Supplemental Information

Table S1 : Si-O-Si angles (deg) of T_{10} (types defined in Figure 1a) with absorption by the molecules. O-Si-O angles are also shown for structures with the molecules at the face. Where different angles were found for the same type, the angle that showed the largest modification from the POSS cage without an absorbate was chosen. Angles are in degrees. At the B3LYP (6-311++(d,p)) level of theory.

	Center		Face		
	side	face	side	face	O-Si-O
O_2 (up)	159.3	151.3	151.8	157.4	117.8
O_2 (side)	150.6	156.4			
N_2 (up)	157.1	153.2	149.95	155.7	117.43
N_2 (side)	156.4	147.1			
H_2	152.0	155.3	154.2	154.1	113.0
CO	160.0	151.65	153.7 (C-out)	153.1 (C-out)	116.7 (C-out)
			149.7 (C-in)	156.5 (C-in)	116.9 (C-in)
CO_2	173.5	145.3	160.0	149.9	116.8
Water	145.5	163.9	147.9	141.0	154.1
He	153.2	155.3	153.7	155.0	111.1
CH_4	151.6	155.8	158.2	144.68	123.5

Brackets indicate the configuration defined in the text.

Table S2 : Si-O-Si angles (deg) of T_{12} (types defined in Figure 1b) with absorption by the molecules. Where different angles were found for the same type, the angle that showed the largest modification from the POSS without an absorbate was chosen. Angles are in degrees. At the B3LYP (6-311++(d,p)) level of theory.

	Center				Face				
	Face	FE1	FE2	edge	Face	FE1	FE2	edge	O-Si-O
O_2 (up)	162.1	161.6	159.5	147.3	159.6	170.4	151.0	146.0	118.6
O_2 (side)	172.5	160.3	155.9	151.5					
N_2 (up)	161.5	162.2	156.6	152.1	167.6	168.9	152.3	141.9	118.3
N_2 (side)	162	162.2	156.6	152.1					
H_2	167.2	163.0	157.2	152.0	156.9	165.2	153.2	148.8	113.0
CO	172.1	160.8	156.2	151.1	161.2 (C-out)	164.3 (C-out)	152.3 (C-out)	145.9 (C-out)	117.9 (C-out)
					169.8 (C-in)	170.5 (C-in)	146.3 (C-in)	139.5 (C-in)	117.9 (C-in)
CO_2	177.5	150.5	151.0	150.2	161.1	164.0	159.1	147.4	115.1
Water	160.3	155.8	149.6	152.2	145.88	162.15	155.13	143.53	156.71
He	164.5	162.6	156.7	151.1	164.9	163.4	154.6	148.6	111.5
CH_4	163.7	161.3	157.3	150.4	—	—	—	144.7	124.5

Parentheses indicate the configuration defined in the text.

Table S3: The NBO charges derived of adsorbate atoms within T_{10} from DFT calculations using the B3LYP functional

diatomic	Out	In	Both	Isolated
O_2	0.032	-0.104	-0.02033 (-0.00992)	0
N_2	0.066	-0.093	-0.028 (-0.021)	0
CO - O	-0.575 [C-in]	-0.619 [C-out]	-0.967 (-0.987)	-0.478 (-0.488)
CO - C	0.562 [C-out]	0.475 [C-in]	0.764 (0.790)	0.478 (-0.488)
H_2	0.064	-0.076	-0.009 (-0.0091)	0
non-diatomic				
Water O	—	-0.973 [at plane]	-0.979 (-0.98634)	-0.913 (-0.913)
Water H	0	0.523 [at plane]	0.483 (0.487,0.487)	0.457 (0.457)
CO_2 - O	0.126 [at plane]	-0.832	-0.543 (-0.552)	-0.495 (-0.503)
CO_2 - C	-0.808	—	1.068 (1.09148)	0.990 (1.007)
He	—	0.005 [at plane]	-0.001 (0.00084)	0
CH_4 – H	0.229	0.156	0.188,0.241	0.202
CH_4 – O	—	-0.787 [at plane]	-0.858	-0.806

Parentheses indicate results using the ωB97XD functional.
Brackets indicate the configuration defined in the text. "at plane" is an atom within the plane of the Si_5 face.

Table S3 shows the NBO charges of of adsorbate atoms within T_{10} from DFT calculations using the B3LYP functional. The "out" column shows charges of the atom of the absorbate molecules when it is at the face but outside the POSS (atom 1 in Figure 2) and "in" when it is inside (atom 2) the POSS. "both" is when the atom is at the center of POSS and "isolated" denotes the free absorbate (zero for homonuclear diatomic atoms). Atoms indicated in brackets as "at plane" are atoms that are in the plane of the Si_5 face.

