Supporting Information.

Adsorptive desulfurization with CPO-27/MOF-74: an experimental and computational investigation

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Details about the computational modelling

Basis sets

The pseudopotential-based correlation-consistent valence-X-ξ basis sets with polarization functions by Peterson et al.,[1] cc-pVXZ-PP, were employed for transition metal ions while Dunning's[2] correlation-consistent valence-X-ξ basis sets with polarization functions, cc-pVXZ, were used for the other atoms. X stands for multiple basis functions describing valence atomic orbitals (valence double (D), triple (T), quadruple-ξ, etc.). The corresponding augmented correlation-consistent valence-X-ξ basis sets with polarization functions, aug-cc-pVZX-CC and aug-cc-pVXZ, were also used. The above-mentioned basis sets are abbreviated as VXZ, AVXZ for standard and augmented basis sets, respectively.

Electronic structure of *cus* sites of CPO-27(X) and $F_2W(X)$

The theoretical description of adsorbate interactions with transition metal structures (Cu^{2+}, Co^{2+} and Ni^{2+}) in the CPO-27(X) framework is complicated due to (i) the possibility of multi-reference character of the wave function and (ii) spin coupling of unpaired electrons within the structure. The relative stability of a high-spin and low-spin states was evaluated for Co^{2+} and Ni^{2+} for $F_2W(X)$ cluster models and $F_2W(X)$-S complexes at the multi-reference CASPT2/VTZ level, using geometries of $F_2W(X)$ clusters optimized in a high-spin electronic configuration. The high-spin electronic configuration (Triplet for Ni^{2+} and Quadruplet for Co^{2+}) is preferred for both; the energetic splitting is 163 kJ mol^{-1} and 179 kJ mol^{-1} for

$F_2W(Ni)$ and $F_2W(Ni)$-S and 155 kJ mol^{-1} and 156 kJ mol^{-1} for $F_2W(Co)$ and $F_2W(Co)$-S. Therefore, the high-spin electronic configuration, which can be described with just a single-reference wavefunction, is employed on each X^{2+} ion in all the following calculations.

The spin coupling between Cu^{2+} ions with an unpaired electron in the CPO-27(Cu) framework can be either ferromagnetic (high-spin configuration, whereby spins on every Cu^{2+} are aligned in the parallel way) or antiferromagnetic (low-spin configuration, whereby spins on every Cu^{2+} are aligned in the antiparallel way). The calculated interaction energies for CPO-27(Cu) were -56.9 kJ mol^{-1} for both high-spin/low-spin electron configurations and -56.8 kJ mol^{-1} for the closed-shell solution, which does not consider spin-polarization. Therefore, the high-spin configuration on the X^{2+} ions describes well the proposed CPO-27(X) models, and will be used for all calculations.

CCSD(T)/CBS with AVTZ/AVQZ extrapolation scheme

The accuracy of CCSD(T)/CBS results with AVTZ/AVDZ extrapolation scheme was verified with higher-level AVTZ/AVQZ extrapolation for $F_2W(Mg)$ and $F_2W(Zn)$ models containing metal ions with closed-shell electronic structure. The CCSD(T) interaction energies for the $F_2W(Zn)$ model are -12.5 kJ mol^{-1}and -12.7 kJ mol^{-1}for AVDZ/AVTZ and AVTZ/AVQZ extrapolation scheme, respectively. The interaction energies for $F_2W(Mg)$ model are -13.9 kJ mol^{-1}and -14.2 kJ mol^{-1} for AVDZ/AVTZ and AVTZ/AVQZ extrapolation scheme, respectively. The energy difference between CCSD(T)/CBS results extrapolated to lower/higher-order basis sets is less than 0.3 kJ mol^{-1}. Thus, the CCSD(T)/CBS results obtained with AVDZ/AVTZ basis sets can serve as the benchmark calculations which can be used to evaluate the accuracy of other methods.
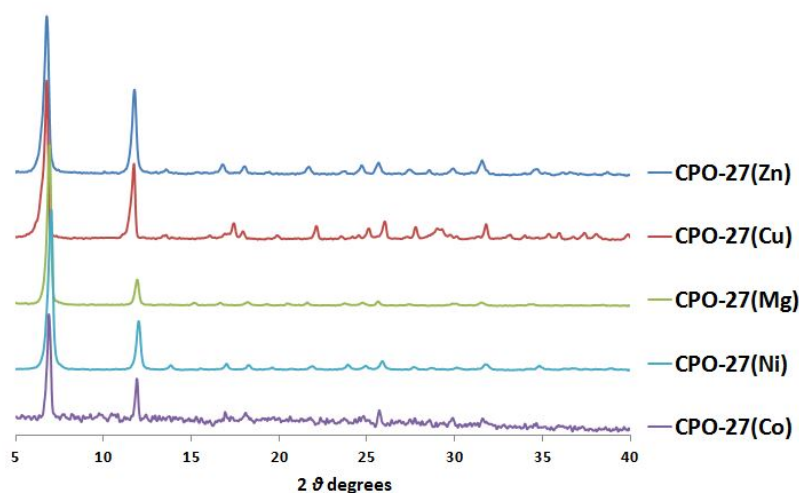
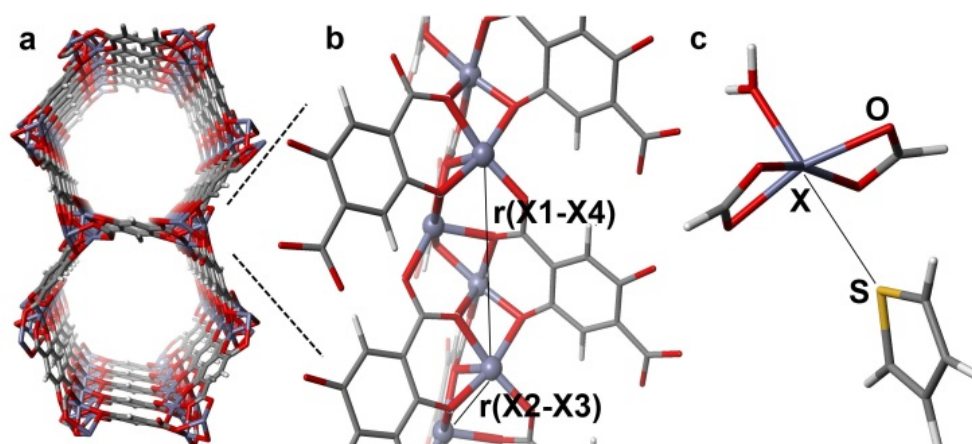**Figure S1.** XRD patterns of the synthesized CPO-27 samples

