SAW based CO_2 sensor; influence of functionalizing MOF crystal size on the sensor's selectivity.

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Presenter resume

Meddy VANOTTI (M) was born on 23-11-1985 in Le Chenit (Switzerland). He obtained the master's degree of physics in 2010 at the University of Franche-Comté (UFR-ST) in France. Meddy obtained his PhD degree in Engineering Sciences at the University of Franche-Comté in 2015 under the supervision of Sylvain Ballandras during which he studied the development of SAW devices for the detection of toxic gases in the air. After a post-doctoral position at the UCL (Belgium), working on the design of surface acoustic wave resonators for the detection of bacteria in liquid phase, Meddy joined back the FEMTO-ST institute to work as a research engineer on SAW based gas sensors.

Outline

I. MOF ZnTACN
- Formulation
- Adsorption properties

II. SAW sensor
- Structure
- Interrogation strategy
- Response characterization

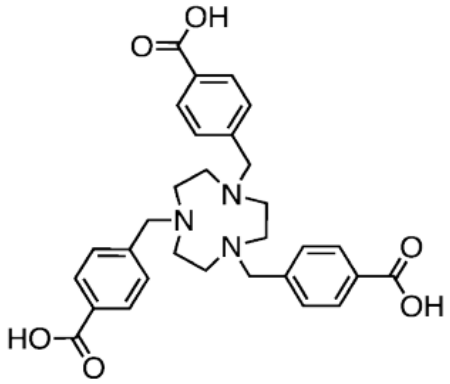
III. Experimental test bench

IV. Gaz measurements and selectivity calculation

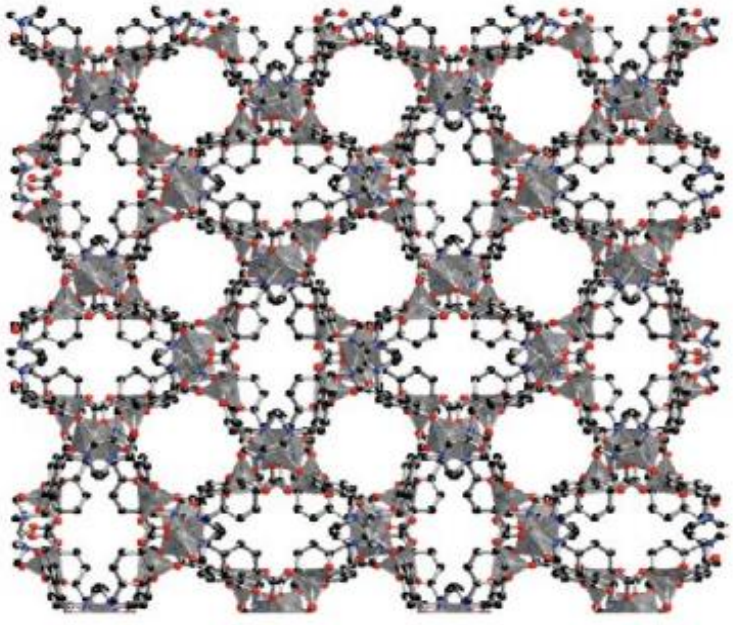
V. Conclusion

CO_2 sensitive layer: MOF ZnTACN

Metal-organic frameworks are of great interest for gas adsorption process because of the numerous structures that can be elaborated [1-4].The MOF used in this study consists in a microporous coordination polymer prepared by self-assembly of zinc and TACN ligand [5].



