Supplementary Information (SI) for Materials Advances.

Supporting information

Rapid, facile synthesis of Fe^{2+}-MOFs in water at ambient conditions

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Materials and Methods

Milli-Q water used for synthesis was degassed by sparging Ar for at least 20 minutes prior to use. Anhydrous and degassed methanol was used for washing under inert conditions. All other chemicals were used as received from commercial suppliers. Standard Schlenk techniques were used during the synthesis and workup of the materials. A PTFE turbine blade (Bohlender C482-12) was used for stirring the reaction mixtures. In situ ATR-IR and synchrotron XRD MOF synthesis experiments (ESRF, ID15A) were performed as described previously using the modified setup depicted in Figure S2.[1] Powder XRD measurements were performed on a D8 Advance diffractometer (Bruker) operating in Bragg–Brentano geometry using CuKα radiation. Diffractograms were collected from 4 to 40° 2θ with a step size of 0.02° and 1 s measurement time per step. An inert atmosphere sample holder with an acrylic dome was used to collect data on the dry Fe-MOF samples.

In situ XRD measurements were performed in transmission geometry at the ID15A beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) at an X-ray wavelength of $\lambda = 0.193725$ Å. Data were collected continuously at a time resolution of 50−100 ms using a DECTRIS Pilatus3 X CdTe 2 M detector. The same reactor cell used for the ATR-IR experiments was modified to replace the bottom part, including the ZnSe crystal, with a stainless steel plate. For this type of measurement, the setup was modified to include a sample loop for online monitoring of the diffraction signal of the reaction mixture through a Kapton capillary (1.2 mm internal diameter). The ligand solution was added via a remotely controlled peristaltic pump (Reglo, Ismatec); a second peristaltic pump (Reglo, Ismatec) was connected in a loop that collected the reactant slurry from the bottom of the reactor, passed it through the Kapton capillary, and returned it to the reactor. In each experiment, this pump was remotely turned on 3 s after the addition of the ligand was finished.

Fe_2(p-dobdc) synthesis

In a Schlenk flask, a solution of 1.2155 g of $Fe(ClO_4)_2 \cdot 6H_2O$ (3.35 mmol, 2.5 eq) in 7.3 mL of degassed water was prepared and brought to 80 °C under Ar with mechanical stirring at 500 rpm. A degassed sodium hydroxide solution was prepared by combining 0.536 mL of 10N NaOH solution (5.36 mmol, 4 eq) with 7.32 mL of water, followed by Ar sparging for 20 minutes. This solution was added via syringe transfer to an Ar-flushed septum vial containing 0.2655 g of H_4(p-dobdc) (1.34 mmol, 1 eq) and a stir bar. The resulting ligand solution was brought to 80 °C and cannula-transferred to the Fe solution. The mixture was allowed to react for 10 minutes, after which it was cooled down to room temperature and filtered on a Schlenk filter, followed by washing with 3x20 mL degassed water and 3x20 mL degassed, anhydrous methanol. Next, the solid was submerged in 20 mL degassed methanol and was kept under methanol for 1 week, exchanging for a fresh solvent every 24 h. Finally, the solid was filtered, vacuum-dried overnight, and stored in a nitrogen-filled glovebox. Yield: 0.365 g.

Fe_2(m-dobdc) synthesis

In a Schlenk flask, a solution of 2.721 g of $Fe(ClO_4)_2 \cdot 6H_2O$ (7.5 mmol, 2.5 eq) in 16.4 mL of degassed water was prepared at 25 °C under Ar with mechanical stirring at 500 rpm. A degassed sodium hydroxide solution was prepared by combining 1.200 mL of 10N NaOH solution (12 mmol, 4 eq) with 5 mL water, followed by Ar sparging for 20 minutes. This solution was added via syringe transfer to an Ar-flushed septum vial containing 0.5944 g of H_4(m-dobdc) (3 mmol, 1 eq) and a stir bar. The resulting ligand solution at 25 °C was cannula-transferred to the Fe solution. The mixture was allowed to react for 40 minutes, after which it was cooled down to room temperature and filtered on a Schlenk filter, followed by washing with 3x20 mL degassed water and 3x20 mL degassed, anhydrous methanol. Next, the solid was submerged in 20 mL degassed methanol and was kept under methanol for 1 week, exchanging for a fresh solvent every 24 h. Finally, the solid was filtered, vacuum-dried overnight, and stored in a nitrogen-filled glovebox. Yield: 0.757 g.

