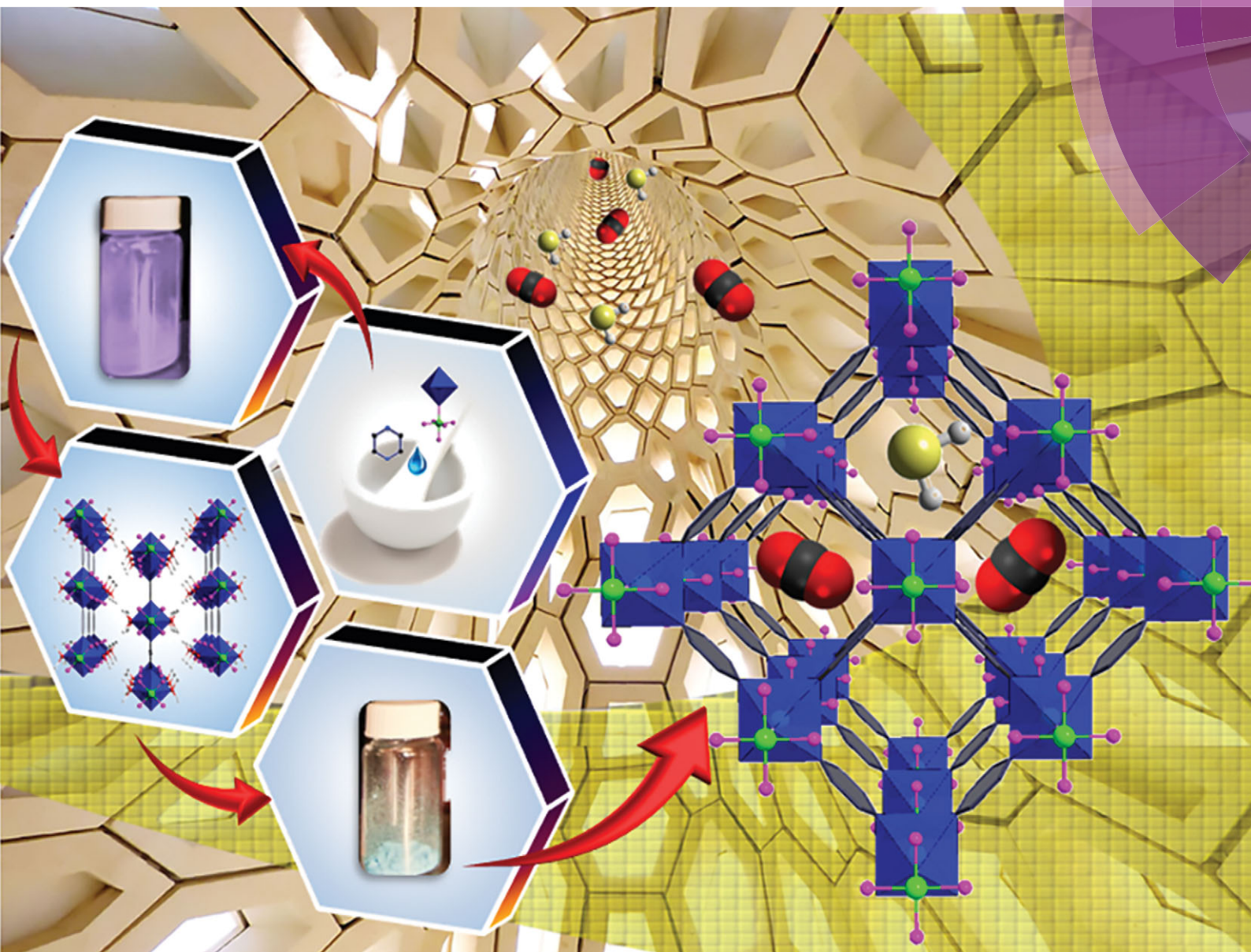


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A facile solvent-free synthesis route for the assembly of a highly CO₂ selective and H₂S tolerant NiSIFSIX metal–organic framework†

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The development of materials for CO₂ capture with high selectivity and high tolerance to H₂S is of prime importance for various industrially relevant gas streams (e.g. natural gas and biogas upgrading as well as pre-combustion capture). Here, we report the successful fabrication of a MOF with combined exceptional CO₂ capture properties and H₂S tolerance, namely the NiSIFSIX-based MOF using both solvothermal and solvent-free methodologies.

