Electronic supplementary information for the paper

Predicting adsorption on metals: Simple yet effective descriptors for surface catalysis

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This document contains the detailed experimental results, additional information on the models reported in the main text and information required to reproduce the reported models. Specifically, all measured adsorption terms are given, the detailed equations of the obtained models, a separate set of models for hydrogen and hydroxyl radical and details on the specific variables and applications included in each model are provided. The additional information provided for the modeling results are sufficient to provide the reader with the means to reproduce any model reported in the main text.

Measured adsorption isotherms

This section contains all measured adsorption isotherms for the gases (CH_4, CO, CO_2, H_2, N_2, and O_2) and solid materials (bare TiO_2 and 1 wt% Ni, Pt and Rh on the same TiO_2) investigated. The data is grouped per adsorptive gas (CH_4 in Figure S1, CO in Figure S2, CO_2 in Figure S3, H_2 in Figure S4, N_2 in Figure S5 and O_2 in Figure S6). The separate plots allow for the widely different scales at which the adsorption events take place.

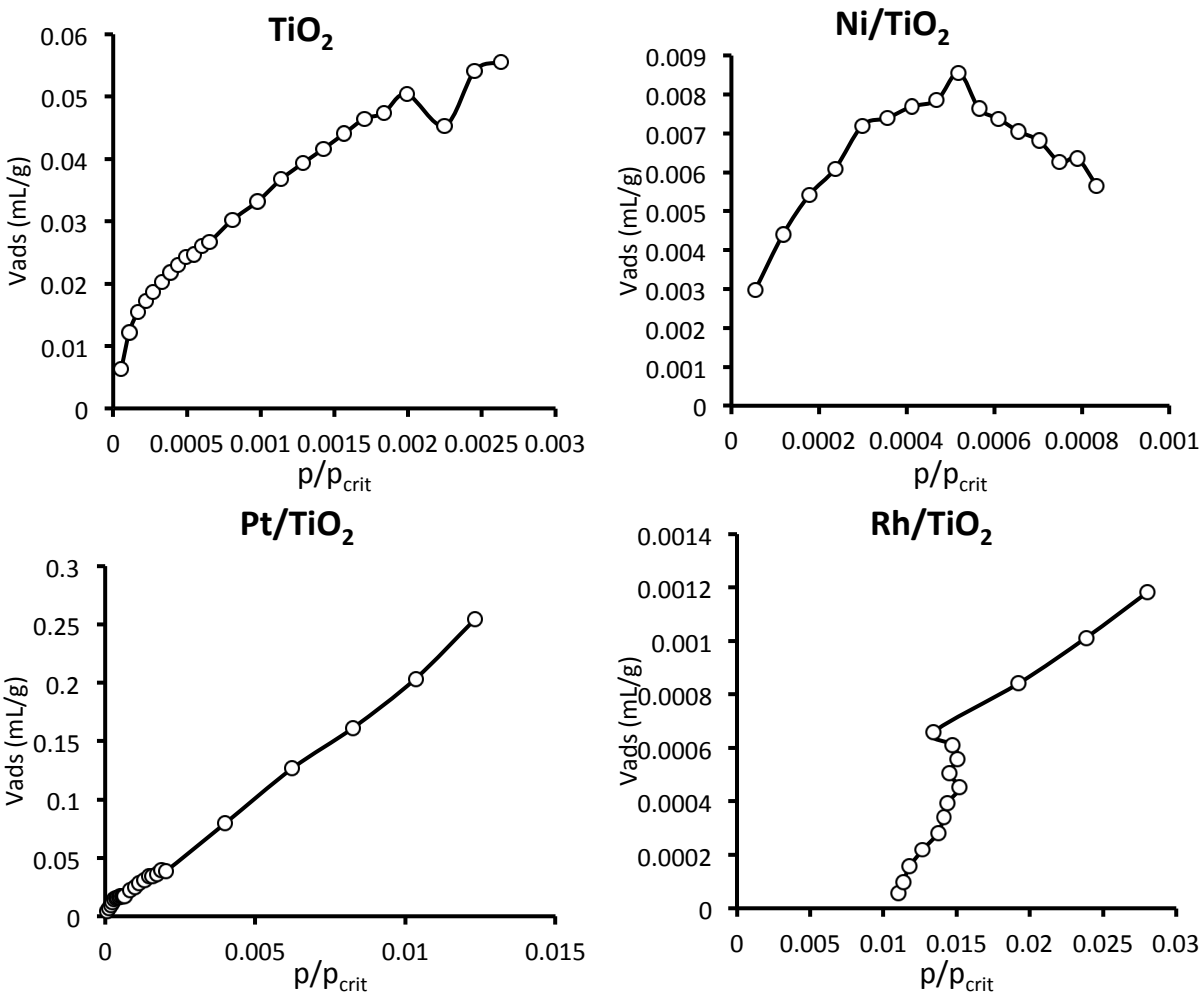

Figure S1 Measured adsorption isotherms for CH_4, as adsorbed volume per unit mass of solid versus p/p_{crit}, for all 4 solid materials (bare TiO_2 and 1 wt% Ni, Pt and Rh on the same TiO_2).

