

Intrusion of Water in ZIF-8: Evidence of the Thermodynamic Instability under High Pressure

Amir Astafan,^{a,b} Céline Dirand,^c Andrey Ryzhikov,^{a,b} Habiba Nouali,^{a,b} T. Jean Daou,^{a,b}
Claire Marichal,^{a,b} Jean-Pierre Bellat,^c Igor Bezverkhyy,^c Gérald Chaplais^{a,b}

^a *Université de Haute-Alsace, CNRS, Institut de Science des Matériaux de Mulhouse (IS2M), UMR 7361, Axe Matériaux à Porosité Contrôlée (MPC), F-68100, Mulhouse, France*

^b *Université de Strasbourg, F-67000 Strasbourg, France*

^c *Université de Bourgogne Franche-Comté, CNRS, Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303, F-21078 Dijon Cedex, France*

List of Figures

| | |
|---|-----|
| Figure S1. Scheme of calorimetric setup..... | S4 |
| Figure S2. Fast and slow intrusion calorimetric procedures..... | S5 |
| Figure S3. a) Simulated XRD pattern of ZIF-8 structure and experimental XRD patterns of b) powder and c) pellet ZIF-8 samples..... | S6 |
| Figure S4. N ₂ adsorption-desorption isotherms at 77 K of the (○) powder and (Δ) pellet ZIF-8 samples. The plots are given with a) a linear scale and b) a logarithmic scale of the relative pressure ... | S6 |
| Figure S5. TG curve of the parent powder ZIF-8 under air at 2 K.min ⁻¹ | S7 |
| Figure S6. SEM image of the parent powder ZIF-8..... | S7 |
| Figure S7. Pressure-volume diagrams of the “ZIF-8–water” systems including samples as a) powder without outgassing under vacuum, b) pellet without outgassing under vacuum, c) powder with outgassing under vacuum and d) pellet with outgassing under vacuum. For a better visibility, the diagrams are shifted by 0.5 mL.g ⁻¹ along the y-axis | S8 |
| Figure S8. a) Simulated XRD pattern of ZIF-8 structure and experimental XRD patterns of the b) parent powder sample, and samples recovered after water intrusion-extrusion experiments involving adsorbent as c) powder without outgassing under vacuum, d) pellet without outgassing under vacuum, e) powder with outgassing under vacuum, and f) pellet with outgassing under vacuum. Marks “o” denote peaks presumably belonging to a structure with doubled conventional lattice of ZIF-8..... | S9 |
| Figure S9. N ₂ adsorption-desorption isotherms at 77 K of ZIF-8 samples recovered after water intrusion-extrusion experiments involving adsorbent as (gray) powder without outgassing under vacuum, (red) pellet without outgassing under vacuum, (green) powder with outgassing under vacuum, and (purple) pellet with outgassing under vacuum. The plots are given with a) a linear scale and b) a logarithmic scale of the relative pressure. Filled and empty symbols correspond to the adsorption and desorption branches, respectively. For clarity, the isotherms for each sample are shifted by 100 cm ³ .g ⁻¹ STP along the y-axis | S10 |
| Figure S10. Integral heat of water/solid interaction determined from fast intrusion experiments as a function of final pressure. Straight lines are just a guide for the eyes to show what we should expect if no thermal effect occurred after intrusion | S11 |
| Figure S11. XRD patterns of ZIF-8 samples after a) fast procedure intrusion-extrusion experiment and b) slow procedure intrusion-extrusion experiment | S12 |
| Figure S12. XRD patterns of the a) simulated ZIF-8 pattern, b) parent ZIF-8 sample, c) ZIF-8 sample after 9 days in oil of compression-decompression cycles under high pressure, and d) ZIF-8 sample after 12.5 days in water under atmospheric pressure..... | S12 |
| Figure S13. XRD patterns of ZIF-8 samples after a) water intrusion-extrusion experiment and b) oil intrusion-extrusion experiment..... | S13 |
| Figure S14. N ₂ adsorption-desorption isotherms at 77 K of ZIF-8 parent sample (black), the sample after 9 days of oil compression-decompression experiments under high pressure (red), and the sample after 12.5 days in water under low pressure (blue). The plots are given with a) a linear scale and b) a logarithmic scale of the relative pressure. Filled and empty symbols correspond to the adsorption and desorption branches, respectively..... | S13 |

List of Tables

| | |
|---|-----|
| Table S1. Textural properties of powder and pellet ZIF-8 samples | S6 |
| Table S2. Characteristics of the “ZIF-8–water” system, intrusion (P_{int}) and extrusion (P_{ext}) pressures, intruded (V_{int}) and extruded (V_{ext}) volumes, and stored (E_s) and restored (E_r) energies..... | S8 |
| Table S3. Textural properties of powder and pellet intruded ZIF-8 samples, microporous volume (V_{μ}) and BET surface (S_{BET}) of post-intruded ZIF-8 samples..... | S10 |
| Table S4. Heats of water/ZIF-8 interaction measured for three successive intrusion-extrusion cycles performed on the same sample | S11 |

