Supporting Information

Mapping acid-base sites on anatase titania (100) and (101) surfaces by DFT: The link between Lewis acidity and the surface ability to flex

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Table S1. Energy for pyridine adsorption on (100) anatase titania surface.

Map of Ti atoms hosting Py	Geometry optimized Energy, a.u.	Single point energy after Pyridine removed, a.u.	Lattice distortion energy per surface Ti atom kcal/mol	Lattice distortion energy per one adsorbate kcal/mol	Adsorption energy per adsorbate kcal/mol	Adsorption energy per adsorbate, corrected kcal/mol	coverage %	Distance between adsorbates, Å	
Pristine surface	-97357.68480								
3-5-7-11-13-15	-98847.58548	-97357.65351	1.23	3.27	-39.60	-42.87	37.50%		
3-7-11-13-15	-98599.26547	-97357.65786	1.06	3.38	-39.20	-42.58	31.25%		
3-7-11-15	-98350.94397	-97357.66249	0.88	3.50	-38.35	-41.86	25.00%		
9-11-13-15	-98350.96415	-97357.6602	0.97	3.86	-41.52	-45.38	25.00%		
11-13-15	-98102.64191	-97357.66568	0.75	4.00	-41.02	-45.02	18.75%		
11-15	-97854.31794	-97357.67184	0.51	4.07	-39.47	-43.54	12.50%	7.68	Same island
12-15	-97854.31829	-97357.67152	0.52	4.17	-39.58	-43.75	12.50%	6.30	
13-15	-97854.32273	-97357.67128	0.53	4.25	-40.97	-45.22	12.50%	3.84	
3-15	-97854.31834	-97357.67163	0.52	4.14	-39.59	-43.73	12.50%	12.33	Different islands
4-15	-97854.31775	-97357.67214	0.50	3.97	-39.41	-43.38	12.50%	9.17	
5-15	-97854.31787	-97357.67191	0.51	4.05	-39.45	-43.49	12.50%	10.38	
7-15	-97854.31726	-97357.67218	0.50	3.96	-39.26	-43.22	12.50%	9.64	
6-15	-97854.31777	-97357.67252	0.48	3.85	-39.41	-43.27	12.50%	7.36	

Table S2. Bond length for pyridine adsorbed on (100) anatase titania surface

Map of Ti atoms hosting Pyridine	O_{3fc}-H	Ti-N	O_{2fc}-H	O-H average	C-N-C angle	
	Bond Length					
3-5-7-11-13-15	2.423	2.332	2.118	2.270		
3-7-11-13-15	2.428	2.329	2.121	2.274		
3-7-11-15	2.432	2.318	2.120	2.276		
9-11-13-15	2.434	2.332	2.119	2.276		
11-13-15	2.437	2.314	2.113	2.275		
11-15	2.443	2.308	2.126	2.285	118.830	Same island
12-15	2.427	2.310	2.136	2.281	118.809	
13-15	2.440	2.310	2.120	2.280	118.818	
3-15	2.445	2.305	2.125	2.285	118.824	Different islands
4-15	0.13	2.307	2.145	1.135	118.803	
5-15	0.13	2.306	2.125	1.125	118.827	
7-15	2.441	2.308	2.124	2.283	118.814	

Fig. S1. Ti-N Bond distances as function of coverage on (100) surface.

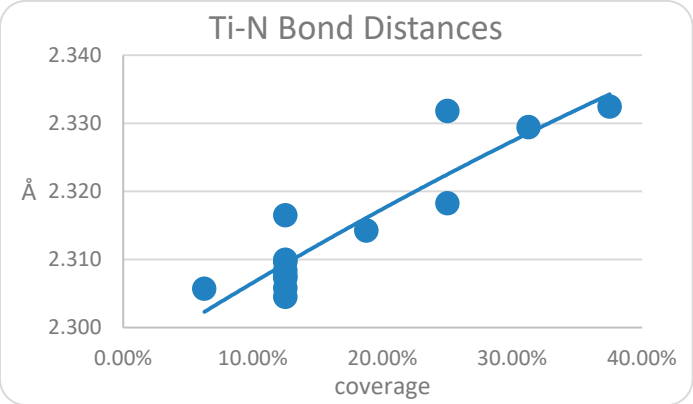


Fig. S2. The lattice distortion energy per each adsorbate for adsorption of a pair of pyridine molecules on (100) anatase titania surface as the function of the distance between them.

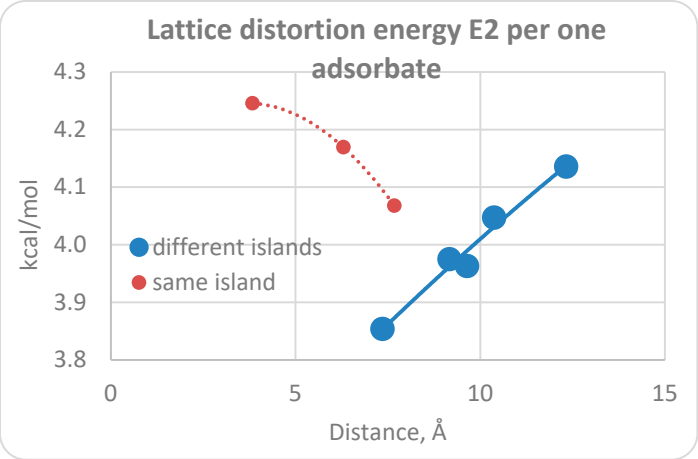


Table S3. DFT Calculated energy of substituted pyridines in the gas phase.

