Robust Co_3O_4 nanocatalysts supported on biomass-derived porous N-doped carbon toward low-pressure hydrogenation of furfural

Lin Zhang, Lanlan Cheng, Yechen Hu, Qingguang Xiao, Xiufang Chen (✉), and Wangyang Lu

National Engineering Lab for Textile Fiber Materials & Processing Technology (Zhejiang), Zhejiang Sci-Tech University, Hangzhou 310018, China

E-mail: chenxf@zstu.edu.cn

Supplementary material

Experimental

1 Materials and reagents

Bamboo shoot were purchased from Huangshan Base. $Co(NO_3)_2·6H_2O$ (>99.0%), furfuryl alcohol (>97.0%), benzaldehyde (>98.0%), isobutyraldehyde (>98.0%), p-anisaldehyde (>99.0%), cyclopentanone (>99.0%) and 5-hydroxymethyl-2- furaldehyde (>99.0%) were purchased from Aladdin Industrial Corporation. Furfural (>99.0%) and 2,5-furan dimethyl alcohol (>98.0%) were purchased from Shanghai Macklin Biochemical Co., Ltd., China. 2-propanol (>99.7%), DMF (>99.5%), ethanol (>99.7%), n-butanol (>99.5%), ethyl acetate (>99.5%), n-hexane (>99.5%) and THF (>99.5%) were purchased from Hangzhou Gaojing Fine Chemical Co., Ltd., China. Commercial carbon (Vulcan XC-72R) was purchased from Cabot Corporation, USA.

2 Preparation of the bamboo shoot-derived porous N-doped carbon

The hydrothermal carbonization process of bamboo shoots powder is carried out in a Teflon-inner stainless-steel autoclave. 2 g of bamboo shoot powder and 20 mL deionized water were added into the autoclave, then heating at 180 °C for 6 h to obtain hydrochars. It was washed thoroughly with deionized water, filtered, and dried under vacuum oven at 70 °C. Finally, the obtained brown biochars were pyrolyzed at 800 °C for 2 h, under an N_2 atmosphere for 2 h to obtain porous N-doped carbon material (NC).

3 Preparation of the Co_3O_4@NC catalyst

The synthesis steps of Co_3O_4@NC catalysts were according to the following steps: Firstly, $Co(NO_3)_2·6H_2O$ and NC were added into deionized water, with ultrasound for 3 h and stirring for 6

h at room temperature. After that, they were stirred at 60 °C to remove water and pyrolyzed at 300 °C for 4 h under an N_2 atmosphere. The Co_3O_4@NC catalyst can be obtained. Besides, catalysts with different proportions of Co_3O_4 can be obtained by changing the mass ratio of $Co(NO_3)_2 \cdot 6H_2O$ and NC material (30, 40, and 50 wt.%). Co_3O_4@C was also prepared by the similar process.

4 Characterization

The morphologies and surface structures were examined by high-resolution scanning electron microscopy (SEM, ZEISS GeminiSEM 500). The high-resolution transmission electron microscopy (HRTEM) images were obtained by JEOL JEM 2100Plus. Low-temperature N_2 adsorption–desorption isotherms of the materials were measured using a Micromeritics ASAP 2460 instrument. Before testing, the samples were vented at 200 °C for 8 h. The specific surface areas of samples were evaluated by the Brunauer–Emmett–Teller (BET) method. The X-ray diffraction (XRD) patterns of the catalysts were recorded on a Bruker D8 Advance X-ray diffraction diffractometer equipped with Cu Kα radiation (operating conditions, λ = 1.5147 Å, scanning speed of 15(°)/min, 40 kV, and 40 mA). Fourier transform infrared (FTIR) spectra of the catalysts were measured by a Nicolet iS50 spectrometer. X-ray photoelectron spectroscopy (XPS) experiments were carried out with the aid of Thermo Scientific K-Alpha instrument. The content of Co element was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using an Agilent 720ES(OES) instrument.

5 Catalytic activity for FAL hydrogenation

The catalytic hydrogenation of furfural was carried out in a 100 mL magnetic stirring autoclave. In a typical experiment, 1 mmol of furfural, 10 mL of 2-propanol, and 100 mg of catalyst were added into the autoclave. Then, the air in the autoclave was replaced with hydrogen gas for 3 times and retained 1 bar of hydrogen before the reaction. The autoclave was heated at 160 °C for several hours. After the reaction, the reaction mixture was cooled to room temperature and depressurized. Then, the catalyst was separated and dodecane was added into the reaction liquid as internal standard, which was analyzed by gas chromatography (GC, Agilent 7890B GC). The liquid mixtures were quantitatively analyzed by internal standard method. The standard curves of furfural and furfuryl alcohol were shown in Fig. S6.

