Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Energetic Performances of the Metal-Organic Framework ZIF-8 by High Pressure Water Intrusion-Extrusion Experiments

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Water Intrusion-Extrusion Experiments

The intrusion-extrusion experiments of water on ZIF-8 samples were performed at room temperature using a modified mercury porosimeter (Micromeritics Model Autopore IV). ZIF-8 powder was directly introduced in the cell. This latter, which contains the "MOF-water" system, consists in a polypropylene cylinder of 2 cm^3 sealed by a mobile piston. Then this cell is introduced in a 15 cm^3 penetrometer of the porosimeter which is filled with mercury. The volume variation is determined through a capacity measurement which depends on the mercury height in the capillary tube of the penetrometer. The experimental intrusion-extrusion curve is obtained after correction of the curve corresponding to the compressibility of pure water. The value of the intrusion (P_{int}) and extrusion (P_{ext}) pressures correspond to the pressure where the variation of the intruded / extruded volume is maximal. Pressure is expressed in MPa, and volume variation in mL per gram of sample. The experimental error is estimated to 1 % on the pressure and on the volume.

Powder X-ray Diffraction

The powder XRD patterns of the different samples was collected between 5 and 50° (2θ) (step 0.01°) on a STOE STADI-P diffractometer in Debye-Scherrer geometry, equipped with a linear position-sensitive detector (6° in 2θ) and employing Ge monochromated CuKα_1 radiation (λ= 1.5406 Å).

Thermogravimetric Analyses

The measures were performed under air until 900 °C (rate of 2 °C min^{-1}) using a METTLER-TOLEDO TGA 851e apparatus.

Scanning Electron Microscopy

The size and the morphology of ZIF-8 nanoparticles were determined using a Philips XL 30 FEG microscope.

Nitrogen Adsorption-Desorption Measurements

Nitrogen adsorption-desorption isotherms were carried out using a Micromeritics ASAP 2420 apparatus. Prior to the adsorption measurements, samples were outgassed at 90 °C overnight under vacuum. BET surface (S_{BET}) areas for ZIF-8, before and after water intrusion-extrusion experiments, were calculated according to the criteria given in the literature,[1, 2] namely in the $0.001 \leq P/P_0 \leq 0.018$ range. Langmuir surface (S_{Lang}) areas were calculated by the apparent Langmuir equations assuming a monolayer coverage of N_2 and a cross-sectional area of 16.2 $Å^2$ per molecule in the same range as BET surface. The micropore volume (V_{micro}) was determined by *t*-plot method.