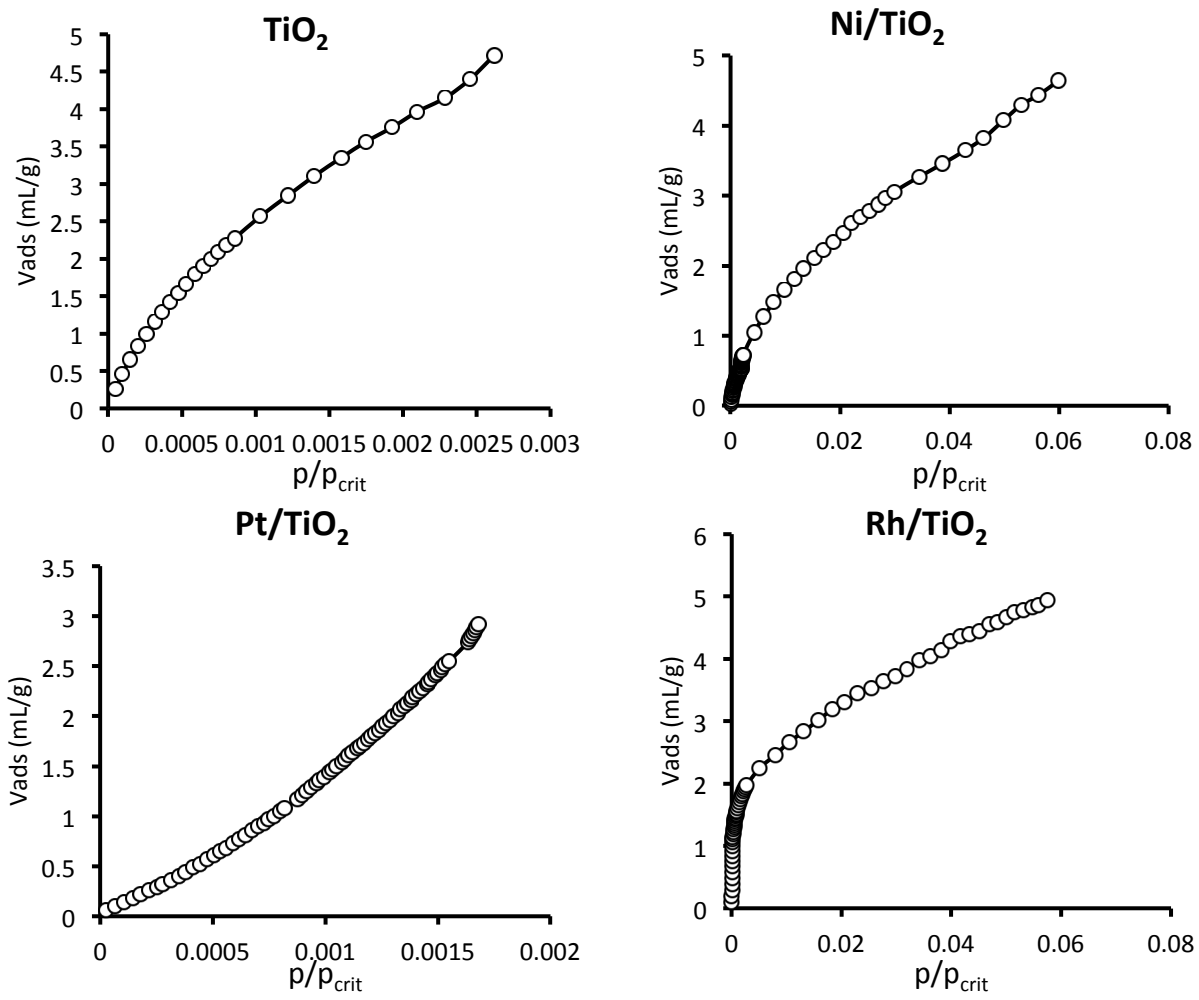

Figure S2 Measured adsorption isotherms for CO, as adsorbed volume per unit mass of solid versus p/p_{crit}, for all 4 solid materials (bare TiO_2 and 1 wt% Ni, Pt and Rh on the same TiO_2).

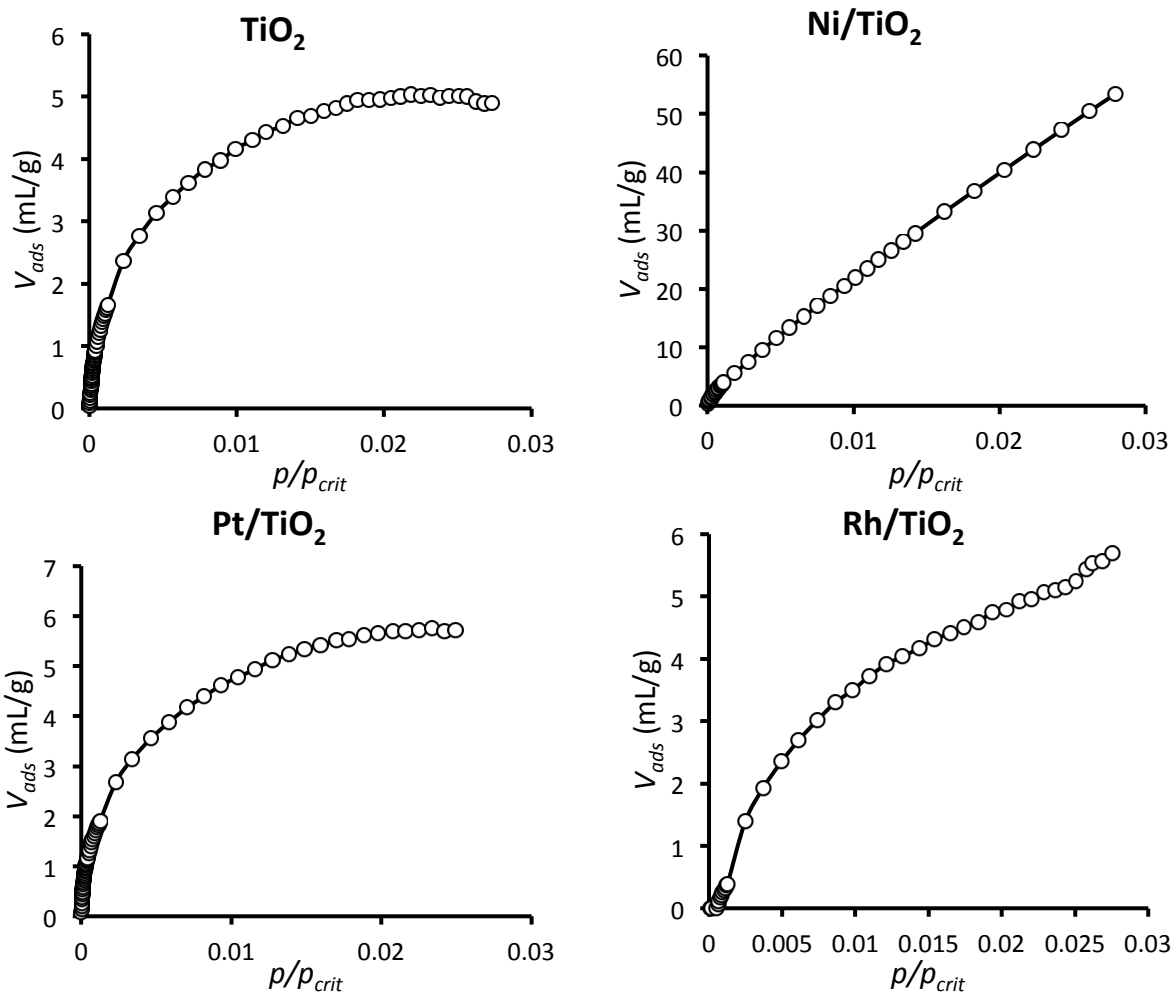

Figure S3 Measured adsorption isotherms for CO_2, as adsorbed volume per unit mass of solid versus p/p_{crit}, for all 4 solid materials (bare TiO_2 and 1 wt% Ni, Pt and Rh on the same TiO_2).

