Supporting Information for

Characterization of acid and basic sites on zirconia surfaces and nanoparticles by adsorbed probe molecules: A theoretical study

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Contents

Table S1 The Bader charges (q, |e|) of the CO adsorption attached to Zr atom for the structures shown in Figure 2 and Table 1 in the manuscript.

	Fig.	Site	q_{CO}	q_{C}	q_{Zr}
m-ZrO_2 ($\bar{1}11$)	2(a)	Zr_{6c}A	-0.03	1.02	2.69
	2(b)	Zr_{6c}B	-0.01	1.07	2.69
	2(c)	Zr_{6c}C	-0.02	1.07	2.70
t-ZrO_2 (101)	2(d)	Zr_{7c}	-0.03	1.03	2.73
m-ZrO_2 ($\bar{2}12$)	2(e)	Zr_{5c}	0.03	0.75	2.12
	2(f)	Zr_{6c}	-0.03	0.70	2.11
t-ZrO_2 (134)	2(g)	Zr_{6c}	0.03	0.75	2.12
	2(h)	Zr_{7c}	-0.03	1.07	2.75

Table S2 The Bader charges (q, |e|) of the pyrrole adsorption attached to O atom for the structures shown in Figure 6 and Table 2 in the manuscript.

	Fig.	Site	$q_{pyrrole}$	q_{H}	q_{O}
m-ZrO_2 ($\bar{1}11$)	6(a)	O_{2c}(O1)	-0.04	0.52	-1.26
	6(b)	O_{3c} (O2)	-0.03	0.51	-1.36
	6(c)	O_{3c} (O4)	-0.04	0.53	-1.39
t-ZrO_2 (101)	6(d)	O_{3c}	-0.05	0.48	-1.38
	6(e)	O_{3c}	-0.05	0.49	-1.38
m-ZrO_2 ($\bar{2}12$)	6(f)	O_{3c}	-0.03	0.52	-1.35
	6(g)	O_{2c}	0.01	0.51	-1.31
	6(h)	O_{3c}	-0.04	0.54	-1.39
t-ZrO_2 (134)	6(i)	O_{3c}	0.04	0.56	-1.38
	6(j)	O_{3c}	0.06	0.53	-1.35
	6(k)	O_{3c}	-0.04	0.53	-1.38
	6(l)	O_{3c}	-0.04	0.55	-1.38

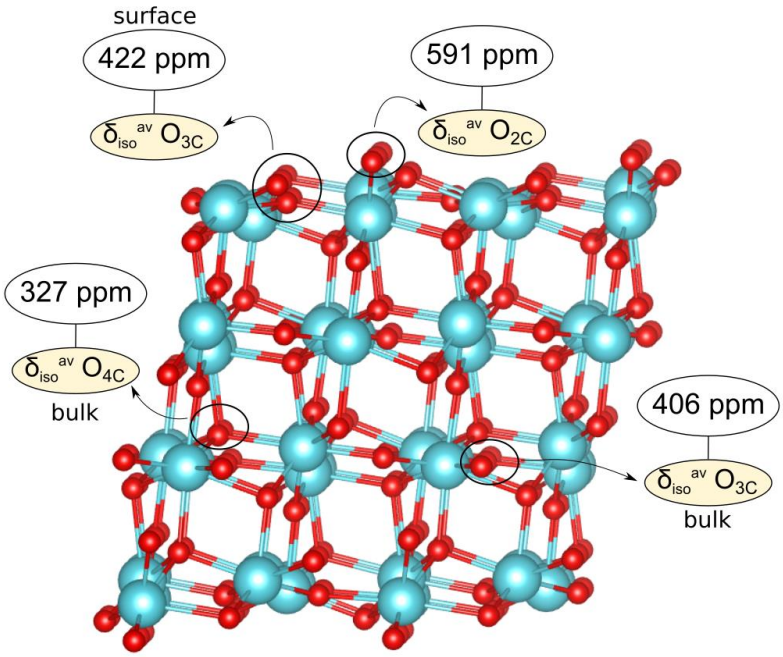


Fig. S1. ^{17}O NMR average chemical shift (δ_{iso}^{av}, ppm) of various oxygen atoms in regular m-ZrO_2 ($\bar{1}11$) slab

