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## Nanoscale

## COMMUNICATION

## Contaminant-resistant MOF-Pd composite for H<sub>2</sub> separation

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**The drive to use hydrogen as energy carrier or reducing agent to synthesise hydrocarbons boosts its demand, requiring affordable and reliable separation methods. In this work, the combination of a selective but vulnerable Pd thin film with a robust metal-organic framework (MOF) yielding a contaminant-resistant composite membrane for hydrogen separation is reported.**

Pure hydrogen is used in many industrial applications requiring costly separation processes through *i*) pressure-swing adsorption (PSA),<sup>[1]</sup> *ii*) fractional/cryogenic distillation or *iii*) membrane separation.<sup>[2]</sup> PSA and distillation are costly, energy demanding and yield insufficient gas purity for energy applications, *cf.* fuel cells. On the other hand, membrane separation affords high efficiency and low energy consumption and operational and investment costs.<sup>[3]</sup> The current, polymer-based, membrane market is limited by short lifetimes, poor selectivity, thermal and chemical stability. Palladium membranes on the other hand display complete perm-selectivity.<sup>[4]</sup> While most concerns related to pure Pd membranes, *e.g.* embrittlement<sup>[5]</sup> or poisoning by sulfurous compounds<sup>[6]</sup> can be addressed by alloying,<sup>[7]</sup> carbon-monoxide contamination remains a critical issue. Carbon monoxide, a ubiquitous impurity in hydrogen gas, is prohibitive for a broad range of applications.<sup>[8]</sup> The development of composite Pd membranes with protective layers<sup>[9]</sup> separating H<sub>2</sub> from contaminants, such as CO, would thus be desirable for non-ideal operational conditions.

MOFs have tailored topology, pore geometry, specific interactions through chemical functionalities and flexibility. In addition, their gas separation may take place through specific interactions or size exclusion.<sup>[10]</sup> Small apolar molecules such as CO and H<sub>2</sub> typically do not adsorb enter strong specific interactions. Separation based on size exclusion, controlled by the pore size, is therefore

advantageous. Also, separation via size exclusion is generally independent of gas concentrations.<sup>[11]</sup> MOF interpenetration, *i.e.* entangling of crystallographically equal sub-lattices,<sup>[12]</sup> is critical for the separation of small inert gases as the pore sizes are limited by the building-blocks. Consequently, H<sub>2</sub> selectivity of MOFs cannot rival that of Pd.<sup>[10b,13]</sup> However, by carefully adjusting the MOF pore size, CO can be excluded from H<sub>2</sub>-CO mixtures, providing excellent surface-protective layers, inhibiting Pd-CO interactions, which block dissociative H<sub>2</sub> absorption.

In the present work, we investigated the use of a MOF thin film as a pre-sieving layer able to separate H<sub>2</sub> and CO.<sup>†</sup> The CO/H<sub>2</sub> separation efficiency was assessed by measuring the optical property changes of the underlying Pd through hydrogen absorption, according to the following considerations: *i*) the optical transparency of Pd increases upon hydrogenation.<sup>[14]</sup> *ii*) If CO reaches the Pd surface it will prevent the dissociation and absorption of H<sub>2</sub>, and consecutive optical changes. *iii*) MOF thin films on Pd are not detrimental to its H<sub>2</sub>-sorption<sup>[15]</sup> and *iv*) if the H<sub>2</sub>/CO selectivity MOF is too low, hydrogen will not be absorbed and we will not be able to observe optical changes in the Pd. This approach is also used to develop suitable MOF protective layers on Pd for optical hydrogen sensing.<sup>[15b]</sup>

