

Supporting Information:

Cu^{2+} @Metal-Organic Framework Derived Amphiphilic Sandwich
Catalysts for Enhanced Hydrogenation Selectivity of Ketenes at
Oil-Water Interface

Jia-Lu Sun, Feng-Di Ren, Yu-Zhen Chen* and Zhibo Li*

*College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao
266042, Shandong, P. R. China*

E-mail: yzchen@qust.edu.cn

1 Materials and Instrumentation.

Cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%), copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99%), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99%), zinc(II) nitrate tetrahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%), terephthalic acid (>99.0%), methanol (>99%), 2-methylimidazole (>98.0%), ethanol (>99%), ethyl acetate ($\geq 99.5\%$) and dichloromethane ($\geq 99.5\%$) were provided by Sinopharm Chemical Reagent Co., Ltd. Multifarious alkene compounds with high-purity were bought from Energy Chemical. All chemicals were obtained from commercial sources and used without further purification. Distilled water with the specific resistance of $18.25 \text{ M}\Omega \cdot \text{cm}$ was produced by reversed osmosis followed by ion-exchange and filtration (Cleaned Water Treatment Co., Ltd., Qingdao). All reactions were heated by metal sand bath (WATTCAS, LAB-500, <https://www.wattcas.com>). Column chromatography was performed on silica gel (200-300 mesh).

The authors would like to thank Shiyanjia Lab (www.shiyanjia.com) for the materials characterization. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo ESCALAB 250Xi high-performance electron spectrometer using monochromatized AlK α ($h\nu = 1486.7 \text{ eV}$) as the excitation source. Power X-ray diffraction (PXRD) were measured on a Rigaku Saturn 70 diffractometer at 113 K with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Nitrogen sorption measurements were conducted using a Micromeritics ASAP 2020 system at 77 K. Transmission electron microscopy (TEM) images were acquired on JEOL-2010 with an electron acceleration energy of 200 kV. Scanning electron microscopy (SEM) was conducted using a Zeiss Supra 40 at an acceleration voltage of 5 kV. Reaction yields were traced by gas chromatography (GC, Panna A91 Plus). The content of Cu, Fe and Co in samples was analyzed by an Agilent ICP-

OES 730 inductively coupled plasma atomic emission spectrometer (ICP-AES). Static water/oil contact angles were measured at room temperature using an Optical Contact Angle & Interface Tension Meter SL200KL. Once a drop of water or oil was deposited on sample surface and the contact angle parameter determined from pictures was immediately recorded.

2 Preparation of catalysts.

2.1 Preparation of ZIF-67 polyhedrons: We adopted a typical approach to prepare ZIF-67.¹ 0.45 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 3 mL of distilled water and mixed with a solution of 2-methylimidazole (5.5 g) in 20 mL of water, then vigorously stirred for 6 h at room temperature (20 °C). The purple products were collected after centrifugation; the product was adequately washed at least three times with water and methanol and finally dried under vacuum at 75 °C for 12 h.

2.2 Preparation of ZIF-8 nanocrystals: A mixture of 80 mL methanol with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.68 g) was added to another 80 mL of methanol with 3.70 g of 2-methylimidazole and stirred for 24 h.² The white powder was obtained from solution via centrifugation, washed thoroughly with methanol three times, and dried in vacuo at 75 °C.

2.3 Preparation of BMZIF-5: The synthetic procedure of BMZIF-5 was similar to the preparation of ZIF-8. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with a $\text{Co}^{2+}/\text{Zn}^{2+}$ molar ratio of five was dissolved in 80 mL of methanol.³ Another solution with 2-methylimidazole (3.70 g) and 80 mL methanol was added into the above solution and stirred for 24 h at room temperature. The total mole of (Zn + Co) was fixed at 5.65 mmol. The purple material was collected by centrifugation and washed

with methanol three times, dried under vacuum at 75 °C overnight. BMZIF-5 powder was dried at 200 °C under vacuum for 24 h prior to use.

2.4 Preparation of Fe-MIL-88A: $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (800 mg, 2 mmol) and fumaric acid (210 mg, 1.8 mmol) were dissolved in 40 mL of N,N-dimethylacetamide (DMA).⁴ The mixture heated for 30 min at 110 °C, then cooled to room temperature. The product was collected after centrifugation, washing with DMA and methanol three times. Finally, the Fe-MIL-88A product was dried under vacuum at room temperature overnight.

