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Modulation Enhanced Diffraction experiments were carried out on single crystals of Me-D5 to study the atomic displacement parameters response to a thermal. A zeolite MFI and a zeolite Y were also studied with temperature modulation to describe the adsorption of Xe and CO_2 gas as test case for dye adsorption. Dye-loaded zeolite samples resulted too disordered. The zeolite samples were in powder form except for one experiment carried out on a zeolite Y single crystal.

These experiments were carried out on the single crystal diffractometer equipped with Pilatus 2M detector:

EXP	Sample	Modulation	Notes	Stimulus	DC Strategy
1) Me-D5 -1	Me-D5 Single crystal	Atomic displacement parameters (ADPs)		Temperature ramp 100K-300K	1 full sphere dataset every 3K from 100 to 150K then 1 dataset every 10K.
2) Me-D5-2	Me-D5 Single crystal	ADPs		Temperature ramp 100 – 120K	Full sphere dataset collected at 100; 100.56; 102.19; 104.72; 107.89; 111.35; 114.69; 117.48; 119.34; 120K
3) Xe-MFI HP	MFI Powder	Occupancy	P=100 mbar of Xe gas	Temperature ramp 200→300K 100K/h	1 pattern every 20 sec, i.e every 0.6K
4) Xe-MFI LP	MFI Powder	Occupancy	P= 10 mbar of Xe gas		
5) Xe-Y	Zeo Y Powder	Occupancy	P=100 mbar of Xe gas	Temperature ramp 200→300K 100K/h	1 pattern every 20 sec, i.e every 0.6K
6) CO2-Y	Zeo Y Powder	Occupancy	P= 100mbar of CO_2 gas		
7) CO2-Y (SC)	Zeo Y Single crystal	Occupancy	P= 100mbar of CO_2 gas	Temperature ramp 300 → 200K	1 full sphere dataset every 2K (plus 1 preliminary dataset collected in vacuum)

Table 1.

All the powder data collected were integrated using Fit2D and the data reduction of all single crystal datasets performed using Crysalis. The structures for every dataset of experiment 2 were solved using Shelx2013. The data will be then processed and demodulated by phase sensitive detection to achieve a better signal to noise ratio and to select the variation in the atomic displacement parameters induced by a small temperature modulation to achieve chemical selectivity in the diffraction experiment.

The powder diffractograms from exp. 3 and 4 were analyzed by sequential Rietveld refinement and the variation of the occupancy of Xe atoms was determined also using innovative approaches, apt to treat huge amount of data, such as principal component analysis. The data reduction of the single crystal datasets from experiment 7 was performed and allowed to point out the changes in the cell parameters upon cooling and CO_2 adsorption as shown in Fig.1. The cell parameter increases as the temperature decreases, this could be due to the adsorption of CO_2 within the pores. The structures at temperatures of 300K, 254K and 200K were solved independently to have a first quick look on the experiment and show progressive filling of the channels. At 300K there is already some CO_2 inside the channels but the occupancy is too low to see the Carbon atoms. TOPAS academic was then used to analyze all the datasets automatically refining the framework atoms positions and ADPs and exporting the CO_2 occupancy as a result.