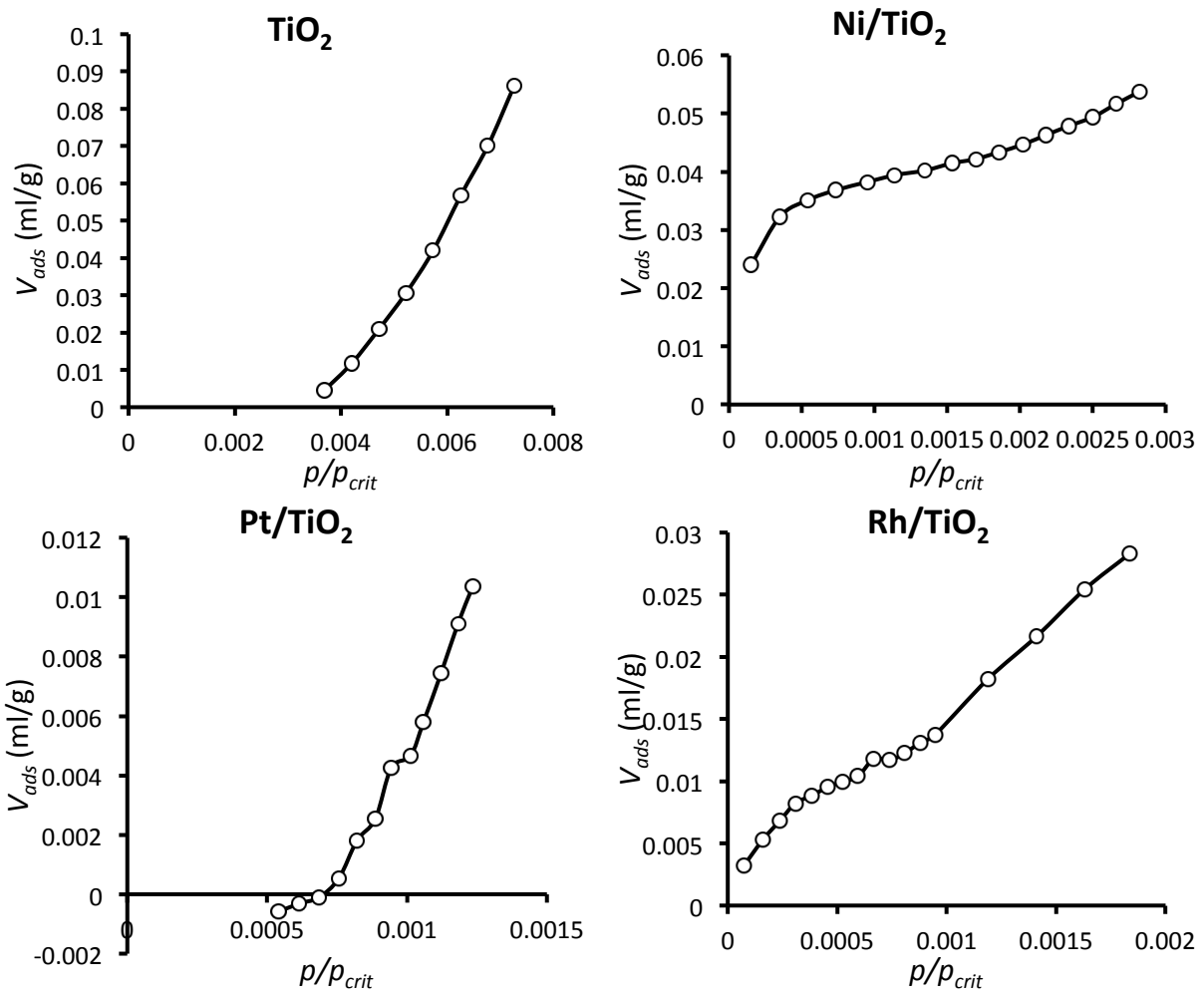

Figure S4 Measured adsorption isotherms for H_2, as adsorbed volume per unit mass of solid p/p_{crit}, for all 4 solid materials (bare TiO_2 and 1 wt% Ni, Pt and Rh on the same TiO_2).