Metal–organic frameworks (MOFs), a special class of solid-state materials, have been considered to be one of the most burgeoning porous materials in the last two decades.¹ MOFs are very attractive due to their modular nature, e.g. large porosity, chemical and topological versatility and structural diversity, which offer potential in various applications such as catalysis, gas storage, gas sensing, greenhouse gas emission mitigation and many other challenging gas separations.^{2,3}

Recently, MOFs were intensively investigated for CO₂ capture from various gas streams such as post-combustion, pre-combustion capture, natural gas and biogas upgrading.⁴ In spite of the large number of studies, only few reports focused on traces or low CO₂ concentration removal applications (i.e. CO₂ removal from air, hydrogen purification, and medical applications such as anaesthesia machines).^{5–7} Furthermore, development of materials capable of selective CO₂ removal, in CO₂ diluted streams, with high tolerance to H₂S is of prime practical importance.

Our quest for made-to-order materials that can address efficiently the separation and capture of CO₂ at different concentrations has prompted us to explore the potential of various MOFs with different structural properties and chemical compositions.^{4d,7–9}

Recently, the successful practice of reticular chemistry allowed us to fabricate a series of isorecticular very stable MOFs with

periodically arrayed hexafluorosilicate (SIFSIX) pillars, called SIFSIX-3-Zn^{4d} and SIFSIX-3-Cu.⁷

These aforementioned porous MOFs disclose unique features for carbon capture, namely uniformly aligned strong CO₂ adsorption sites in an idealized and contracted pore system with high localized charge density. Particularly the use of a relatively small cation, i.e. Cu²⁺, led to an isorecticular analogue with a very high selectivity toward CO₂ adsorption at very low CO₂ partial pressures when compared to other physical adsorbents reported in the open literature.^{4d,7}

These unique materials offer great potential for air-capture applications due to the periodically aligned very high (non-reactive) CO₂ adsorption energetic sites, resulting in a fully reversible physically driven adsorption–desorption operation under very mild conditions. The contracted pore system associated with a localized high charge density had afforded the selective CO₂ adsorption with relatively much faster rates and stronger interactions than H₂, CH₄ and N₂, and subsequently the attainment of unprecedented separation performances based on a unique synergistic mechanism involving both thermodynamics and kinetics in a wide range of CO₂ concentrations.

It is worth noting that commonly hybrid porous solid-state materials are synthesized using solvo/hydrothermal routes.^{10,11} Various other synthetic approaches have been explored and reported for the construction of MOF materials such as (i) microwave-assisted solvothermal methods,¹¹ (ii) micro-fluidics,^{11c} (iii) ionic liquids,^{11d} and (iv) electro-chemistry.^{11e} Nevertheless, all these synthetic practices are found to be practical for the lab-scale research but are hardly implemented, and not often economically applicable, at the pilot or larger industrial scales. Mainly, the scale-up of MOF materials is hindered by the expensive cost, safety and the negative environmental impact associated with the use of organic solvents. Furthermore, MOF solution-based synthesis approaches suffer from additional drawbacks such as the plausible toxic and/or corrosive character associated with dissolved metal salts, generating acids as byproducts and often susceptible to solvolysis and must be disposed.¹¹ Additionally, the need to dispose or recycle large quantities of solvents is not