TACN ligand

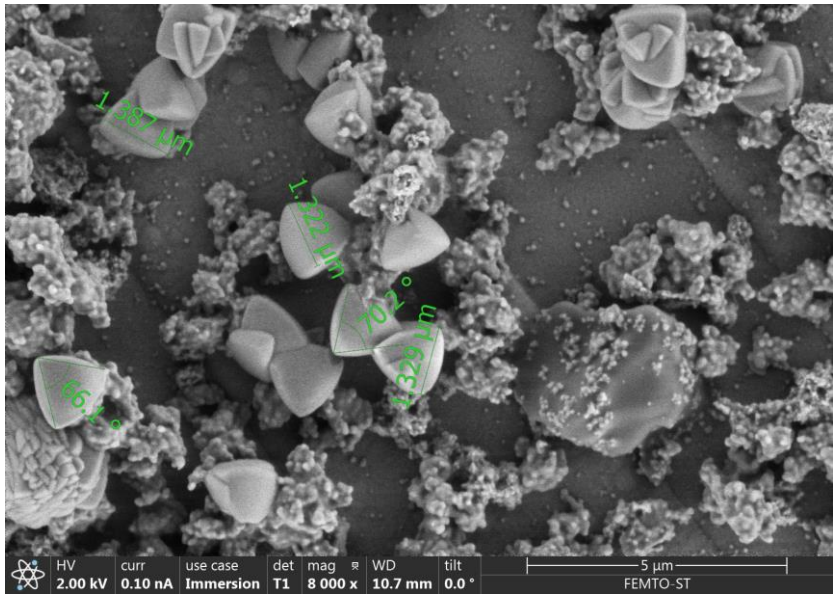


ZnTACN MOF porous framework

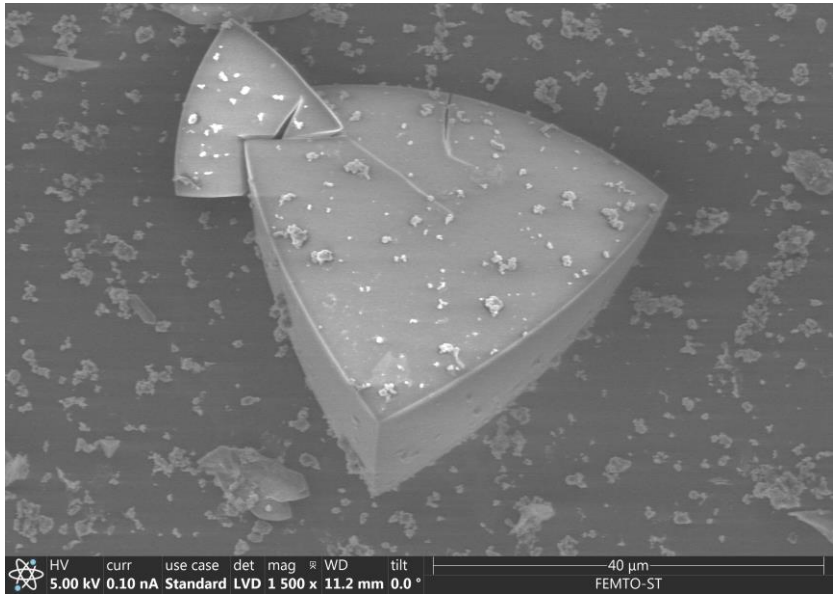
[1] M. Eddaoudi, J. Kim, R. Nathaniel, D. Vodak, J. Wachter, M. OKeefe, O. M. Yaghi, Science 2002, 295, 469 – 472.
[2] G. Frey, Chem. Soc. Rev. 2008, 37, 191 – 214.
[3] S. L. James, Chem. Soc. Rev. 2003, 32, 276 – 288.
[4] S. Kitagawa, R. Kitaura, S. Noro, Angew. Chem. 2004, 116, 2388–2430; Angew. Chem. Int. Ed. 2004, 43, 2334 – 2375.
[5] G. Ortiz, S. Brandès, Y. Rousselin, R. Guilard, Chemistry–A European Journal 2011, 17(24), 6689-6695.

CO_2 sensitive layer: MOF ZnTACN

- Depending on the scale of the synthesis, the crystals had sizes between 1 and 40 µm.
- SEM observation of the sensor's surface confirm the presence of the MOF.
- The characteristic trigonal prismatic-like morphology with curved edges of the ZnTACN MOF was observed assessing the proper functionalization of the surface.