2.5 Preparation of Cu@Co@GC/NC and Cu@Fe@GC/C: Activated Cu^{2+} @BMZIF-5 powder (500 mg) was heated to 250 °C for 5 h at a heating rate of 5 °C/min under flowing 20% H_2/Ar atmosphere, further pyrolyzed at 500 °C for 2 h, followed by calcination at 800 °C for 2 h to obtain the final derived carbon materials. To examine the generality of the synthetic protocol, Cu^{2+} @Fe-MIL-88A was further employed to synthesize Cu@Fe@GC/C.

2.6 Preparation of CuCo@GC/NC: Activated Cu^{2+} @BMZIF-5 powder (500 mg) was heated to 500 °C for 2 h at a heating rate of 5 °C/min under flowing 20% H_2/Ar , pyrolyzed by calcination at 800 °C for 2 h at the same condition and finally cooled to room temperature naturally to obtain CuCo@GC porous carbon materials.

2.7 Preparation of Cu/NC and Co@GC/NC: The 500 mg of activated Cu^{2+} @ZIF-8 or BMZIF-5 was heated to 250 °C for 5 h followed by 500 °C for 2 h at a heating rate of 5 °C/min under flowing 20% H_2/Ar atmosphere; and then the materials were heated to 800 °C and remained there for 2 h. After cooling to room temperature, Cu@NC or Co@GC/NC was obtained.

2.8 Preparation of Cu@Co/BMZIF-5: The BMZIF-5 and a certain amount of $\text{Cu}^{2+}/\text{Co}^{2+}$ precursors were added into aqueous solution (20 mL) containing NH_3BH_3 (30 mg). During hydrolysis, Cu

ions were first reduced to give Cu(0) NPs as cores followed by subsequent reduction of Co^{2+} to provide Co NPs as outer shell. Then the Cu@Co/BMZIF-5 catalyst was obtained.

3 Catalytic Activity Evaluation.

3.1 Catalytic Study of Cu@Co@GC/NC, Cu/NC, Co@GC/NC, CuCo@GC/NC and Cu@Co/BMZIF-

5 Catalysts Toward Dehydrogenation of Ammonia Borane: At moderate temperature, Cu@Co@GC/NC and 20 mL of ultrapure water were put in a round-bottomed flask (25 mL). The reaction was carried out when 30 mg of NH_3BH_3 was placed into above flask under constant stirring. To examine the stability of catalysts, another 30 mg of NH_3BH_3 was replenished under the same reaction conditions. For comparison, Cu/NC, Co@GC/NC, CuCo@GC/NC or Cu@Co/BMZIF-5, were investigated for catalytic activity while retaining all other reaction conditions. General isolated procedure products: i) After completion of the reaction indicated by GC, the resulting mixture was extracted with ethyl acetate; ii) The combined organic layers were dried with anhydrous Na_2SO_4 , and then concentrated under vacuum to remove the solvent; iii) The residue was purified by column chromatography on silica gel, and eluting with n-hexane to obtain the product.

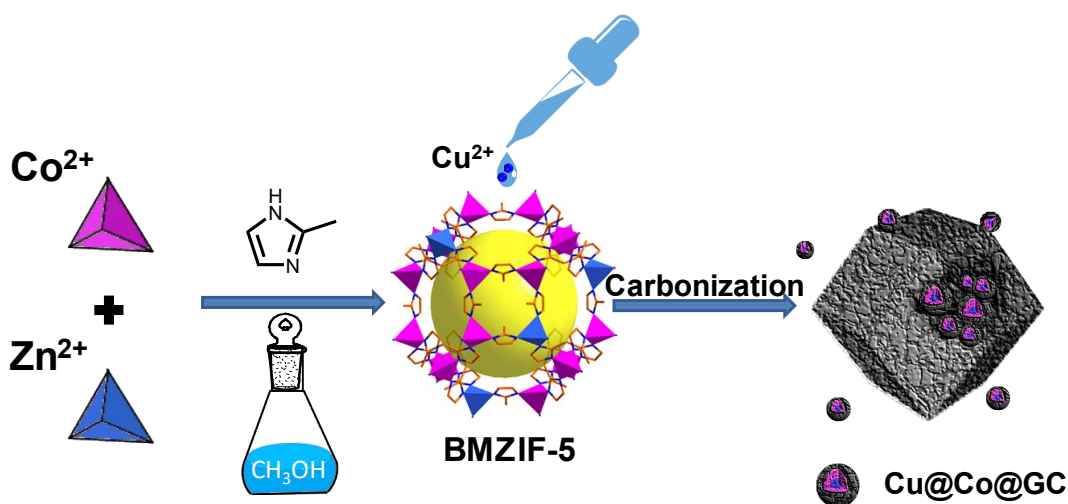
3.2 Catalytic Performance Test of Cu@Co@GC/NC, Cu/NC, Co@GC/NC, CuCo@GC/NC and

