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# One-step fabrication of mixed matrix metal–organic framework membranes for sustainable catalytic processes

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Mixed-matrix membranes with either pristine or defective UiO-66 metal–organic framework fillers were fabricated *via* a novel one-step process. On top of a simpler, more sustainable preparation, these membranes also exhibit remarkable catalytic activity for a sulfur oxidation reaction when compared to those produced by the traditional filler dispersion process.

Membrane technology has garnered significant attention across various fields due to its versatility and broad industrial applicability. Membranes are extensively studied for use in fuel cells, drug delivery systems, water purification, and, most notably, gas separation processes, particularly in the context of carbon capture and utilization.<sup>1–4</sup> Compared to conventional separation techniques, membrane-based processes offer high energy efficiency, operational simplicity, and modular design, making them attractive for developing more sustainable industrial solutions.<sup>5</sup> Mixed-matrix membranes (MMMs), which combine polymer matrices with inorganic fillers, have been developed to address some of the limitations of traditional polymer membranes, such as membrane fouling, limited selectivity, and the well-known trade-off between permeability and selectivity. By incorporating porous materials into the polymer structure, MMMs benefit from improved mass transport properties, mechanical stability, and selective molecular recognition. Beyond separation applications, the use of catalytically active inorganic fillers in MMMs opens up new opportunities in catalytic process engineering. The resulting membranes offer increased surface area for catalytic reactions, while the polymer matrix enables better handling, enhanced reusability, and improved control over reaction environments.<sup>6</sup> These structural

## Sustainability spotlight

The acceleration of global energy demand due to the increase of population will require an exponential consumption of fuels for transportation. Unfortunately, fossil fuels still need to be used to meet the main energy needs in the next decades, mainly for maritime and aviation transportation. Therefore, it is crucial to develop novel technologies able to remove the sulfur from fuels, using low-cost and highly sustainable processes. Oxidative desulfurization is one of the most effective technologies. This work proposes an innovative procedure to prepare advanced catalysts able to desulfurize fuels, avoiding losses and waste to prepare greener fuels for transportation. This goal falls within point 7 of the UN Sustainable Development Goals, Affordable and Clean Energy.

and functional advantages help mitigate issues such as catalyst deactivation and material loss during recovery, making MMMs highly attractive for heterogeneous catalytic systems.<sup>7</sup> Traditionally, MMMs are fabricated either by dispersing pre-formed inorganic fillers into a polymer casting solution<sup>8–14</sup> or by growing the fillers directly on a membrane support *via in situ* methods.<sup>15,16</sup> The two approaches can be labor-intensive and require multiple processing steps, often leading to non-uniform filler distribution or limited control over filler crystallinity. Herein, a novel one-step fabrication of MOF MMMs, which offers significant advantages in both efficiency and sustainability compared to the aforementioned traditional methods, is reported and discussed. While the traditional approaches involve either the time-consuming and resource-intensive steps of separately preparing MOFs and then dispersing them into the casting solution, or multiple cycles of membrane exposure to metal and linker solutions to ensure proper *in situ* growth, our method streamlines the process by achieving the synthesis of the MOF fillers during the solvent evaporation step of the membrane fabrication. We achieve this by preparing a single solution with the MOF's precursors and the membrane polymer and, after proper dissolution, casting this metal/linker/polymer solution on an adequate support which is then placed in a drying oven at a set temperature, ensuring the MOF forms during the evaporation of the solvent, producing the MMM.

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Fig. 1 (a) Stacked ATR-FTIR spectra and (b) stacked XRD patterns obtained for the one-step UiO-66@PVDF membranes prepared under different temperatures and support diameters in the presence and absence of a synthesis modulator.

This minimizes the use of reagents and solvents, leading to a reduction in hazardous waste and lower environmental impact. This one-step method also allows for some degree of *ab initio* control of the MOF filler's crystallinity, thus ensuring it can be used for the preparation of MMMs for different applications. The UiO (Universitetet i Oslo) MOF family, known for its exceptional thermal and chemical stability, consists of zirconium-based MOFs.<sup>17</sup> In particular, UiO-66 offers high porosity, robustness, versatility and significant surface areas, making it ideal for applications such as gas storage and separation,<sup>18</sup> drug delivery<sup>19</sup> and catalysis.<sup>20–22</sup> We prepared different UiO@polyvinylidene fluoride (PVDF) membranes using the traditional method of dispersing a pre-prepared UiO filler and our one-step method either with or without a synthesis modulator, at different solvent evaporation temperatures and support diameters (see the SI, document for details).

