Supporting Information

Hydrogen-catalyzed acid-transformation for the hydration of alkenes and epoxy alkanes over Co-N frustrated Lewis pair surface

Qiang Deng[1]†, Xiang Li[1†], Ruijie Gao[2,3]†, Jun Wang[1], Zheling Zeng[1], Ji-Jun Zou[2]*, Shuguang Deng[4]*, Shik Chi Edman Tsang[5]*

[1]School of Resource, Environmental and Chemical Engineering, Nanchang University, Nanchang 330031, PR China

[2]School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China

[3]Engineering Research Center of Nano-Geomaterials of Ministry of Education, China University of Geosciences, Wuhan 430074, PR China

[4]School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ 85287, USA

[5]Wolfson Catalysis Centre, Department of Chemistry, University of Oxford, Oxford OX1 3QR, UK

*Corresponding Authors. E-mail: edman.tsang@chem.ox.ac.uk; Shuguang.Deng@asu.edu; jj_zou@tju.edu.cn.

† The authors contributed equally to this work.

Materials

Potassium hexacyanocobaltate (III) ($K_3Co(CN)_6$), zinc chloride ($ZnCl_2$), 3-chlorostyrene, 2-chlorostyrene, cyclohexene, cyclohexanol, 1-methyl cyclohexene, 3-carbonyl cyclohexene, 1-phenyl-1-cyclohexene, 1-(2-cyclohexanone)-cyclohexene, cyclopentene, cyclooctene, cyclododecene, 1-hexene, epoxy styrene, cyclohexene epoxide, epoxyethane, 2-(chloromethyl)oxirane, epoxypropane, ethylethylene oxide, pentane, sulphuric acid, sulfolane and acidic resin amberlyst-15 were supplied by Aladdin Reagent Company. Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly-(ethylene glycol) (P_{123}, average molecular weight=5800), ethanol, n-hexane, deuterium oxide (D_2O), trimethylphosphine oxide (TMPO), D_6-benzene, and cobaltous nitrate ($Co(NO_3)_2$) were purchased from Sigma-Aldrich. All chemicals were used without further purification. Acidic zeolites Hβ (SiO_2/Al_2O_3 = 25), and HZSM-5 (SiO_2/Al_2O_3 = 27) were obtained from Nankai Catalysts Co., China, and calcined in air for 3 h at 580 °C before the use.

Characterizations

The powder X-ray diffraction patterns of the samples were characterized on a Panalytical Empyrean diffractometer with monochromatized Cu-Kα radiation. The elemental contents of Co and Zn were determined by inductively coupled plasma optical emission spectrometry on a PerkinElmer Optima 8000 spectrometer. The contents of C and N elements were determined by an elemental analyzer (Vario MICRO). The morphology of all as-synthesized samples was determined by a JEM-2100 transmission electron microscope and a JEOL ARM 200F aberration-corrected high-angle annular dark-field scanning transmission electron microscope. X-ray photoelectron spectroscopy data were measured on an ESCALAB 250Xi instrument using Al Kα

radiation. The specific surface area was obtained from the results of N_2 physisorption at 77 K at -196 °C on an ASAP 2046 surface analyzer by using the Brunauer-Emmett-Teller (BET) method. Raman spectra were collected using a HR Evolution Raman microscope with 473 nm (1.96 eV) laser excitation. The Co K-edge X-ray absorption near edge structure (XANES) was documented in the fluorescence mode. Co K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) experiments were carried out at beamline BL07A1 of the National Synchrotron Radiation Research Center (NSRRC), China. EXAFS data were collected by a Si (111) double-crystal monochromator. XANES and EXAFS data reduction and analysis were processed by Athena software. D_2-H_2O exchange was actualized in a fixed bed reactor equipped with an 8.0 mm (inner diameter) quartz tube. 20 mg of Co-NC catalyst was pretreated in 30 mL/min N_2 at 150 °C for 1 h. Then, the gas was transferred to a mixture of D_2 (6 mL/min), H_2O (6 mL/min), and N_2 (18 mL/min) to start the D_2-H_2O exchange reaction at a defined temperature (i.e., 120, 150 °C). The outlet gases were monitored by an online MS.

The in situ attenuated total reflection infrared (ATR-IR) measurement was acquired with a Nicolet iS 50 spectrometer equipped with a highly sensitive MCT detector and a heating chamber equipped with CaF windows. An ethanol suspension of Co-NC was added dropwise onto the surface of the diamond probe equipped on the instrument, dried at 150 °C, and the background spectrum was recorded. ATR-IR spectra were recorded by averaging 32 scans at a resolution of 2 cm^{-1}. Then, a D_2/Ar gas stream was inlet with a flow rate of 20 mL/min at 150 °C, and the in situ spectrum of D_2-activated Co-NC was recorded. Subsequently, D_2O was introduced by bubbling with an Ar gas stream (20 mL/min), and the spectrum of D_2-D_2O-activated Co-NC was obtained.

