

Supplementary Information

Abatement of dichloromethane with high selectivity over defect-rich MOFs derived Ru/TiO₂ catalysts

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Catalyst characterization procedures

X-ray diffraction (XRD) patterns of the catalysts were measured with a Smartlab using Cu K α radiation. The specific surface area (SSA) was calculated by the N₂ adsorption–desorption isotherms at 77 K by the Brunauer-Emmett-Teller (BET) method with a SSA-7300 (Builder,

China), all the catalysts were outgassed under vacuum at 150 °C for 8 h prior to the measurement. The weight percent of ruthenium in the catalysts was determined by an inductively coupled plasma-optical emitting spectrometer (ICP-OES, Agilent 5110, USA). The scanning electron spectroscopy was carried on JSM-7800 (Prime) to obtain the surface morphology of the samples. Transmission electron microscopy (TEM) images were collected on JEOL 2100F. X-ray absorption of fine structures (XAFS) measurements of Ru K-edge were performed at Beijing Synchrotron Radiation Facility (BSRF). X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250 Xi spectrometer) was used to determine the binding energies (BEs) of Ti 2p, Ru 3d, O 1s, N 1s and C 1s, and the spectra were calibrated with the C1s peak at 284.8 eV as an internal standard. NH₃-temperature programmed desorption (NH₃-TPD), O₂-temperature programmed desorption (O₂-TPD) and H₂-temperature programmed reduction (H₂-TPR) were carried out on a Micromeritics Autochem II 2920 equipped with a thermal conductivity detector (TCD). As for NH₃-TPD, the catalysts (100 mg) were firstly pretreated in N₂ flow at 200 °C for 1 h. Upon cooling down to 50 °C, the absorption of NH₃ was performed in a flow of 10% NH₃/He over the catalysts for 1 h following the remove of physically absorbed NH₃ by purging with He for 0.5 h. Then NH₃ desorption was carried out from 50 °C to 700 °C with a heating rate of 10 °C /min. The O₂-TPD and H₂-TPR experiments were carried out under

pulse 5% O₂/He, and 10% H₂/He, respectively, and other steps and conditions of experiment were same as NH₃-TPD. Pyridine adsorbed IR spectroscopy (Py-IR) was conducted using an FT-IR (Tensor 27, Bruker, Germany) equipped with a custom-made IR cell that was connected by a vacuum adsorption apparatus. The catalyst was first heated at a rate of 10 °C /min to 300 °C and then cooled down to room temperature in a vacuum (10⁻³ Pa). After that, pyridine vapor was introduced until the adsorption approached saturation. The desorption process was conducted by heat-treatment of the adsorbed catalyst with the heating rate of 10 °C/min to 150 °C. The amount of Lewis acid and Bronsted acid are calculated based on the area of characteristic absorption peaks at 1450 cm⁻¹ and 1540 cm⁻¹, respectively, the extinction coefficient ratio of Lewis acid and Brønsted acid is 1.32 according to $\epsilon_{1450} / \epsilon_{1540}$.