The IR spectra of the prepared UiO-66 samples (Fig. 1a) exhibit similar characteristic bands, particularly at lower frequencies, where the C–H vibration, C=C stretch, OH bend and OCO bend in the linker can be found between 810 and 710  $\text{cm}^{-1}$ . The band at 551  $\text{cm}^{-1}$  belongs to the Zr–(OC) asymmetric stretch, and the bands around 659 and 480  $\text{cm}^{-1}$  belong to the  $\mu_3$ -O stretch and the  $\mu_3$ -OH stretch.<sup>23</sup> All UiO-66@PVDF samples also display the expected infrared bands for PVDF, particularly those at 835, 1164 and 1399  $\text{cm}^{-1}$  ( $\beta$  phase) and at

877 and 1066  $\text{cm}^{-1}$  ( $\alpha$  phase).<sup>24</sup> The XRD pattern of as-prepared UiO-66 membrane samples (Fig. 1b) matches well with the reported patterns of microcrystalline UiO-66,<sup>25</sup> particularly evident in the diffraction peaks at  $2\theta = 7.4^\circ$  and  $8.5^\circ$ . The diffraction peak of varying intensity at  $2\theta = 17.3^\circ$  can be attributed to unreacted, recrystallized terephthalic acid linker.<sup>26</sup> The varying intensity of this peak, along with the different full-width at half-maximum of the characteristic UiO-66 peaks in the prepared samples, suggests different degrees of crystallinity can be achieved by adjusting the membrane preparation conditions. It appears evaporating the solvent at 90 °C yields more crystalline UiO-66, whereas 70 °C is insufficient for acceptable crystallinity. At 120 °C, the materials exhibit the lowest crystallinity, likely due to the rapid solvent evaporation, which hinders the formation of crystalline MOFs. A lower degree of crystallinity is also apparent for the wider substrates (9 cm  $\phi$ ) which we also attribute to the higher rate of solvent evaporation. Finally, using formic acid as a synthesis modulator appears to produce the most crystalline UiO-66, a result consistent with literature reports. Modulators alter crystal size and morphology while improving crystallinity, probably by controlling the rate and kinetics of nucleation and thus crystal growth through competitive coordination between the monocarboxylate and the bridging linker to the Zr clusters.<sup>27,28</sup> This result highlights the versatility of our one-step method for preparing MOF MMMs, as



the crystallinity of the fillers can be adjusted for different applications.

The SEM images provide critical insights into the structural characteristics of the membranes and their catalytic functionality (Fig. 2). When pre-prepared UiO-66 was dispersed in the PVDF matrix, the resulting membrane showed that the MOF was almost entirely encapsulated within the polymer matrix. This encapsulation likely impedes the access of catalytic substrates to the active sites of the MOF, as suggested by the smooth surface morphology observed in the SEM images. The inability to expose these catalytic sites on the membrane surface correlates with the expected lower catalytic activity of this membrane, as the substrates cannot efficiently reach the encapsulated MOF particles. In contrast, the novel one-step synthesis method, performed at 90 °C and using a 7 cm wide support, produces a membrane where UiO-66 particles with an average size of approximately 100 nm are clearly visible on the membrane's surface. The SEM images confirm that the surface accessibility of UiO-66 particles on the membrane interface directly enhances its catalytic performance by allowing substrates direct access to the catalytically active sites. Furthermore, when a synthesis modulator was introduced in the one-step method, the SEM images reveal the formation of larger UiO-66 crystals on the membrane surface, with an average particle size of around 470 nm. SEM cross-section images (Fig. S3) of the different membranes also showed a uniform morphology with MOF distribution through the membrane thickness. It is also well clear that the membrane prepared using modulator showed a higher granulometry through the membrane vertical section caused by the higher particles size of MOF crystals incorporated in to PVDF membrane. Performing the cross-section analysis was also possible to determine the thickness of the membranes prepared by the different methodologies. The one-step method using modulator to prepare UiO-66@PVDF membrane resulted in the highest membrane thickness with *ca.* 190  $\mu\text{m}$ . Smaller thickness were found using pre-prepared UiO-66 methodology (80  $\mu\text{m}$ ) and once-step method without modulator (110–130  $\mu\text{m}$ ). The highest thickness of one-step method using modulator correlated with the higher size of MOF crystals formed in this case. EDS was used to determine the atomic ratios in the prepared samples and, as expected, the membrane prepared

without a modulator exhibits the highest Cl/Zr ratio (0.10), while the one prepared with a modulator exhibits the lowest (0.04). Residual chlorine in UiO-66 samples can be correlated to their number of defect sites. These defects arise from missing terephthalate ligands, creating charge and coordination deficiencies. Chloride anions can compensate these deficiencies by bonding to exposed zirconium sites.<sup>29</sup> This is, once again, consistent with literature reports on modulated MOF synthesis.