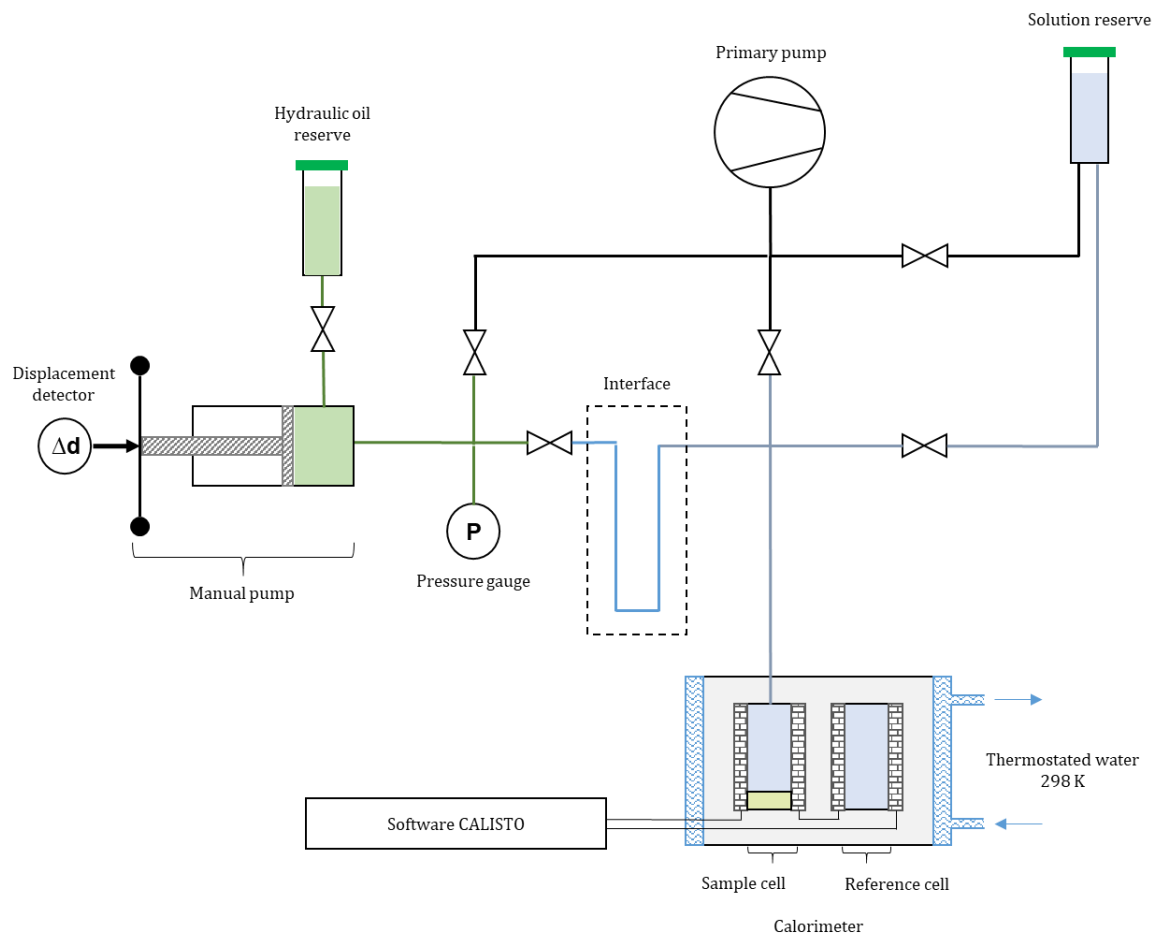


Figure S1. Scheme of calorimetric setup

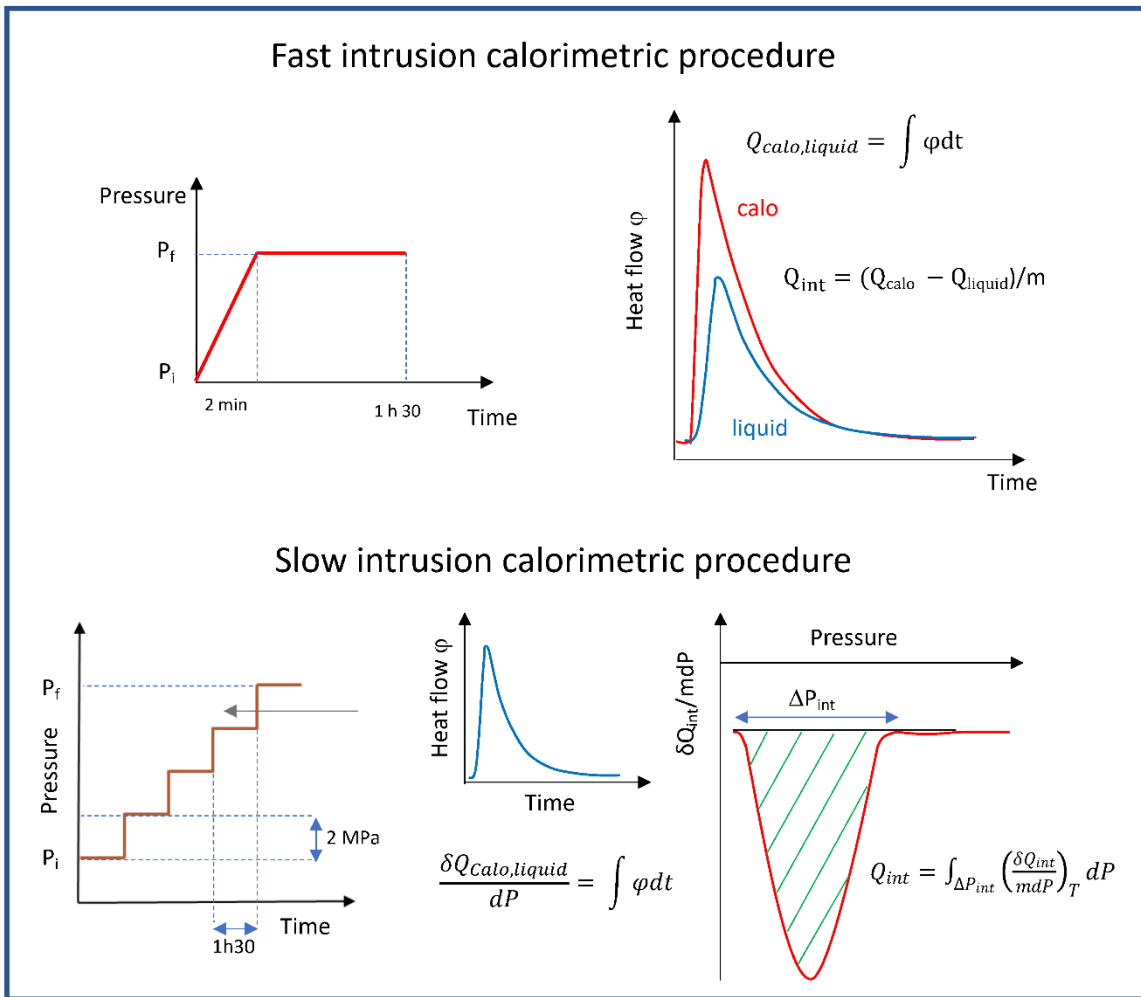


Figure S2. Fast and slow intrusion calorimetric procedures

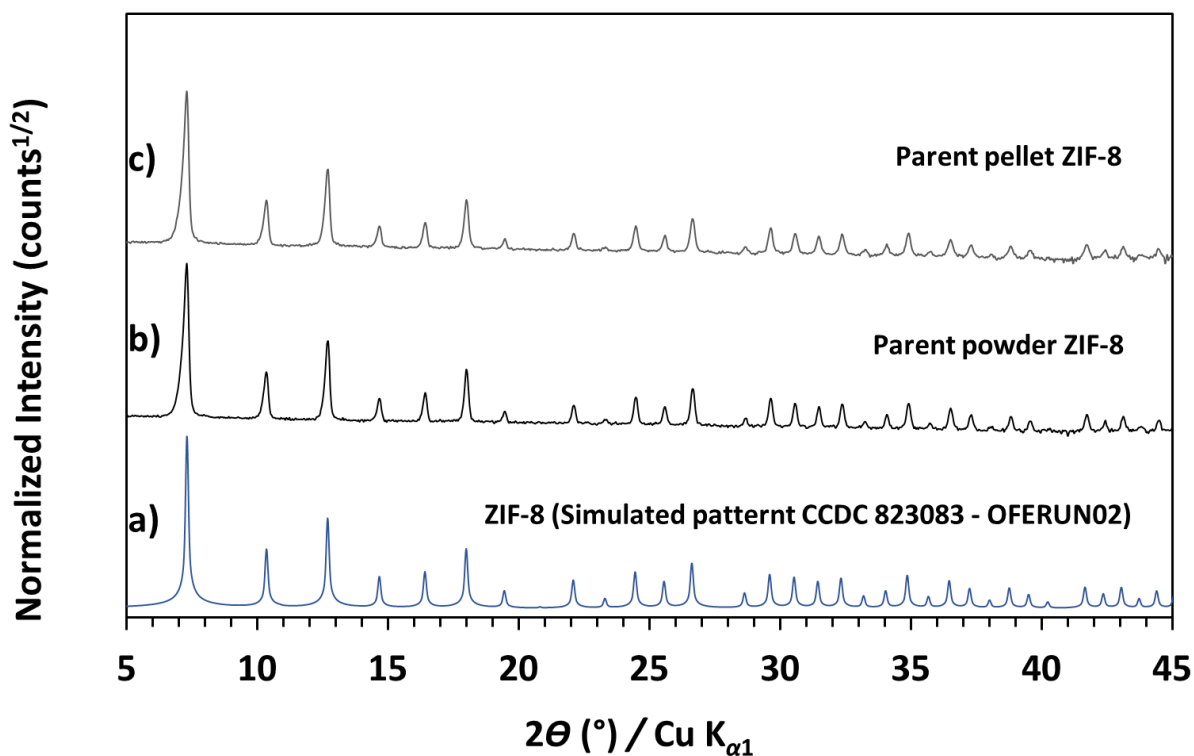


Figure S3. a) Simulated XRD pattern of ZIF-8 structure and experimental