Report:

The main goal of the proposed experiment was to understand the gas adsorption induced structural modification in single and mixed metal MOF-74 frameworks and probe the cooperativity effect present if any. We investigated the adsorption of 3 different gases on 5 different single and mixed metal MOF-74 samples. Successful experiments performed during the beamtime are enlisted in Table 1. Two of the experiments, performed on Ni-rich MOF-74s, were not successful due to the beam damage of the samples. Gained information is, though, essential for the future investigations design.

100Ni	100Mg	90Ni10Mg	90Mg10Ni	mixed Ni-Mg
activation	activation			
500mbar CO	500mbar CO			
1000mbar CO	1000mbar CO			
2500mbar CO	2500mbar CO			
desorption	desorption			
	activation			
	630 mbar H_2			
	desorption			
	activation	activation	activation	activation
	1bar CO_2	1bar CO_2	1bar CO_2	1bar CO_2
	desorption	desorption	desorption	desorption

The samples were heated in 0.5 mm capillary up to 500 K under vacuum in order to remove solvents. Typical diffractogram changes during the activation is shown on Figure 1.

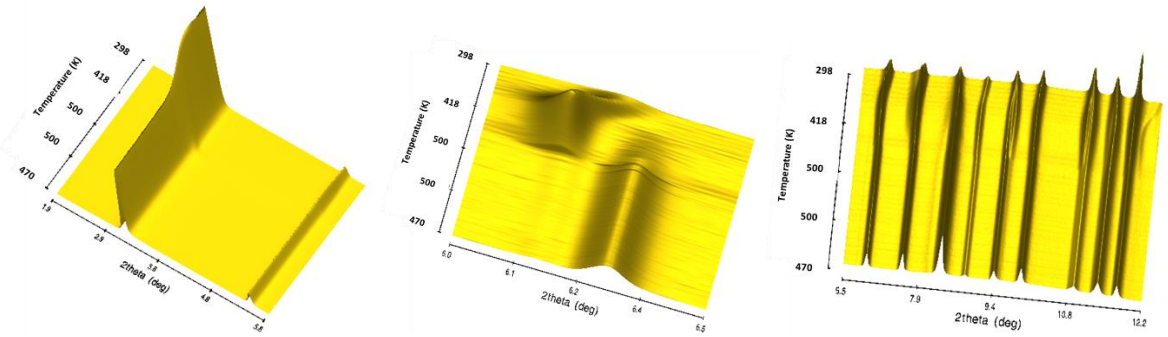

Figure 1. Fragments of the diffractogram changes during the activation of the 100Mg MOF-74 sample.

After activation the temperature was set to 290 K (in case of CO and H2 adsorption) and 470K (in case of CO_2 adsorption), and respective pressure of the gas was added. Data on CO and H_2 adsorption on the 100Ni MOF-74 and 100Mg MOF-74 were gained in the 'step mode' and will be used for the cooperativity investigation. 'Step mode` implies waiting for the settling of the temperature and making a 1 minute pause before recording the diffractogram, to avoid any influence of the kinetic effects. This way diffractograms were collected with a 2K step (290-120-290 for CO adsorption and 290-90-290 for H_2 adsorption).

For the CO_2 adsorption on all the samples data was measured in a 'ramp mode' with a 2K/min ramp in the 470-195-470K temperature range. This set of experiments will help answer the question of the true phasic nature of the as prepared mixed metal MOF-74 frameworks. In combination with other experimental techniques we will also conclude if mixed metal Ni,Mg MOF-74 is more efficient for the carbon capture and storage then a reported single metal MOF-74.

The isobars of gases adsorption will be constructed from in situ synchrotron powder diffraction. Rietveld refinement of the diffractograms will be performed and by comparing the gas adsorption on isostructural MOFs with single metal, bimetallic and physical mixture from the structural point of view we are looking into the possibility to answer the true phasic nature of the as prepared mixed metal MOF-74 frameworks. These sets of experiments would also allow us to characterize the isosteric heat of absorption, associated entropy change, and cooperativity in gas adsorption in the MOF-74 family from rather unique in situ diffraction site-sensitive data.

Additionally, we have discovered an interesting phenomenon of the 'phase transition' at lower temperature for the CO/100Mg MOF-74 system. Example of fragments of the diffractograms are shown on Figure 2. This is a rather unusual result and additional careful investigation of this system will be performed.

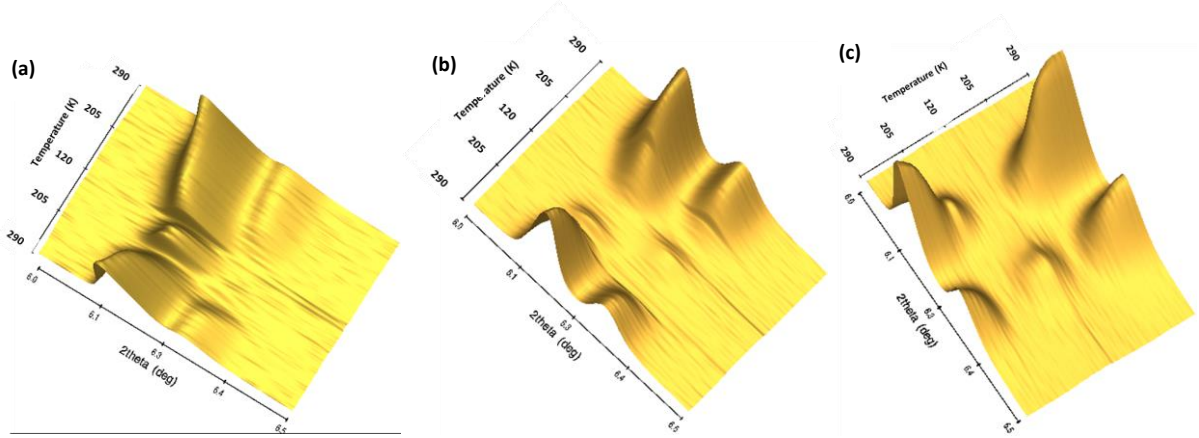

Figure 2. fragments of the in situ diffractograms taken for the CO/100Mg MOF-74 system at different pressures: 500mbar (a), 1000mbar (b) and 2500mbar (c) of CO (from 4% CO 96%He gas mixture).

Data analysis is in progress. In parallel we have performed additional characterisation with BET, TGA, Raman and SEM-EDS analysis of all the samples. Overall, the beamtime was successful. We are grateful for the help from the BM01 local contacts and hope for the further fruitful cooperations.