The conversion (η) was calculated by:

$$\eta/\% = \frac{n_{\mathrm{rf}}}{n_{\mathrm{if}}} \times 100 \tag{1}$$

where n_{rf} is the mole number of reacted furfural, and n_{if} is the mole number of initial furfural.

The selectivity of furfuryl alcohol (S_{fa}) was calculated by:

$$S_{\mathrm{fa}}/\% = \frac{n_{\mathrm{pfa}}}{n_{\mathrm{rf}}} \times 100 \tag{2}$$

where n_{pfa} is the mole number of produced furfuryl alcohol, and n_{rf} is the mole number of reacted furfural.

The yield of furfuryl alcohol (Y_{fa}) was calculated by:

$$Y_{fa}/\% = \frac{n_{pfa}}{n_{if}} \times 100 \quad (3)$$

where n_{pfa} is the mole number of produced furfuryl alcohol, and n_{if} is the mole number of initial furfural.

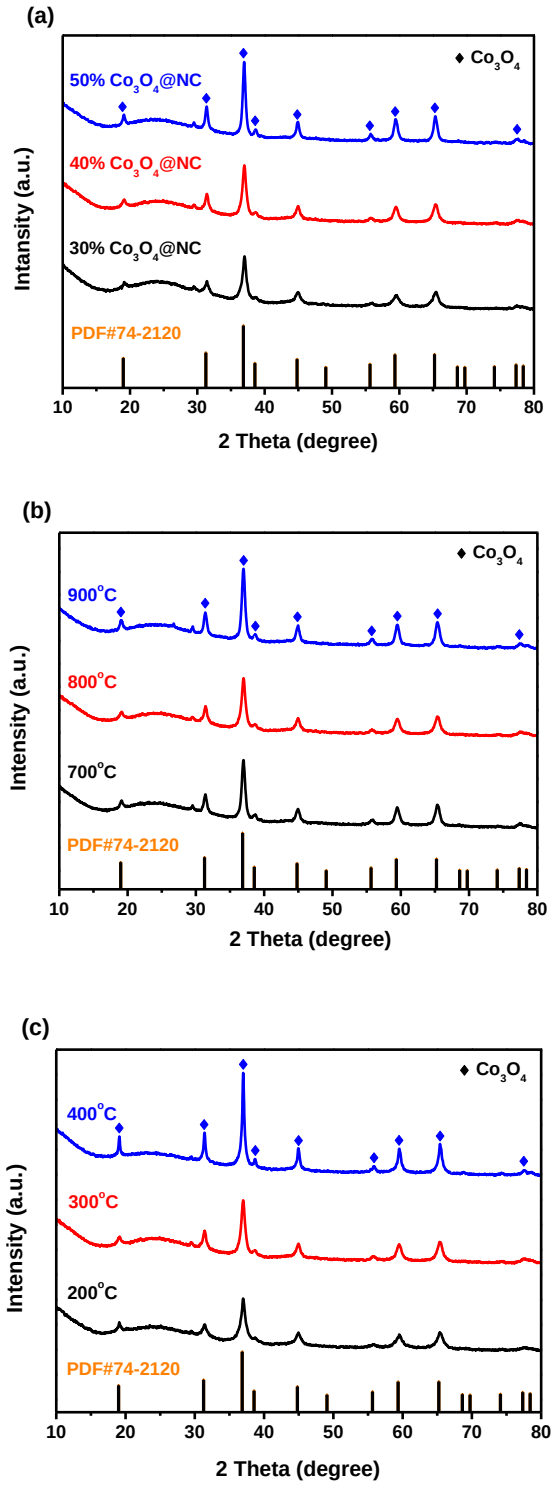


Fig. S1 XRD patterns of different Co_3O_4@NC samples: **(a)** different Co_3O_4 contents; **(b)** different carbonization temperatures; **(c)** different nitrate decomposition temperatures.

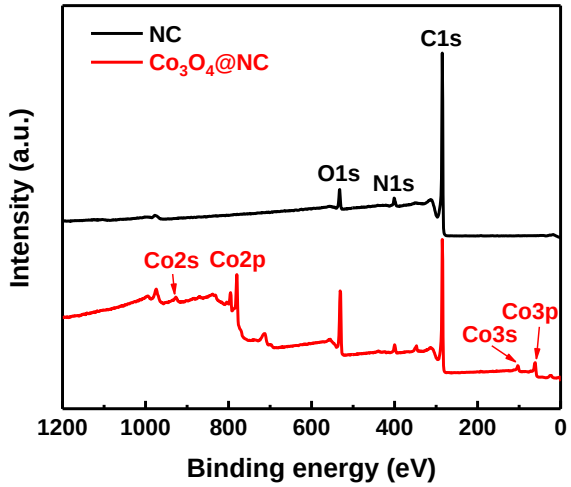


Fig. S2 The XPS survey scan of NC and Co_3O_4@NC.