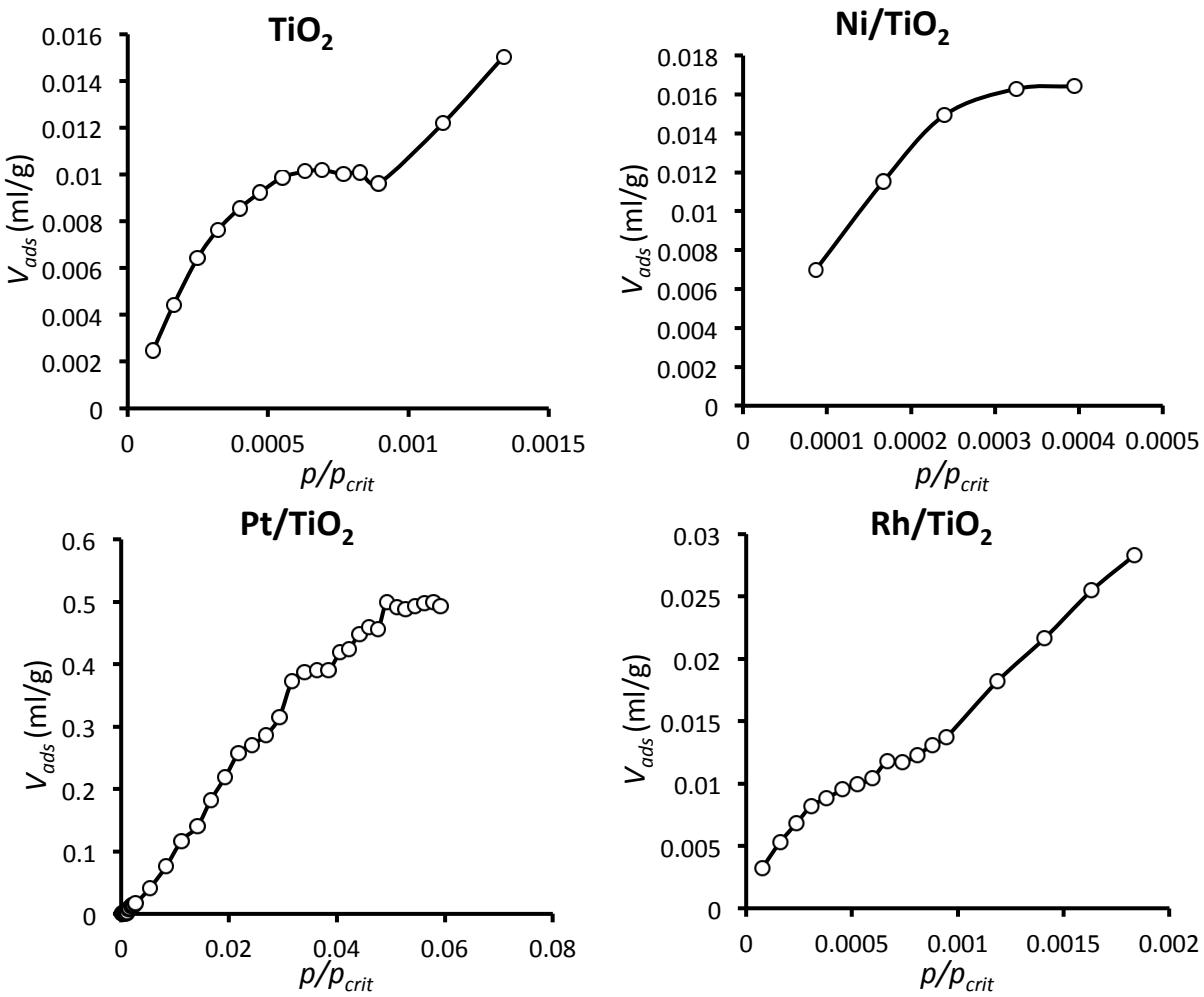

Figure S5 Measured adsorption isotherms for N_2, as adsorbed volume per unit mass of solid versus p/p_{crit}, for all 4 solid materials (bare TiO_2 and 1 wt% Ni, Pt and Rh on the same TiO_2).

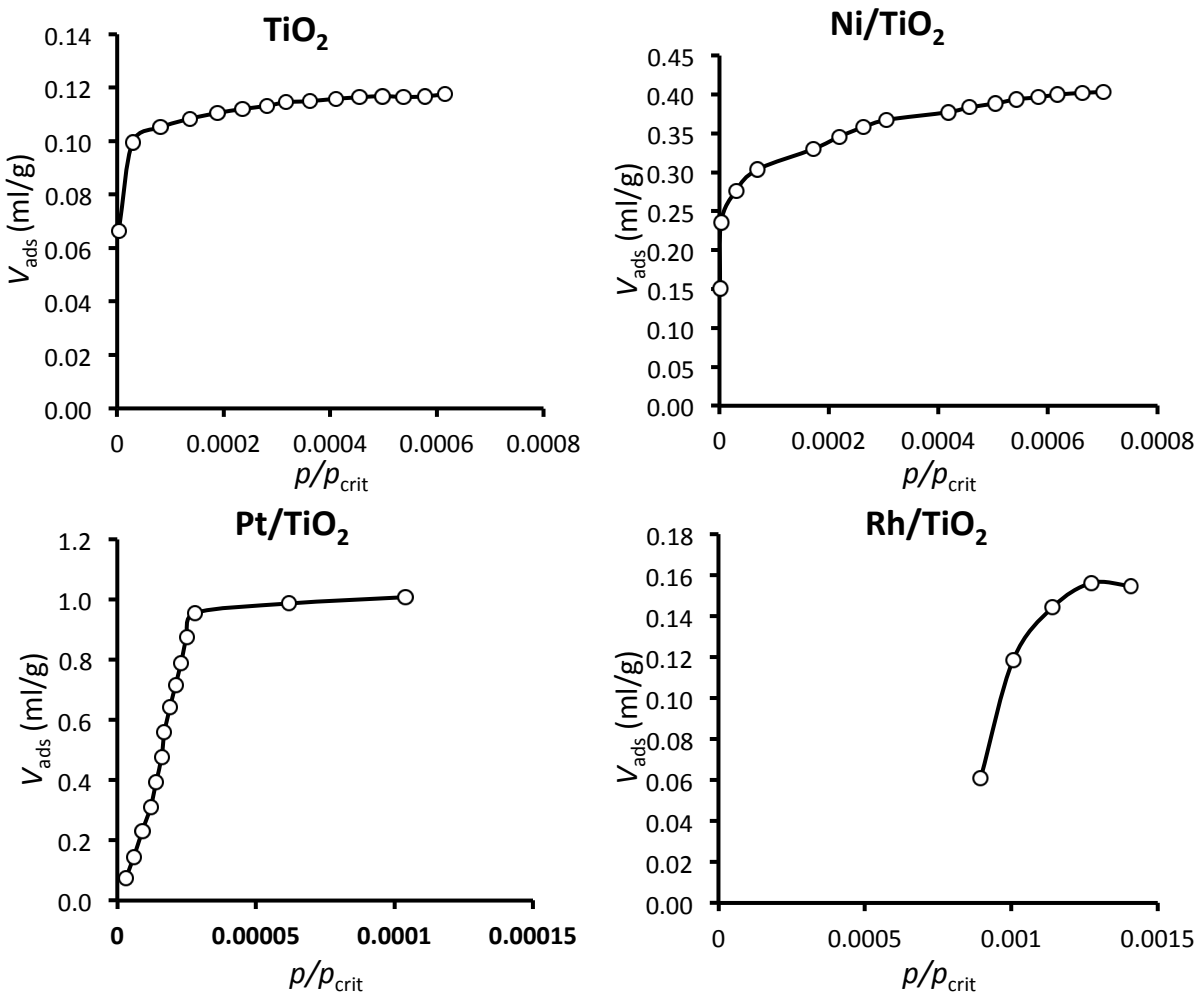

Figure S6 Measured adsorption isotherms for O_2, as adsorbed volume per unit mass of solid versus p/p_{crit}, for all 4 solid materials (bare TiO_2 and 1 wt% Ni, Pt and Rh on the same TiO_2).

Equations for best models

Below the coefficients are given for the best models (out of the 27 possibilities, from A1B1C1 to A3B3C3) based on DFT data as indicated in Table 3 in the main text. Each table gives the variable identifier, the scaled model coefficients for comparing the importance of each parameter within a model and the real model coefficients to apply the model to calculate heat of adsorption values. As an example, the full equation for model A1B2C1:

$$\Delta H_{ads} = -7.3122 - 2.4519 \cdot x_4 - 0.0860 \cdot x_5 + 0.0296 \cdot x_7 + 0.0427 \cdot x_1 \cdot x_2 + 0.0115 \cdot x_1 \cdot x_9 - 0.0150 \cdot x_2 \cdot x_7 - 0.0311 \cdot x_2 \cdot x_9 + 0.1591 \cdot x_4 \cdot x_8 + 0.0012 \cdot x_5 \cdot x_6 + 0.0018 \cdot x_7 \cdot x_8$$

Table S1 Scaled and real coefficients for the best model obtained for the full data set (A1B2C1).

