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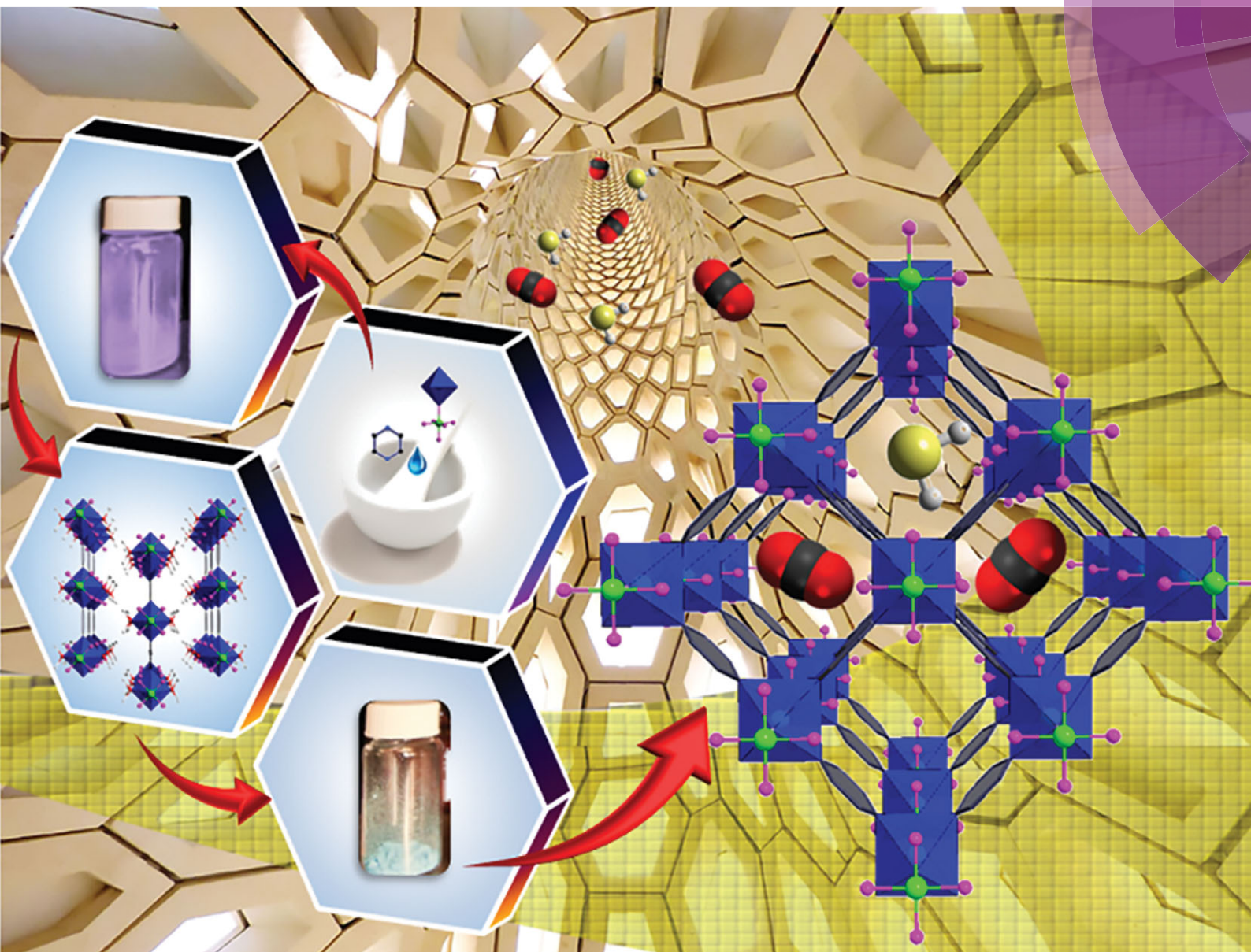
COMMUNICATION
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A facile solvent-free synthesis route for the assembly of a highly CO$_2$ selective and H$_2$S tolerant NiSIFSIX metal–organic framework†

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The development of materials for CO$_2$ capture with high selectivity and high tolerance to H$_2$S 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 CO$_2$ capture properties and H$_2$S 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 CO$_2$ 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 CO$_2$ concentration removal applications (*i.e.* CO$_2$ removal from air, hydrogen purification, and medical applications such as anaesthesia machines).[5–7] Furthermore, development of materials capable of selective CO$_2$ removal, in CO$_2$ diluted streams, with high tolerance to H$_2$S is of prime practical importance.

