

Controllable transformation from 1D Co-MOF-74 to 3D CoCO₃ and Co₃O₄ with ligand recovery and tunable morphologies: assembly process and boosting VOCs degradation

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1. Experimental Procedures

Catalyst preparation

Synthesis of tricobalt tetroxide nanorods (Co₃O₄-N):

In a typical process, Cobalt tetrahydrate 0.44 g (1.77 mmol) was dissolved in 60 mL methanol followed by adding 0.12 g (6.1 mmol) 2,5-dihydroxyterephthalic acid (DHTP), and the resulting mixture was further ultrasonicated for 10 min, then centrifuged, the obtained precipitate was washed by methanol and distilled water for several times to remove the unreacted compositions for further use, denoted as Co-mof-74 nanoparticles. The as-prepared Co-mof-74 nanorods was transferred into a ceramic boat and placed in a tube furnace under an O₂ flow, by heating up to 350 °C at a rate of 1 °C/min and maintained at this temperature for 3.5 h to obtain the tricobalt tetroxide nanowires, denoted as Co₃O₄-N.

Synthesis of hydrangeas like tricobalt tetroxide (Co₃O₄-H):

The as-prepared precursors were dispersed in 60 mL distilled water, followed by adding amount of urea 0.25g (4.2 mmol), the mixture was then transferred into a 100 mL Teflon-lined autoclave and placed in an oven at 140 °C for 24 h, after cooling down to room temperature, centrifuged, and the products were rinsed by distilled water and ethanol to form fuchsia hydrangea like structure (CoCO₃-H), then calcined in the same process to obtain hydrangea like tricobalt tetroxide, denoted as Co₃O₄-H.

Synthesis of capsules like tricobalt tetroxide capsule (Co₃O₄-C):

The preparation methods were the same as that of Co₃O₄-H, the only difference was that changed urea by adding 0.25 g (1.8 mmol) hexamethylenediamine (HMT), after cooling down to room temperature, the dark brown capsule like structure (CoCO₃-C) was collected and washed by

distilled water and ethanol, then calcined in the same process to obtain capsule like tricobalt tetroxide capsule, denoted as $\text{Co}_3\text{O}_4\text{-C}$.

Synthesis of time-dependent, urea content and temperature dependent tricobalt tetroxide catalysts:

The synthesis conditions were similar to that of $\text{Co}_3\text{O}_4\text{-H}$, except that the reaction conditions were controlled under hydrothermal conditions by controlling the reaction time, adding different amount of urea content and regulating the reaction temperature. The products were subsequently centrifuged and washed with distilled water and ethanol, then calcined in the same process to obtain time-dependent, different urea content and reaction temperature catalysts.

Catalyst characterization and catalytic evaluation

N_2 adsorption-desorption measurement was performed on a Micromeritics ASAP 2020 instrument at $-196\text{ }^\circ\text{C}$. Prior measurement, every sample was outgassed at $150\text{ }^\circ\text{C}$ for 3h. PXRD analysis was conducted on Bruker D8 ADVANCE X-ray diffractometer, with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.1541\text{ nm}$) in the 2θ range of $10\text{-}85^\circ$ (40 Kv, 40 mA, scanning step = $0.02^\circ/\text{min}$). Scanning electron microscopy (SEM) images were collected on a ZEISS scanning microscope, whereas TEM images were taken on a JEOL JEM-1010/2010F transmission electron microscope operated at 200 kV.

Where H_2 -TPR measurement was performed in a U-shape quartz reactor with the sample (50 mg) kept under a $\text{H}_2\text{-Ar}$ mixture (vol 5% H_2/Ar). Before switching the gas feed to $\text{H}_2\text{-Ar}$ stream, the sample was pretreated in Ar stream at $120\text{ }^\circ\text{C}$ for 1 h, and then cooled down to room temperature. The TPR profile was recorded with temperature programming from $50\text{ to }800\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C}/\text{min}$. H_2 consumption was monitored by a thermo-conductive detector. O_2 -TPD was carried out in the U-shape quartz reactor. 50 mg of the catalyst was pretreated in He flow at $300\text{ }^\circ\text{C}$ for 1h (30 mL/min) to remove physically adsorbed molecules, and then cooled down to room temperature. Then, the gas was switched to a flow of 5 vol % O_2/He (30 mL/min) in the tube for 1 h, followed by purging with pure He at the same temperature for 30 min to remove the unabsorbed O_2 molecules. Then, the catalysts were heated from room temperature to $750\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C min}^{-1}$ in pure He (30 mL/min).

The XPS patterns were tested on a Thermo ESCALAB 250Xi electron spectrometer with Al K α ($h\nu = 1486.8\text{ eV}$) being the excitation source. The binding energies of all the elements were referenced to the C 1s line at 284.8 eV from carbon impurities.

The photoluminescence (PL) spectra of these catalysts were measured at room temperature using FluoroMax-4 fluorescence spectrophotometer (HORIBA Japan) with an excitation wavelength at $\lambda_{\text{exc}} = 320$ nm.

Raman spectroscopy was performed on a LabRAM HR system (HORIBA Scientific) with a CCD detector and a spectral resolution of 1 cm^{-1} , 532 nm laser was employed as the excitation source with an 1800 groove mm^{-1} grating and 80 holes. The laser power was maintained at 6 mW and the exposure time was 60 s in the wavenumber region measured from 100 to 850 cm^{-1} .

ESI-MS measurements were conducted with a Thermo Exactive spectrometer in negative ion modes at a capillary temperature of $275 \text{ }^\circ\text{C}$. Aliquots of the solution were injected into the device at 0.3 mL/h. The spectrometer was calibrated with the standard tune mix to give a precision of ca. 2 ppm in the region of 100-1000 m/z. The capillary voltage was 50 V, the tube lens voltage was 150 V, and the skimmer voltage was 25 V. The in-source energy was set 0 eV with a gas flow rate at 10% of the maximum.

