Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information: Role of the OH-group in the Adsorption Properties of Methanol, Ethanol, and Ethylene Glycol on 15-atom $3d$, $4d$, and $5d$ Transition-metal Clusters

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Contents

1 Introduction

Several additional data are reported in this electronic supplementary information (ESI) file, which complement our results reported within the manuscript. Below, we list the most important data:

1. The computational parameters, in particular, the PAW projectors technical details.
2. The energetic, structural, electronic and charge properties for the gas-phase clusters and alcohols.
3. All configurations of the adsorbed systems are available along the relative energies.
4. An example of clustering technique employed for the selection of the representative configurations of the adsorbed systems.
5. The energetic, structural and electronic properties for the representative configurations of the adsorbed systems.

2 Computational Parameters

2.1 Technical Details of the PAW projectors

The selected PAW projects selected from VASP are listed in Table S1 with their respective number of valence electrons and maximum recommended cutoff energies, e.g., `ENMAX` obtained

from the employed POTCAR files. From our experience using VASP in the last 25 years, we found out that the recommended ENMAX cutoff energies should be increases slightly to yield accurate results. Thus, from a large number of convergence tests along the years, we employed as standard a cutoff energy of 12.50 % higher than highest maximum recommended cutoff energy among the chemical species within a given system, $\texttt{ENMAX}_{max}$.

For example, for the adsorption of methanol, ethanol, ethylene glycol on transition-metal clusters, the highest recommended cutoff energy is from the O atom, i.e., 434.431 eV, and hence, we employed for all those calculations a cutoff energy, ENCUT, of 488.734 eV. This particular cutoff energy is used for all total energy, geometric optimizations, density of states, etc. We understand that this particular choose increase the computational cost, however, it provides accurate results and proper approach to compare the results within all group members instead that every group member decide to use a slightly different cutoff energy.

For stress tensor calculations to obtain the equilibrium volume of crystal structures, we employed a cutoff energy from 1.50 up to 2.00 the highest recommended cutoff energy in POTCAR, which yields accurate results for the lattice parameters. Furthermore, lattice constant calculations can require even larger cutoff energies, e.g., 2.50 times the highest recommended cutoff energies. Those rules based on empirical experience looks simple, however, combined with the information within the POTCAR files, they provide guidelines for consistent calculations for a wide range of materials, which is the case of the present study.

2.2 Definitions: Structural, Energetic and Electronic Parameters

- To obtain the average structural parameters for transition-metal clusters, we employed the effective coordination concept, which yields the effective coordination number (ECN^i) and the weighted bond length distance (d^i_{av}) for each atom i in the cluster. The effective coordination number (in Number of Nearest Neighbors - NNN) for a given atom i is given by the following equation,

$$\text{ECN}^i = \sum_{\substack{j=1,\\ i\neq j}}^{N} w_{ij} = \sum_{\substack{j=1,\\ i\neq j}}^{N} exp\left[1 - \left(\frac{d_{ij}}{(d^i_{av} + d^j_{av})/2}\right)^6\right], \qquad (1)$$

Table S1: PAW-PBE Projectors: chemical specie, `POTCAR` for the calculations, number of valence electrons, Z_{val}, and default recommended cutoff energy for the plane waves.

Specie	PAW Projector	Z_{val}	`ENMAX` (eV)
C	C_GW_new 19Mar2012	4	413.992
O	O_GW 19Mar2012	6	434.431
H	H_GW 21Apr2008	1	300.000
Ag	Ag_GW 06Mar2008	11	249.844
Au	Au_GW 23Mar2010	11	248.344
Co	Co_GW 31Mar2010	9	323.400
Cu	Cu_GW 19May2006	11	417.039
Fe	Fe_GW 31Mar2010	8	321.007
Ir	Ir_sv_GW 23Mar2010	17	319.843
Ni	Ni_GW 31Mar2010	10	357.323
Os	Os_sv_GW 23Mar2010	16	319.773
Pd	Pd_GW 06Mar2008	10	250.925
Pt	Pt_GW 10Mar2009	10	248.408
Rh	Rh_GW 06Mar2008	9	247.408
Ru	Ru_sv_GW 05Dec2013	16	348.106

where the sum runs over all atoms and the d_{av}^{i} parameters are obtained for each atom using a self-consistent procedure. N is the number of transition-metal atoms within the cluster. Thus, the average coordination for a given cluster can be obtained by the following equation,

$$\mathrm{ECN}_{av} = \frac{1}{N}\sum_{i=1}^{N}\mathrm{ECN}_{i}\ . \tag{2}$$

- The weighted bond length (in Å) can be obtained by the following equation,

$$d_{av}^{i,new} = \frac{\sum_{\substack{j=1,\\ i\neq j}}^{N} d_{ij} exp\left[1-\left(\frac{d_{ij}}{(d_{av}^{i}+d_{av}^{j})/2}\right)^{6}\right]}{\sum_{\substack{j=1,\\ i\neq j}}^{N} exp\left[1-\left(\frac{d_{ij}}{(d_{av}^{i,old}+d_{av}^{j,old})/2}\right)^{6}\right]}\ . \tag{3}$$

The present equation is solved using a self-consistent framework, where the smallest distance between the atoms are the initial values. Thus, the average weighted bond lengths are given by the following equations,

$$d_{av} = \frac{1}{N}\sum_{i=1}^{N} d_{av}^{i}\ . \tag{4}$$

- The binding energy (in eV) per cluster can be obtained by the following equation,

$$E_b = E_{tot}^{TM15} - \sum_i E_{tot}^{i\ free-atom}\ , \tag{5}$$

where E_{tot}^{TM15} and $E_{tot}^{i\ free-atom}$ are the total energies of the cluster and the free-atoms, respectively, obtained from spin-polarized calculations.