To ensure H<sub>2</sub>/contaminant separation by size exclusion, MOF pore apertures need to match with molecular kinetic diameters (H<sub>2</sub> 2.8 Å, and typical contaminants: CO 3.76 Å and H<sub>2</sub>S 3.6 Å). Therefore, the doubly interpenetrated Cu(FMA)(Bpe)<sub>0.5</sub> with 2.0×3.2 Å<sup>2</sup> pore apertures<sup>[16]</sup> was selected. Zhu *et al.* demonstrated that in the bulk Cu(FMA)(Bpe)<sub>0.5</sub> selectively adsorbs H<sub>2</sub> over Ar (3.4 Å), N<sub>2</sub> (3.64 Å) and CO.<sup>[16]</sup> Cu(FMA)(Bpe)<sub>0.5</sub> crystal structure was solved at 195 K while adsorption isotherms were measured at 195 and 77 K, and as the PXRD data did not reveal any major structural changes up to 298 K, ambient-temperature gas-separation studies are thus justified.<sup>[16]</sup> For H<sub>2</sub> separation, thin films need the same selectivity as the bulk at low temperature, which means that the interpenetrated structure must be preserved as the MOF's selectivity is a consequence thereof. MOF thin-film synthesis routes, such as layer-by-layer or multi-sequential assembly were shown to yield preferentially oriented, non-interpenetrated thin films,<sup>[17]</sup> unfavourable for H<sub>2</sub> separation. To obtain the desired properties a

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direct synthetic route was thus adapted. Solvothermal synthesis of Cu(FMA)(Bpe)<sub>0.5</sub> using various solvents and self-assembling monolayers (SAM) resulted in the formation of a loose powder unattached to the Pd. Therefore, the microwave-assisted technique was employed, allowing the direct deposition of MOF films on the substrate through the unique absorption of microwaves in Pd, heating the solution locally.<sup>[18]</sup>

Cu(FMA)(Bpe)<sub>0.5</sub> formation on Pd substrates was confirmed (Fig. S1, ESI). In addition, SEM micrographs (Figure 1) of the composite suggest that the MOF's interpenetrated bulk structure was preserved in the thin films. The reason for this is that preferential orientation, *i.e.* when the crystal-growth direction is limited to one crystallographic axis, of MOF thin films is closely related to lattice interpenetration<sup>[12,19]</sup> and it is also reflected in the particle morphology.<sup>[17b]</sup>

Synthetic conditions were optimised for a single microwave shot to maximise coverage while preserving substrate integrity. Surface coverage was found to improve with increasing reaction-mixture temperature up to 70 °C (solution temperature, Pd surface temperature would be higher). At 80 °C, the formation of cracks and buckles compromised the Pd membrane integrity, while at 100 °C the Pd layer detached from the glass wafer.

In addition our X-ray diffraction data (Fig. S2 ESI) also confirmed that the MOF thin film indeed preserved the bulk-like structure published.<sup>[16]</sup> In conclusion, microwave-assisted deposition of Cu(FMA)(Bpe)<sub>0.5</sub> on Pd substrate yields randomly oriented thin layers, critical for H<sub>2</sub> separation. To probe the composite's selectivity, repetitive cycles of absorption and desorption of H<sub>2</sub> from H<sub>2</sub>-CO mixtures were performed while measuring the optical reflection and the results were compared with those obtained on the pristine Pd substrate (after the same microwave-treatment, without reagents).

Uncontaminated Pd is highly reflective when metallic, whereas it is more transparent as a hydride, in H<sub>2</sub> atmosphere (Figure 2, in dark blue).<sup>[20]</sup> This process is reversible under vacuum and reproducible (Fig. 2). However, when exposed to CO the pristine Pd film is immediately contaminated and no longer absorbs H<sub>2</sub> (Fig. 2, in turquoise). On the other hand, Pd coated with Cu(FMA)(Bpe)<sub>0.5</sub> shows some initial loss of response intensity upon exposure to a H<sub>2</sub>/CO mixture, compared with its response to pure H<sub>2</sub>, then the signal stabilises (Fig. 2, in grey). The MOF thin layer's density sheds light on the initial loss of response intensity. Partial surface coverage left some of the Pd surface directly exposed to CO, which was subsequently poisoned, lowering the optical response. However, where the MOF particles were attached to the Pd surface, no poisoning could occur, as reflected by the stabilised optical signal.

