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

Electronic Supplementary Information to A theoretical study of adsorption on iron sulfides towards nanoparticles modeling

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1 Slab Models

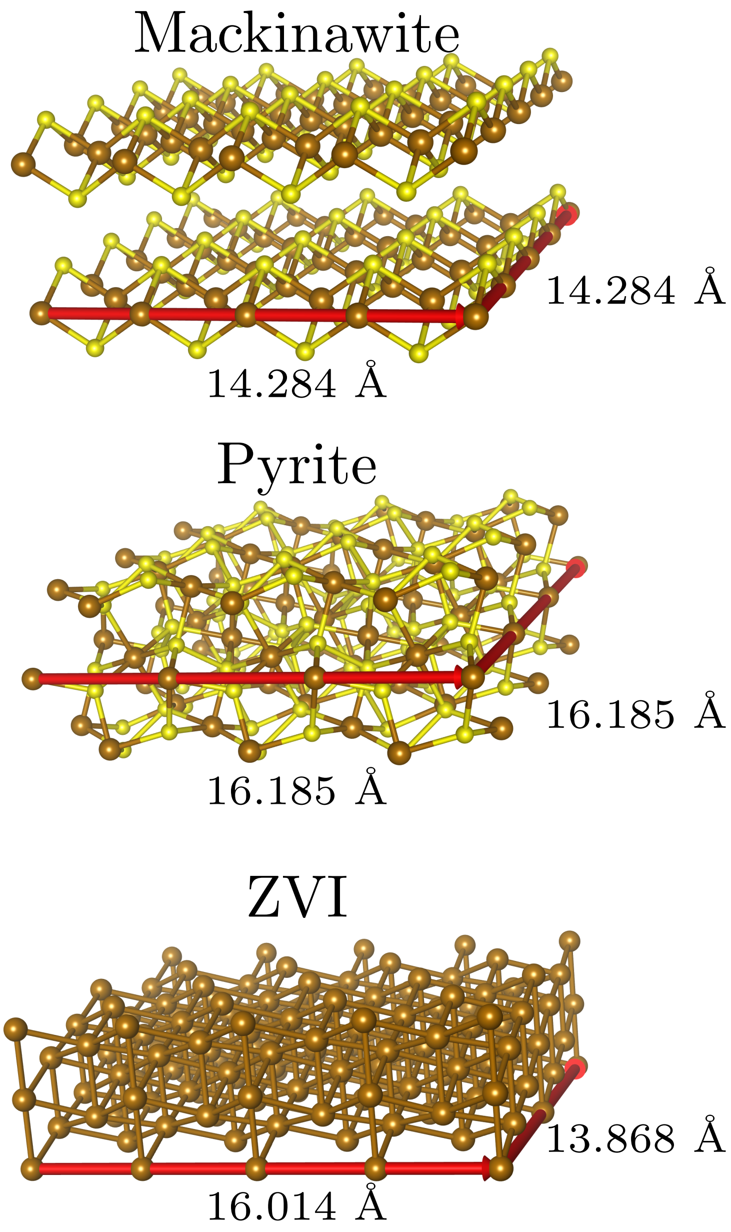

Figure S1: Slab supercells used for calculations: mackinawite(001), pyrite(001) and zero valent iron(111).

2 Testing of Dispersion Corrections

It is worthy to note that we observed empirical correction to dispersion as important also for mackinawite a lattice constant which was not desirable. We therefore calculated how various type of empirical correction to PBE DFT affect the a lattice constant in 2D mackinawite (monolayer FeS). The changes in a lattice constant (collected in Table S1) were in hundredths of Å which we considered as non-negligible. Usage of these correction should be therefore always carefully considered and, for instance, tested with fixed a lattice constant, as was done in present study.

Table S1: Calculated c and a lattice constants (in Å) of bulk mackinawite and a lattice constant (in Å) of 2D (monolayer) mackinawite obtained by PBE density functional in conjunction with several corrections schemes for dispersion.[1] Two different PAW pseudopotentials for Fe atoms were compared.

	standard PAW^a		small-core PAW^b		2d structure	
Method	c	a	c	a	a^a	a^b
PBE	5.765	3.595	5.276	3.576	3.5926	3.5882
PBE-D2	4.903	3.564	4.789	3.551	3.5536	3.5500
PBE-D3	**5.046**	3.584	**4.924**	3.571	3.5823	3.5747
PBE-D3/BJ^c	4.868	3.568	4.756	3.555	3.5648	3.5589
PBE-TS	4.897	3.578	4.810	3.564	3.5713	3.5657
PBE-TS/HI^d	4.939	3.584	4.861	3.568	3.5810	3.5740
PBE-dDsC	4.984	3.568	4.857	3.556	3.5673	3.5635
Exp.[2]	5.080	3.680				
Exp.[3]	5.033	3.674				

^{a} Fe PAW pseudopotential with $4s3d$ configuration (8 electrons are explicitly treated), ^{b} Fe PAW_sv pseudopotential with $3s3p4s3d$ configuration (16 electrons are explicitly treated), ^{c}D3 method with Becke-Jonson damping, ^{d}Tkatchenko-Scheffler method with iterative Hirshfeld partitioning.