Cu@Co/BMZIF-5 Catalysts Toward Chemo-selective Hydrogenation Reactions: The catalyst (50 mg), olefine compound (0.5 mmol) and ultrapure water (20 mL) were highly dispersed in a 25 mL round-bottomed flask. The reaction started when NH_3BH_3 (30 mg) was added to the flask with high-speed stirring under 50 °C. The olefine hydrogenation yield was determined using GC-

Panna A91 Plus analysis. Otherwise, to test the reusability of Cu@Co@GC/NC, the same amount of NH_3BH_3 (30 mg) and olefin compound (0.5 mmol) were put into the recycled reaction solution to start the reaction.

3.3 Catalytic Performance Test of Cu@Co@GC/NC Catalyst Toward the CO Oxidation

Reaction: 25 mg of Cu@Co@GC/NC catalyst was placed in a thin quartz tube filled with the mixed reaction gas (1% CO/Dry air) at a gas flow rate of 30 mL/min. The catalytic system warmed up to the target reaction temperatures at a heating rate of 2 °C/min and kept constant for 30 min to reach a steady state. In the meantime, the composition of effluent gas was on-line identified with Panna A91 Plus gas chromatograph. The CO conversion was calculated based on the CO concentration change in the outlet gases.



Scheme S1. The synthesis process for Cu@Co@GC/NC by a simple calcination of Cu^{2+} @BMZIF-5 at designed temperature under H_2/Ar atmosphere.

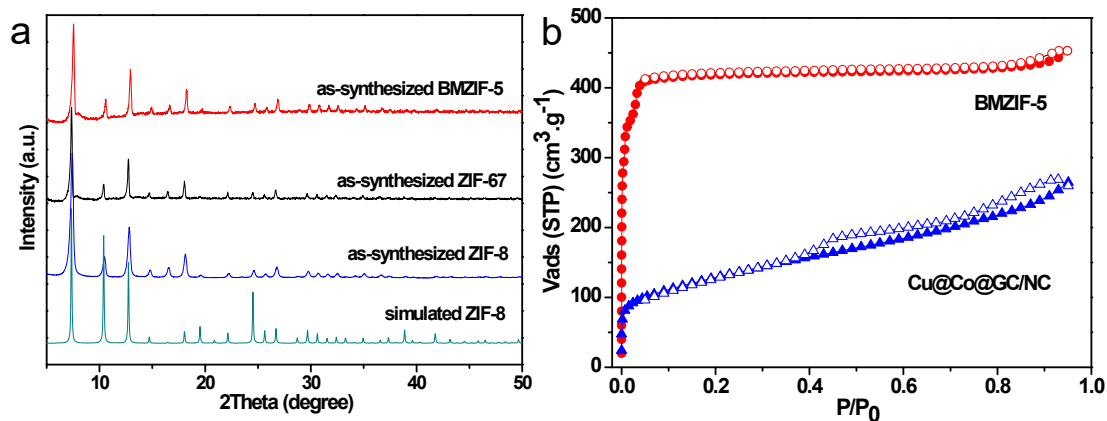


Fig. S1 (a) Powder X-ray diffraction (PXRD) patterns for as-synthesized MOFs. (b) N₂ sorption isotherms for BMZIF-5 and Cu@Co@GC/NC.

