

Supporting Information

Carbon-supported Co/Co₃O₄ hybrid catalyst: an efficient non-noble metal catalyst for the hydrodeoxygenation of vanillin

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Experimental

Materials.

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, benzimidazole, and all substrates were purchased from Aladdin Chemicals Co. Ltd (Beijing, China). All the solvents were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The commercially available reagents were used directly without further purification.

Catalyst synthesis.

Cobalt (II) benzimidazole complex (ZIF-9) was first synthesized by dissolving cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2.4 mmol) and benzimidazole (4.8 mmol) into 60 mL dimethylformamide (DMF). After being treated in a hydrothermal reactor at 140 °C for 24 h, the cobalt (II) benzimidazole complex was obtained by centrifuging, washing with acetone, and dried at 60 °C overnight. Co/C was then obtained by pyrolysis of cobalt (II) benzimidazole complex ZIF-9 at 500 °C under N_2 atmosphere for 1 h, following evaluating to 750 °C with a ramping rate of 5 °C min^{-1} and staying for 2 h. Afterward, the pyrolysis product was oxidized in air for 24 h to generate Co- Co_3O_4 /C-T (**Scheme 1**).

Catalyst characterizations.

The morphology of all samples is characterized by transmission electronic microscopy (TEM, Tecnai G2 F20 S-TWIN). TEM samples were prepared by picking samples in dilute ethanol suspensions using copper grids. X-ray diffraction (XRD) patterns of all samples are collected on a diffractometer (Bruker D8 ADVANCE) with Cu k_α ($\lambda = 1.5418 \text{ \AA}$). Diffraction patterns were obtained within the 2θ range of 10° to 90° at a scan rate of 4° min^{-1} . XPS data were recorded on an X-ray photoelectron spectrometer (Thermo ESCALAB 250XI). Temperature-programmed reduction (TPR) of catalysts was performed on BELCAT-II with 10 % H_2 /Ar gas as reducing gas (30 mL min^{-1}). The TPR process was conducted from room temperature to 600 °C with a ramp of 10 °C min^{-1} . Inductively coupled atomic emission

spectrometer (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation) was used to determine the Ni content in the catalysts.

Catalytic testing.

Typically, vanillin (0.5 mmol) and the catalyst (20 mg) were introduced into a 20 mL stainless steel autoclave containing the solvent of *i*-PrOH (10 mL) and a magnetic stirrer. The air in the autoclave was removed by the flush of H₂ for several times and then charged to the setting H₂ pressure (1-3 MPa). Then the reactor was heated to a designed temperature and kept for a certain time (2-24 h) under stirring at 1000 RPM. After the reaction, the autoclave was cooled down to room temperature quickly before the deflated process. The products in the reaction mixture were characterized by gas chromatography-mass spectrometry (GC-MS). The conversion of vanillin and the yield of products were calculated according to the calibration curves.

Recycling experiment.

After each experiment, the used catalyst was thoroughly washed with ethyl alcohol, dried in vacuum before the next turn of the HDO of vanillin.

Supplementary Figures

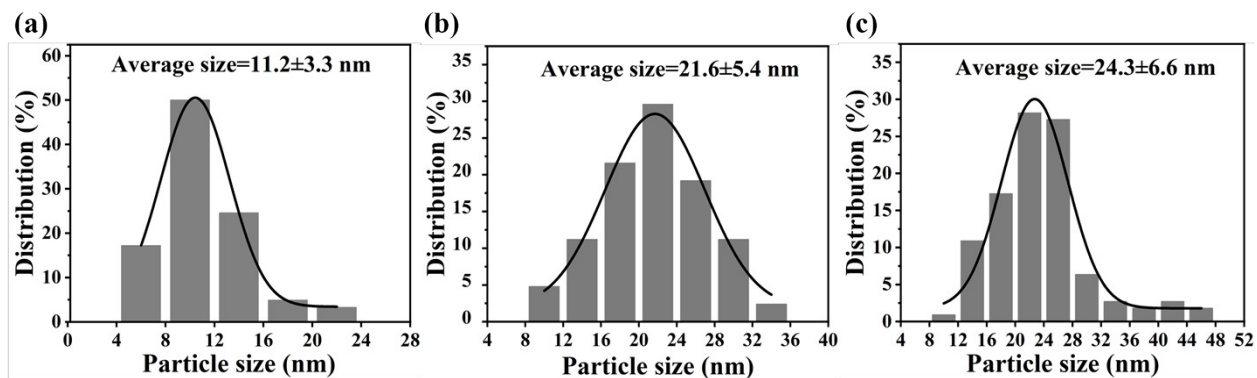


Figure S1. The particle size distribution for (a) Co/C; (b) Co-Co₃O₄/C-230; (c) Co-Co₃O₄/C-250.

