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Fabrication of a freestanding metal organic framework predominant hollow fiber mat and its potential applications in gas separation and catalysis†

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Recently, metal–organic framework (MOF)-based polymeric substrates show promising performance in many engineering and technology fields. However, a commonly known drawback of MOF/polymer composites is MOF crystal encapsulation and reduced surface area. This work reports a facile and gentle strategy to produce self-supported MOF predominant hollow fiber mats. A wide range of hollow MOFs including MIL-53(Al)–NH₂, Al-PMOF, and ZIF-8 are successfully fabricated by our synthetic method. The synthetic strategy combines atomic layer deposition (ALD) of metal oxides onto polymer fibers and subsequent selective removal of polymer components followed by conversion of remaining hollow metal oxides into freestanding MOF predominant hollow fiber structures. The hollow MOFs show boosted surface area, superb porosity, and excellent pore accessibility, and exhibit a significantly improved performance in CO₂ adsorption (3.30 mmol g⁻¹), CO₂/N₂ separation selectivity (24.9 and 21.2 for 15/85 and 50/50 CO₂/N₂ mixtures), and catalytic removal of HCHO (complete oxidation of 150 ppm within 60 min).

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Introduction

Metal–organic-frameworks (MOFs) are highly crystalline and porous materials consisting of metal ions or clusters which are coordinated with organic linkers.^{1,2} Impressive progress has been made using MOFs in gas storage and separation,^{3,4} volatile organic compound (VOC) adsorption,^{5–7} heterogeneous catalysis,^{8–15} and environmental decontamination.¹⁶ These advances result from the unique advantages of MOFs, such as controllable pore size, high surface areas and porosity, well-dispersed active centers, and tailorable functionalities.

Because MOF powders are difficult to handle and utilize,¹⁷ significant research effort is focused on integrating MOFs into robust MOF-fibers,^{18,19} and membranes.^{20,21} A polymer fiber or membrane provides mechanical support and can substantially

reduce MOF aggregation, leading to improvement in functional performance on a per-gram of MOF basis. MOF/fiber composites have shown marked advantages in catalysis,²² pollution control,²³ gas separation,²⁴ and sensing²⁵ applications. Moreover, MOF/fiber composites enable more than one type of MOF to be coupled together to simultaneously perform multiple functions.¹⁹

Despite the reported advances in MOF polymer composites, there are several common challenges to create high performance structures. For example, during formation, the polymer from the fiber can infuse or otherwise unfavorably interact with the MOF to block pore access.²⁶ Also, for biomedical applications, biocompatible polymers (*e.g.*, polyvinylpyrrolidone, polyvinylalcohol, poly(lactic-co-glycolic acid), and gelatin)²⁷ must be used to construct the MOF polymer composites, thereby limiting the substrate selection.

While several groups have demonstrated MOF/fiber composites, very few reports describe approaches to produce free-standing MOF fiber mats or provide quantified functional performance of the products. Li and coauthors reported a strategy applying soft ceramic oxide fibers as MOF conversion templates, and suggested that resulting MOF fibers would retain the original fiber flexibility and softness.^{26,28} Dwyer *et al.* demonstrated a unique synthetic approach to create hollow TiO₂ cylinders with dense MOF crystals on the inner and outer surfaces.²⁹ These methods possess some drawbacks such as low

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surface area, and time- and energy-consuming material processing.

Here, we report a facile and unique approach to synthesize freestanding MOF enriched hollow structures *via* oxide-to-MOF conversion, also known as coordination replication.^{30,31} The metal oxides used here, Al₂O₃ and ZnO, are formed conformally on starting polymer fibers using low-temperature atomic layer deposition (ALD).^{18,19,22,32} These oxides allow successful synthesis of MIL-53(Al)-NH₂, Al-PMOF, and ZIF-8 MOFs. In this work, cellulose diacetate (CDA), a cost-effective polymer that readily dissolves in acetone or DMF, was selected as the sacrificial polymer for freestanding MOF fabrication. First, a stable metal oxide layer is formed on the fiber surface by ALD, and then the polymer is selectively dissolved in acetone solution leaving only the metal oxide hollow structure. The oxide tube is then converted to a hollow MOF by reacting with organic linkers. The process yields hollow fibers with a small (~500 nm) diameter suitable for filtration structure, but size and mechanical handling inhibit testing as hollow fiber separator systems. This work further describes the versatility and performance of the freestanding MIL-53(Al)-NH₂ predominant hollow fiber mats as filters for CO₂ adsorption, CO₂/N₂ separation, and VOC removal. This work is the first to report synthesis of a freestanding MOF fiber with the feature of a hollow structure, and it directly demonstrates a novel and unique approach to MOF crystal size and pore configuration control which is a common challenge in MOF powder growth. In addition, this study highlights the importance of MOFs in gas separation and VOC heterogeneous catalysis, and may contribute to the design of high-performance adsorbents.

Experimental

Materials

Electrospinning polymer: cellulose diacetate (CDA, Eastman Chemicals); **ALD precursors:** diethyl zinc (DEZ, 95% STREM Chemicals Inc.) and trimethyl aluminum (TMA, 98% STREM Chemicals Inc.); **metal sources:** aluminum chloride hexahydrate (AlCl₃·6H₂O, Alfa Aesar) and copper nitrate trihydrate (Cu(NO₃)₂·3H₂O, 99–104%, Sigma-Aldrich); **linkers:** 2-aminoterephthalic acid (99%, Acros Organics), 2-methylimidazole (99%, Sigma-Aldrich), and *meso*-tetra(4-carboxyphenyl) porphine (H₂TCPP, >97% Frontier Scientific); **organic solvents:** acetone (Fisher), *N,N*-dimethylformamide (DMF, Fisher), *N,N*-dimethylacetamide (DMAc, 99.8%, Sigma-Aldrich), and anhydrous ethanol (200 proof, VWR) were purchased from commercial sources and used without further treatment. Melt-blown polypropylene (PP) fiber mats with a density of 40 gsm were used as received from the Nonwovens Cooperative Research Center (NCRC), North Carolina State University.