3 Structural, Electronic, and Energetic Properties of the Gas-phase Clusters

Our group has worked on the adsorption of molecular systems on finite size particles for long time, and hence, we have identified several descriptors, which play a crucial role in the study of gas-phase clusters and adsorption of molecular species on clusters. For example, in Table S2, we summarized the total magnetic moment for every cluster, binding energy per atom, and several average properties such as the effective coordination number, weighted bond lengths, center of gravity of the *d*-states. Furthermore, we indicated also the size of the cubic box employed for all calculations, which includes also the alcohol adsorption studies.

Table S2: Energetical, structural, and electronic properties of gas-phase 15-atom transition-metal (TM) clusters: chemical specie; total energy, E_{tot} (eV); total magnetic moment, m_{tot} (μ_B); total energy of the free atom, $E_{tot}^{free-atom}$; binding energy, E_b (eV); average effective coordination number, ECN_{av} (number of nearest neighbours - NNN); average weighted bond length, d_{av} (Å); size of the cubic box (Å); d-states center for the up-, down-, and average spin-components, ε_d^{up}, ε_d^{dn}, ε_d^{av}, (eV) for the TM_{15} clusters.

TM	E_{tot}	m_{tot}	$E_{tot}^{free-atom}$	E_b	ECN_{av}	d_{av}	box	ε_d^{up}	ε_d^{dn}	ε_d^{av}
Fe	−102.163 847 08	48	−3.363 535 34	−3.45	6.16	2.45	21.70	−2.34	−1.25	−1.80
Ru	−100.982 778 54	8	−2.193 157 02	−4.54	5.39	2.50	23.00	−2.53	−2.64	−2.58
Os	−145.061 822 56	2	−3.993 441 23	−5.68	4.68	2.48	23.30	−3.03	−3.03	−3.03
Co	−81.006 446 15	29	−2.051 749 74	−3.35	5.67	2.34	23.70	−2.46	−1.49	−1.97
Rh	−82.057 473 47	15	−1.518 323 79	−3.95	5.68	2.57	22.60	−2.33	−2.05	−2.19
Ir	−108.219 767 11	5	−2.090 354 07	−5.12	5.12	2.54	23.90	−2.72	−2.63	−2.67
Ni	−60.197 277 79	12	−0.741 682 59	−3.27	5.95	2.37	23.30	−1.79	−1.31	−1.55
Pd	−60.074 638 51	8	−1.477 067 34	−2.53	5.94	2.68	23.50	−1.78	−1.67	−1.73
Pt	−69.787 685 99	2	−0.562 626 72	−4.09	4.96	2.61	24.20	−2.42	−2.37	−2.40
Cu	−40.664 776 41	1	−0.244 794 59	−2.47	5.89	2.46	22.70	−2.26	−2.24	−2.25
Ag	−40.664 776 41	1	−0.198 762 47	−1.81	5.44	2.81	23.90	−3.74	−3.71	−3.73
Au	−37.655 072 43	1	−0.183 428 37	−2.33	5.37	2.78	25.10	−2.84	−2.87	−2.85

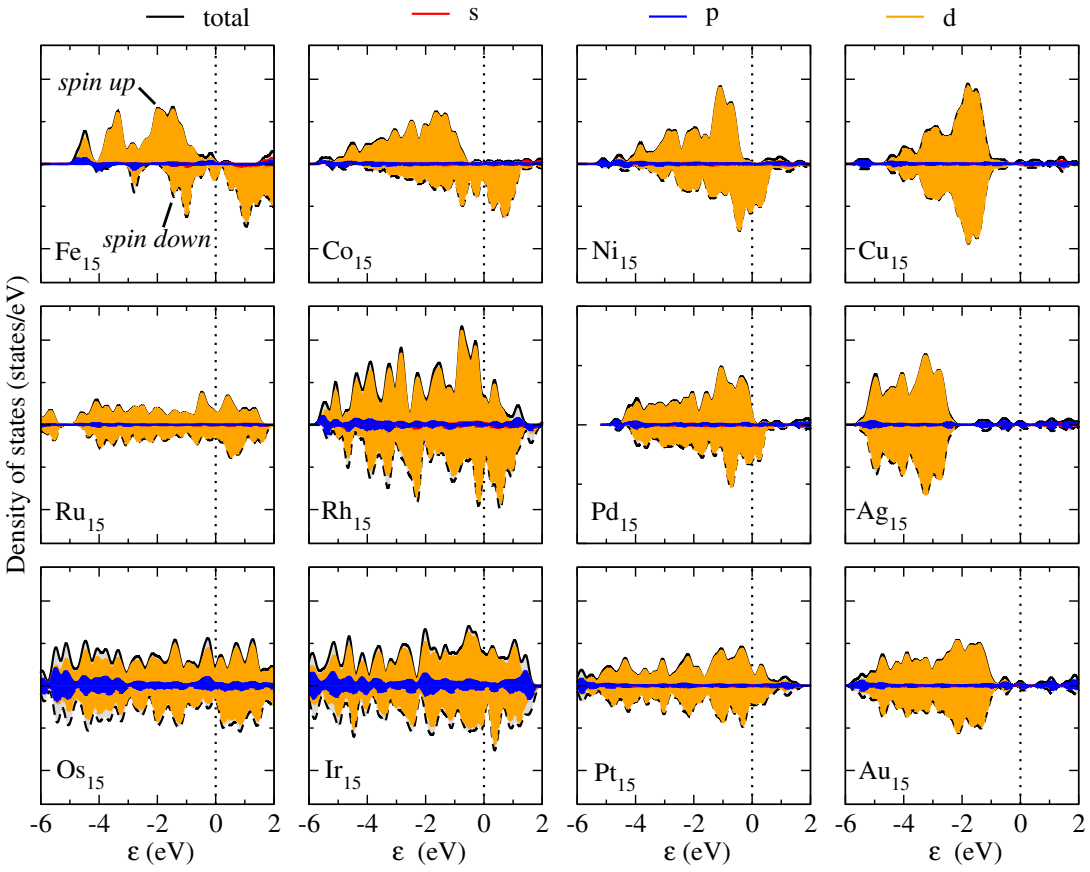

Figure S1: Density of states (DOS) for the gas-phase TM_{15} clusters.