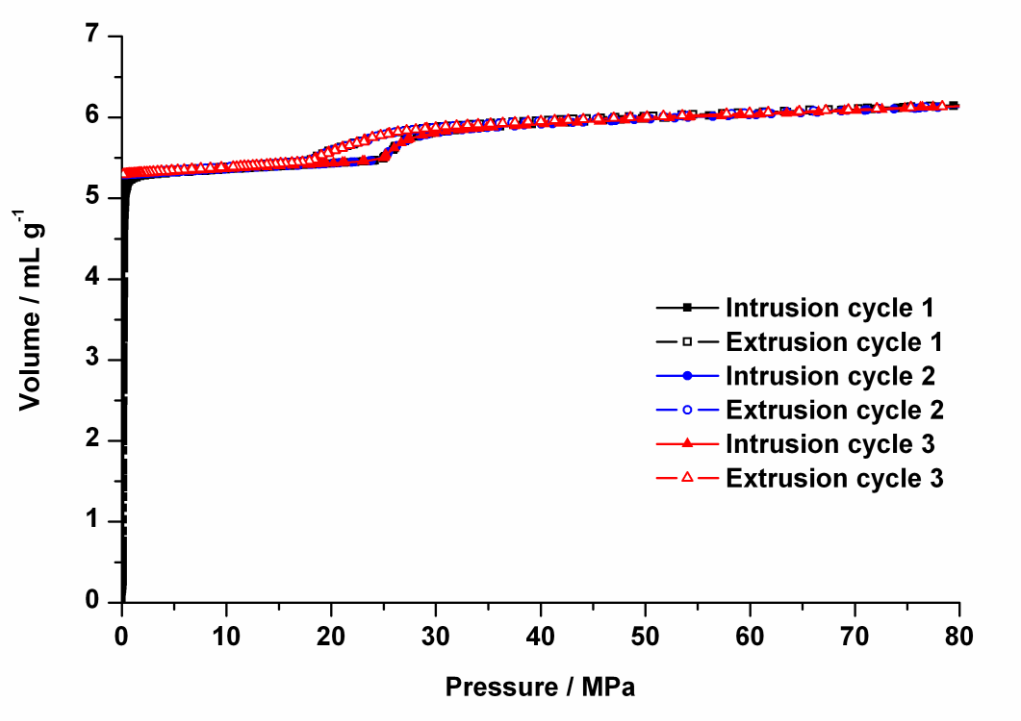

Figure S1. Water intrusion-extrusion diagrams of the "ZIF-8-water" system in linear scale for pressure values.

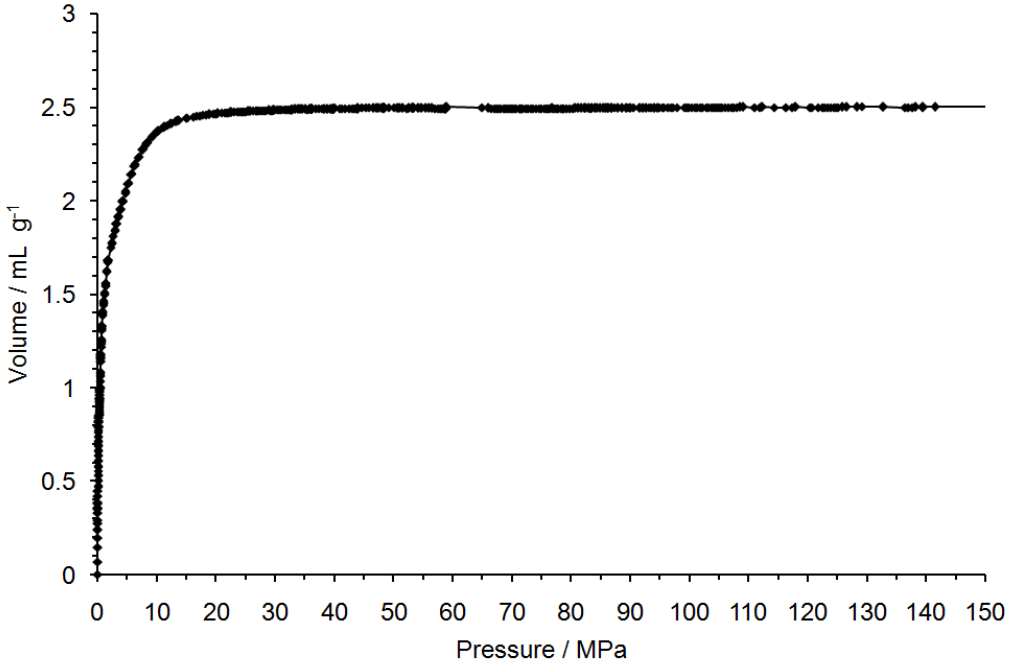

Figure S2. Mercury porosimetry on ZIF-8.