Figure S2. (a) Unit cell of CPO-27(X) viewed along the one-dimensional channel; (b) Detail of a helical chain of CPO-27(X) formed by *cis*-oriented DHBDC organic linkers connected to the *cus* sites of the metal X^{2+} ions; r(X2-X3) denotes the distance between adjacent *cus* centres and r(X1-X4) is the distance between the two closest metal ions along *c* accessible from the same channel. (c) The cluster model denoted $F_2W(X)$-S. X, O and S atoms are depicted in blue, red, and yellow, respectively.
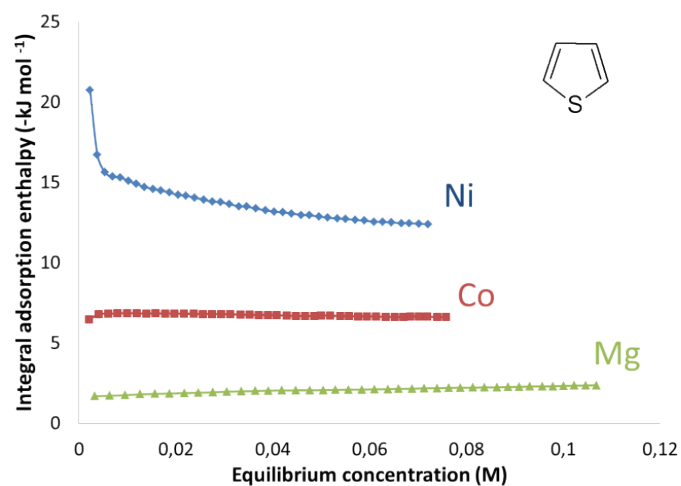
Figure S3. Integral adsorption enthalpies ΔH ($-$kJ mol^{-1}) of thiophene as a function of equilibrium concentration (mol L^{-1}) for CPO-27(Ni,Co,Mg).
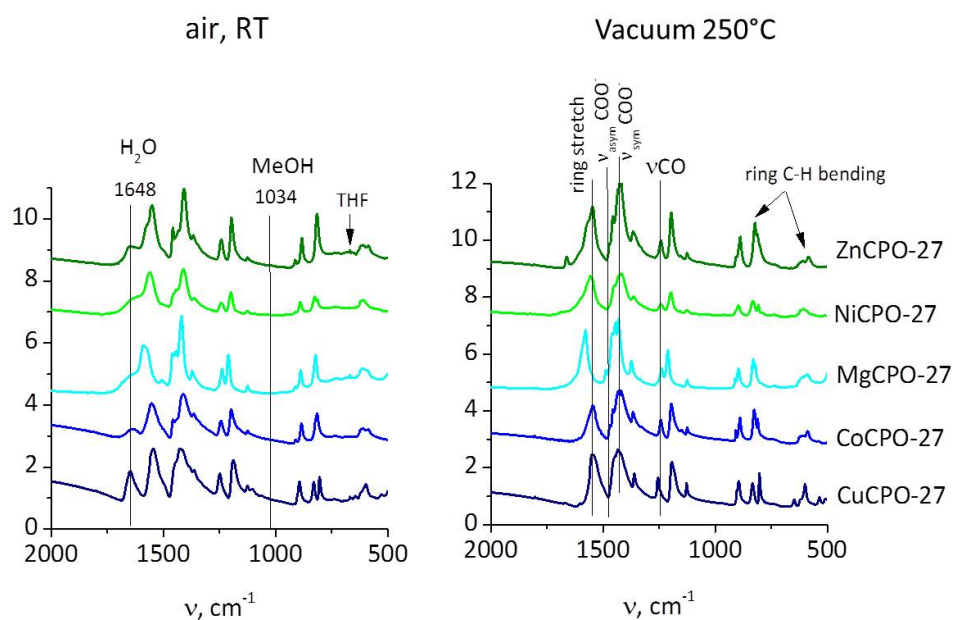