Catalytic evaluation

Catalytic activities of the samples were evaluated in a continuous flow quartz tube ($\Phi=6$ mm) micro-reactor and 50 cm length. To minimize the effect of hot spots, the sample (100 mg, 40-60 mesh) was mixed with 400 mg silicon (40-60 mesh). All the particles were packed at the bed of the reactor. The total flow rate of the reactant mixture (1000 ppm Toluene, 20% O_2/N_2) was 100 ml min^{-1} , corresponding to the weight hourly space velocity (WHSV) at $60000 \text{ ml}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. The reactant and product gases were analyzed by an on-line gas chromatograph (GC-2014C, Shimadzu, Japan) equipped with FID at a given temperature after stabilizing for 30 min. Catalytic activities of the samples were evaluated using the temperature (T_{50} and T_{90}) required for achieving toluene conversions of 50% and 90%, respectively. The range of catalytic activity testing temperatures were from 180 to $280 \text{ }^\circ\text{C}$. The complete conversion of toluene (η -toluene) was calculated according to the following equation:

$$\eta_{\text{toluene}} = \frac{[C_{\text{toluene}}]_{\text{out}}}{[C_{\text{toluene}}]_{\text{in}}} * 100\%$$

$$\eta_{\text{acetone}} = \frac{[C_{\text{acetone}}]_{\text{out}}}{[C_{\text{acetone}}]_{\text{in}}} * 100\%$$

$$\eta_{\text{methanol}} = \frac{[C_{\text{methanol}}]_{\text{out}}}{[C_{\text{methanol}}]_{\text{in}}} * 100\%$$

Activation energies were calculated at low temperatures for toluene conversions lower than 20%, which were determined by means of the following Arrhenius relationship.

$$\ln \kappa = -\frac{Ea}{RT} + \ln A$$

Where κ , Ea , R and T were the toluene oxidation rate ($\text{mol}\cdot\text{s}^{-1}$), activation energy ($\text{J}\cdot\text{mol}^{-1}$), universal gas constant ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) and reactor temperature (K), respectively.

Table S1. The BET data for different Co-based samples

Samples	Crystallite size (nm)	Pore Size (nm)	Pore volume ($\text{m}^3\cdot\text{g}^{-1}$)	BET ($\text{m}^2\cdot\text{g}^{-1}$)
$\text{Co}_3\text{O}_4\text{-N}$	18.1	22.2	0.11	22.7
$\text{Co}_3\text{O}_4\text{-H}$	24.7	18.1	0.14	32.6
$\text{Co}_3\text{O}_4\text{-C}$	21.5	22.2	0.20	36.8

Table S2. The reaction temperature of VOCs oxidation.

Catalyst	Acetone		Methanol	
	T_{50} ($^{\circ}\text{C}$)	T_{90} ($^{\circ}\text{C}$)	T_{50} ($^{\circ}\text{C}$)	T_{90} ($^{\circ}\text{C}$)
$\text{Co}_3\text{O}_4\text{-N}$	188	205	126	151
$\text{Co}_3\text{O}_4\text{-H}$	166	187	100	133
$\text{Co}_3\text{O}_4\text{-C}$	175	194	116	140

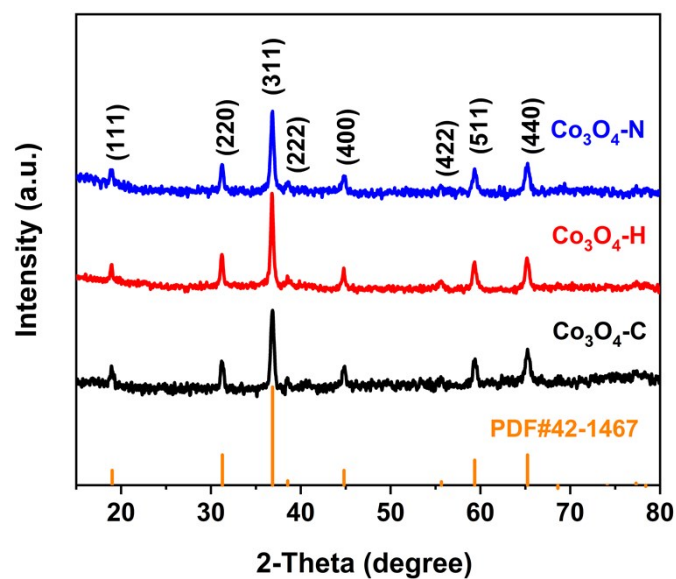


Figure S1. PXRD patterns of the as-prepared catalysts.

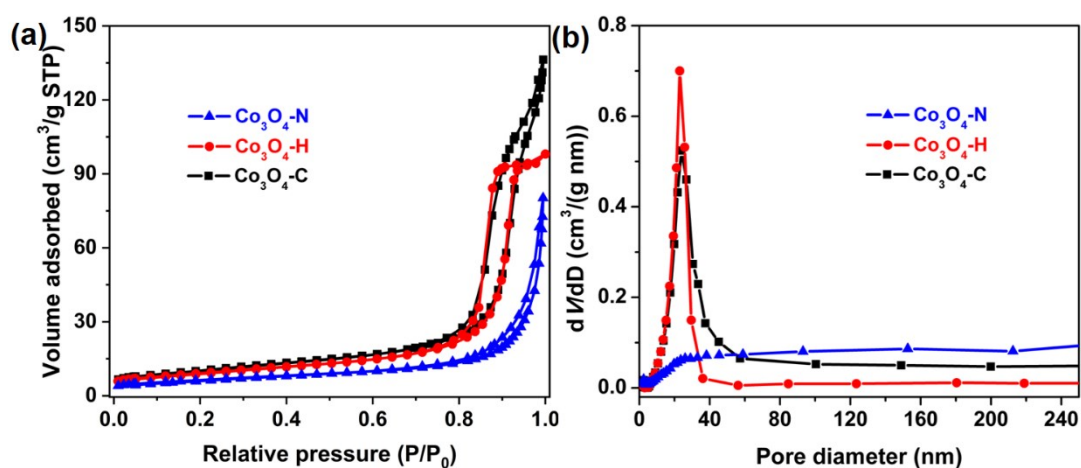


Figure S2 (a) N_2 adsorption-desorption isotherms and (b) BJH pore size distributions of the as-obtained catalysts.