4 Gas-phase Alcohols

Table S3: Energetic and geometric properties of the alcohols: total energy, E_{tot} in eV; relative energy, ΔE_{tot} in meV; binding energy per atom, E_b in eV and bond length distances, C–C, C–O, C–H and O–H in Å.

Alcohol	E_{tot} (eV)	ΔE_{tot} (meV)	E_b (eV)	d_{C-C} (Å)	d_{C-O} (Å)	d_{C-H} (Å)	d_{O-H} (Å)
methanol	−30.272 091 94		−3.76		1.429	1.098 1.105 1.105	0.970
ethanol (gauche)	−46.977 242 07	0	−3.96	1.522	1.434	1.100 1.107 1.102 1.099 1.101	0.972
ethanol (trans)	−46.974 645 46	3	−3.96	1.516	1.436	1.107 1.107 1.099 1.099 1.099	0.971
EG (isomer 1)	−53.469 141 61	0	−4.02	1.521	1.438 1.424	1.106 1.100 1.111 1.102	0.973 0.976
EG (isomer 2)	−53.336 536 96	133	−4.01	1.513	1.431 1.431	1.108 1.106 1.106 1.108	0.970 0.970

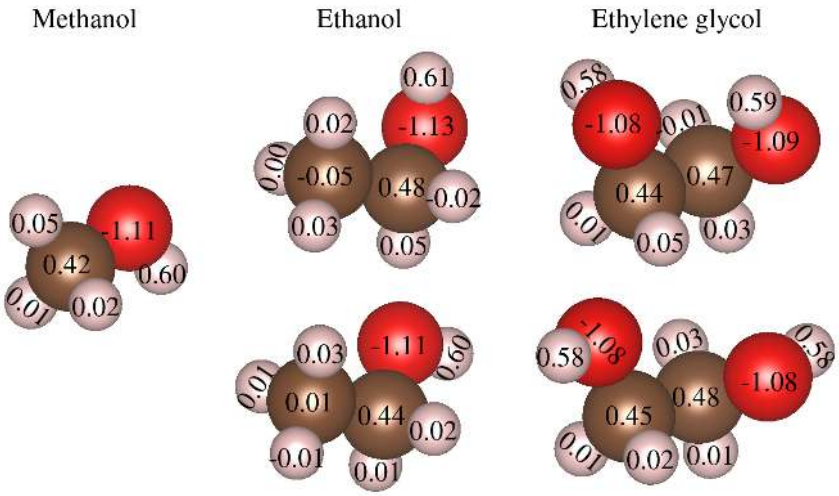

Figure S2: Effective charges in the alcohol molecules: methanol, ethanol and ethylene glycol.