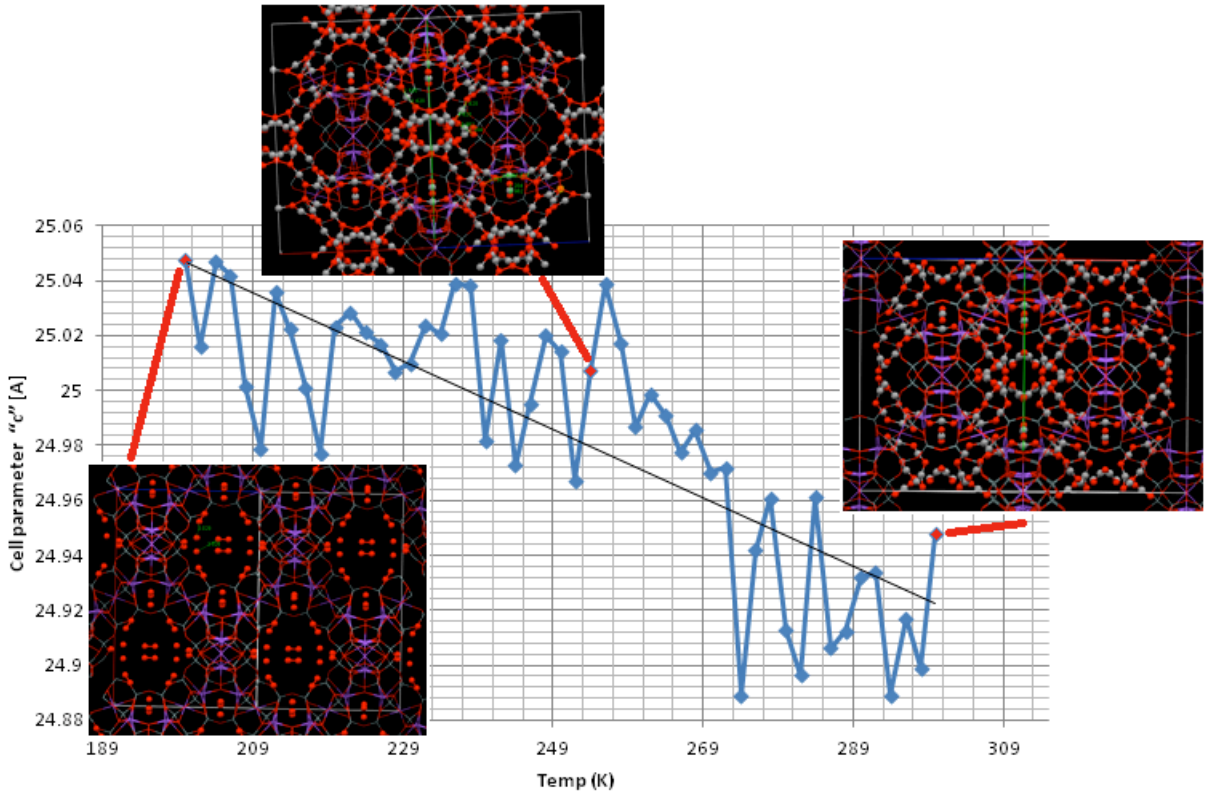

Figure 1 – Cell parameter plotted against temperature and, in the insets, structural models of zeolite –Y with 100ml CO_2 at 200K – 254K and 300K.

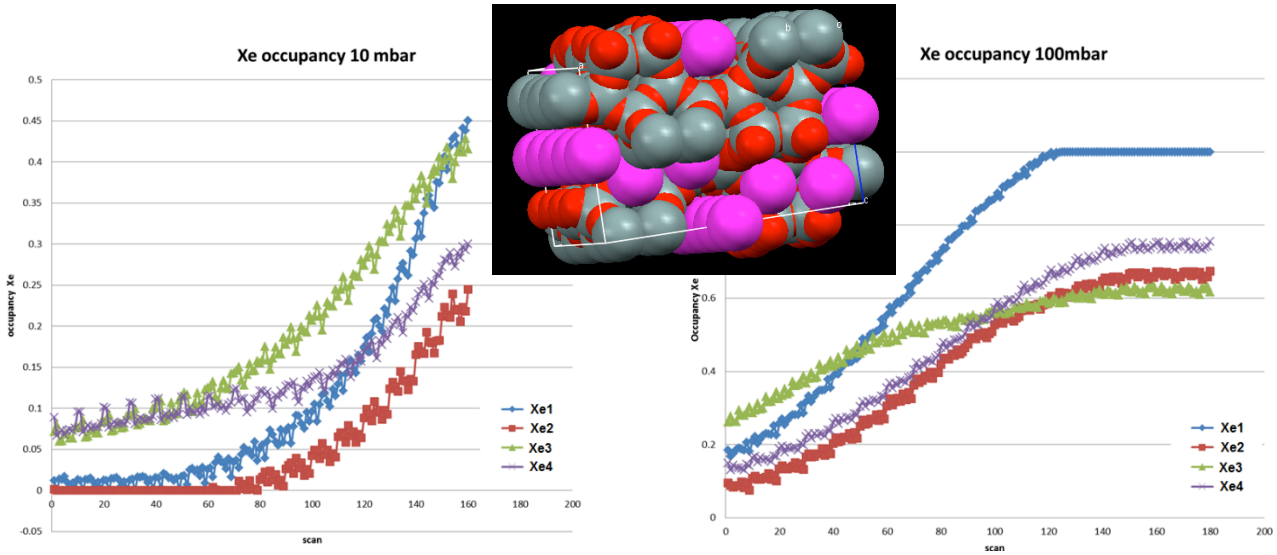

Figure 2 – Occupancy of Xe atoms in zeolite MFI plotted against scan number and structural model in the inset.

Three paper are in preparation:

1) Gas adsorption in zeolites by MED analysis of powder diffraction data
2) Gas adsorption in zeolites by MED analysis of single crystal diffraction data
3) MED analysis of Me-D5 dye by exploiting ADP modulation