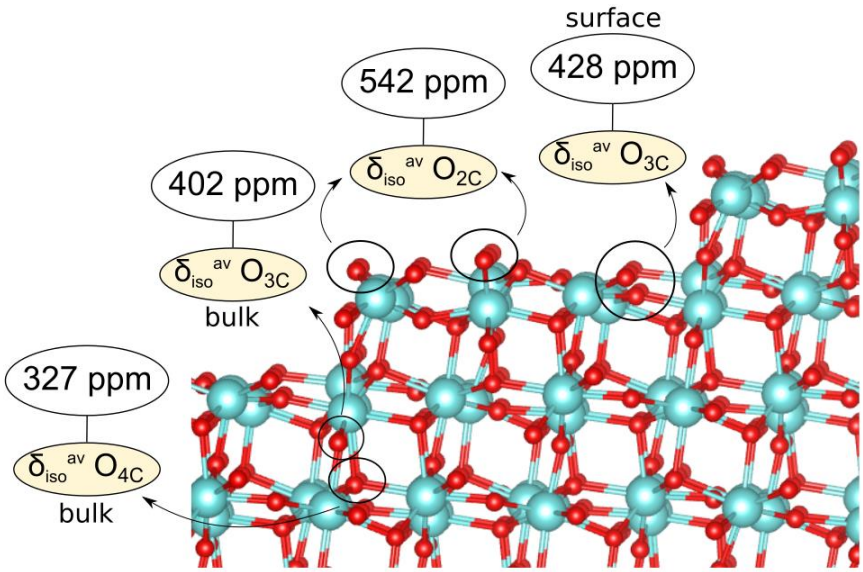


Fig. S2. ^{17}O NMR average chemical shift (δ_{iso}^{av}, ppm) of various oxygen atoms in stepped m-ZrO_2 ($\bar{2}12$) slab

Table S3. δ_{iso}^{av} ^{17}O NMR (ppm) of m-ZrO_2 surfaces.

	δ_{iso}^{av} m-ZrO_2 ($\bar{1}11$)	**δ_{iso}^{av} m-ZrO_2 ($\bar{2}12$)**	**δ_{iso}Exp [1]**
O_{2C} (surface)	591	542	-
O_{3C} (surface)	422	428	426
O_{3C} (bulk)	406	402	402
O_{4C} (bulk)	327	327	325

[1] L. Shen, X.-P. Wu, Y. Wang, M. Wang, J. Chen, Y. Li, H. Huo, W. Hou, W. Ding, X.-Q. Gong, L. Peng, ^{17}O Solid-State NMR Studies of ZrO_2 Nanoparticles, J. Phys. Chem. C 123 (2019) 4158-4167.

Table S4. δ_{iso} ^{17}O NMR (ppm) of m-ZrO_2 ($\bar{1}11$) surface.

