Metal-Organic Frameworks with Potential Application for SO_2-Separation and Flue Gas Desulfurization

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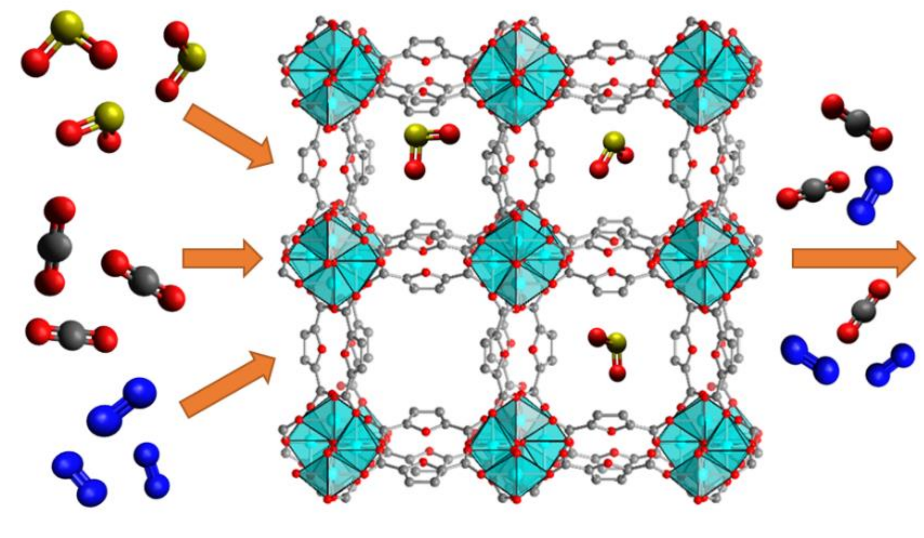
Introduction

Sulfur dioxide (SO_2) is an acidic and toxic gas and its emission from utilizing energy from fossil fuels or in industrial processes harms human health and environment.[1] Therefore, it is of great interest to find new materials for SO_2-sorption to improve classic flue gas desulfurization (FGD). We present SO_2 sorption investigations for MOF-177, NH_2-MIL-125(Ti) and MIL-160. MOF-177 shows exceptional maximal loadings for SO_2 whereas NH_2-MIL-125(Ti) and MIL-160 are examined in more detail for their potential in selective separation of SO_2 gas from other flue gas components.