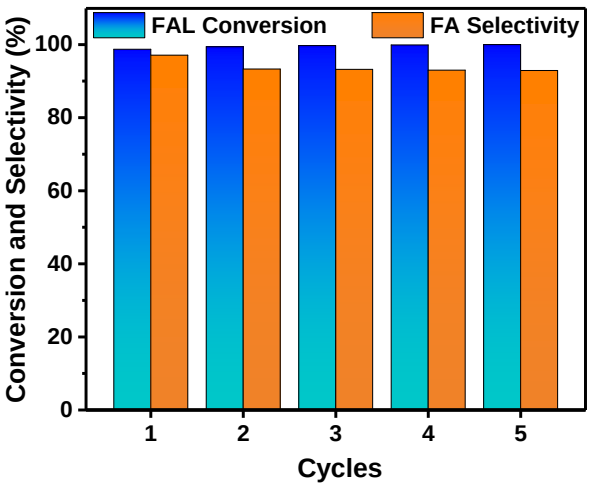


Fig. S3 The reusability of Co_3O_4@NC in the hydrogenation of FAL.

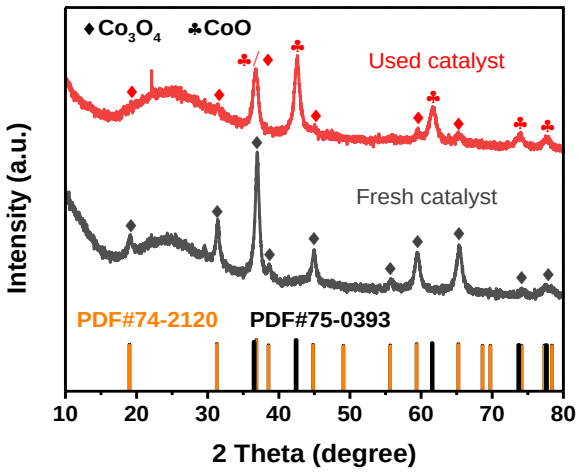


Fig. S4 XRD patterns of Co_3O_4@NC before and after the reaction.

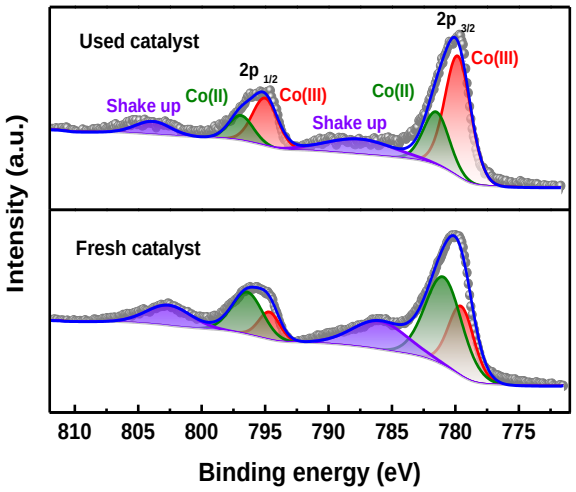
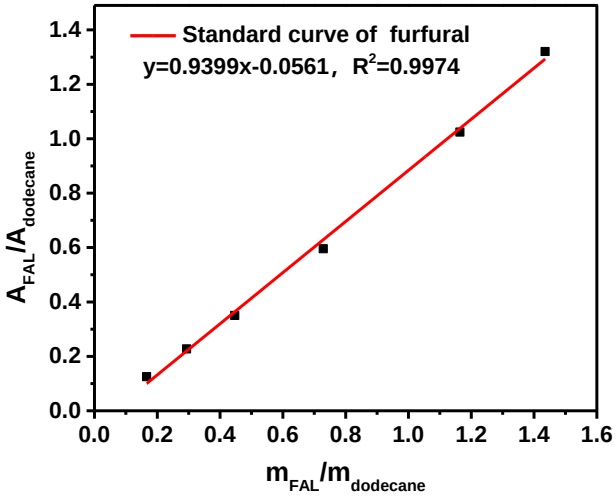


Fig. S5 XPS spectra of Co 2p for Co_3O_4@NC before and after the reaction.



