— Supporting Information —

Real-Time Observation of the Exchange Process between H_2O and NO in the Metal Organic Framework Ni-MOF-74

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Sample Preparation:

The Ni-MOF-74 sample was synthesized by following the modified procedure from Ref. [1]. A mixture of nickel nitrate hexahydrate (0.24 g, 0.8 mmol), 2,5-dihydroxyterephthalic (0.08 g, 0.4 mmol), 9 ml DMF, and 1 ml H_2O was prepared in a 28 ml Teflon-lined autoclave. The autoclave was then sealed and heated to 100 ℃ for 3 days. After filtering and washing with 20 ml DMF, the product was collected and exchanged with methanol every 2 h during daytime for at least 3 days. Then the MOF sample was stored in a N_2 glove box. The crystal structure of Ni-MOF-74 was confirmed by PXRD measurement as shown in Fig. S1. After thorough solvent exchange, the BET surface area reaches 913 m^2/g (see Fig. S2)

In situ Infrared (IR) spectroscopy:

In situ IR measurements were performed on a Nico-let 6700 FTIR spectrometer using a liquid N_2-cooled mercury cadmium telluride (MCT-A) detector. A vacuum cell is placed in the sample compartment of the infrared spectrometer with the sample at the focal point of the beam. The MOFs (powder, ~5 mg) were gently pressed onto a tungsten mesh (~1 cm diameter, wire diameter: 0.001″; width opening: 0.0090″; % open area: 81.0) and placed in a cell for in-situ activation by evacuation overnight at 180 ℃, and then cooling back to room temperature for NO and H_2O vapor exposure measurement.

Ab initio Calculations:

All *ab initio* calculations were performed using density functional theory (DFT) in VASP (Vienna Ab Initio Simulation Package) [2,3], with the vdW-DF functional [4–7] to consider important van der Waals interactions. All MOF unit cells were optimized, with an SCF convergence of 0.1 meV and the plane wave energy cut-off set at 600 eV. The unit-cell parameters and ions were allowed to move untill the force acting between atoms were below 5 meV/Å. NO and H_2O binding was studied by placing molecules in the Ni-MOF-74 at various sites and then relaxing all atoms in accordance with the convergence condition. To study the interactions between the competing NO and H_2O molecules at the binding sites, induced charge densities were calculated by subtracting the individual charge densities of the binding molecules from the density of the combined system, which maps the variation in charge density upon introduction of the guest molecules. Transition-state searches were performed to study the NO–H_2O exchange process by using the climbing-image nudged elastic band (cNEB) method [8,9]. Intermediate structures were optimized to generate a minimum energy path between known initial and final structures and gave the transition states and the energy barrier for the exchange process. Vibrational frequencies were calculated using a finite-difference approach, using a displacement of 0.1 Å, and diagonalizing the resulting dynamical matrix under the constraint of applicable sum-rules.

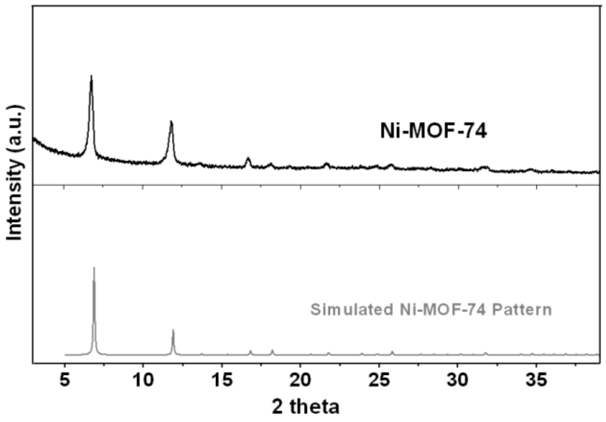

Figure S1. Powder X-ray diffraction pattern of Ni-MOF-74 (after solvent exchange), compared with the simulated pattern from single crystal data (See Ref. [10]).