XRD patterns of b) powder and c) pellet ZIF-8 samples

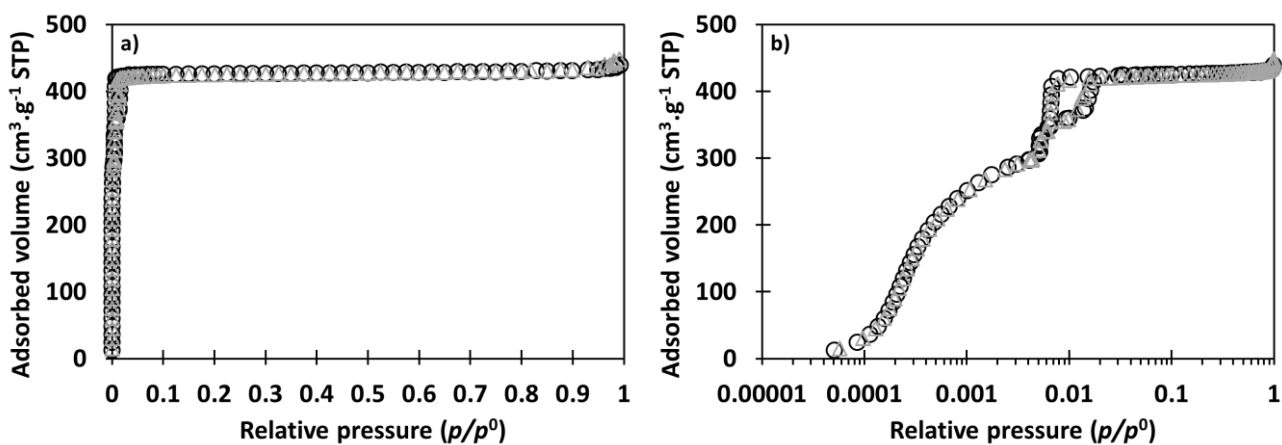


Figure S4. N₂ adsorption-desorption isotherms at 77 K of the (○) powder and (Δ) pellet ZIF-8 samples. The plots are given with a) a linear scale and b) a logarithmic scale of the relative pressure