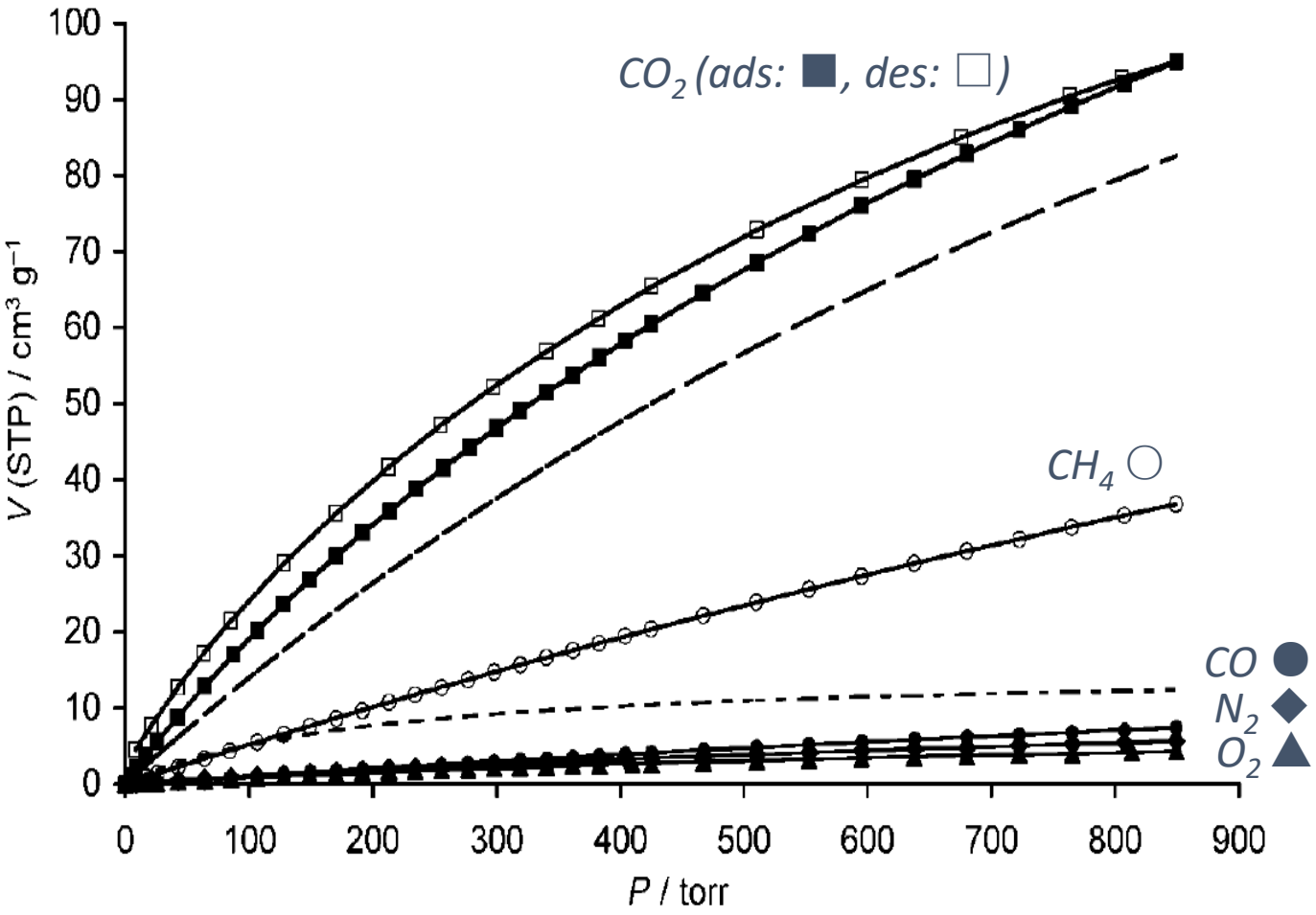


1,3 µm MOF crystals



40 µm MOF crystals

CO_2 sensitive layer: MOF ZnTACN



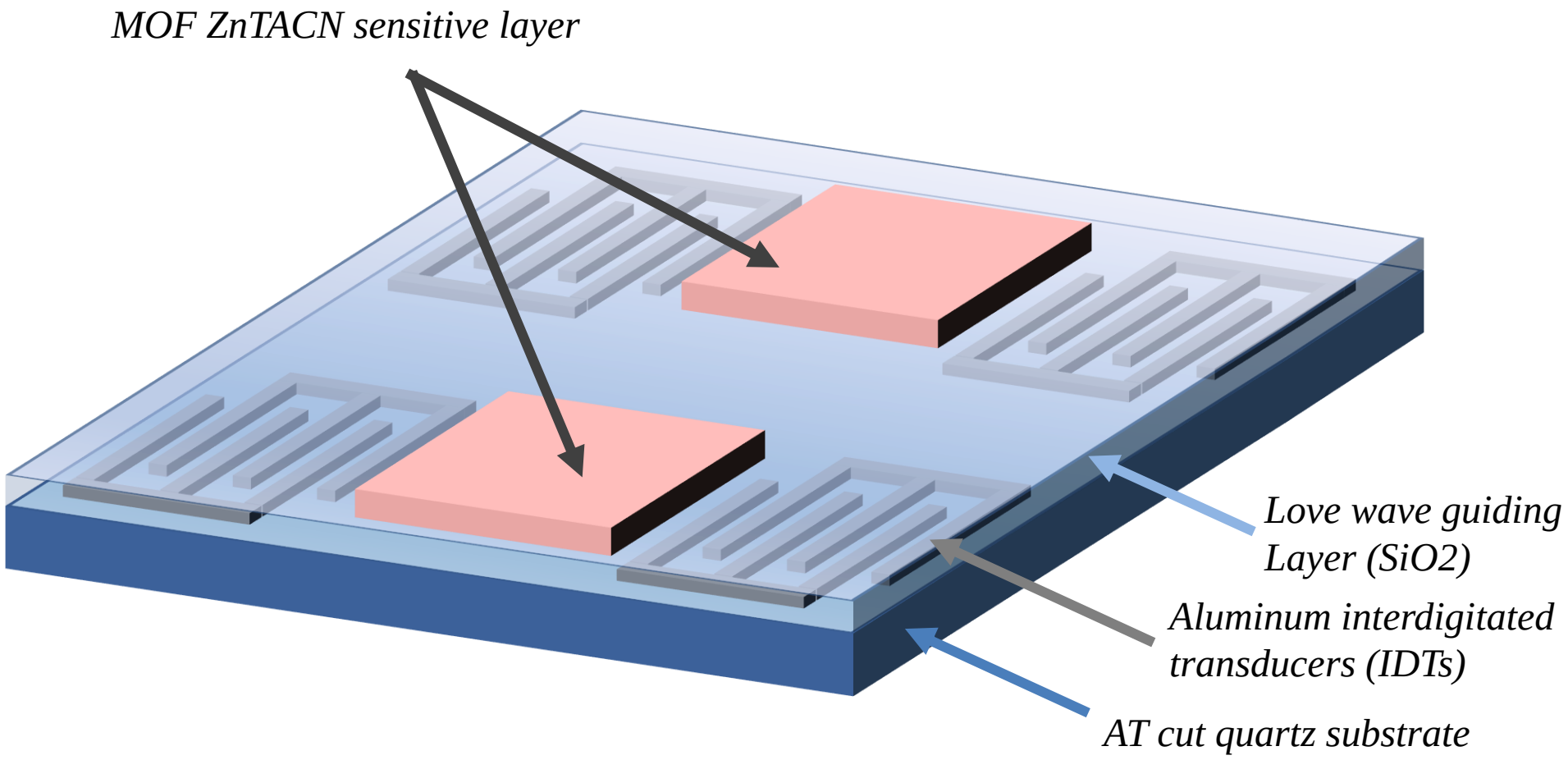
Adsorption–desorption isotherms for ZnTACN MOF at 298 K with CO_2 (ads: ■, des: □), CH_4 (○), CO (●), N_2 (◆), and O_2 (▲). [5]