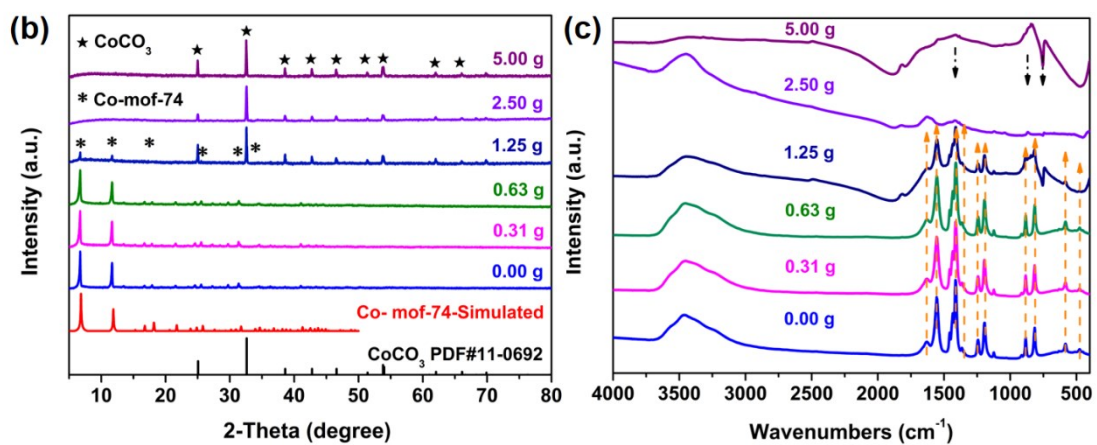
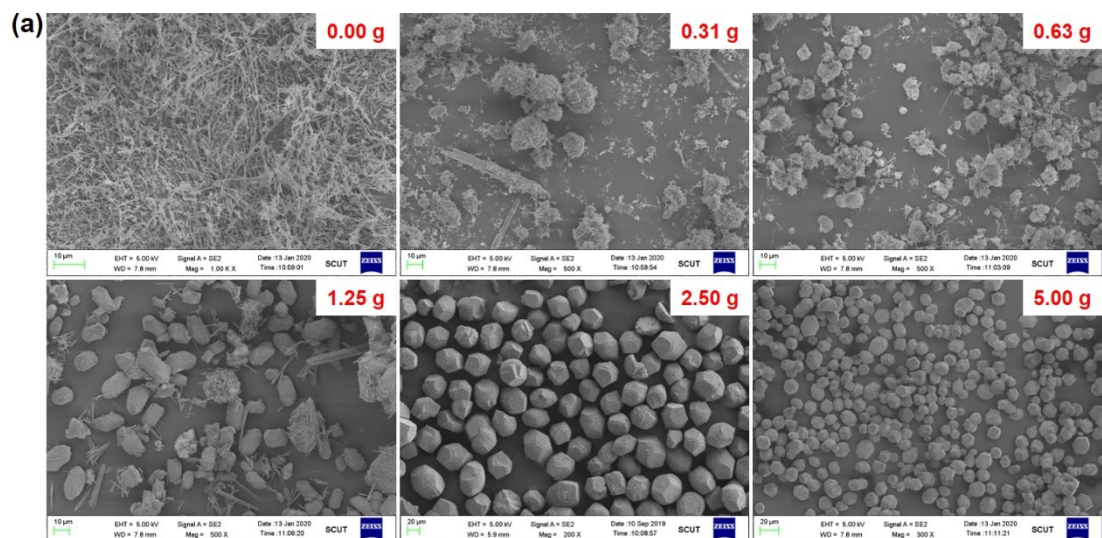
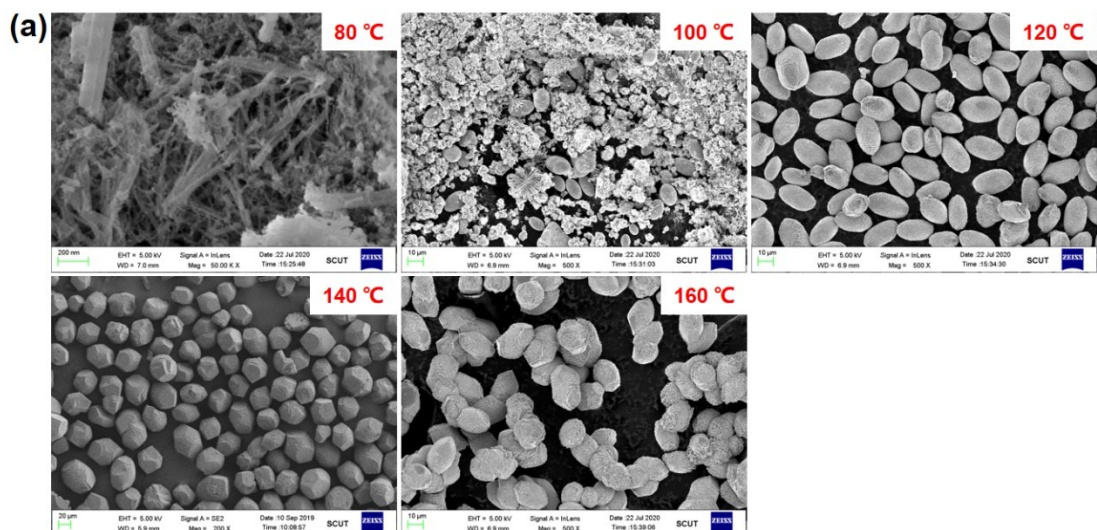


Figure S3. (a) SEM, (b) PXRD and (c) FT-IR with adding different amount of urea.