Parameter	Scaled coefficient	Real coefficient
Intercept	-0.0918243	-7.31229
x4	-0.0709649	-2.45185
x5	-0.0595861	-0.0859984
x7	0.256484	0.0296089
x1*x2	0.0463655	0.0427118
x1*x9	0.458749	0.0115422
x2*x7	-0.531661	-0.0150488
x2*x9	-0.364033	-0.0311441
x4*x8	0.234732	0.159055
x5*x6	0.244552	0.0012333
x7*x8	0.390236	0.0018444

Table S2 Scaled and real coefficients for the best model obtained for the data set excluding H_2 (A2B2C1).

Parameter	Scaled coefficient	Real coefficient
intercept	-0.0263352	-9.89117
x7	0.0486255	0.0091438
x9	-0.0319799	-0.0111913
x1*x7	0.286961	0.0031395
x1*x9	0.174436	0.0062212
x2*x5	-0.291259	-0.122037
x2*x9	-0.231181	-0.0255706
x4*x7	0.0750419	0.0093469
x4*x8	0.140208	0.108952
x4*x9	-0.0232902	-0.0058702
x5*x7	0.0888695	0.0008441
x5*x8	0.13099	0.0082944
x6*x7	0.112894	5.19E-05
x8*x9	0.0275215	0.0004433

Table S3 Scaled and real coefficients for the best model obtained for the data set excluding H_2 and HO▪ (A3B2C1).

Parameter	Scaled coefficient	Real coefficient
intercept	0.010702	-14.3304
x3	0.107007	0.484081
x8	0.151839	0.164672
x9	-0.03308	-0.01067
x1*x7	0.294707	0.003223
x1*x9	0.127356	0.004145
x2*x5	-0.22764	-0.09666
x2*x6	-0.10331	-0.00235
x2*x9	-0.20979	-0.0235
x4*x8	0.186132	0.135114
x5*x6	0.136066	0.000737
x5*x8	0.192965	0.011867
x6*x9	0.064007	9.99E-05
x8*x9	0.035087	0.000516

Individual models for H_2 and HO▪

The heats of adsorption for H_2 and HO▪ have been identified as potential outliers in the models describing multiple metals an adsorptives. To demonstrate that the descriptors proposed here are still valid to describe the adsorption of these species, they have been modeled separately using the best combination of descriptors identified (Table S3). Since in this case a model only describes a single adsorptive species, descriptors related to the adsorptive (*x*7, *x*8 and *x*9) have been discarded. The modeling results for H_2 (R^2 = 0.95 and RMSEE = 0.14 eV) and HO▪ (R^2 = 0.91 and RMSEE = 0.48 eV) are shown in Figure S7 and Figure S8.

Table S4 Model coefficients in real scale for the individual models describing heat of adsorption of H_2 and HO▪.

Parameter	Model for H_2	Model for HO▪
intercept	0.8496234	2.9236674
x3	-0.1654974	-0.4563958
x2*x5	-0.0175603	-0.1530765
x2*x6	-0.0037634	-0.0022056
x5*x6	0.0010038	0.0020596

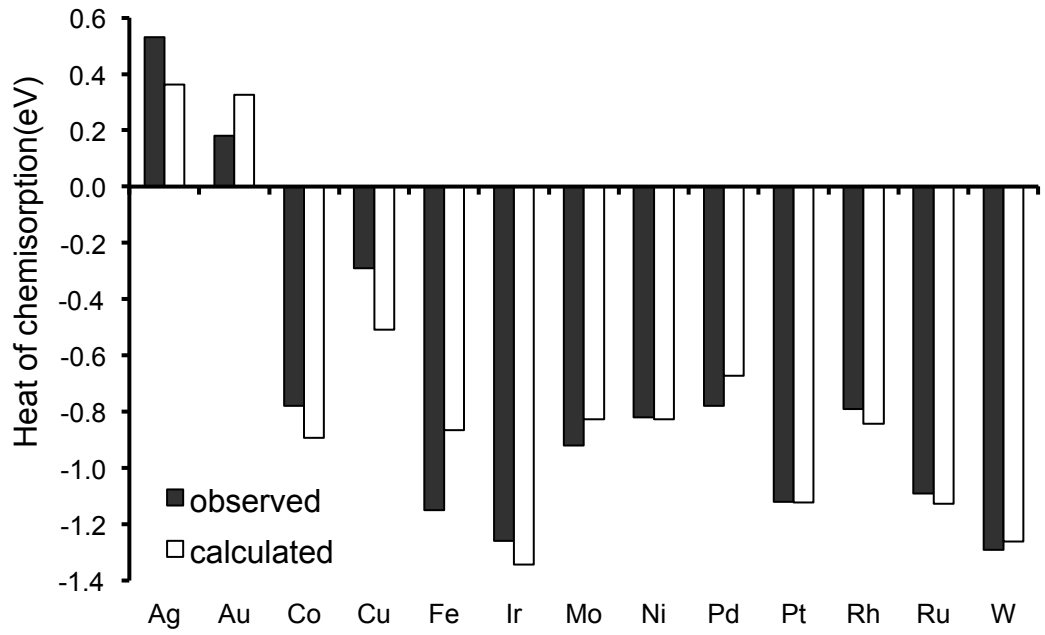

Figure S7 Chemisorption energies of hydrogen derived from DFT (solid bars) and calculated by descriptor model (open bars) for the 13 metals considered.