Table S1. Textural properties of powder and pellet ZIF-8 samples

| ZIF-8 sample | S_{BET} $\text{m}^2\cdot\text{g}^{-1}$ | V_{μ} $\text{cm}^3\cdot\text{g}^{-1}$ |
|---------------|--|--|
| Powder | 1421 | 0.68 |
| Pellet | 1361 | 0.65 |

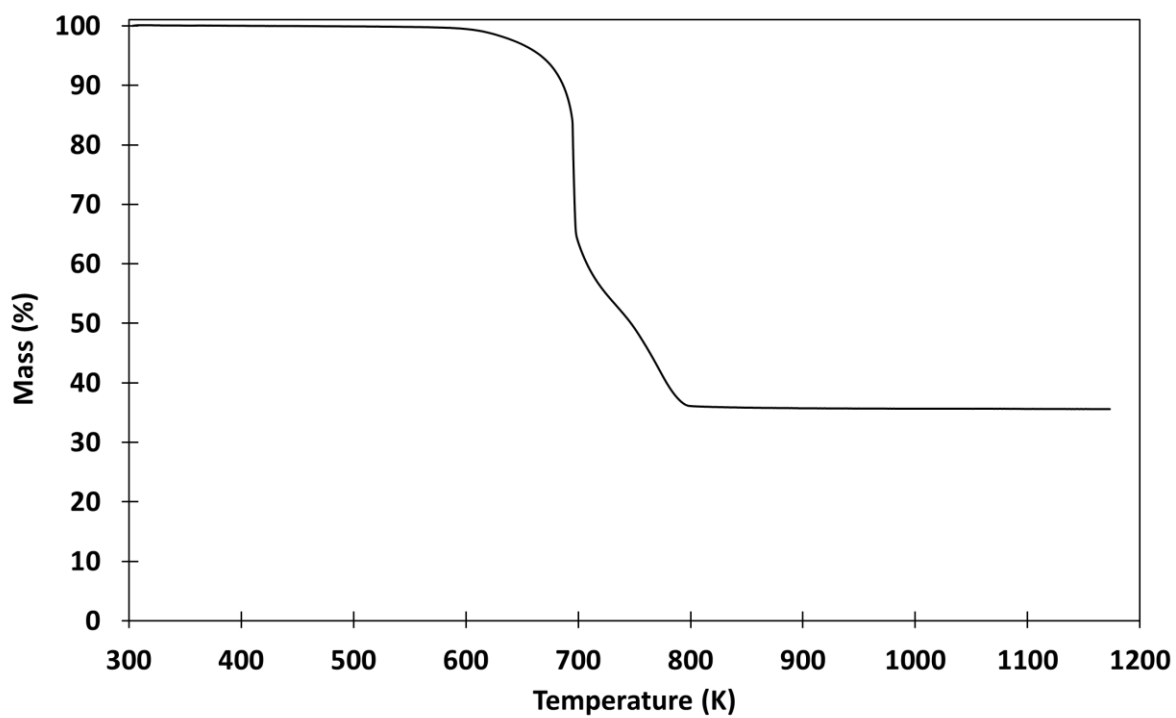


Figure S5. TG curve of the parent powder ZIF-8 under air at 2 K.min⁻¹

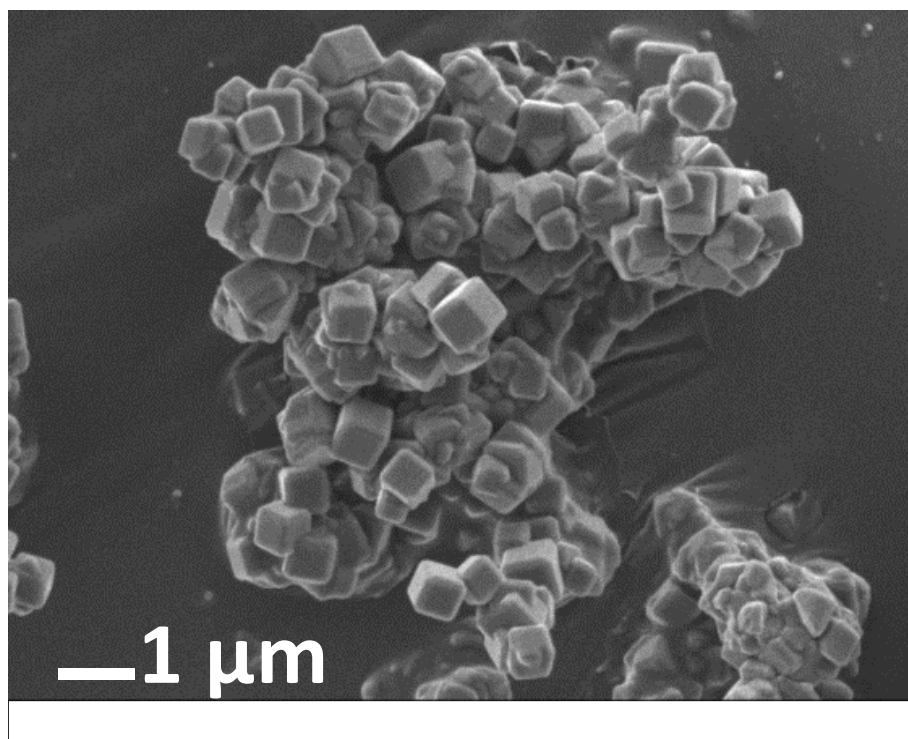


Figure S6. SEM image of the parent powder ZIF-8

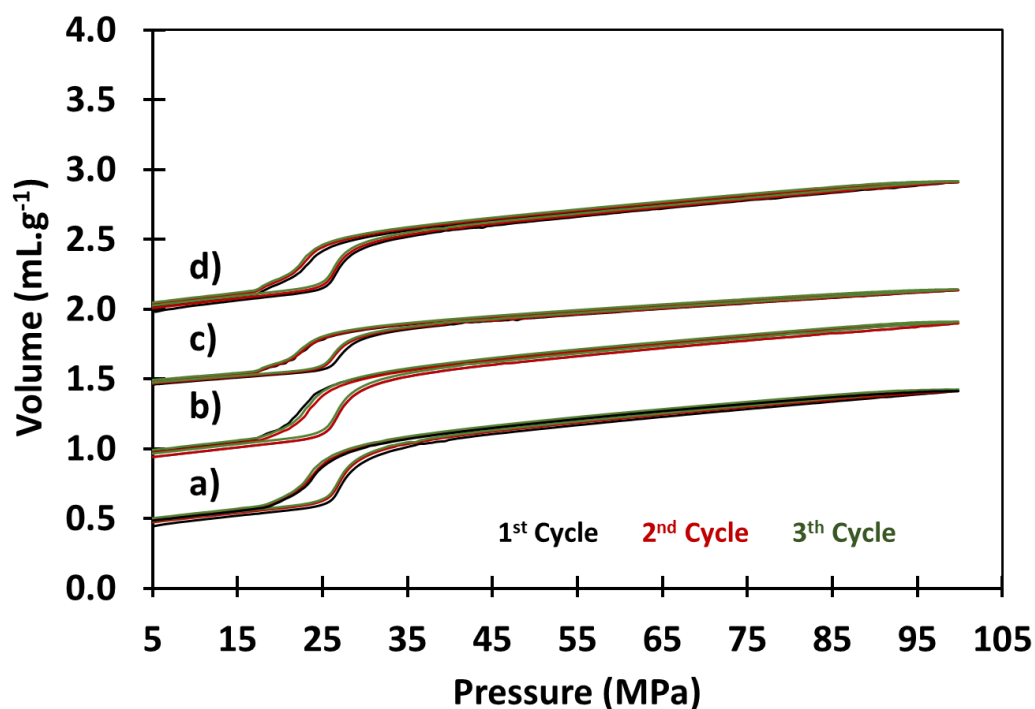


Figure S7. Pressure-volume diagrams of the “ZIF-8–water” systems including samples as a) powder without outgassing under vacuum, b) pellet without outgassing under vacuum, c) powder with outgassing under vacuum and d) pellet with outgassing under vacuum. For a better visibility, the diagrams are shifted by 0.5 mL.g⁻¹ along the y-axis

Table S2. Characteristics of the “ZIF-8–water” system, intrusion (P_{int}) and extrusion (P_{ext}) pressures, intruded (V_{int}) and extruded (V_{ext}) volumes, and stored (E_s) and restored (E_r) energies