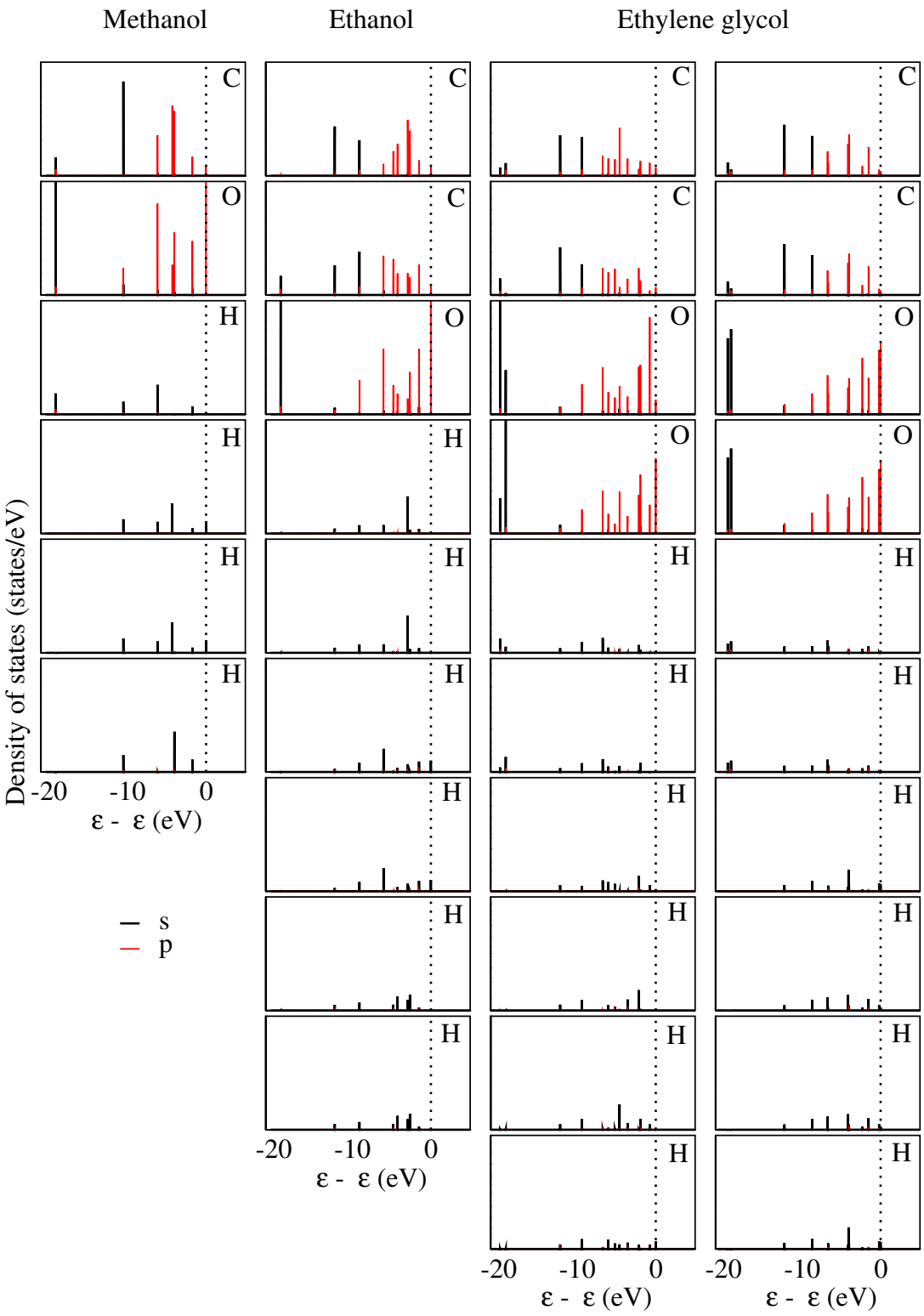

Figure S3: Electronic states for methanol, ethanol and ethylene glycol in gas-phase.

5 All optimized structures for the adsorption of the methanol, ethanol and ethylene glycol on TM_{15}lusters

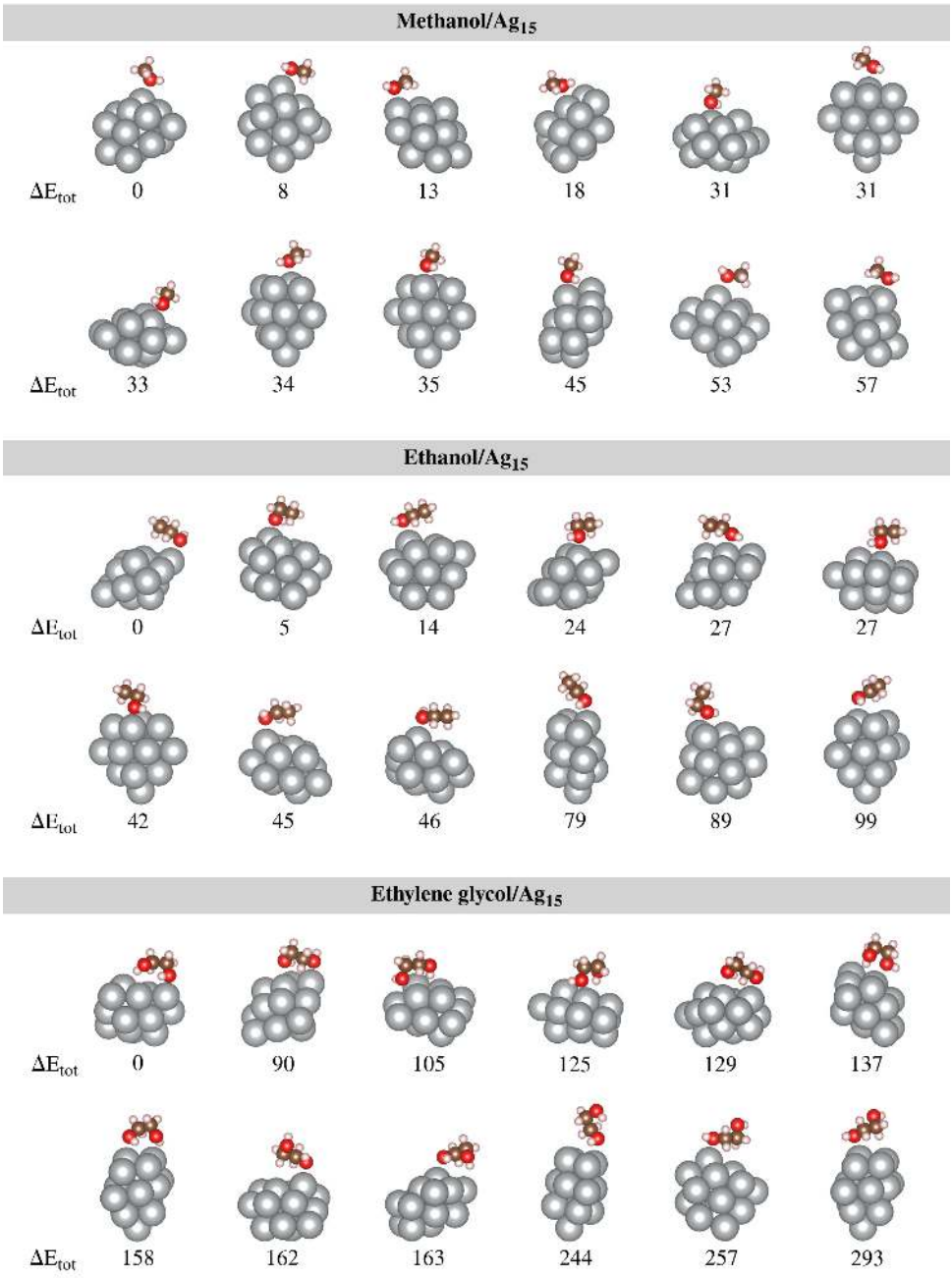

Figure S4: The Alcohols/Ag_{15} configurations and their relative energies in meV with respect to the lowest energy configuration.

