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Short communication

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Isorecticular rare earth fcu-MOFs for the selective removal of H₂S from CO₂ containing gases

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Highlights

- Stable Metal Organic Frameworks (MOFs) with **fcu** underlying topology (UiO-66 like) for H₂S capture
- Ideal for selective capture of H₂S from natural gas even in the presence of CO₂
- Excellent H₂S/CO₂ selectivity with good uptake
- Can be used to produce pure H₂S, with acceptable levels of CO₂, for Claus process

Graphical abstract

Abstract

In this work, we present the implementation of reticular chemistry and the molecular building block approach to unveil the appropriateness of Rare Earth (RE) based Metal-Organic Frameworks (MOFs) with **fcu** topology for H₂S removal applications. Markedly,

RE-**fcu**-MOFs, having different pore apertures sizes in the range of 4.7-6.0 Å and different functionalities, showed excellent properties for the removal of H₂S from CO₂ and CH₄ containing gases such as natural gas, biogas and landfill gas. A series of cyclic mixed gas breakthrough experiments were carried out on three isorecticular **fcu**-MOFs, containing linkers of different lengths (between 8.4 and 5 Å), by using simulated natural gas mixture containing CO₂/H₂S/CH₄ (5%/5%/90%) under different adsorption and regeneration conditions. The **fcu**-MOF platform has good H₂S removal capacity with a high H₂S/CO₂ selectivity, outperforming benchmark materials like activated carbon and Zeolites in many aspects. The comparison of H₂S removal performance with the related structures of the RE-**fcu**-MOFs provides insightful information to shed light on the relationship between the structural features of the MOF and its associated H₂S separation properties. The excellent H₂S/CO₂ and H₂S/CH₄ selectivity of these materials offer great prospective for the production of pure H₂S, with acceptable levels of CO₂ for Claus process to produce elemental sulfur.

Keywords: Metal-organic frameworks (MOFs), Natural gas upgrading, Hydrogen sulfide, Rare Earth **fcu**-MOFs, Claus process

1. Introduction

Hydrogen sulfide (H₂S) is a corrosive, toxic and odorous gas that can be present at variable concentrations from ppm level to more than 20% in different natural gas (NG) wells. The H₂S is also produced during the anaerobic digestion at wastewater treatment plants or fermentation of biodegradable materials,¹ leading to a gas rich of CH₄, but also containing variable concentrations of H₂S and CO₂. The presence of acid gases and particularly H₂S is problematic in the conversion of NG, biogas, and landfill gas to valuable energy vectors. As noted in the occupational safety and health administration (OSHA) standards, exposure to H₂S can be acutely fatal to workers in gas plants, refinery and production sites at concentrations between 500 and 1,000 ppm or higher. The maximum allowable daily exposure without appreciable risk of deleterious effects during a lifetime is 10 ppm as recommended by OSHA for prolonged exposure.² In addition, the lack of controlling H₂S emissions in the industry can affect the capital cost due to the plausible damage of mechanical and electrical equipment used for process control, energy

generation, and heat recovery. When the gas emissions containing H_2S are flared, the combustion of hydrogen sulfide results in the release of sulfur dioxide, another harmful gas pollutant. Therefore, H_2S needs to be removed before any foreseen processing of gas mixtures. There is a variety of deployed methods for the removal of H_2S from NG and biogas and these processes are either physicochemical or biological.¹

Among these processes, the most famous are aqueous amine scrubbing, membrane based separation, and adsorption based separation. The last technology can be divided into two types, depending on the nature of the deployed sorbent; chemical and physical adsorbents. Activated carbons were extensively investigated as physical as well as chemical adsorbents or a combination of both for this purpose.³⁻⁸ Activated charcoal is generally regarded to have one of the best $\text{H}_2\text{S}/\text{CO}_2$ selectivity, owing to its low affinity for CO_2 . Among other traditional adsorbents, zeolites show a high affinity towards both H_2S and CO_2 leading to a low $\text{H}_2\text{S}/\text{CO}_2$ selectivity. Inspired by the liquid amine scrubbing, various studies report on the potential of amine supported materials for tuning the $\text{H}_2\text{S}/\text{CO}_2$ selectivity in relation with the appended amine functionality.⁹⁻¹⁰ The captured H_2S is generally used in Claus process to produce elemental sulfur; however, this H_2S should have none or very low amounts of CO_2 in order to achieve high efficiency conversion.¹¹ Materials that can remove H_2S preferentially over CO_2 can be therefore useful for obtaining H_2S with acceptable quality for Claus process.

Owing to their hybrid character and modular nature, MOFs are regarded as the new generation of porous materials with great prospective to address persisting challenges pertinent to energy and environmental sustainability.¹²⁻¹⁹ Only few examples are reported to show H_2S adsorption on MOFs and even lesser studies pertaining to the MOF stability in the presence of H_2S .²⁰⁻²⁴ It is to be noted, to the best of our knowledge, until very recently²⁴, that no work was carried out on the selective removal of H_2S from CH_4 and CO_2 containing gas streams.