Synthesis of MIL-53(Al)-NH₂ predominant hollow fiber mats

To synthesize MIL-53(Al)-NH₂ predominant hollow fiber mats, the Al₂O₃ ALD coated CDA nanofiber mats (denoted as Al₂O₃@CDA) were first immersed in acetone and heated up to 120 °C for 24 h in a sealed Teflon-lined stainless-steel autoclave

reactor to dissolve and remove the CDA polymers. After the heat treatment in acetone, the majority of CDA polymers (~90%) were removed from the Al₂O₃@CDA nanofiber mats, which can be calculated by the mass change before and after acetone treatment, leaving the Al₂O₃ hollow fiber mats with tiny polymer residuals. For the conversion of MIL-53(Al)-NH₂ using Al₂O₃ hollow fiber mats as the metal source, 0.106 g 2-aminoterephthalic acid was firstly added to a 20 mL DMF/water mixture (3/1, v/v), and then the mixture was sonicated and stirred for 20 min until complete dissolution. Subsequently, a piece of Al₂O₃ hollow fiber mat (0.030 g) was gently soaked in the prepared solution and transferred into a 100 mL Teflon-lined stainless-steel autoclave reactor. This reactor was then heated at 120 °C for 20 h to finish the solvothermal synthesis. After reaction completed, the as-received MIL-53(Al)-NH₂ hollow fiber mat was washed twice with hot DMF, followed by another 2 times of anhydrous ethanol washing. The MIL-53(Al)-NH₂ hollow fiber mat was finally dried under vacuum at 200 °C for 10 h and stored in a desiccator before test. As a control group, the Al₂O₃@CDA nanofiber mat was also converted into MIL-53(Al)-NH₂ directly using the same recipe mentioned above without the pretreatment in acetone solution. The as-prepared sample was denoted as MIL-53(Al)-NH₂ (CDA).

Characterization

Scanning electron microscopy (SEM) was conducted using a FEI Verios 460 L field emission SEM. X-ray diffraction (XRD) data were collected using a Rigaku SmartLab X-ray diffraction tool (Cu K α X-ray source) for crystalline structure characterization. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Analytical Axis Ultra system equipped with an aluminum source (Al K α = 1486.6 eV radiation). The voltage and current of the X-ray gun were 15 kV and 20 mA. All the binding energies were calibrated using the signal from adventitious carbon (C 1s = 284.6 eV). *In situ* diffuse reflectance infrared Fourier transform spectrometry (DRIFTS) was performed on a Fourier transform infrared (FTIR) spectrometer (Model Nicolet 6700, Thermo Fisher, USA). The spectra were recorded with a resolution of 4 cm⁻¹ and an accumulation of 64 scans. During the HCHO oxidation process, ~80 ppm of HCHO was injected into the DRIFTS cell carried by a synergetic gas (80% N₂, 20% O₂) at a flow rate of 30 mL min⁻¹ at room temperature.

Low-pressure gas adsorption measurements

Gas adsorption isotherms in the pressure range of 0–1.1 bar were measured by a volumetric method using a Micromeritics 3Flex Surface Characterization Analyzer. Before analysis, all samples were fully degassed under vacuum at 120 °C for 20 h by using the Smart Vacprep (Micromeritics), a gas adsorption sample preparation device. After the degassing process was completed, the sample tubes were weighed and then carefully transferred to the analysis port of the gas adsorption instrument. N₂ adsorption–desorption isotherms at 77 K were measured in liquid nitrogen. N₂ and CO₂ adsorption–desorption isotherms at 273 K were measured using an ice water bath and isotherms at 298 K were measured using water baths. All

temperatures were monitored before and after the measurement and no temperature change was detected in all cases.

Thermogravimetric analysis and CO₂ cycling measurement

CO₂ cycling experiments were carried out on a TA instruments SDT 650. 15% CO₂/N₂ (Acro) and N₂ (99.999%) were used in this experiment. In a typical test, ~10 mg of the target sample was loaded into an alumina pan, with a flow rate of 100 mL min⁻¹ for both gases. The sample was first heated at 100 °C for 40 min under a N₂ atmosphere to complete degassing, and after the temperature was cooled to 25 °C, the MOF sample was swept continuously with CO₂ for 20 min, and then flowing N₂ was maintained for 40 min at 100 °C to activate the MOF sample in every cycle. All ramp rates were set as 10 °C min⁻¹.

Adsorption and catalytic activity test

The HCHO adsorption and catalytic activities were evaluated in the static state using reported procedures.³³ Specifically, a polytetrafluoroethylene layer stainless steel reactor (0.5 L) was used, at the bottom of which was placed a quartz Petri dish which held the material under test. After putting the dish into the reactor, 300 ppm of HCHO, generated using an S-4000 Gas Mixing system (EnviroNics, USA), was injected into the reactor. After the concentration of HCHO was stabilized to 150 ppm, the cover of the dish was removed to start the adsorption and catalytic reaction of HCHO. HCHO, CO₂, CO and water vapor were recorded online by a photoacoustic IR multigas monitor (INNOVA AirTech Instruments Model 1412i) during the test at 25 °C. The yield of CO₂ (Δ CO₂) and the concentration variation of HCHO were calculated to analyze the HCHO removal ratio.

Results and discussion

Synthesis and characterization of MIL-53(Al)-NH₂ hollow fiber mats

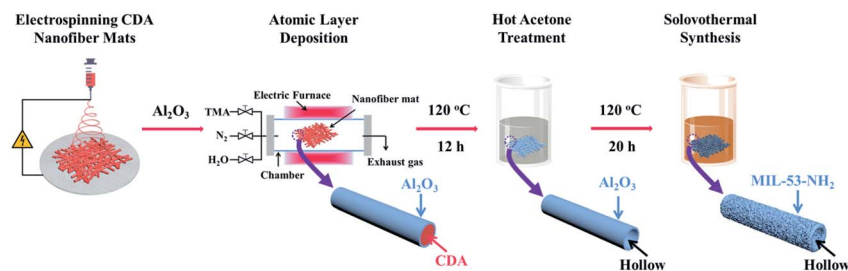
The procedure developed here for synthesizing freestanding hollow MOFs is shown in Scheme 1. Using MIL-53(Al)-NH₂ as an example, the first step was the electrospinning of a CDA nanofiber mat with a fiber diameter in the range of 300–500 nm. The as-prepared CDA nanofiber mat was transferred to a lab-made ALD reactor and coated with a conformal metal oxide layer to construct a core–sheath structure. This Al₂O₃ ALD layer

functions as a metal source for MOF structure synthesis by reacting with organic linkers. For most experiments, before MOF synthesis, the Al₂O₃@CDA mat was immersed in acetone at 120 °C for 12 h to dissolve the CDA, yielding an Al₂O₃ hollow fiber mat (Fig. S1 and S2†). Then, the hollow Al₂O₃ structure was transferred into the solution containing the 2-amino-terephthalic acid linker dissolved in the water/DMF mixed solvent and heated to 120 °C for 20 h. Using this solvothermal synthesis method, the Al₂O₃ hollow structure transformed into MIL-53(Al)-NH₂ and the initial hollow structure remained intact (Fig. 1A and B).