The acid and base strength was characterized by determining the temperature-programmed desorption of ammonia and carbon dioxide on a Micromeritics AutoChem II 2920 instrument. For the H_2-H_2O-activated sample, Co-NC was pretreated in a tubular furnace at 150 °C for 1 h in a mixed atmosphere of H_2-H_2O (volume ratio of 1:1). Acid properties were analyzed by the infrared spectroscopy of adsorbed pyridine using a Thermo Fisher Nicolet iS50 FTIR spectrometer. The sample was tabled to a wafer (10 mg/cm^2) and degassed under vacuum at 120 °C for 1 h, and pyridine adsorption was performed at 60 °C for 30 min. Then, the temperature was gradually increased to 150 and 250 °C, and the spectra were recorded. The signals detected at 150 and 250 °C were attributed to total acid sites and strong acid sites, respectively. Meanwhile, the acid type can also be monitored by reference to the ^{31}P NMR chemical shift of chemisorbed trimethylphosphineoxide on the acidic samples. Typically, a mixture of 0.05 g of Co-NC, 0.02 g of TMPO and 20 mL of pentane was stirred for 2 h and then dried at 50 °C under vacuum. ^{31}P nuclear magnetic resonance (NMR) spectra were obtained on a Bruker 400 MHz NMR spectrometer.

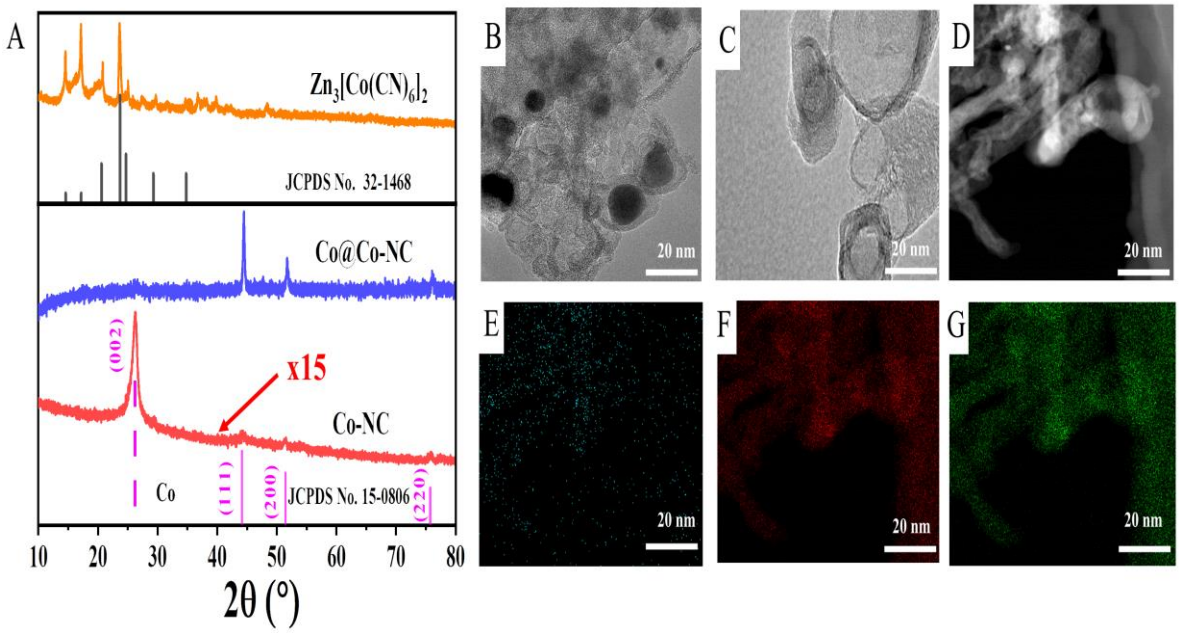


Figure S1. XRD patterns of (A) $Zn_3[Co(CN)_6]_2$, Co@Co-NC and Co-NC. TEM micrographs of (B) Co@Co-NC, (C, D) Co-NC, EDS mappings of Co (E), N (F) and C elements (G).