MIL–160

Results

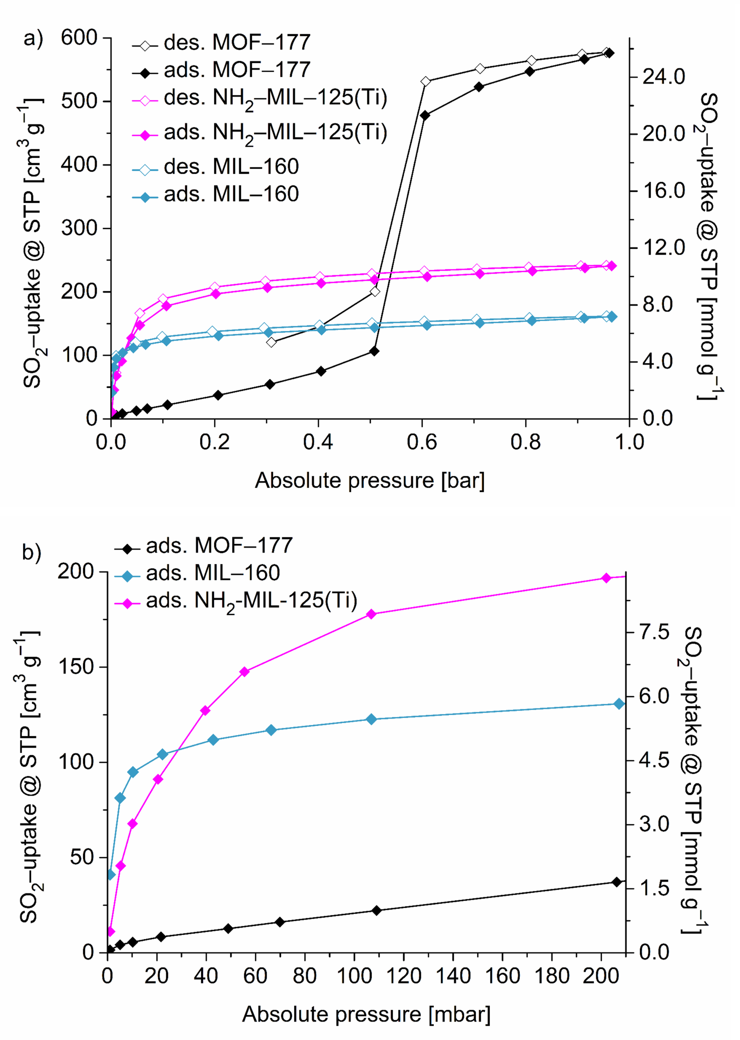


Fig. 1: SO_2-isotherms of MOF-177, NH_2-MIL-125(Ti) and MIL-160 at 293 K.

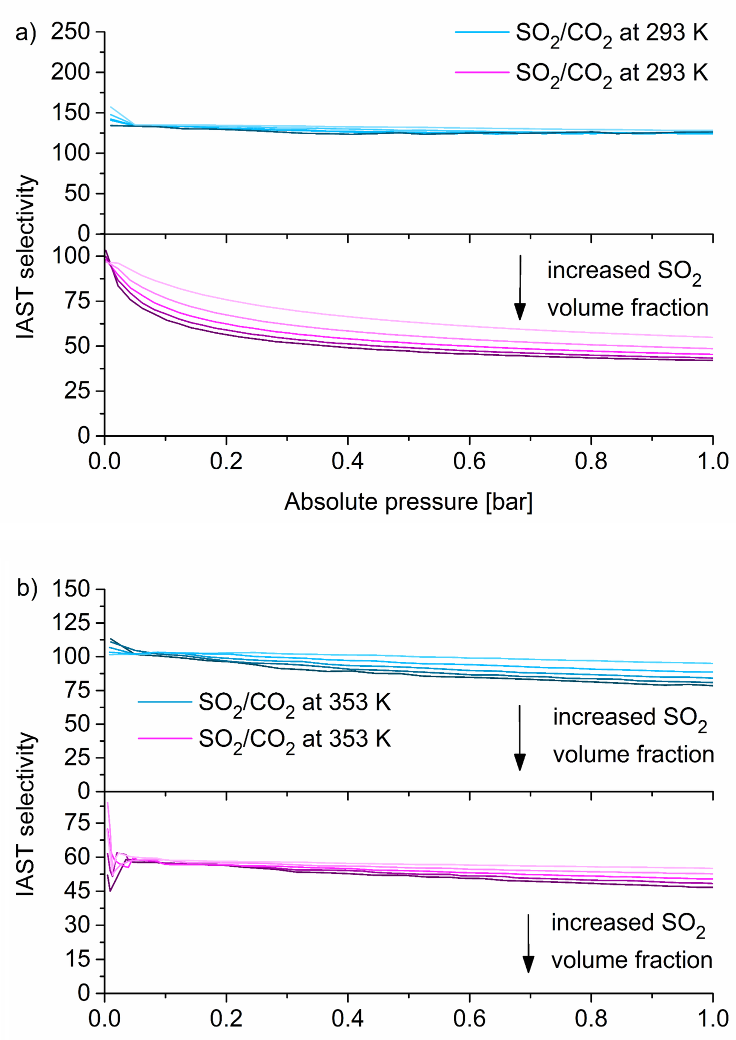


Fig. 2: IAST selectivities of MIL-160 and NH_2-MIL-125(Ti) with SO_2/CO_2 10/90-50-50; v:v at 293 K (a) and 353 K (b).