		Shielding (VASP)	δ_{iso} δ_{ref}= -17	Layer
1	O_{2C}	-608	591	**1**
2	O_{2C}	-608	591	
3	O_{2C}	-608	591	
4	O_{2C}	-608	591	
5	O_{3C}	-443	426	
6	O_{3C}	-443	426	
7	O_{3C}	-443	426	
8	O_{3C}	-443	426	
9	O_{3C}	-438	421	
10	O_{3C}	-438	421	
11	O_{3C}	-438	421	
12	O_{3C}	-438	421	
13	O_{3C}	-435	418	
14	O_{3C}	-435	418	
15	O_{3C}	-435	418	
16	O_{3C}	-435	418	
17	O_{3C}	-439	422	
18	O_{3C}	-439	422	
19	O_{3C}	-439	422	
20	O_{3C}	-439	422	
21	O_{4C}	-343	326	
22	O_{4C}	-343	326	
23	O_{4C}	-343	326	
24	O_{4C}	-343	326	
25	O_{4C}	-353	336	
26	O_{4C}	-353	336	
27	O_{4C}	-353	336	
28	O_{4C}	-353	336	
29	O_{3C}	-430	413	
30	O_{3C}	-430	413	
31	O_{3C}	-430	413	
32	O_{3C}	-430	413	
33	O_{3C}	-415	398	**2**
34	O_{3C}	-415	398	
35	O_{3C}	-415	398	
36	O_{3C}	-415	398	
37	O_{4C}	-338	321	
38	O_{4C}	-338	321	
39	O_{4C}	-338	321	
40	O_{4C}	-338	321	
41	O_{4C}	-349	332	
42	O_{4C}	-349	332	
43	O_{4C}	-349	332	
44	O_{4C}	-349	332	
45	O_{3C}	-422	405	
46	O_{3C}	-422	405	
47	O_{3C}	-422	405	
48	O_{3C}	-422	405	
49	O_{3C}	-425	408	
50	O_{3C}	-425	408	
51	O_{3C}	-425	408	
52	O_{3C}	-425	408	
53	O_{4C}	-340	323	
54	O_{4C}	-340	323	
55	O_{4C}	-340	323	
56	O_{4C}	-340	323	
57	O_{4C}	-341	324	
58	O_{4C}	-341	324	
59	O_{4C}	-341	324	
60	O_{4C}	-341	324	
61	O_{3C}	-424	407	
62	O_{3C}	-424	407	
63	O_{3C}	-424	407	
64	O_{3C}	-424	407	
65	O_{3C}	-424	407	**3**
66	O_{3C}	-424	407	
67	O_{3C}	-424	407	
68	O_{3C}	-424	407	
69	O_{4C}	-341	324	
70	O_{4C}	-341	324	
71	O_{4C}	-341	324	
72	O_{4C}	-341	324	
73	O_{4C}	-340	323	
74	O_{4C}	-340	323	
75	O_{4C}	-340	323	
76	O_{4C}	-340	323	
77	O_{3C}	-425	408	
78	O_{3C}	-425	408	
79	O_{3C}	-425	408	
80	O_{3C}	-425	408	
81	O_{3C}	-422	405	
82	O_{3C}	-422	405	
83	O_{3C}	-422	405	
84	O_{3C}	-422	405	
85	O_{4C}	-349	332	
86	O_{4C}	-349	332	
87	O_{4C}	-349	332	
88	O_{4C}	-349	332	
89	O_{4C}	-338	321	
90	O_{4C}	-338	321	
91	O_{4C}	-338	321	
92	O_{4C}	-338	321	
93	O_{3C}	-415	398	
94	O_{3C}	-415	398	
95	O_{3C}	-415	398	
96	O_{3C}	-415	398	
97	O_{3C}	-430	413	**4**
98	O_{3C}	-430	413	
99	O_{3C}	-430	413	
100	O_{3C}	-430	413	
101	O_{4C}	-353	336	

102	O_{4C}	-353	336
103	O_{4C}	-353	336
104	O_{4C}	-353	336
105	O_{4C}	-343	326
106	O_{4C}	-343	326
107	O_{4C}	-343	326
108	O_{4C}	-343	326
109	O_{3C}	-439	422
110	O_{3C}	-439	422
111	O_{3C}	-439	422
112	O_{3C}	-439	422
113	O_{3C}	-435	418
114	O_{3C}	-435	418
115	O_{3C}	-435	418
116	O_{3C}	-435	418
117	O_{3C}	-438	421
118	O_{3C}	-438	421
119	O_{3C}	-438	421
120	O_{3C}	-438	421
121	O_{3C}	-443	426
122	O_{3C}	-443	426
123	O_{3C}	-443	426
124	O_{3C}	-443	426
125	O_{2C}	-608	591
126	O_{2C}	-608	591
127	O_{2C}	-608	591
128	O_{2C}	-608	591

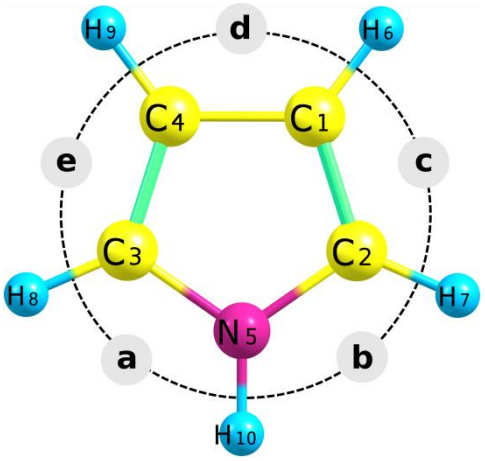
Table S5. δ_{iso} ^{17}O NMR (ppm) of m-ZrO_2 ($\bar{2}12$) surface.