| “ZIF-8–water” system | | P_{int} (MPa) | P_{ext} (MPa) | V_{int} (mL.g ⁻¹) | V_{ext} (mL.g ⁻¹) | E_s (J.g ⁻¹) | E_r (J.g ⁻¹) |
|----------------------------------|---------|--------------------|--------------------|------------------------------------|------------------------------------|-------------------------------|-------------------------------|
| Powder without outgassing | Cycle-1 | 26.9 | 24.1 | 0.40 | 0.40 | 10.8 | 9.6 |
| | Cycle-2 | 26.9 | 23.9 | 0.40 | 0.40 | 10.8 | 9.6 |
| | Cycle-3 | 26.9 | 23.9 | 0.40 | 0.40 | 10.8 | 9.6 |
| Pellet without outgassing | Cycle-1 | 26.9 | 23.4 | 0.40 | 0.40 | 10.8 | 9.4 |
| | Cycle-2 | 26.9 | 23.4 | 0.40 | 0.40 | 10.8 | 9.4 |
| | Cycle-3 | 26.5 | 23.4 | 0.40 | 0.40 | 10.6 | 9.4 |
| Powder with outgassing | Cycle-1 | 26.9 | 23.5 | 0.40 | 0.40 | 10.8 | 9.4 |
| | Cycle-2 | 26.9 | 23.5 | 0.40 | 0.40 | 10.8 | 9.4 |
| | Cycle-3 | 26.4 | 23.5 | 0.40 | 0.40 | 10.7 | 9.4 |
| Pellet with outgassing | Cycle-1 | 26.9 | 23.4 | 0.40 | 0.40 | 10.8 | 9.4 |
| | Cycle-2 | 26.9 | 23.4 | 0.40 | 0.40 | 10.8 | 9.4 |
| | Cycle-3 | 26.9 | 23.4 | 0.40 | 0.40 | 10.8 | 9.4 |