NO adsorption experiments

Inside a nitrogen-filled glovebox, a sample of ca. 10 mg of a MOF was dispersed in 0.5-1 mL of anhydrous, degassed n-heptane. The resulting slurry was deposited on top of a ZnSe ATR crystal (30°, 50 × 20 × 2 mm) and was allowed to dry inside the glovebox. The crystal was then mounted inside an in situ cell (Figure S3) and connected to the gas dosing setup under a flow of Ar. After stabilization in Ar, a background spectrum of the MOF layer on the ZnSe crystal was collected in Ar. Then, a 10 mL/min flow of 1 vol% NO in Ar was dosed to the MOF layer for 30 minutes while ATR-IR spectra were collected continuously at a resolution of 4 cm^{-1} using a FTIR spectrometer (Nicolet 6700) to obtain the signature of NO adsorbed on the Fe-MOF materials.

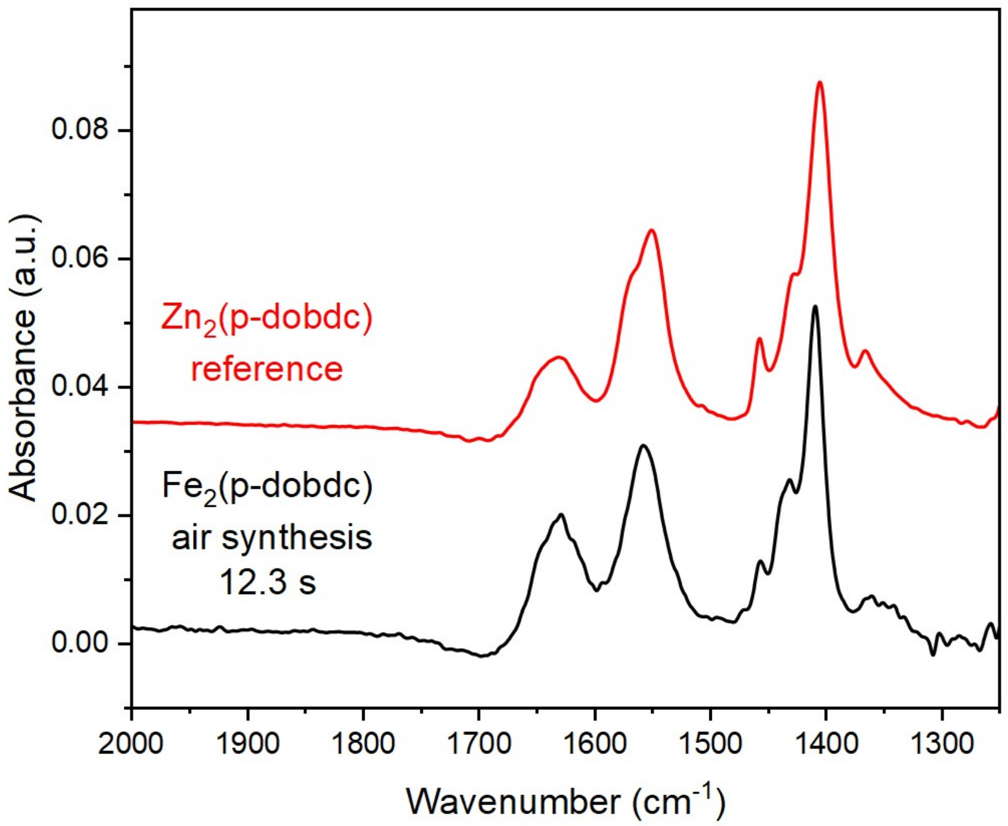

Figure S1. Comparison plot of the in situ ATR-IR spectrum of Fe_2(p-dobdc) synthesis product under air after 12.3 s with the reference ATR-IR spectrum of Zn_2(p-dobdc).