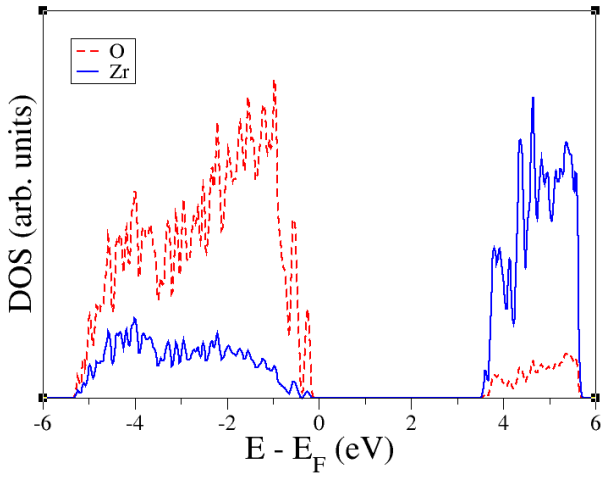
		Shielding (VASP)	δ_{iso} δ_{ref}= -17	Layer
1	O_{2C}	-544	527	1
2	O_{2C}	-544	527	
3	O_{2C}	-574	557	
4	O_{2C}	-574	557	
5	O_{3C}	-433	416	
6	O_{3C}	-433	416	
7	O_{3C}	-451	434	
8	O_{3C}	-451	434	
9	O_{3C}	-454	437	
10	O_{3C}	-454	437	
11	O_{3C}	-469	452	
12	O_{3C}	-469	452	
13	O_{3C}	-442	425	
14	O_{3C}	-442	425	
15	O_{4C}	-357	340	
16	O_{4C}	-357	340	
17	O_{3C}	-442	425	
18	O_{3C}	-442	425	
19	O_{3C}	-422	405	
20	O_{3C}	-422	405	
21	O_{3C}	-425	408	
22	O_{3C}	-425	408	
23	O_{4C}	-345	328	
24	O_{4C}	-345	328	
25	O_{4C}	-339	322	
26	O_{4C}	-339	322	
27	O_{3C}	-445	428	
28	O_{3C}	-445	428	
29	O_{3C}	-411	394	
30	O_{3C}	-411	394	
31	O_{4C}	-346	329	
32	O_{4C}	-346	329	
33	O_{4C}	-334	317	2
34	O_{4C}	-334	317	
35	O_{3C}	-403	386	
36	O_{3C}	-403	386	
37	O_{3C}	-416	399	
38	O_{3C}	-416	399	
39	O_{4C}	-339	322	
40	O_{4C}	-339	322	
41	O_{4C}	-341	324	
42	O_{4C}	-341	324	
43	O_{3C}	-433	416	
44	O_{3C}	-433	416	
45	O_{3C}	-422	405	
46	O_{3C}	-422	405	
47	O_{4C}	-343	326	
48	O_{4C}	-343	326	
49	O_{4C}	-349	332	
50	O_{4C}	-349	332	
51	O_{3C}	-419	402	
52	O_{3C}	-419	402	
53	O_{3C}	-420	403	
54	O_{3C}	-420	403	
55	O_{4C}	-345	328	
56	O_{4C}	-345	328	
57	O_{4C}	-344	327	
58	O_{4C}	-344	327	
59	O_{3C}	-425	408	
60	O_{3C}	-425	408	
61	O_{3C}	-425	408	3
62	O_{3C}	-425	408	
63	O_{4C}	-344	327	
64	O_{4C}	-344	327	
65	O_{4C}	-345	328	
66	O_{4C}	-345	328	
67	O_{3C}	-420	403	
68	O_{3C}	-420	403	
69	O_{3C}	-419	402	
70	O_{3C}	-419	402	
71	O_{4C}	-349	332	
72	O_{4C}	-349	332	
73	O_{4C}	-343	326	
74	O_{4C}	-343	326	
75	O_{3C}	-422	405	
76	O_{3C}	-422	405	
77	O_{3C}	-433	416	
78	O_{3C}	-433	416	
79	O_{4C}	-341	324	
80	O_{4C}	-341	324	
81	O_{4C}	-339	322	
82	O_{4C}	-339	322	
83	O_{3C}	-416	399	
84	O_{3C}	-416	399	
85	O_{3C}	-402	385	
86	O_{3C}	-402	385	
87	O_{4C}	-334	317	
88	O_{4C}	-334	317	
89	O_{4C}	-346	329	4
90	O_{4C}	-346	329	
91	O_{3C}	-411	394	
92	O_{3C}	-411	394	
93	O_{3C}	-445	428	
94	O_{3C}	-445	428	
95	O_{4C}	-339	322	
96	O_{4C}	-339	322	
97	O_{4C}	-345	328	
98	O_{4C}	-345	328	
99	O_{3C}	-425	408	
100	O_{3C}	-425	408	
101	O_{3C}	-422	405	