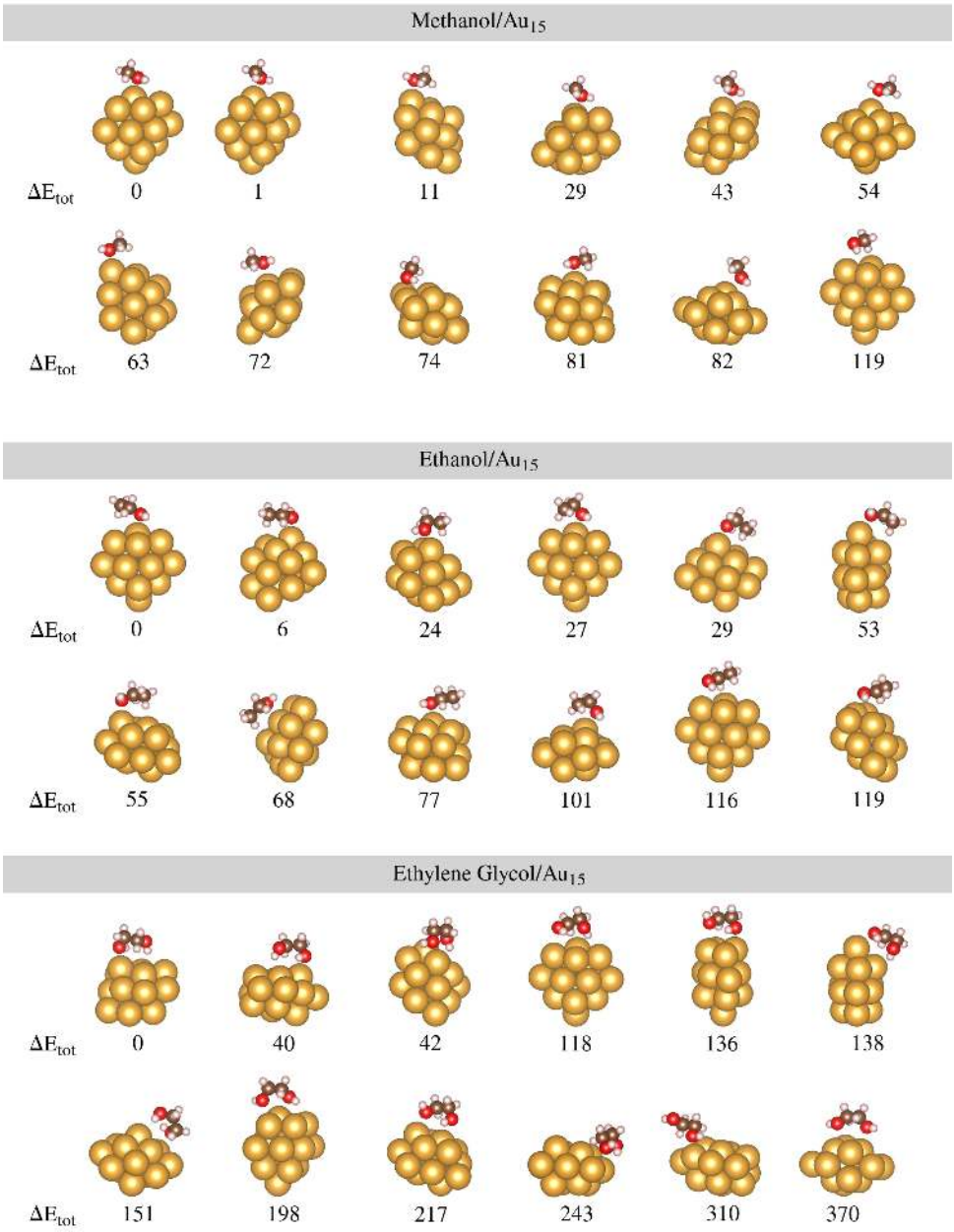

Figure S5: The Alcohols/Au_{15} configurations and their relative energies in meV with respect to the lowest energy configuration.