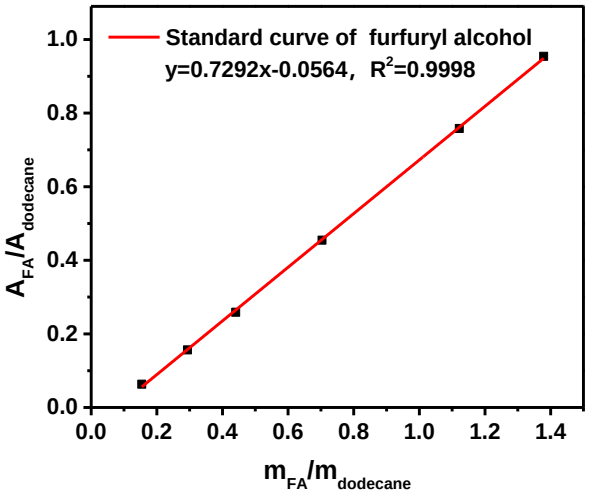


Fig. S6 The standard curve of furfural and furfuryl alcohol.

Table S1 The physical properties of NC and Co_3O_4@NC

Sample	A_{sur}/($m^2 \cdot g^{-1}$)	V_p/($cm^3 \cdot g^{-1}$)	d_{ap}/nm	r_{ap}/nm
NC	221.7	0.06	2.4	8.5
Co_3O_4@NC	242.6	0.12	3.3	11.9

Notes: A_{sur} is the surface area obtained from the N_2 adsorption isotherm; V_p is the pore volume estimated from the BJH adsorption cumulative volume of pores; d_{ap} is the average pore diameter estimated from the adsorption average pore diameter; r_{ap} is the BJH desorption average pore radius.

Table S2 Diameters of metal oxide particles calculated by XRD

Entry	Sample	Diameter/nm
1	30%Co_3O_4@NC	12.0
2	40%Co_3O_4@NC	12.7
3	50%Co_3O_4@NC	16.9
4	40%Co_3O_4@NC/700	14.8
5	40%Co_3O_4@NC/800	12.7
6	40%Co_3O_4@NC/900	15.6
7	40%Co_3O_4@NC-200	11.1
8	40%Co_3O_4@NC-300	12.7
9	40%Co_3O_4@NC-400	20.8

Notes: Entries 1–3 show Co_3O_4@NC catalysts with different Co_3O_4 NP loading (30, 40, and 50 wt.%), in which the NC was carbonized at 800 °C and the Co_3O_4@NC catalyst was pyrolyzed at 300 °C; Entries 4–6 show 40%Co_3O_4@NC catalysts pyrolyzed at 300 °C, with NC carbonized at different temperatures; Entries 7–9 show 40%Co_3O_4@NC catalysts pyrolyzed at different temperatures, with NC carbonized at 800 °C.

Table S3 Results of elemental compositions

Catalyst	Content/mol.%			
	C [a)]	N [a)]	O [a)]	Co [b)]
NC	91.66	3.22	5.12	–
Co_3O_4@NC	57.40	2.95	14.09	25.4

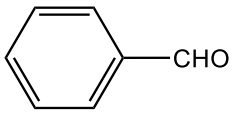
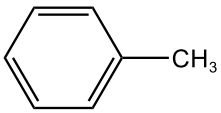
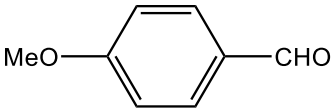
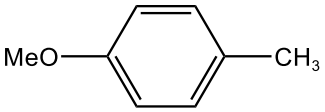
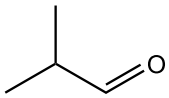
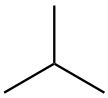
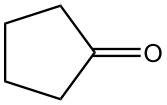
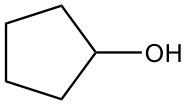
Note: The unit of Co content is wt.%.
a) Measured by XPS. b) Measured by ICP-MS.

Table S4 The effect of valence states of cobalt particles on furfural hydrogenation

Entry	Catalyst	Conversion/%	Selectivity/%			
			FA	THFA	MF	Others
1	Co_3O_4@NC	98.7	97.1	1.6	1.3	0
2	Co@NC	73.2	90.8	1.2	3.2	4.8

Note: Reaction conditions — FAL (1 mmol), catalyst (100 mg), 2-propanol (10 mL), 1 bar H_2, 160 °C, 6 h.

Table S5 The catalytic hydrogenation reaction of different carbonyl compounds over the Co_3O_4@NC catalyst

Entry	Reactant	Product	Time/h	Conversion/%	Selectivity/%
1			8	> 99	> 99
			8	> 99	65.9
3			6	97.3	> 99
4			6	85.3	> 99

Note: Reaction conditions — 1 mmol reactant, 100 mg catalyst, 10 mL 2-propanol, 1 bar H_2, 160 °C.