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

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***Abstract*— The potential impact of indoor air quality on human health has become an increasingly important topic of public health and, thus, has stimulated an interest in hazardous compounds survey such as carbon dioxide. To address this issue, we started the development of a Surface Acoustic Wave device functionalized with metal-organic framework for the selective detection of carbon dioxide. Here, we propose preliminary results on the influence of the size of the metal-organic framework crystals on the sensor's selectivity and on its evolution with the ageing of the sensor.**

Keywords-Carbon dioxide sensor; SAW device; metal-organique framework.

I. INTRODUCTION

Road traffic considerably contributes to the exposure of human to air pollutants like carbon dioxide (CO_2). In traffic environments, the concentrations of traffic related pollutants are higher than in other environments and a considerable amount of time, on average from 4 % to 8 % of total hours of the day, is spent in traffic in developed countries. This points to the need for an air quality monitoring system in vehicle cabins, especially for CO_2. Here we propose preliminary results on a Surface acoustic Wave (SAW) based sensor for the selective detection of CO_2. In this work, we focus on the influence of the size of the ZnTACN Metal-Organic Framework (MOF) crystals used for the functionalization of its surface on the selectivity toward interferent such as carbon monoxide (CO) et oxygen (O_2). The evolution of the calculated selectivity with the ageing of the sensor is also discussed.

II. MATERIALS AND METHODS

We have developed a CO_2 sensor based on the potential of Surface Acoustic Waves (SAW) to probe mass variations [1] in CO_2 sensitive porous material. We used Love wave based SAW delay line built on a temperature compensated substrate of (YXlt)/36°/90° quartz. IDTs were made of aluminum and shaped by mean of a lift-off technique using negative photoresist. In order to allow the Love-mode acoustic wave to propagate at the surface of the device, a silica guiding layer was deposited on the top of the chip. We have selected a delay line configuration shown in Fig. 1 for the sensors because of the large functionalization area that it offers. Also, the robustness of such a device allows for the deposition of a sensitive layer compatible with its normal operating conditions [2, 3].

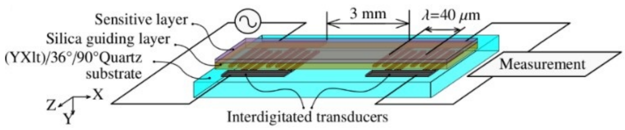


Figure 1. SAW device used for the manufacturing of the CO2 sensors.

The SAW device was than functionalized with metal-organic framework to reach sensitivity toward CO_2. The ZnTACN MOF represented in Fig. 2 was selected because of its high affinity with this gas described in the literature [4].

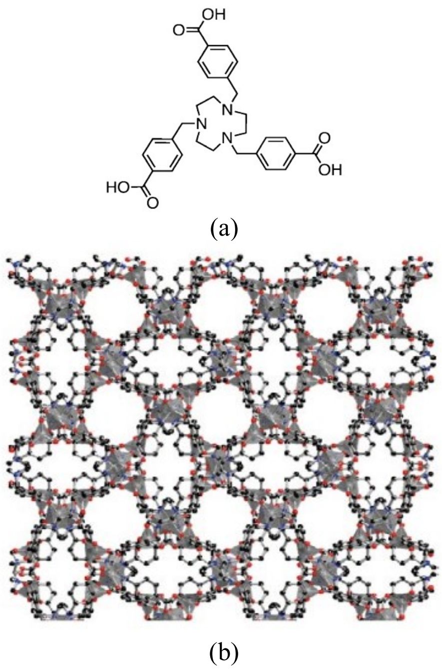
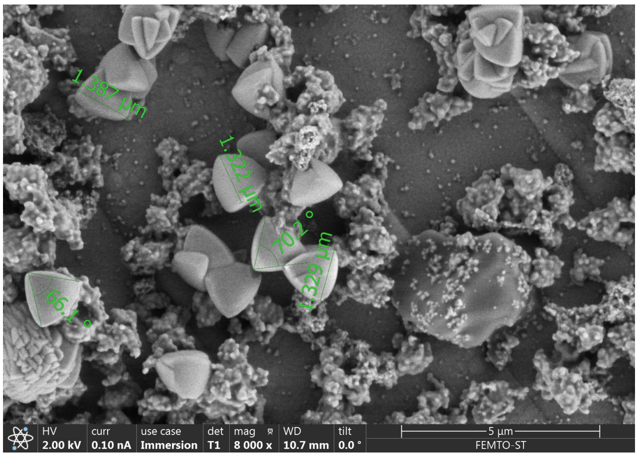