UiO-66 has predominantly been employed in the catalytic field as a solid support for catalytically active species, including metallic nanoparticles<sup>30–32</sup> and polyoxometalates,<sup>33–35</sup> due to its robust framework and high surface area. However, our research group has previously demonstrated that non-functionalized UiO-66 can exhibit intrinsic catalytic activity when optimal concentration and distribution of coordination-defective sites are present.<sup>20,36,37</sup> These previously mentioned defect sites, typically resulting from missing linker defects, produce under-coordinated Zr atoms that serve as Lewis acid sites, enhancing the MOF's ability to activate hydrogen peroxide.<sup>38</sup> This activation is crucial for the oxidative desulfurization (ODS) process, where the generated reactive oxygen species oxidize sulfur compounds, thereby demonstrating that UiO-66's catalytic performance can be harnessed without additional functionalization. The UiO-66@PVDF membranes were tested as catalysts in the ODS of a model diesel containing 2000 ppm of sulfur from four different sources (benzothiophene, dibenzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene) (Fig. 3). These reactions were performed at 70 °C and at room pressure in a two-phase system, using 3  $\mu\text{mol}$  of UiO-66 (determined from ICP-OES analysis) from each catalyst, with the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF<sub>6</sub>) as an extraction solvent and 30% w/w hydrogen peroxide as the oxidant. The oxidant is added to the reaction medium after 10 minutes of stirring, during which a percentage of the sulfur compounds present in the model fuel are extracted into the [BMIM]PF<sub>6</sub> ionic liquid. The oxidation of these extracted compounds produces insoluble sulfoxides and sulfones, thus allowing the extraction of further sulfur compounds into the ionic liquid and their subsequent oxidation. Membrane samples were cut into sections of known area and mass and directly placed into the reaction vessel in contact with the two-phase system. No specialized support or holder was used; the membrane remained fully immersed throughout the reaction to ensure efficient contact with the substrates. The powdered UiO-66 exhibited desulfurization performance comparable to that previously reported by our research group, achieving near complete desulfurization ( $\geq 93\%$ ) of the model fuel,<sup>36</sup> however, when this active catalyst was dispersed in a PVDF matrix, the resulting membrane showed no significant catalytic activity for ODS (54% sulfur removal after 2 hours). We attribute this lack of activity to the inaccessibility of the active catalytic sites in UiO-66 after immobilization within the PVDF matrix. Notably, the membrane prepared using our novel one-step method, at 90 °C and over a 7 cm wide substrate, achieved 96% total desulfurization, performing similarly to powdered UiO-66. We ascribe this to a high density of coordination-defective active

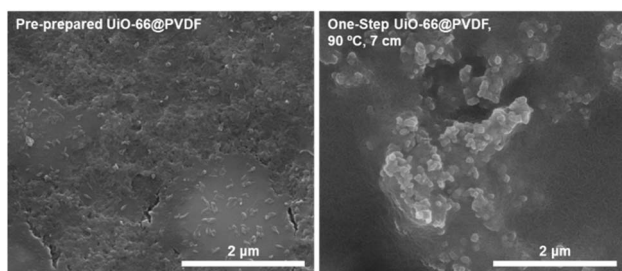


Fig. 2 SEM images obtained for the UiO@PVDF membranes prepared by dispersing pre-synthesized UiO-66 in a PVDF solution (left) and using the one-step method (right). Note how the one-step method ensures MOF particles are present in the membrane's surface.



