

Effect of Cu modification to Ru/HZSM-5 catalysts on the catalytic combustion of vinyl chloride

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Catalysts characterization

The chemical compositions of all catalysts were measured quantitatively using inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an Agilent 725 spectrometer. Prior to the measurement, each sample was dissolved in a mixed solution of hydrofluoric acid and aqua regia and then diluted before measurement.

To obtain X-ray diffraction (XRD) measurements, we used a Bruker D8 Focus diffractometer with Cu K α radiation (40 kV, 40 mA, $\lambda = 1.5406 \text{ \AA}$) and a scanning rate of $6^\circ/\text{min}$ at $2\theta = 5\text{-}80^\circ$.

Nitrogen adsorption and desorption isotherms were recorded at low temperatures (77 K) using a Micromeritics ASAP 2020 M instrument after degassing the sample at 180°C for 1 hour prior to analysis. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method, and pore size distribution was calculated using the Barrett-Joyner-Halanda (BJH) method.

Scanning transmission electron microscopy (STEM) was recorded with a ThermoFisher Talos F200X (FETEM, 200 kV), and high angle annular dark field (HAADF)-STEM images were acquired with a convergence semi-angle of 11 mrad, and inner- and outer collection angles of 59 and 200 mrad, respectively. Energy dispersive X-ray spectroscopy (EDS) was carried out using 4 in-column Super-X detectors.

The analysis of X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Scientific ESCALAB 250Xi electron spectrometer. Al K α ($h\nu = 1486.6 \text{ eV}$) radiation was used as the excitation source in ultra-high vacuum ($6.7 \times 10^{-8} \text{ Pa}$), and a pass energy of 30 eV was applied. The C1s peak (284.8 eV) originating from the adventitious carbon was used as a reference.

Ultraviolet and visible diffuse reflectance spectroscopy (UV-vis) were determined on a Lambda 950 UV-vis spectrophotometer.

The temperature-programmed reduction of hydrogen (H_2 -TPR) was performed in a PX 200 apparatus (Tianjin Pengxiang Technology Co., Ltd.) equipped with a thermal conductivity detector (TCD). A total of 40 mg of the catalyst was loaded into a quartz reactor and gradually heated from 30°C to 800°C at a rate of $10^\circ\text{C}/\text{min}$ while being exposed to a flow of 10 vol.% H_2/N_2 gas mixture, flowing at a flow rate of 40 mL/min. The amount of H_2 consumed was quantified by utilizing high purity CuO as a reference sample.

The PX 200 apparatus, manufactured by Tianjin Pengxiang Technology Co., Ltd., was used for the temperature-programmed desorption of ammonia (NH_3 -TPD). Initially, 50 mg of the catalyst

was placed in a quartz reactor and treated with Ar for 1 hour at 450 °C with a flow rate of 50 mL/min. Following cooling down to 90 °C, the adsorption of ammonia was executed in a flow of 10 vol.% NH₃/Ar at a flow rate of 50 mL/min and preserved at 90 °C for 30 minutes. Desorption was carried out by ramping the temperature from 90 °C to 600 °C at a rate of 10 °C /min. A TCD detected the corresponding NH₃ desorption signal.

Temperature-programmed desorption of oxygen (O₂-TPD) was conducted using a Micromeritics AutoChem II 2920 chemisorption analyzer. A mass of 50 mg of the catalyst underwent pretreatment at 400 °C for 1 hour in 3 vol.% O₂/He gas with a flow rate of 40 mL/min. Upon cooling to room temperature, the catalyst was purged with pure He at a flow rate of 40 mL/min for 40 minutes. The reactor was then heated from room temperature to 800 °C at a rate of 10 °C/min. The Hiden HPR20 mass spectrometer (MS) was used to record the signal.

The in-situ DRIFT measurement of VC oxidation was performed on a Nicolet Nexus 6700 FT-IR spectrometer with an MCT detector, and the sample cell was equipped with BaF₂ windows and a heating chamber. The sample was pretreated at 300 °C for 1 hour in O₂/Ar at a 40 mL/min flow rate, then cooled to 60 °C to collect the backgrounds at 40 °C intervals. Subsequently, the gas flow consisting of stoichiometric VC/O₂ mixture was introduced into the IR cell at 60 °C and the infrared signals were collected after stabilizing for 30 minutes. Then the temperature was increased, and the spectra of VC oxidation were collected at 40 °C intervals.