4-NH2-pyridine	-303.6360414
4-methoxyPyridine	-362.8848614
4-MethylPyridine	-287.5605232
Pyridine	-248.2536706
acetylPy	-401.0001142
4-nitroPyridine	-453.0292653

Table S4. Adsorption of 4-substituted pyridines on Ti_{5c} atom of pristine (100) anatase surface.

Substituent	F3	F1	E2	E1	E3
4-NH2	-48982.56473	-48678.85218	5.08	-42.93	-48.01
4-methoxy	-49041.81216	-48678.85302	4.55	-42.06	-46.61
4-Methyl	-48966.48667	-48678.85354	4.23	-41.33	-45.56
H	-48927.17701	-48678.85393	3.98	-39.57	-43.55
4-acetyl	-49079.92549	-48678.85462	3.55	-40.85	-44.40
4-nitro	-49131.94900	-48678.85566	2.90	-37.31	-40.21

Fig. S3. Bond length for 4-substituted pyridines adsorption on Ti_{5c} atom of pristine (100) anatase surface.

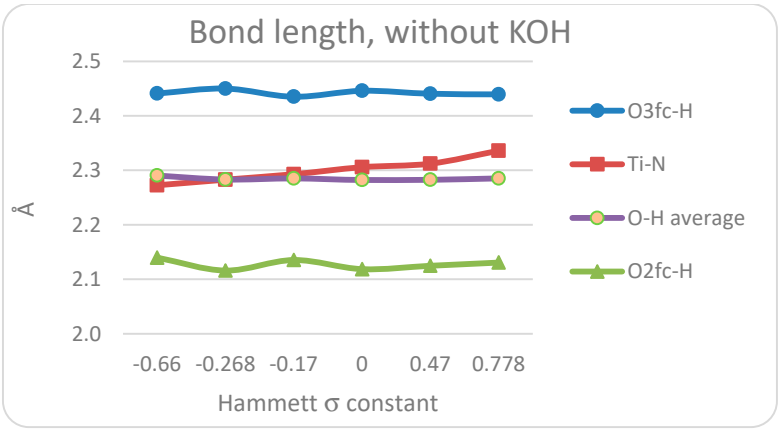


Fig. S4. Energy E1 of 4-substituted pyridines adsorption on (100) anatase surface in the presence of water, KOH, or in absence of those as a function of substituent's Hammett sigma constant.

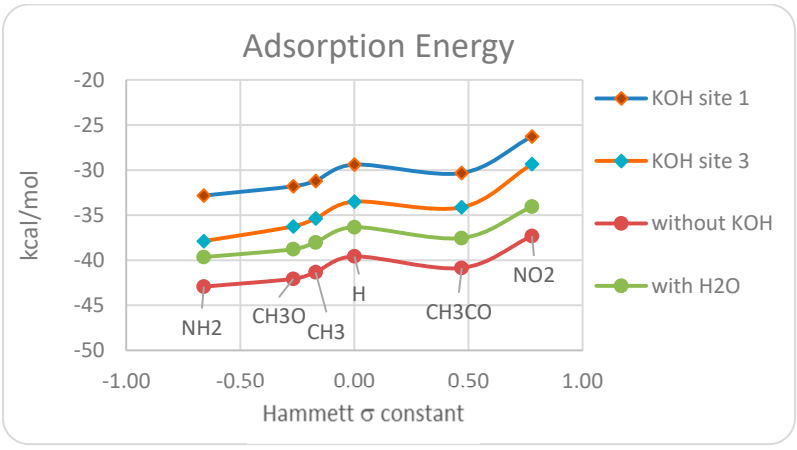


Table S5. Adsorption of 4-substituted pyridines on site 1 of (100) anatase surface in presence of KOH.

site 1 with KOH	F3, a.u.	F1, a.u.	E2, kcal/mol	E1, kcal/mol	E3, kcal/mol
4-NH2	-49672.56862	-49368.87221	5.06	-32.83	-37.88
4-methoxy	-49731.8158	-49368.87318	4.44	-31.80	-36.24
4-Methyl	-49656.49051	-49368.87362	4.17	-31.20	-35.37
H	-49617.18076	-49368.87371	4.12	-29.38	-33.50
4-acetyl	-49769.92871	-49368.87421	3.80	-30.32	-34.13
4-nitro	-49821.95139	-49368.87539	3.06	-26.27	-29.33

Table S6. Adsorption of 4-substituted pyridines on site 2 of (100) anatase surface in presence of KOH.

site 2 with KOH	F3, a.u.	F1, a.u.	E2, kcal/mol	E1, kcal/mol	E3, kcal/mol
4-NH2	-49672.57619	-49368.87337	4.33	-37.58	-41.90
4-methoxy	-49731.82152	-49368.87368	4.13	-35.39	-39.52
4-Methyl	-49656.49672	-49368.87415	3.84	-35.10	-38.94
H	-49617.18855	-49368.87469	3.50	-34.27	-37.77
4-acetyl	-49769.93667	-49368.87558	2.94	-35.32	-38.26
4-nitro	-49821.95993	-49368.87635	2.46	-31.63	-34.08