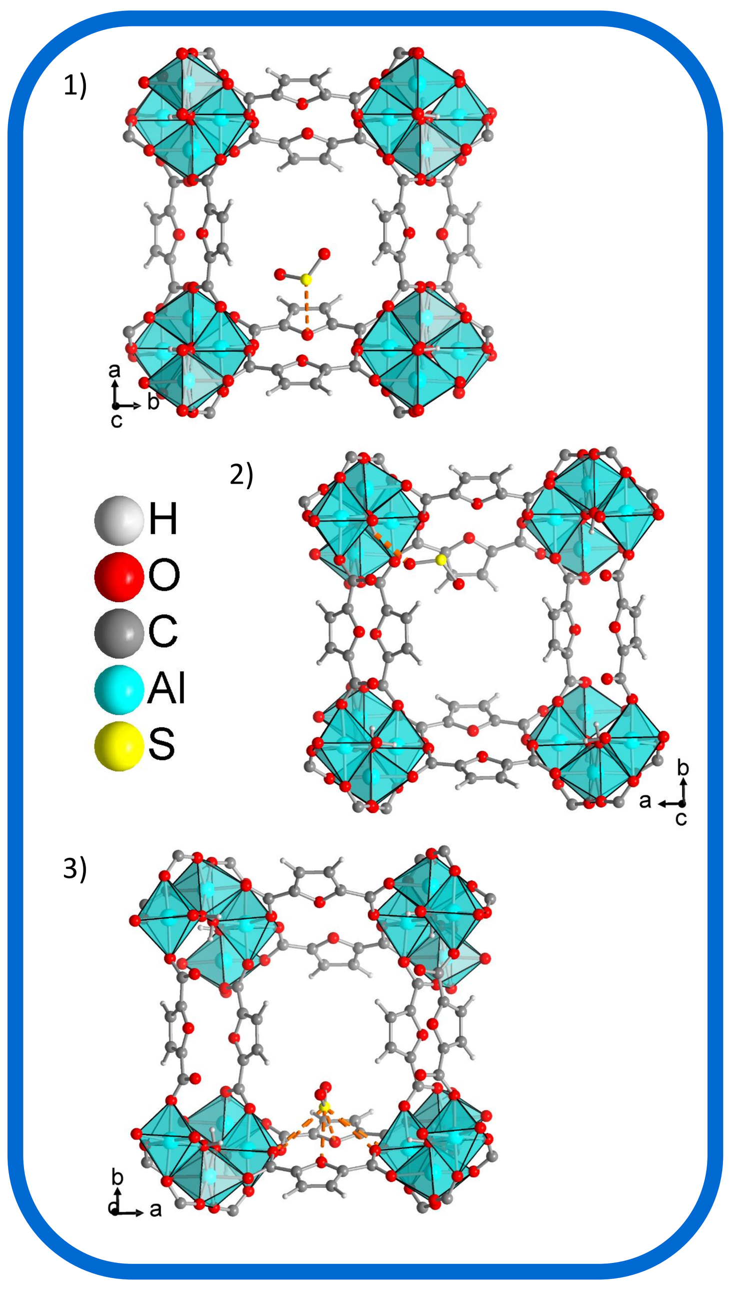


Fig. 3: Density functional theory (DFT) simulated binding sites of SO_2 in MIL-160: 1) $O_{furan}\cdots S_{SO2}$, 2) $O_{HAl\text{-}chain}\cdots O_{SO2}$ and 3) $O_{furan/carboxylate}\cdots S_{SO2}$.