Scanning electron microscopic (SEM) imaging and X-ray diffraction (XRD) confirmed successful formation of MIL-53(Al)-NH₂ hollow fiber mats. As shown in Fig. 1B, a rod-like morphology was observed for hollow MIL-53(Al)-NH₂. The MOF crystals with the average size of around 200 nm length and 5 nm diameter were conformally formed along the surface of the fiber cylinders. In Fig. 1C, the observed characteristic peaks resemble those expected for the MOF with large pore (lp) configuration although the narrow pore (np) structure has been obtained previously for the MIL-53(Al)-NH₂ powder.^{34,35}

To obtain the highest quality of hollow MOF fiber mats, systematic experiments were conducted by tuning the thickness of the Al₂O₃ ALD layer. Using 100, 200, and 300 cycles of ALD treatment, that thickness ranges from 12 nm to 40 nm (Table S1 and Fig. S3†), denoted as MIL-53(Al)-NH₂ (100), MIL-53(Al)-NH₂ (200), and MIL-53(Al)-NH₂ (300), respectively. By analyzing the results from SEM, XRD, N₂ isotherms, and XPS we found around the 200 cycle sample with a thickness of 28 nm was optimal to transform into a high quality MOF. As shown in Fig. 1D–F, MIL-53(Al)-NH₂ (100), MIL-53(Al)-NH₂ (200), and MIL-53(Al)-NH₂ (300) exhibit similar morphologies. Moreover, thicker ALD layers tend to produce MOFs with a larger crystal size. XRD patterns of the samples prove that there is a slight loss in crystallinity with the increase of the ALD layer thickness (Fig. 1G). In addition, XRD patterns corresponding to the lp configuration were observed in all MOFs.

A high surface area was calculated from N₂ adsorption isotherms at 77 K for the hollow MOF-fibers and the relation between the MOF surface area and the starting thickness of ALD Al₂O₃ was elucidated. For all hollow MIL-53(Al)-NH₂ fibers, the N₂ adsorption–desorption isotherms at 77 K exhibit slight hysteresis (at higher pressure, $P/P_0 > 0.4$) (Fig. 1H) reflecting



Scheme 1 Schematic illustration of the fabrication of the hollow MIL-53(Al)-NH₂ fiber mat. The Al₂O₃ hollow fiber mat (obtained from dissolving Al₂O₃@CDA into acetone) was employed as the metal source, and was then transferred into the water/DMF mixed solution containing the 2-amino-terephthalic acid linker, which was heated to 120 °C for 20 h.

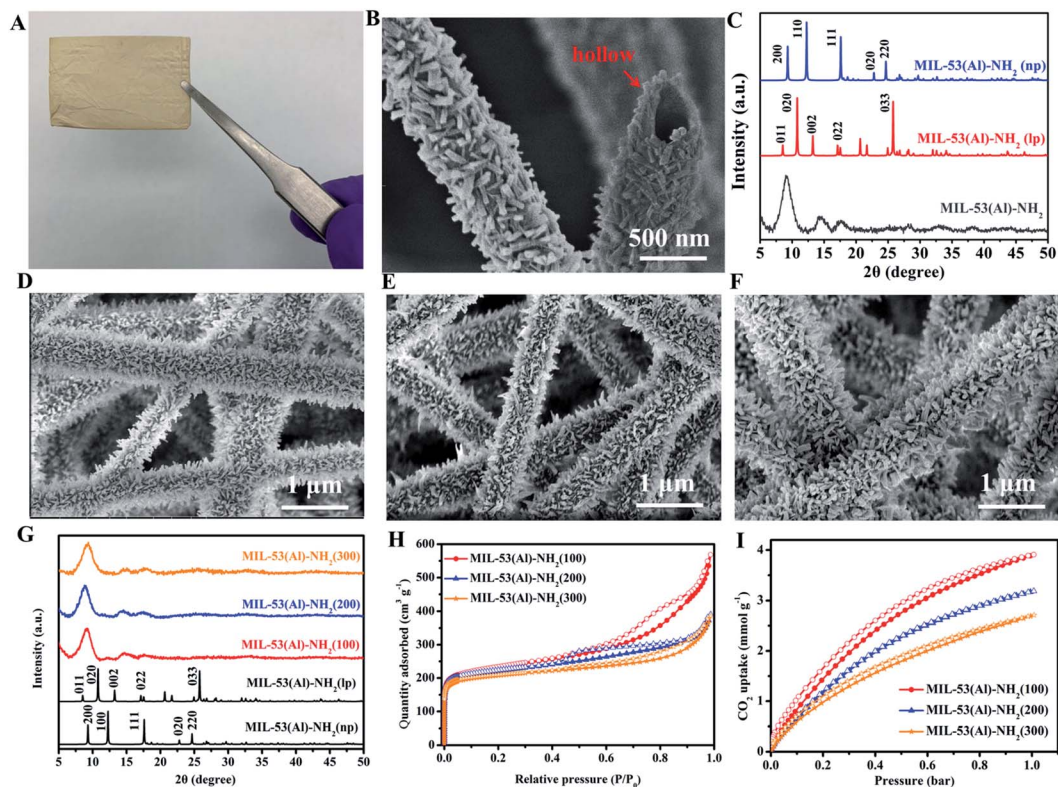


Fig. 1 (A) Optical photograph of the freestanding hollow MIL-53(Al)-NH₂. (B) Cross-sectional SEM image of the hollow MIL-53(Al)-NH₂ fiber mat. (C) XRD pattern of the MIL-53(Al)-NH₂ fiber mat with the simulated patterns for the lp and np configurations of MIL-53(Al)-NH₂.³⁶ SEM images of the (D) MIL-53(Al)-NH₂ (100), (E) MIL-53(Al)-NH₂ (200) and (F) MIL-53(Al)-NH₂ (300). Rod-like crystals are observed in all cases, and as the ALD layers get thicker, the obtained MOF crystal sizes increase. (G) XRD pattern of the hollow MIL-53(Al)-NH₂ fiber mat fabricated with different ALD thicknesses. All XRD patterns reveal an lp configuration. (H) N₂ isotherms at 77 K. (I) CO₂ isotherms at 273 K.