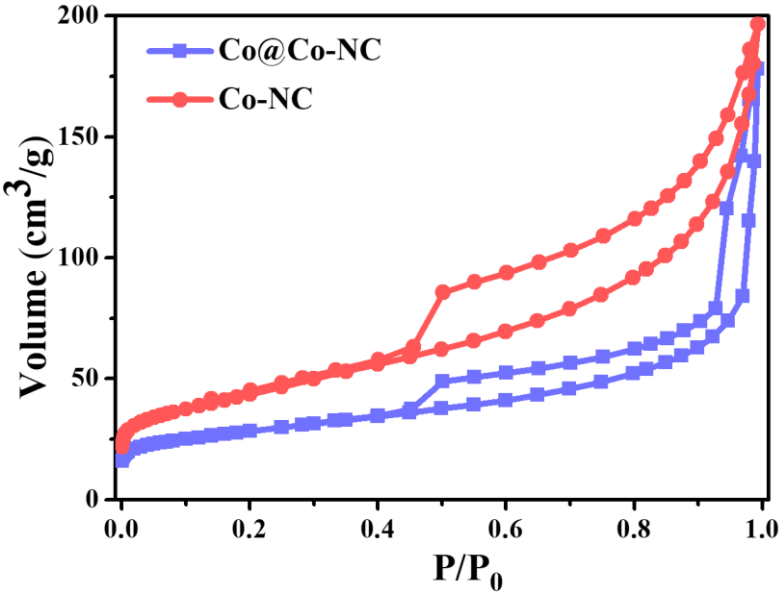


Figure S2. N_2 adsorption and desorption isotherms of Co@Co-NC and Co-NC.

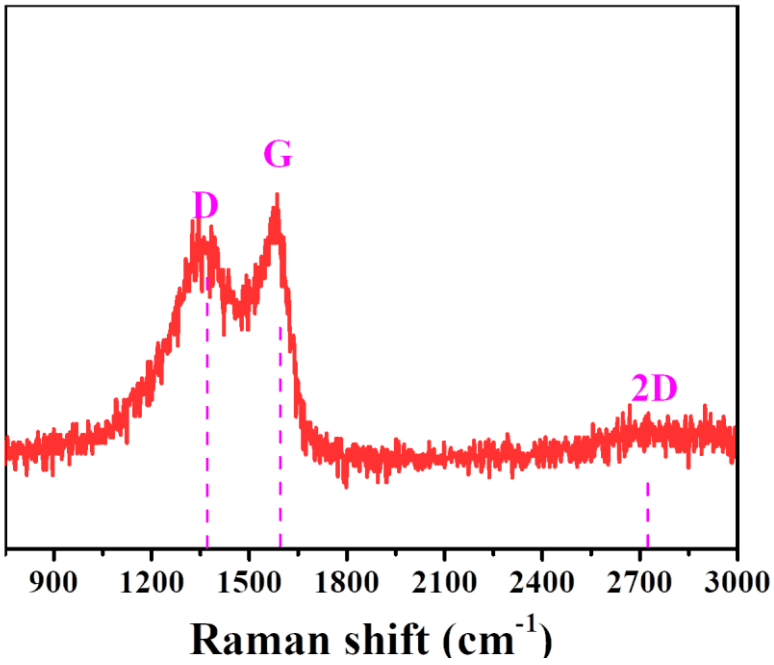


Figure S3. Raman spectra of the Co-NC.

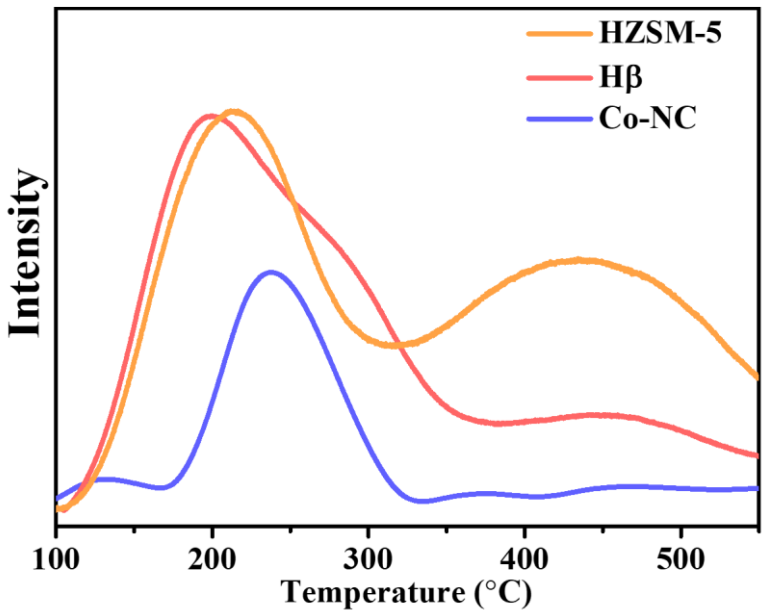


Figure S4. NH_3-TPD profiles of various solid acids.