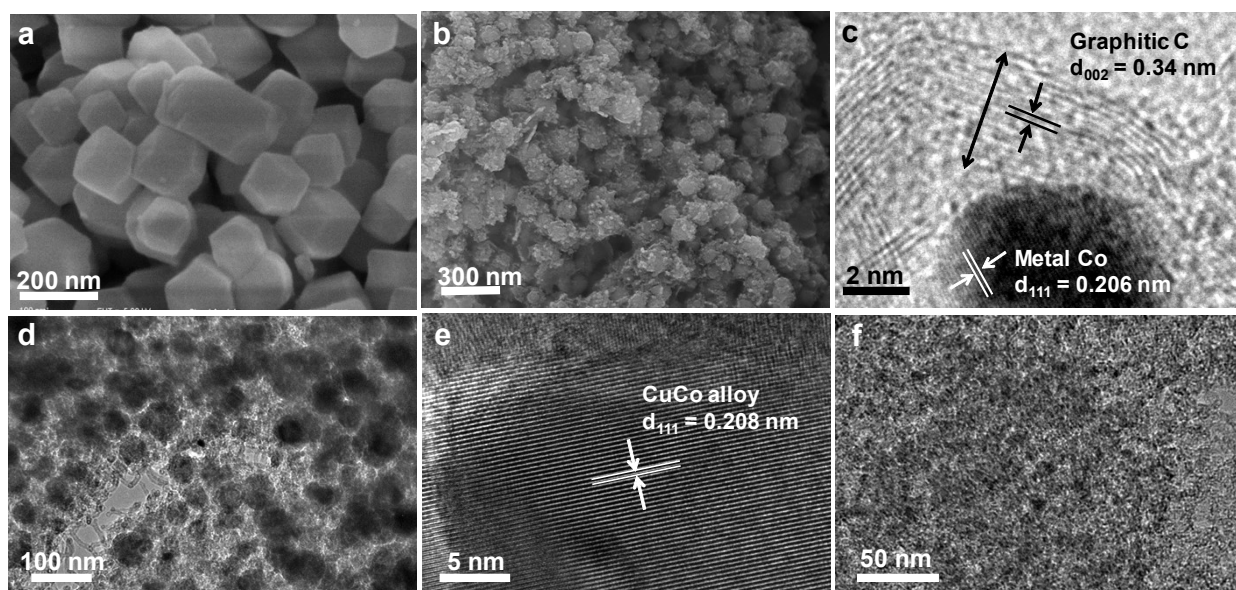


Fig. S2 SEM images of (a) BMZIF-5, (b) Cu@Co@GC/NC. (c) HRTEM image of carbon shell around Cu@Co NP in Cu@Co@GC/NC, showing Cu@Co NP was tightly wrapped by the well-developed graphitization layers. (d) TEM image of CuCo@GC/NC. (e) HRTEM image of CuCo@GC/NC. (f) TEM image of Cu/NC.