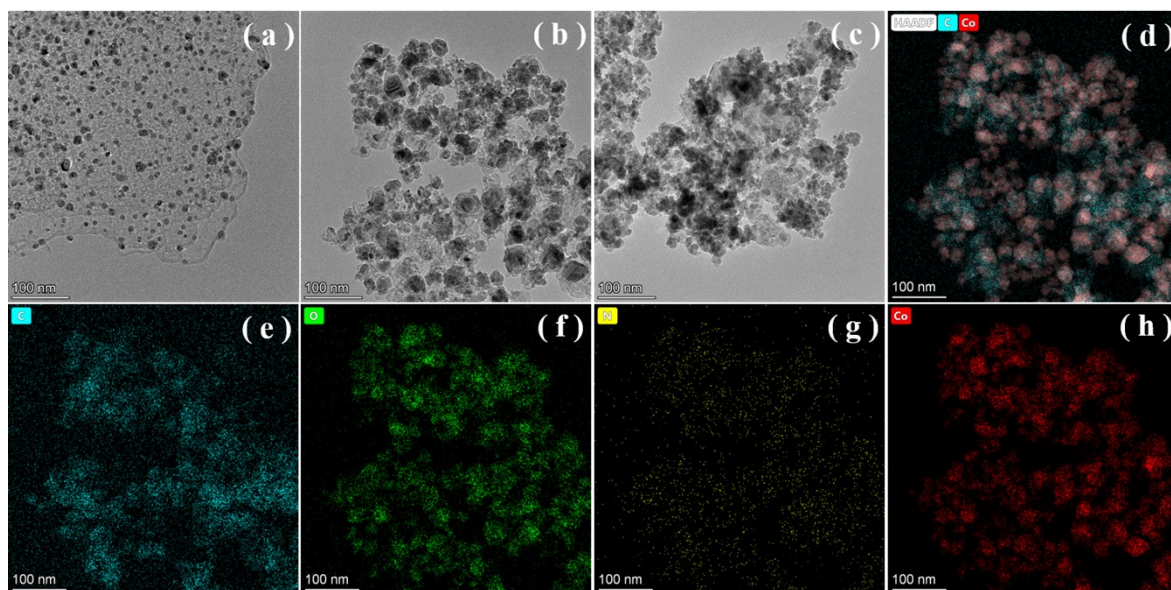


Figure S2. TEM images for Co/C and Co-Co₃O₄/C-T catalysts: (a) Co/C; (b) Co-Co₃O₄/C-230; (c) Co-Co₃O₄/C-250 and energy-dispersive X-ray (EDS) elemental mapping (d-h) images of the Co-Co₃O₄/C-230 catalyst.

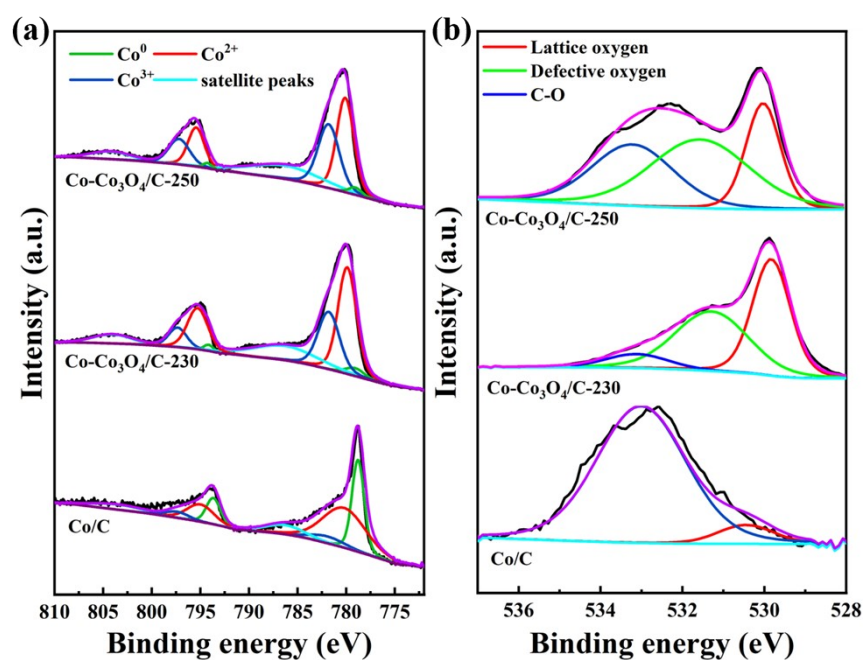


Figure S3. XPS spectra of Co/C and Co-Co₃O₄/C-T. (a) Co 2p, (b) O 1s.