a hierarchical pore structure, involving micro, meso- and macro-porosity. The MIL-53(Al)-NH₂ crystals contribute to the microporous structure, whereas the spaces between these crystals, hollowness of the fibers, and fibrous mats give rise to meso- and macro-porosity.²² These meso-macro-porosities with complex pore geometry are consistent with the observed hysteresis in the isotherms, and may lead to capillary condensation at high relative pressure.^{37,38} As shown in Fig. 1H, the Brunauer-Emmett-Teller (BET) surface area of MIL-53(Al)-NH₂ (100), MIL-53(Al)-NH₂ (200), and MIL-53(Al)-NH₂ (300) is $880 \pm 30 \text{ m}^2 \text{ g}^{-1}$, $842 \pm 28 \text{ m}^2 \text{ g}^{-1}$, and $720 \pm 40 \text{ m}^2 \text{ g}^{-1}$, respectively. The resulting DFT pore diameter distribution curves (Fig. S4†) show that the pore size of all MIL-53(Al)-NH₂ fiber mats is predominantly microporous (0.5–2 nm).^{39–41} The textural parameters derived from the N₂ isotherms are included in Table S1.†

CO₂ isotherms at 273 K in Fig. 1I display the same trend of decreasing adsorption capacity on a per-gram basis for hollow MIL-53(Al)-NH₂ materials synthesized with thicker Al₂O₃ layers. Notably, all CO₂ adsorption capacities at 273 K are improved compared to those of MIL-53(Al)-NH₂ powder samples reported,^{42,43} due to the more stable lp configuration, indicating the great potential of our materials in CO₂ capture or other gas separations.

Analysis of MOF conversion yield

Mass measurements were used to examine MOF quality. The MOF conversion yield was calculated using measured mass, following a procedure adapted from previous reports,⁴⁴ and the results are given in Table S1.† The yield values given in Table S1† reveal 100% conversion for the thinnest Al₂O₃ layer, with somewhat decreased yield for thicker oxides.

X-ray photoelectron spectroscopy (XPS) analysis was also used to qualitatively confirm the elemental composition of the MOFs. As illustrated in Fig. 2, the XPS data reflected a similar trend to the mathematical calculation. Two peaks are detected at the Al 2p high resolution scan of MIL-53(Al)-NH₂ (300) (Fig. 2A), where the component at 74.50 eV corresponds to octahedral AlO₄(OH)₂ clusters in MOFs, and the component at 75.35 eV is attributed to the unreacted aluminum oxide or byproducts of hydroxide in the hollow structure.⁴⁵

Notably, when thinner Al₂O₃ layers are used, the peak areas for unreacted aluminum oxide at 75.4 eV decrease significantly and no peak is detected for MIL-53(Al)-NH₂ (100) (Fig. 2G). As observed in the yield calculation, the XPS result also denotes 100% conversion into MIL-53(Al)-NH₂ from the Al₂O₃ film with 12 nm thickness. In addition, the O 1s spectra can be divided into two peaks. As shown in Fig. 2B, E and H, the first peak at 531.5 eV is attributed to the coordination of the Al cations with the oxygen

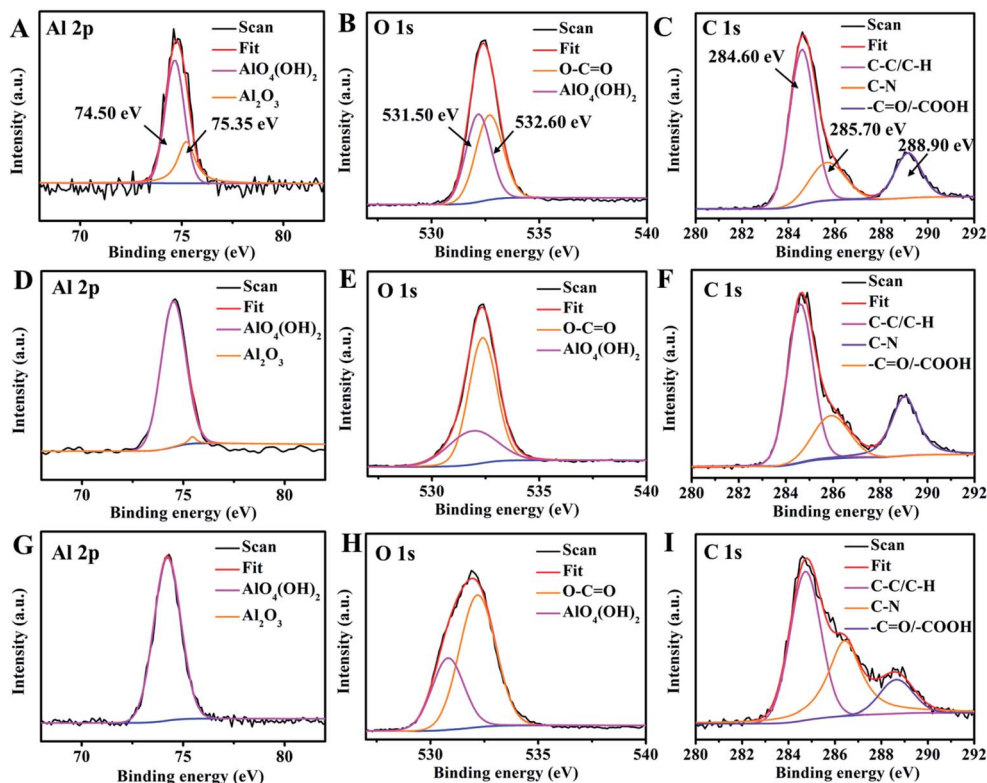


Fig. 2 High resolution XPS scans of (A) Al 2p (B) O 1s and (C) C 1s for MIL-53(Al)-NH₂ (300). (D) Al 2p (E) O 1s and (F) C 1s for MIL-53(Al)-NH₂ (200). (G) Al 2p (H) O 1s and (I) C 1s for MIL-53(Al)-NH₂ (100).

anion of the 2-amino-terephthalic acid linker, whereas the latter one at 532.6 eV is assigned to the oxygen in O-C=O. There are three peaks in C 1s emission spectra (Fig. 2C, F and I), which can be assigned to the non-oxygenated ring carbon (284.6 eV), C-N bond (285.7 eV), and carboxylate carbon (288.6 eV), respectively.

As shown in Fig. S5,† MIL-53(Al)-NH₂ (200) and MIL-53(Al)-NH₂ (300) form as robust mats, whereas MIL-53(Al)-NH₂ (100) is evidently fragile due to the ultrathin Al₂O₃ shell. In view of structure robustness and MOF quality, MIL-53(Al)-NH₂ (200) was chosen for the application tests. With this information in mind, 200 cycles of ALD Al₂O₃ (*i.e.* a thickness of 28 nm) are fixed to provide the consumptive metal oxide source in the following experiments.

