Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2015

Supporting Information

First principles study of the adsorption and dissociation mechanisms of H_2S on TiO_2 anatase (001) surfaces

Naeem Shahzad[a,c], Akhtar Hussain[b,c,d], Naeem Mustafa[b], Nisar Ali[e], Mohammed Benali Kanoun[f], Souraya Goumri-Said[f,*]

[a] *National University of Sciences and Technology, Islamabad, Pakistan*
[b] *TPD, Pakistan Institute of Nuclear Science and Technology (PINSTECH), P. O. Nilore, Islamabad, Pakistan*
[c] *National Centre for Physics, Quaid-e-Azam Univwersity Campus, Islamabad, Pakistan*
[d] *NED, Pakistan Institute of Engineering and Applied Sciences (PIEAS), P. O. Nilore, Islamabad, Pakistan*
[e] *Department of Physics, GPG Jehanzeb College Swat, Pakistan*

[f] *College of Science, Physics department, Al Faisal University, Riyadh 11533, Saudi Arabia*

[*]Email of corresponding author: souraya.goumri-said@chemistry.gatech.edu, sosaid@alfaisal.edu

Additional Data File

Table 1S: Adsorption energies and different geometric parameters of all the species computed

Surface	Species	Site	E_{ads}	Bond lengths (Å)	Bond angles(degrees)
TiO_2 (p2x2)	H	Ti_{5c}	1.09	H-Ti_{5c} = 5.14	
		O_{3c}	0.29	H-O_{3c} = 1.6	
		hollow	-2.29	O_{2c}-H-O_{2c} = 1.99	
		O_{2c}	-2.75	H-O_{2c} = 0.97	
	OH	O_{3c} (tilted)	-1.01	H-O_{2c} = 0.99; O-Ti_{5c} = 2.12	Ti_{5c}-O-H = 108
		Ti_{5c}(linear)	-1.47	H-O_{2c} = 0.97; O-Ti_{5c} = 1.82	Ti_{5c}-O-H = 180
		Ti_{5c}(tilted)	-1.85	H-O_{2c} = 0.98; O-Ti_{5c} = 1.85	Ti_{5c}-O-H = 108
	S	Ti_{5c}	-0.91	S-Ti5c = 2.22	
		hollow	-1.04	O_{2c}-S-O_{2c} = 1.78	
		O_{3c}	-1.67	S-O_{2c} = 1.72	
		O_{2c}	-2.46	S-O_{3c} = 1.73	
	HS	O_{2c}	0.16	S- O_{2c} = 3.31; S-H = 1.36	O_{2c} -S-H = 180
		Ti_{5c}	0.15	S- Ti_{5c} = 3.01; S-H = 1.36	Ti_{5c} -S-H = 180