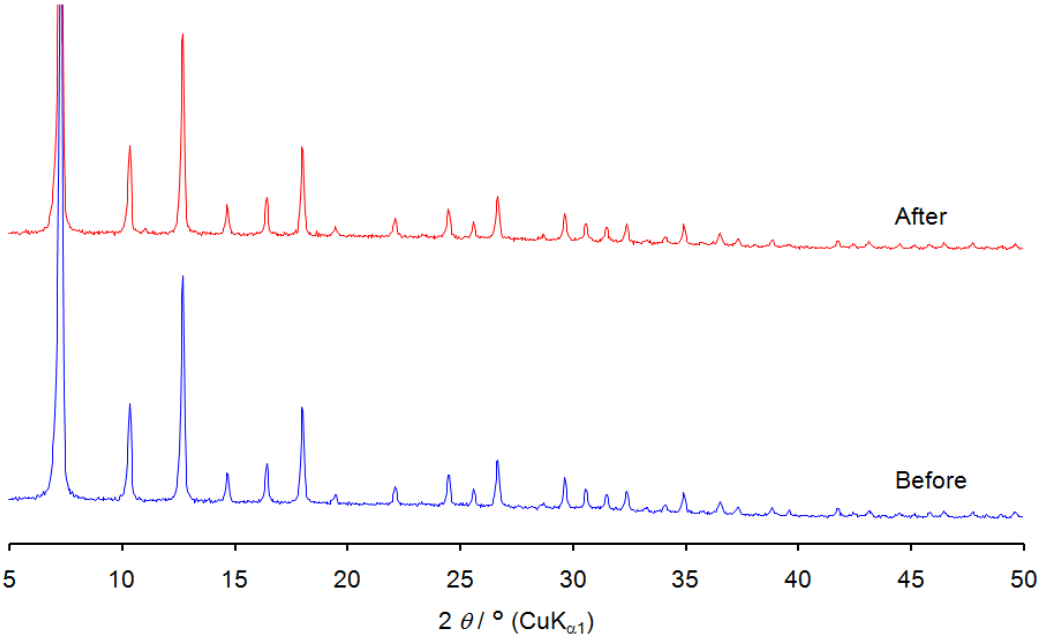

Figure S3. Powder X-ray diffraction patterns of ZIF-8 before (blue line) and after (red line) three water intrusion-extrusion cycles.

(a) (b)

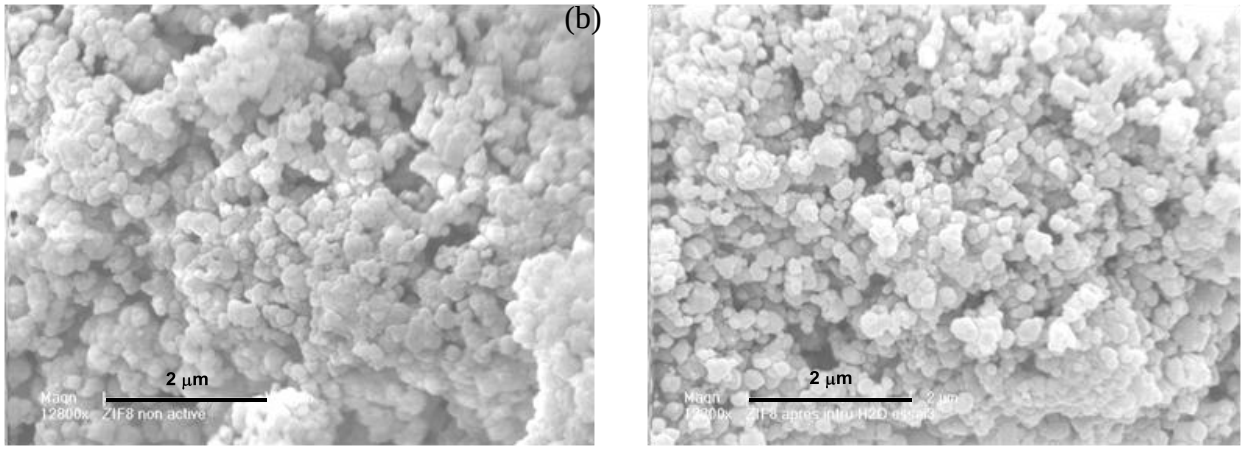

Figure S4. SEM images of ZIF-8 before (a) and after (b) three water intrusion-extrusion cycles.