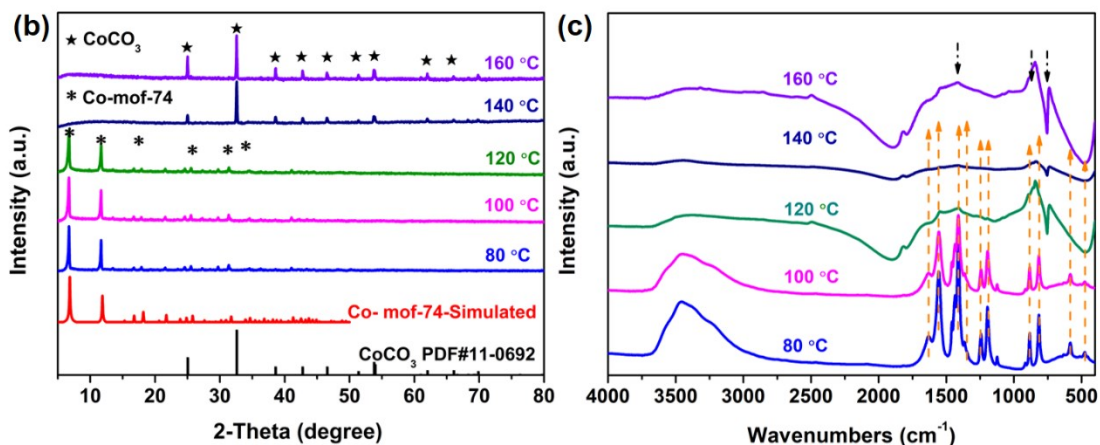


Figure S4. (a) SEM, (b) PXRD and (c) FT-IR with adding 2.5 g urea in different reaction temperature.

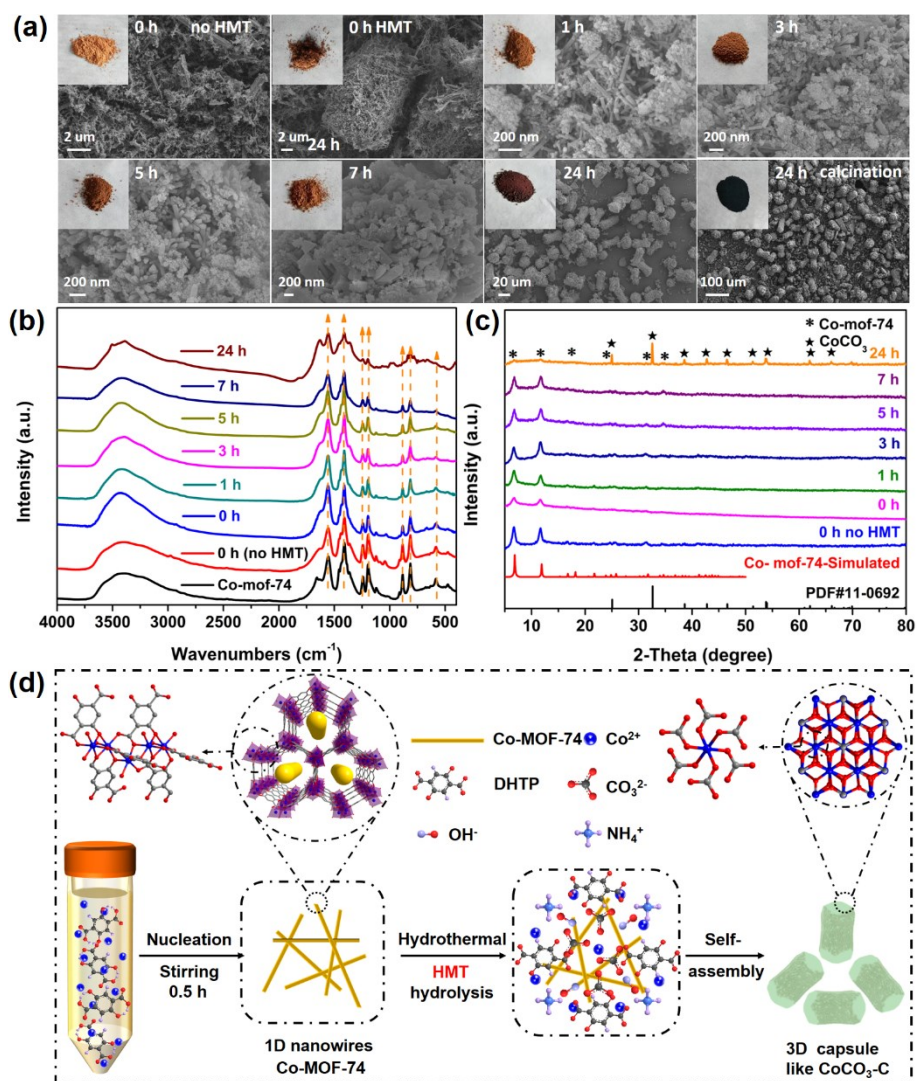


Figure S5. (a) Time-dependent process precipitation photograph, (b) infrared spectra, (c) PXRD

and (d) illustration of the synthesis procedure for conversion of 1D Co-MOF-74 to $\text{CoCO}_3\text{-C}$.

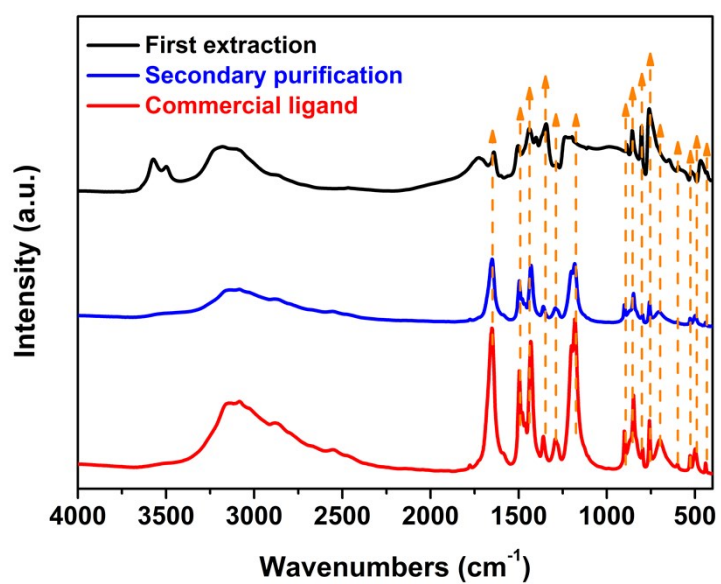


Figure S6. Infrared spectra of ligand extraction from mother liquor.