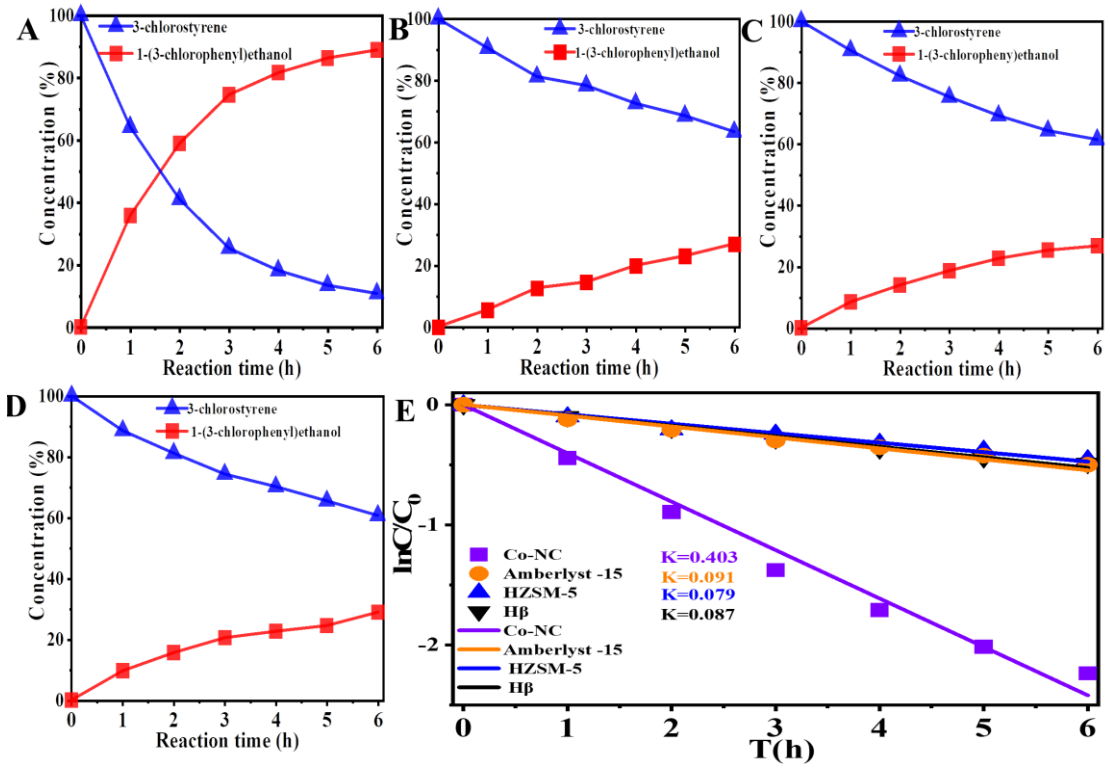


Figure S5. Time-dependent product concentration distribution (A, B, C, D) and kinetics studies (E) for hydration of 3-chlorostyrene. Reaction conditions: 3-chlorostyrene (10 mmol), water (10 mL); catalyst (Co-NC 50 mg, ZSM-5 19.2 mg, Hβ 23.6 mg, Amberlyst-15 2 mg), 150 °C, 4.0 MPa H_2, (A) Co-NC; (B) HZSM-5; (C) Hβ; (D) Amberlyst-15.

