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# MOF-74 and UTSA-16 film growth on monolithic structures and their $CO_2$ adsorption performance

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## HIGHLIGHTS

- Coating MOF-74 and UTSA-16 on cordierite monolith.
- $CO_2$ adsorption performance of MOF-coated monoliths.
- Good $CO_2$ capture capacity and fast kinetics for MOF-coated monoliths.

## ARTICLE INFO

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## ABSTRACT

Monolithic structures offer a cost-effective and practical platform for scaling up gas separation processes in comparison to traditional packing systems. In this study, the immobilization of several metal-organic frameworks (MOFs) namely, MOF-74(Ni) and UTSA-16(Co) on commercial cordierite monolith (600 cpsi) was investigated and their corresponding adsorptive performance in $CO_2$ capture was assessed systematically. To gain control over crystal nucleation and growth, various bottom-up growth techniques were employed and optimized with respect to loading, thickness, and adsorption characteristics of the MOFs films. Our results indicated that the choice of suitable coating procedure depends primarily on the type of the MOF material used. It was shown that layer-by-layer technique followed by a secondary growth is a suitable method for MOF-74(Ni) film growth on the monolith walls which gives rise to ~52 wt% MOF loading, whereas for UTSA-16(Co), *in-situ* dip coating was found to be a promising coating method which results in ~55 wt% MOF weight gain. Moreover, the MOF-coated monoliths displayed relatively moderate $CO_2$ adsorption capacity with fast kinetics.

## 1. Introduction

Carbon capture, utilization, and sequestration (CCUS) technologies are considered as potentially viable solutions to combat anthropogenic $CO_2$ emissions and thus climate change in the 3rd millennia [1,2]. To capture $CO_2$ from gas streams before emitting into the atmosphere, several strategies such as membrane, adsorption, and chemical looping processes have been proposed aiming at addressing the challenges associated with the current benchmark technology (*i.e.*, amine scrubbing), however, these technologies are yet to become cost-effective and suitable for large-scale implementation [3,4]. In particular, $CO_2$ capture by adsorption which has been demonstrated to offer a more efficient solution than the other methods, suffers primarily from the lack of an efficient and scalable process configuration [5]. Applying adsorbent materials into scalable contactors such as monolithic structures and composites introduces a cost-effective platform for practical applications in comparison to traditional packing systems [6,7]. To date, several zeolites monoliths such as 13X, and 5A have been fabricated by either coating a thin layer on an inactive support or by extruding into monoliths with binders or additives [8–12]. Moreover, activated carbon monoliths have been widely investigated as a structured adsorbent for various gas separation applications [13–17].

Metal-organic frameworks (MOFs) with exceptional textural properties and framework structures have been extensively studied for gas adsorption and storage applications in particular, $CO_2$ capture [18–24]. Despite significant promises, the scalability of MOFs adsorbents for practical applications has not been fully addressed. There are only a few studies that have focused on fabrication of MOFs monoliths and their utilization in adsorption processes [25–27]. For instance, the immobilization of $Cu_3(BTC)_2$ on

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cordierite monolith was demonstrated by Kusgens et al. [25] through an *in-situ* synthesis of $Cu_3(BTC)_2$. However, the uniform deposition of the MOF on the cordierite support was not successful by this method and the crystals were deposited only on the cutting edge of the honeycomb. Therefore, the authors fabricated extruded $Cu_3(BTC)_2$ monoliths by a two-step procedure and showed that the extruded monoliths have relatively high specific surface area (ca. 370 $m^2/g$) with high mechanical stability. In another study, Ramos-Fernandez et al. [26] immobilized MIL-101(Cr) on a 400 cpsi cordierite monolith using a secondary seeded growth. The authors reported a uniform deposition of ~9 wt% MOF on the monolith channels and used the coated substrate for selective oxidation of tetralin in the liquid phase. Most recently, Hong et al. [27] manufactured MIL-101(Cr) monoliths by paste extrusion technique and demonstrated that the resulting MIL-101(Cr) monoliths have comparable $CO_2$ adsorption capacity to the pristine MIL-101 (Cr) powder.

In coating crystalline MOF film on a ceramic support, the ability to fully control MOF crystallisation is achieved by improved control over the location of crystal formation, crystal orientation, particle size distribution, and optimization of growth conditions in two dimensions (2D), while substrate itself can be modified in order to increase the compatibility and functionality through the processes like chemical etching or self assembly of monolayers (SAM) [28–30]. Polycrystalline MOF films can be grown through a variety of procedures including liquid-phase epitaxy (LPE), direct synthesis, *in-situ* crystallization, seeded growth, and electrochemical growth [28,29,31]. LPE consists of layer-by-layer adsorption of chemical components from liquid phase onto the surface in which the substrate is frequently placed in organic linker and metal connector solutions [32]. The obtained films originated from stepwise building block deposition process are highly crystalline and oriented based on underlying functionalized surface. In light of these previous studies, MOFs can be immobilized on monolithic substrates by using monolayer deposition and bottom-up growth techniques which offer precise control over crystal nucleation and growth.