Table S7. Adsorption of 4-substituted pyridines on site 3 of (100) anatase surface in presence of 12.5% KOH coverage (Fig. S5).

site 3 with KOH	F3, a.u.	F1, a.u.	E2, kcal/mol	E1, kcal/mol	E3, kcal/mol
4-NH2	-49672.57604	-49368.87287	4.64	-37.48	-42.13
4-methoxy	-49731.82378	-49368.87381	4.05	-36.80	-40.86
4-Methyl	-49656.49821	-49368.87403	3.91	-36.03	-39.94
H	-49617.18912	-49368.87431	3.74	-34.63	-38.37
H*	-119425.13876 eV	-118301.94700 eV	5.56	-32.93	-38.49
4-acetyl	-49769.93764	-49368.87479	3.44	-35.93	-39.37
4-nitro	-49821.96183	-49368.87587	2.76	-32.82	-35.58

* Calculated for comparison using HSE06 functional. The energy for unit cell with 12.5% KOH coverage before pyridine adsorption is -118302.18800 eV.

Table S8. Adsorption of 4-substituted pyridines on site 3 of (100) anatase surface in presence of water (Fig. S6).

	F3, a.u.	F1, a.u.	E2, kcal/mol	E1, kcal/mol	E3, kcal/mol
4-NH2	-49059.12683	-48755.41646	6.99	-39.65	-46.64
4-methoxy	-49118.37425	-48755.41721	6.52	-38.77	-45.29
4-Methyl	-49043.04871	-48755.41795	6.05	-38.02	-44.07
H	-49003.73918	-48755.41821	5.89	-36.34	-42.23
4-acetyl	-49156.48753	-48755.41891	5.45	-37.54	-42.99
4-nitro	-49208.51113	-48755.41997	4.78	-34.05	-38.84

Fig. S5. Adsorption of pyridine on site 3 of (100) surface doped with KOH, a) side view, b) top view

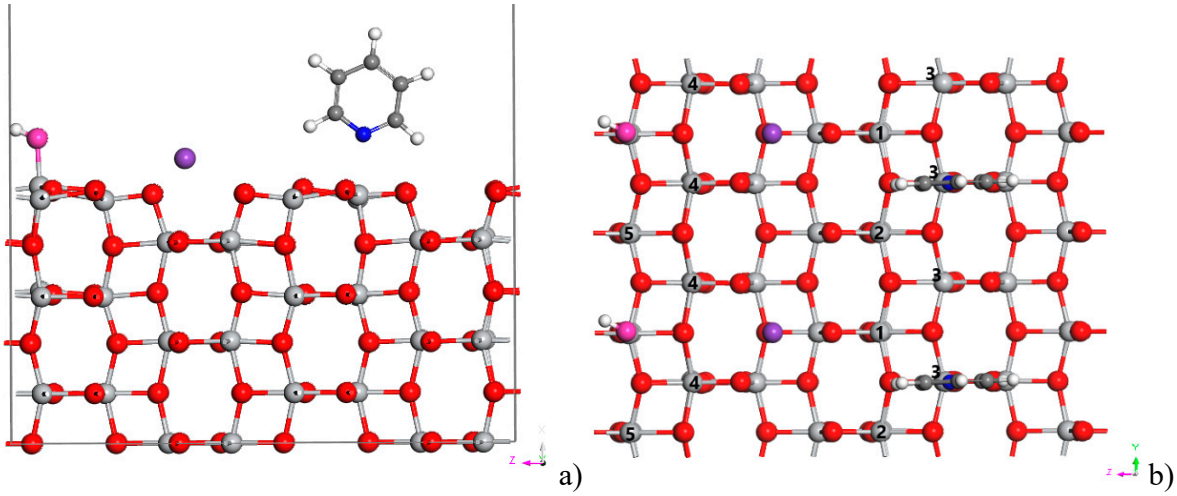


Fig. S6. Adsorption of pyridine on site 3 of (100) anatase surface in presence of water dissociated to H and OH.