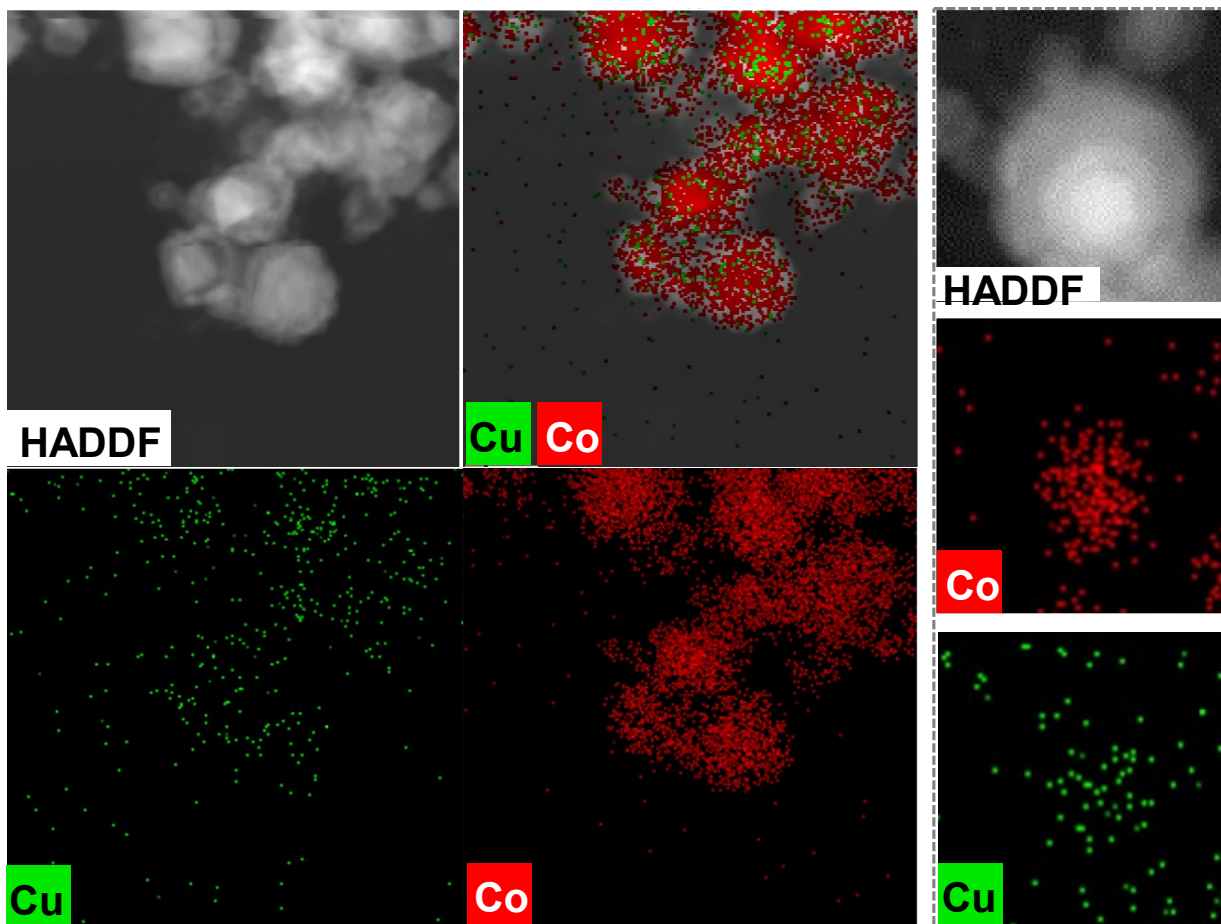


Fig. S3 HAADF-STEM image of Cu@Co@GC/NC and the corresponding element mappings of Cu and Co.

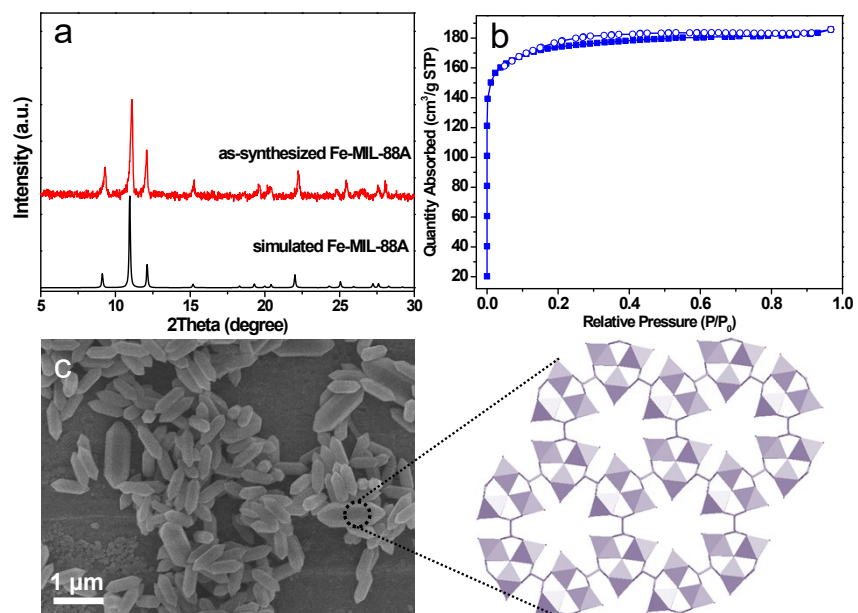


Fig. S4 (a) PXRD patterns, (b) N₂ sorption isotherms and (c) SEM image and the structure for as-synthesized Fe-MIL-88A.

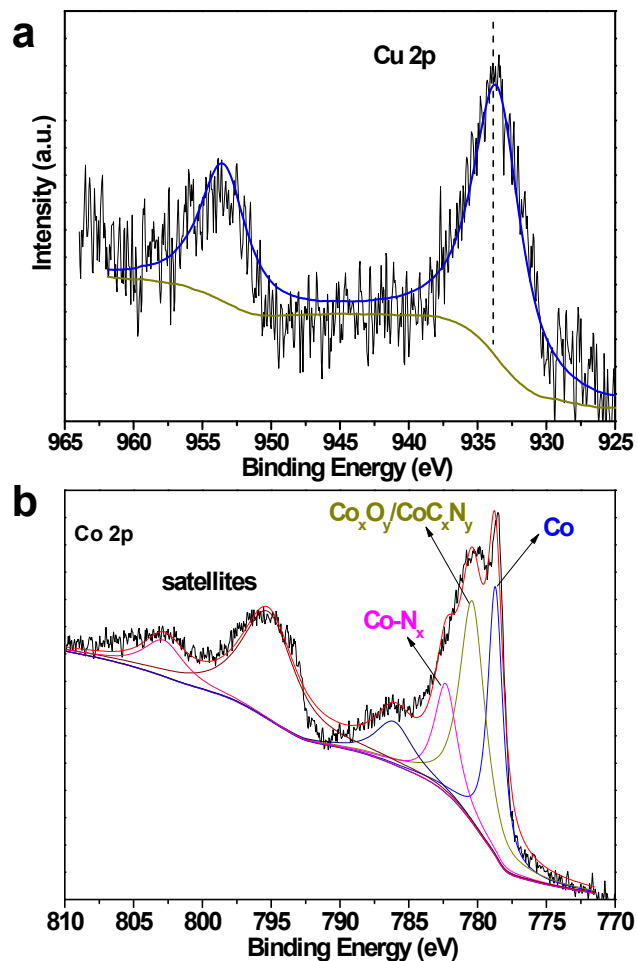


Fig. S6 X-ray photoelectron spectroscopy (XPS) spectra of (a) Cu 2p and (b) Co 2p for as-synthesized Cu@Co@GC/NC.



