



	Experiment title: Unexpected behavior of ethylene adsorption in metal-organic framework CPO-54	Experiment number: CH-6191
Beamline: BM01	Date of experiment: from: 16.6.2022 to: 20.6.2022	Date of report: 10.3.2023
Shifts: 12	Local contact(s): Chloe Fuller	<i>Received at ESRF:</i>
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Report:

Experiments were performed of samples exposed to various gases and prepared ex situ and under thermodynamic equilibrium conditions and experiments under in situ conditions to study the kinetics of the adsorption process. For the latter, samples were desolvated in the home lab in advance of the experiment time. Gases of interest were C₂H₄, CO₂, CH₄ (as a less bulky hydrocarbon) and C₂H₆ (as more bulky hydrocarbon with a similar space requirement as C₂H₄). In situ measurements were performed using the gas dosing equipment and experimental setup available at SNBL, where the temperature is controlled using a cryostream. Gases of interest were C₂H₄, CO₂, CH₄ (as a less bulky hydrocarbon) and C₂H₆ (as more bulky hydrocarbon with a similar space requirement as C₂H₄).

Ex situ experiments

Samples of several synthesis batches of the best diffracting compound in the MOF series under investigation were filled into capillaries, evacuated under heating, and flame sealed in vacuum or exposed to predetermined pressures of C₂H₄ and then flame sealed prior to the experiment. Several synthesis batches were used to make sure to obtain useable data in case there were deviations between syntheses and confirm reproducibility. By the time the diffraction data was collected (at room temperature), these samples had sufficient time to achieve thermodynamic equilibrium of the adsorption. The intention was to use the data to determine the static host-guest structure at different loadings of ethylene. Another advantage of this approach is that one avoids potential exposure to unwanted atmosphere during sample preparation at ESRF.

Overview of the measurements:

Sample ID	Preparation	Comment
IMB-1-015	Flame sealed in vacuum	Expected to yield the desolvated MOF structure. Rietveld analysis

		indicates ~20 % of water is still on open metal site.
IMB-1-015	Dosed with 95 kPa C ₂ H ₄	Two capillaries measured (in case of leakage)
IMB-1-015	Dosed with 5 kPa C ₂ H ₄	
IMB-1-010	Dosed with 95 kPa C ₂ H ₄	Also run with temperature program from 298-170 K

In situ experiment under isobaric conditions

Samples were desolvated in dynamic vacuum under heating in the home lab and transported to ESRF under inert atmosphere. They were transferred into the glove box of the Chemistry Lab, where the capillaries for the individual experiments were filled. Variable temperature powder diffraction data was collected for the following samples and conditions:

Sample ID	Measurement program	Comment
IMB-1-015	Aborted	Several capillaries were prepared and tested. They all turned out to be degraded, i.e. the compound had decomposed in between preparation in the home lab and experiment time (less than 1 week). In contrast, the compound in the pre-sealed capillary used in the ex situ experiment was fine.
IMB-1-010	<ol style="list-style-type: none"> 1. Vacuum, heated to 423 K, later increased to 473 K 2. CO₂, 1 bar, 423-195 K, hold for 30 min, 195-298 K 3. Vacuum, 473 K 4. C₂H₆, 1 bar, 473-184 K, hold for 30 min, 184-298 K 5. Vacuum, 473 K 6. CH₄, 1 bar, 473-110 K, hold for 30 min, 110-298 K 7. Vacuum, 473 K 8. C₂H₄, 1 bar, 473-170 K, hold for 30 min, 170-298 K 	<p>Same compound as IMB-1-015, but much older (~1 year). This sample was fine!</p> <p>Despite being pre-treated in the home lab and extended time of heating in vacuum on the beam, there was still water on the open metal site.</p>
IMB-1-016	<ol style="list-style-type: none"> 1. Vacuum, 423 K 2. C₂H₄, 1 bar, 473-170 K, hold for 30 min, 170-298 K 3. Vacuum, 423 K 4. C₂H₆, 1 bar, 473-184 K, hold for 30 min, 184-298 K 	Worse resolved pattern. Only the main adsorptives of interest were measured therefore.
TSO-1-033	<ol style="list-style-type: none"> 1. Vacuum, 473 K 2. C₂H₄, 1 bar, 473-170 K, hold for 30 min, 170-298 K 3. Vacuum, 473 K 4. C₂H₆, 1 bar, 473-184 K, hold for 30 min, 184-298 K 5. Vacuum, 473 K 6. CH₄, 1 bar, 473-110 K, hold for 30 min, 110-298 K 7. Vacuum, 473 K 8. CO₂, 1 bar, 423-195 K, hold for 30 min, 195-298 K 	

VMS-1-019/020/021	9. Vacuum, 448-473 K 10. C ₂ H ₄ , 1 bar, 473-170 K, hold for 30 min, 170-298 K 11. Vacuum, 423 K 12. C ₂ H ₆ , 1 bar, 473-184 K, hold for 30 min, 184-298 K 13. Vacuum, 423 K 14. CO ₂ , 1 bar, 423-195 K, hold for 30 min, 195-298 K	Some problems with sample stability and impurities that only show up at the synchrotron. Selected in the end a sample (019) with good pattern, but with impurity present. Sample was spread in capillary during gas changing which lead to lower than possible intensities.
IMB-1-010	Vacuum, 298-473 K with ramp	End of experiment time, performed to check whether there is any change in water occupancy over time. Initial occupancy is ~35 %, drops to ~23 % during heating ramp, and remains constant at 473 K.

Preliminary conclusions

Unlike structurally similar compounds we previously investigated, we found clear evidence of solvent molecules (water) on the open metal site, despite extensive heating at the maximum permissible temperature (before the compounds start to degrade thermally) in dynamic vacuum. A possibility is that the pressure drop through the small diameter PEEK tubing linking the capillary on the diffractometer and the gas dosing system is too large and it will take too long to affect the occupancy of water in the sample. This appears unlikely because the sample prepared in vacuum at the home lab for the ex situ didn't suffer from this restriction, but also has remaining water. This indicates that it is not possible to remove all solvent from the open metal site by heating in vacuum below the decomposition temperature of the framework. This is further corroborated by the final experiment where a sample was just heated in vacuum and the change in solvent occupancy monitored. This would be an explanation for some of the deviation observed in heat of adsorption versus loading for these materials. Unfortunately, it also complicates the continuing structure analysis of the data collected because every pattern has to be considered as a mixture of two phases of the same material with different adsorbates now.