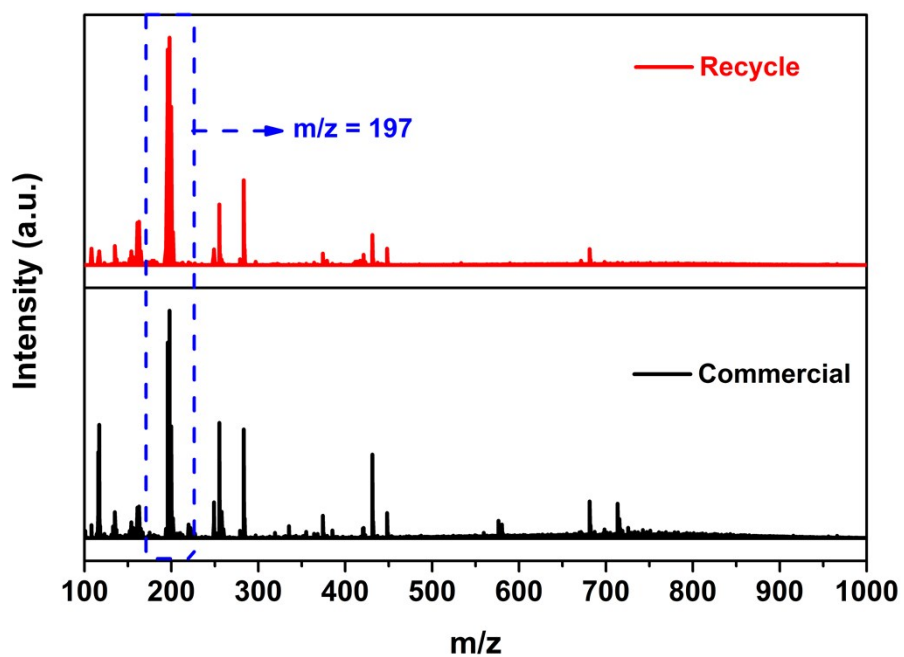
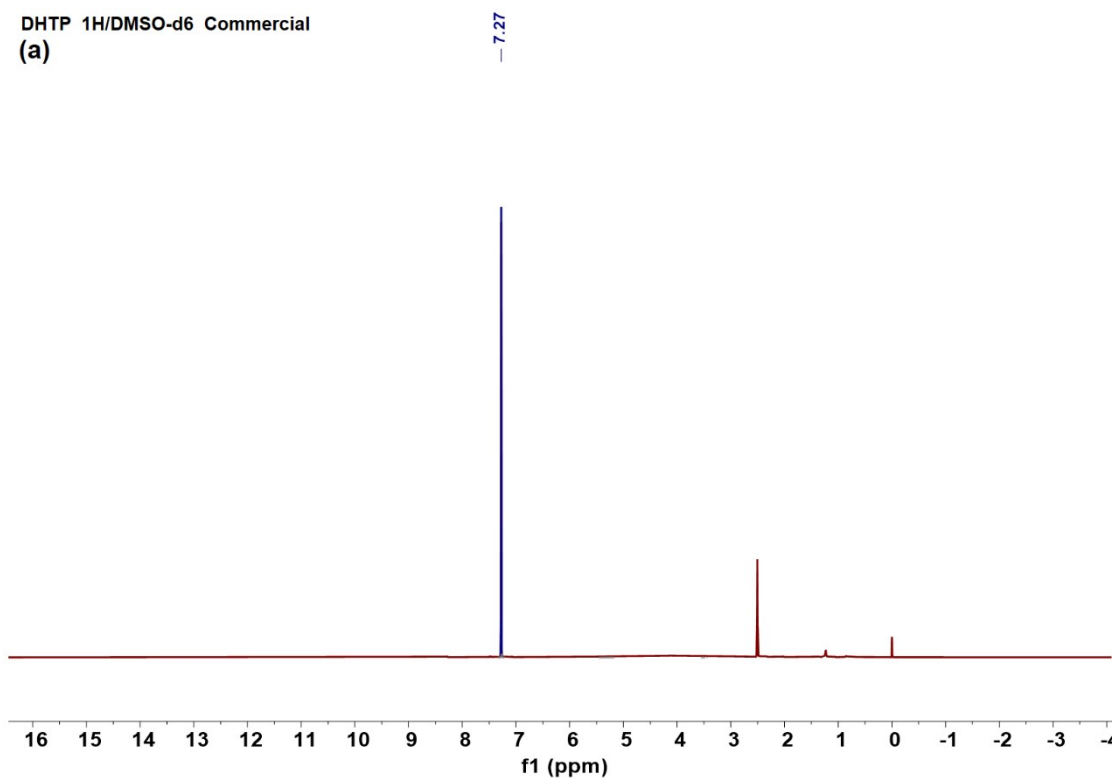