- The CO, CH_4, O_2 and N_2 adsorption isotherms at 298 do not show significant uptake of these gases with respect to CO_2.
- The selectivity for CO_2 towards other gases was calculated from the Henry constants [5] and values were 21.1, 4.2, 26.0 and 22.6 over CO, CH_4, O_2 and N_2, respectively.

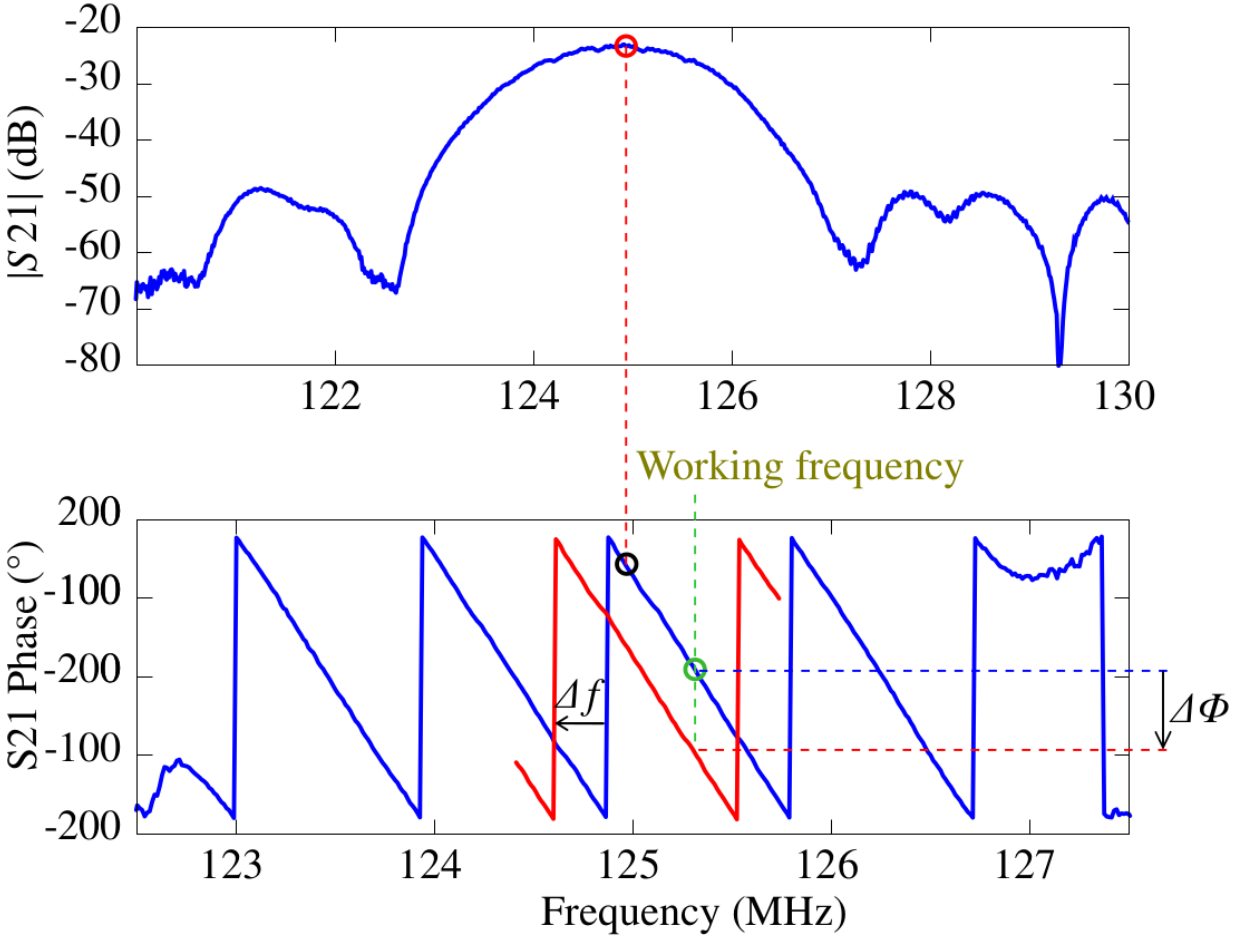
[5] G. Ortiz, S. Brandès, Y. Rousselin, R. Guilard, Chemistry–A European Journal 2011, 17(24), 6689-6695.