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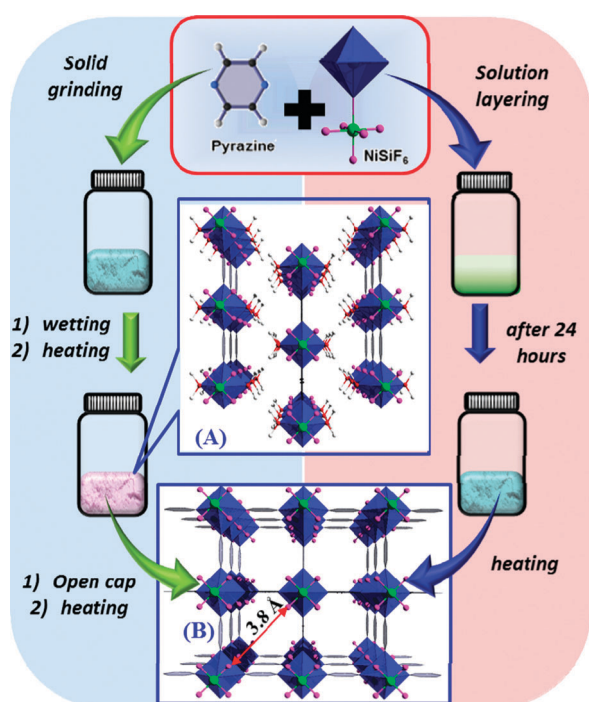
cost effective. All the above mentioned downfalls have hindered the timely progress in the scale-up of MOFs and their successful deployment in industrial applications.¹² Accordingly, the successful use of the solvent-free synthesis route for the construction of MOFs can be regarded as a plausible route toward the requisite cost-effective scale-up of MOFs, a critical step for MOF industrial deployment.^{11a}

Here, we report the solvent-free synthesis of a new H₂S tolerant MOF material, namely **SIFSIX-3-Ni**, isostructural to the Zn and Cu based **SIFSIX-3-M**,^{4d-7} with very high CO₂ selectivity in a wide range of CO₂ concentrations. After countless failed attempts to develop solvent-free procedures for the synthesis of the previously isolated Zn and Cu **SIFSIX** analogues (**SIFSIX-3-Zn** and **SIFSIX-3-Cu**),^{4d-7} we extended our focus and efforts to other metal sources that can also potentially form **SIFSIX-3-M** isostructures. Accordingly, first we opted to target and confirm the construction of the nickel analogue using the conventional solvothermal route and then subsequently explore the ability to fabricate this Ni-analogue using a free-solvent process.

Indeed, the **SIFSIX-3-Ni** analogue (**B** in Scheme 1) was prepared successfully by layering a methanol solution of pyrazine (pyz) in a glass tube onto a methanol solution of NiSiF₆·xH₂O. Upon layering, a slow formation of light blue powder was observed, and the powder was left for 24 hours in the mother solution. Before the gas adsorption study, the powder was first collected, washed extensively with methanol and then heated to 105 °C, dried under vacuum and characterized using powder X-ray diffraction (PXRD) (Fig. S1, ESI†). The structure of this expected new analogue is in very good agreement with those of the Zn and Cu analogues

reported previously,^{4d,7} but with a slightly smaller unit cell (378 Å³) than the Zn (388 Å³) analogue which is attributed to the relatively strong bonding between the Ni²⁺ and the pyrazine as compared to Zn²⁺ (Table S1, ESI†).^{7,8} The unit cell size of the Ni analogue was found to be between the Zn and the Cu analogues, in good agreement with the relatively sharp pore size distribution (PSD) centred at 3.8 Å (average pore size), as determined from the CO₂ adsorption isotherm analysis using the NLDFT model (Fig. 1b). This result is in good agreement with the associated crystal structure and as anticipated is situated between the observed values for **SIFSIX-3-Zn** (3.8–4 Å) and **SIFSIX-3-Cu** (3.5 Å).

The steepness of variable temperature adsorption isotherms at low pressure for the newly isolated Ni analogue (Fig. 1a) is another indication of the relatively small pore size as compared to the Zn analogue. The intermediate steepness of CO₂ adsorption isotherms is also an indication of stronger/weaker CO₂–**SIFSIX-3-Ni** interactions as compared to the Zn/Cu analogues. Accordingly, the Q_{st} of CO₂ adsorption for **SIFSIX-3-Ni** (Fig. 2) is 7% and 8% higher/lower (48 kJ mol⁻¹) than the Zn and the Cu analogues, respectively. The Q_{st} of CO₂ adsorption is an intrinsic property that dictates the affinity of the MOF toward CO₂, which in turn plays an important role in determining the necessary energy to release CO₂ during the regeneration step. The Q_{st} for CO₂ is in the range of fully reversible CO₂ adsorption (30–50 kJ mol⁻¹),^{4d} in agreement with the full evacuation of **SIFSIX-3-Ni** at 298–323 K in a vacuum. As in the case of **SIFSIX-3-Zn** and **SIFSIX-3-Cu**, the Q_{st} for CO₂ adsorption was relatively



Scheme 1 Schematic representation of the two different preparation procedures for **SIFSIX-3-Ni**. (right) Solvothermal route based on layering methanol solutions of both precursors. (left) Solvent-free route that involves the grinding of precursors, wetting and heating.

