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Supporting information

G-C_3N_4 coated activated carbon supported Pd catalyst for 4-CBA hydrogenation：effect of nitrogen species

Zhiwei Wang[a], Jianren Wei[a], Gonggang Liu[a], Yonghua Zhou[a]*, Kai Han[a]*, Hongqi Ye[a]

a. Chemistry and Chemical Engineering College, Central South University Changsha, 410083, China.
Fax: 0086-731-88879616; Tel:0086-731-88879616;
E-mail: zhouyonghua@mail.csu.edu.cn , hankai@mail.csu.edu.cn

Preparation of samples

g-C_3N_4(H) preparation The g-C_3N_4 sample in this paper was prepared by two steps. The bulk g-C_3N_4 was firstly synthesized by melamine condensation at 550 ℃ for 4 h. Then the bulk g-C_3N_4 was treated in a basic solution. The base treatment details are as follows. 1 g of bulk g-C_3N_4, 0.2 g of NaOH, and 50 g of distilled water were mixed and then kept in an autoclave at 100 ℃ for 20 h, followed by filtration, washing, and drying at 60 ℃ overnight. The resulting powder was denoted as g-C_3N_4(H).

g-C_3N_4(L) preparation The g-C_3N_4(L) sample in this paper was obtained by treating g-C_3N_4(H) in distilled water at 200 ℃ in a hydrothermal reactor for 20 h.

Pd-g-C_3N_4(H)/AC catalyst preparation The Pd-g-C_3N_4(H)/AC catalyst was prepared by two steps. Firstly, we loaded Pd on g-C_3N_4(H) by impregnation with 0.01M H_2PdCl_4 aqueous solution, followed by calcination in air at 350 ℃ for 2 h and reduction in potassium borohydride (KBH_4) solution. Then, 0.3 g of Pd-g-C_3N_4(H) was dispersed in 50 ml distilled water under sonication and 1.74 g of coconut shell activated carbon was added. The slurry was finally filtered, dried under vacuum at 50 ℃ overnight. The resulting sample was denoted as Pd-g-C_3N_4(H)/AC.

Pd-g-C_3N_4(L)/AC catalyst preparation 0.3 g of g-C_3N_4(L) was impregnated in 0.01M H_2PdCl_4 aqueous solution for 30 minutes. Then 1.74 g of coconut shell activated carbon was added. The slurry was then stirred to dry followed by calcination in air at 350 ℃ for 2 h and reduction in potassium borohydride (KBH_4) solution. The resulting sample was denoted as Pd-g-C_3N_4(L)/AC.

Characterizations

X-Ray diffraction (XRD) was carried out using a Japan Rigaku D/MAX-2500 instrument with a Cu Ka radiation and a scanning rate 5°/min for crystal structure detection. Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrophotometer using KBr pellets. X-ray photoelectron spectroscopy (XPS) analysis of catalyst was carried out on an ESCALAB 250Xi X-ray Photoelectron Spectroscopy. The morphology and size of palladium particles on catalysts were recorded by Transmission Electron Microscopy (TEM) on a JEOL JEM-2100 (Japan) operated at 200 kV. The Scanning Transmission Electron Microscopy（STEM）was performed with a Titan G2 60-300 operated at 300 kV. The Pd loading was determined by an Optima 5300 inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Catalytic reactions

The hydrogenation of 4-CBA was conducted in a batch-type reactor operated under a hydrogen pressure of 0.3 MPa and 90°C. Experiments were conducted using a stirred autoclave in the presence of 0.1 g catalyst, 0.10 g CBA and 100ml of de-ionized water. Nitrogen was introduced into the reactor to remove air with a magnetic stirrer, and the reaction mixture was then heated to the temperature 90°C. The reaction occurs with an inlet of hydrogen (0.15MPa). The samples were withdrawn at specific intervals. Then NH_4OH was added to dissolve the components (including 4-CBA, PT, 4-(hydroxy-methyl) benzoic acid in the solution, and nitric acid was used to control pH 7. Then component compositions were determined with a Dionex U3000 HPLC apparatus (Dionex, Sunnyvale, CA, USA) high performance liquid chromatography equipped with a C-18 column and a MWD-3000RS multiple wavelength detector (wavelength 254 nm). Then the catalyst was aged under a similar condition to reference. In detail, 0.30 g of catalyst were kept in an autoclave at 200 ℃ for 25 h with a hydrogen pressure of 1.5 MPa. After aging, the activity of the catalysts was tested under the same conditions. The stability of catalyst is evaluated by comparing the activity drop via keeping the catalyst in a severe aging condition, which is common used in the studies on this reaction.

Hydrogenation of 4-CBA is a first order reaction for 4-CBA. Thus, the concentration of 4-CBA can be described by the following equation.

$$\ln\frac{C_0}{C_t} = kt$$

where C_0 is the initial concentration of 4-CBA, C_t is its instantaneous concentration at a given reaction time t , and k is the reaction rate constant. Since the Pd loading is the same for each catalyst, the activity can be reflected by reaction rate constant k.