Catalyst performance evaluation for EDC oxidation

The catalytic activity of EDC oxidation was evaluated by a fixed bed reactor. 100 mg of the catalysts were placed in a quartz tube with an inner diameter of 6 mm. A mixture of EDC and air, with a concentration of 1000 ppm of EDC, was passed through the tube with a weight hourly space velocity (WHSV) of 30,000 mL·h⁻¹·g_{cat}⁻¹. The outlet gas was detected online using a GC2060 gas chromatography. It equipped a flame ionization detector (FID) to test EDC and the organic by-products of the reaction. The conversion of EDC was calculated by the following equation:

$$X_{\text{EDC}}(\%) = \frac{[\text{EDC}]_{\text{in}} - [\text{EDC}]_{\text{out}}}{[\text{EDC}]_{\text{in}}} \times 100\%$$

Where [EDC]_{in} and [EDC]_{out} represent the concentrations of EDC at the inlet and outlet, respectively.

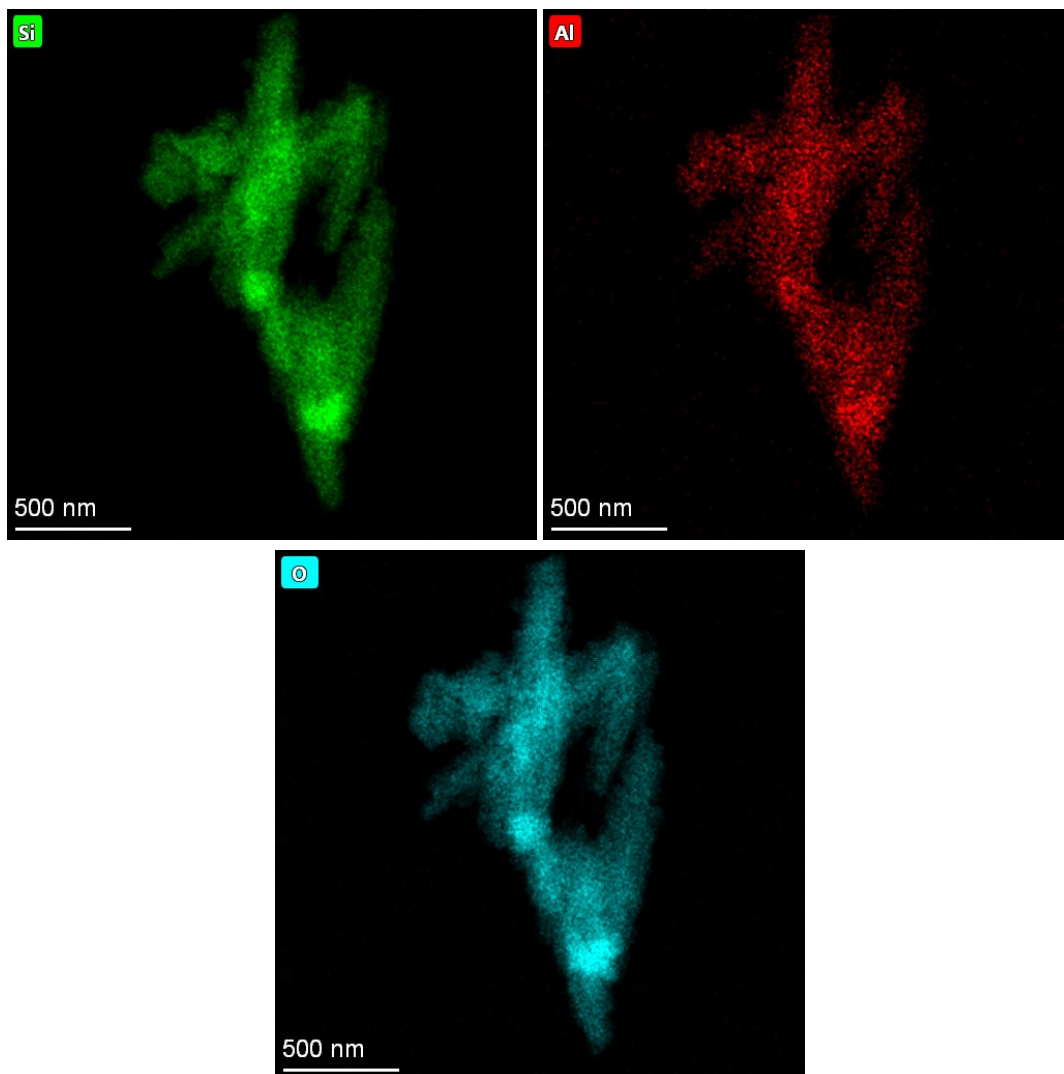


Fig. S1 EDS mapping images of Ru/HZSM-5 catalyst.