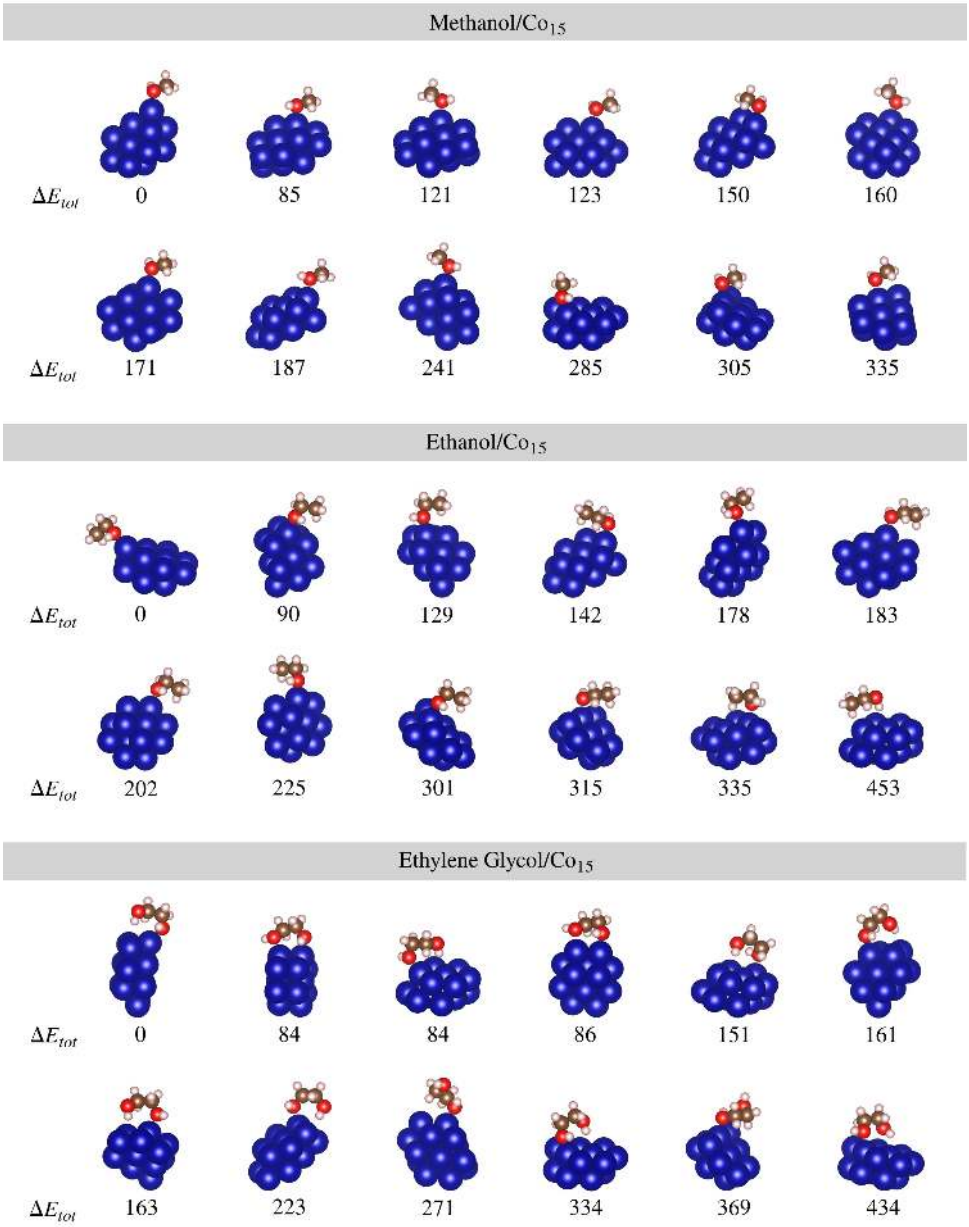

Figure S6: The Alcohols/Co_{15} configurations and their relative energies in meV with respect to the lowest energy configuration.

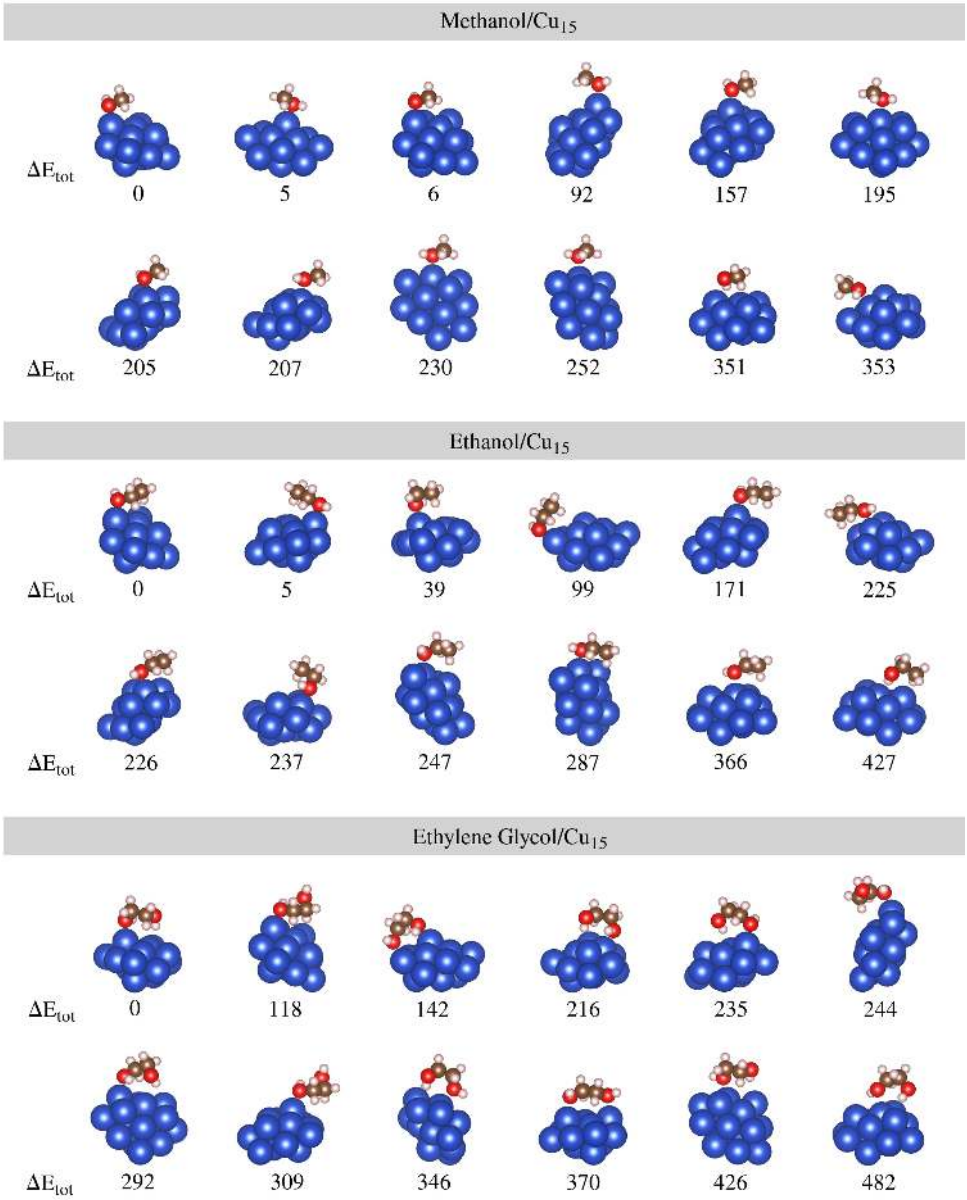

Figure S7: The Alcohols/Cu_{15} configurations and their relative energies in meV with respect to the lowest energy configuration.