Our quest for made-to-order materials that can address efficiently the separation and capture of CO$_2$ 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 isoreticular very stable MOFs with

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periodically arrayed hexafluorosilicate (**SIFSIX**) pillars, called **SIFSIX**-3-Zn[4d] and **SIFSIX**-3-Cu.[7]
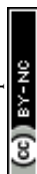
These aforementioned porous MOFs disclose unique features for carbon capture, namely uniformly aligned strong CO$_2$ adsorption sites in an idealized and contracted pore system with high localized charge density. Particularly the use of a relatively small cation, *i.e.* Cu^{2+}, led to an isoreticular analogue with a very high selectivity toward CO$_2$ adsorption at very low CO$_2$ 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) CO$_2$ 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 CO$_2$ adsorption with relatively much faster rates and stronger interactions than H$_2$, CH$_4$ and N$_2$, and subsequently the attainment of unprecedented separation performances based on a unique synergistic mechanism involving both thermodynamics and kinetics in a wide range of CO$_2$ 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

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 H_2S tolerant MOF material, namely **SIFSIX**-3-Ni, isostructural to the Zn and Cu based **SIFSIX**-3-M,[4d–7] with very high CO_2 selectivity in a wide range of CO_2 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 $NiSiF_6 \cdot xH_2O$. 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 Ni^{2+} and the pyrazine as compared to Zn^{2+} (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 CO_2 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 CO_2 adsorption isotherms is also an indication of stronger/weaker CO_2–**SIFSIX**-3-Ni interactions as compared to the Zn/Cu analogues. Accordingly, the Q_{st} of CO_2 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 CO_2 adsorption is an intrinsic property that dictates the affinity of the MOF toward CO_2, which in turn plays an important role in determining the necessary energy to release CO_2 during the regeneration step. The Q_{st} for CO_2 is in the range of fully reversible CO_2 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 CO_2 adsorption was relatively
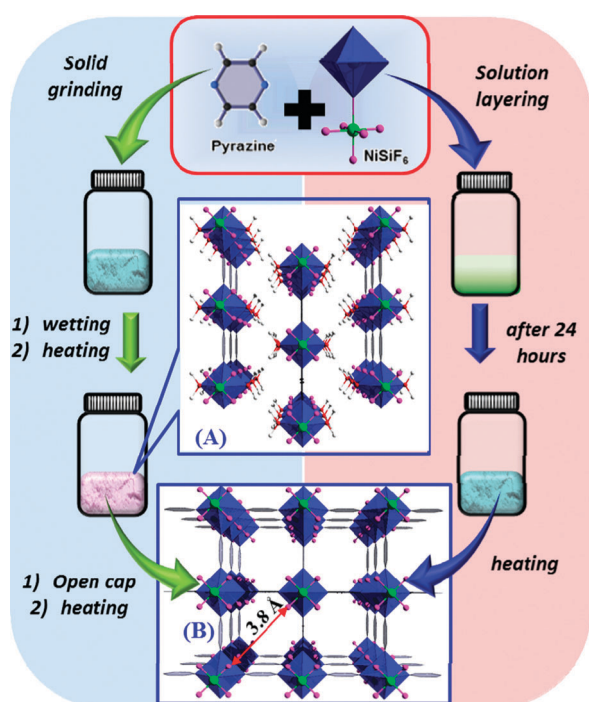
Scheme 1 Schematic representation of the two different preparation procedures for **SIFSIX**-3-Ni. (right) Solvothermal route based on layering methanol solutions of both precursors. (left) Solvent-free route that involves the grinding of precursors, wetting and heating.
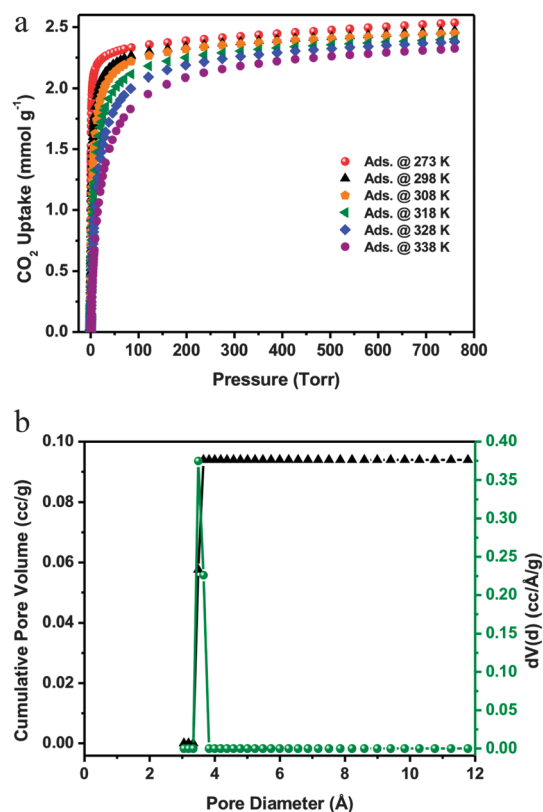