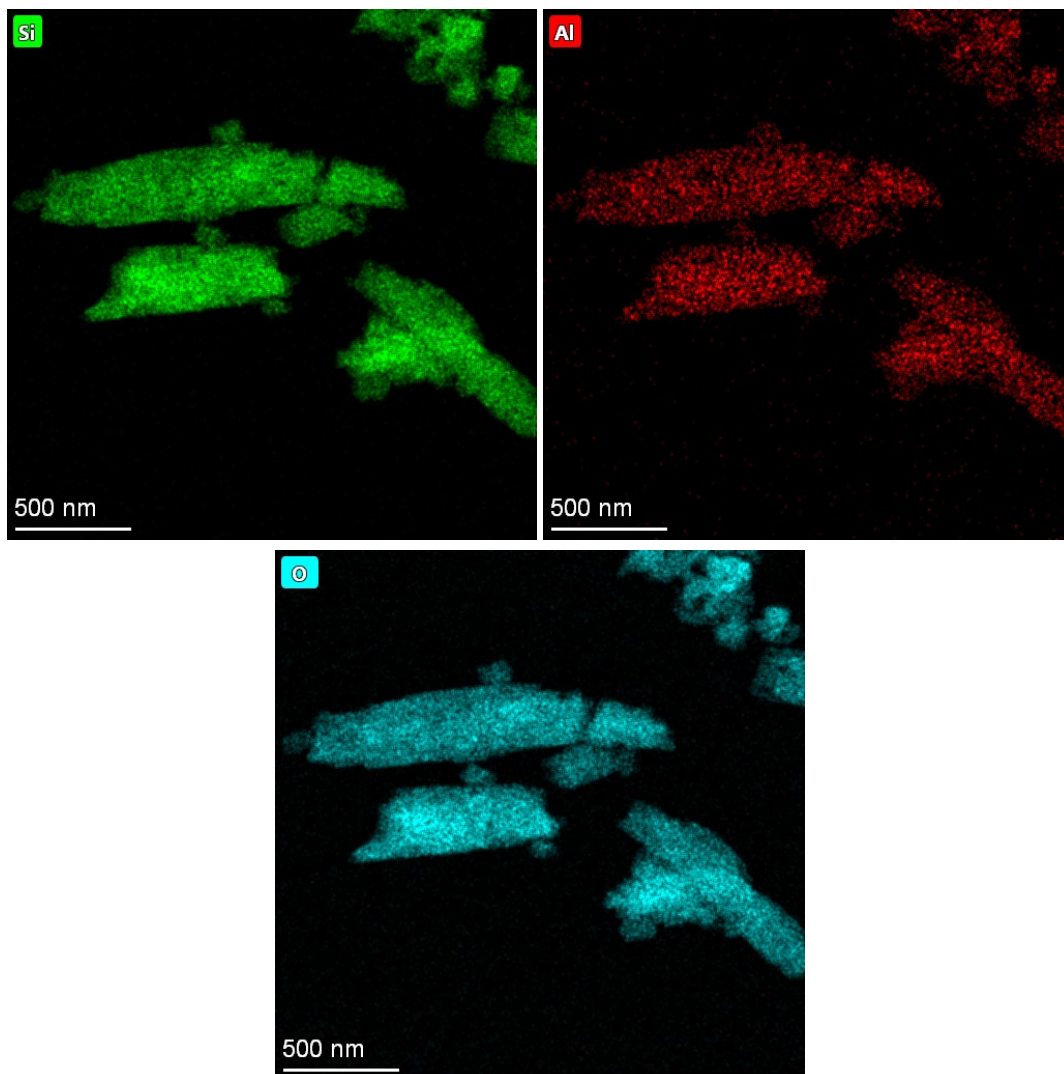


Fig. S2 EDS mapping images of Ru-2Cu/HZSM-5 catalyst.