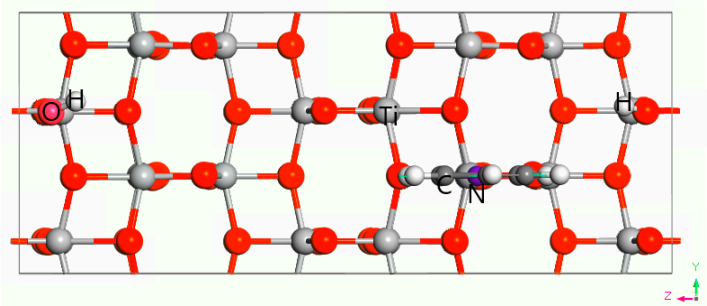
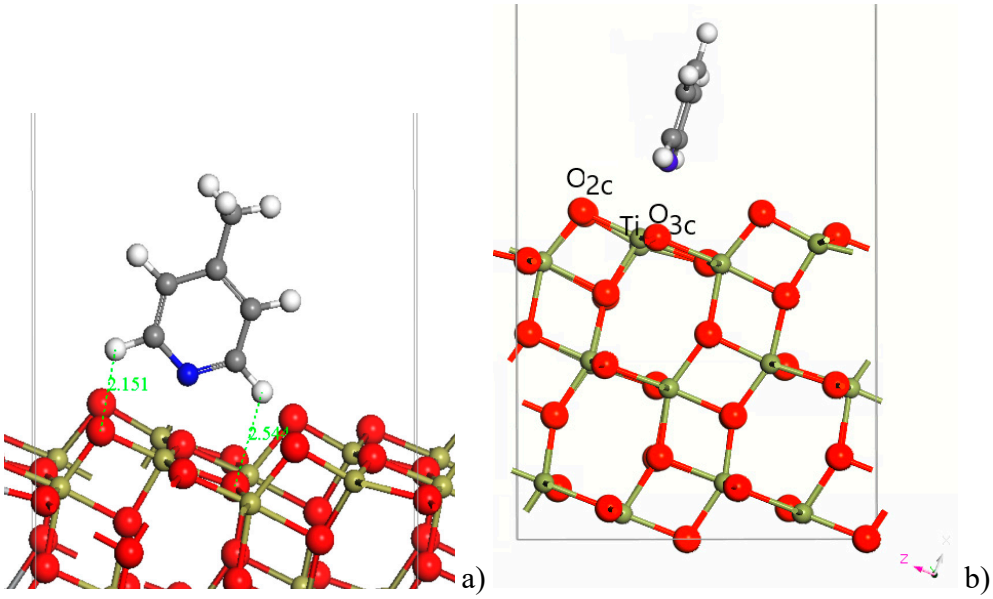


Table S9. Hammett constant for 4-substituted pyridines.[42]

Pyridine	Hammett σ constant
4-Aminopyridine	-0.66
4-Methoxypyridine	-0.27
4-Methylpyridine	-0.17
Pyridine	0.00
4-Acetylpyridine	0.47
4-Nitropyridine	0.78

Fig. S7. Adsorption of pyridine on pristine (101) anatase surface a) strong interaction mode b) weak interaction mode.

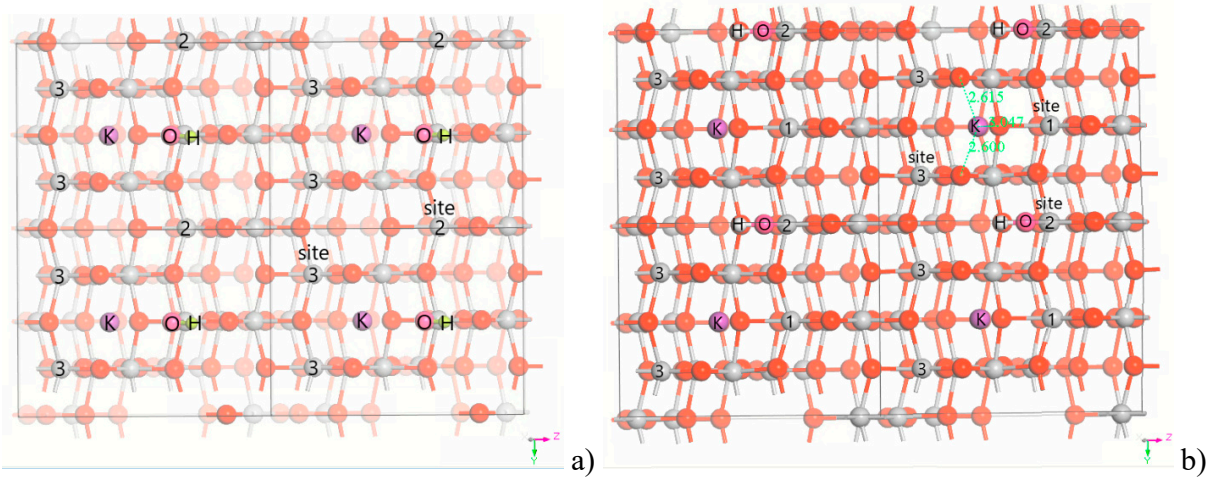


a) b)

Table S10. Adsorption of 4-substituted pyridines on pristine (101) anatase surface.

	F3, a.u.	F1, a.u.	E2, kcal/mol	E1, kcal/mol	E3, kcal/mol
4-NH2	-24643.18702	-24339.46613	6.53	-46.71	-53.24
4-methoxy	-24702.43444	-24339.46732	5.78	-45.83	-51.61
4-Methyl	-24627.10903	-24339.46802	5.35	-45.16	-50.50
H	-24587.79895	-24339.46847	5.07	-43.13	-48.20
4-acetyl	-24740.54792	-24339.46901	4.73	-44.72	-49.45
4-nitro	-24792.57075	-24339.46981	4.22	-40.75	-44.98
H (orientation with weaker adsorption, Fig. S7b)	-24587.79498	-24339.46959	4.36	-40.64	-45.00

Fig. S8. KOH doping on anatase (101) surface, with a) more stable adsorption of OH on site 1, and b) less stable, by 6.9 kcal/mol, adsorption of OH on site 2.



a) b)

Table **S11**. Adsorption of 4-substituted pyridines on site 3 of KOH doped (101) anatase surface.