Fig. 1 (a) Variable temperature adsorption isotherms of CO_2 for **SIFSIX**-3-Ni, (b) pore size distribution from CO_2 sorption isotherms at 77 K for **SIFSIX**-3-Ni.
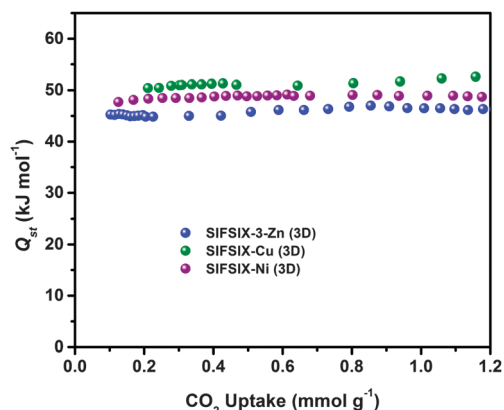
Fig. 2 Isosteric heats of adsorption at low coverage for **SIFSIX**-3-Cu, **SIFSIX**-3-Zn and **SIFSIX**-3-Ni.

Fig. 3 (a) Variable temperature PXRD for phase transition of the 2D ($NiSiF_6 \cdot xH_2O$) to the 3D **SIFSIX**-3-Ni structure, and (b) CO_2 sorption at 298 K during phase transition at different temperatures.

