

Supporting Information

Effective catalytic elimination of dichloromethane under humid environment over Co based oxides

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Text S1. Catalytic activity tests.

Catalytic ozonation of DCM was conducted in a self-designed platform that has described before. DCM was supplied by a cylinder gas (1000 ppm DCM with N₂ balanced) and further diluted into 100 ppm in the simulated gas mixture. O₂ flowed into a dielectric barrier discharger (HTU-500E) to produce ozone that was injected into the gas mixture. The initial ozone concentration was measured by ozone concentration analyzer (BMT-964BT). The total gas flow rate was 100 mL/min and O₂ concentration was 10 vol.%. The catalyst dosage was fixed at 50 mg, corresponding to a gas-time space velocity (GHSV) of 30000 h⁻¹. Water vapor is produced by N₂ bubbling in a thermostatic bath. Water was injected into reaction system with N₂ bubbling at a certain temperature. The DCM reaction products were monitored and analyzed online by gas chromatograph (GC9790II). DCM ozone catalytic oxidation activity test reference text, DCM conversion rate and CO₂ yield are calculated by **Eqs. 1~2**.

$$\text{Acetone Conversion} = ([\text{ACE}]_{\text{initial}} - [\text{ACE}]_{\text{outlet}}) / [\text{ACE}]_{\text{initial}} \times 100\% \quad (1)$$

$$\text{CO}_2 \text{ Yield} = ([\text{CO}_2]_{\text{outlet}} / [\text{ACE}]_{\text{initial}} \times 3) \times 100\% \quad (2)$$

where [ACE]_{initial} and [ACE]_{outlet} are the initial and outlet DCM concentration (ppm), respectively, [CO]_{outlet} and [CO₂]_{outlet} are the outlet CO and CO₂ concentration (ppm), respectively.

The reaction rate (*r*, mol g⁻¹ s⁻¹) of acetone oxidation was calculated according to **Eq. 3**⁴.

$$r = C \cdot X \cdot F / m \quad (3)$$

Where X denotes the DCM conversion, C is the DCM concentration in the gas mixture (mol/mL), F is the total flow rate (mL/s), and m is the weight of the catalyst (g). When the DCM conversion is lower than 20%, the reaction rate can be expressed by **Eq. 4**⁵. Accordingly, the slope of the linear relationship between ln*r* and 1/T is the activation energy (E_a).

$$\ln r = - E_a / RT + C \quad (4)$$

TOF was calculated based on the converted mole number of DCM per second per mole of surface chemisorbed oxygen at 120°C, respectively. Example for TOF calculation on 0.003 CoO_x-UF10 catalyst

Co content of CoO_x-UF10: 0.6402 × 0.003/59 = 3.26 × 10⁻⁵ mol (determined by +9

Co content of CoO_x-U: $0.7525 \times 0.003/59 = 3.82 \times 10^{-5}$ mol (determined by **Table S3**)

TOF (Co) of CoO_x-UF10 (dry) = DCM concentration \times flow rate \times DCM conversion / (22.4 \times Co content \times 60) = $100 \times 10^{-6} \times 100 \times 10^{-3} \times 6.5 \times 10^{-2} / (22.4 \times 3.26 \times 10^{-5} \times 60) = 1.48 \times 10^{-5} \text{ s}^{-1}$.

TOF (Co) of CoO_x-U (dry) = DCM concentration \times flow rate \times DCM conversion / (22.4 \times Co content \times 60) = $100 \times 10^{-6} \times 100 \times 10^{-3} \times 4.5 \times 10^{-2} / (22.4 \times 3.82 \times 10^{-5} \times 60) = 8.76 \times 10^{-6} \text{ s}^{-1}$.

TOF (Co) of CoO_x-UF10 (wet) = DCM concentration \times flow rate \times DCM conversion / (22.4 \times Co content \times 60) = $100 \times 10^{-6} \times 100 \times 10^{-3} \times 8.9 \times 10^{-2} / (22.4 \times 3.26 \times 10^{-5} \times 60) = 2.03 \times 10^{-5} \text{ s}^{-1}$.

TOF (Co) of CoO_x-U (wet) = DCM concentration \times flow rate \times DCM conversion / (22.4 \times Co content \times 60) = $100 \times 10^{-6} \times 100 \times 10^{-3} \times 5.4 \times 10^{-2} / (22.4 \times 3.82 \times 10^{-5} \times 60) = 1.05 \times 10^{-5} \text{ s}^{-1}$.