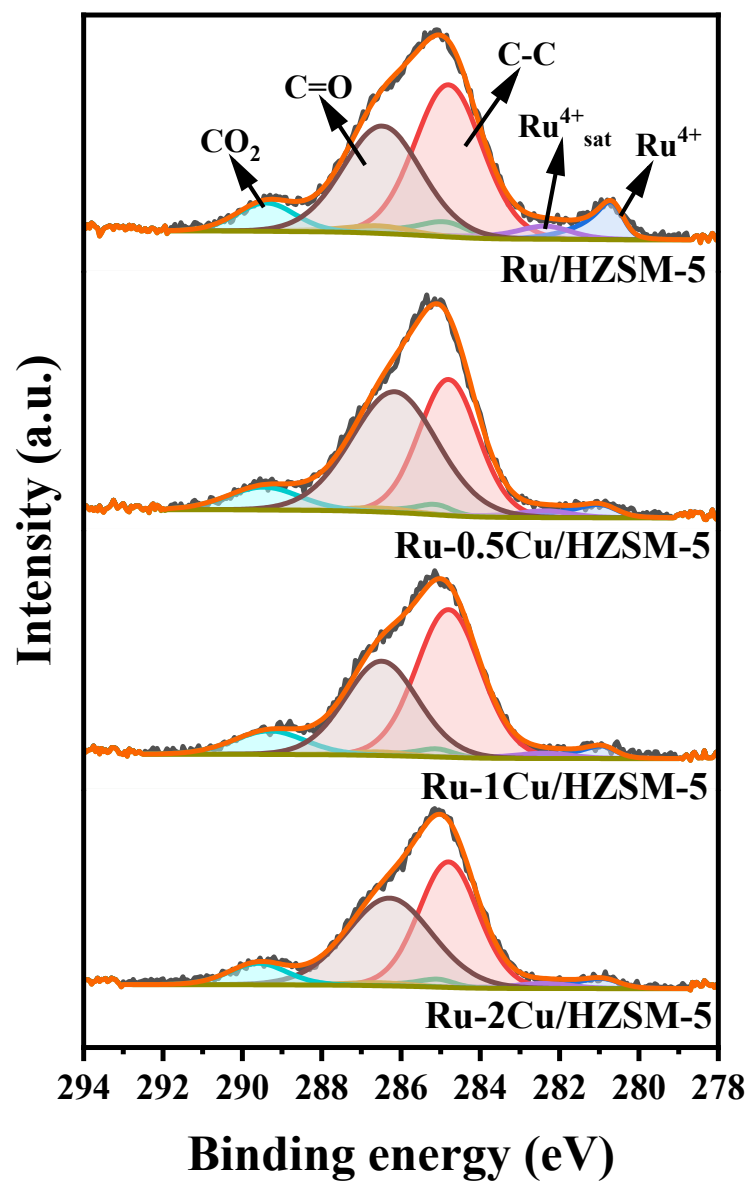


Fig. S3 Ru 3d XPS spectra of zeolite-based catalyst.

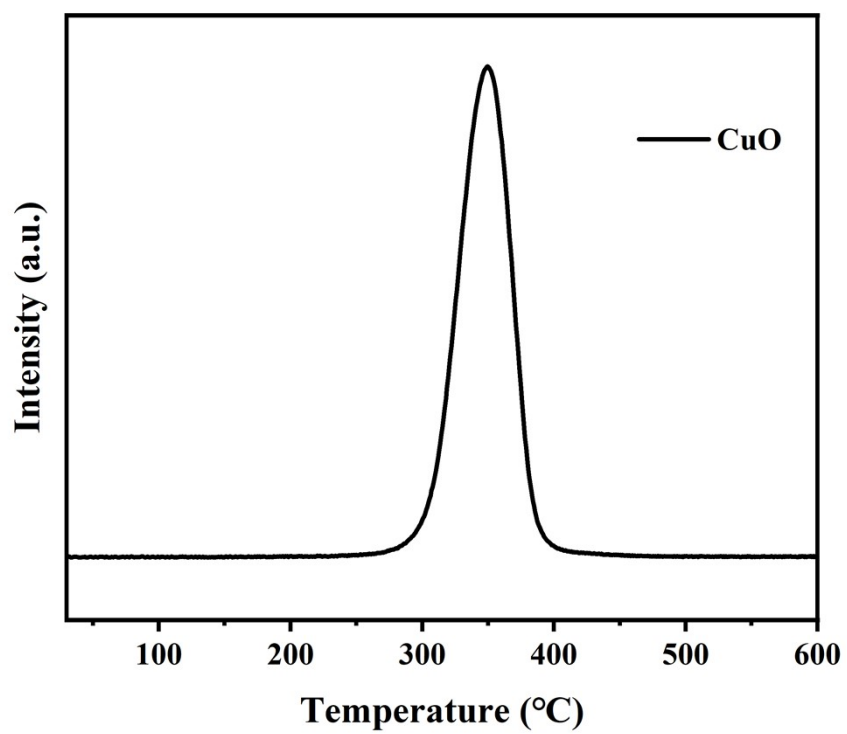


Fig. S4 H₂-TPR profiles of CuO sample.