These observations highlight that *i*) thin Cu(FMA)(Bpe)<sub>0.5</sub> layers obtained by microwave-assisted synthesis preserve bulk selectivity, as expected from their morphology and structure; *ii*) the MOF-Pd contact is firm and intimate, as the CO molecules could not penetrate onto the Pd surface even after several gas-exposure cycles and, most importantly, *iii*) the MOF-on-Pd composite proved an efficient and robust hydrogen-selective membrane no longer displaying the pristine Pd membrane's vulnerability towards contaminants such as carbon monoxide. It should be noted that control experiments were carried out on both as-synthesised and

microwave-treated Pd samples. As these measurements were identical, the effect of microwave treatment in H<sub>2</sub>/CO separation can be neglected. In addition, previous work on Cu-BTC deposition onto Pd highlights that neither the interactions of Pd with cupric ions nor with carboxylate groups result in increased Pd resistivity towards contaminants.<sup>[15a]</sup> Also, since the functionality of the coating relies on its filtering effect, we do not believe that the nature of the Pd (alloyed or not) would make much difference. However, subtle effects on the hydrogen absorption process may occur due to the particular nature of the MOF-Pd interaction.<sup>[21]</sup>

As this is a proof-of-principle study, the applied CO concentration (0.019-0.025 mbar) was lower than those encountered in industrial processes (>0.5 mbar).<sup>[22]</sup> As Cu(FMA)(Bpe)<sub>0.5</sub> coating operates on the principle of size exclusion CO concentration should not affect the operation conditions of the MOF-on-Pd composite significantly. However, reaction conditions need yet to be optimised to fully cover the Pd surface with the MOF.

We expect that the greatest limitation of the composite is the thermal stability of both the MOF (Cu(FMA)(Bpe)<sub>0.5</sub> is stable up to 270 °C) and the Pd-MOF bond. Although thermal stability of MOF-substrate bonds has not been studied in detail, there is evidence that the careful choice of synthetic method and/or SAM, may improve thermal stabilities.<sup>[23]</sup> Industrial processes benefiting from reliable and robust hydrogen-separation membranes include the Water-Gas Shift reaction, Steam Reforming, Proton-Exchange Membrane Fuel Cells (PEMFC) and hydrogen sensing. While the operating temperature for hydrogen sensing (near ambient temperature) and PEMFC (*ca.* 80 °C) is ideal for a MOF-on-Pd membrane to be considered, hydrogen separation from low-temperature gas shift<sup>[24]</sup> and hydrogen recovery from tail-gas stream (Claus reaction),<sup>[25]</sup> both in the 100-300 °C region, may also be achieved with the suggested composite. Finally, some MOFs display very good thermal stability, up to 500 °C,<sup>[26]</sup> which suggests that MOF-on-Pd hydrogen-separation membranes can be developed for Steam Reform from Combustion Engine, below 450 °C.<sup>[27]</sup>

## Conclusions

We have shown that robust hydrogen-selective composite membranes can be obtained by the deposition of a protective pre-sieve thin film of an adequate MOF on Pd membranes. Such composite membranes can have immediate applications in a number of industrial processes, such as hydrogen production from biomass or hydrocarbons, PEMFC and protective layer for optical fibre-sensors.