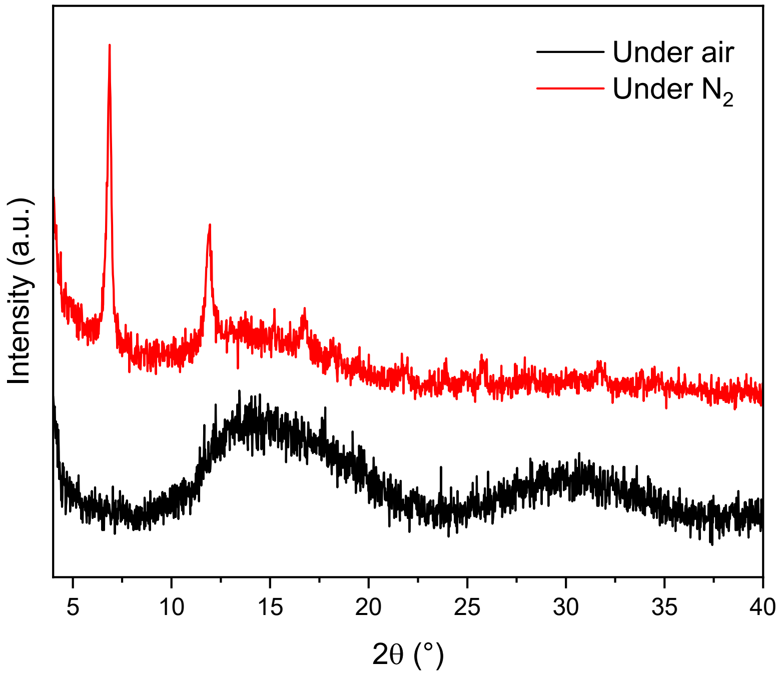

Figure S2. XRD patterns of the reaction products from the ATR-IR reactor produced under air (bottom) and under N_2 (top).