2. Materials and methods

Detailed description of experimental techniques is given in ESI

3. Results and discussion

At this point, we decided to investigate highly stable and tunable rare earth based **fcu**-MOF platform (**RE-fcu-MOF**) developed in our group for the H₂S removal related applications. The series of **RE-fcu-MOFs** were synthesized by applying the molecular building block (MBB) approach,²⁵⁻²⁶ where hexanuclear RE clusters serve as 12-connected MBBs, joined by fluorinated/non-fluorinated and/or homofunctional/heterofunctional ditopic linkers assisted by the modulator and structural directing agent, namely 2-fluorobenzoic acid (2-FBA) as shown in figure 1.²⁵⁻²⁶ Recently, we reported the modular nature of **RE-fcu-MOFs** by deliberately fine-tuning the triangular windows for size exclusion separation of paraffins.²⁶

Figure 1. Assembly strategy for different analogs of **fcu**-MOFs with different linear linkers leading to isorecticular **fcu**-MOFs with different pore-aperture sizes.

We selected three **RE-fcu-MOFs** from the available library of the **RE-fcu-MOF** platform based on their extraordinary stability and structural diversity. The selected MOFs are (i) **Y-FTZB-fcu-MOF**, assembled by using fluorinated and relatively longer ligand 2-fluoro-4-(1H-tetrazol-5-yl)benzoic acid (H₂FTZB)²⁵ (ii) **Y-1,4-NDC-fcu-MOF**, by using 1,4-naphthalenedicarboxylic acid (1,4-H₂NDC), a bulkier linker with a relatively medium length²⁶ and (iii) **Y-fum-fcu-MOF**, by using the shorter fumaric acid (fum) ligand.²⁷

These MOFs differ in pore-aperture size, pore volume and charge density distribution inside the pore system. Precisely, Y-FTZB-**fcu**-MOF has the biggest window pore aperture, large pore volume and a high localized charge density within the pore system due to the mutual presence of tetrazole and fluorine functionalities; on the other hand Y-fum-**fcu**-MOF has the smallest window pore aperture, medium pore volume and a relatively lower localized charge density within its pore system, while Y-1,4-NDC-**fcu**-MOF has medium window pore aperture combined with the smallest pore size and channels decorated with aromatic naphthyl moieties. The apparent BET surface areas and pore volumes for these three MOFs, calculated from Ar adsorption data at 87 K,²⁵⁻²⁷ are presented in Table 1. The powder X-ray diffraction (PXRD) experiments carried out on these MOFs before and after the H₂S exposure, indicated good stability towards H₂S exposure (Figures S1-S3) in addition to the already reported excellent water stability (hydrolytic stability).²⁵⁻²⁷

Table 1. The apparent BET surface areas, pore volumes, H₂S and CO₂ uptake, and H₂S/CO₂ selectivities for the evaluated **fcu**-MOFs

Materials	BET (m ² g ⁻¹)	PV (cm ³ g ⁻¹)	H ₂ S uptake (mmol g ⁻¹)	CO ₂ uptake (mmol g ⁻¹)	H ₂ S/CO ₂
Y-FTZB- fcu -MOF	1310	0.56	0.9	0.22	4
Y-fum- fcu -MOF	691	0.28	1.1	0.17	6.4
Y-1,4-NDC- fcu -MOF	546	0.21	1.5	0.24	6.3

In order to assess the potential of these MOFs for H₂S removal from natural gas, a protocol of cyclic adsorption tests was derived by means of adsorption breakthrough column set-up using simulated natural gas (5%H₂S/5%CO₂/90%CH₄) as shown in Scheme S2. The primary objective of the protocol is to investigate the effect of adsorption and regeneration temperatures and establish the appropriate/optimal adsorption-desorption mode (temperature and vacuum swing modes) as well as asserting the

recyclability of the evaluated MOF. The protocol (Scheme S2) for testing the materials is comprised of six cycles of adsorption-desorption based on the combination of temperature swing regeneration (TSR) and vacuum swing regeneration (VSR) modes. In the first and second cycles, adsorption breakthrough experiments were carried out at 25 °C and 50 °C, respectively, after optimal activation of YFTZB-**fcu**-MOF, Y-1,4-NDC-**fcu**-MOF and Y-fum-**fcu**-MOF at 160 °C. In the third and fourth cycles, adsorption breakthrough experiments were carried out at 25 °C after regeneration at 50 °C and 25 °C, respectively. The fifth cycle was carried out at 50 °C after 50 °C regeneration, while the sixth cycle was carried out under the same condition as the first cycle in order to demonstrate the recyclability of the evaluated material.

