

Controllable Synthesis of Co/NC Catalysts with High-density Co-Nx Active Site Derived from Co/Zn-ZIF for Cyclopropanation

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1. Preparation of Catalysts

Co@N doped carbon materials labeled as Co_x/NC-T (x represents the molar ratio, T is the mark of calcined temperature) were synthesized using a simple method, as shown in Figure S1. Co/Zn-ZIFs were synthesized from an aqueous solution at room temperature. Typically, 10 mmol mixture of Zn(NO₃)₂·6H₂O and Co(NO₃)₂·6H₂O with designed molar ratio, like 0%, 25%, 50%, 75% and 100%, and 80 mmol 2-methylimidazole were separately dissolved in 200 mL methanol. Two solutions were quickly mixed and changed into brown. The mixture was stirred continuously for 12 h at room temperature. After centrifugation, the product was washed by methanol several times and dried at 80 °C overnight. Then, these Co/Zn-ZIF precursors were annealed under nitrogen atmosphere for carbonization by thermal treatment at 900°C, and the samples were denoted as Co₀/NC-900, Co_{0.25}/NC-900, Co_{0.50}/NC-900, Co_{0.75}/NC-900 and Co_{1.00}/NC-900.

Preparation of Fe /NC

2mmol mixture of Fe(NO₃)₂·6H₂O and 1,10-phenanthroline (J&K Scientific, ≥99%, 990 mg, 5.5 mmol) were stirred in ethanol (90 mL) for 3 h at room temperature. Then, Carbon black powder (Alfa Aesar, 5g) was added and the whole mixture was kept stirring at room temperature for 6h. Ethanol was removed by vacuum. The obtained pink solid sample was dried at 80 °C for 24 hours, after which it was grinded to a fine powder in an agate mortar. Then, the grinded powder was transferred into a corundum crucible and placed in the oven. The oven was heated to 800 °C at the rate of 10 °C per minute, and held at 800 °C for 2 hours under flowing nitrogen gas. The oven was allowed to cool to room temperature naturally in a nitrogen atmosphere. The resultant black material was grinded again so as to obtain a fine powder.

2. Catalytic Tests

The supported catalyst (10.0 mg) was placed in an oven dried Schlenk tube which was evacuated and backfilled with nitrogen (Figure S2). Solvent 1,2-dichloroethane (2 mL) was added followed by styrene (2.50 mmol) and a stock solution of ethyl diazoacetate (EDA, 0.5 mmol). The mixture was heated at 60°C under N₂ atmosphere, then the cyclopropanation reaction lasted for 4 h with stirring. After the reaction, the catalyst was separated by centrifugation, enantiomeric excess and yields were determined by chiral gas chromatography (GC) using a AgilentJ&WDB-35 column on a Shimadzu GC-2014C instrument equipped with an FID detector. The flow rate was set to 3.0 mL/min for all tested compounds. Injector was in split mode 100:1, injection volume was 1 µL and injector temperature was set to 100 °C, whereas the detector temperature was set to 280 °C. The conditions for separation of individual product enantiomers can be found in the compound characterization section.

3. Catalysts Characterization

X-ray powder diffractometer (XRD, Rigaku D/Max 2500 VB2+PC) with 2θ range from 10 ° to 90 ° characterizes the crystal. Raman spectra were recorded on a LabRAM HR Evolution (Renishaw Invia Raman, UK). X-ray photoelectron spectroscopy (XPS, Pekin-Elmer PHI-1600) characterizes the surface elemental composition and valence. Transmission electron microscopy (TEM, FEI Tecnai-G2F20) characterizes the microstructure, combine with Energy Dispersive X-Ray Spectroscopy (EDS) to obtain the elemental mapping within the micro-region of the material. The nitrogen adsorption-desorption were performed using a Micromeritics ASAP 2020 at 77 K. Brunauer-Emmett-Teller (BET) equation was used to calculate the final specific surface area and the corresponding pore size distribution.

Typical XPS survey of Co/NC catalysts

The surface elements composition and chemical states of Co/NC samples were shown in Table S1.

Catalyst	C[at.%]	N[at.%]	O[at.%]	Co[at.%]
Co _{0.25} /NC-900	81.55	10.77	6.65	0.74
Co _{0.50} /NC-900	79.72	11.71	7.57	0.94
Co _{0.75} /NC-900	87.08	7.64	4.81	0.28
Co _{1.0} /NC-900	95.33	0.20	4.33	0.14

Table S1. Typical XPS survey of Co/NC catalysts

Texture properties of Co/NC catalysts

The N₂ gas adsorption–desorption isotherm and the corresponding pore size distribution curve of Co/NC-900 are reported.

Catalyst	S _{BET} (m ² /g)	V _p (cm ³ /g)	d _p (nm)
Co _{0.25} /NC-900	667	0.387	48.5
Co _{0.50} /NC-900	607	0.378	49.7
Co _{0.75} /NC-900	449	0.346	61.2
Co _{1.0} /NC-900	400	0.150	30.1

Table S2. Texture properties of Co/NC catalysts

4. Proposed reaction mechanism

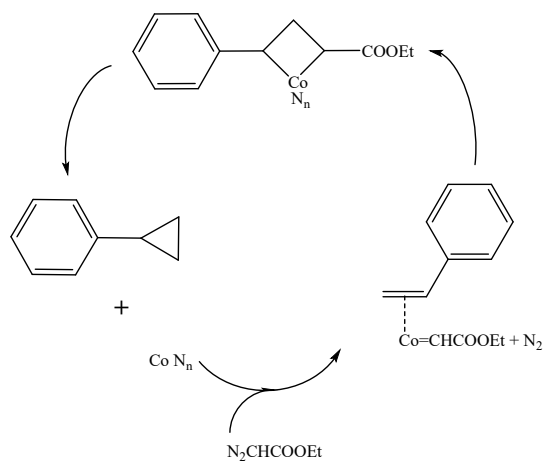


Figure S1. Proposed catalytic mechanism of cyclopropanation

5. NMR Spectra ¹H-NMR and ¹³C-NMR Spectra

For trans isomer:

¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, J = 7.1 Hz, 2H), 7.24 – 7.17 (m, 1H), 7.15 – 7.05 (m, 2H), 4.17 (q, J = 7.1 Hz, 2H), 2.52 (ddd, J = 9.4, 6.5, 4.2 Hz, 1H), 1.90 (ddd, J = 8.4, 5.3, 4.2 Hz, 1H), 1.67 – 1.51 (m, 1H), 1.34 – 1.30 (m, 1H), 1.28 ppm (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 173.40, 140.13, 128.45, 126.45, 126.17, 60.69, 26.16, 24.17, 17.04, 14.26 ppm.

For cis isomer:

¹H NMR (400 MHz, CDCl₃) δ 7.27 (s, 4H), 7.22 – 7.15 (m, 1H), 3.87 (q, J = 7.1 Hz, 2H), 2.58 (q, J = 8.7 Hz, 1H), 2.08 (ddd, J = 9.1, 7.9, 5.7 Hz, 1H), 1.72 (dt, J = 7.4, 5.4 Hz, 1H), 1.33 (td, J = 8.2, 5.1 Hz, 1H), 0.97 ppm (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 170.96, 136.57, 129.29, 127.86, 126.62, 60.15, 25.45, 21.81, 14.02, 11.10 ppm.