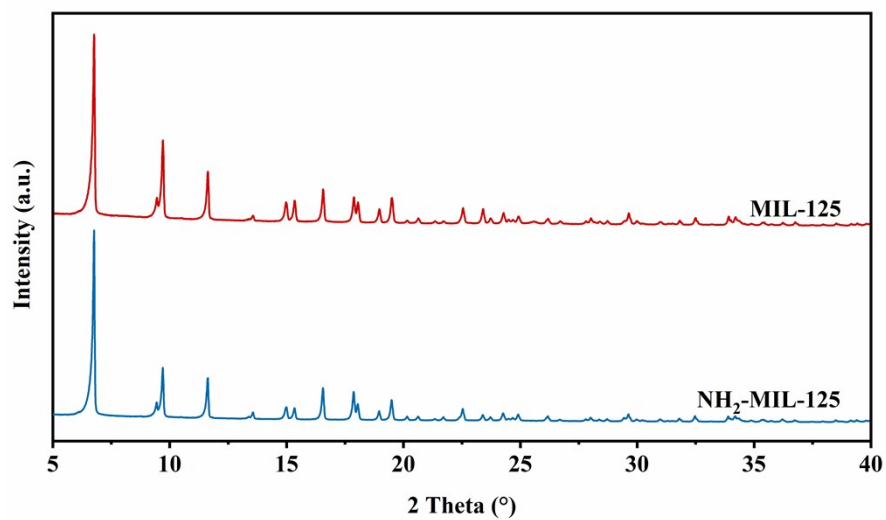


Fig. S1 XRD patterns of MIL-125 and NH₂-MIL-125

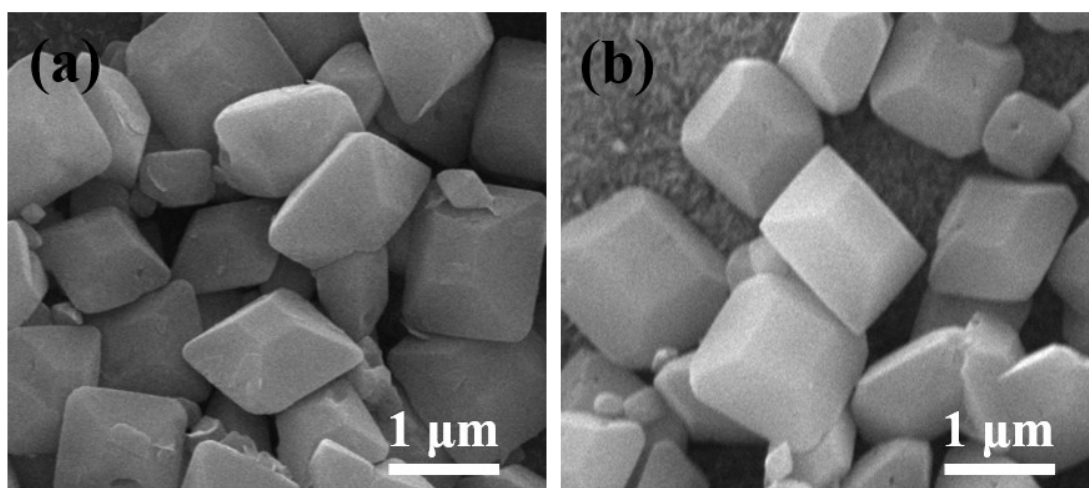


Fig. S2 SEM images of MIL-125 (a) and NH₂-MIL-125 (b)