3 Magnetic States of Mackinawite

Table S2: Adsorption energies E_{ads} for H_2O, H_2S and TCE molecules on surfaces of nonmagnetic (NM) mackinawite (mac) and stripe anti-ferromagnetic (SAFM) mackinawite slab. All energies are in kcal/mol. Note that SAFM mackinawite a lattice constant obtained from optimization is significantly larger ($a = 3.823$ Å) than experimental one ($a = 3.674$ Å) used for NM calculations.

System	E_{ads}	System	E_{ads}
$\mathrm{mac_{NM}} \cdots \mathrm{OH_2}$	-5.1	$\mathrm{mac_{SAFM}} \cdots \mathrm{OH_2}$	-4.2
$\mathrm{mac_{NM}} \cdots \mathrm{SH_2}$	-6.1	$\mathrm{mac_{SAFM}} \cdots \mathrm{SH_2}$	-5.4
$\mathrm{mac_{NM}} \cdots \mathrm{TCE}$	-14.1	$\mathrm{mac_{SAFM}} \cdots \mathrm{TCE}$	-10.7

4 Molecular Isomers

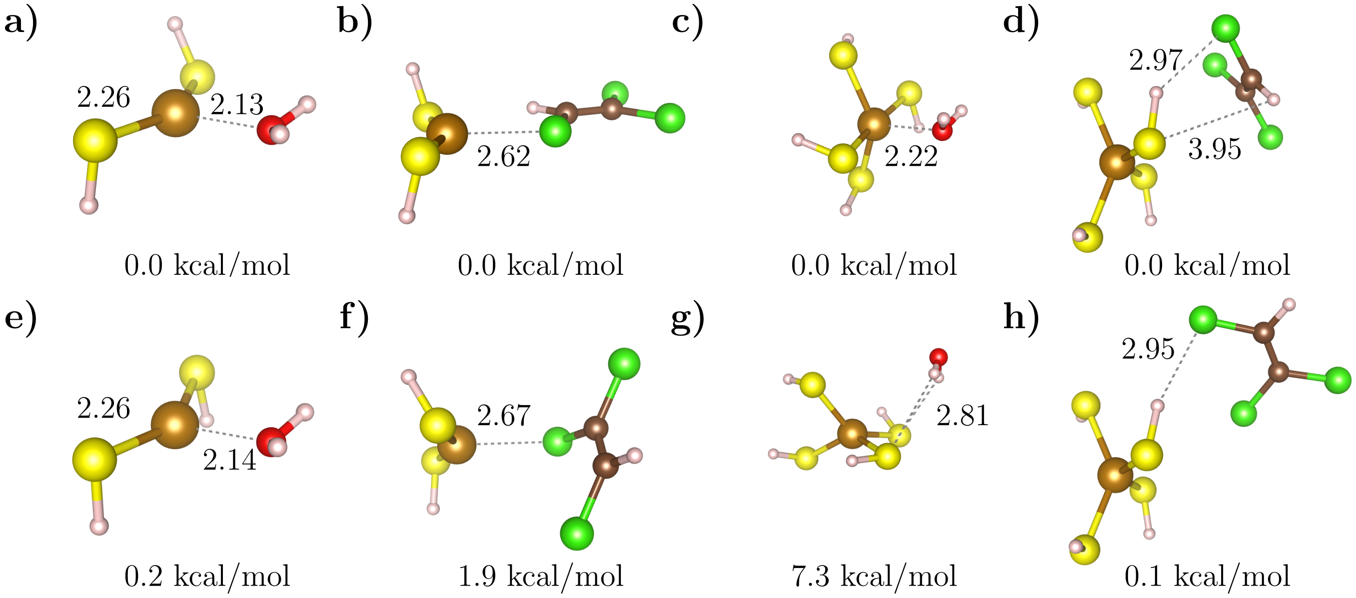

Figure S2: Selected examples of Fe complex isomers (local minima on potential energy surface): a),e) $Fe(SH)_2 \cdots H_2O$, b),f) $Fe(SH)_2 \cdots$TCE, c),g) $Fe(SH)_4 \cdots H_2O$ and d),h) $Fe(SH)_4 \cdots$TCE. Energy difference for both configurations is referenced with respect to lower one (0.0 kcal/mol). Selected distances are shown (in Å). Gold, yellow, red, brown, pink and green balls are used for Fe, S, O, C, H, and Cl atoms, respectively.