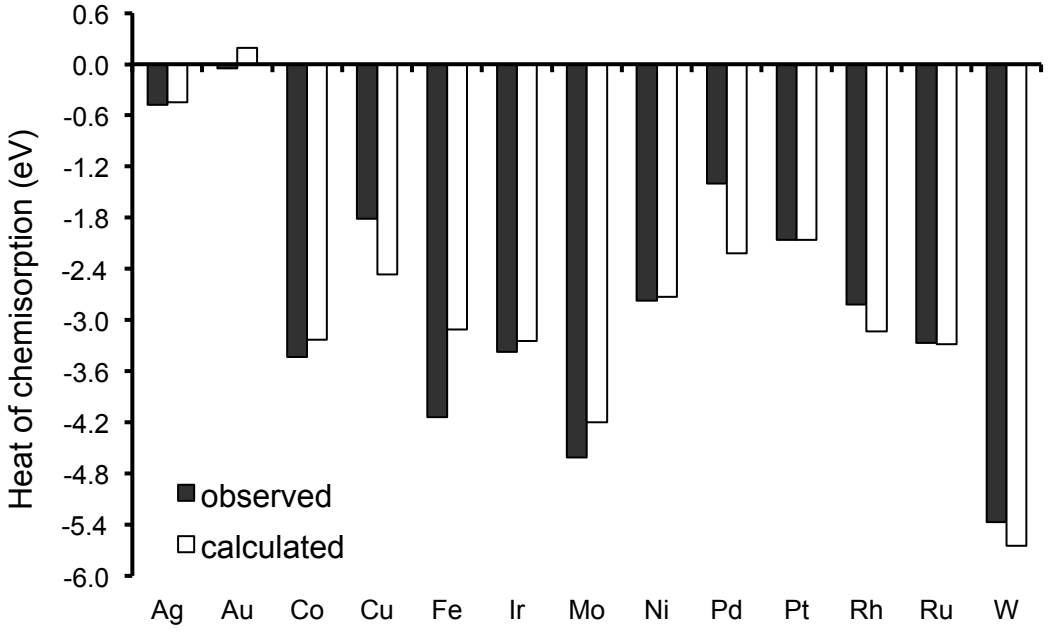

Figure S8 Chemisorption energies of hydroxyl radical derived from DFT (solid bars) and calculated by descriptor model (open bars) for the 13 metals considered.

Detailed modeling results

This section contains the modeling results detailed to a level sufficient to reproduce any of the models discussed in the main text[1]. In the diagram below, the work flow for reproducing a scenario of choice is shown. One simply needs to combine information from Table S5 (data set), Table S6 (variable selection) and (training set selection) and regress a PLS model using one's software of choice to reproduce the models from the main text (main text Table 2). Using an appropriate implementation of the PLS algorithm, regression of a model with the same number of latent variables as indicated in the text will produce a model of similar quality and stability. Due to small differences in the various implementations of the PLS algorithm, small numerical differences in the results can be expected. One aspect in particular to keep in mind is scaling. After partitioning the data into a training and a test set, the training set should be scaled to zero mean and unit variance[2]. The column means and standard deviation obtained in scaling the training set should then be used to scale the validation set. Most commercial software packages will do this automatically.

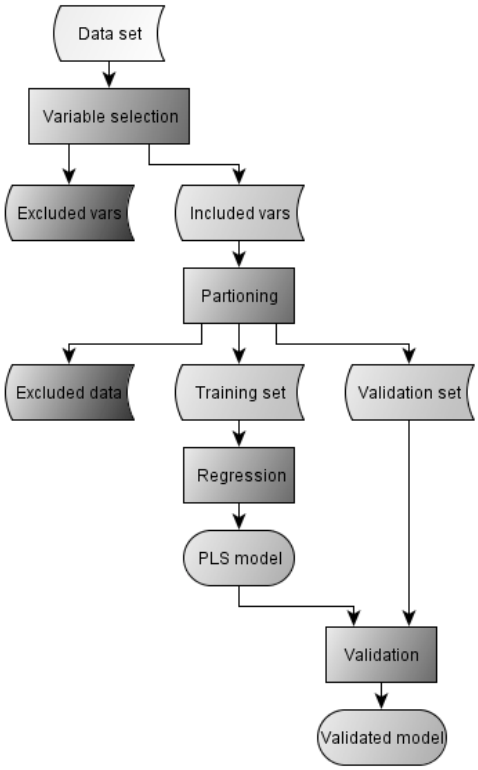

Diagram 1 Flow chart describing the workflow to reproduce any modeling scenario from the main text

[1] To facilitate the use of the modeling results the tables from this document can also be obtained in Microsoft Excel format from the publishers' website.

[2] To scale the training set, first calculate the average and standard deviation for each column. The training set data is then scaled by first subtracting the column mean and then dividing by column standard deviation for each entry in a column. To achieve the same scaling for the validation set, apply the procedure above to the validation set using the column means and standard deviations obtained for the training set.

Table S5 Heat of adsorption (y) and descriptor values (*x*1-*x*9) for all 130 metal-adsorptive pairs

