Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

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.

Additional figures and tables

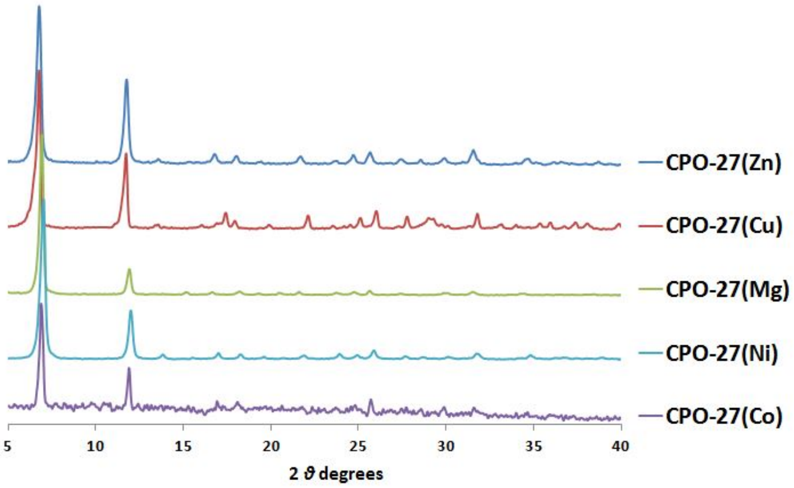

Figure S1. XRD patterns of the synthesized CPO-27 samples

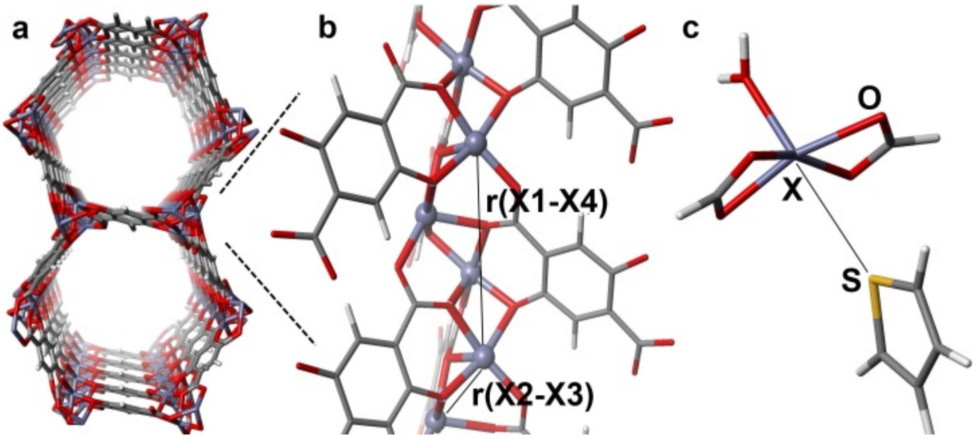

Figure S2. (a) Unit cell of CPO-27(X) viewed along the one-dimensional channel; (b) Detail of a helical chain of CPO-27(X) formed by *cis*-oriented DHBDC organic linkers connected to the *cus* sites of the metal X^{2+} ions; r(X2-X3) denotes the distance between adjacent *cus* centres and r(X1-X4) is 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.

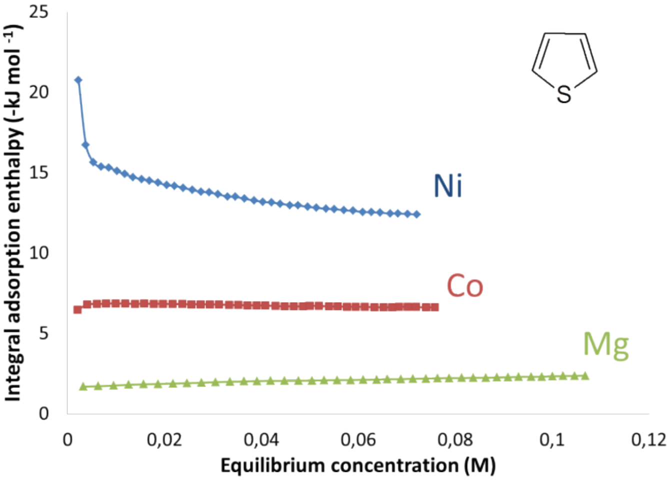

Figure S3. Integral adsorption enthalpies ΔH (−kJ mol^{-1}) of thiophene as a function of equilibrium concentration (mol L^{-1}) for CPO-27(Ni,Co,Mg).