SAW sensor structure

A Surface Acoustic Wave sensor in double delay-line configuration has been selected. This provides a large functionnalisation area and permits to average the measurements. This configuration will also allow to achieve a differential sensor to improve selectivity.



Interrogation strategy



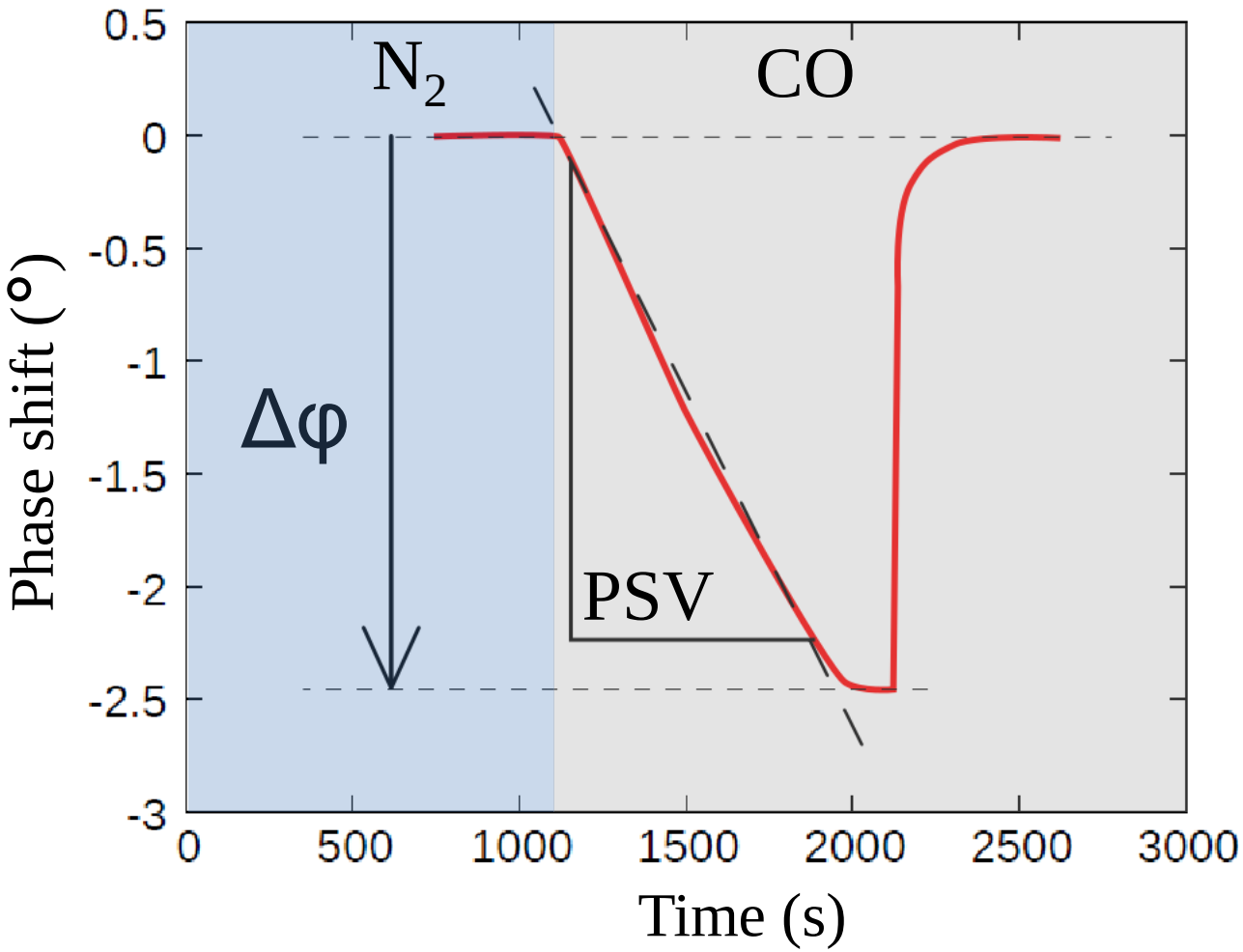
Phase monitoring principle; blue and red curves respectively represent the phase response of the transfer function of the delay line before and after the sorption of the target gas on the sensitive layer.

The blue and red curves represent the phase before and after the sorption of the target gas respectively.

Δf, represents the frequency shift induced by the mass-loading effect.

Since the phase is linear with the frequency in the vicinity of the working frequency, the frequency shift Δf can be revealed by a phase shift $\Delta\varphi$ measurement at constant frequency, represented here as the working frequency.

Signal characterization



Typical phase response of the sensor.