102	O_{3C}	-422	405
103	O_{3C}	-442	425
104	O_{3C}	-442	425
105	O_{4C}	-357	340
106	O_{4C}	-357	340
107	O_{3C}	-442	425
108	O_{3C}	-442	425
109	O_{3C}	-469	452
110	O_{3C}	-469	452
111	O_{3C}	-454	437
112	O_{3C}	-454	437
113	O_{3C}	-451	434
114	O_{3C}	-451	434
115	O_{3C}	-433	416
116	O_{3C}	-433	416
117	O_{2C}	-573	556
118	O_{2C}	-573	556
119	O_{2C}	-543	526
120	O_{2C}	-543	526

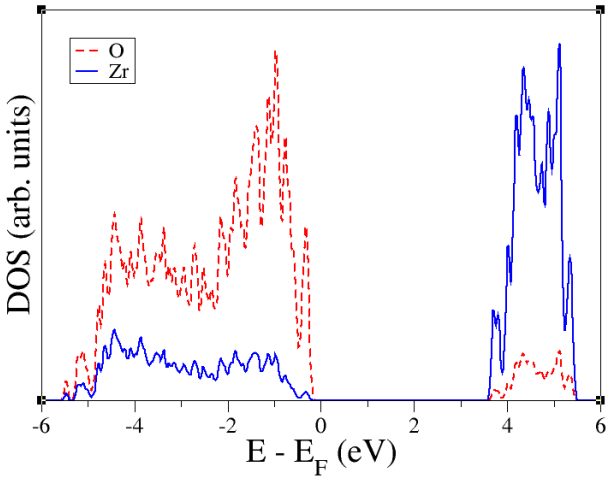
Table S6. Dihedral angles (a to e, ˚) of pyrrole on ZrO_2 surfaces, see Figure 6 in the paper.

	Figure	a	b	c	d	e
m-ZrO_2 ($\bar{1}11$)	6(a)	0.24	0.08	0.08	0.05	0.04
	6(b)	0.57	0.51	0.29	0.21	0.04
	6(c)	5.32	5.81	1.08	0.16	0.26
t-ZrO_2 (101)	6(d)	0.36	0.63	0.23	0.04	0.12
	6(e)	1.61	1.56	0.09	0.05	0.01
m-ZrO_2 ($\bar{2}12$)	6(f)	4.74	5.31	2.49	0.04	1.67
	6(g)	8.84	0.46	10.31	1.17	0.11
	6(h)	0.77	0.16	0.46	0.08	0.31
t-ZrO_2 (134)	6(i)	26.56	27.47	4.29	2.53	7.75
	6(j)	5.37	26.78	18.64	2.36	3.64
	6(k)	1.01	0.87	0.61	0.05	0.71
	6(l)	0.14	0.08	0.05	0.02	0.09