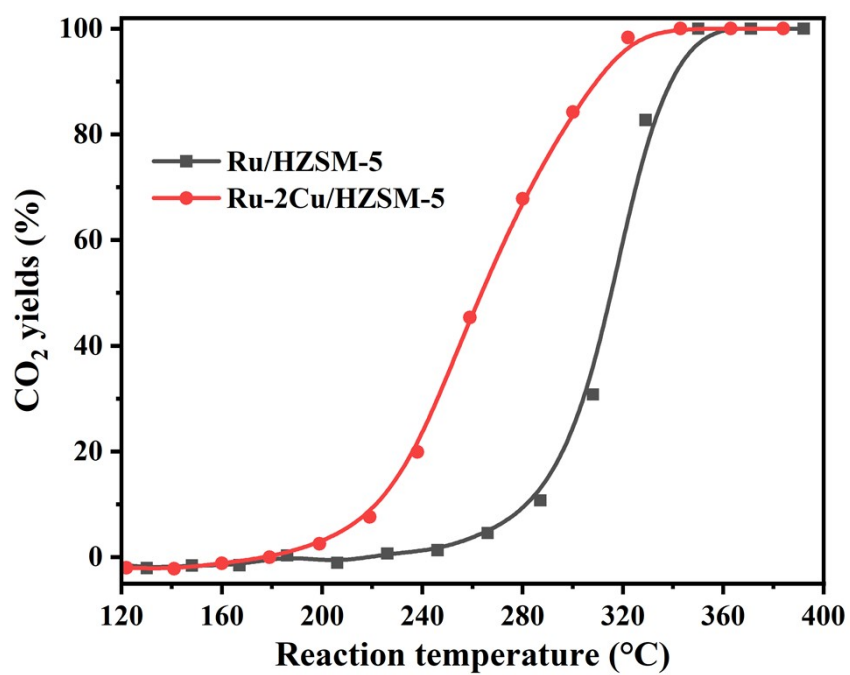


Fig. S5 CO₂ yields of the Ru/HZSM-5 and Ru-2Cu/HZSM-5 catalysts in the catalytic combustion of VC.

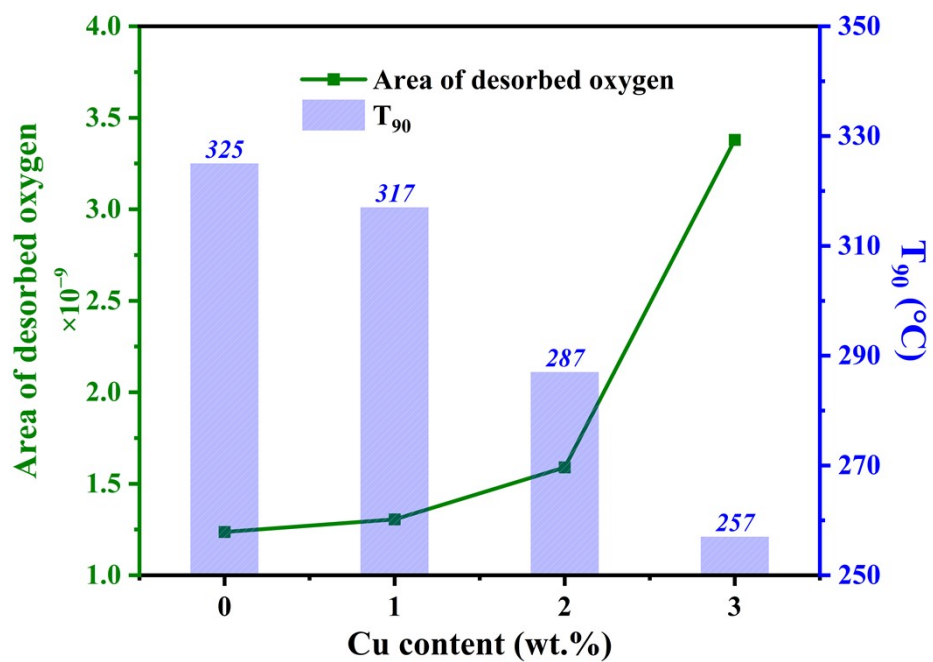


Fig. S6 Relationship between surface oxygen desorption peak area and T₉₀ values over Ru/HZSM-5 and Ru-xCu/HZSM-5 catalysts.

