic performance is attributed to the synergistic effect between graphitic nitrogen and pyridinic nitrogen, and they are stable in the experimental conditions. We investigated the composition of CN-900 after reaction (Fig S4 and Table S3). It still has a high graphitic N content after the reaction, indicating the CN-900 had a strong absorption of nitrobenzene in the recycle experiment and ensured the smooth process of the reduction. [4] Additionally, the content of pyridinic N didn't decrease after reaction. It showed that the CN-900 still had the activation capacity of formic acid in the recycle experiments. [5,6] The reaction did not change the property of catalysts. Hence it exhibited a good stability in the reaction.

Reference

1. R. Gao, L. Pan, J. Lu, J. Xu, X. Zhang, L. Wang and J.-J. Zou, *ChemCatChem*, 2017, **9**, 4287-4294.
2. V. V. Phatake, A. A. Mishra and B. M. Bhanage, *Inorganica Chimica Acta*, 2020, **501**, 1-7.
3. Z. Yu, A. Yoshida, J. Shi, T. Wang, S. Yang, Q. Ye, X. Hao, A. Abudula, Y. Fang and G. Guan, *ACS Sustainable Chemistry & Engineering*, 2020, **8**, 13956-13963.
4. F. Yang, C. Chi, C. Wang, Y. Wang and Y. Li, *Green Chemistry*, 2016, **18**, 4254-4262.
5. Y. Wang, Y. Zhang, J. Wang, M. Wang, H. Cui, W. Yi, F. Song, P. Zhao, X. Sun and Y. Xie, *Catalysis Letters*, 2020, **150**, 3184-3195.
6. B. Li, X. Sun and D. Su, *Phys Chem Chem Phys*, 2015, **17**, 6691-6694.