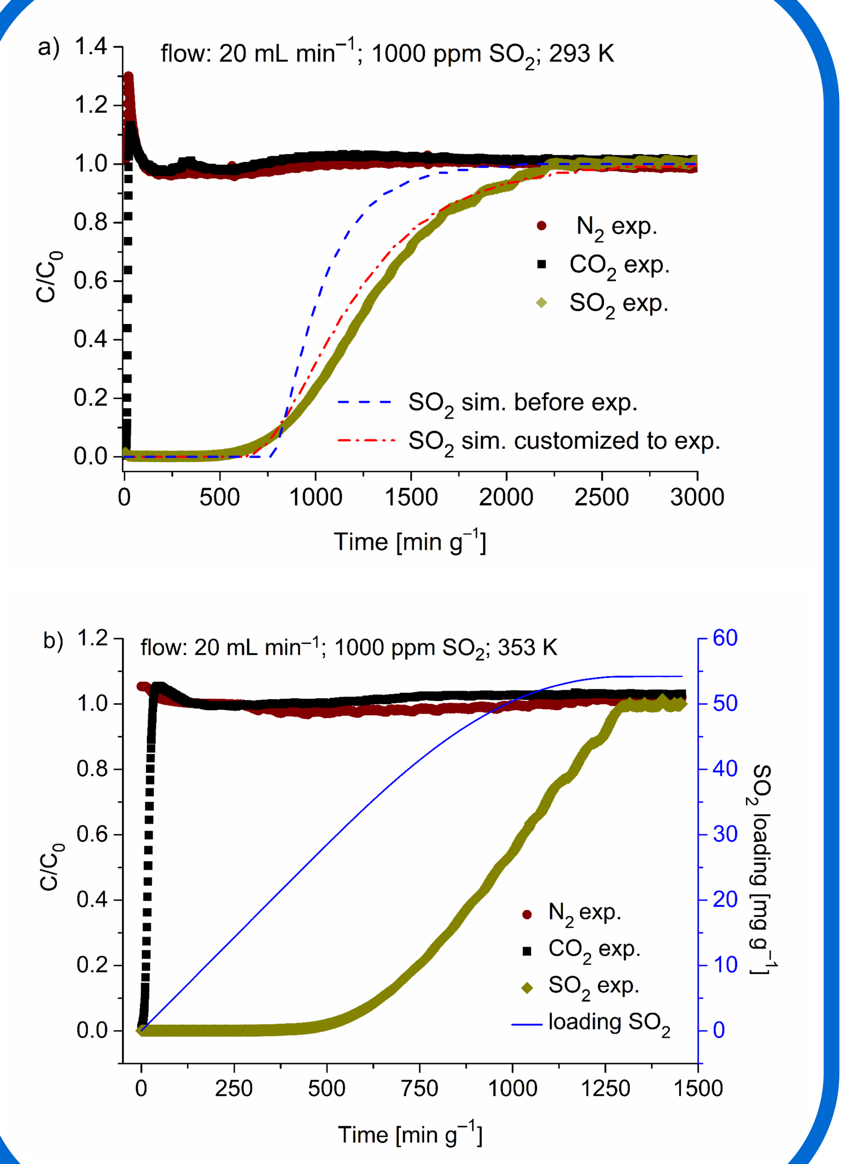


Fig. 4: Experimental an simulated breakthrough curves for MIL-160 at 293 K (a) and 353 K (b).

a) Simulations are in good agreement with experiments

b) High retention time for SO_2, even at elevated temp. (353 K)

gas mixture: according to flue gas composition from air-fired coal combustion ($N_2/CO_2/SO_2$; 84.9/15.0/0.1; v:v:v).[2]

Tab. 1: Overview of stability and sorption performance for MIL-160.

Material	BET [m² g⁻¹]	BET after dry SO_2 [m² g⁻¹]	BET after humid SO_2 (175 ppm h at 75% RH) [m² g⁻¹]	SO_2-uptake (isotherm) at 0.001; 0.01, 1 bar at 293 K [mmol g⁻¹]	SO_2-uptake (breakthrough exp.) with 0.1; 1; 100% SO_2 at 293 K [mmol g⁻¹]
MIL-160	1170	1170	1130	1.8; 4.2; 7.2	1.2; 3.7; not measured

High stability

High performance at low SO_2 concentrations

Conclusion

MOF-177 showed a record maximum SO_2 uptake of 25.7 mmol g^{-1} at 293 K and 1 bar but turned out to be unsuitable for flue gas desulfurization (FGD) applications due to its chemical instability and low adsorption at low partial pressures of SO_2. NH_2-MIL-125(Ti) showed promising properties in IAST selectivity and breakthrough simulations for SO_2 but not as good as MIL-160, which exhibited outstanding performances in terms of SO_2/CO_2 selectivity, onset breakthrough time, stability towards SO_2 under dry and humid conditions. These properties make MIL-160 a promising material for FGD applications.

References

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[2] Jia, L.; Tan, Y.; Anthony, E. J. Emissions of SO_2 and NO_x during Oxy–Fuel CFB Combustion Tests in a Mini-Circulating Fluidized Bed Combustion Reactor. *Energy Fuels* **2010**, *24*, 910–915.

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