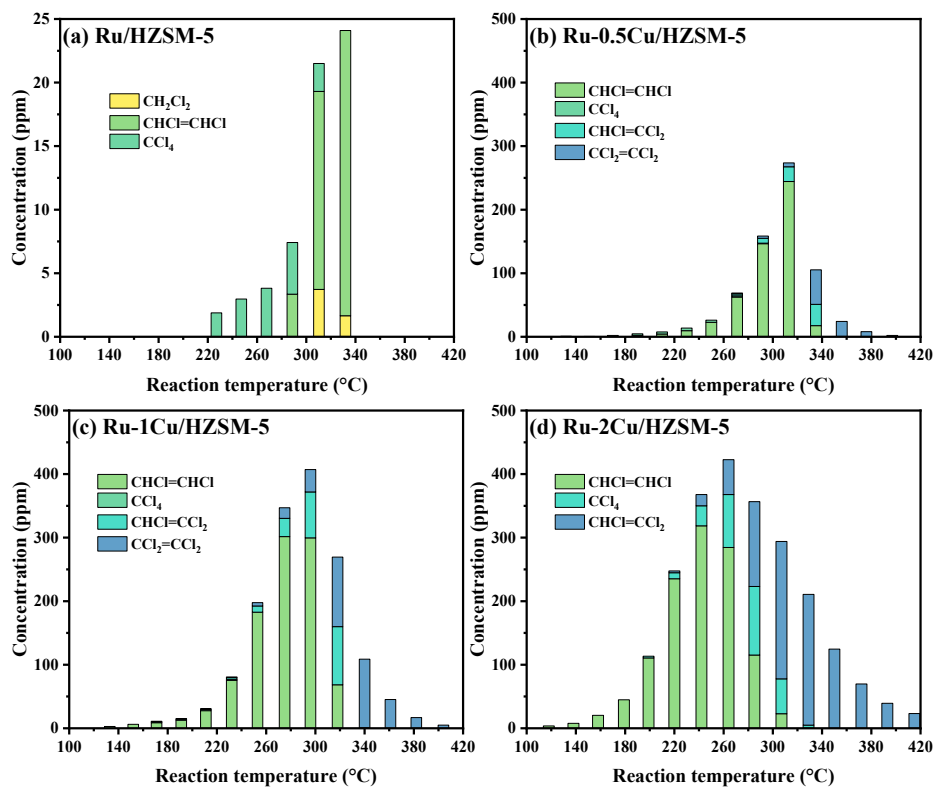


Fig. S7 The concentrations of chlorinated by-products as a function of temperature for VC oxidation over the zeolite-based catalysts. The reaction conditions were 1000 ppm VC, and air balance, and the WHSV was $30,000 \text{ mL} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$.

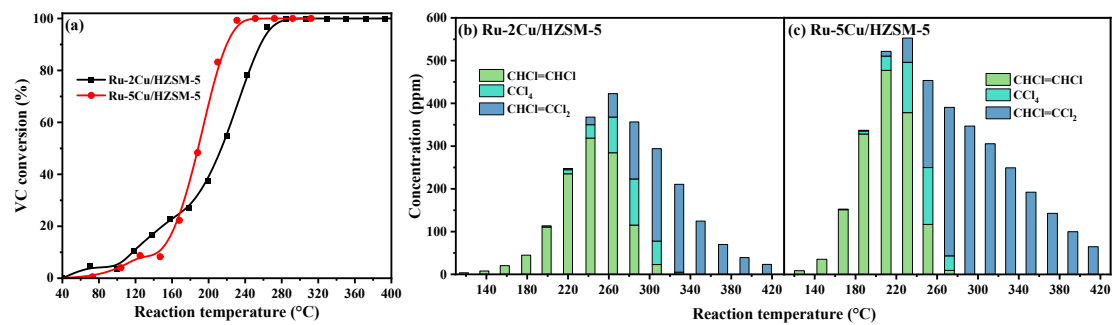


Fig. S8 (a) Catalytic activity of VC for the Ru-2Cu/HZSM-5 and Ru-5Cu/HZSM-5 catalysts. (b) The concentrations of chlorinated byproducts as a function of temperature over the Ru-2Cu/HZSM-5 and Ru-5Cu/HZSM-5 catalysts.