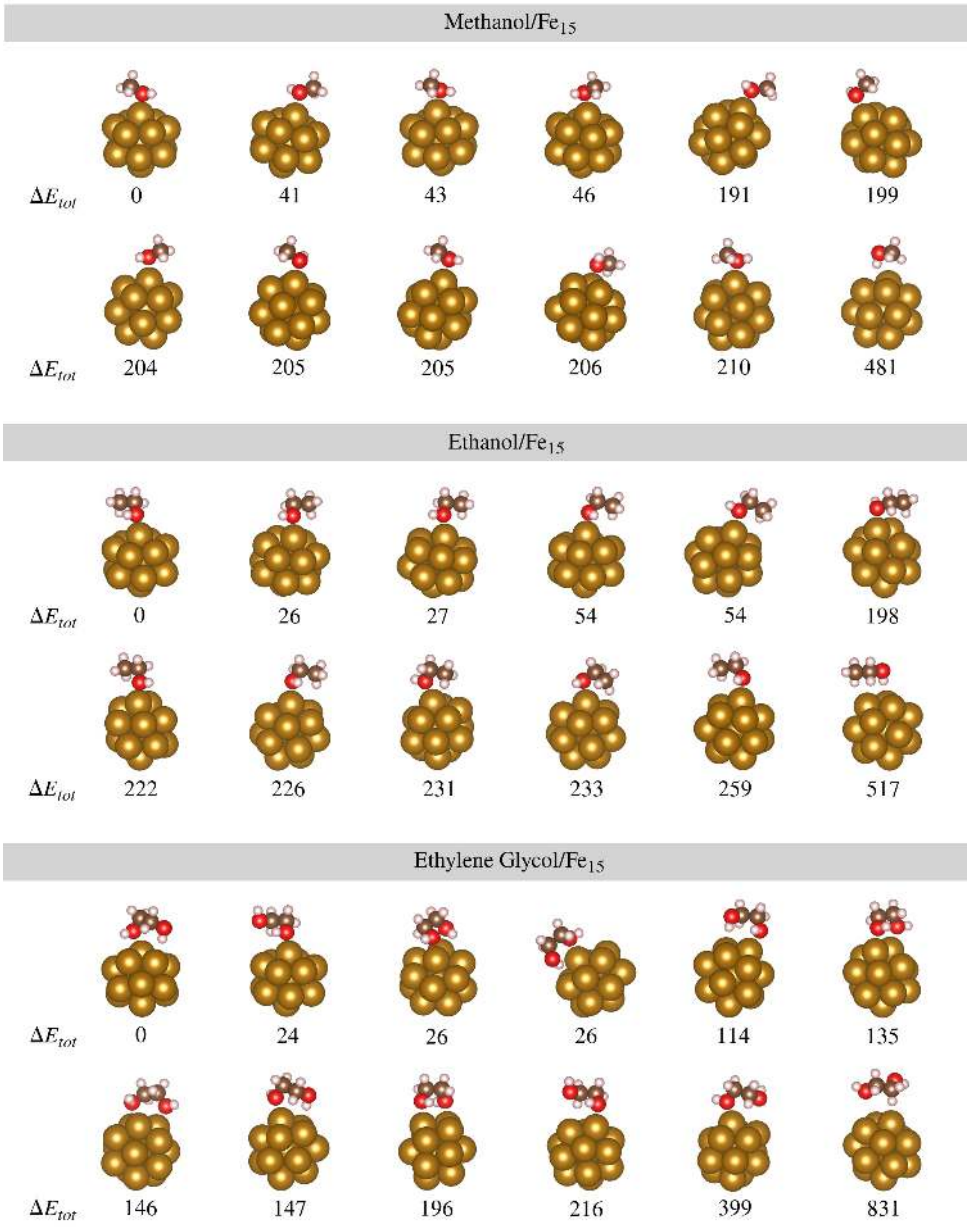

Figure S8: The Alcohols/Fe_{15} configurations and their relative energies in meV with respect to the lowest energy configuration.