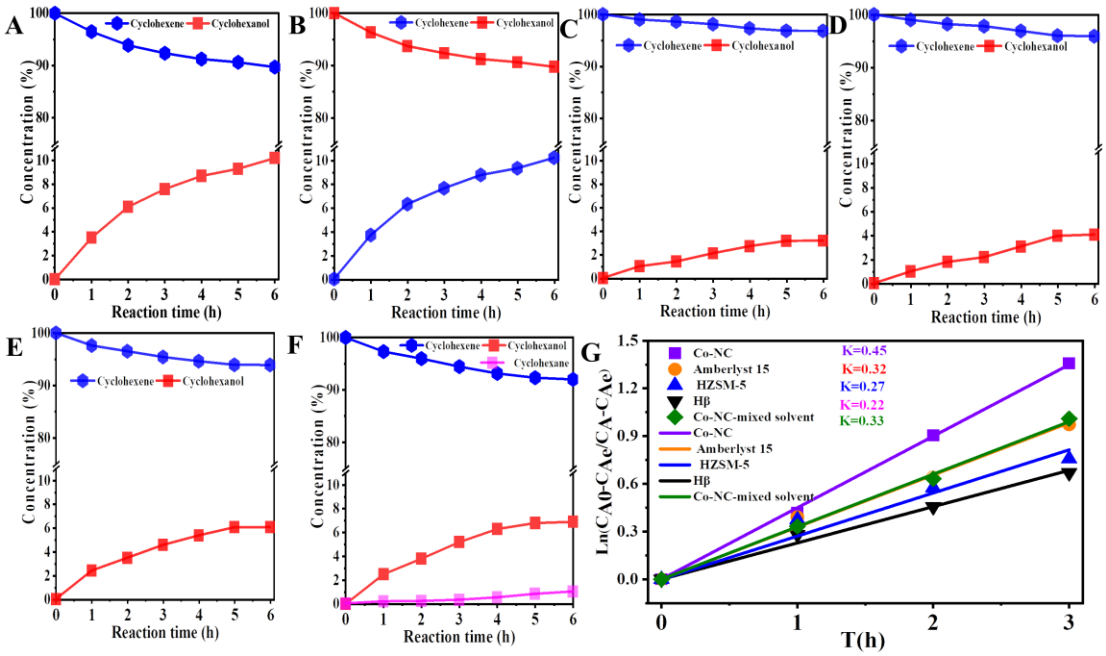


Figure S6. Time-dependent product concentration distribution (A, B, C, D, E, F) and kinetics studies (G) for hydration of cyclohexene and dehydration of cyclohexanol. Reaction conditions: substrate (10 mmol), water (10 mL); catalyst (Co-NC 50 mg, ZSM-5 19.2 mg, Hβ 23.6 mg, Amberlyst-15 2 mg), 150 °C, 4.0 MPa H_2, (A) cyclohexene, Co-NC; (B) cyclohexanol, Co-NC; (C) cyclohexene, HZSM-5; (D) cyclohexene, Hβ; (E) cyclohexene, Amberlyst-15 (F) cyclohexene, Co-NC, mixed solvent (water 7 mL and sulfolane 3 mL); (G) Comparison of the normalized activity per acid site over given samples.

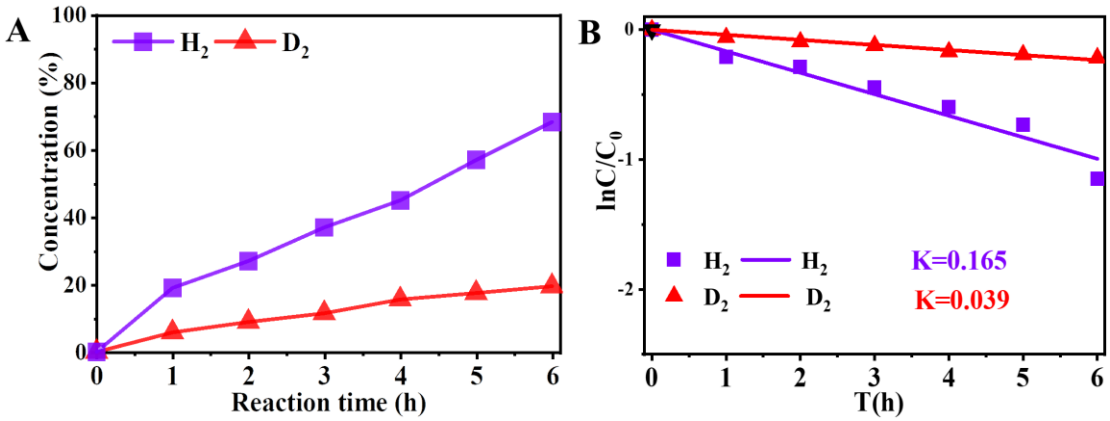


Figure S7. Time-dependent product concentration distribution (A) and kinetics studies (B) for hydrogenation of 3-chlorostyrene. Reaction conditions: 3-chlorostyrene (10 mmol), *n*-hexane (10 mL); 150 °C, 4.0 MPa H_2 or D_2, Co-NC 50 mg.