Results and discussion

The successful immobilization of Pd-g-C_3N_4 on activated carbon can be identified by XRD pattern of Pd-g-C_3N_4(H)/AC as shown in Fig.S1, The broad peaks at 23.8° and 43.2° were attributed to the amorphous carbons, and the peak at 27.3°

was the characteristic peak of g-C_3N_4. It was shown that g-C_3N_4 can be immobilized on the surface of coconut shell activated carbon via ultrasonic method. Pd characteristic peaks cannot be detected probably due to the tiny size and low content.

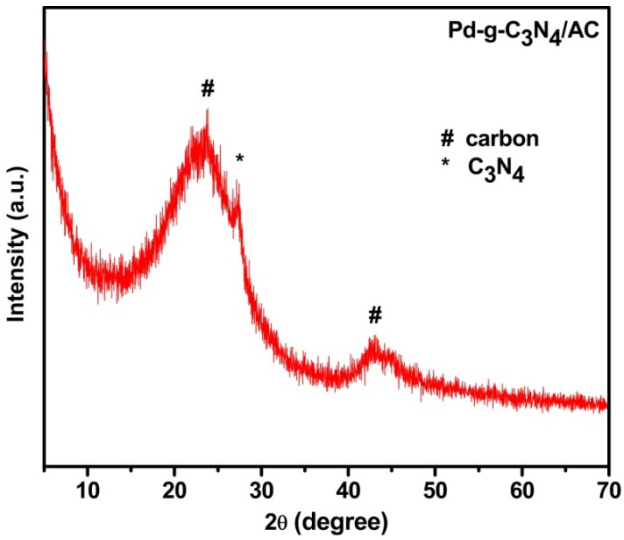

Fig.S1 XRD pattern of Pd-g-C_3N_4(H)/AC

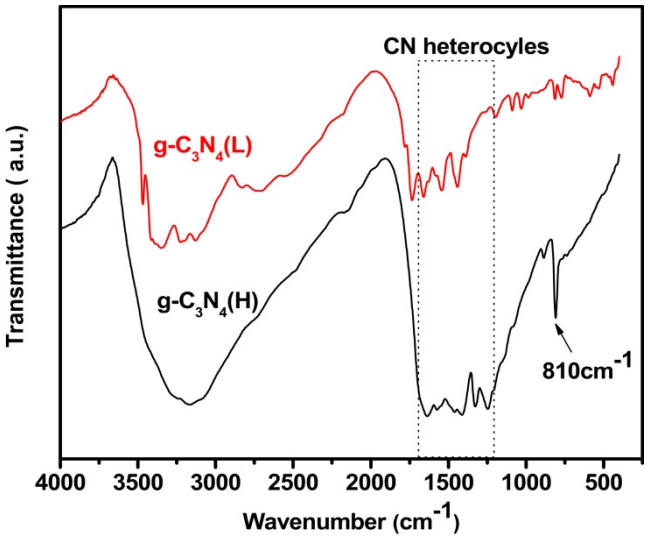

Fig.S2 FT-IR spectra of g-C_3N_4(H) and g-C_3N_4(L)

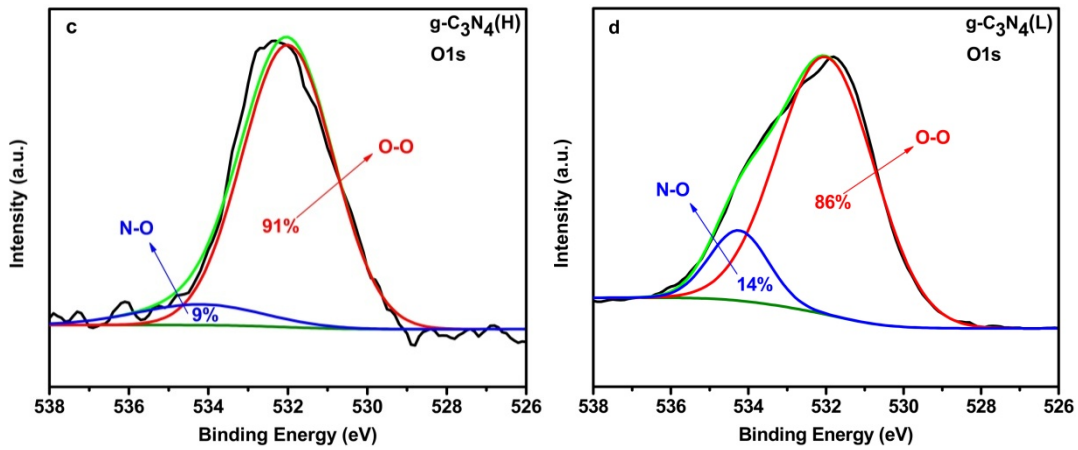

Fig.S3 XPS O1s spectra of g-C_3N_4(H) (c) and g-C_3N_4(L) (d)

Table S1 Elemental analysis of C_3N_4(H) and Pd-g-C_3N_4(L)

Material	Atomic (%)		
	C	N	O
g-C_3N_4(H)	42.1	55.7	2.2
g-C_3N_4(L)	39.2	44.9	15.9

Table S2 Pd loading before and after aging of Pd-g-C_3N_4(H)/AC and Pd-g-C_3N_4(L)/AC catalysts

Catalyst	Pd loading (%)		Pd leaching
	Before	After aging	(%)
Pd-g-C_3N_4(H)/AC	0.0175	0.0169	3
Pd-g-C_3N_4(L)/AC	0.0191	0.0151	21