Growth mechanism

The mechanism for MOF syntheses from Al₂O₃ proceeds *via* a dissolution-growth process.^{30,46} In detail, the reaction originates from fast dissolution and hydration of the surface oxide in DMF:water cosolvent; Al³⁺ species are then generated by the reaction between hydroxylated aluminum and adsorbed H⁺ in the near-surface region yielding an aluminum aqua complex ([Al(H₂O)₆]³⁺). Finally, MOF nucleation is promoted by the coordination between the aluminum aqua complex and the linkers.⁴⁶ However, as the MOF crystal growth consumes the outer Al₂O₃ layer, MOF crystals on the fiber surface can inhibit ligand diffusion into the inner region of the oxide layer,³⁰ thereby limiting MOF growth.^{47,48}

Comparison to powders and extension to other fiber substrates

We further studied MIL-53(Al)-NH₂ powders produced *via* solvothermal synthesis (denoted as MIL-53(Al)-NH₂ (powder)), as well as MOF-fibers formed *via* oxide conversion on CDA and PP fibers (Materials and Synthesis ESI†). The latter materials are referred to as MIL-53(Al)-NH₂ (CDA) and MIL-53(Al)-NH₂ (PP), respectively. In these cases, the polymer was not removed before oxide-to-MOF conversion. Results of these materials, and comparison to MIL-53(Al)-NH₂ (200) fibers produced with the pre-dissolved polymer are shown in Fig. 3.

As shown in Fig. 3A, MIL-53(Al)-NH₂ powder samples produced rice-shaped crystals with crystal size in the range of 500–700 nm length and 80–150 nm diameter (Fig. 3A). For the case of MIL-53(Al)-NH₂ (CDA), the SEM image (Fig. 3B) shows a predominantly hollow MOF structure indicating that the CDA polymer scaffold was dissolved during the MOF synthesis. For MIL-53(Al)-NH₂ (PP), the polymer was not dissolved, yielding a conformally integrated MOF on PP fibers, as shown in Fig. 3C.

It is also important to note that in contrast to the relatively large MIL-53(Al)-NH₂ crystals produced as powders, the crystals converted from ALD Al₂O₃ on fibers (Fig. 3B and C) are more well defined and smaller, less than 250 nm in length, which was consistent with the proposed growth mechanism. For all cases, the XRD patterns (Fig. 3D) of MIL-53(Al)-NH₂ (powder), MIL-53(Al)-NH₂ (CDA), and MIL-53(Al)-NH₂ (PP) show the characteristic peaks, indicating the successful MOF synthesis. The

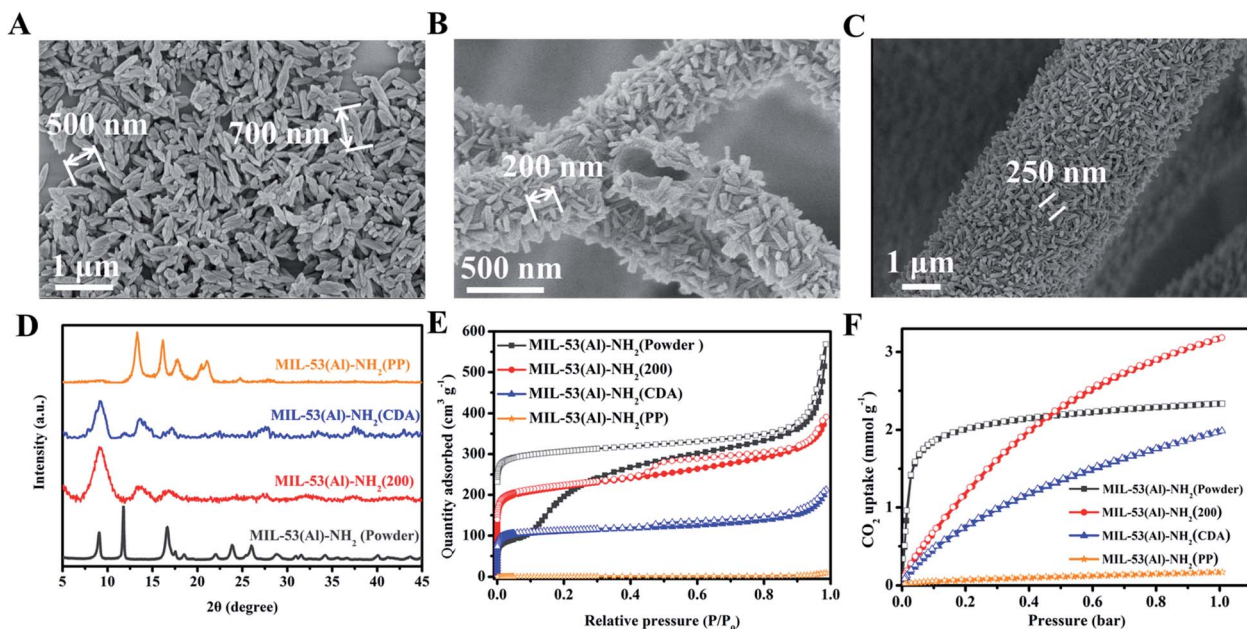


Fig. 3 SEM images of the (A) MIL-53(Al)-NH₂ (powder), (B) MIL-53(Al)-NH₂ (CDA) and (C) MIL-53(Al)-NH₂ (PP). MIL-53(Al)-NH₂ converted from the metal oxide source given by an ALD process shows a reduced crystal size (D) XRD patterns of MIL-53(Al)-NH₂ materials fabricated by different methods. MIL-53(Al)-NH₂ (200), MIL-53(Al)-NH₂ (CDA) and MIL-53(Al)-NH₂ (PP) can be assigned to the lp configuration, whereas MIL-53(Al)-NH₂ (powder) is much closer to the np configuration. (E) N₂ isotherms at 77 K. (F) CO₂ isotherms at 273 K.

powder samples show features consistent with the np structure, whereas like the materials shown in Fig. 1C, the MOF-fibers show spectra consistent with the lp configuration. The structural changes detected by XRD analysis show flexibility and breathing behavior in the MOFs. The flexibility is expected to arise from the parallel arrangement of the Al^{III}(OH)(RCOO)₂ chains and possibly some interpenetrated coordination.^{49,50} This distinction is important as it influences the performance of the MOF-fibers relative to the free MOF powder.