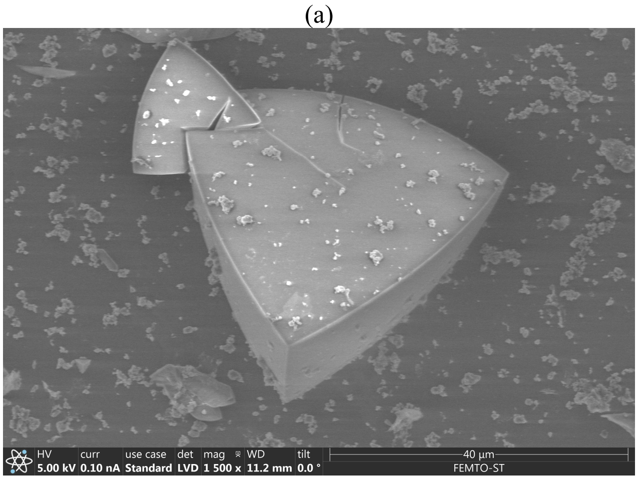
Figure 2. ZnTACN metal-organic framework (b) obtained by self assembly of TACN ligand (a) and zinc.

Depending on the scale of the synthesis, the crystals had sizes between 1 μm and 40 μm. The characteristic trigonal prismatic-like morphology with curved edges of the

ZnTACN MOF was observed by SEM assessing the proper synthesis and the functionalization of the surface (Fig. 3).



(a)



(b)

Figure 3. SEM images of the ZnTACN MOF with crystal size between 1.3 µm (a) and 40 µm (b).

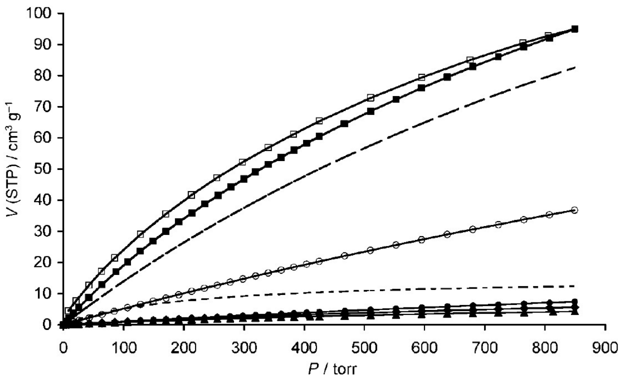


Figure 4. SEM Adsorption–desorption isotherms for ZnTACN MOF at 298 K with CO_2 (ads: ■, des: □), CH_2 (○), CO (●), N_2 (◆), and O_2 (▲).

The CO_2, CO, CH_4, O_2 and N_2 adsorption isotherms at 298 K are illustrated in Fig. 4. The thin solid lines are related to the calculated dual-site Langmuir isotherm model for CO_2 and single-site Langmuir-type isotherms for the other gases. Dashed and dotted lines indicate the two contributions for the calculated CO2 isotherm. The large uptake of CO2 compared to other gases, especially in the low-pressure range, clearly evidence the selective adsorption of CO_2. These isotherms were obtained with MOFs whose size is between 10 µm and 30 µm. Five sensors were coated with MOF of different sizes in the range [1-40] µm. SEM observations of the sensor's surface, shown on Fig. 3, were made to assess the presence of the MOF at the surface of the device and measure the crystal size. The evaluation of the coverage rate of the sensors was also made with a high-resolution digital microscope 4 K Serie VHX-7000 KEYENCE.

III. Results and Discussion

The sensors were exposed to CO_2, CO and O_2 diluted in pure N_2. The phase decrease observed during the exposures were characterized by means of the derived phase at the beginning of the phase decrease. This derived phase is referred to as 'Phase Shift Velocity' (PSV). This approach allows to measure gas concentration within a few tens of seconds [1]. The responses are normalized by the coverage rate of the sensor's surface and the gas concentration. The measurements of the three gases are plotted against the MOF crystals size in Fig. 5. It shows that the sensitivity of the sensor to CO_2 is inversely proportional to the crystal size. As expected from the adsorption isotherms presented in Fig. 4, the sensitivity to O_2 is virtually null. However, we observed an unexpected non-zero sensitivity to CO which tends to be linear with the MOF crystal size.