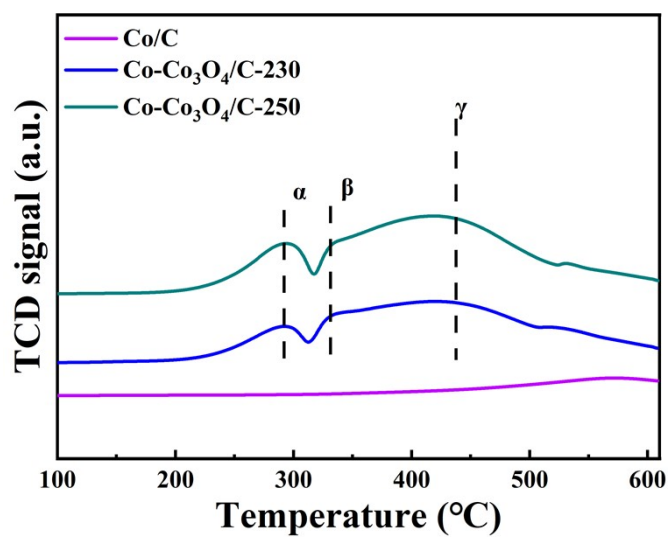


Figure S4. H₂-TPR profiles of the Co/C and Co-Co₃O₄/C-T catalysts.

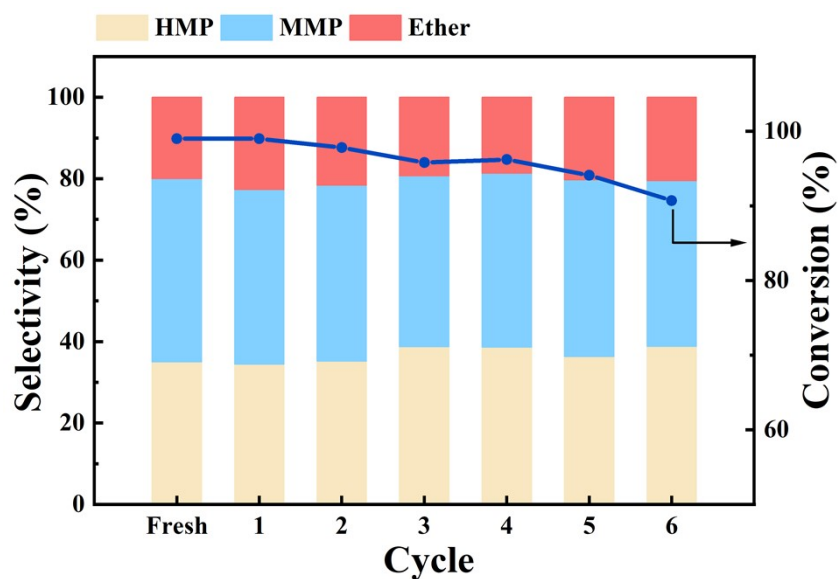


Figure S5. Summary of the results of recycling experiments conducted under H_2 (2 MPa) at 100 °C, reaction time (8 h).