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## Notes and references

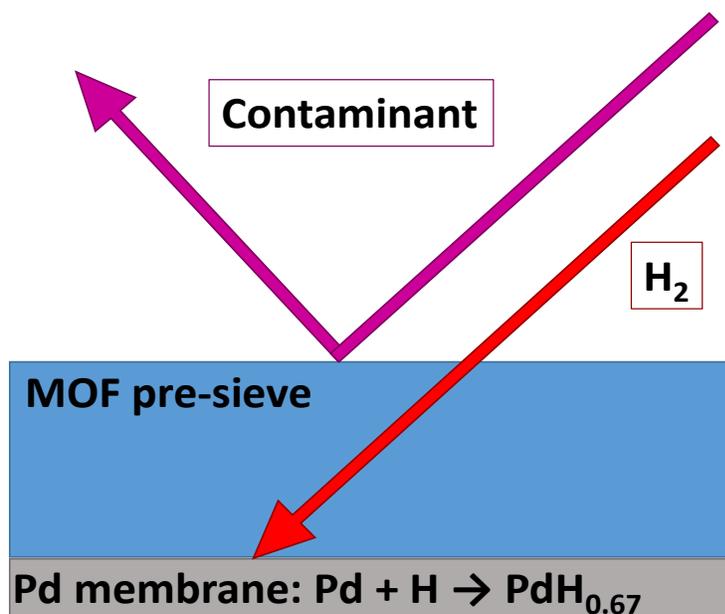
‡ Cu(FMA)(Bpe)<sub>0.5</sub> should also separate H<sub>2</sub> and H<sub>2</sub>S, another Pd poison. Its presence may cause further complications, cf. reactions with the MOF, as H<sub>2</sub>S is more reactive than CO. Current Health and Safety regulations did not permit to verify the composite membrane's H-H<sub>2</sub>S separation capacity.