	F3, a.u.	F1, a.u.	E2, kcal/mol	E1, kcal/mol	E3, kcal/mol
4-NH2	-25333.17726	-25029.4624	5.37	-44.09	-49.46
4-methoxy	-25392.42395	-25029.46326	4.84	-42.75	-47.58
4-Methyl	-25317.09871	-25029.46349	4.69	-42.18	-46.87
H	-25277.78907	-25029.46341	4.74	-40.43	-45.17
4-acetyl	-25430.53824	-25029.46396	4.40	-42.15	-46.55
4-nitro	-25482.56095	-25029.46497	3.76	-38.10	-41.86

Table **S12**. Adsorption of 4-substituted pyridines on site 2 of KOH doped (101) anatase surface.

	F3, a.u.	F1, a.u.	E2, kcal/mol	E1, kcal/mol	E3, kcal/mol
4-NH2	-25333.18015	-25029.46332	4.80	-45.90	-50.69
4-methoxy	-25392.42802	-25029.46396	4.40	-45.30	-49.70
4-Methyl	-25317.10204	-25029.46426	4.21	-44.27	-48.48
H	-25277.79261	-25029.4645	4.05	-42.65	-46.71
4-acetyl	-25430.5398	-25029.46503	3.72	-43.13	-46.85
4-nitro	-25482.56511	-25029.46593	3.16	-40.72	-43.87

Table S13. Adsorption of 4-substituted pyridines on site 2 of (101) anatase surface in presence of dissociated water with OH on site 1 and H on O2c site 1 (Fig. S9a).

	F3, a.u.	F1, a.u.	E2, kcal/mol	E1, kcal/mol	E3, kcal/mol
4-NH2	-24719.74759	-24416.02614	2.83	-50.76	-53.60
4-methoxy	-24778.99516	-24416.02715	2.20	-49.98	-52.18
4-Methyl	-24703.66949	-24416.0276	1.92	-49.14	-51.06
H	-24664.35955	-24416.02798	1.68	-47.20	-48.88
4-acetyl	-24817.10864	-24416.0285	1.36	-48.86	-50.22
4-nitro	-24869.13204	-24416.02937	0.81	-45.26	-46.06

Table S14. Adsorption of 4-substituted pyridines on site 2 of (101) anatase surface in presence of dissociated water with OH on site 1 and H on O2c site 2 (Fig. S9b).

	F3, a.u.	F1, a.u.	E2, kcal/mol	E1, kcal/mol	E3, kcal/mol
4-NH2	-24719.75101	-24416.02058	5.84	-53.39	-59.23
4-methoxy	-24778.99831	-24416.02149	5.27	-52.44	-57.70
4-Methyl	-24703.67256	-24416.02182	5.06	-51.55	-56.61
H	-24664.36244	-24416.02213	4.87	-49.50	-54.37
4-acetyl	-24817.11172	-24416.02259	4.58	-51.28	-55.86
4-nitro	-24869.13431	-24416.02371	3.87	-47.16	-51.04

Table S15. Adsorption of 4-substituted pyridines on site 2 of (101) anatase surface in presence of dissociated water with OH on site 1 and H on O2c site 3 (Fig. S9c).

	F3, a.u.	F1, a.u.	E2, kcal/mol	E1, kcal/mol	E3, kcal/mol
4-NH2	-24719.74801	-24416.02504	6.51	-48.04	-54.55
4-methoxy	-24778.99584	-24416.02524	6.39	-47.42	-53.81
4-Methyl	-24703.66973	-24416.02645	5.62	-46.31	-51.93
H	-24664.3597	-24416.02692	5.33	-44.31	-49.64
4-acetyl	-24817.10898	-24416.02768	4.85	-46.09	-50.95
4-nitro	-24869.13183	-24416.02843	4.38	-42.14	-46.52

Table S16. Adsorption of 4-substituted pyridines on site 4 of (101) anatase surface in presence of dissociated water with OH on site 1 and H on O2c site 3 (Fig. S10a).

	F3, a.u.	F1, a.u.	E2, kcal/mol	E1, kcal/mol	E3, kcal/mol
4-NH2	-24719.74481	-24416.02471	6.72	-46.03	-52.75
4-methoxy	-24778.99187	-24416.02561	6.15	-44.92	-51.08
4-Methyl	-24703.66644	-24416.02616	5.81	-44.24	-50.05
H	-24664.35649	-24416.02663	5.51	-42.30	-47.81
4-acetyl	-24817.10542	-24416.02722	5.14	-43.86	-49.00
4-nitro	-24869.12853	-24416.02835	4.43	-40.07	-44.50

Table S17. Adsorption of 4-substituted pyridines on site 3 of (101) anatase surface in presence of dissociated water with OH on site 1 and H on O2c site 3 (Fig. S10b).

	F3, a.u.	F1, a.u.	E2, kcal/mol	E1, kcal/mol	E3, kcal/mol
4-NH2	-24719.75051	-24416.02248	8.12	-49.61	-57.73
4-methoxy	-24778.99716	-24416.02316	7.69	-48.25	-55.94
4-Methyl	-24703.67119	-24416.02349	7.48	-47.22	-54.70
H	-24664.36101	-24416.02407	7.12	-45.13	-52.25
4-acetyl	-24817.11097	-24416.02498	6.55	-47.34	-53.89
4-nitro	-24869.13223	-24416.02597	5.93	-42.39	-48.31

Table S18. Adsorption of 4-substituted pyridines through nitrogen protonation by the OH group of KOH doped (101) anatase surface (Fig. S11a).