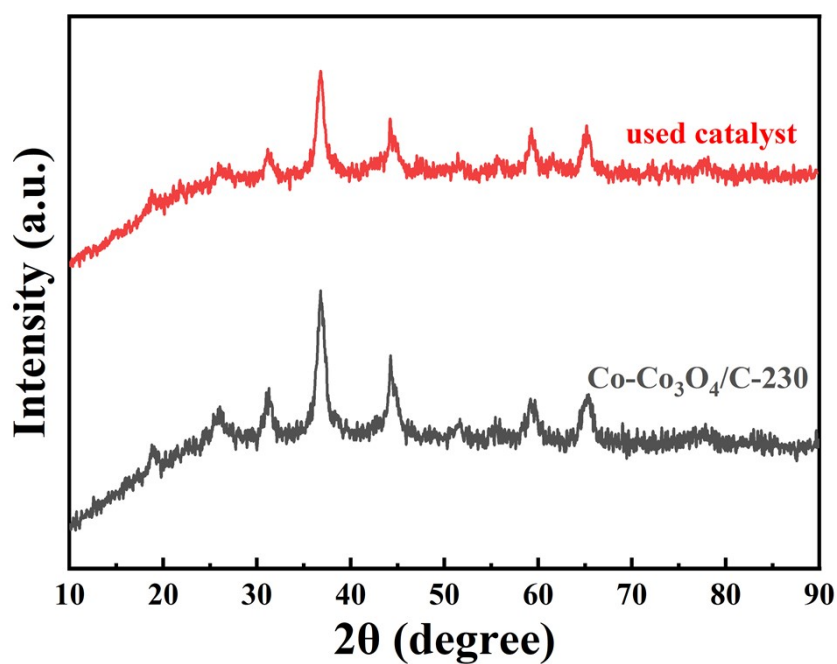


Figure S6. XRD pattern of the fresh and used catalyst.

Supplementary Tables

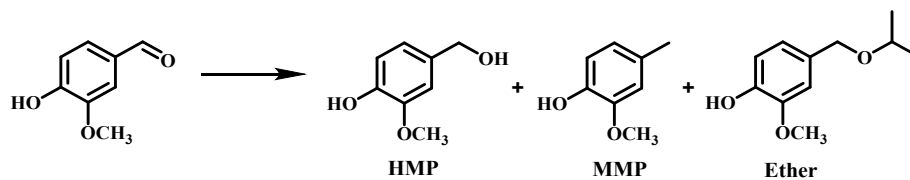
Table S1. Summary of fitting data for the XPS spectrum for Co 2p orbital of Co/C and Co-Co₃O₄/C-T catalysts.

Cat.	2p3/2								2p1/2							
	Co ⁰		Co ²⁺		Co ³⁺		Sat.		Co ⁰		Co ²⁺		Co ³⁺		Sat.	
	(%)	B.E.	(%)	B.E.	(%)	B.E.	(%)	B.E.	(%)	B.E.	(%)	B.E.	(%)	B.E.	(%)	B.E.
Co/C	24.18	778.79	36.30	780.22	5.16	782.02	7.76	786.27	7.96	793.66	9.94	794.99	3.05	797.41	5.64	803.59
Co-Co ₃ O ₄ /C-230	2.53	779.10	33.58	779.9	21.02	781.80	15.55	786.24	1.01	794.16	14.31	795.29	6.03	797.33	5.98	804.06
Co-Co ₃ O ₄ /C-250	1.73	779.05	29.35	780.10	24.52	781.81	17.03	786.26	0.85	794.26	11.52	795.43	9.53	797.19	5.46	804.20

Table S2. Summary of fitting data for the XPS spectrum for O 1s orbital of Co/C and Co-Co₃O₄/C-T catalysts.

Cat.	Lattice oxygen		Defective oxygen (O _v)		C-O		O _v /(O _L + O _{C-O})
	(%)	B.E.	(%)	B.E.	(%)	B.E.	
Co/C	8.10	530.42	\	\	91.90	533.01	\
Co-Co ₃ O ₄ /C-230	45.78	529.83	45.25	531.31	8.97	533.11	0.83
Co-Co ₃ O ₄ /C-250	23.70	530.03	43.81	531.57	32.49	533.22	0.78

Table S3. Optimization of reactions conditions of HDO of vanillin with Co-Co₃O₄/C-230 catalyst^a.



Entry	Solvent	Pressure of H ₂ (MPa)	Conversion (%)	Selectivity (%)		
				HMP	MMP	Ether
1	<i>i</i> -PrOH	2	>99.0	34.2	45.8	20.0
2	EtOH	2	>99.0	20.9	30.5	48.6
3	MeOH	2	>99.0	10.3	7.5	82.2
4	Toluene	2	12.2	100	\	\
5	Hexane	2	54.2	74.8	25.2	\
6	<i>i</i> -PrOH	1	87.1	54.3	32.2	13.5
7	<i>i</i> -PrOH	3	>99.0	25.1	48.7	26.2
8	<i>i</i> -PrOH	N ₂	5.3	\	2.9	2.4

^a Reaction conditions: 10 mL of solvent, 0.5 mmol of vanillin, 20 mg of Co-Co₃O₄/C-230, 2 MPa H₂, 100 °C, 8

h.