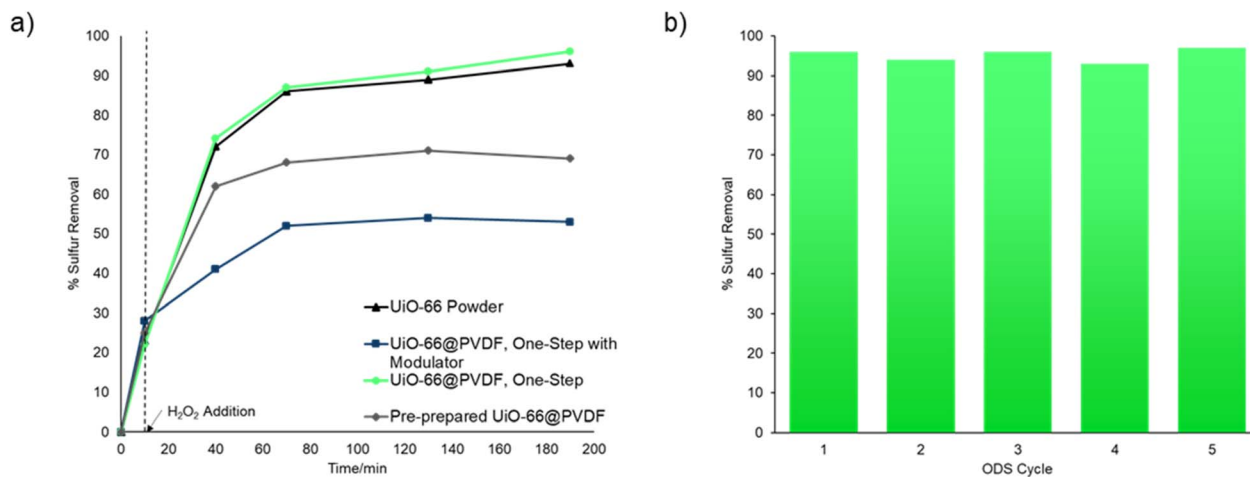


Fig. 3 (a) Desulfurization profiles for the multicomponent, 2000 ppm S model diesel using the powdered 3  $\mu\text{mol}$  of UiO-66 MOF, the same pre-prepared MOF dispersed in PVDF and the UiO-66@PVDF membranes obtained from the one-step method with and without a synthesis modulator as catalysts. (b) Desulfurization performance of the UiO-66@PVDF membrane prepared using the one-step method without a synthesis modulator, demonstrating its reusability over 5 consecutive ODS cycles.

catalytic sites and their enhanced accessibility to the substrates, as proven by the SEM images. The membrane prepared using a modulator in the one-step method, which resulted in a more crystalline form of UiO-66, exhibited some catalytic activity, achieving 69% sulfur removal, but performed worse than its non-modulator counterpart. This outcome is also consistent with the results our research group reported for powdered UiO-66.<sup>36</sup> The catalytic stability of the UiO-66@PVDF membrane was evaluated by simple recycling tests: at the end of each cycle, the catalyst was recovered, washed thoroughly by ultrasonication in ethanol, dried and reused in a new cycle under the same experimental conditions. Remarkably, this novel catalyst retained its catalytic activity over 5 consecutive ODS cycles with very similar kinetic profiles for each reaction, which suggests no structural degradation occurs. The heterogeneity of the one-step UiO-66@PVDF membrane was further examined using a leaching test, where the membrane was removed from the reaction medium 15 minutes after the start of the oxidation step. The reaction was then allowed to proceed with only the remaining filtrate. As shown in the leaching test results, the desulfurization of the model diesel ceased nearly immediately following the catalyst's removal. Furthermore, the X-ray diffraction pattern obtained for the membrane after the 5 consecutive reaction cycles still displays the main diffraction peaks of UiO-66 in the same positions and with similar relative intensities (Fig. S6), indicating the preservation of the MOF structure as a consequence of the remarkable robustness of UiO-66 in PVDF, even when prepared using the novel one-step method.

In summary, our study demonstrates the successful development of a novel one-step method for fabricating MOF@PVDF MMMs with superior catalytic activity, particularly in oxidation processes. The SEM analysis confirmed that this method effectively positions UiO-66 particles on the membrane surface, making catalytically active sites readily accessible, which significantly enhances the membrane's performance. In contrast, membranes prepared by traditional methods failed to exhibit

comparable catalytic activity due to the encapsulation of UiO-66 within the polymer matrix. X-ray diffraction (XRD) analysis further corroborated these findings, revealing that the UiO-66 crystals formed *via* the one-step method exhibit appropriate crystallinity, which is crucial for maintaining high catalytic activity. Overall, the one-step UiO-66@PVDF membranes not only achieve high catalytic activity but also maintain structural integrity and reusability, as shown by consistent XRD patterns after multiple reaction cycles, making them a promising candidate for sustainable industrial applications. Additionally, the introduction of a synthesis modulator in the one-step process resulted in larger, more crystalline UiO-66 particles, consistent with literature reports. While these membranes exhibit reduced catalytic efficiency compared to their non-modulated counterparts, this result demonstrates that, using our novel method, MOF@PVDF MMMs for different applications can be prepared, as the degree of filler crystallinity can be somewhat tuned *ab initio* by adjusting the membrane fabrication conditions.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

All data have been provided in the main article and the supplementary information (SI). Supplementary information: experimental details, additional characterization of membranes, extra ODS studies and catalyst stability investigation. See DOI: <https://doi.org/10.1039/d5su00231a>.

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