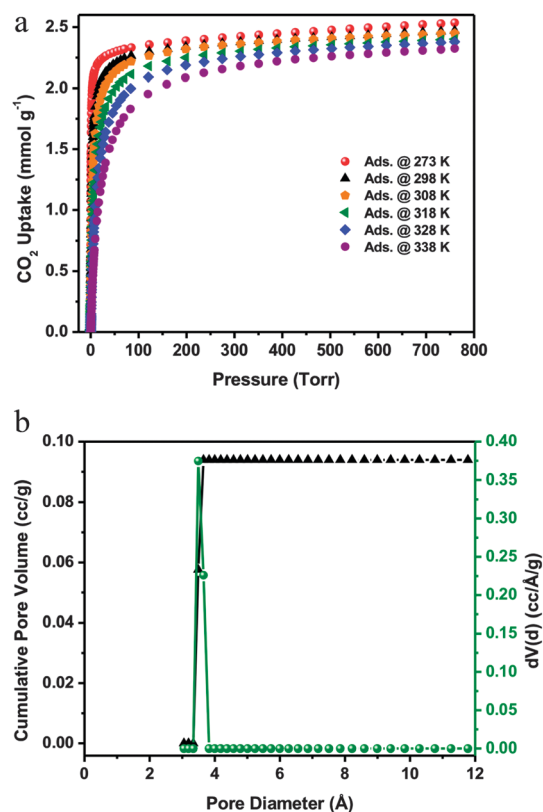


Fig. 1 (a) Variable temperature adsorption isotherms of CO₂ for **SIFSIX-3-Ni**, (b) pore size distribution from CO₂ sorption isotherms at 77 K for **SIFSIX-3-Ni**.



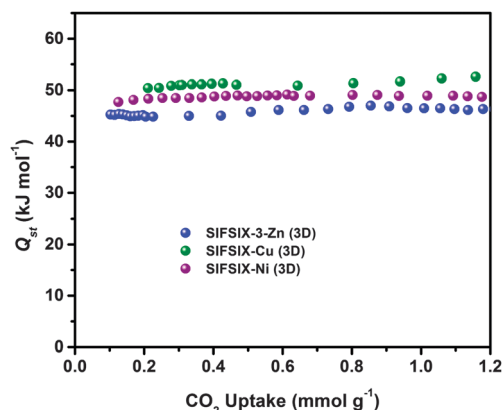


Fig. 2 Isosteric heats of adsorption at low coverage for **SIFSIX-3-Cu**, **SIFSIX-3-Zn** and **SIFSIX-3-Ni**.

constant indicating homogenous energetic sites over the full range of CO₂ loading (Fig. 2).^{4d,7} By analogy and based on the full mixed gas adsorption and kinetics study carried out on the Zn and Cu analogues,^{4d,7} it is logically expected that **SIFSIX-3-Ni** will perform at least similarly as the Zn analogue^{4d} in terms of CO₂ separation from N₂, O₂, CH₄ and H₂ containing mixtures. The anticipated high selectivity toward CO₂ in the case of **SIFSIX-3-Ni** is projected to be driven by the unique optimal combination between thermodynamics and kinetics, *i.e.*, the occurrence of strong/homogenous CO₂–MOF interactions and the relatively fast CO₂ adsorption than those of other relevant gases.^{4d,7}

The successful isolation of the new Ni analogue solvothermally had encouraged us to explore its plausible isolation using a solvent-free route. After few attempts, and in contrast to the case of Zn and Cu analogues, we successfully discovered the appropriate conditions that permit a solvent-free route synthesis of **SIFSIX-3-Ni**. This extremely facile methodology is based first on mechanically mixing both the organic and inorganic solid precursors *i.e.* pyrazine and NiSiF₆ with a molar ratio of 4:1 respectively, followed by a wetting procedure with few drops of water and then a careful heating procedure (Scheme 1).