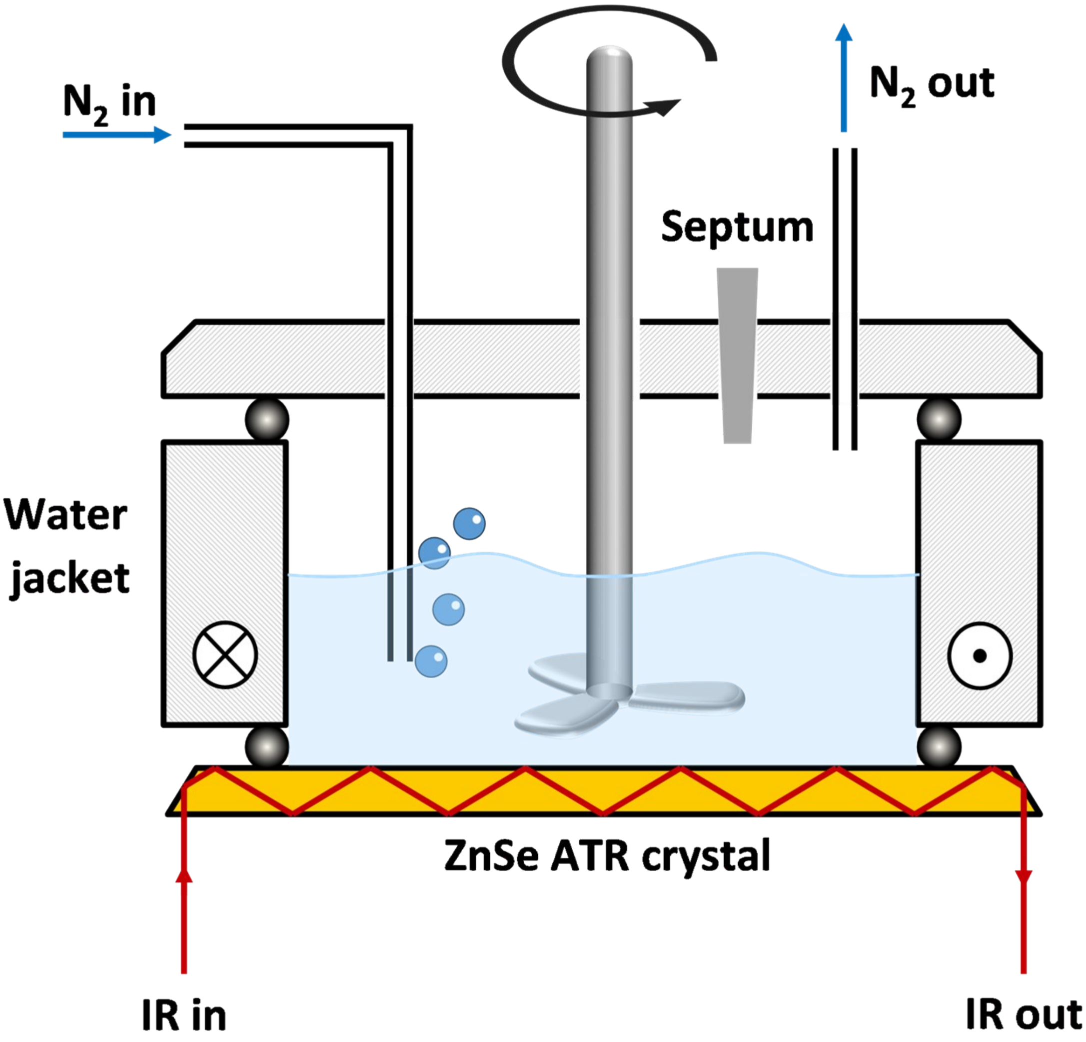

Figure S3. A modified in situ ATR-IR cell was used for studying the synthesis reactions under an inert atmosphere.