Fig. S7 The wettability of Cu@Co@GC/NC in a biphasic solution ($V_{H_2O}/V_{oil} = 1:1$) before and after 2 days, the organic upper layer (ethyl acetate or n-hexane) and aqueous bottom layer (water).

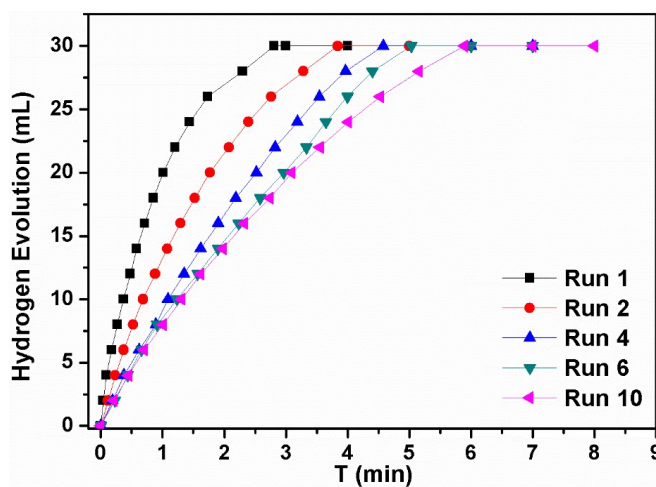


Fig. S8 Recycling performance for the hydrogen generation from an aqueous NH_3BH_3 solution (15 mg in 20 mL H_2O , $T = 25\text{ }^\circ\text{C}$) over the Cu@Co/NC .

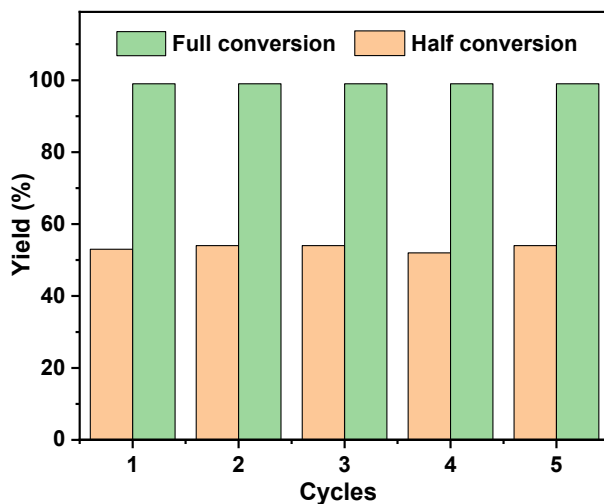


Fig. S9 Recycling stability of Cu@Co@GC/NC toward the cascade reaction of the hydrolysis of NH_3BH_3 and hydrogenation of styrene. Reaction conditions: 0.5 mmol styrene, 30 mg NH_3BH_3 , 50 mg Cu@Co@GC/NC , 20 mL H_2O , and $T = 50\text{ }^\circ\text{C}$.

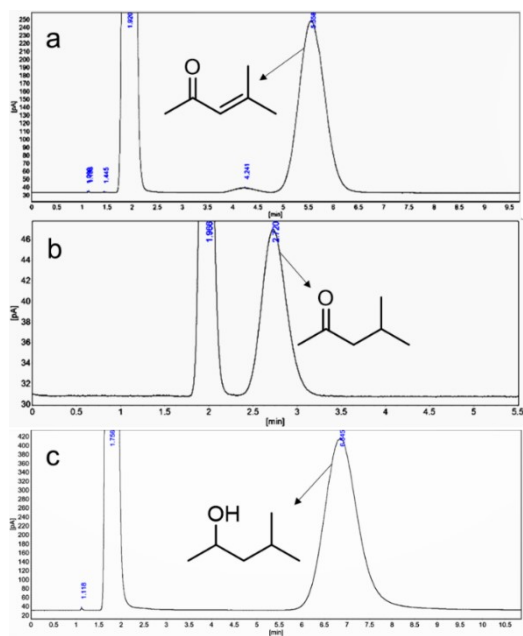


Fig. S10 Gas chromatography (GC) spectra of (a) 4-methyl-3-penten-2-one, (b) 4-methyl-2-pentanone, and (c) 4-methyl-2-pentanol, respectively.