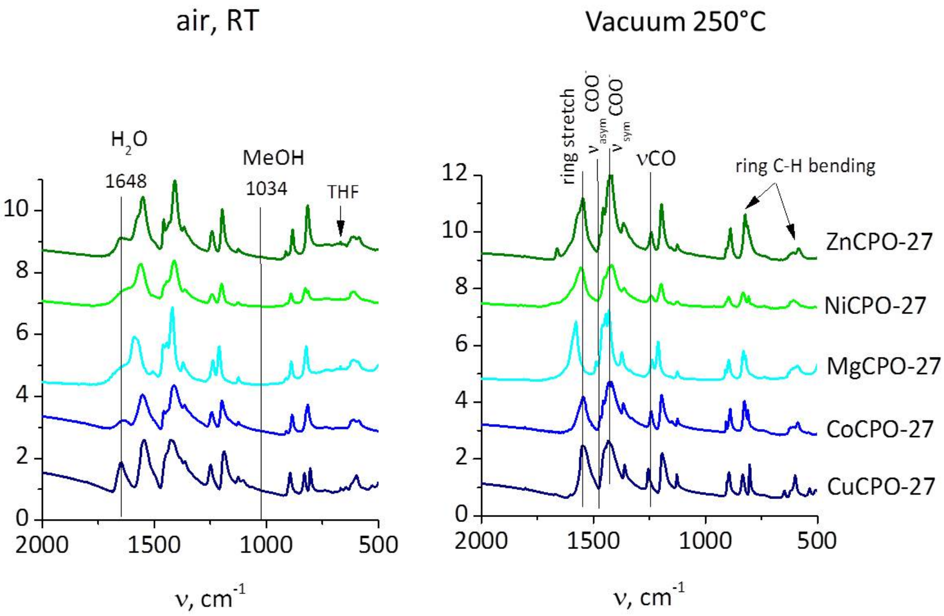

Figure S4. IR spectra of CPO-27 materials at room temperature in air (left) and under vacuum at 250 C (right).

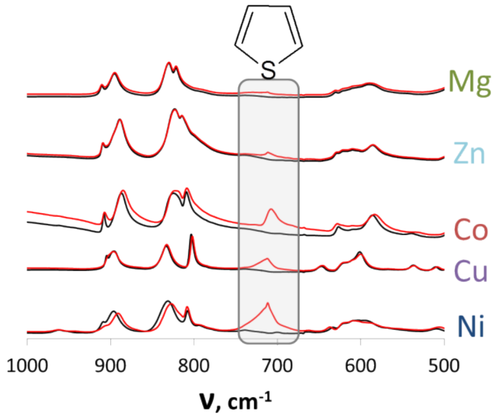

Figure S5. Normalized FTIR spectra at room temperature of an empty framework (black lines) and after adsorption of thiophene (red lines) from the vapour phase (80 mbar) monitoring a complex thiophene interaction band between 730-680 cm^{-1}.

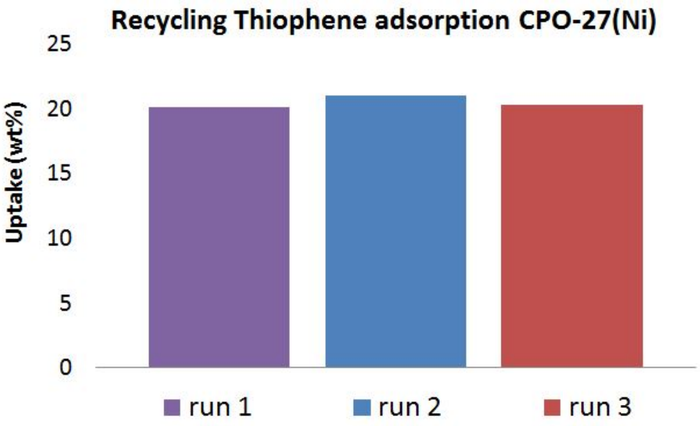

Figure S6. Consecutive adsorption runs for a 0.3M solution of thiophene from heptane:toluene (80:20) on CPO-27(Ni)

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.

	ΔE_{int}							r(XS)[b]
	CCSD(T)	MP2		PBE		B3LYP	vdW	PBE
F2W(X)	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.