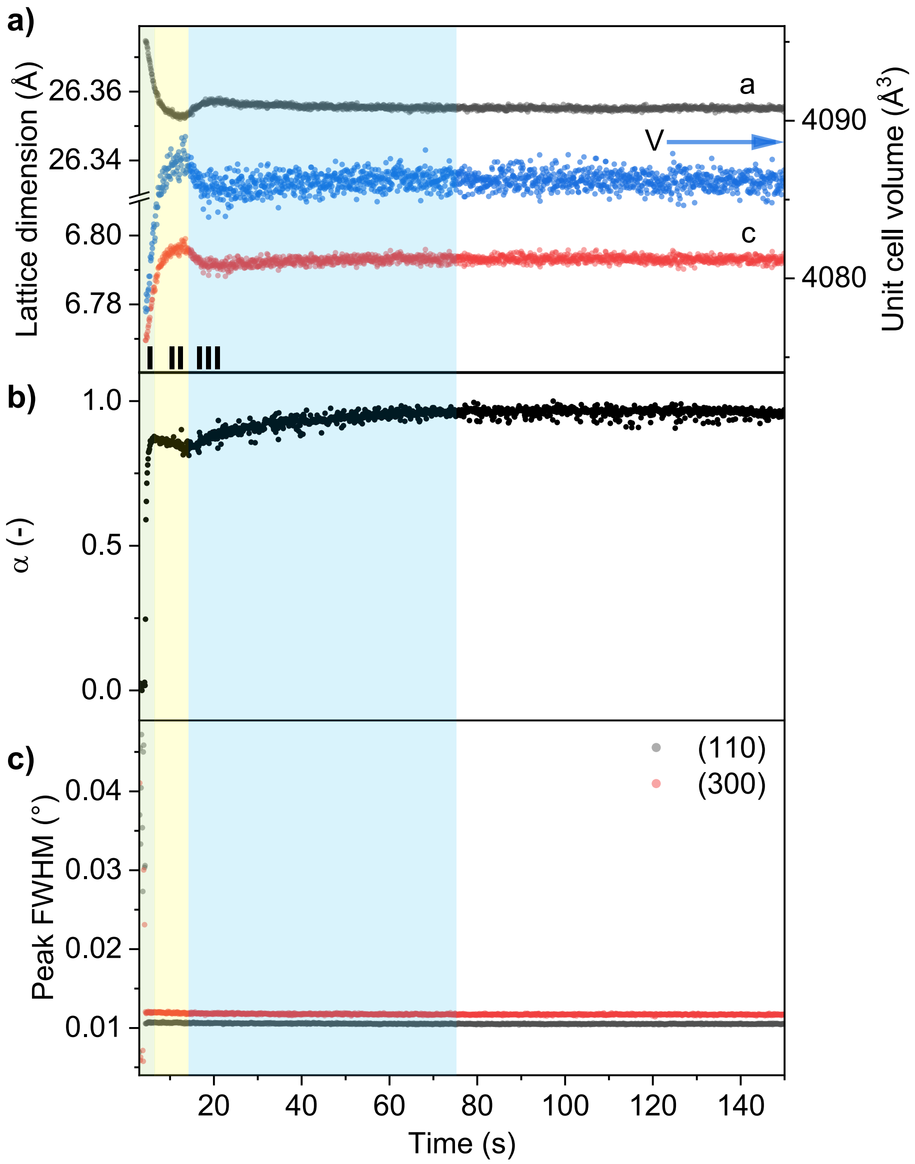

Figure S4. (a) Lattice parameters, (b) degree of crystallinity (α), (c) FWHM of the 110 and 300 peaks vs. time during the synthesis of Fe_2(p-dobdc) at 80 °C.

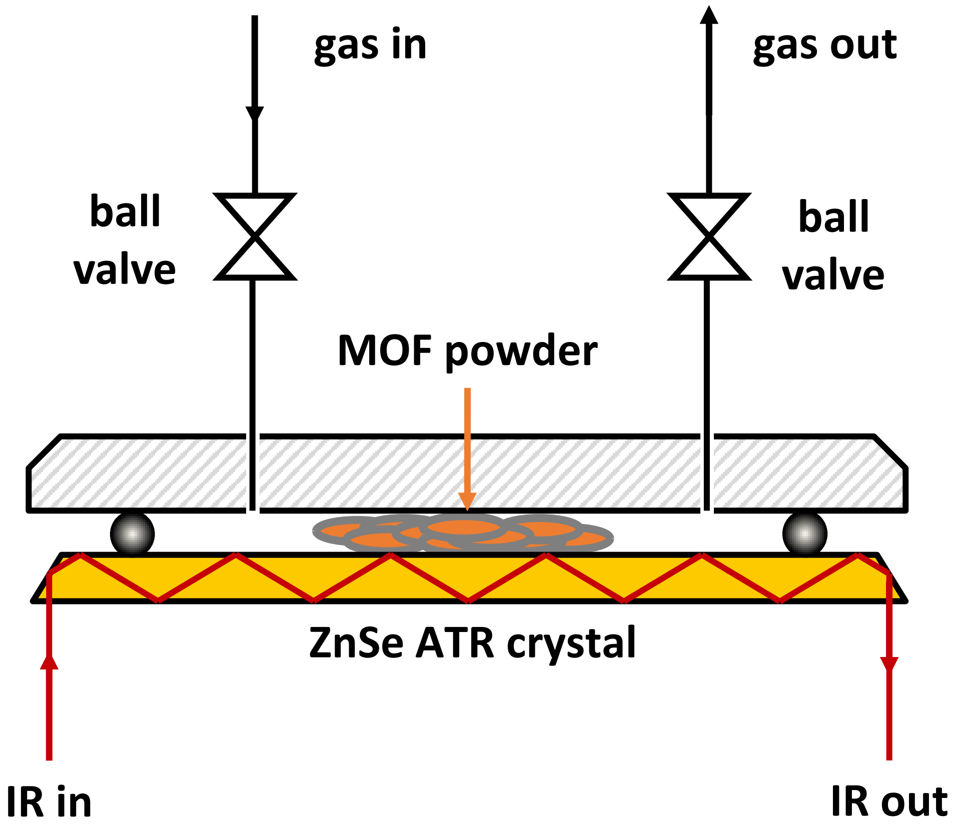

Figure S5. A modified in situ ATR-IR cell used for studying the NO adsorption on MOF materials.

References

(1) Kochetygov, I.; Maggiulli, L.; Ranocchiari, M.; Ferri, D. The Mechanism of Rapid and Green Metal–Organic Framework Synthesis by in Situ Spectroscopy and Diffraction. *Chem. Mater.* **2024**, *36* (14), 6877-6887. DOI: 10.1021/acs.chemmater.4c00879.