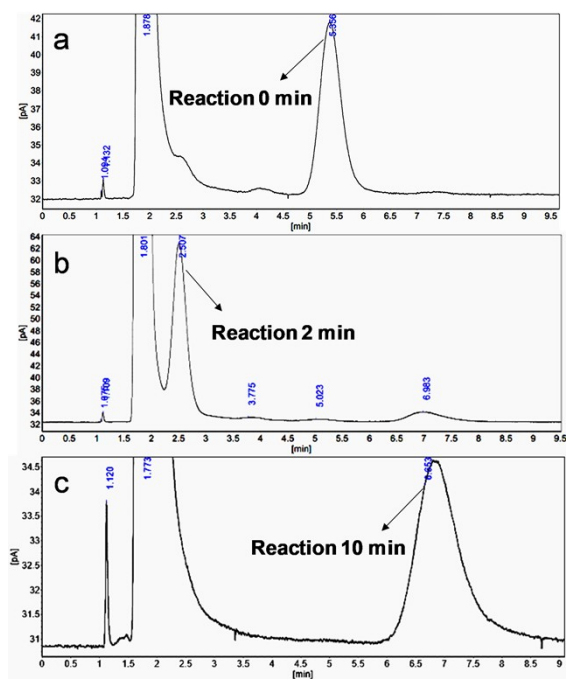


Fig. S11 Gas chromatography (GC) spectra of 4-methyl-3-penten-2-one catalyzed by Cu@Co@GC/NC at (a) 0 min, (b) 2 min and (c) 10 min, respectively.

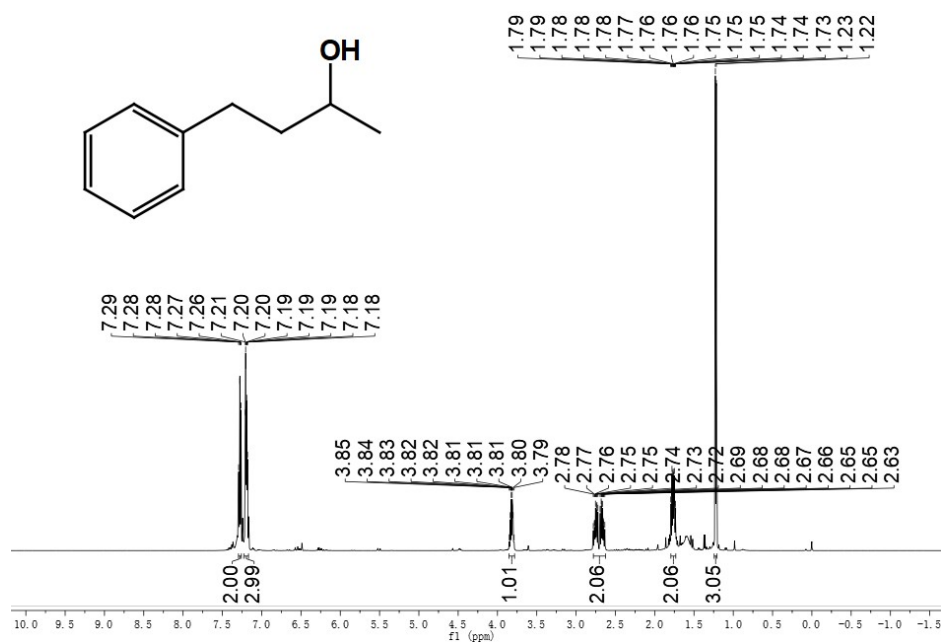


Fig. S12 Nuclear magnetic resonance (NMR) for product. Reaction conditions: 0.25 mmol methyl cinnamate, 20 mg NH_3BH_3 , 20 mg Cu@Co@GC/NC , 2 mL H_2O , 50 °C, 40 min.