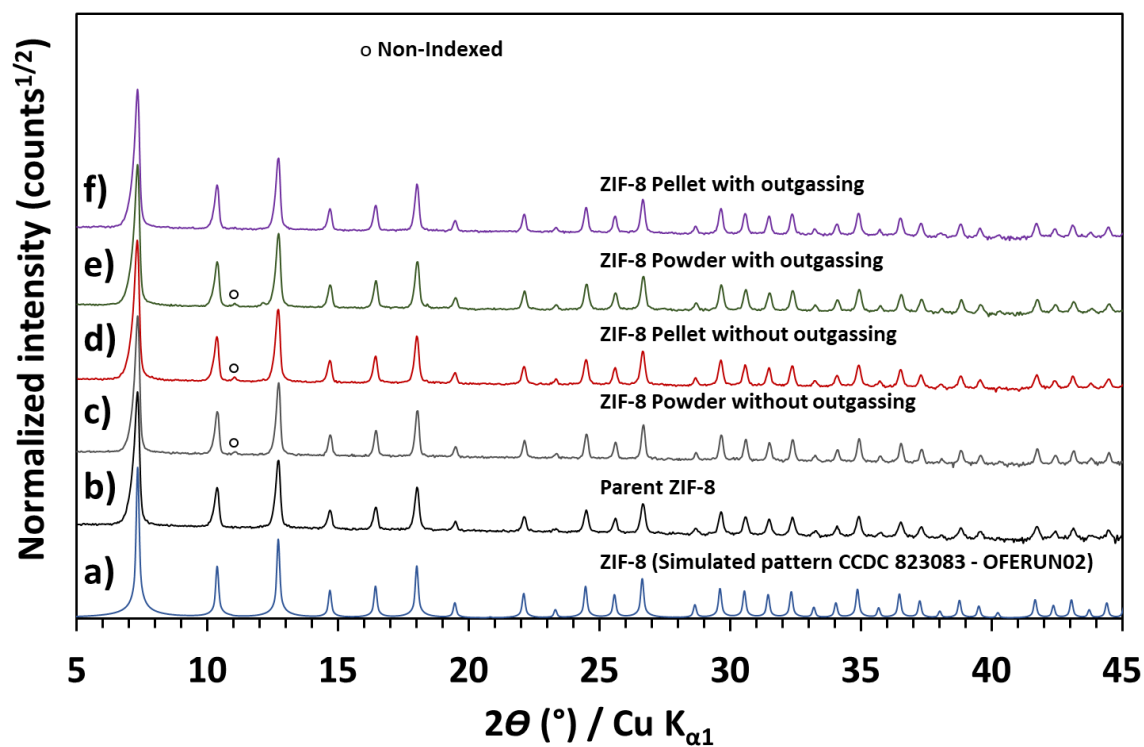


Figure S8. a) Simulated XRD pattern of ZIF-8 structure and experimental XRD patterns of the b) parent powder sample, and samples recovered after water intrusion-extrusion experiments involving adsorbent as c) powder without outgassing under vacuum, d) pellet without outgassing under vacuum, e) powder with outgassing under vacuum, and f) pellet with outgassing under vacuum. Marks “o” denote peaks presumably belonging to a structure with doubled conventional lattice of ZIF-8

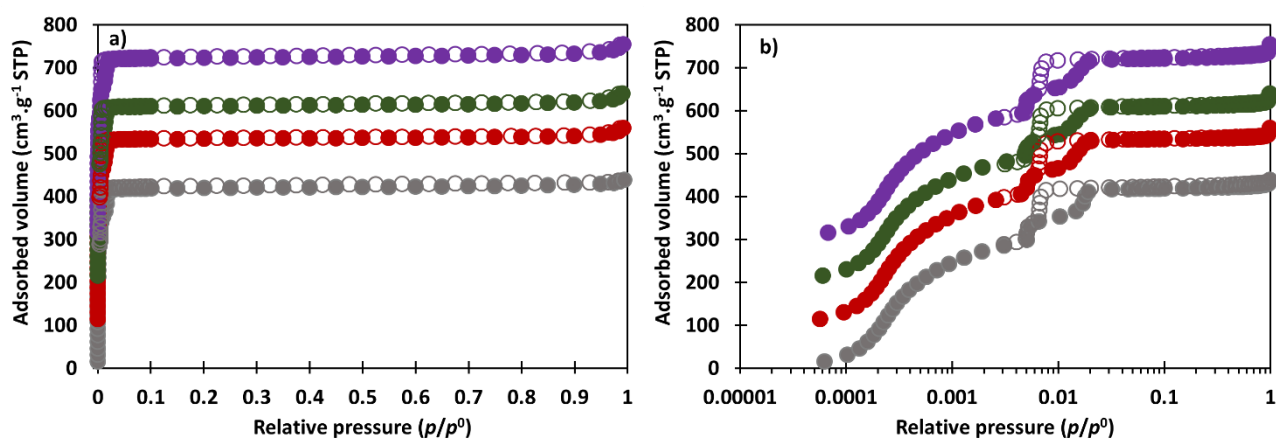


Figure S9. N₂ adsorption-desorption isotherms at 77 K of ZIF-8 samples recovered after water intrusion-extrusion experiments involving adsorbent as (gray) powder without outgassing under vacuum, (red) pellet without outgassing under vacuum, (green) powder with outgassing under vacuum, and (purple) pellet with outgassing under vacuum. The plots are given with a) a linear scale and b) a logarithmic scale of the relative pressure. Filled and empty symbols correspond to the adsorption and desorption branches, respectively. For clarity, the isotherms for each sample are shifted by 100 cm³.g⁻¹ STP along the y-axis

Table S3. Textural properties of powder and pellet intruded ZIF-8 samples, microporous volume (V_{μ}) and BET surface (S_{BET}) of post-intruded ZIF-8 samples

| ZIF-8 sample | S_{BET} m ² .g ⁻¹ | V_{μ} cm ³ .g ⁻¹ |
|---------------------------|---|---|
| Parent Pellet | 1361 | 0.65 |
| Powder without outgassing | 1342 | 0.65 |
| Pellet without outgassing | 1384 | 0.66 |
| Powder with outgassing | 1331 | 0.64 |
| Pellet with outgassing | 1344 | 0.65 |