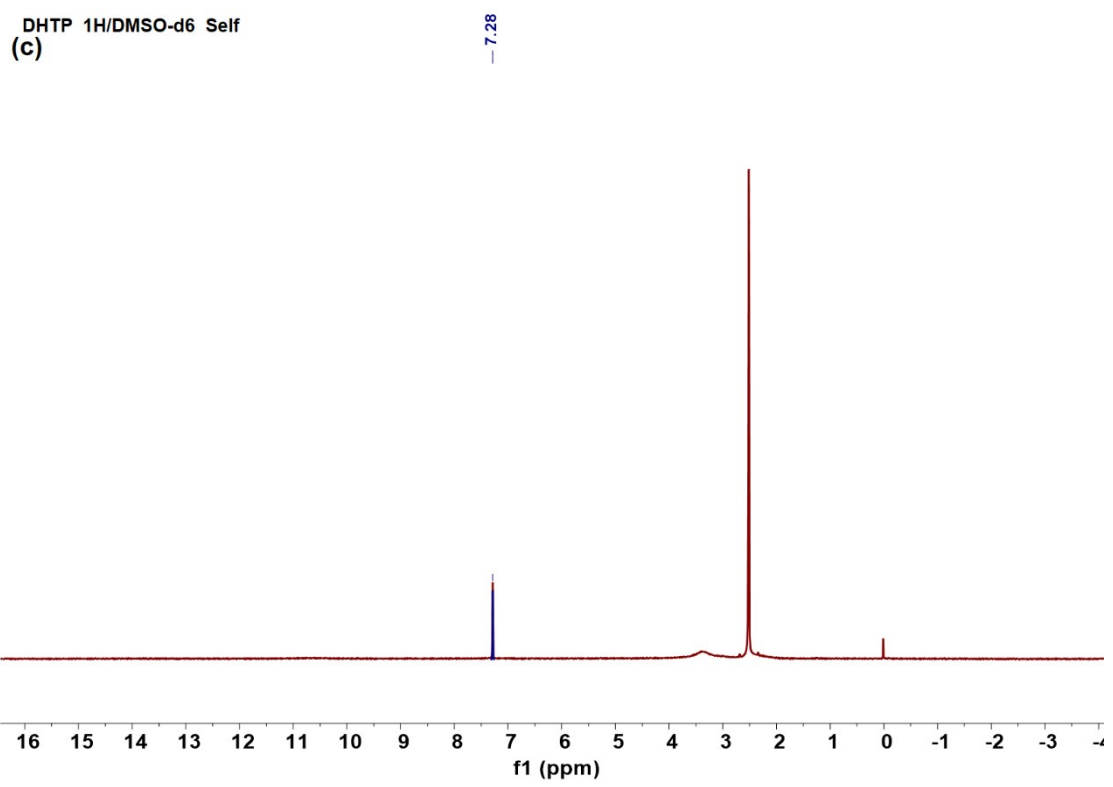
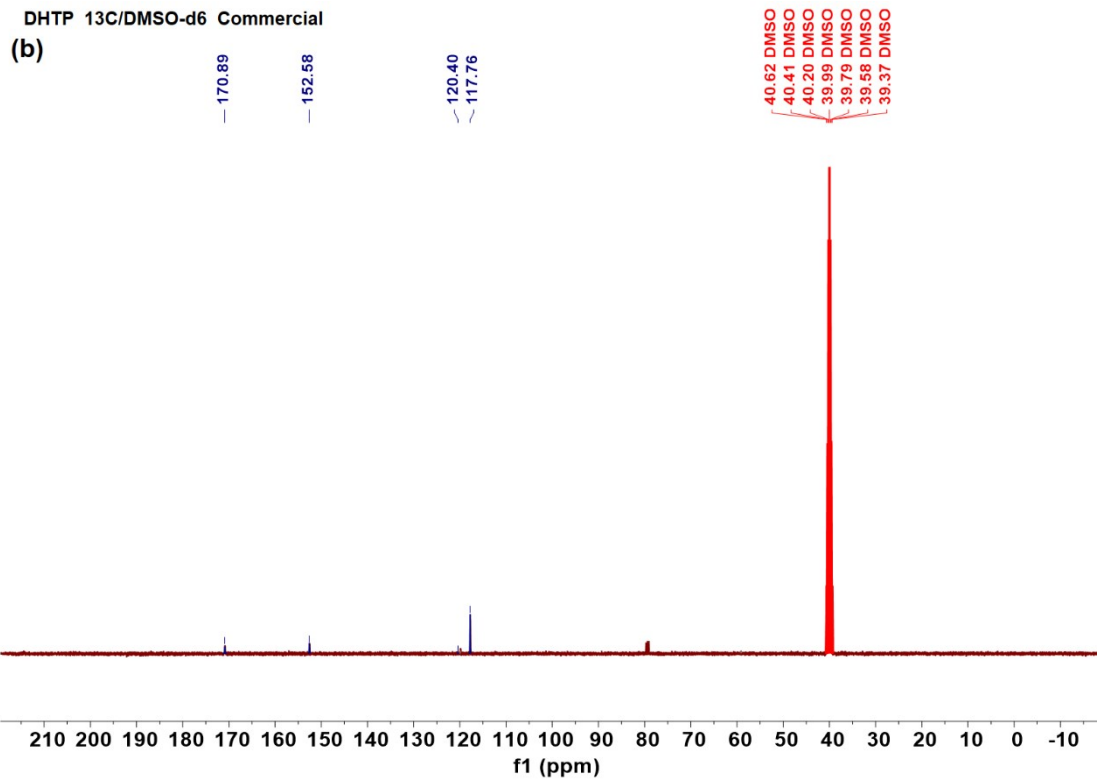