The gravimetric sensitivity of the sensor, deduced from the Sauerbrey formula [6], is given by following equation :

$$S = \frac{df}{f_0} \cdot \frac{A}{dm}$$

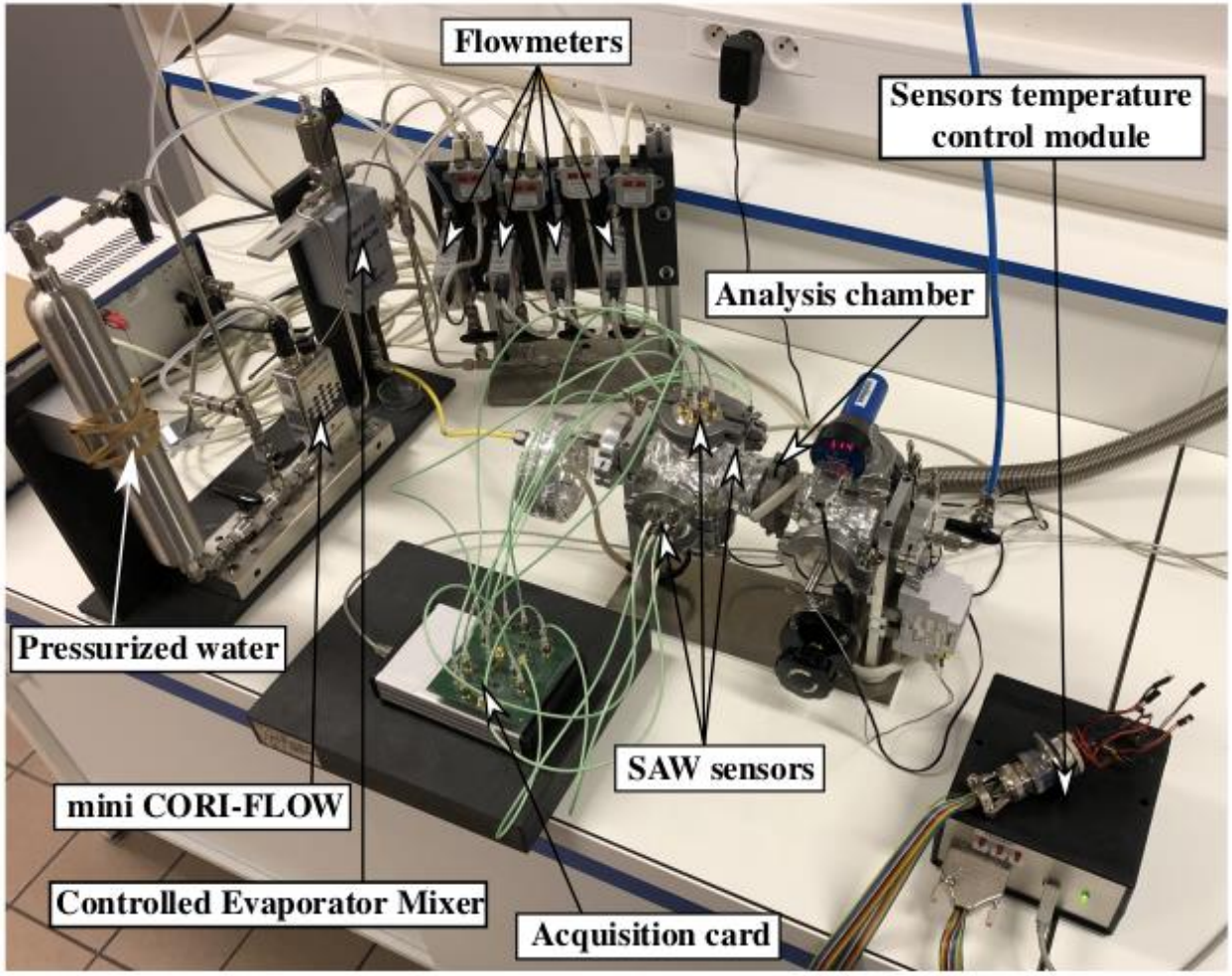
The CO concentration and flow rate being kept constant during the exposure, the gas concentration is proportional to the phase variation in respect of time:

$$C \sim \frac{d\varphi}{dt} .$$

CO concentrations can consequently be determined by means of the derived phase at the beginning of its decrease. This derived phase is referred to as 'Phase Shift Velocity' (PSV). This approach allows to measure gas concentrations within a few tens of seconds.

[6] G. Sauerbrey, Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung, Z. Physik. 155 (1959) 206–222. https://doi.org/10.1007/BF01337937.