Low-pressure gas adsorption analysis

MIL-53(Al)-NH₂ is known to be flexible with breathing behavior associated with lp–np transitions even at room temperature. The breathing behavior of MIL-53(Al)-NH₂ powders can be triggered by various gases such as CO₂, CH₄, and C₂H₆.⁵¹ Kitagawa and co-workers described a close relationship between the MOF crystal size and the framework flexibility; that is, nanometer-scale crystals provide stability to the pore configuration in a flexible MOF structure, resulting in a thermodynamic and/or kinetic suppression in pore transitions.^{25,52} Therefore, the smaller 200 nm lp dominated MIL-53(Al)-NH₂ (200) MOFs are expected to possess a much more stable pore configuration and be restricted further from breathing.

N₂ adsorption–desorption isotherms (Fig. 3E) confirm the hypothesis that MIL-53(Al)-NH₂ (200) features a much more stable pore structure than the powder phase. For MIL-53(Al)-NH₂ (powder), it shows an np configuration at room temperature, and the np–lp transition is evidently triggered at 120 °C by the degassing process.^{53,54} In Fig. 3E, the N₂ adsorption isotherm at 77 K for MIL-53(Al)-NH₂ (powder) shows two

plateaus, one at around 0.02–0.1 *P/P*₀ associated with the lp–np transition, and another at 0.4–0.6 *P/P*₀ associated with the np–lp transition.^{55,56}

In separate tests, hollow MOF-fibers were produced from Al₂O₃ ALD layers either before or after removing the CDA fiber substrate. Removing the polymer before oxide-to-MOF conversion led to N₂ isotherms with a much more stable pore configuration and BET surface area of 842 ± 28 m² g⁻¹. This surface area is ~2× larger than 480 ± 21 m² g⁻¹ measured for MIL-53(Al)-NH₂ formed with the CDA not removed before oxide to MOF conversion. The small surface area for MOFs formed before polymer removal is ascribed to infusion of dissolved CDA into the MOF to partly block the pore volume (Table S1†). This highlights the significance of the pre-dissolution treatment in formation of a hollow structure MOF with fewer impurities and higher crystallinity. The pore size distribution results indicate that the MIL-53(Al)-NH₂ powder and MIL-53(Al)-NH₂-PP fiber show a hierarchical pore structure, whereas the MIL-53(Al)-NH₂ (CDA) fiber only shows a microporous structure (Fig. S6†).^{39–41}

From the CO₂ isotherms, it can be observed that MIL-53(Al)-NH₂ (200) spans a higher range at a relative pressure at 0.4 bar over MIL-53(Al)-NH₂ (powder) isotherms, exhibiting a more stable pore configuration and higher CO₂ uptake (Fig. 3F). That is because, after the lp–np transition at 0–0.1 bar, MIL-53(Al)-NH₂ (powder) still forms in the np phase, and is unable to have additional gas uptake. In comparison, MIL-53(Al)-NH₂ (200) is stabilized in the lp phase and has continued adsorption throughout this region.^{53,54}

Furthermore, among the four samples studied, MIL-53(Al)-NH₂ (200) shows the highest CO₂ uptake at 1 bar, reaching 3.30

$\pm 0.05 \text{ mmol g}^{-1}$ (Table S1†) which is significantly higher than those reported in previous studies.^{42,57}

Extension to other MOF materials

To confirm that our synthetic approach can be extended to other materials, we synthesized other hollow MOF fibers including Zn and Al based structures (Methods, ESI†). Fig. 4 shows Al-PMOF and ZIF-8 structures formed by transformation from the Al_2O_3 hollow structure, yielding freestanding MOF predominant nanofiber mats. The SEM images, XRD patterns, and N_2 adsorption-desorption isotherms (Fig. 4) confirm successful fabrication of the MOF structure.

Potential applications on MIL-53(Al)- NH_2 hollow fiber mats

The performances of the MIL-53(Al)- NH_2 fiber mats and powders were evaluated in gas separation and VOC removal applications. Over the past decade, experimental and computational analyses show promising potential for MOFs in CO_2 capture⁵⁸⁻⁶⁰ and CO_2/N_2 and CO_2/CH_4 separation.^{49,61,62} For the MIL-53(Al)- NH_2 hollow fiber samples produced here, volumetric gas adsorption analysis shown in Fig. 3F confirms high CO_2 adsorption capacities, showing promise for advanced applications.

To analyze CO_2/N_2 selectivity, we applied the ideal adsorbed solution theory (IAST) using adsorption data of single-

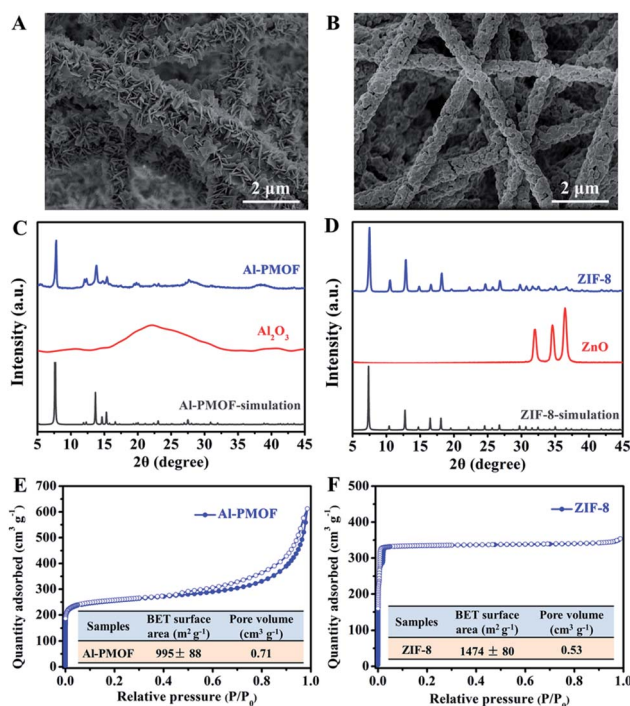


Fig. 4 SEM images of the (A) Al-PMOF predominant fiber mat and (B) ZIF-8 predominant fiber mat. Freestanding fiber structures are retained from their parent phases of Al_2O_3 and ZnO nanofibers, respectively. XRD patterns of (C) Al-PMOF and (D) ZIF-8, which confirm that both Al-PMOF and ZIF-8 have been converted successfully and the characteristic peaks are identical to the simulation patterns. N_2 isotherms of (E) Al-PMOF and (F) ZIF-8 at 77 K. Inset shows the decent BET surface areas and pore volumes of Al-PMOF and ZIF-8.