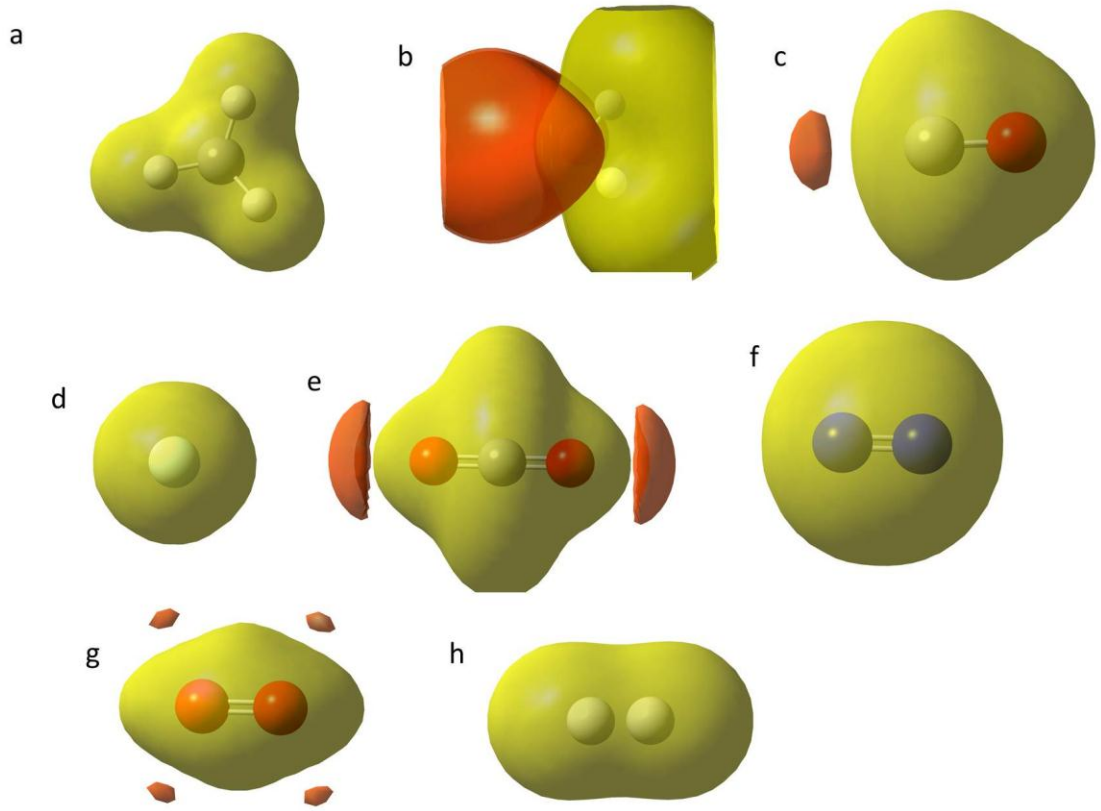

Figure S1 : The electrostatic potential surfaces of the absorbate molecules. Red is negatively charged, yellow is positively charged. The surfaces are set with an isovalue of 0.02 electrons. a) CH_4, b) H_2O, c) CO, d) He, e) CO_2, f) N_2, g) O_2, h) H_2

Figure S1 shows the electrostatic potential surfaces of the absorbate molecules**.** The interesting points to note are: CH_4, He, and H_2 do not show any negative charge but are positively charged shapes, roughly the shape of the respective molecule. O_2 has patches of negative charge positioned away from the oxygen atoms, probably due to the oxygen lone pairs. H_2O has negative charge on the oxygen atom and positive charge on the hydrogen atoms. CO has positive charge over the molecule except it has a negative charge patch positioned away from the carbon atom due to the dipole. CO_2 has two negative charged patches positioned away from the oxygen atoms.

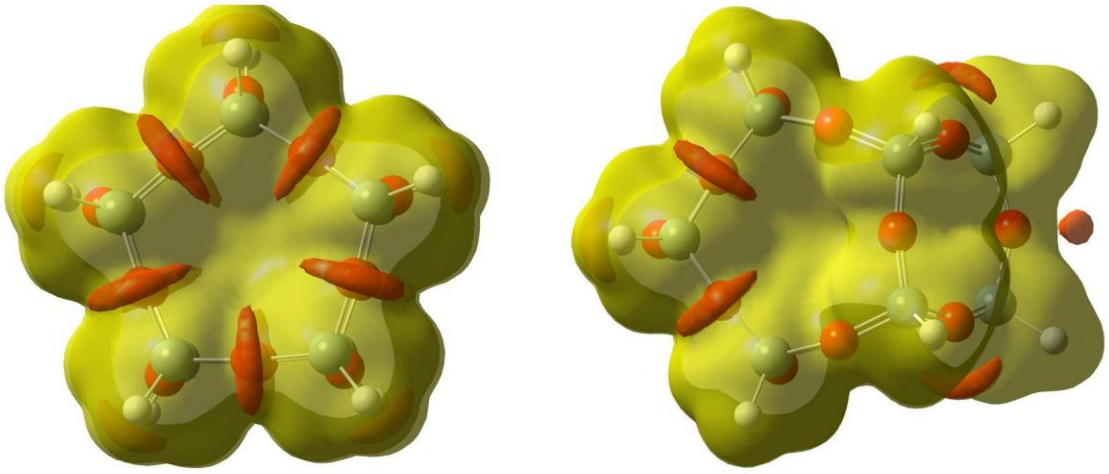

Figure S2 : The electrostatic potential surfaces of the POSS cages. Red is negatively charged, yellow is positively charged. The surfaces are set with an iso-value of 0.02 electrons.

Figure S2 shows the electrostatic potential surfaces of the POSS cages. Both POSS cages mostly have a positively charged surface except for patches of negative charge close to the oxygen atoms. For T_{12} there are only negative patches close to atoms that are part of FE2 and 'Edge' Si-O-Si angles defined in Figure 1.