ID	Metal	Adsorptive	Y	x1	x2	x3	x4	x5	x6	x7	x8	x9
1	Fe	H_2	-1.15	6	2.45	7.902	1.25	8.18	55.85	86.98	22.82	2
2	Fe	HO▪	-4.14	6	2.45	7.902	1.25	8.18	55.85	106.24	21.05	17
3	Fe	N_2	-1.27	6	2.45	7.902	1.25	8.18	55.85	139.66	21.79	28
4	Fe	CO	-2.53	6	2.45	7.902	1.25	8.18	55.85	147.35	19.43	28
5	Fe	NO	-4.66	6	2.45	7.902	1.25	8.18	55.85	134.87	14.07	30
6	Fe	O_2	-6.3	6	2.45	7.902	1.25	8.18	55.85	122.71	13.51	32
7	Fe	H_2O	-1.98	6	2.45	7.902	1.25	8.18	55.85	118.53	19.4	18
8	Fe	CO_2	-2.51	6	2.45	7.902	1.25	8.18	55.85	165.03	20.96	44
9	Fe	NH_3	-1.45	6	2.45	7.902	1.25	8.18	55.85	138.04	17.48	17
10	Fe	CH_4	-1.07	6	2.45	7.902	1.25	8.18	55.85	155.79	21.82	16
11	Co	H_2	-0.78	7	2.53	7.881	1.26	8.38	58.93	86.98	22.82	2
12	Co	HO▪	-3.43	7	2.53	7.881	1.26	8.38	58.93	106.24	21.05	17
13	Co	N_2	-0.38	7	2.53	7.881	1.26	8.38	58.93	139.66	21.79	28
14	Co	CO	-1.51	7	2.53	7.881	1.26	8.38	58.93	147.35	19.43	28
15	Co	NO	-3.63	7	2.53	7.881	1.26	8.38	58.93	134.87	14.07	30
16	Co	O_2	-5.07	7	2.53	7.881	1.26	8.38	58.93	122.71	13.51	32
17	Co	H_2O	-0.99	7	2.53	7.881	1.26	8.38	58.93	118.53	19.4	18
18	Co	CO_2	-0.83	7	2.53	7.881	1.26	8.38	58.93	165.03	20.96	44
19	Co	NH_3	-0.43	7	2.53	7.881	1.26	8.38	58.93	138.04	17.48	17
20	Co	CH_4	0.09	7	2.53	7.881	1.26	8.38	58.93	155.79	21.82	16
21	Ni	H_2	-0.82	8	2.42	7.64	1.21	7.42	58.69	86.98	22.82	2
22	Ni	HO▪	-2.77	8	2.42	7.64	1.21	7.42	58.69	106.24	21.05	17
23	Ni	N_2	-0.1	8	2.42	7.64	1.21	7.42	58.69	139.66	21.79	28
24	Ni	CO	-1.05	8	2.42	7.64	1.21	7.42	58.69	147.35	19.43	28
25	Ni	NO	-2.87	8	2.42	7.64	1.21	7.42	58.69	134.87	14.07	30
26	Ni	O_2	-3.9	8	2.42	7.64	1.21	7.42	58.69	122.71	13.51	32
27	Ni	H_2O	-0.45	8	2.42	7.64	1.21	7.42	58.69	118.53	19.4	18
28	Ni	CO_2	0.17	8	2.42	7.64	1.21	7.42	58.69	165.03	20.96	44
29	Ni	NH_3	-0.37	8	2.42	7.64	1.21	7.42	58.69	138.04	17.48	17
30	Ni	CH_4	-0.13	8	2.42	7.64	1.21	7.42	58.69	155.79	21.82	16
31	Cu	H_2	-0.29	10	1.81	7.726	1.38	11.01	63.55	86.98	22.82	2
32	Cu	HO▪	-1.81	10	1.81	7.726	1.38	11.01	63.55	106.24	21.05	17
33	Cu	N_2	2.88	10	1.81	7.726	1.38	11.01	63.55	139.66	21.79	28
34	Cu	CO	1.77	10	1.81	7.726	1.38	11.01	63.55	147.35	19.43	28
35	Cu	NO	-0.68	10	1.81	7.726	1.38	11.01	63.55	134.87	14.07	30
36	Cu	O_2	-2.51	10	1.81	7.726	1.38	11.01	63.55	122.71	13.51	32
37	Cu	H_2O	0.78	10	1.81	7.726	1.38	11.01	63.55	118.53	19.4	18
38	Cu	CO_2	3.69	10	1.81	7.726	1.38	11.01	63.55	165.03	20.96	44
39	Cu	NH_3	1.92	10	1.81	7.726	1.38	11.01	63.55	138.04	17.48	17
40	Cu	CH_4	3.06	10	1.81	7.726	1.38	11.01	63.55	155.79	21.82	16
41	Mo	H_2	-0.92	5	2.96	7.092	1.45	12.77	95.94	86.98	22.82	2
42	Mo	HO▪	-4.61	5	2.96	7.092	1.45	12.77	95.94	106.24	21.05	17
43	Mo	N_2	-2.76	5	2.96	7.092	1.45	12.77	95.94	139.66	21.79	28
44	Mo	CO	-3.61	5	2.96	7.092	1.45	12.77	95.94	147.35	19.43	28
45	Mo	NO	-5.99	5	2.96	7.092	1.45	12.77	95.94	134.87	14.07	30
46	Mo	O_2	-7.48	5	2.96	7.092	1.45	12.77	95.94	122.71	13.51	32
47	Mo	H_2O	-2.33	5	2.96	7.092	1.45	12.77	95.94	118.53	19.4	18
48	Mo	CO_2	-4.18	5	2.96	7.092	1.45	12.77	95.94	165.03	20.96	44
49	Mo	NH_3	-1.84	5	2.96	7.092	1.45	12.77	95.94	138.04	17.48	17
50	Mo	CH_4	-1.09	5	2.96	7.092	1.45	12.77	95.94	155.79	21.82	16
51	Ru	H_2	-1.09	7	3.05	7.36	1.26	8.38	101.07	86.98	22.82	2
52	Ru	HO▪	-3.27	7	3.05	7.36	1.26	8.38	101.07	106.24	21.05	17
53	Ru	N_2	-0.84	7	3.05	7.36	1.26	8.38	101.07	139.66	21.79	28
54	Ru	CO	-1.62	7	3.05	7.36	1.26	8.38	101.07	147.35	19.43	28
55	Ru	NO	-3.6	7	3.05	7.36	1.26	8.38	101.07	134.87	14.07	30
56	Ru	O_2	-4.62	7	3.05	7.36	1.26	8.38	101.07	122.71	13.51	32
57	Ru	H_2O	-1.08	7	3.05	7.36	1.26	8.38	101.07	118.53	19.4	18
58	Ru	CO_2	-0.77	7	3.05	7.36	1.26	8.38	101.07	165.03	20.96	44
59	Ru	NH_3	-1.14	7	3.05	7.36	1.26	8.38	101.07	138.04	17.48	17
60	Ru	CH_4	-0.88	7	3.05	7.36	1.26	8.38	101.07	155.79	21.82	16
61	Rh	H_2	-0.79	8	2.68	7.459	1.35	10.31	102.91	86.98	22.82	2