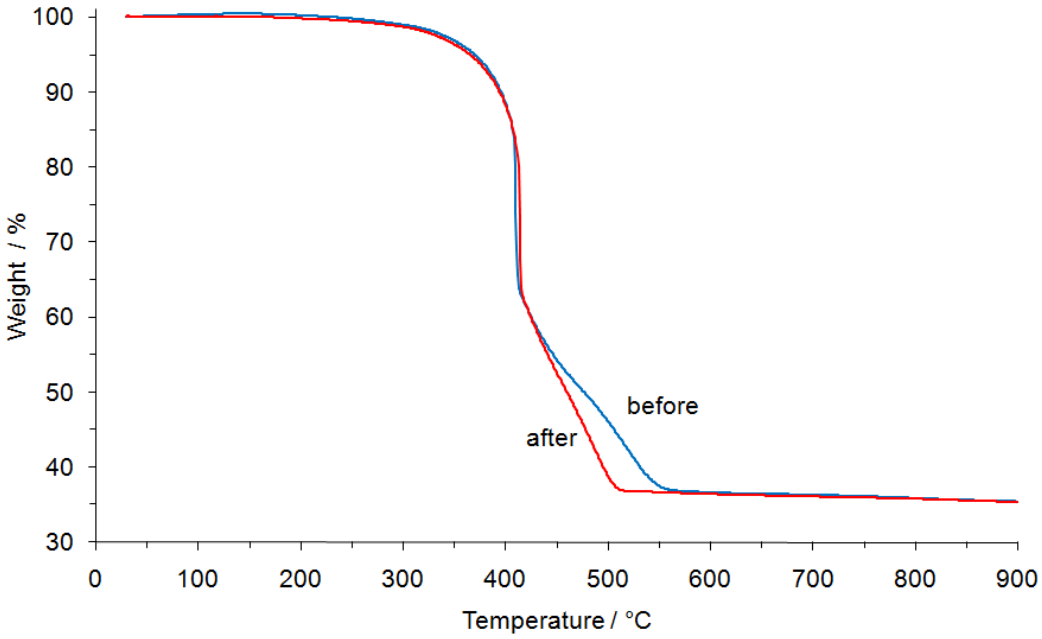

Figure S5. TG curves under air of ZIF-8 before (blue line) and after (red line) three water intrusion-extrusion cycles.

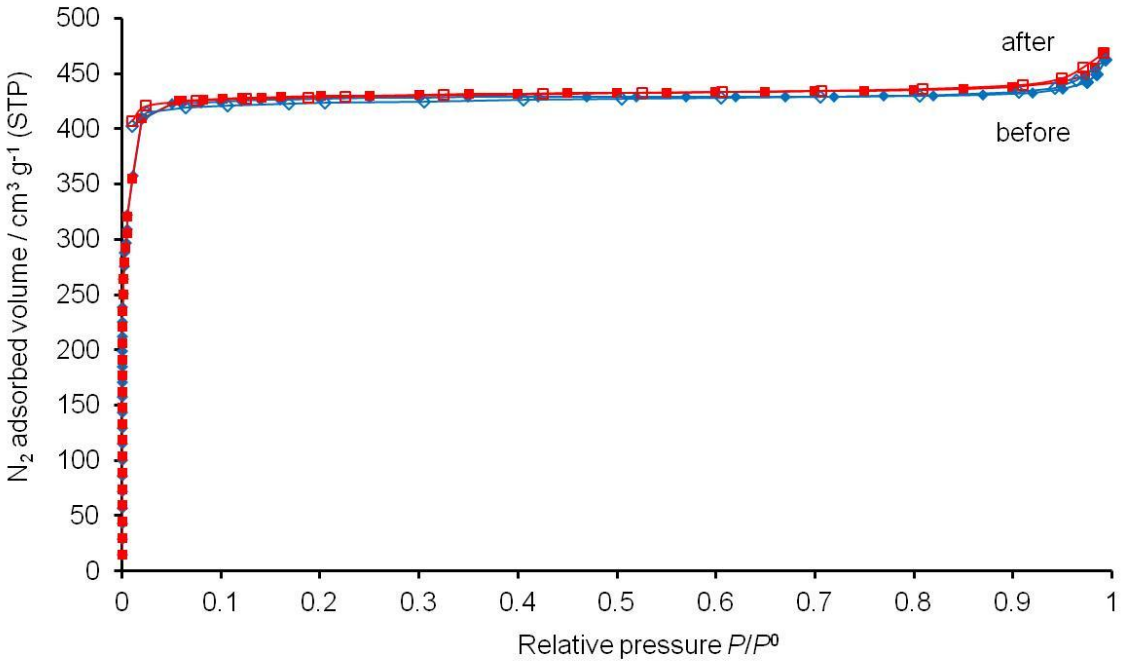

Figure S6. Nitrogen adsorption (full square)-desorption (empty square) isotherms of ZIF-8 before (blue line) and after (red line) water intrusion-extrusion experiments.

References

1. J. Rouquerol, P. Llewellyn and F. Rouquerol, *Stud. Surf. Sci. Catal.*, 2007, **160**, 49.

2. K. S. Walton and R. Q. Snurr, *J. Am. Chem. Soc.*, 2007, **129**, 8552.