In this study, two well-known $CO_2$ sorbent MOFs, namely MOF-74(Ni) and UTSA-16(Co) were immobilized on the walls of commercial cordierite monolith (600 cpsi) and their equilibrium and dynamic $CO_2$ adsorption behavior were assessed by adsorption isotherm measurements and breakthrough tests. To gain control over crystal nucleation and growth, various bottom-up growth techniques were employed and optimized with respect to loading, thickness, and adsorption characteristics of the MOFs films. Accordingly, reliable coating approaches for each MOF were introduced.

## 2. Experimental section

### 2.1. MOFs powders synthesis and support pretreatment

MOF-74(Ni) and UTSA-16(Co) were synthesized according to well-established methods in the literature [33–36] with some modifications in post-synthesis and activation steps. Detailed information about MOFs powder synthesis is provided in Supporting Information.

Cordierite monolith with a cell density of 600 cpsi (Corning Inc.) was used as the bare support for the MOFs materials. Pretreatment of the substrate was performed in aqueous solutions containing dentate groups (–OH, –COOH, $-NH_2$) to decorate the substrate surface with functional groups. First the substrate was repeatedly rinsed and washed with toluene and acetone to remove any contaminants. It was then soaked in NaOH 0.1 M, $NH_4OH$ 0.25 M, or $HNO_3$ 1 M aqueous solutions or ethanol solutions of the –COOH functionalized terphenylmethanethiol CTPMT for 5 h. The treated substrate was then washed by DI water and kept in the oven overnight at 110 °C.

### 2.2. MOFs growth on cordierite monolith

The coating methods employed in this study were based on LPE techniques in which layer-by-layer (LBL) assembly plays a major role in forming secondary building unites followed by a secondary growth step (LBL + secondary growth) [37]. Moreover, *in-situ* dip coating (ISDC) was also employed to grow the MOF building unites. The schematic of these coating procedures is presented in Fig. 1. The LBL assembly and secondary growth methods were carried out by first dissolving 10 mL $Ni(AC)_2{\cdot}4H_2O$ in THF (metal solution) and 10 mL DHTA in water (ligand solution). A piece of treated support was then placed in ligand solution for 40 min and then the support was washed with ethanol and placed in metal solution for 20 min, as schematically illustrated in Fig. 1. This process was repeated 4 times to achieve high seed loading on the monolith walls. Subsequently, the substrate was immersed in original metal and linker reaction solution (twice the original concentration) to further induce the secondary growth on top of epitaxial layers formed on the surface. Post synthetic modification of MOF-74 (Ni)-coated substrates was carried out in a similar manner as for MOF-74(Ni) powder (see Supporting Information). It should be noted here that the coating conditions such as number of steps, soaking duration, and ligand and metal solution concentrations were systematically varied to find the optimum coating conditions (those stated above) based on the characteristics of the obtained materials (*i.e.*, weight gain, film thickness and uniformity).

In the ISDC method, the pretreated cordierite monoliths were simply dipped into the reaction solution consisting of organic linker (DHTA in the case of MOF-74(Ni), or citric acid in the case of UTSA-16(Co)) and metal ($Ni(AC)_2{\cdot}4H_2O$ in the case of MOF-74 (Ni), or $Co(OAc)_2{\cdot}4H_2O$ in the case of UTSA-16(Co)) prior to solvothermal reaction in acid digestion vessel. The metal and linker molecules were self-assembled on the anchored surface of substrate followed by bottom-up growth (see Fig. 1).

UTSA-16(Co) thin layer deposition on the cordierite support was performed only by the ISDC technique, mainly because this technique was successful in yielding high MOF loading (as will be shown later), whereas for MOF-74(Ni), both ISDC and LBL+ secondary growth techniques were employed to deposit a thick film of MOF on the support. It is also worth noting here that the conventional coating techniques [38] commonly used for zeolitic materials such as wash coating, dip coating, and spin coating were initially utilized for MOFs film growth, however, they were proved to be unsuccessful in yielding a high mass loading on the cordierite support.

### 2.3. Characterization of materials

$N_2$ physisorption measurements were performed by using a Micromeritics 3Flex gas analyzer to determine the textural properties of the coated and the powder samples. Prior to analysis, the adsorbents were degassed at 250 and 90 °C (corresponding degassing temperatures for MOF-74(Ni) and UTSA-16(Co), respectively) under vacuum for 5 h. The surface areas were estimated by the BET method whereas pore volumes were estimated using the total $N_2$ adsorbed at $P/P_0 = 0.99$. The pore sizes were also estimated using Horvath–Kawazoe method. Powder X-ray diffraction (PXRD) analysis was performed to determine the degree of crystallinity of both bare and coated substrates as well as the corresponding MOFs powders using a diffractometer with $CuK_\alpha$ ($\lambda = 1.5406$ Å) radiation and 30 kV/15 mA current. Moreover, the surface morphology of all materials was evaluated by high resolution scanning electron