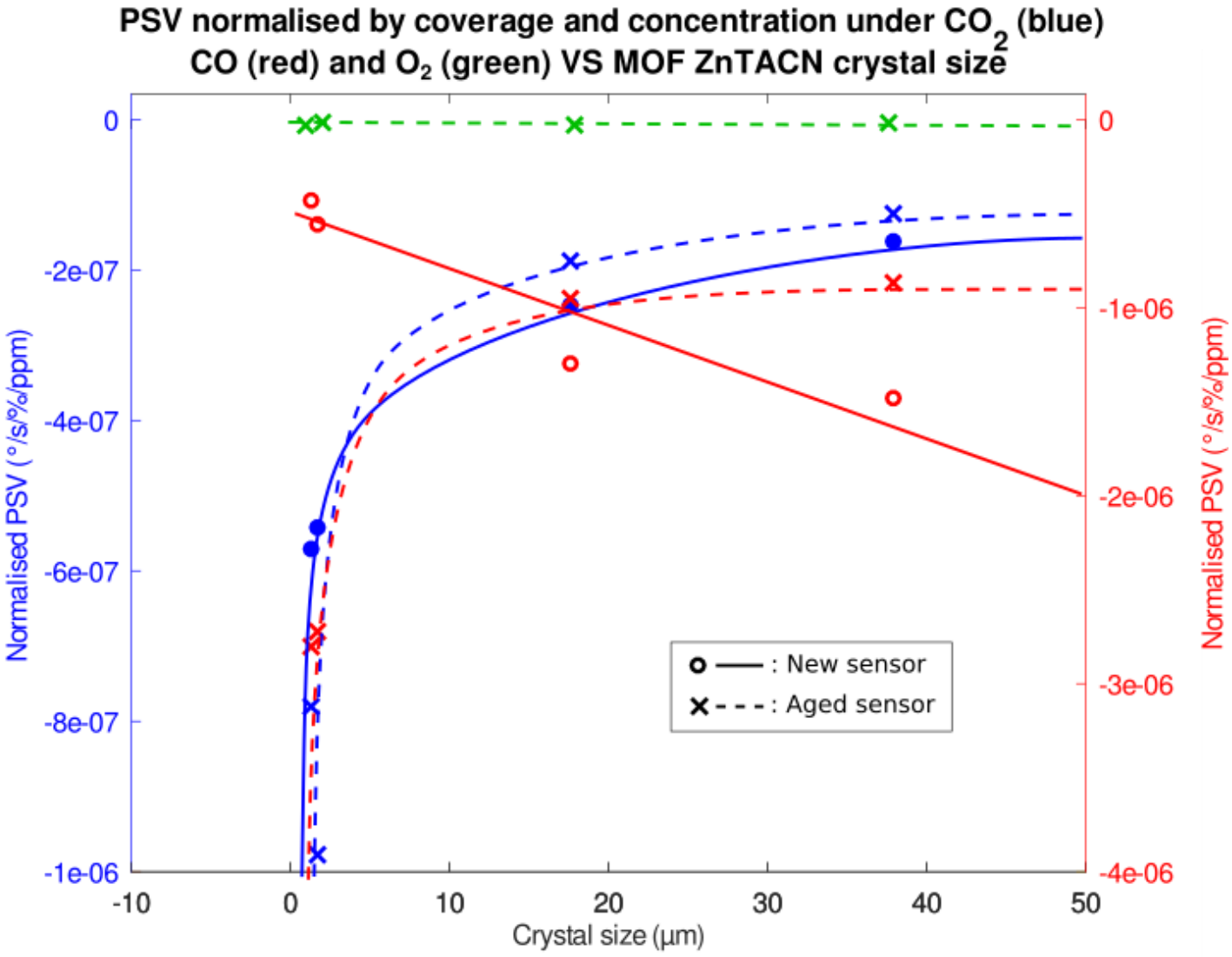
Experimental bench



Four mass-flow meters operating in the range 2-500 $mL.min^{-1}$ were used to generate the mixture from gas cylinders with calibrated concentration of target molecules. A Controlled Evaporation Mixing module (CEM) was used to generate a controlled relative humidity in the gas flow. The latter then flowed through a dedicated test chamber, which volume is approximately one liter, with a constant flow rate equal to 500 $mL.min^{-1}$. A primary pump is also connected to the chamber to activate the sensors under 30.10^{-3} mbar before use.
A dedicated electronic [7] that delivers similar information to that from a network analyzer was implemented to monitor the phase signals.

[7] D. Rabus, G. Martin, E. Carry, S. Ballandras, Eight channel embedded electronic open loop interrogation for multi sensor measurement, 2012 European Frequency and Time Forum. (2012). https://doi.org/10.1109/EFTF.2012.6502420.