	F3, a.u.	F1, a.u.	E2, kcal/mol	E1, kcal/mol	E3, kcal/mol
4-NH2	-25333.14254	-25029.46484	3.84	-22.30	-26.14
4-methoxy	-25392.38861	-25029.46472	3.92	-20.57	-24.49
4-Methyl	-25317.06434	-25029.4665	2.80	-20.61	-23.42
H	-25277.7548	-25029.46657	2.75	-18.93	-21.68
4-acetyl	-25430.50347	-25029.46632	2.91	-20.32	-23.24
4-nitro	-25482.52355	-25029.46792	1.91	-14.63	-16.54

Fig. S9. Adsorption of pyridine on site 2 of (101) anatase surface in presence of water with OH bound to site 1 and H on a) site 1, b) site 2, c) site 3)

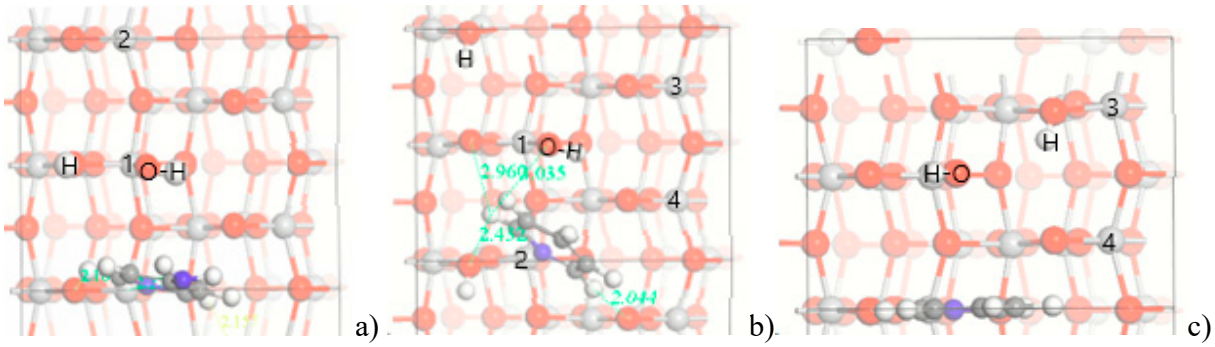


Fig. S10. Adsorption of pyridine on a) site 4, b) site 3 of (101) anatase surface in presence of water with OH bound to site 1 and H on site 3.

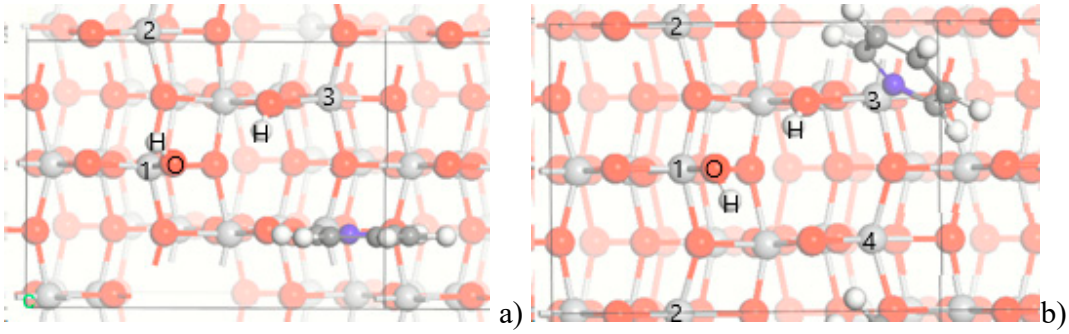
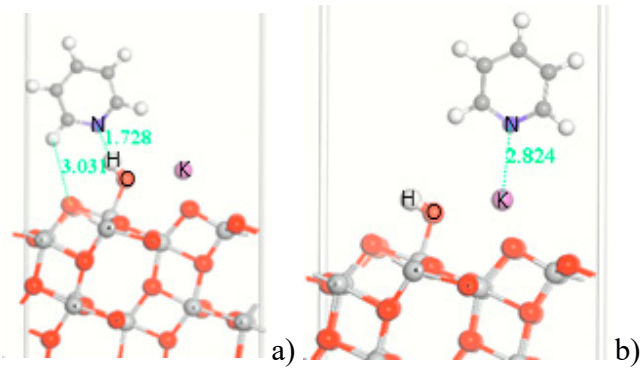


Fig. S11. Adsorption of pyridine on a) OH bound to site 1, b) K of KOH doped (101) anatase surface.



a) b)

Fig. S12. Lattice distortion energy E2 caused by adsorption of 4-substituted pyridines on Ti sites 2-4 of anatase (101) surface in presence of dissociated water with OH on site 1.