Text S2. Catalytic activity tests.

The specific surface area of catalysts was measured by Brunauer-Emmett-Teller (BET) model from N₂ adsorption-desorption isotherms on a gas adsorption apparatus (BELSORP-max, Japan). Besides, Barrett-Joyner-Halenda (BJH) method was used to analyze pore structures. X-ray diffraction (XRD) patterns were obtained on an X'Pert Pro MRD (PANalytical, Netherlands) instrument using a Cu K α radiation ($\lambda=1.54056 \text{ \AA}$, $10^\circ \text{ min}^{-1}$ from 10 to 80°) with the voltage of 40 kV and current of 40 mA . The micro-morphologies of catalysts were conducted on a JEOL JSM-7800F field emission scanning electron microscopy (SEM). The transmission electron microscopy (TEM) images and elements scanning maps were detected on JEM-2800 electron microscopy (JEOL, Japan) and energy dispersive spectrometer (EDS), respectively. X-ray photoelectron spectra (XPS) were recorded on a Thermo Scientific Escalab 250Xi S4 spectrometer and all binding energies were corrected by referring to the C 1s peak at 284.6 eV . H₂ temperature-programmed reduction (H₂-TPR), NH₃ temperature-programmed desorption (NH₃-TPD), and O₂ temperature-programmed desorption (O₂-TPD) were conducted on a chemical adsorption analyzer (PCA-1200) to analyze various surface chemical properties. All the samples were purged at $150 \text{ }^\circ\text{C}$ for 1 h under 50 mL/min He. For NH₃-TPD and O₂-TPD tests, $\sim 100 \text{ mg}$ purged catalysts were treated with a 30 mL/min of $5 \text{ vol.}\% \text{ NH}_3/\text{N}_2$ and $5 \text{ vol.}\% \text{ O}_2/\text{He}$, respectively, to reach saturated adsorption. Subsequently, the programs were heated up to 1173 K (10 K/min) under 30 mL/min N₂ to collect the desorbed NH₃/O₂ signals. For H₂-TPR, $\sim 50 \text{ mg}$ pretreated samples were heated up to $800 \text{ }^\circ\text{C}$ ($10 \text{ }^\circ\text{C/min}$) under 30 mL/min $10 \text{ vol.}\% \text{ H}_2/\text{He}$ and the signal intensity was recorded by a TCD detector. Raman spectra was obtained by LabRAM HR Evolution-Raman spectrometer (Jobin Yvon S.A.S, France). Electron paramagnetic resonance (EPR) was carried out to analyze the oxygen vacancy of catalysts using an EMXPlus instrument. The contact angle was measured by Dataphysics-OCA20.

Text S3. In-situ DRIFTS details.

In-situ diffused reflectance infrared Fourier transform spectroscopy (in-situ DRIFTS) measurements of DCM catalytic ozonation with presence of water vapor were conducted on an iS50 spectrometer equipped with a reaction chamber (Praying Mantis). Prior to tests, the catalyst was purged by 100 mL/min N_2 at 120 °C for 30 min. Subsequently, DCM and O_2/O_3 flows were introduced according to experimental settings. Water vapor was also injected by bubbling method. All the in-situ spectra were recorded from 600~4000 cm^{-1} at a resolution of 4 cm^{-1} .



Fig. S1. Real picture of catalyst crystallization effect after hydrothermal process