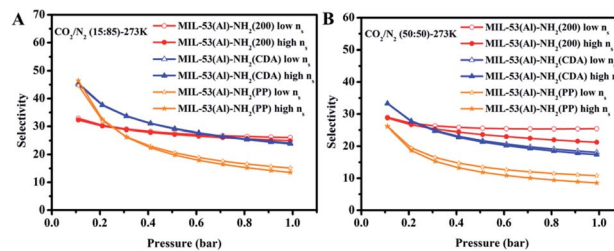


Fig. 5 Selectivity by the IAST calculations at 273 K with CO_2 and N_2 molar ratios of (A) 15/85 and (B) 50/50 in the gas phase.

component gases (Table S2 and Fig. S7–S10†).⁶³⁻⁶⁸ As shown in Fig. 5, the MIL-53(Al)- NH_2 (200) material shows a moderate CO_2/N_2 selectivity. The values of IAST selectivity at 273 K and 1 bar for 15/85 and 50/50 CO_2/N_2 mixtures are about 24.9 and 21.2, respectively. It should be pointed out that MIL-53(Al)- NH_2 (200) shows much lower selectivity compared with MIL-53(Al)- NH_2 (powder) (Fig. S11†). We attribute this to the inherent low N_2 uptake on the powder, which results in ultrahigh CO_2/N_2 selectivity on MIL-53(Al)- NH_2 (powder) both in 15/85 and 50/50 CO_2/N_2 mixtures at 1 bar.

The CO_2/N_2 selectivity is further confirmed by a binary gas-adsorption experiment *via* a gravimetric method, where the CO_2/N_2 mixture (15/85) is utilized to simulate the major components of flue gas. As shown in Fig. 6A, no apparent capacity loss is observed after 21 cycles with a mass change of 4.5%, indicating that MIL-53(Al)- NH_2 (200) is capable of withstanding cyclic exposure to the gas mixture and able to remove CO_2 from flue gases.

Beyond application in gas separation, MIL-53(Al)- NH_2 hollow fibers produced under several conditions were further investigated for their catalytic activity for VOC formaldehyde (HCHO) oxidation.⁶⁹⁻⁷¹ Results were compared to those of the MIL-53(Al)- NH_2 powder. HCHO removal performance was measured statically in an airtight reactor, with samples cyclically and automatically taken at 1 minute intervals and monitored by utilizing a photoacoustic IR multigas monitor for appearance of CO_2 and decrease of HCHO.⁷² The data clearly indicate a heterogeneous removal of HCHO⁶⁹⁻⁷¹ on each MIL-53(Al)- NH_2 sample. The adsorption-degradation-desorption process active in this system produces the expected HCHO reduction and CO_2 generation (Fig. 6B and C).⁷⁰ The catalytic activity performance is determined by the variation of HCHO concentration after 60 min (Fig. 6B). Results confirm that MIL-53(Al)- NH_2 (200) with the hollow structure shows the best HCHO catalytic activity, followed by MIL-53(Al)- NH_2 (CDA), MIL-53(Al)- NH_2 (powder) and MIL-53(Al)- NH_2 (PP). The superior performance of MIL-53(Al)- NH_2 (200) is ascribed to the unique hollow fiber structure. In part, the radial growth of MOF crystals along with fiber cylinders can diminish most aggregation effects seen in the powder phase. The hollow structure facilitates HCHO molecule flow into the inner side of the cylinders, thereby encountering more active sites. It is worth noting that MIL-53(Al)- NH_2 (200) exhibits excellent reproducibility in HCHO removal analysis, even with a tiny dosage (*ca.* 35

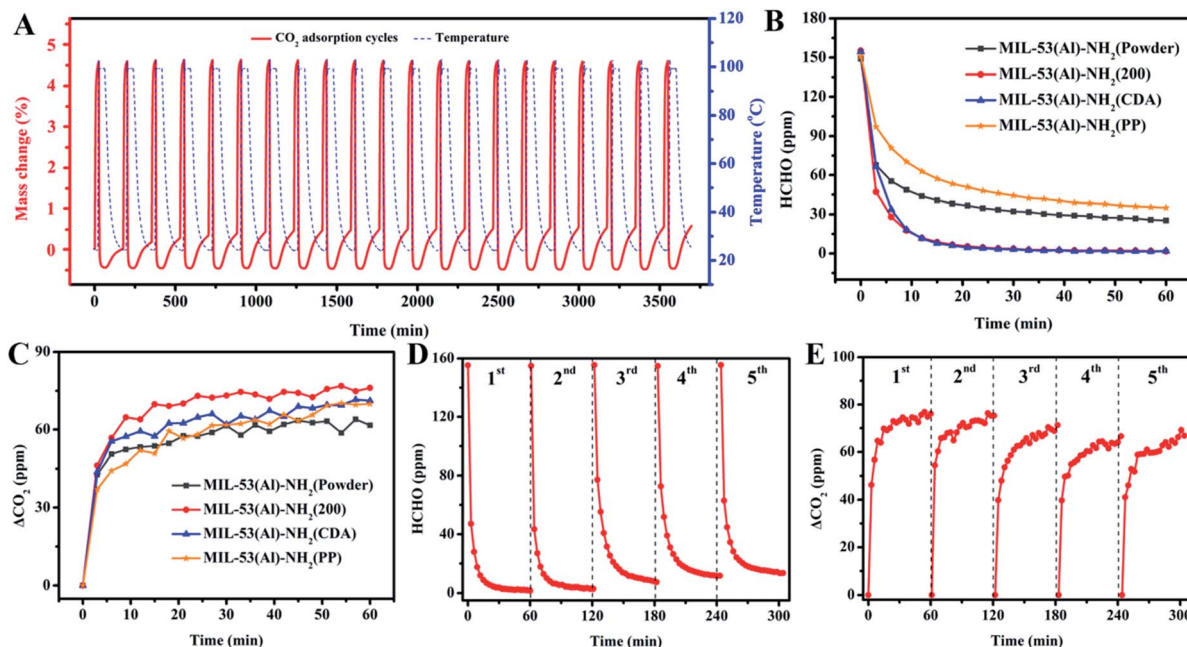


Fig. 6 (A) Cyclic CO₂ adsorption behavior measured by the thermogravimetric method with introducing a 15% CO₂ mixture in N₂ at 25 °C. The initial mass was normalized to 0% at 25 °C under a N₂ atmosphere. HCHO removal tests over MIL-53(Al)-NH₂ (powder), MIL-53(Al)-NH₂ (200), MIL-53(Al)-NH₂ (CDA) and MIL-53(Al)-NH₂ (PP): variation of the concentration of (B) HCHO; (C) CO₂. Reproducibility tests of HCHO removal performance on MIL-53(Al)-NH₂ (200): variation of the concentration of (D) HCHO; (E) CO₂. (F) Proposed heterogeneous catalytic mechanism in HCHO removal using MIL-53(Al)-NH₂ (200) as a catalyst.