		O_{3c}	-0.29	S-O_{3c} = 2.61; S-H = 1.36	Ti_{5c} -S-H = 126.5
		hollow	-1.26	S- O_{2c} = 1.67; S-H = 1.36	O_{2c} -S-H = 98.3
	H_2S	hollow	2.66	S-O_{2c} = 1.6; H-S-H = 1.38	H-S-H = 87.2; O_{2c}-S-H = 100.5
		O_{2c}	0.04	S-O_{2c} = 3.33; H-S-H = 1.35	H-S-H = 91.6
		Ti_{5c}	-0.13	S- Ti_{5c} = 2.73; H-S-H = 1.35	H-S-H = 96.5
		O_{3c}	-0.17	S- O_{3c} = 3.27; H-S-H = 1.35	H-S-H = 93.6
	H_2S-H_2S	Ti_{5c}-Ti_{5c}	-0.25	S- Ti_{5c} = 2.72; H-S-H = 1.35-- S-Ti_{5c} = 2.72; H-S-H = 1.35	H-S-H = 97-- H-S-H = 97
		Ti_{5c}-O_{2c}	-0.47	S- Ti_{5c} = 2.72; H-S-H = 1.35-- S-O_{2c} = 3.08; H-S-H = 1.35	H-S-H = 97-- H-S-H = 92.9; O_{2c}-S-H = 73.2
	S-H_2S	Ti_{5c}-O_{2c}	-0.16	S- Ti_{5c} = 2.23--S- O_{2c} = 3.02; H-S-H = 1.35	H-S-H = 93; O_{2c}-S-H = 75
		Ti_{5c}-Ti_{5c}	-0.18	S- Ti_{5c} = 2.23--S- Ti_{5c} = 2.71; H-S-H = 1.35	H-S-H = 97.3
		Ti_{5c}-O_{2c}	-0.21	S- O_{2c} = 1.72-- S- Ti_{5c} = 2.65; H-S-H = 1.35	H-S-H = 98
		O_{2c}-O_{3c}	-0.91	S- O_{2c} = 1.62--S- O_{3c} = 2.47; H-S-H = 1.41	H-S-H = 89.9
	S-HS	Ti_{5c}-Ti_{5c}	0.23	S- Ti_{5c} = 2.22-- S- Ti_{5c} = 2.76; S-H = 1.35	
		Ti_{5c}-O_{2c}	-0.04	S- Ti_{5c} = 2.31-- S- O_{2c} = 2.57; S-H = 1.36	
		O_{2c}-Ti_{5c}	-0.33	S- O_{2c} = 1.66--S- Ti_{5c} = 2.41--; S-H = 1.34	Ti_{5c}-O_{2c}-S = 138.6
		O_{2c}-O_{3c}	-0.9	S- O_{2c} = 1.66--S- O_{3c} = 2.56; S-H = 1.36	
	H_2S+OH	no S, H_2S-O_{2c},OH-Ti_{5c}	-0.33	S-Ti_{5c} = 3.03; H-S-H =1.35; H-S-H = 1.42--O-Ti_{5c} = 1.92;O-H = 0.97	O_{2c}-Ti_{5c}-S = 68.4; H-S-H = 92.9--Ti_{5c}-O-H = 112.4
	H_2S+OH-90	no S,H_2S-Ti_{5c}, with H atoms 90° rotated, OH-O_{2c}	-0.09	S-Ti_{5c} = 2.92; H-S-H = 1.35--O-Ti_{5c} = 1.87; O-H = 0.97	Ti_{5c}-S-H = 91.6; H-S-H = 91.1--Ti_{5c}-O-H = 108.9
	S+H_2S+OH	S-O_{2c}, H_2S-O_{2c},OH-Ti_{5c}	-1.54	S-O_{2c} = 1.6-- S-Ti_{5c} = 2.78; H-S-H =1.35; H-S-H = 1.42-- O-Ti_{5c} = 1.92; O-H = 0.97	O_{2c}-S-Ti_{5c} = 65.1; O_{2c}-Ti_{5c}-S =79.1; H-S-H = 93.4°--H-O-Ti_{5c} = 113
	S+H_2S+OH-90	S-O_{2c},H_2S-O_{2c}, with H atoms 90° rotated,OH-O_{2c}	-1.07	S-O_{2c} = 1.63-- S-Ti_{5c} = 2.91; H-S-H =1.36-- O-Ti_{5c} = 1.87; O-H = 0.97	H-S-Ti_{5c} = 91.76;H-S-H = 91.4--H-O-Ti_{5c} = 113.2°
Surface	**Species**	**Site**	**E_{ads}**	**Bond lengths (Å)**	**Bond angles(degrees)**
Defected Surface	H_2S	no S, H_2S-Ti_{5c}	-0.20	S-Ti_{5c} = 2.69; H-S-H = 1.35	H-S-H = 93.6
	H_2S	no S, H_2S-$O_{2c(vac)}$	-0.27		H-S-H = 92.7
	H_2S	no S,H_2S-O_{3c}	-0.31	S-O_{3c} = 3.0; H-S-H = 1.35	H-S-H = 93.6
	S + H_2S	S-O_{2c},H_2S- $O_{2c(vac)}$	-0.21	S-O_{2c} = 1.73	H-S-H = 98
	S + H_2S	S-O_{2c},H_2S-Ti_{5c}	-0.24	S-O_{2c} = 1.72-- S-Ti_{5c} = 2.67;H-S-H = 1.35	
	S + H_2S	S-O_{2c},H_2S-O_{3c}	-0.96	S-O_{2c} = 1.66-- S-O_{3c} = 2.98;H-S-H = 1.35	S-O_{2c}-Ti=66.5°
	S + H_2S + OH	S-O_{2c},H_2S-Ti_{5c}, OH-O_{2c}	-4.64	S-O_{2c} = 1.67-- S-Ti_{5c} = 2.61; H-S-H =1.35&1.4-- O-Ti_{5c} = 1.9; O-H = 0.97	O_{2c}-S-Ti_{5c} = 69.4-- H-S-H = 96.5; H-S-Ti_{5c} = 103.6--H-O-Ti_{5c} = 142.5
	S + H_2S(90°) + OH	S-O_{2c},H_2S- $O_{2c(vac)}$, with H atoms 90° rotated,OH-O_{2c}	-2.67	S-O_{2c} = 1.72-- H-S-H =1.35-- O-Ti_{5c} = 1.87; O-H = 0.97	O_{2c}-S-Ti_{5c} = 43.1-- H-S-H = 107.8; Ti_{5c}-S-Ti_{5c}=101.1-- H-O-Ti_{5c} = 148.2
	H_2S(90°) + OH	no S,H2S- $O_{2c(vac)}$, with H atoms 90° rotated, OH-O_{2c}	-2.25	S-Ti_{5c} = 2.52; H-S-H =1.35&1.4-- O-Ti_{5c} = 1.87; O-H = 0.96	Ti_{5c}-S-Ti_{5c}=94.1; H-O-Ti_{5c}=151.7
Perfect surface TiO_2 (p2x2)	S+HS+H(l)	S-O_{2c}, one H of H_2S-Ti_{5c} on left O_{2c}	-1.49	S-O_{2c} = 1.72-- S-Ti_{5c} = 2.39; H-S =1.34-- O-H = 1.0	Ti_{5c}-O-H=72.7
	S+HS+H(r)	S-O_{2c}, one H of H_2S-Ti_{5c} on right O_{2c}	-1.49	S-O_{2c} = 1.72-- S-Ti_{5c} = 2.41; H-S =1.34-- O-H = 1.0	Ti_{5c}-O-H=98.1
	S+S+H+H	S-O_{2c}, one H each of H_2S-		S-O_{2c} = 1.73-- S-Ti_{5c} = 2.26-- O_{2c}-	Ti_{5c}-O-H=72.7