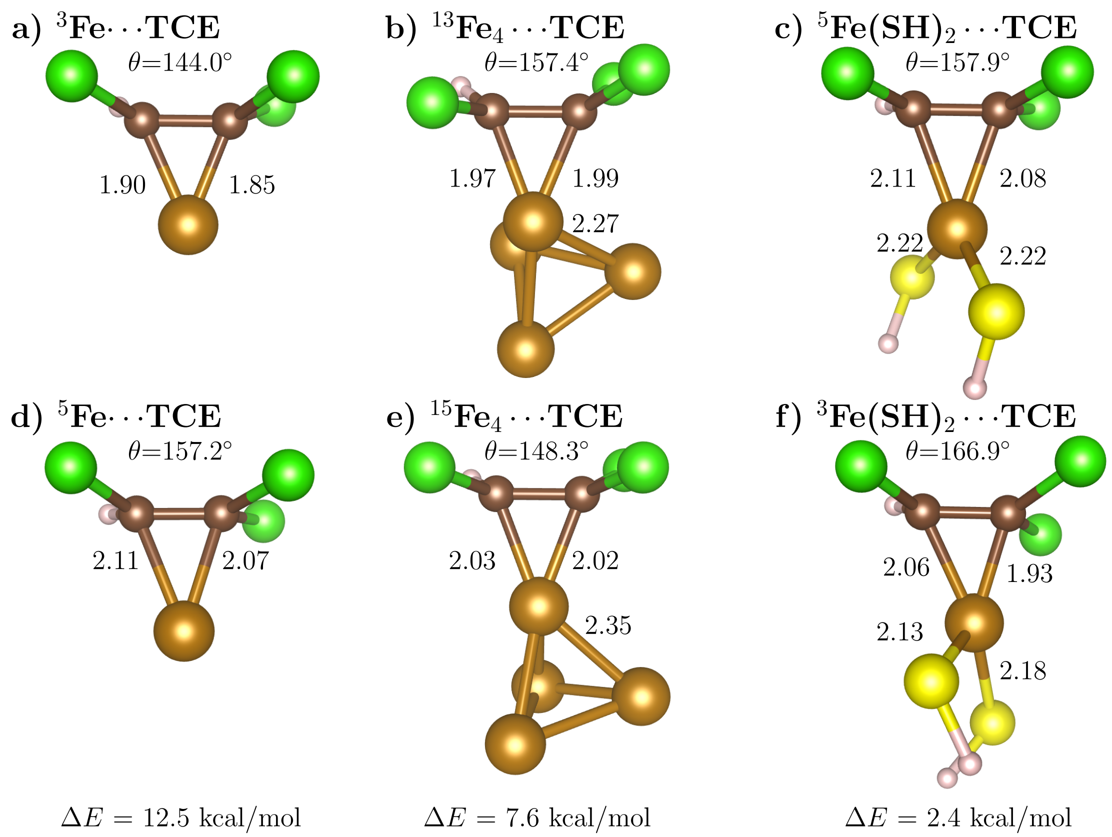

Figure S3: Selected examples of TCE chemisorbed on Fe compounds (Fe atom, Fe_4 cluster, $Fe(SH)_2$) in two spin states as obtained from PBE-D3 method. Energy difference ΔE for both spin configurations is referenced with respect to lower one (ground magnetic states a)-c)). Selected distances (in Å) and dihedral angles θ(trans Cl-C-C-Cl) are shown. Gold, yellow, brown, pink and green balls are used for Fe, S, C, H, and Cl atoms, respectively.

5 Adsorption Energy vs. K-point Grid

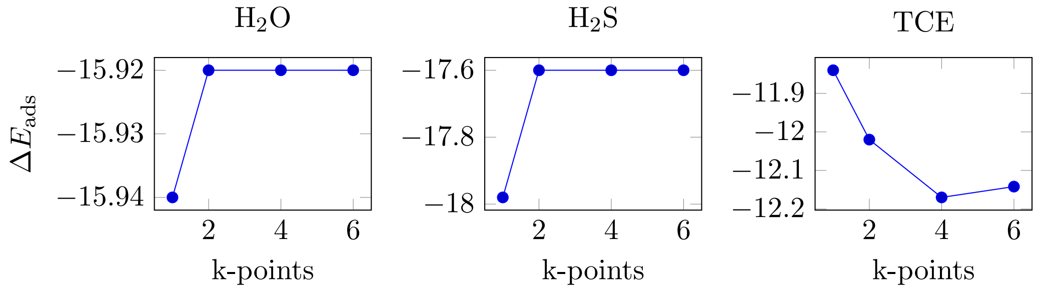

Figure S4: Convergence of adsorption energy of molecules on ZVI surface with respect to number of k-points.