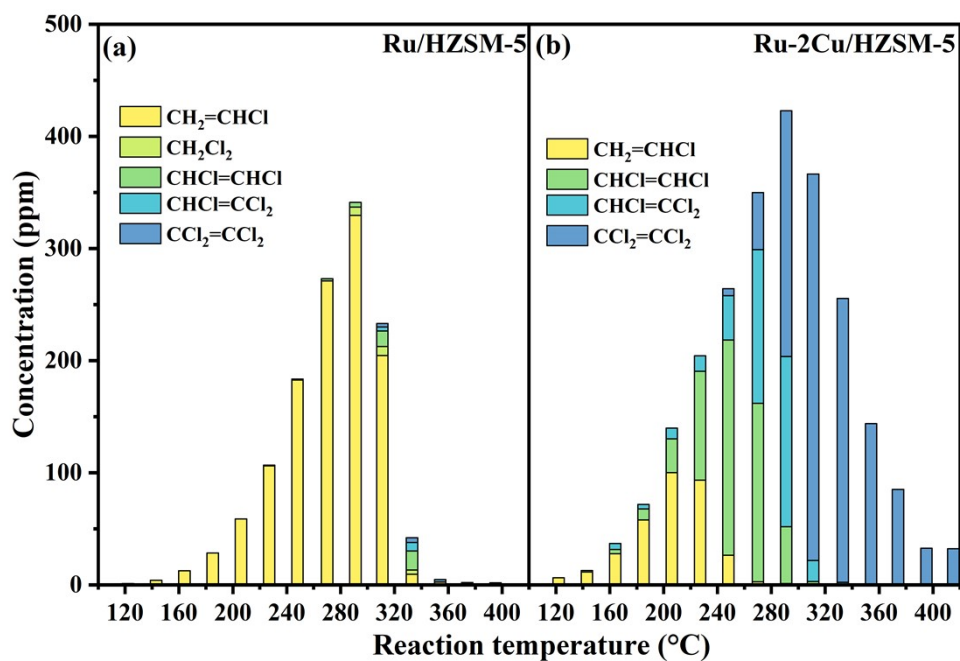


Fig. S9 The concentrations of chlorinated by-products as a function of temperature for EDC oxidation over (a) Ru/HZSM-5 and (b) Ru-2Cu/HZSM-5 catalysts. The reaction conditions were 1000 ppm EDC, and air balance, and the WHSV was 30,000 mL·h⁻¹·g_{cat}⁻¹.

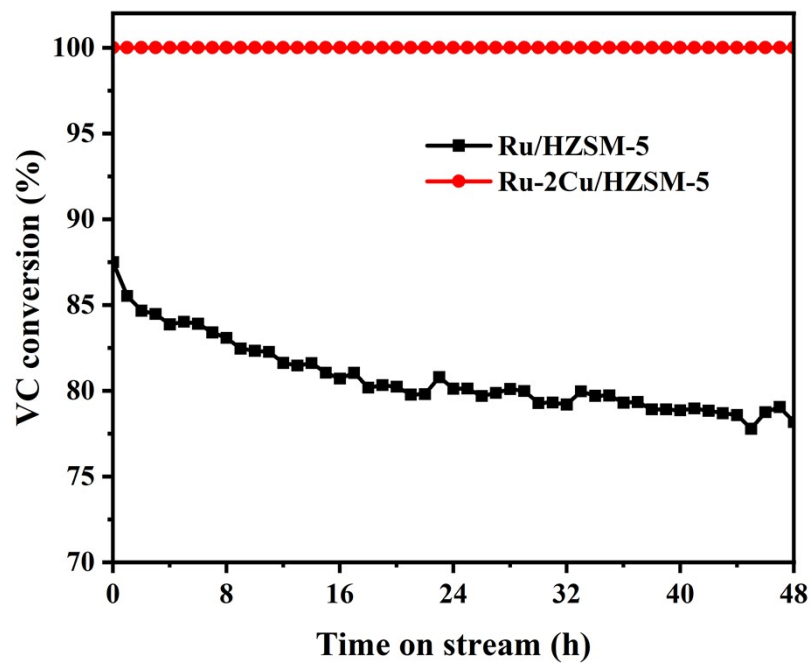


Fig. S10 Catalytic stability for VC oxidation of Ru/HZSM-5 and Ru-2Cu/HZSM-5 catalysts at 320 °C.