		O_{3c} on left O_{2c} and on right O_{2c}		H-S =1.22-- O-H = 0.98	
Defected Surface	S + HS + H(lt)	S-O_{2c}, one H of H_2S-Ti_{5c} on left $O_{2c(vac)}$	-1.6	S-O_{2c} = 1.72-- S-Ti_{5c} = 2.27; H-S =1.34-- H-Ti_{5c} =1.75	Ti_{5c}-O-Ti_{5c} =147.7
	S + HS + H(rt)	S-O_{2c}, one H of H_2S-Ti_{5c} on right O_{2c}	-1.6	S-O_{2c} = 1.72-- S-Ti_{5c} = 2.35; H-S =1.34-- H-O_{2c} = 0.98	Ti_{5c}-O-H=101.1
	HS (90°) + H_2O	no S,H_2S-O_{2c}(vac), with H atoms 90° rotated and one H of H_2S added to OH-O_{2c}	-3.62	H-S = 1.36--O-Ti_{5c} = 2.4; H-O-H = 0.98	Ti_{5c}-S-Ti_{5c} = 109-- H-O-H = 109.3
	S + HS (90°) + H_2O	S-O_{2c},H_2S- $O_{2c(vac)}$, with H atoms 90° rotated one H of H_2S added to OH-O_{2c}	-3.79	S-O_{2c} = 1.72-- S-O_{2c} = 1.72-- H-S = 1.36--O-Ti_{5c} = 2.32; H-O-H = 0.98	Ti_{5c}-S-Ti_{5c} = 109.9-- H-O-H = 110.2