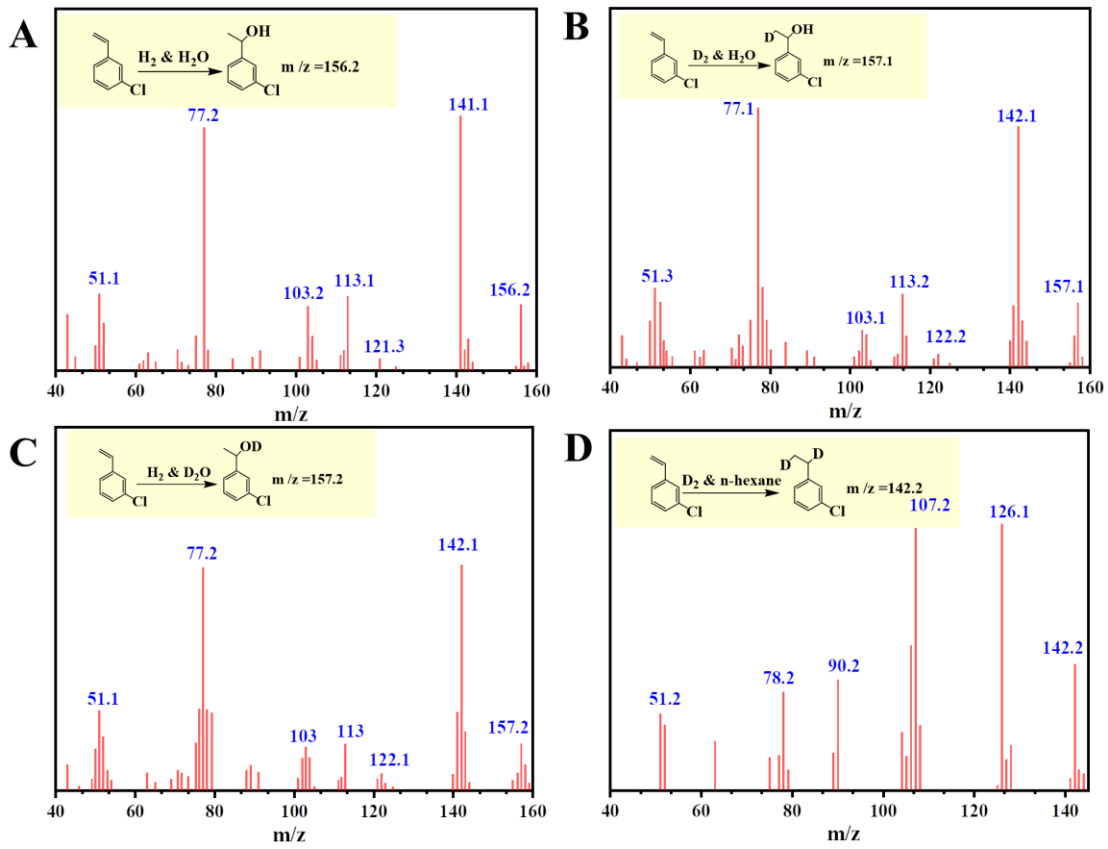


Figure S8. Isotope studies for the (A, B, C) 3-chlorophenylethane hydration to 1-(3-chlorophenyl)ethanol and (D) hydrogenation to 3-chlorophenylethane catalyzed by Co-NC. Reaction conditions: 3-chlorophenylethane (10 mmol), Co-NC 50 mg, and solvent (10 mL), 150 °C, 4.0 MPa H_2. (A) H_2 and H_2O; (B) D_2 and H_2O; (C) H_2 and D_2O; (D) D_2 and *n*-hexane.

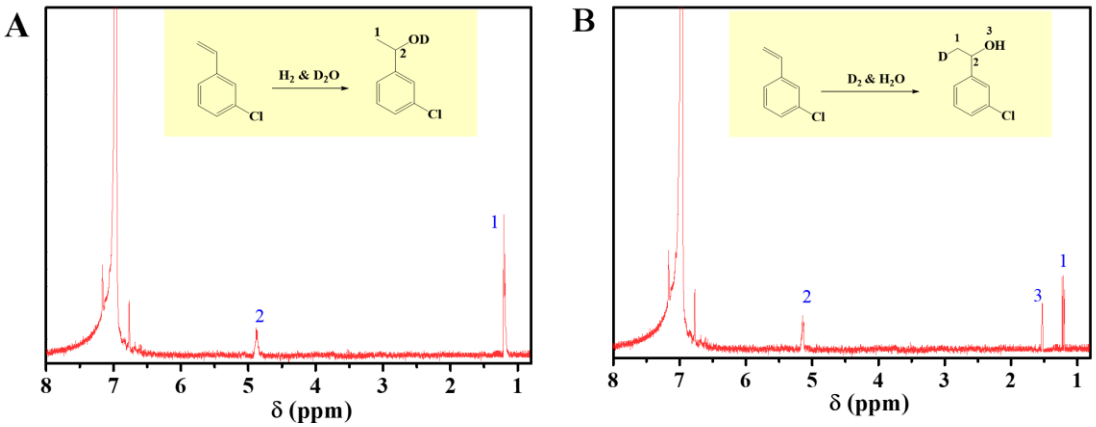


Figure S9. ^{1}H NMR of (A) hydroxyl-deuterated and (B) ethyl-deuterated 1-(3-chlorophenyl)ethanol. Reaction conditions: 3-chlorophenylethane (10 mmol), Co-NC 50 mg, solvent (10 mL), 4.0 MPa atmosphere. (A) H_2 and D_2O, (B) D_2 and H_2O.