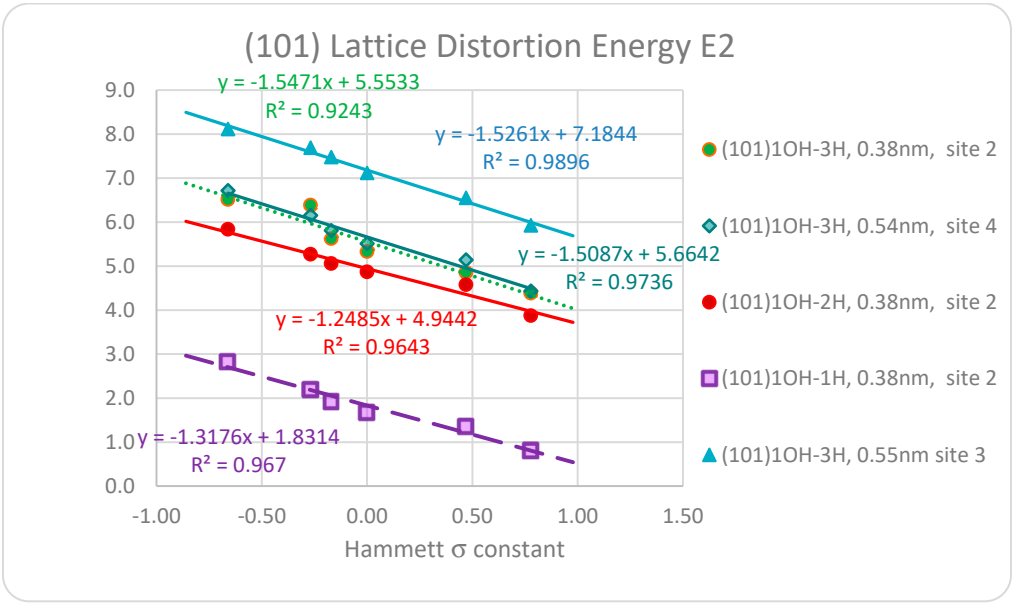


Fig. S13. Energy correlation between Pyridine and CO adsorption on various sites of (101) surface, in the presence of dissociated water, or KOH, a) Lattice distortion energy E2, b) adsorption energy E1. Data points are taken from Table 1.

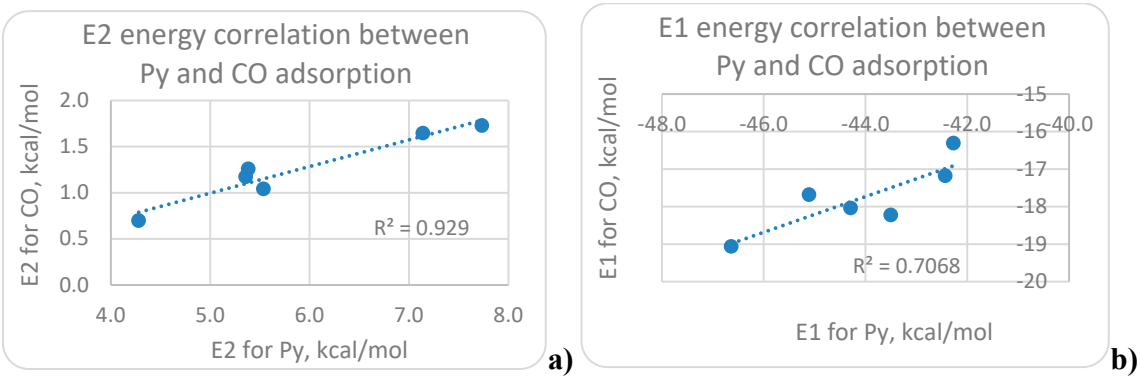


Fig. S14. Lattice distortion energy E2 correlation with the bond length of CO adsorbed on various (101) surface Titanium Lewis acid sites in the presence of dissociated water, or KOH, a) CO bond length, b) Ti-CO bond length. Data points are taken from Table 1.

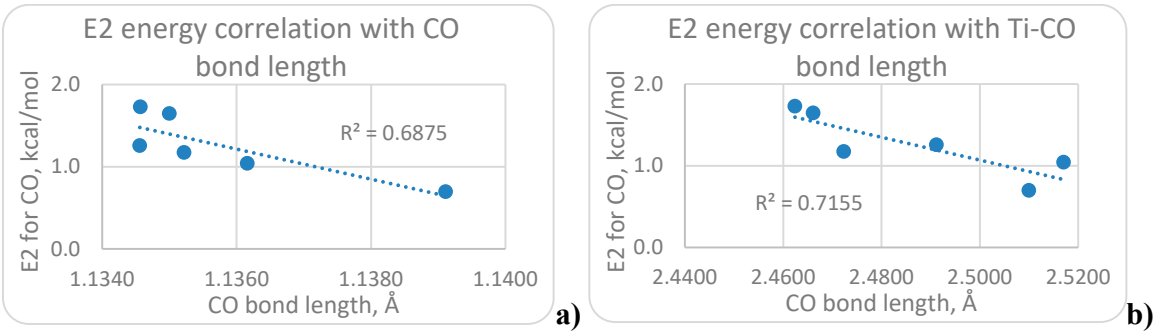
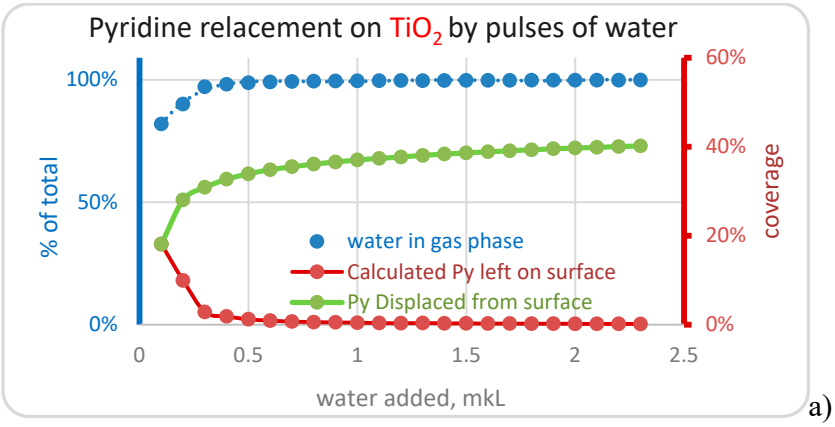
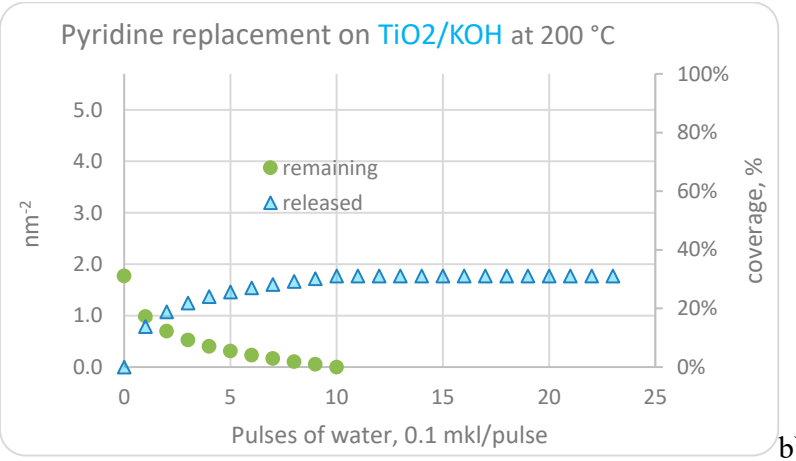