The adsorption column breakthrough experiments (cycles 1 and 2) with (5% H_2S /5% CO_2 /90% CH_4) gas mixture (flow rate 10 cm^3/min) for Y-FTZB-**fcu**-MOF at 25 °C and 50 °C after optimal activations are shown in Figure 2. It can be seen that at 25 °C, H_2S is adsorbed almost four times higher than CO_2 as evidenced by the retention times of ≈ 42 min/g for H_2S and of ≈ 10 min/g for CO_2 . The retention times correspond to ≈ 0.9 and 0.22 mmol/g uptake of H_2S and CO_2 , respectively. Upon increasing the temperature of adsorption to 50 °C, H_2S retention time decreases by almost half (25 min/g), while CO_2 retention time remains almost unaltered (9 min/g). This is in good agreement with the reported high CO_2 / framework interactions at lower loading for FTZB-**fcu**-MOF.²⁴ The Y-FTZB-**fcu**-MOF can be completely regenerated at 50 °C, while regeneration at 25 °C resulted in a small decrease ($\approx 10\%$) of the H_2S removal performance (Figure S4). The excellent recyclability of the material is confirmed by the unaltered performance after the completion of six cycles (Figures S5).

Figure 2. Column breakthrough tests (cycles 1 and 2) for Y-FTZB-**fcu**-MOF with H₂S/CO₂/CH₄ (5%/5%/90%) at 25 °C and 50 °C at 1 bar total pressure (10 cm³/min flow rate).

Interestingly, Y-1,4-NDC-**fcu**-MOF showed a much higher retention time for H₂S (≈ 70 min/g) under similar experimental conditions at 25 °C but with a similar retention time for CO₂ (≈ 11 min/g) as compared to Y-FTZB-**fcu**-MOF (Figure 3). The corresponding uptake derived from retention times of H₂S and CO₂ is 1.5 mmol/g and 0.24 mmol/g respectively. The H₂S/CO₂ selectivity of ≈ 6 -7 for Y-1,4-NDC-**fcu**-MOF was found to be among the highest values reported so far, suggesting that the Y-1,4-NDC-**fcu**-MOF is a suitable adsorbent for the selective removal of H₂S in presence of CO₂. Upon increasing the temperature to 50 °C, retention times for both H₂S (≈ 40 min/g) and CO₂ (≈ 6 min/g) decreased significantly; however, H₂S/CO₂ selectivity remained unchanged. This relative enhancement of H₂S/CO₂ selectivity upon substitution of FTZB by 1,4-NDC linker can be explained by the lessened CO₂/framework interactions, combined with the enhanced H₂S condensability induced by the reduced pore system size and the presence of naphthalene moiety. Remarkably, Y-1,4-NDC-**fcu**-MOF can be completely regenerated at 25°C (Figure S9), promoting this adsorbent as a strong candidate for industrially important and

economical processes, vacuum swing regeneration (VSR) or pressure swing regeneration (PSR). Moreover, after the six cycles, the performance of the Y-1,4-NDC-**fcu**-MOF was unaltered, affirming its excellent recyclability (Figure S10). It is worth to be mentioned that unlike these RE-**fcu** MOFs, Cu-based MOFs described in the open literature for H₂S adsorption are not recyclable. Reported studies showed that H₂S reacts irreversibly with the copper center of the CuBTC MOF to form copper sulfide.^{28,29} In addition, it is admitted that CuBTC MOF suffers from its limited stability in the presence of moisture.³⁰

Figure 3. Column breakthrough tests (cycles 1 and 2) for Y-1,4-NDC-**fcu**-MOF with H₂S/CO₂/CH₄ (5%/5%/90%) at 25 °C and 50 °C at 1 bar total pressure (10 cm³/min flow rate).

In order to assert the plausible effect of the naphthalene moiety on the H₂S/CO₂ removal capabilities, we evaluated the adsorption properties of another isorecticular **fcu**-MOF encompassing a relatively shorter linker. Namely, Y-fum-**fcu**-MOF, another isorecticular analog of Y-1,4-NDC-**fcu**-MOF with close pore size and volume but lacking the naphthalene moiety, showed a similar behavior as of Y-1,4-NDC-**fcu**-MOF with slightly lower retention times for H₂S (50 min/g) and CO₂ (8 min/g) at 25 °C (Figure 4). The Y-fum-**fcu**-MOF can be also easily regenerated at 25 °C (Figure S11) and its

performance remained unaltered after the six cycles (Figure S12). In this case, the corresponding uptake derived from retention time for H₂S and CO₂ is 1.1 mmol/g and 0.17 mmol/g respectively

Figure 4. Column breakthrough tests (cycles 1 and 2) for Y-fum-fcu-MOF with H₂S/CO₂/CH₄ (5%/5%/90%) at 25 °C and 50 °C at 1 bar total pressure (10 cm³/min flow rate).