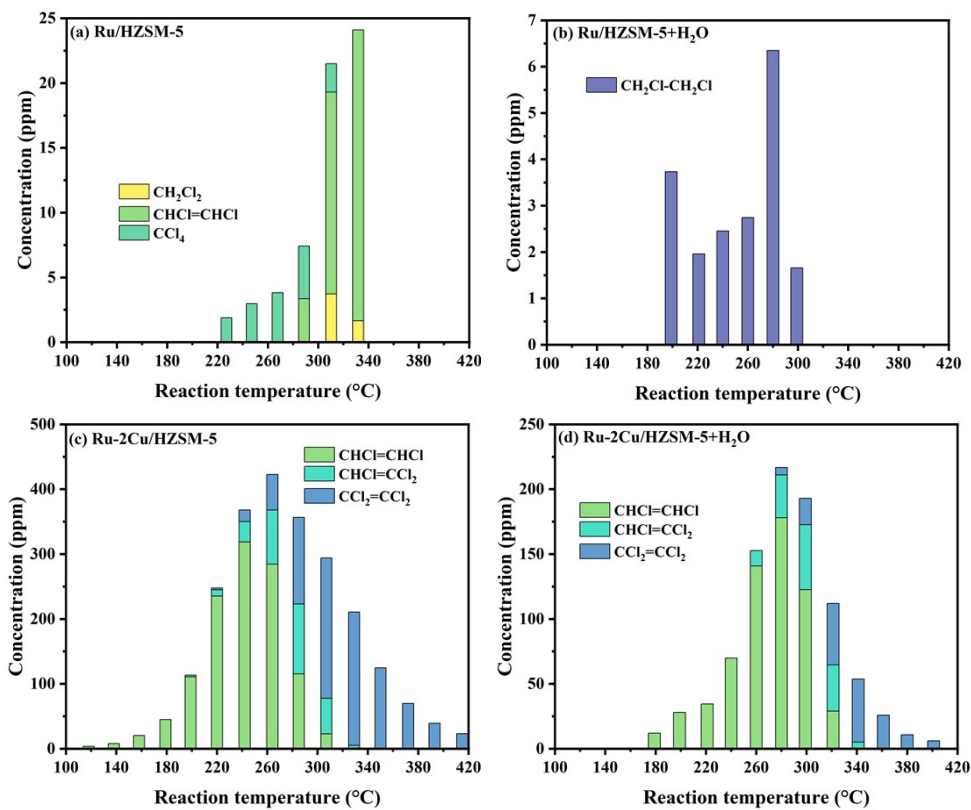


Fig. S11 The concentrations of chlorinated by-products as a function of temperature for VC oxidation over the zeolite-based catalysts under dry and wet conditions.

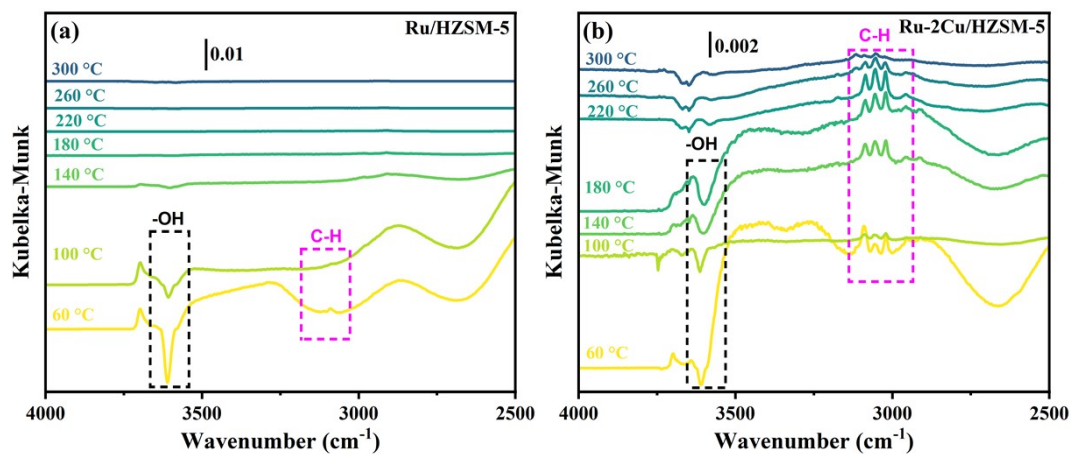


Fig. S12 In situ DRIFTS of VC oxidation over (a) Ru/HZSM-5 and (b) Ru-2Cu/HZSM-5 catalysts in the wavenumber range of 2500-4000 cm^{-1} at different temperatures.

Table S1 Calculation results of H₂-TPR and NH₃-TPD for the catalysts

Catalysts	H ₂ consumption (mmol/g)	NH ₃ desorption (mmol/g)		
	RuO ₂ →Ru	Weak	Strong	Total
Ru/HZSM-5	0.110	0.28	1.11	1.39
Ru-0.5Cu/HZSM-5	0.118	0.20	0.20	0.40
Ru-1Cu/HZSM-5	0.123	0.23	0.17	0.40
Ru-2Cu/HZSM-5	0.136	0.26	0.13	0.39

Table S2 Comparison of the catalytic activity of the Ru-2Cu/HZSM-5 catalyst for VC oxidation with those catalysts reported in the literatures

Catalysts	VC concentration (ppm)	WHSV (mL·h ⁻¹ ·g _{cat} ⁻¹)	T ₉₀ (°C)	Reference
Mn _{0.4} Ti _{0.6} O _x	1000	15,000	262	[1]
Co(0.7)CeO _x	1000	15,000	282	[2]
Ru-CeO ₂	1000	30,000	262	[3]
0.5% Ru/Co ₃ O ₄ -F-10	1000	30,000	251	[4]
1% RuO _x /HZ5-3d	1000	30,000	297	[5]
1% Ru/CoPO-MCF	1000	48,000	313	[6]
Ru/Sn-MFI	1000	30,000	306	[7]
Ru-2Cu/HZSM-5	1000	30,000	257	This work

Reference

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