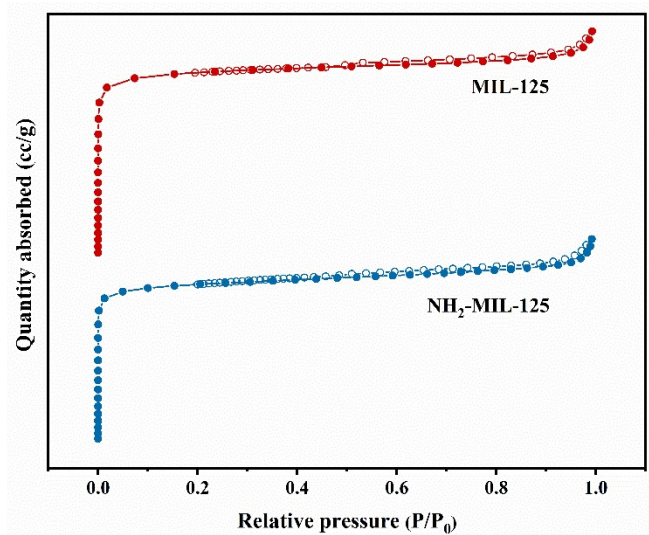


Fig. S3 N₂ adsorption-desorption isotherms of MIL-125 and NH₂-MIL-125

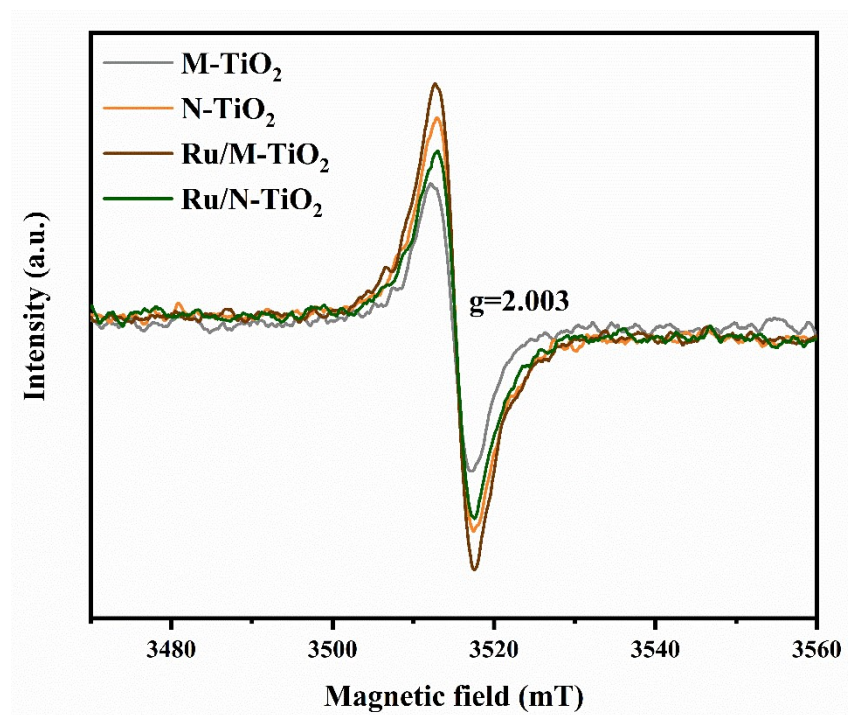


Fig. S4 ESR spectra of catalysts

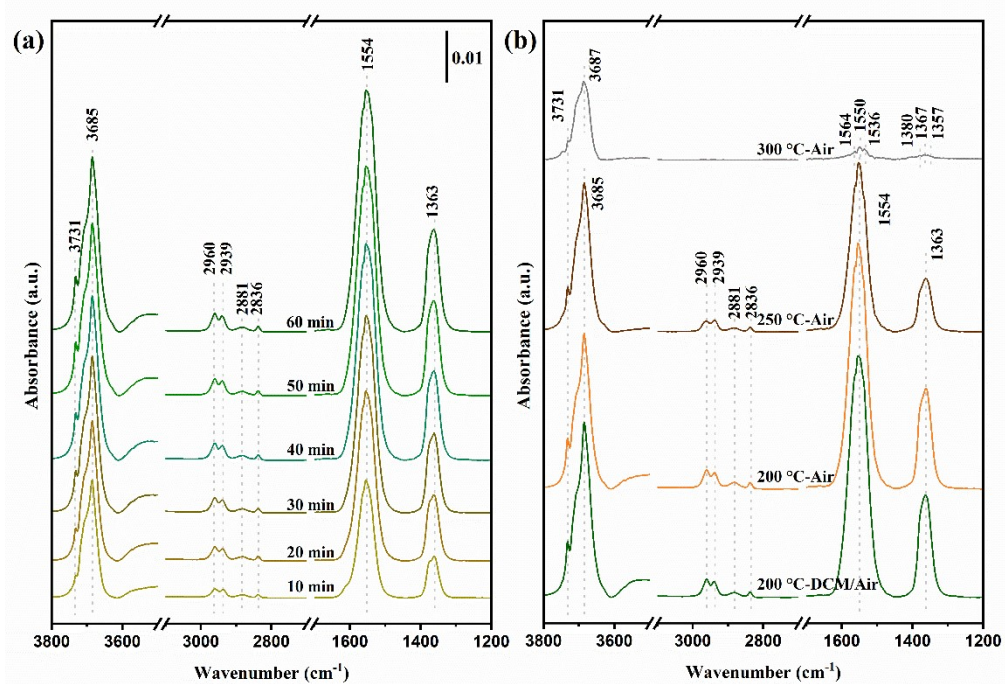


Fig. S5 In situ DRIFT spectra of (a) DCM oxidation over M-TiO₂ at 200 °C and (b) intermediates over M-TiO₂ exposed to air from 200 to 300 °C

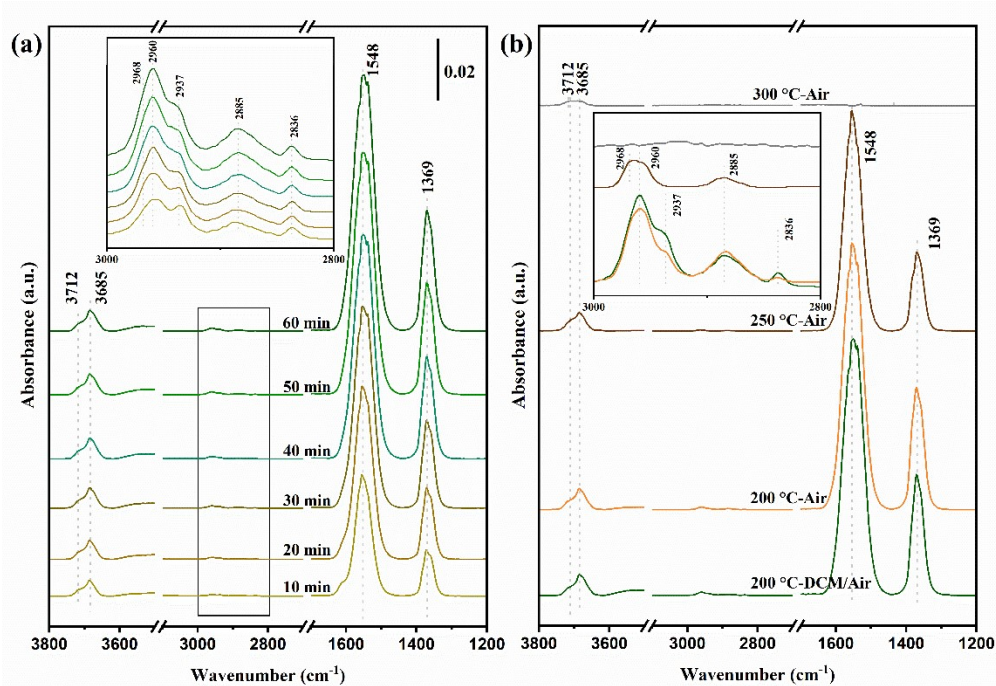


Fig. S6 In situ DRIFT spectra of (a) DCM oxidation over Ru/M-TiO₂ at 200 °C and (b) intermediates over Ru/M-TiO₂ exposed to air from 200 to 300 °C