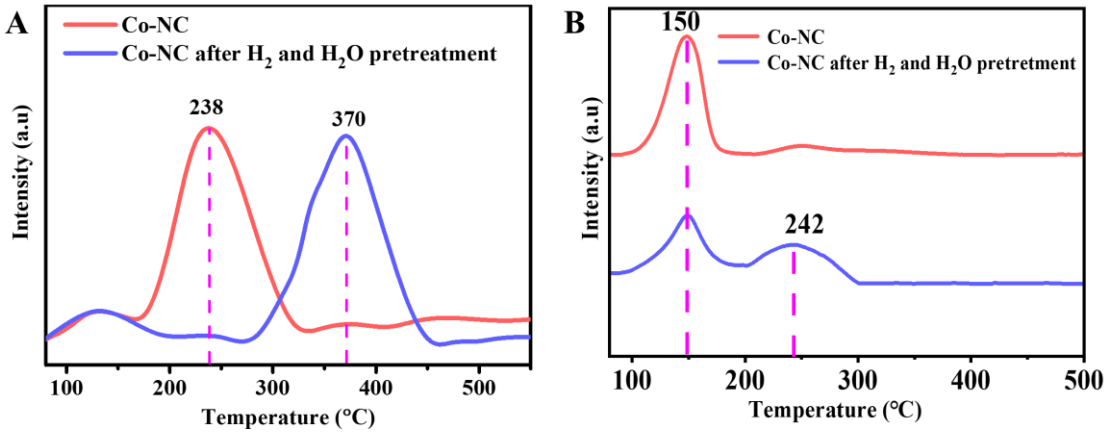


Figure S10. (A) NH_3-TPD and (B) CO_2-TPD profile of Co-NC before and after hydrogen and water treatment under 150 °C.

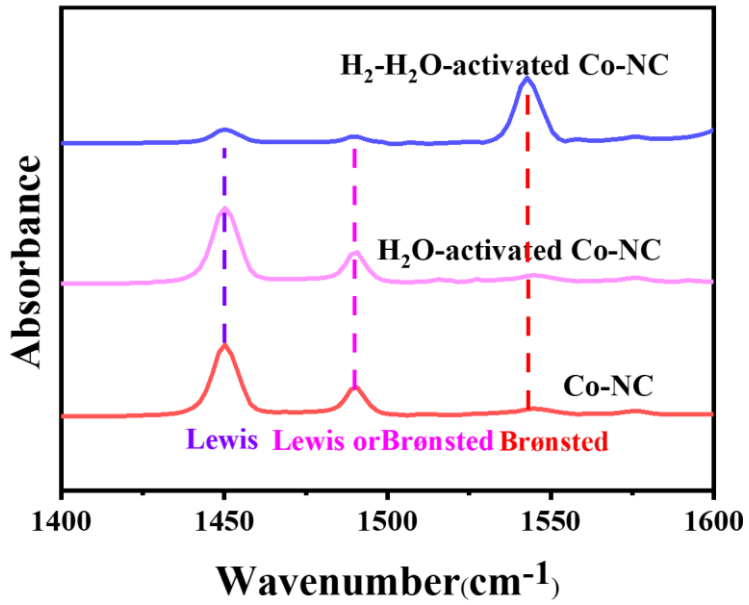


Figure S11. In situ IR spectra of adsorbed pyridine detected at 250 °C over Co-NC.

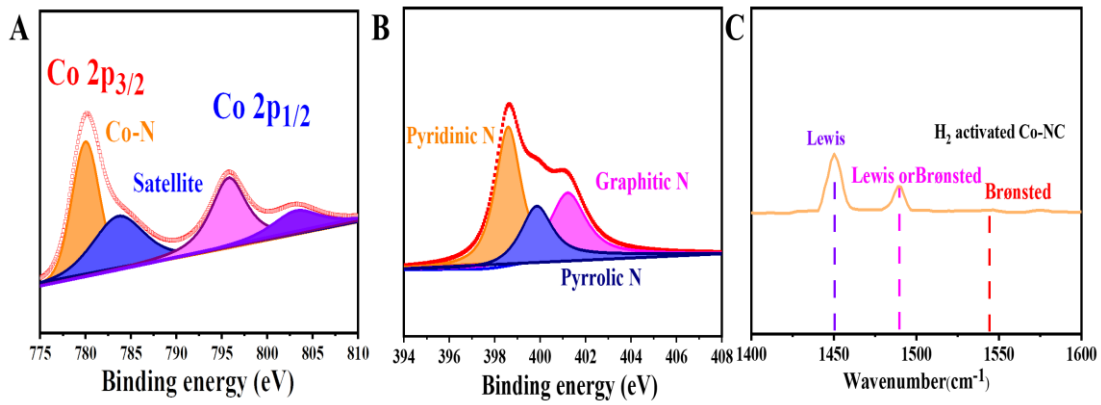


Figure S12. (A) Co 2p, (B) N 1s XPS spectra of the H_2-activated Co-NC, and (C) in situ IR spectra of adsorbed pyridine detected at 150 ℃ over the H_2 activated Co-NC.