6 Structural Parameters of Molecules on Surfaces

Table S3: Structural properties of H_2S molecule

	H_2S	H_2S on mac	H_2S on pyr	H_2S on ZVI
H-S (Å)	1.349	1.352	1.360	1.360
H-S (Å)	1.349	1.353	1.361	1.362
H-S-H (°)	91.6	91.0	91.1	91.9

Table S4: Structural properties of water molecule

	H_2O	H_2O on mac	H_2O on pyr	H_2O on ZVI
H-O (Å)	0.973	0.974	0.982	0.990
H-O (Å)	0.973	0.974	0.977	0.987
H-O-H (°)	104.5	103.8	105.0	103.0

Table S5: TCE Structural properties.

	TCE	TCE on mac	TCE on pyr	TCE on ZVI
C-C (Å)	1.344	1.345	1.343	1.343
C-H (Å)	1.089	1.089	1.089	1.089
C-Cl1 (Å)	1.708	1.706	1.709	1.722
C-Cl2 (Å)	1.710	1.710	1.716	1.725
C-Cl3 (Å)	1.723	1.720	1.714	1.718
Cl2-C-Cl3 (°)	115.9	115.9	115.7	116.3
H-C-Cl1 (°)	115.5	115.5	115.4	115.3

7 Charge Analysis

Table S6: Atomic charge (in e) in absorbed molecules (mol = H_2O, H_2S, TCE) provided by Bader charge analysis and using PBE-D3. Values are rounded-off to the two decimal places.

		molecule	on mackinawite	on pyrite	on ZVI
H_2O	H_1	0.59	0.59	0.61	0.59
	H_2	0.61	0.61	0.63	0.61
	O	-1.2	-1.21	-1.20	-1.25
	total	0.00	-0.01	0.04	-0.05
H_2S	H_1	0.00	0.01	0.04	0.04
	H_2	-0.01	0.01	0.04	0.06
	S	0.01	0.00	0.03	-0.06
	total	0.00	0.02	0.11	0.04
TCE	C_1	0.10	0.12	0.18	0.09
	C_2	0.33	0.23	0.17	0.22
	H	0.12	0.13	0.16	0.14
	Cl_1	-0.20	-0.18	-0.18	-0.22
	Cl_2	-0.18	-0.15	-0.14	-0.15
	Cl_3	-0.17	-0.14	-0.16	-0.17
	total	0.00	0.01	0.03	-0.09

Table S7: Atomic charge (in e) in absorbed molecules (mol = H_2O, H_2S, TCE) provided by Natural Bond Orbital (NBO) analysis and using PBE-D3/aug-cc-pVTZ method. Values are rounded-off to the two decimal places.

		free mol	$Fe\cdots mol$	$HFeSH\cdots mol$	$Fe(SH)_2\cdots mol$	$Fe(SH)_4\cdots mol$
H_2O	O	-0.90	-0.93	-0.89	-0.87	-0.82
	H	0.45	0.49	0.50	0.51	0.50
	H	0.45	0.49	0.50	0.51	0.51
	total	0.00	0.05	0.11	0.15	0.19
H_2S	S	-0.29	-0.27	-0.17	-0.14	-0.02
	H	0.14	0.18	0.17	0.19	0.17
	H	0.14	0.18	0.19	0.18	0.19
	total	0.00	0.09	0.19	0.23	0.34
TCE	C	-0.10	-0.12	-0.11	-0.12	-0.15
	C	-0.25	-0.27	-0.27	-0.25	-0.29
	Cl	0.05	0.07	0.08	0.13	0.09
	Cl	0.03	0.04	0.09	0.06	0.08
	Cl	0.04	0.05	0.08	0.08	0.05
	H	0.23	0.24	0.27	0.24	0.24
	total	0.00	0.01	0.14	0.14	0.02

References

[1] See VASP manual at http://www.vasp.at for definitions of empirical corrections and references. Advanced semi-empirical schemes have been implemented in VASP by T. Bučko *et al.*, Phys. Rev. B **87**, 064110 (2011); J. Phys.: Condens. Matter **28**, 045201 (2016).

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[3] A. R. Lennie, S. A. T. Redfern, P. F. Schofield and D. J. Vaughan, *Mineral. Mag.*, 1995, **59**, 677–683.