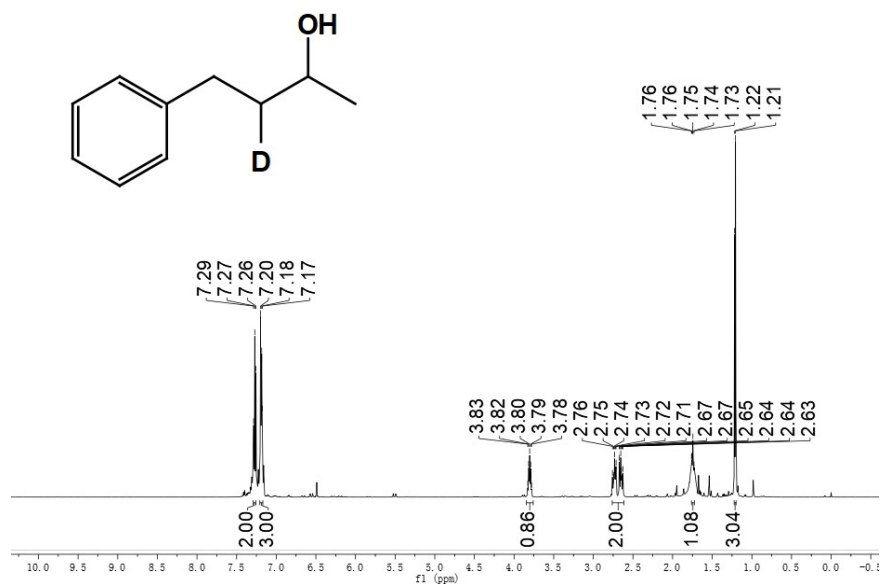


Fig. S13 Nuclear magnetic resonance (NMR) for product. Reaction conditions: 0.25 mmol methyl cinnamate, 20 mg NH_3BH_3 , 20 mg Cu@Co@GC/NC , 2 mL D_2O , 50 °C, 40 min.



Fig. S14 Metal sand bath (WATTCAS, LAB-500).

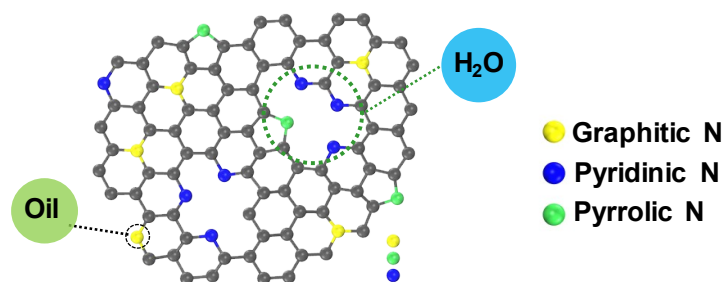
Table S1. Inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis result for samples. The results have confirmed that the actual contents of Cu, Co are close to the nominal values.

Sample	Low percentage			High percentage	
	Cu (wt%)	Co (wt%)	Zn (wt%)	Cu (wt%)	Co (wt%)
Cu@Co@GC/NC	1.83	46.54	0.039	24.38	46.54
CuCo@GC/NC	2.05	45.62	0.028	-	-
Co@GC/NC	-	47.22	0.036	-	-

Table S2. The peak positions of different N types and their relative atomic ratios based on XPS analyses for Cu@Co@GC/NC sample.

Structure	Graphitic-N	Pyridinic-N	Pyrrolic-N	Co-N _x
BE (eV)	401.3	398.9	400.9	399.3
Area	1075.56	633.17	101.88	87.53
Ratio (%)	56.7	33.3	5.4	4.6

Table S3. The total adsorption energy of styrene and H₂O molecules on the NG systems with the basis set superposition error (BSSE) correction at the M06-2X/6-31(d,p) level.



Adsorbed molecule	Graphitic-N	Pyridinic-N	Pyrrolic-N
	Inter. (eV)	Inter. (eV)	Inter. (eV)
Styrene	-0.55456814	-0.10189255	-0.23684597
H ₂ O	-0.43408052	-0.41992546	-0.3097256

Table S4. Performance comparison of Cu@Co@GC/NC with previously reported catalysts for the selective hydrogenation of C=C in ketene compounds.

Catalyst	Sol.	Con. (%)	Sel. (%)	Yield (%)	Ref.
Cu@Co@GC/NC	H ₂ O	100	100	100	This work
Au/Fe ₂ O ₃	ethanol	48.2	25.3	12.2	1
1,3,2-diazaphospholene	CH ₃ CN	-	-	81	2
Pd/N,O-Carbon	Toluene	100	99	99	3
10 wt% Pd/C	EtOAc	50	73	37	Commercially available
Pd nanocatalyst	H ₂ O	55	99	55	4
Cu ₅₀ Pd ₅₀ /C ₃ N ₄	MeOH/H ₂ O	50	99	50 (5h)	5
Cu NPs/CB	Dioxane	-	-	90 (80 °C)	6
Amorphous Ni-P	H ₂ O	89.6	71.9	64.4	7

3-Pt/MOF	isopropanol	53	58.6	31	8
MIL-101(Cr)@Pt	THF	45.0	40.0	18	9

4 References

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