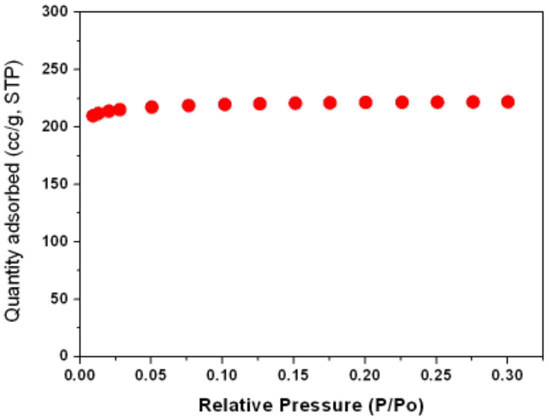

Figure S2. N_2 adsorption isotherm in Ni-MOF-74 at 77 K.

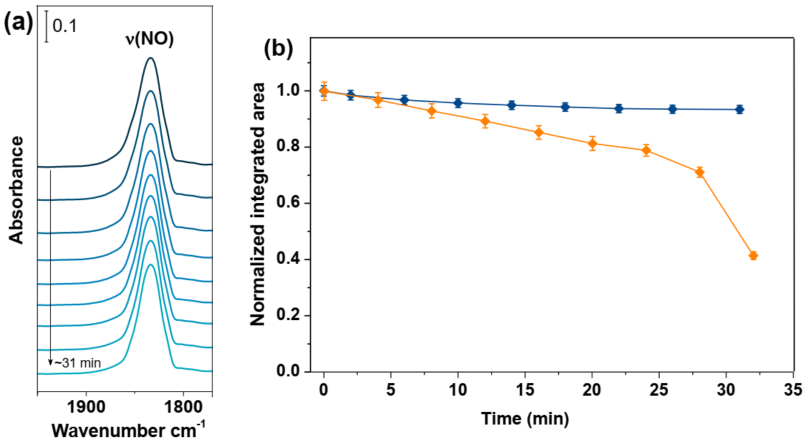

Figure S3. **(a)** IR spectra of ν(NO) band in Ni-MOF-74 under evacuation in vacuum. The NO gas was loaded into Ni-MOF-74 at 40 Torr and 25 °C. **(b)** Evolution of ν(NO) band intensity under vacuum (blue square) and upon exposure to water moisture from 1 Torr to 8 Torr (orange diamond).

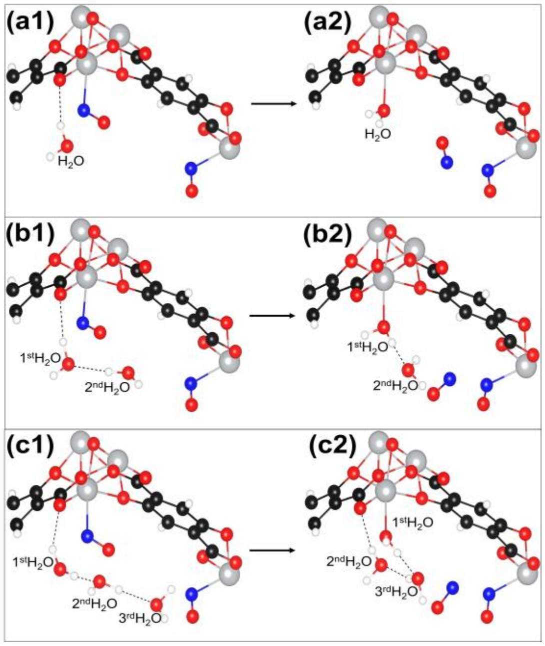

Fig. S4. Initial and final configuration of the H_2O → NO exchange process in Ni-MOF-74 for the cases of (a1/a2) one H_2O, (b1/b2) two H_2O and (c1/c2) three H_2O guest molecules.

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