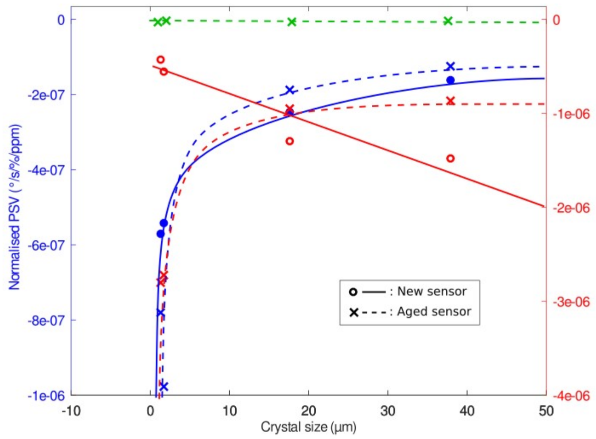


Figure 5. Phase shift velocity normalized by surface coverage and gas concentration measured under CO_2, CO and O_2.

On the basis of these measurements, we estimated that the CO2 vs O2 selectivity is virtually infinite since there is no measurable signal under O2. The CO2 vs CO selectivity was also calculated and plotted against the MOF crystals size on Fig. 6. It appears that is the case of brand-new sensor, the CO2 vs CO selectivity is inversely proportional to the MOF crystal size offering a potentially infinite selectivity in the submicronic range. However, in the studied range, its value isn't quite as high as expected from the measurement made on compacted powder (Fig. 4). This will draw our attention and further work will be engaged to explain the difference in the MOF sensitivity toward CO between the case of a compacted powder and the case of fewer crystals deposited on a surface. In the case of an aged sensor exposed to ambient air for days, the CO_2 vs CO selectivity dramatically decreases for small crystals. This behavior may be attributed to the breakdown of the zinc sites on the MOF structure after the exposure to ambient air.

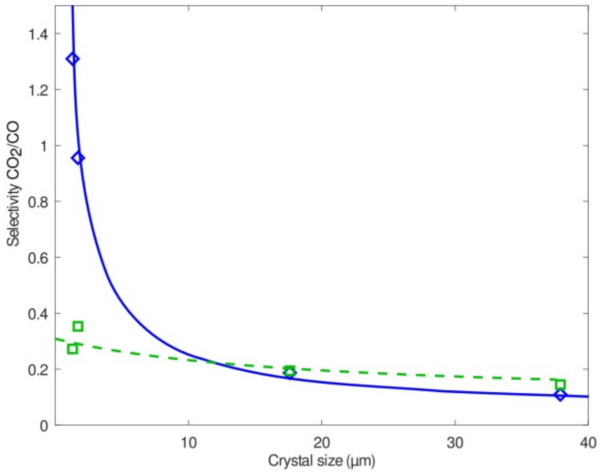


Figure 6. Selectivity CO2/CO versus MOF crystal size for new sensors and aged sensors.

IV. Conclusions

In this work we showed the capability of a SAW based sensor functionalized with ZnTACN metal-organic framework to detect carbon dioxide. Although the measurements that were performed on compacted MOF powder showed high selectivity for CO_2 toward CO, we found a significantly lower selectivity for dispersed MOF crystals on the sensor's surface. More interestingly, we noticed a virtually infinite selectivity toward O_2 in the whole crystal size range and for submicronic crystals in the case of CO_2. These observations induce us to investigate further the potential of the ZnTACN MOF for the development of selective CO_2 sensor.

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References

[1] M. Vanotti, S. Poisson, V. Soumann, V. Quesneau, S. Brandès, N. Desbois, Y. Yang, L. André, C.P. Gros, and V. Blondeau-Patissier. (2021). Influence of interfering gases on a carbon monoxide differential sensor based on SAW devices functionalized with cobalt and copper corroles. Sensors and Actuators B: Chemical, 332, 129507.

[2] M. Vanotti, V. Blondeau-Patissier, V. Moutarlier, and S. Ballandras, Analysis of palladium and yttrium–palladium alloy layers used for hydrogen detection with SAW device, Sens. Actuators B Chem. 217 (2015) 30–35, https://doi.org/10.1016/j.snb.2015.02.049.

[3] P. Zheng, T.-L. Chin, D. Greve, I. Oppenheim, V. Malone, T. Ashok, J. Miller, and L. Cao, Langasite SAW device with gas-sensitive layer, 2010 IEEE International Ultrasonics Symposium (2010) 1462–1465, https://doi.org/10.1109/ULTSYM.2010.5935779.

[4] G. Ortiz, S. Brandès, Y. Rousselin, and R. Guilard. (2011). Selective CO_2 Adsorption by a Triazacyclononane-Bridged Microporous Metalo-Organic Framework. Chemistry - A European Journal, 17(24), 6689-6695.G. Eason, B. Noble, and I. N. Sneddon, "On certain integrals of Lipschitz-Hankel type involving products of Bessel functions," Phil. Trans. Roy. Soc. London, vol. A247, pp. 529–551, April 1955.