Table S4. Heats of water/ZIF-8 interaction measured for three successive intrusion-extrusion cycles performed on the same sample

| Experiments duration | | $Q_{wz,int}$ (J.g ⁻¹) | $Q_{wz,ext}$ (J.g ⁻¹) |
|----------------------|---------|--------------------------------------|--------------------------------------|
| 37.5 days | Cycle-1 | -5.2 | 2.7 |
| | Cycle-2 | -5.5 | 3.6 |
| | Cycle-3 | -3.1 | n.d. |

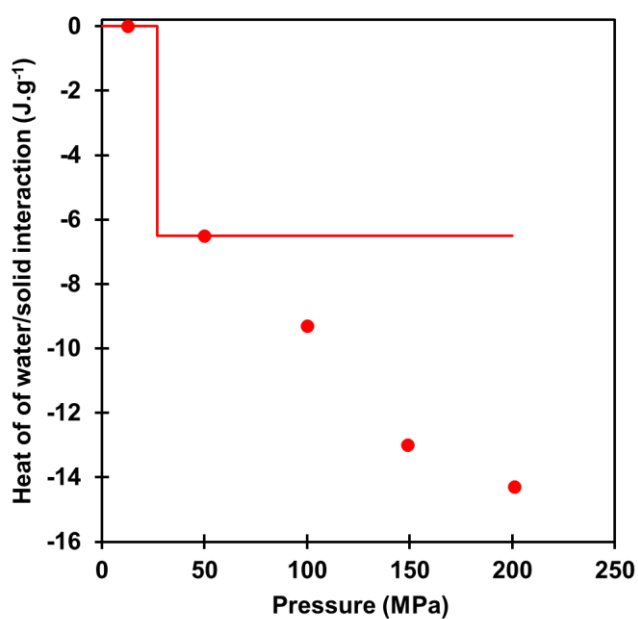


Figure S10. Integral heat of water/solid interaction determined from fast intrusion experiments as a function of final pressure. Straight lines are just a guide for the eyes to show what we should expect if no thermal effect occurred after intrusion

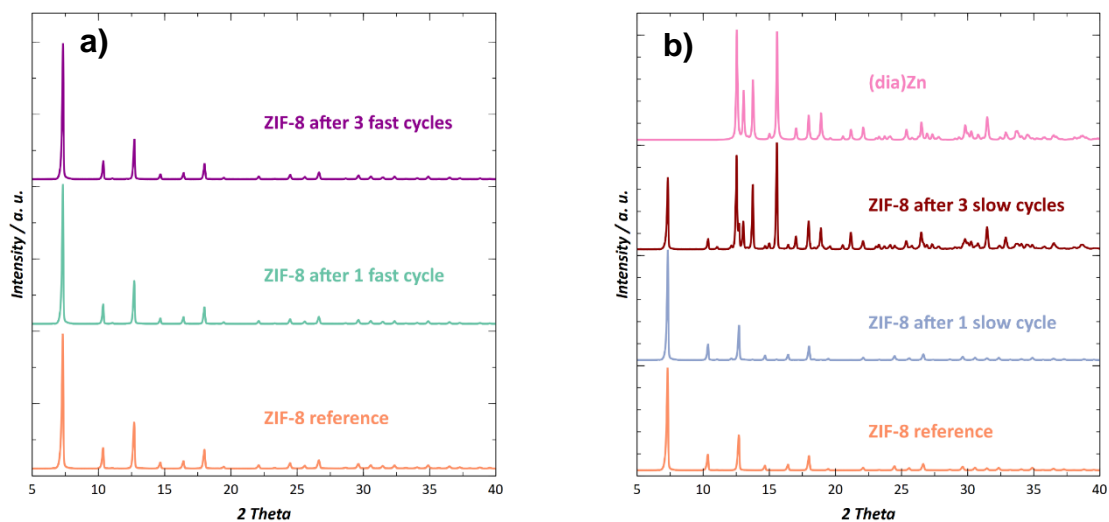


Figure S11. XRD patterns of ZIF-8 samples after a) fast procedure intrusion-extrusion experiment and b) slow procedure intrusion-extrusion experiment