Fig. S15. Typical gas phase titration with pulses of water, 0.1 mkl/pulse, of pyridine covered a) anatase titania TiO_2 at 250 °C, b) TiO_2/KOH at 200 °C.





b)

Fig. S16. GC/MS Calibration at temperatures 200-350 °C using a mixture of pyridine-water in 1:1 molar ratio while monitoring intensity of signals m/z 79 for pyridine and m/z 18 for water.

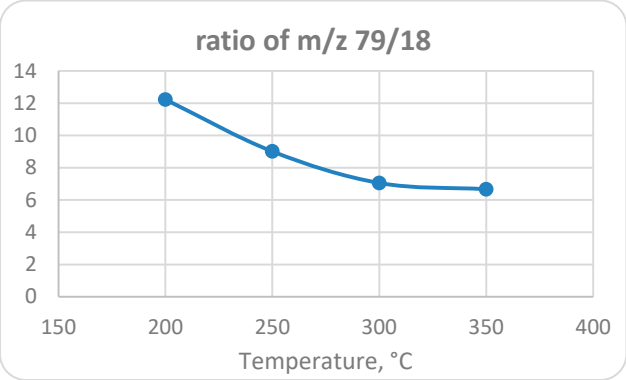


Fig. S17. Fitness test for the 1st order kinetics of pyridine exchange with water on surface.

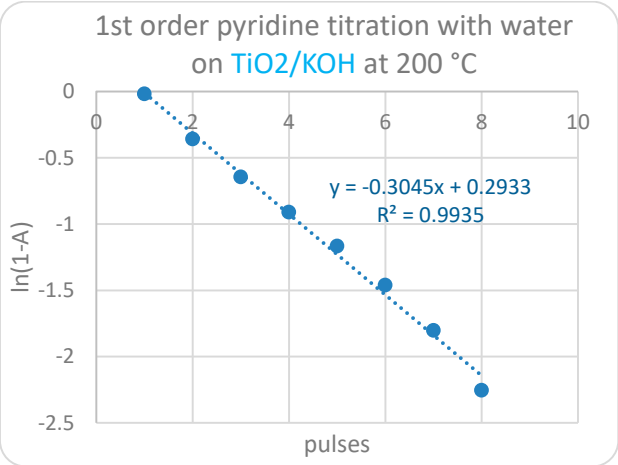
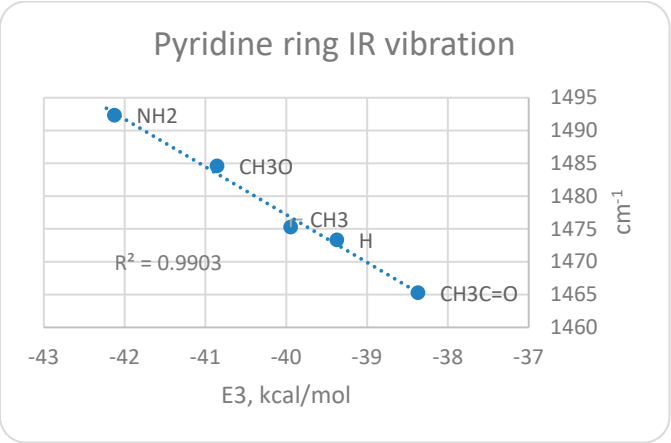



Fig. S18. DFT Calculated frequency of pyridine ring vibration for 4-substituted pyridines adsorbed on site 3 of 12.5% KOH and 12.5% adsorbate coverage of (100) anatase surface as a function of the adjusted energy of adsorption, E3.