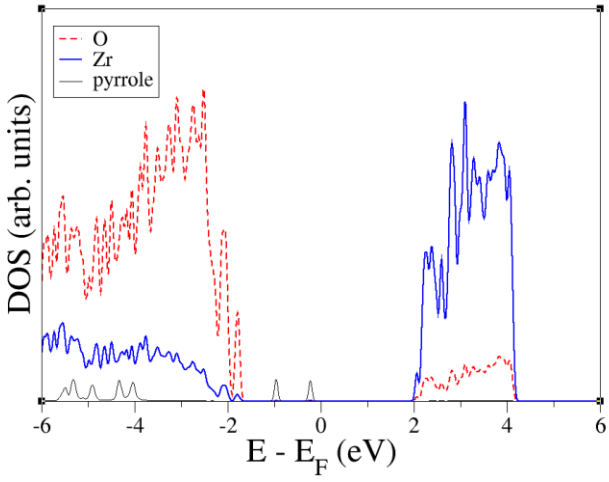




Clean m-ZrO_2 ($\bar{2}12$)



Clean t-ZrO_2 (134)



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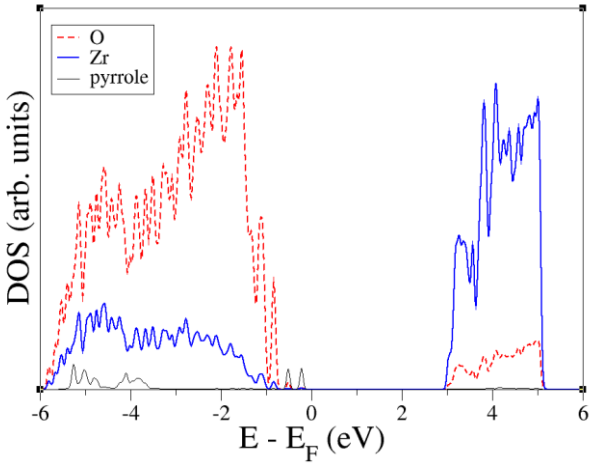
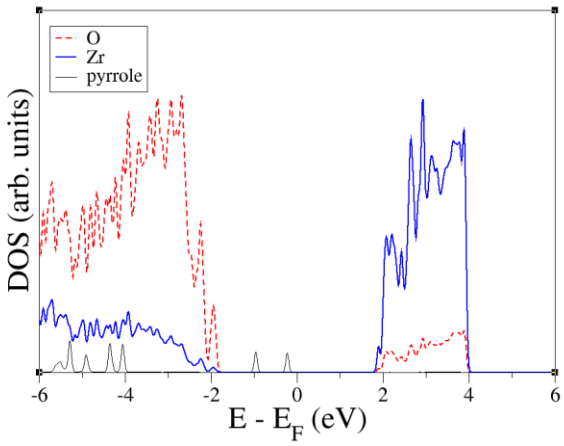


(g)



(h)