The present comparative study pertaining to H₂S/CO₂ separation performance of various fcu-MOFs in relation to their respective structural/functional features, within the same platform, provided some insightful information about the structure/property relationship. For instance, as the surface area and the pore volume decreased from Y-FTZB-fcu-MOF to Y-fum-fcu-MOF to Y-1,4-NDC-fcu-MOF, the H₂S uptake increased at a lower concentration. This suggests that MOFs with small cavities are suitable adsorbent candidates for the removal of H₂S at a relatively low concentrations and pressures, as H₂S is prone to interact more strongly with the framework in the case of narrow pore systems and promote significant adsorption at relatively lower concentrations. In the case of the Y-FTZB-fcu-MOF, the adsorbent offered some additional specific sites (positioning of the tetrazole and fluorine moieties in close

proximity) with a strong affinity for CO_2 ²⁴ that resulted in the observed lessened $\text{H}_2\text{S}/\text{CO}_2$ selectivity as compared to Y-fum-**fcu**-MOF and Y-1,4-NDC-**fcu**-MOF where such CO_2 specific sites were not present. As evidenced by the mild regeneration conditions for these two MOFs, there are no specific adsorption sites in the MOF offering very high affinity for H_2S and CO_2 . Both gases (CO_2 and H_2S) were adsorbed in the octahedral and tetrahedral cages of the **fcu** MOFs and mainly by virtue of conventional weak dispersive interactions between the guests and the framework. Prominently, in the absence of CO_2 specific adsorption sites, a framework with a relatively more confined pore system is envisioned and expected to offer a higher affinity for H_2S than CO_2 by the virtue of the plausible higher condensability of H_2S . Notably, Y-1,4-NDC-**fcu**-MOF and Y-fum-**fcu**-MOF offered a relatively contracted pore system that was found to be in the ideal range for the limited CO_2 adsorption and promoted a more pronounced H_2S adsorption at the given concentrations (5% H_2S /5% CO_2 /90% CH_4), resulting in the high $\text{H}_2\text{S}/\text{CO}_2$ selectivity associated with mild regeneration conditions for these **fcu**-MOF adsorbents.

Markedly, additional experiments on the top performing adsorbent in the **fcu**-MOFs (namely, Y-1,4-NDC-**fcu**-MOF) suggest that the notable H_2S removal performance remained practically unaltered under humid conditions (Figure S6). Comparison of the adsorption breakthrough experiments before and after exposure to humidity asserted that the MOF adsorbent is fully recyclable after exposure to humidity (Figure S7). Adsorption column breakthrough experiments with 5% $\text{H}_2\text{S}/95\%\text{CH}_4$ gas mixture in the absence of CO_2 also resulted in a similar uptake for H_2S , confirming the results with ternary mixture (Figure S8). Comparison of the performance of the Y-1,4-NDC-**fcu**-MOF with other framework materials like Activated Charcoal (NORIT ROW 0.8 SUPRA, Sigma Aldrich) (Figure S13) highlighted further the superior properties of Y-1,4-NDC-**fcu**-MOF. Precisely, the Y-1,4-NDC-**fcu**-MOF adsorbent offers a much higher H_2S uptake and $\text{H}_2\text{S}/\text{CO}_2$ selectivity than the activated charcoal.

4. Conclusions

In summary, we unveiled a series of stable and H_2S selective isorecticular rare earth MOFs with the **fcu** underlying topology, RE-**fcu**-MOFs. These highly stable MOFs were

investigated for H₂S removal from natural gas in the presence of CO₂ by multiple cyclic adsorption breakthrough experiments. The comparison of H₂S removal performance with their respective structures revealed the importance of the pore system size and functionality, e.g. the presence of the naphthalene moiety contributed to the enhanced H₂S uptake. The studies on the relationship between structural features and H₂S/CO₂ adsorption properties of the RE-**fcu**-MOFs allowed for further understanding of the notable H₂S removal performance of these MOF adsorbents. Notably, the evaluated **fcu**-MOFs offer high uptakes with very high H₂S/CO₂ selectivities and outperform benchmark materials like activated charcoal. The unique properties of the **fcu**-MOFs, a high H₂S selectivity vs. CO₂, offer great prospective for the production of high-quality H₂S that can be used in Claus process without loss of efficiency. Prominently, the **fcu**-MOF platform offers great potential for further fine-tuning, adjustment of the pore system size and functionality, in order to achieve efficient removal of H₂S at low or high pressures akin to the operating feed conditions for real natural gas, biogas and landfill gas streams, prior the upgrading process. Further studies are underway and are expected to provide additional insights on the structure-property relationship governing the H₂S/CO₂ separation properties of other highly stable MOF platforms.

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