Indeed, after dry mechanical mixing and wetting, the examination of the resultant powder mixture using powder X-ray diffraction data showed that a very less crystalline product was obtained (Fig. 3a). The resultant powder mixture was heated to 65 °C for 4 hours in a closed vial which resulted in a colour change to light violet. The observed colour change is associated with the formation of the 2D structure of the **SIFSIX-3-Ni** analogue (**A** in Scheme 1). Interestingly, upon heating (drying) at 105 °C for an additional 4 hours, we observed a structural phase transformation. The PXRD diagram of the final material prepared using the solvent-free route method after the drying process was found to match and correspond to the 3D **SIFSIX-3-Ni** structure (**B** in Scheme 1) prepared using the solvothermal method (Fig. S1, ESI†). It is worth mentioning that the application of a similar solvent-free procedure to the Zn and Cu analogues did not permit the observation of the same phase transformation from the 2D to the 3D structure.

Essentially, the Rietveld refinement allowed us to clearly confirm the crystal structure of the resultant crystalline material

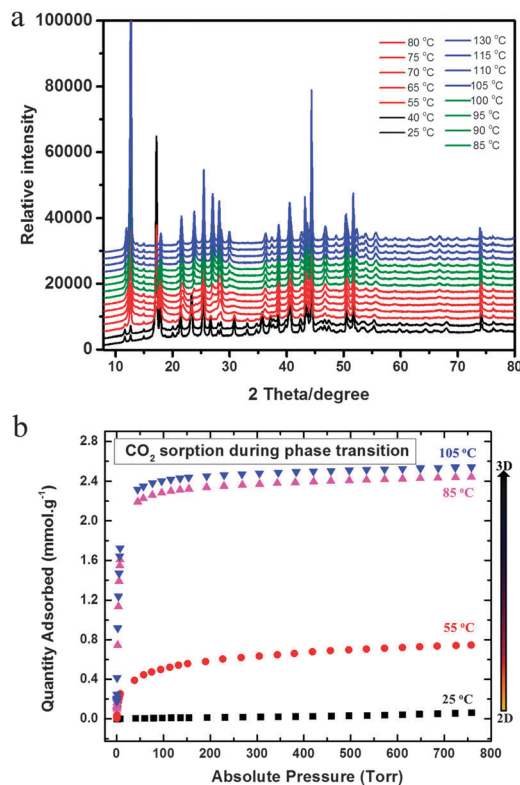


Fig. 3 (a) Variable temperature PXRD for phase transition of the 2D (NiSiF₆·xH₂O) to the 3D **SIFSIX-3-Ni** structure, and (b) CO₂ sorption at 298 K during phase transition at different temperatures.

from the solvent-free synthesis as **SIFSIX-3-Ni** (Fig. S1, ESI†). In order to better understand the crystallisation process affording the formation of **SIFSIX-3-Ni**, variable temperature PXRD was conducted (Fig. 3a) from 25 °C to 130 °C. At low temperature (25–40 °C), a first product with a very low crystallinity appeared which corresponds to a 2D structural analogue that was previously reported (CuSiF₆(pyz)(H₂O)₂ (**A** in Scheme 1).⁷ A further increase in the temperature resulted in a phase transformation that afforded the formation of targeted 3D **SIFSIX-3-Ni** starting at around 55 °C and completed at 70 °C. At higher temperatures, PXRDs confirm the good crystallinity of the 3D material and its associated noticeable stability up to 130 °C.

It is worth noting that the phase transformation was accompanied by a discernible colour change from light violet to light blue when full converted.

Delightfully, the Ni analogue prepared by the solvent-free route showed the same variable temperature adsorption isotherms at low pressure as the Ni analogue prepared by the solvothermal methods which further supports the conformity of the **SIFSIX-3-Ni** materials resulting from both approaches (Fig. 3b). Fig. 3b illustrates the evolution in the CO₂ adsorption uptake, recorded at 25 °C, as a function of the evacuation temperature for the **SIFSIX-3-Ni** analogue prepared by the solvent-free route method. The CO₂ adsorption showed an increase in the CO₂ uptake with increased evacuation temperatures up to 105 °C, corresponding to the optimal CO₂ adsorption isotherm which also correlates with the phase change observed in the VT-PXRD and the