constant indicating homogenous energetic sites over the full range of CO_2 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 CO_2 separation from N_2, O_2, CH_4 and H_2 containing mixtures. The anticipated high selectivity toward CO_2 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 CO_2–MOF interactions and the relatively fast CO_2 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 $NiSiF_6$ 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
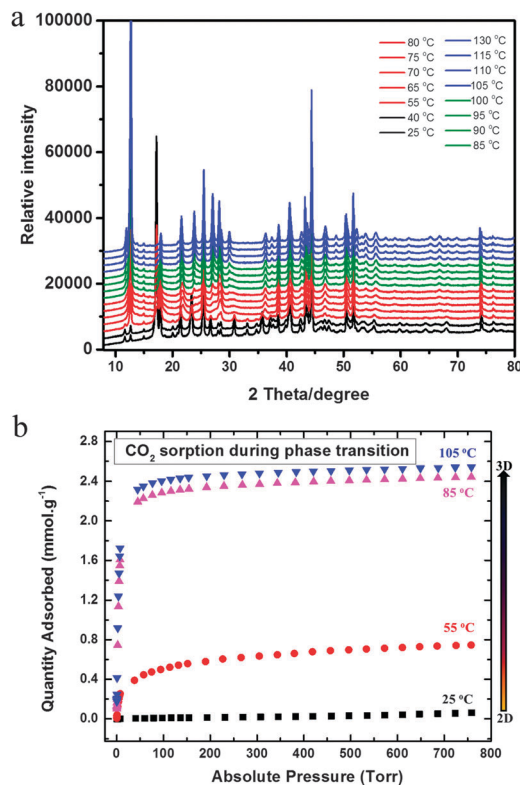
from the solvent-free synthesis as **SIFSIX**-3-Ni (Fig. S1, ESI†). In order to better understand the crystallisation process affording the formation of **SIFSIX**-3-Ni, variable temperature PXRD was conducted (Fig. 3a) from 25 °C to 130 °C. At low temperature (25–40 °C), a first product with a very low crystallinity appeared which corresponds to a 2D structural analogue that was previously reported ($CuSiF_6(pyz)(H_2O)_2$) (**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 CO_2 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 CO_2 adsorption showed an increase in the CO_2 uptake with increased evacuation temperatures up to 105 °C, corresponding to the optimal CO_2 adsorption isotherm which also correlates with the phase change observed in the VT-PXRD and the
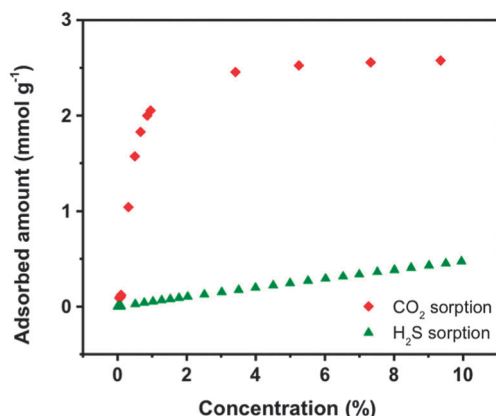
Fig. 4 CO_2 and H_2S sorption isotherms for **SIFSIX**-3-Ni. H_2S uptake remains same after repeated sorption and activation cycles.

complete conversion to 3D **SIFSIX**-3-Ni. The Q_{st} for CO_2 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 CO_2 capture properties of **SIFSIX**-3-Zn and **SIFSIX**-3-Cu[4d,7] analogues, it is expected that the high CO_2 selectivity of **SIFSIX**-3-Ni at intermediate and high CO_2 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 CO_2-humidity and CO_2-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 CO_2 capture, an ideal CO_2 adsorbent should also be tolerant to impurities such as H_2S, since natural gas contains acidic gases in various amounts that can reach high concentration up to 10–20% in the case of H_2S. Accordingly, we have investigated the stability of **SIFSIX**-3-Ni after exposure and adsorption of H_2S. It is worth noting that MOFs known to be stable upon exposure to H_2S are scarce.[13]

The H_2S sorption isotherm was collected for the **SIFSIX**-3-Ni sample and revealed an uptake of H_2S around 1.3 mol g^{-1} at 10% concentration (Fig. 4). The H_2S adsorption isotherm was repeated on the same sample in order to check/confirm the material's stability; the second H_2S 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 H_2S. This unique stability of the **SIFSIX**-3-Ni material in the presence of H_2S was also supported by the similarities between the PXRD patterns before and after the H_2S exposure (Fig. S2, ESI†). The resultant H_2S exposed **SIFSIX**-3-Ni sample was then used for another cycle of CO_2 sorption isotherm studies. Comfortably, the new collected CO_2 adsorption isotherm matched exactly with the adsorption isotherm for the fresh sample not exposed to H_2S as shown in Fig. S5 (ESI†). Certainly, the repeated H_2S exposure did not affect/alter the subsequent capacity of **SIFSIX**-3-Ni for CO_2 and H_2S. It is worth stating that the Cu and Zn analogues are not tolerant to H_2S, unlike the H_2S tolerant **SIFSIX**-3-Ni, and lose their crystallinity and CO_2 uptake capacity upon exposure to H_2S. This further supports the uniqueness of **SIFSIX**-3-Ni and

its prospective use as an excellent adsorbent for CO_2 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 H_2S-tolerant MOF, **SIFSIX**-3-Ni, for practical CO_2 capture in a wide range of CO_2 concentrations, using a solvent-free synthetic approach. The exceptional CO_2 capture and high tolerance to H_2S, 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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