ID	Metal	Adsorptive	y	x1	x2	x3	x4	x5	x6	x7	x8	x9
63	Rh	N_2	-0.7	8	2.68	7.459	1.35	10.31	102.91	139.66	21.79	28
64	Rh	CO	-1.12	8	2.68	7.459	1.35	10.31	102.91	147.35	19.43	28
65	Rh	NO	-3.23	8	2.68	7.459	1.35	10.31	102.91	134.87	14.07	30
66	Rh	O_2	-4.03	8	2.68	7.459	1.35	10.31	102.91	122.71	13.51	32
67	Rh	H_2O	-0.48	8	2.68	7.459	1.35	10.31	102.91	118.53	19.4	18
68	Rh	CO_2	0.03	8	2.68	7.459	1.35	10.31	102.91	165.03	20.96	44
69	Rh	NH_3	-0.61	8	2.68	7.459	1.35	10.31	102.91	138.04	17.48	17
70	Rh	CH_4	-0.06	8	2.68	7.459	1.35	10.31	102.91	155.79	21.82	16
71	Pd	H_2	-0.78	10	2.03	8.337	1.31	9.42	106.42	86.98	22.82	2
72	Pd	HO▪	-1.4	10	2.03	8.337	1.31	9.42	106.42	106.24	21.05	17
73	Pd	N_2	1.78	10	2.03	8.337	1.31	9.42	106.42	139.66	21.79	28
74	Pd	CO	0.38	10	2.03	8.337	1.31	9.42	106.42	147.35	19.43	28
75	Pd	NO	-0.58	10	2.03	8.337	1.31	9.42	106.42	134.87	14.07	30
76	Pd	O_2	-1.2	10	2.03	8.337	1.31	9.42	106.42	122.71	13.51	32
77	Pd	H_2O	0.95	10	2.03	8.337	1.31	9.42	106.42	118.53	19.4	18
78	Pd	CO_2	2.96	10	2.03	8.337	1.31	9.42	106.42	165.03	20.96	44
79	Pd	NH_3	0.64	10	2.03	8.337	1.31	9.42	106.42	138.04	17.48	17
80	Pd	CH_4	0.04	10	2.03	8.337	1.31	9.42	106.42	155.79	21.82	16
81	Ag	H_2	0.53	10	1.28	7.576	1.53	15	107.87	86.98	22.82	2
82	Ag	HO▪	-0.48	10	1.28	7.576	1.53	15	107.87	106.24	21.05	17
83	Ag	N_2	5.86	10	1.28	7.576	1.53	15	107.87	139.66	21.79	28
84	Ag	CO	4.32	10	1.28	7.576	1.53	15	107.87	147.35	19.43	28
85	Ag	NO	1.73	10	1.28	7.576	1.53	15	107.87	134.87	14.07	30
86	Ag	O_2	-0.65	10	1.28	7.576	1.53	15	107.87	122.71	13.51	32
87	Ag	H_2O	2.52	10	1.28	7.576	1.53	15	107.87	118.53	19.4	18
88	Ag	CO_2	7.16	10	1.28	7.576	1.53	15	107.87	165.03	20.96	44
89	Ag	NH_3	4.63	10	1.28	7.576	1.53	15	107.87	138.04	17.48	17
90	Ag	CH_4	6.31	10	1.28	7.576	1.53	15	107.87	155.79	21.82	16
91	W	H_2	-1.29	4	3.47	7.98	1.46	13.04	103.84	86.98	22.82	2
92	W	HO▪	-5.37	4	3.47	7.98	1.46	13.04	103.84	106.24	21.05	17
93	W	N_2	-4.33	4	3.47	7.98	1.46	13.04	103.84	139.66	21.79	28
94	W	CO	-4.73	4	3.47	7.98	1.46	13.04	103.84	147.35	19.43	28
95	W	NO	-7.34	4	3.47	7.98	1.46	13.04	103.84	134.87	14.07	30
96	W	O_2	-8.62	4	3.47	7.98	1.46	13.04	103.84	122.71	13.51	32
97	W	H_2O	-3.27	4	3.47	7.98	1.46	13.04	103.84	118.53	19.4	18
98	W	CO_2	-5.87	4	3.47	7.98	1.46	13.04	103.84	165.03	20.96	44
99	W	NH_3	-3.18	4	3.47	7.98	1.46	13.04	103.84	138.04	17.48	17
100	W	CH_4	-2.37	4	3.47	7.98	1.46	13.04	103.84	155.79	21.82	16
101	Ir	H_2	-1.26	7	3.03	9.1	1.37	10.77	192.22	86.98	22.82	2
102	Ir	HO▪	-3.37	7	3.03	9.1	1.37	10.77	192.22	106.24	21.05	17
103	Ir	N_2	-0.59	7	3.03	9.1	1.37	10.77	192.22	139.66	21.79	28
104	Ir	CO	-1.07	7	3.03	9.1	1.37	10.77	192.22	147.35	19.43	28
105	Ir	NO	-3.49	7	3.03	9.1	1.37	10.77	192.22	134.87	14.07	30
106	Ir	O_2	-4.65	7	3.03	9.1	1.37	10.77	192.22	122.71	13.51	32
107	Ir	H_2O	-1.26	7	3.03	9.1	1.37	10.77	192.22	118.53	19.4	18
108	Ir	CO_2	-0.23	7	3.03	9.1	1.37	10.77	192.22	165.03	20.96	44
109	Ir	NH_3	-1.27	7	3.03	9.1	1.37	10.77	192.22	138.04	17.48	17
110	Ir	CH_4	-0.65	7	3.03	9.1	1.37	10.77	192.22	155.79	21.82	16
111	Pt	H_2	-1.12	9	2.48	9	1.28	8.78	195.08	86.98	22.82	2
112	Pt	HO▪	-2.06	9	2.48	9	1.28	8.78	195.08	106.24	21.05	17
113	Pt	N_2	1.37	9	2.48	9	1.28	8.78	195.08	139.66	21.79	28
114	Pt	CO	0.37	9	2.48	9	1.28	8.78	195.08	147.35	19.43	28
115	Pt	NO	-1.27	9	2.48	9	1.28	8.78	195.08	134.87	14.07	30
116	Pt	O_2	-2.17	9	2.48	9	1.28	8.78	195.08	122.71	13.51	32
117	Pt	H_2O	0.12	9	2.48	9	1.28	8.78	195.08	118.53	19.4	18
118	Pt	CO_2	2.45	9	2.48	9	1.28	8.78	195.08	165.03	20.96	44
119	Pt	NH_3	-0.08	9	2.48	9	1.28	8.78	195.08	138.04	17.48	17
120	Pt	CH_4	-0.18	9	2.48	9	1.28	8.78	195.08	155.79	21.82	16
121	Au	H_2	0.18	10	1.53	9.226	1.44	12.51	196.97	86.98	22.82	2
122	Au	HO▪	-0.05	10	1.53	9.226	1.44	12.51	196.97	106.24	21.05	17
123	Au	N_2	5.89	10	1.53	9.226	1.44	12.51	196.97	139.66	21.79	28
124	Au	CO	4.58	10	1.53	9.226	1.44	12.51	196.97	147.35	19.43	28
125	Au	NO	2.34	10	1.53	9.226	1.44	12.51	196.97	134.87	14.07	30
126	Au	O_2	0.54	10	1.53	9.226	1.44	12.51	196.97	122.71	13.51	32
127	Au	H_2O	2.77	10	1.53	9.226	1.44	12.51	196.97	118.53	19.4	18

ID	Metal	Adsorptive	y	x1	x2	x3	x4	x5	x6	x7	x8	x9
128	Au	CO_2	8.02	10	1.53	9.226	1.44	12.51	196.97	165.03	20.96	44
129	Au	NH_3	4.12	10	1.53	9.226	1.44	12.51	196.97	138.04	17.48	17
130	Au	CH_4	5.28	10	1.53	9.226	1.44	12.51	196.97	155.79	21.82	16