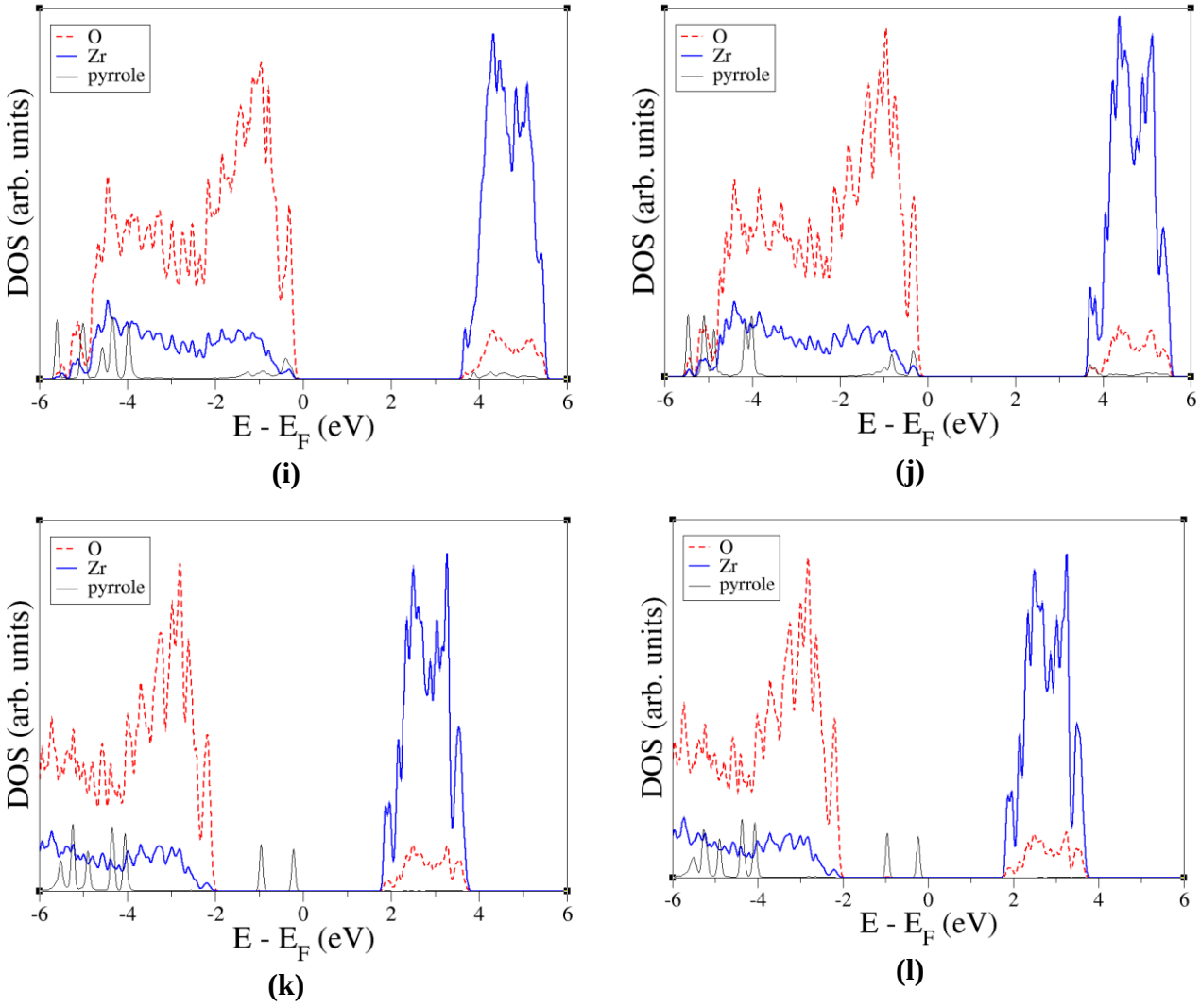


Fig. S3. Density of states (DOS) of the clean and pyrrole adsorption on stepped m- and t-ZrO_2 surfaces

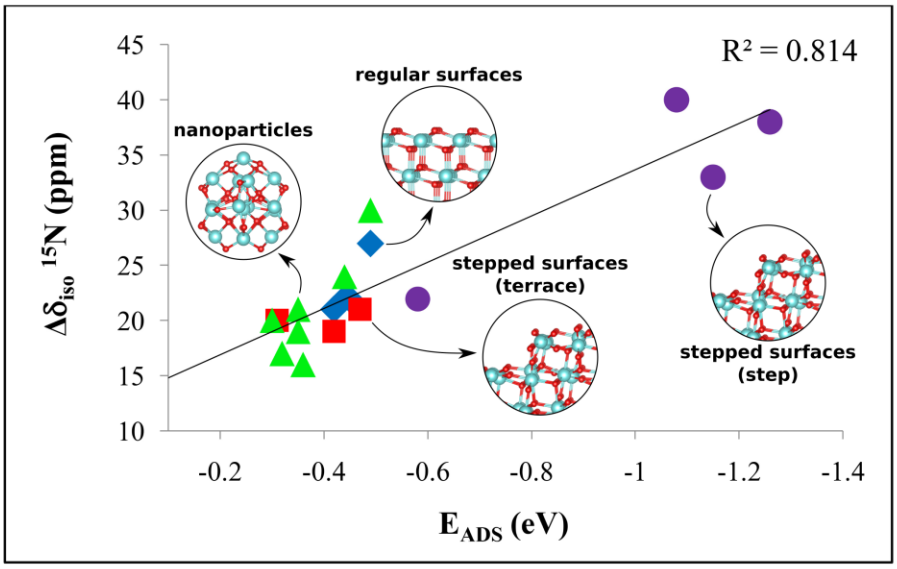


Fig. S4. Correlation between the changes in ^{15}N NMR chemical shift and the adsorption energy of the pyrrole molecule on regular and stepped m-ZrO_2 and t-ZrO_2 surfaces and on zirconia nanoparticles.