Figure S4. IR spectra of CPO-27 materials at room temperature in air (left) and under vacuum at 250 C (right).
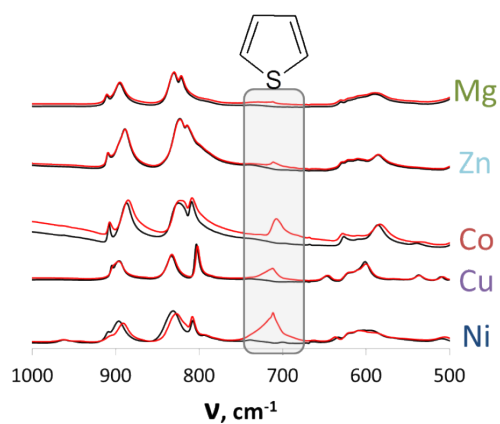
Figure S5. Normalized FTIR spectra at room temperature of an empty framework (black lines) and after adsorption of thiophene (red lines) from the vapour phase (80 mbar) monitoring a complex thiophene interaction band between 730-680 cm^{-1}.
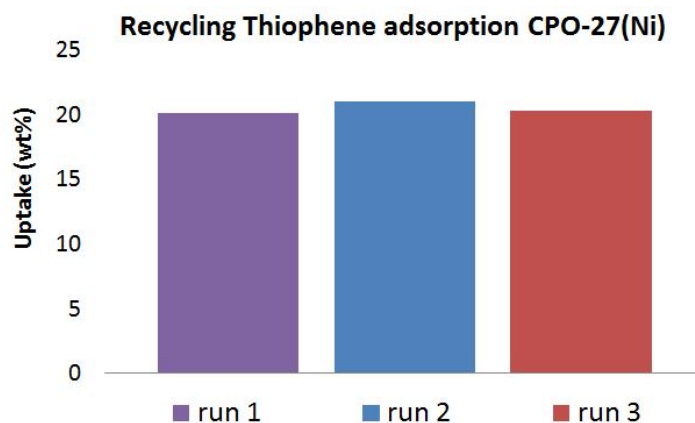

Figure S6. Consecutive adsorption runs for a 0.3M solution of thiophene from heptane:toluene (80:20) on CPO-27(Ni)

Table S1. Affinities of the CPO-27 series of materials for sulfur compounds in L mol^{-1}.

L mol^{-1}	TPH	BT	DBT	DMDBT
CPO-27(Ni)	290	27000	290000	1000
CPO-27(Co)	100	3700	150000	650
CPO-27(Mg)	64	560	11000	160
CPO-27(Cu)	15	400	1400	530
CPO-27(Zn)	18	130	530	20

Table S2. Interaction energies of thiophene with $F_2W(X)$ cluster models[a] calculated at various levels of theory.

| F2W(X) | ΔE_{int} | | | | | | | r(XS)[b] |
| | CCSD(T) | MP2 | | PBE | | B3LYP | vdW | PBE |
	CBS	VTZ	CBS	VTZ	PAW[c]	VTZ	PAW[c]	VTZ
Cu	-11.3	-9.2	-11.9	-2.8	-3.1	0.2	-11.4	3.544
Zn	-12.5	-9.6	-13.1	-3.1	-3.4	0.7	-13.1	3.517
Mg	-13.9	-11.4	-14.8	-4.2	-4.4	0.6	-13.9	3.327
Co	-17.7	-11.7	-19.0	-6.6	-7.8	7.1	-17.6	2.847
Ni	-17.0	-6.8	-17.7	-14.7	-17.1	4.1	-22.7	2.489

[a] In kJ mol^{-1}; all energies corrected for BSSE. [b] X^{2+}-S distance in Å, [c] Energy cut-off 600 eV

REFERENCES

1.   K. Peterson and C. Puzzarini, *Theor. Chem. Acc.*, 2005, **114**, 283–296.

2.   T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007.