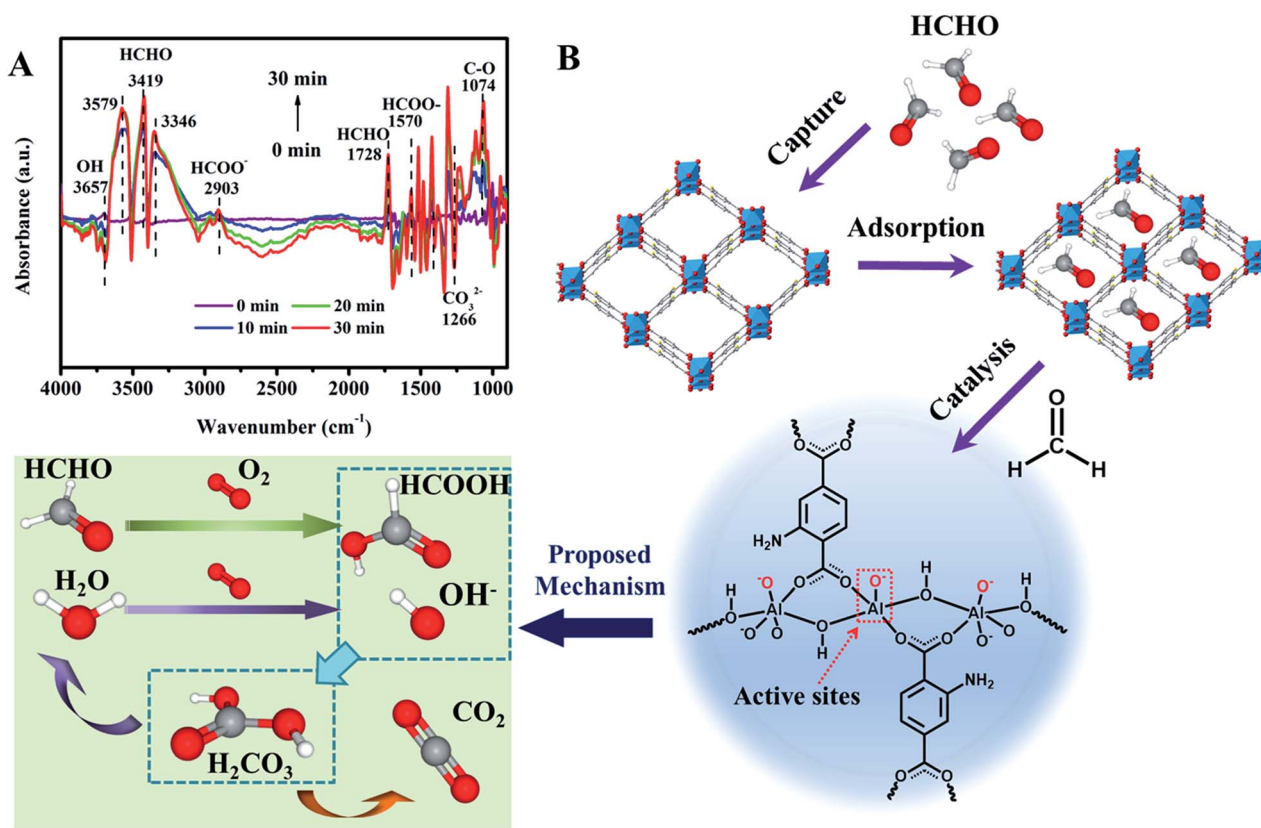


Fig. 7 (A) *In situ* DRIFTS spectra of MIL-53(Al)-NH₂ (200) exposed to a flow of ~80 ppm of HCHO/synergetic air at room temperature. (B) Proposed heterogeneous catalytic mechanism in HCHO removal using MIL-53(Al)-NH₂ (200) as a catalyst.

mg), and still retains the HCHO removal ability of around 92.9% after 5 cyclic tests (Fig. 6D and E). Moreover, the morphology of the MIL-53(Al)-NH₂ (200) fiber mats remains intact after HCHO removal testing (Fig. S12[†]), indicating good stability of the MOF structure. The VOC removal performance of selected MOFs is summarized in Table S3.[†] In comparison with other MOFs, MIL-53(Al)-NH₂ (200) shows competitive performance in overall VOC removal.

To demonstrate the degradation pathway of HCHO on MIL-53(Al)-NH₂ (200), *in situ* observation of DRIFTS spectra exposed to a flow of ~80 ppm HCHO/synthetic air within 30 min was recorded at room temperature. As shown in Fig. 7A, characteristic peaks around 1728 cm⁻¹, 3346 cm⁻¹, 3419 cm⁻¹, and 3579 cm⁻¹ can be ascribed to gas HCHO (National Institute of Standards and Technology (NIST) Standard Reference Database 69), indicating quick adsorption by the porous MOF structure. The formation of formate species (1570 cm⁻¹, 2903 cm⁻¹) and carbonate species (1266 cm⁻¹) can be clearly observed in the spectra, revealing that the formate species are the main intermediates during the HCHO oxidation process.^{73,74} The negative signals around 3657 cm⁻¹ can be assigned to surface hydroxyl groups. Based on the results, the proposed mechanism of HCHO removal on MIL-53(Al)-NH₂ (200) is illustrated in Fig. 7B. The heterogeneous catalytic process is composed of several intermediate details. In detail, HCHO molecules are adsorbed by the porous structures initially and then oxidized by AlO₄(OH)₂ clusters to transform to formate and carbonate species, finally degrading to harmless products of CO₂ and H₂O.

Conclusions

This work demonstrates a novel approach to fabricate free-standing MIL-53(Al)-NH₂ fiber mats in a unique hollow structure with high crystallinity and porosity. The method can also be extended to other MOF systems with a freestanding hollow structure. The freestanding MOF-fiber mat converted from the metal oxide source formed by ALD shows a well-controlled crystal size and more stable pore configuration as well as a restrained breathing behavior in a flexible MOF structure compared with its powder phase. Experimental analysis confirms that predominant MIL-53(Al)-NH₂ hollow fiber mats have promising potential in CO₂ adsorption, CO₂/N₂ separation, and VOC abatement applications.

Conflicts of interest

There are no conflicts to declare.

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