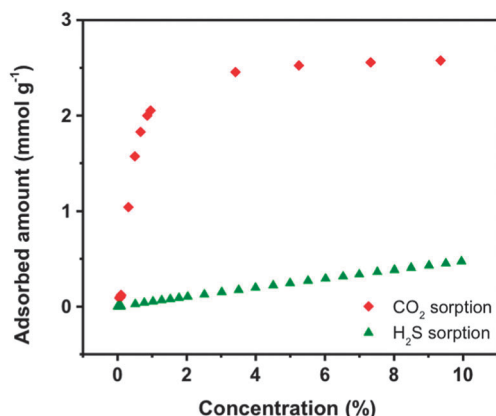


Fig. 4 CO₂ and H₂S sorption isotherms for SIFSIX-3-Ni. H₂S uptake remains same after repeated sorption and activation cycles.

complete conversion to 3D SIFSIX-3-Ni. The Q_{st} for CO₂ was found to be in good agreement with the associated values for SIFSIX-3-Ni prepared using the solvothermal method (Fig. S3, ESI†).

In light of the exceptional CO₂ capture properties of SIFSIX-3-Zn and SIFSIX-3-Cu^{4d,7} analogues, it is expected that the high CO₂ selectivity of SIFSIX-3-Ni at intermediate and high CO₂ concentrations will be similarly high. For the particular case of SIFSIX-3-Ni we found that the structure is stable up to 80% RH both in CO₂-humidity and CO₂-air and undergo phase change to the 2D structure (Scheme 1A) at relative humidity higher than 80% RH (Fig. S2, ESI†).

In addition to favourable adsorption properties for CO₂ capture, an ideal CO₂ adsorbent should also be tolerant to impurities such as H₂S, since natural gas contains acidic gases in various amounts that can reach high concentration up to 10–20% in the case of H₂S. Accordingly, we have investigated the stability of SIFSIX-3-Ni after exposure and adsorption of H₂S. It is worth noting that MOFs known to be stable upon exposure to H₂S are scarce.¹³

The H₂S sorption isotherm was collected for the SIFSIX-3-Ni sample and revealed an uptake of H₂S around 1.3 mol g⁻¹ at 10% concentration (Fig. 4). The H₂S adsorption isotherm was repeated on the same sample in order to check/confirm the material's stability; the second H₂S adsorption isotherm was found to be identical to the first one as shown in Fig. S4 (ESI†), and thus confirming the stability and regeneration/recycling of SIFSIX-3-Ni in the presence of H₂S. This unique stability of the SIFSIX-3-Ni material in the presence of H₂S was also supported by the similarities between the PXRD patterns before and after the H₂S exposure (Fig. S2, ESI†). The resultant H₂S exposed SIFSIX-3-Ni sample was then used for another cycle of CO₂ sorption isotherm studies. Comfortably, the new collected CO₂ adsorption isotherm matched exactly with the adsorption isotherm for the fresh sample not exposed to H₂S as shown in Fig. S5 (ESI†). Certainly, the repeated H₂S exposure did not affect/alter the subsequent capacity of SIFSIX-3-Ni for CO₂ and H₂S. It is worth stating that the Cu and Zn analogues are not tolerant to H₂S, unlike the H₂S tolerant SIFSIX-3-Ni, and lose their crystallinity and CO₂ uptake capacity upon exposure to H₂S. This further supports the uniqueness of SIFSIX-3-Ni and

its prospective use as an excellent adsorbent for CO₂ removal from a gaseous mixture containing acidic gases for natural gas upgrading application.

In conclusion, we showed herein that the successful practice of MOF chemistry had permitted for the first time the fabrication of an H₂S-tolerant MOF, SIFSIX-3-Ni, for practical CO₂ capture in a wide range of CO₂ concentrations, using a solvent-free synthetic approach. The exceptional CO₂ capture and high tolerance to H₂S, in addition to the simplified synthesis procedure, qualify the SIFSIX-3-Ni analogue as a prospective candidate for scale-up and testing at the pilot scale. This projected accomplishment will facilitate the smooth transition to commercialization and will pave the way for this technology technically and economically to be viable.

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