Figure S7. ESI-MS spectra of ligand extraction from mother liquor and commercial.

The ESI-MS of the commercial (black line) and recycle ligand (red line) were dissolved in CH_3OH . Both of them shows a high intensity peak at $m/z = 197$, corresponding to the ligand release one H in negative modes.





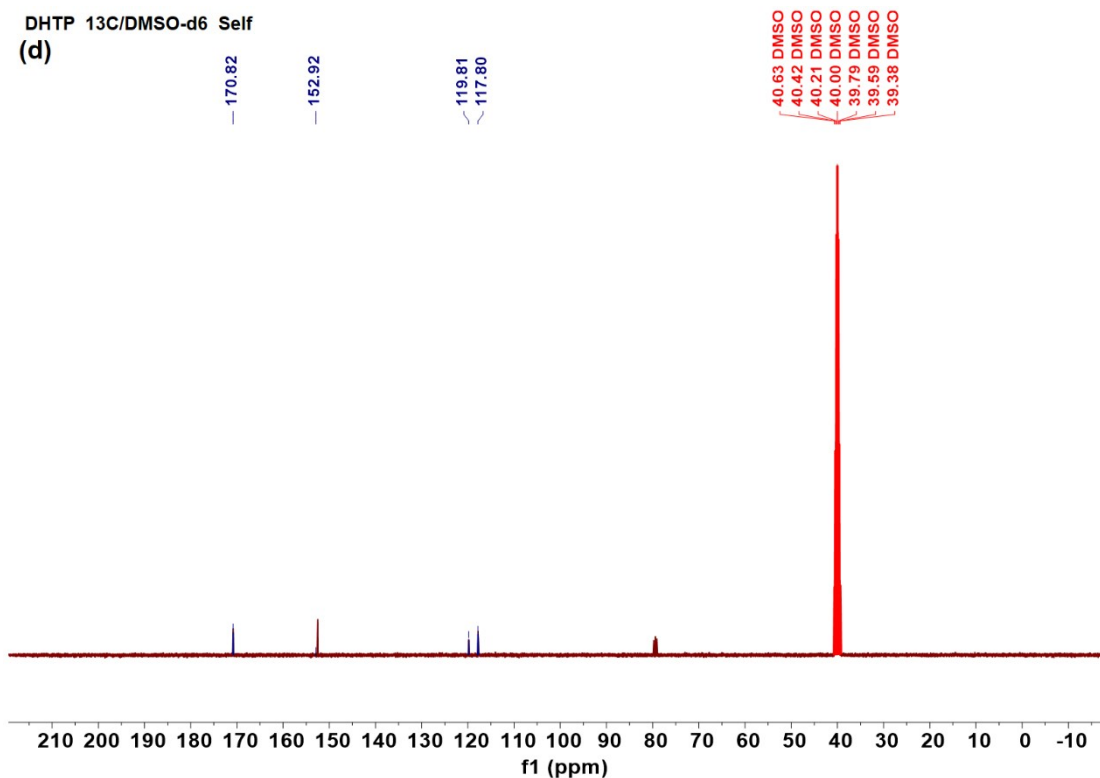


Figure S8. (a) ^1H NMR spectra and (b) ^{13}C NMR spectra of (in DMSO-d_6) commercial ligand; (c) ^1H NMR spectra and (d) ^{13}C NMR spectra of recycle ligand.

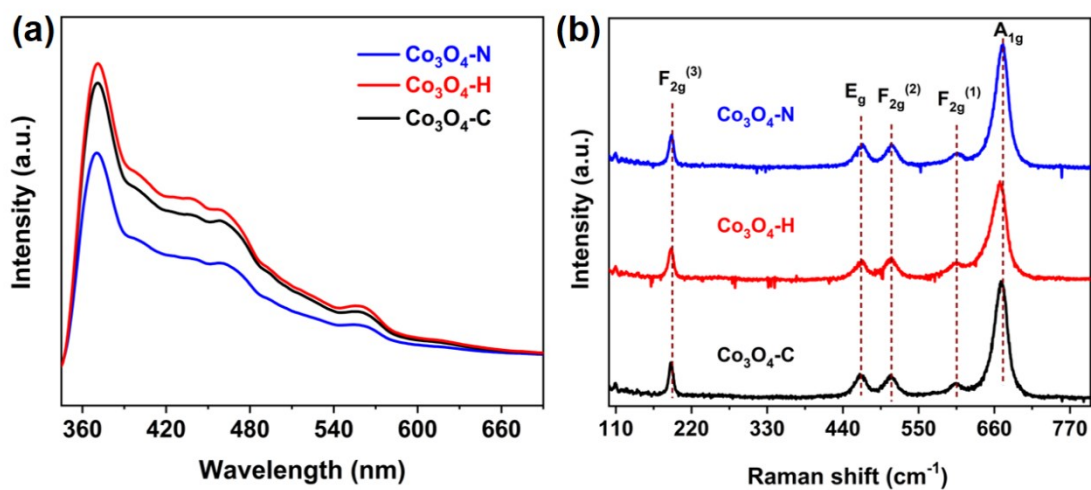


Figure S9. (a) PL emission spectrum and (b) Raman spectra of the as-synthesized Co-based catalysts.

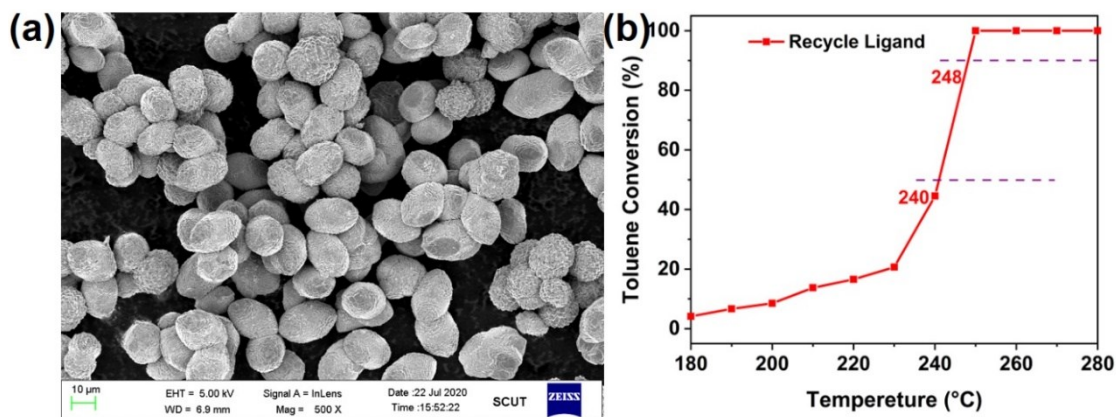


Figure S10. (a) The SEM image of the recovered ligand prepared catalyst use urea as base retardants; (b) Toluene catalytic performance of the recovered ligand prepared catalyst under the following conditions: toluene = 1000 ppm(v), 20 vol.% O₂/N₂, WHSV = 60,000 mL g⁻¹ h⁻¹.