CO_2 and interferents measurements



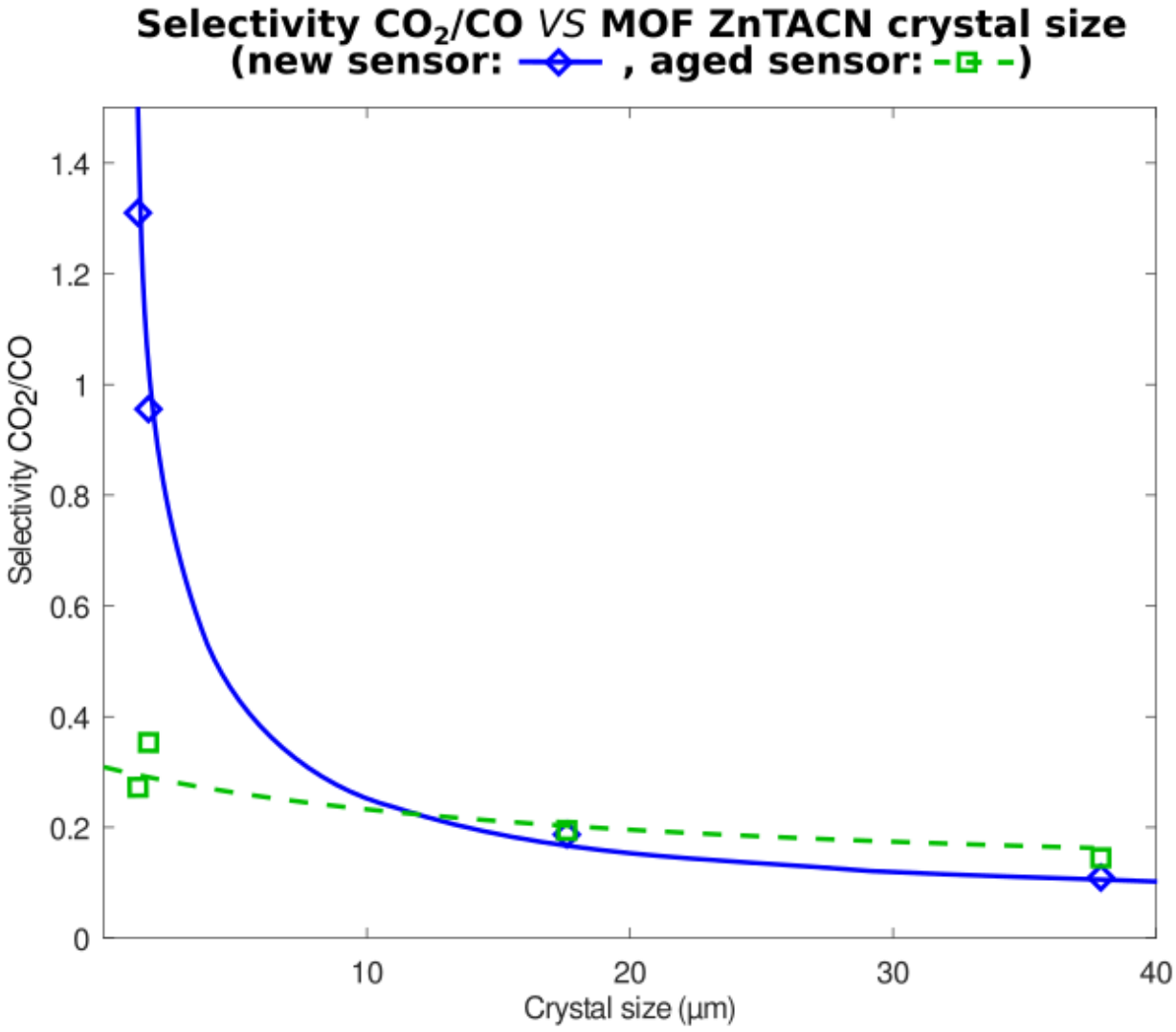
- In the case of a freshly activated sensor;

- the PSV modulus measured under CO_2 is inversely proportional to crystal size in the considered range.

- The PSV modulus measured under CO is proportional to the crystal size

- In the case of a aged sensor exposed for days to ambient air, the response to CO_2 et CO a similar and there is no signal under O_2.

CO_2 and interferents measurements



From the previous results, we estimated the selectivity of the sensors toward the major interferent, O_2 and CO.

- We estimated that the CO_2/O_2 selectivity is virtually infinite since there is no measurable signal under O_2.
- It appears that is the case of brand new sensor, the selectivity is inversely proportional to the crystal size. However, its value isn't quite as high as expected from the measurement on powder.
- In the case of an aged sensor exposed to ambient air for days, the selectivity dramatically decreases for small crystals.

This behavior may be attributed to the breakdown of the zinc site consecutive to the exposure to ambient air.

Conclusions and prospects

- Our SAW based CO_2 sensor functionalized with ZnTACN Metal-Organic Framework showed measurable responses to the target gas with virtually infinite electivity toward O_2 upon the 1 µm to 40 µm crystal size range.

- We observed an important increase of the CO_2/CO selectivity with the reduction of the MOF crystal size offering the prospect of manufacturing highly selective CO_2 sensors based on submicronic MOF crystals.

- The measured selectivity of the sensor toward CO is not as high as expected from the volumetric method based on the adsorption isotherms.

- We observed a rapid aging of the MOF at the sensors surface under ambient air inducing a important decrease of the selectivity toward CO especially for the sensor functionalized with small crystal (< 2 µm).

→ Further works will consist on the synthesis of submicronic ZnTACN MOF to improve its selectivity and stability. The synthesis of alternative MOF structures for the trapping of interferents such as CO to develop a reference to the CO_2 measurement.