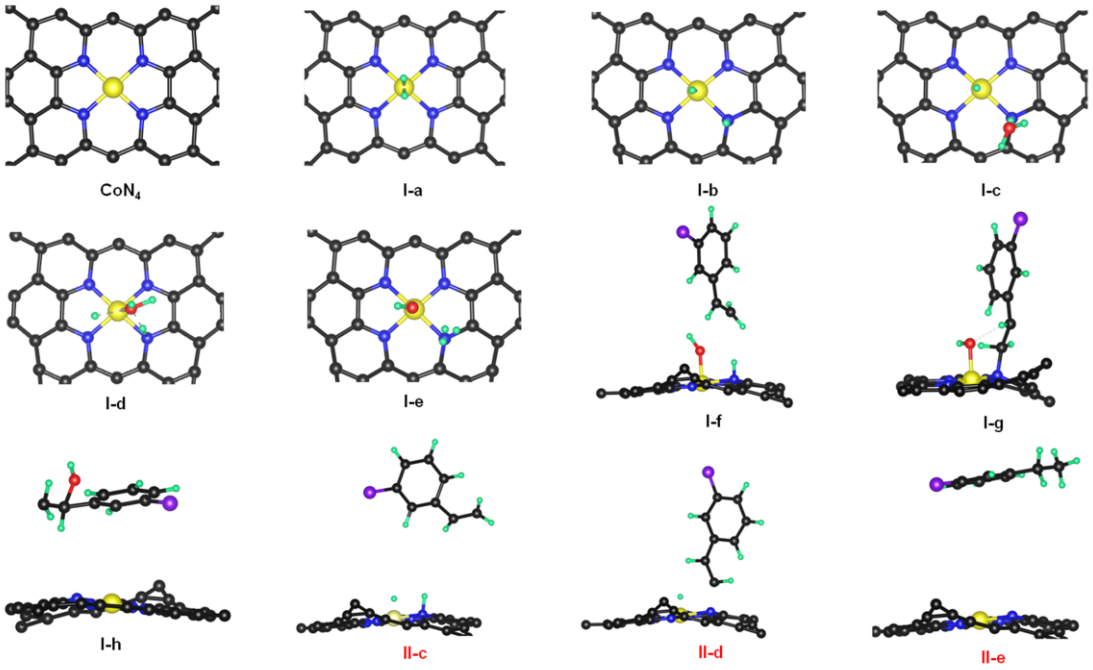


Figure S13. Configurations of energy change profile for hydration and hydrogenation of 3-chlorostyrene on Co-NC catalyst.

Table S1. Physicochemical properties of the $Zn_3[Co(CN)_6]_2$-derived Co-NC.

Samples	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Zn content (wt%)	Co content (wt%)	C content (wt%)	N content (wt%)
Co@Co-NC	97.7	0.143	0	44.6	45.1	5.2
Co-NC	154.6	0.273	0	1.0	94.0	4.5

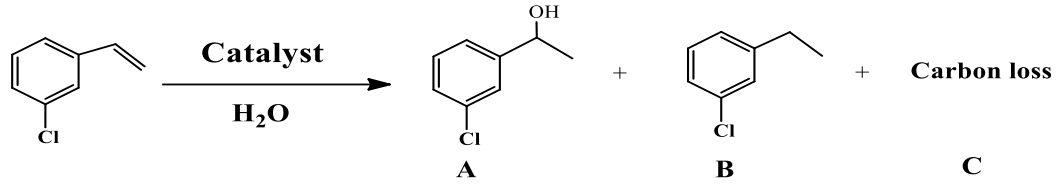
Table S2. Physico-chemical properties of catalysts.

Catalyst	Acid concentration (mmol/g)
HZSM-5	0.421
Hβ	0.341
Amberlyst-15	4.139
Co-NC	0.161

Table S3. Physicochemical properties of $Co_3[Co(CN)_6]_2$-derived Co-NC.

Samples	Co content (wt%)	C content (wt%)	N content (wt%)
Co-NC	1.4	91.9	3.6

Table S4. The catalytic performance of $Co_3[Co(CN)_6]_2$-derived Co-NC on the hydration of 3-chlorostyrene.



Entry	Solvent	Atmosphere	Conversion (%)	Selectivity (%)		
				A	B	C
1	H_2O	N_2	-	-	-	-
2	H_2O	H_2	78.6	99.1	-	0.9
3	*n*-hexane	H_2	72.3	-	99.9	-

Reaction conditions: 3-chlorostyrene (10 mmol), catalyst (50 mg), solvent (10 mL), 150 °C, 4.0 MPa atmosphere, 6 h. Quantified by GC.

Table S5. Acid properties of the H_2-H_2O activated Co-NC.

Samples	Total Acid Amount (mmol/g)	Total Strong Acid Amount (mmol/g)	Total Lewis Acid Amount (mmol/g)	Strong Lewis Acid Amount (mmol/g)	Total Brønsted Acid Amount (mmol/g)	Strong Brønsted Acid Amount (mmol/g)
Co-NC	0.161	0.043	0.159	0.042	0.002	0.001
H_2-H_2O activated Co-NC	0.160	0.063	0.085	0.013	0.075	0.050