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A functional metal-organic framework for dual gas sensing (CH_4/CO_2) using a quartz crystal microbalance

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Unchecked gas leaks from pipeline infrastructure can lead to disastrous consequences.[1] Compact sensors deployed near pipelines could mitigate this problem by continuously monitoring potential leaks. Existing methane sensors suffer from lack of selectivity, irreversible poisoning and short lifespan under non-ideal conditions. Metal-organic frameworks (MOFs) are porous materials that ideal for this application. These consist of metal clusters that coordinate with organic linkers, thus, generating porous frameworks with tunable pore sizes and morphologies.[2] When incorporated into a quartz-crystal microbalance (QCM), a CH_4-selective MOF would work as a low-power cost-effective sensor. QCMs can continuously monitor frequency changes (on the order of a few Hz) and typically have a high mass sensitivity (4.4 ng Hz^{-1} cm^{-2} for 10 MHz quartz resonators) that facilitates ppm-level of analyte detection.[3]

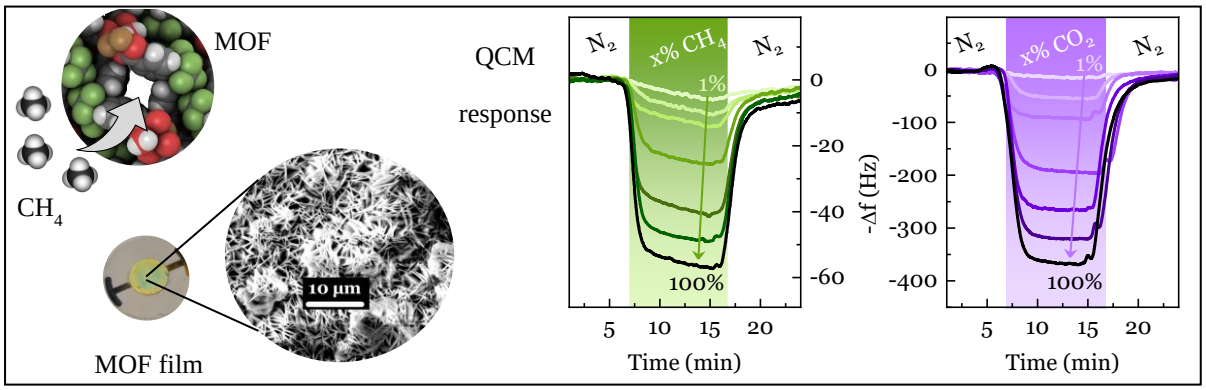

Fig. 1. MOF framework pores, MOF thin film on quartz sensor and QCM sensing response for CH_4 and CO_2

We use a microporous MOF $[Cu(hfipbb)(H_2O)]_n$ (hfipbb = 4,4′ (hexafluoroisopropylidene) bis(benzoic acid)) which shows a favorable adsorption of up to 4-C straight-chain hydrocarbons, including CH_4.[4] The framework consists of 5 Å pores connected via 3 Å gates as investigated via PoreBlazer4.0.[5] Thin films of this MOF were directly synthesized on thiol-functionalized gold electrodes of 10 MHz quartz sensors (thiol = 16-mercaptohexadecanoic acid) via epitaxial growth. Grazing angle powder X-ray diffraction confirmed the phase of the MOF. Atomic force and scanning electron microscopies show a rough surface with needle-like morphology of the crystals on the film.

An open source QCM device (OpenQCM Next)[6] and a syringe setup for gas flow were used to study the sensor's response towards CH_4. A fast regenerative response (t_{90} = 181 s) towards CH_4 was observed when measured against a baseline of N_2 flow. A Freundlich-type adsorption isotherm was obtained for Δf vs CH_4 concentration with a limit of detection at 1% methane (v/v in N_2). The sensor also shows cross-sensitivity towards CO_2 (6:1 by mass) but not with other atmospheric gases as evident from the sensor's response towards methane when

measured against a baseline of air flow at atmospheric conditions. Frequency deviation of the 3rd and 5th overtones, allows to distinguish between CH_4 and CO_2 response, as CO_2 having a smaller kinetic diameter (3.3 Å) than CH_4 (3.8 Å), penetrates deeper within the film. We are currently working on investigating response from CH_4-CO_2 mixtures using chemometrics and multivariate regression to quantify mixture compositions. Stored at standard atmospheric conditions, the sensor shows a stable response over time (at least 80 days).

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