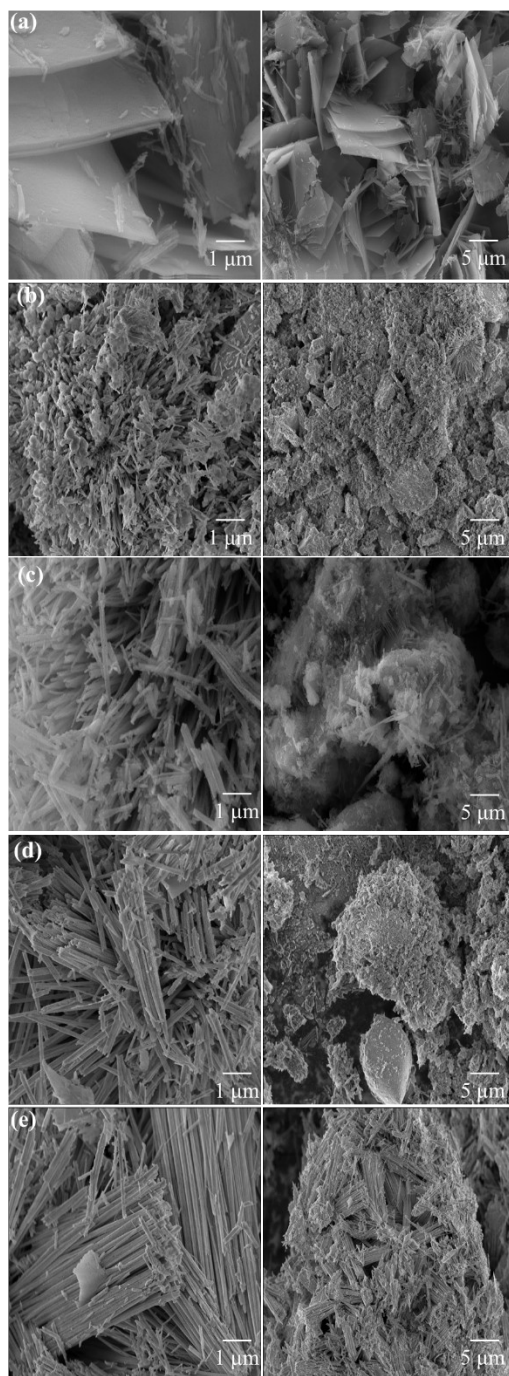


Fig. S2. SEM of CoOx-U (a), CoOx-UF5 (b), CoOx-UF10 (c), CoOx-UF15 (d), CoOx-UF20 (e).

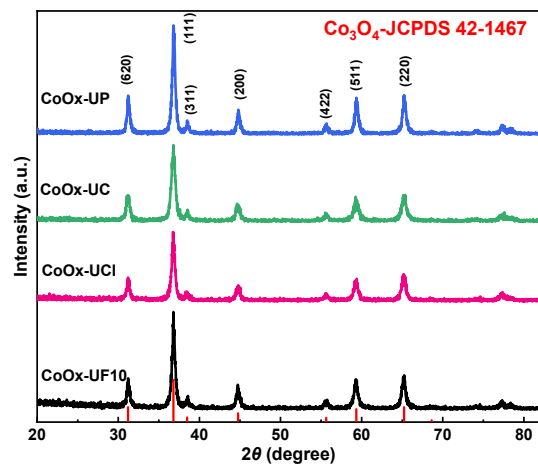


Fig. S3. XRD patterns of catalysts with varied template agents.

Table S1. Pore structure parameters of catalysis.

Catalysts	BET specific surface area (m ² /g)	Total pore volume ^a (cm ³ /g)	Average pore size ^b (nm)
CoO _x -U	65.1	0.20	9.6
CoO _x -UF5	52.0	0.16	12.4
CoO _x -UF10	68.3	0.20	17.3
CoO _x -UF15	43.5	0.29	17.1
CoO _x -UF20	49.8	0.25	16.8

^a BET specific surface area obtained at $P/P_0 = 0.05-0.30$; ^b Total pore volume estimated at $P/P_0 = 0.98$ ^b BJH pore diameter calculated from the N₂ adsorption branch.

Table S2. Textural property and semi-quantitative results of synthesized catalysts.

Catalysts	H ₂ consumption ^a (a.u.)	O ₂ desorption ^a (a.u.)	NH ₃ desorption ^a (a.u.)
CoO _x -U	10992439	373401	373401
CoO _x -UF5	8927688	377695	6500
CoO _x -UF10	10376518	373376	418734
CoO _x -UF15	11634308	428764	311824
CoO _x -UF20	11615282	358908	394890

^aPeak areas of H₂ consumption, O₂ desorption, and NH₃ desorption obtained from H₂-TPR, O₂-TPD and NH₃-TPD results, respectively.

Table S3. The content of Co element measured by ICP.

	CoO _x -U	CoO _x -UF5	CoO _x -UF10	CoO _x -UF15	CoO _x -UF20
Co content (%)	75.25	72.81	64.02	75.56	77.84