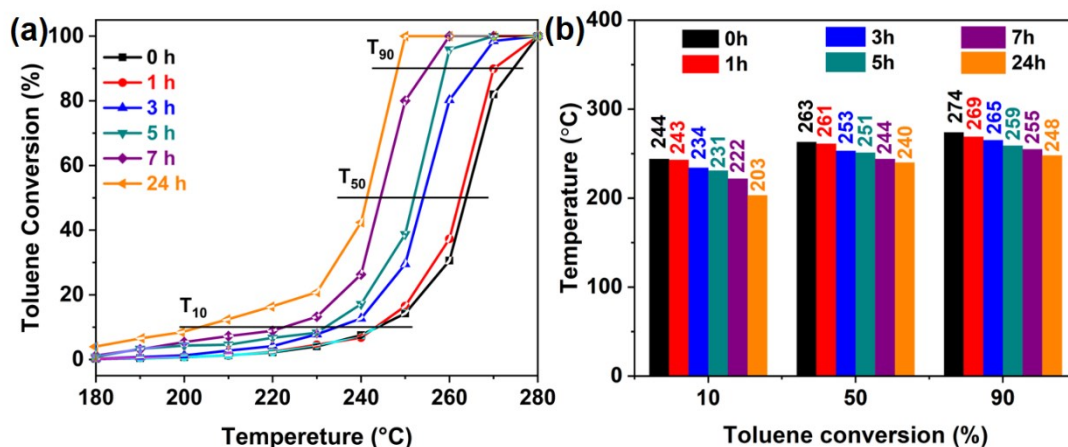


Figure S11. (a) Toluene catalytic performance (b) 2D histogram of the 10%, 50%, 90% toluene conversion vs reaction temperatures of the time-dependent Co₃O₄ under the following conditions: toluene = 1000 ppm(v), 20 vol.% O₂/N₂, WHSV = 60,000 mL g⁻¹ h⁻¹.

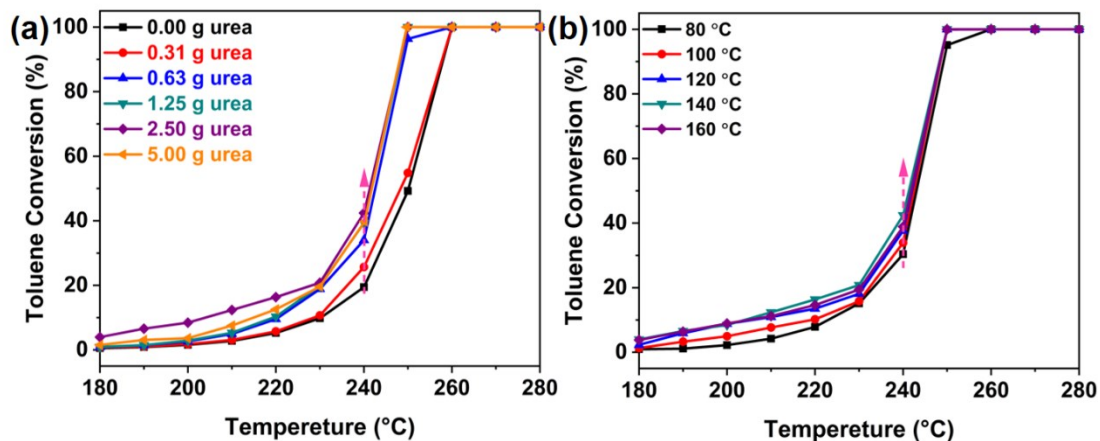


Figure S12. (a) Toluene catalytic performance over different reaction temperature; (b) Toluene catalytic performance over the different urea content.

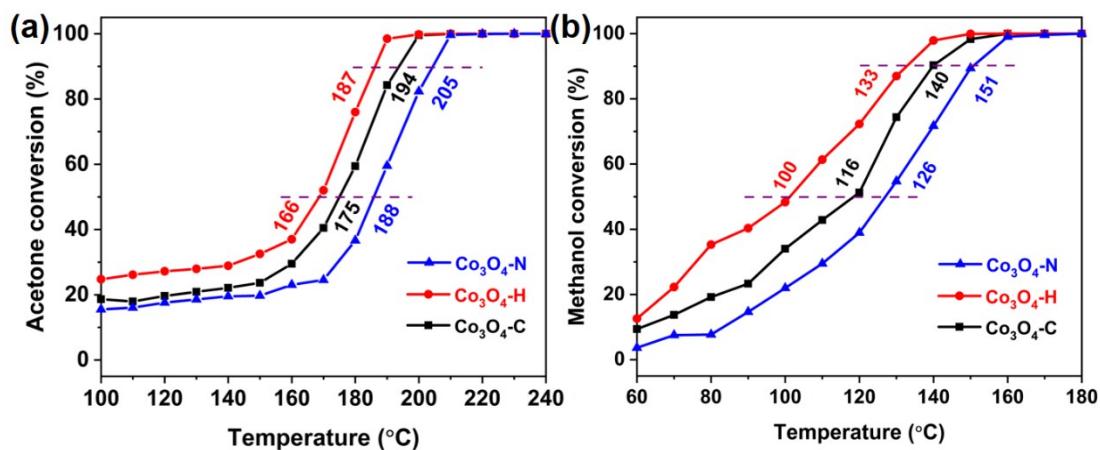


Figure S13. (a) Acetone and (b) methanol catalytic performance of the as-prepared morphologies Co₃O₄ under the following conditions: acetone = 400 ppm, methanol = 500 ppm, 20 vol.% O₂/N₂, WHSV = 60,000 mL g⁻¹ h⁻¹.