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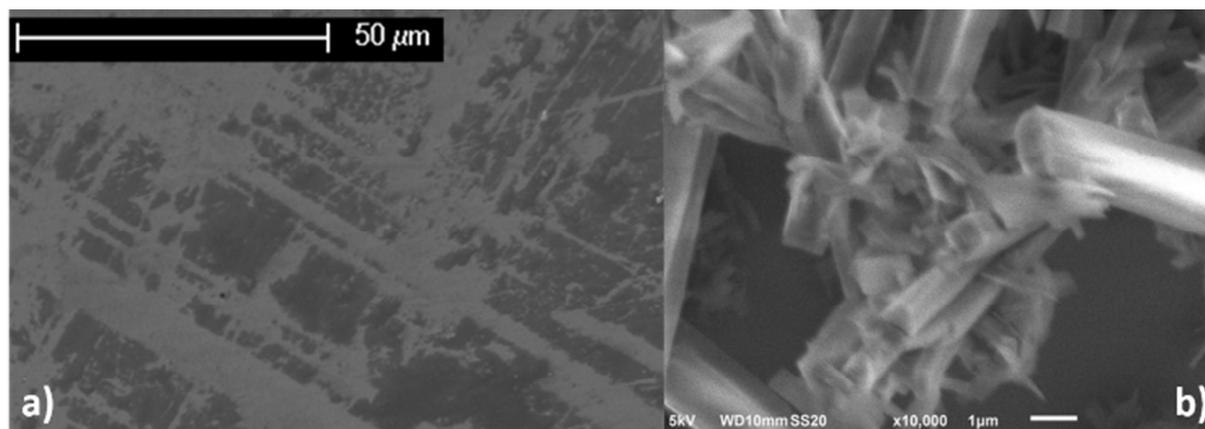
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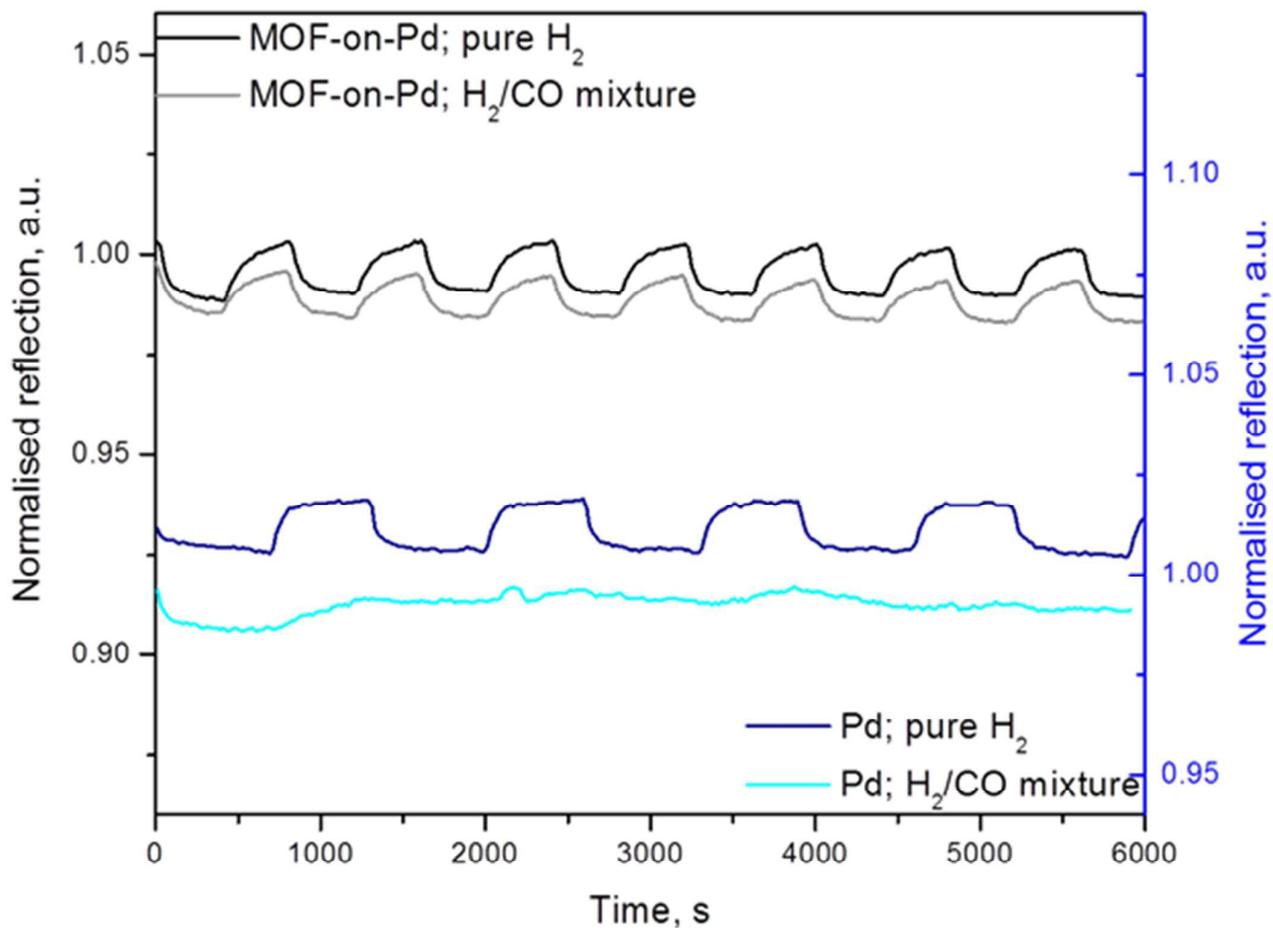
## Figures



**Table of Content** Working principle of a contaminant-resistant MOF-on-Pd composite membrane for hydrogen separation



**Figure 1** SEM micrographs of selected Cu(FMA)(Bpe)<sub>0.5</sub>-on-Pd composite films showing **a)** partial surface coverage and **b)** particle shapes



**Figure 2** Hydrogen-sorption spectra of a Pd membrane from pure H<sub>2</sub> (dark blue) and H<sub>2</sub>-CO mixture (turquoise); and of selected Cu(FMA)(Bpe)<sub>0.5</sub>-on-Pd composite from pure H<sub>2</sub> (black) and H<sub>2</sub>-CO mixture (grey) at H<sub>2</sub> 1% (10 mbar) and CO 0.0019-0.0025% (0.019-0.025 mbar).