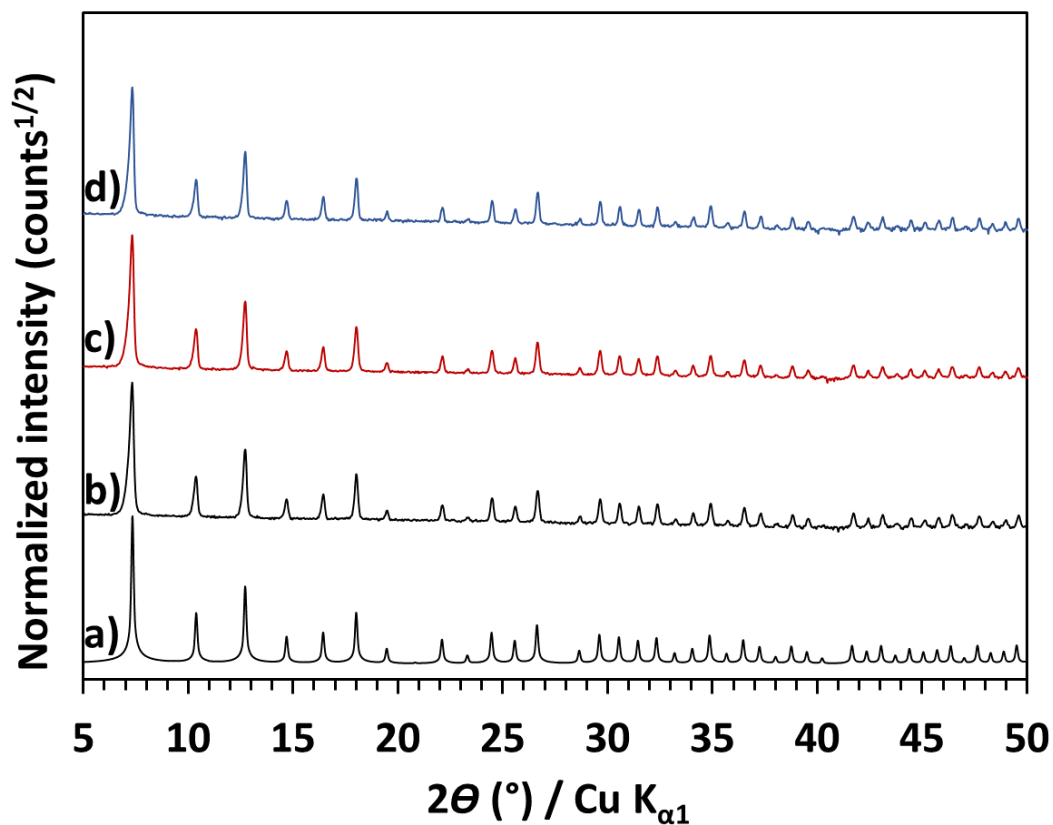


Figure S12. XRD patterns of the a) simulated ZIF-8 pattern, b) parent ZIF-8 sample, c) ZIF-8 sample after 9 days in oil of compression-decompression cycles under high pressure, and d) ZIF-8 sample after 12.5 days in water under atmospheric pressure

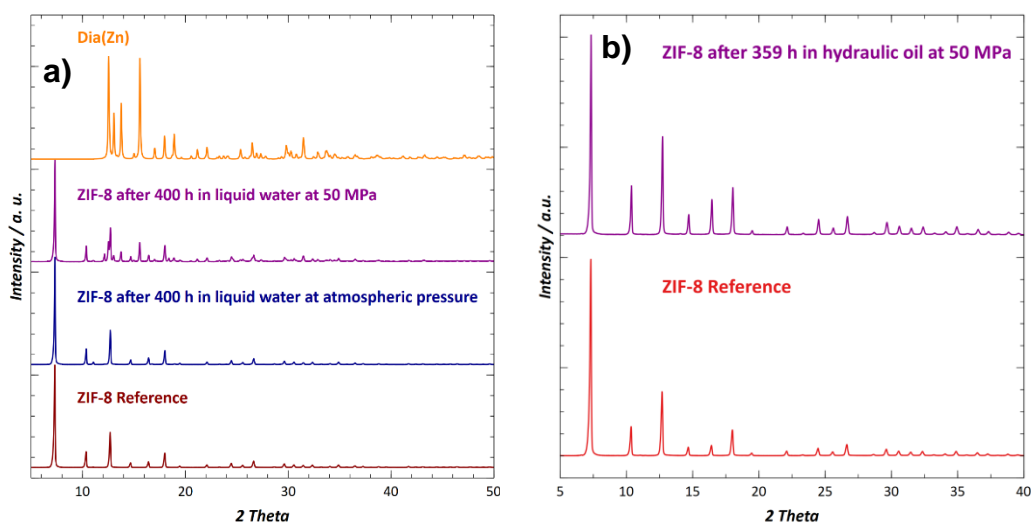


Figure S13. XRD patterns of ZIF-8 samples after a) water intrusion-extrusion experiment and b) oil intrusion-extrusion experiment

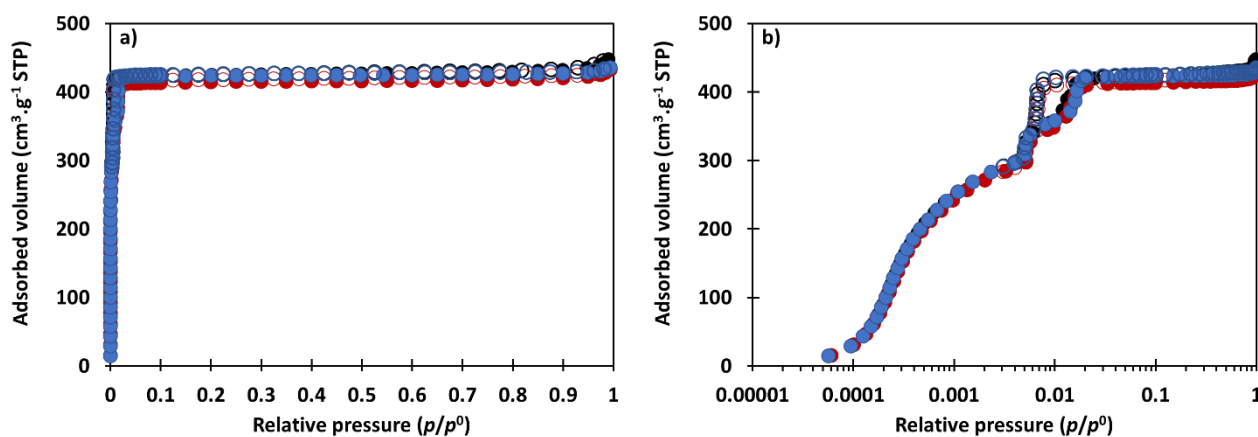


Figure S14. N₂ adsorption-desorption isotherms at 77 K of ZIF-8 parent sample (black), the sample after 9 days of oil compression-decompression experiments under high pressure (red), and the sample after 12.5 days in water under low pressure (blue). The plots are given with a) a linear scale and b) a logarithmic scale of the relative pressure. Filled and empty symbols correspond to the adsorption and desorption branches, respectively