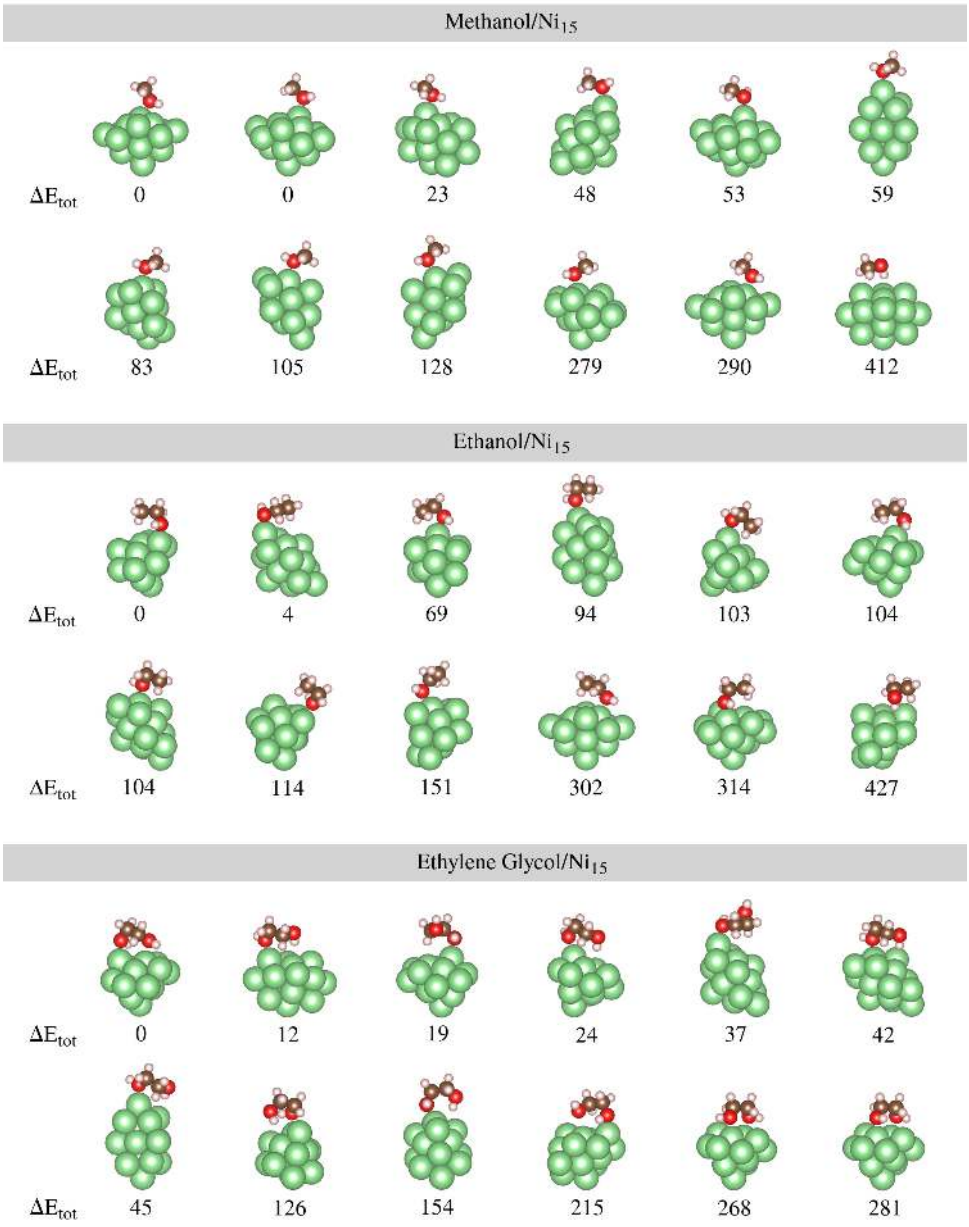

Figure S9: The Alcohols/Ni_{15} configurations and their relative energies in meV with respect to the lowest energy configuration.

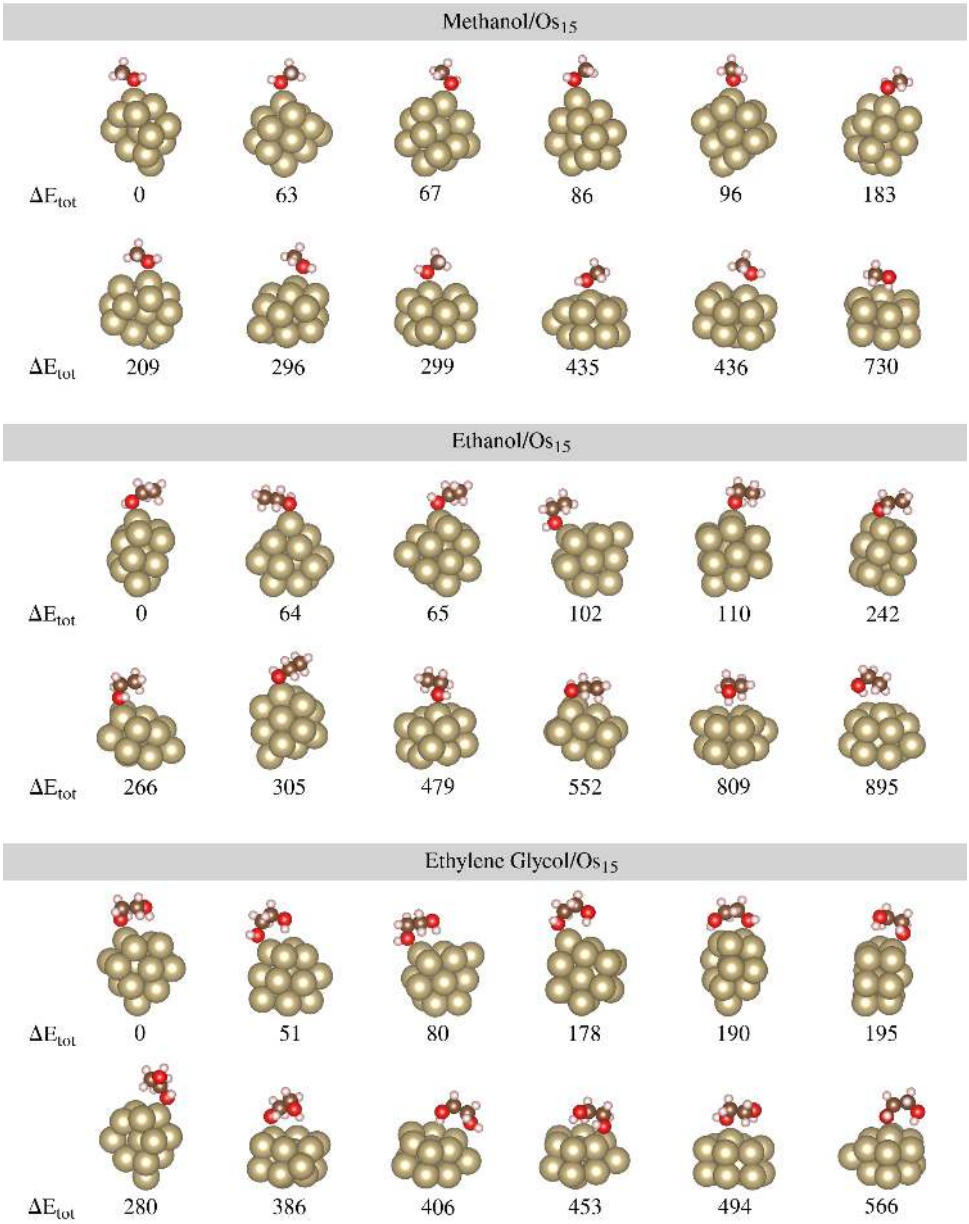

Figure S10: The Alcohols/Os_{15} configurations and their relative energies in meV with respect to the lowest energy configuration.

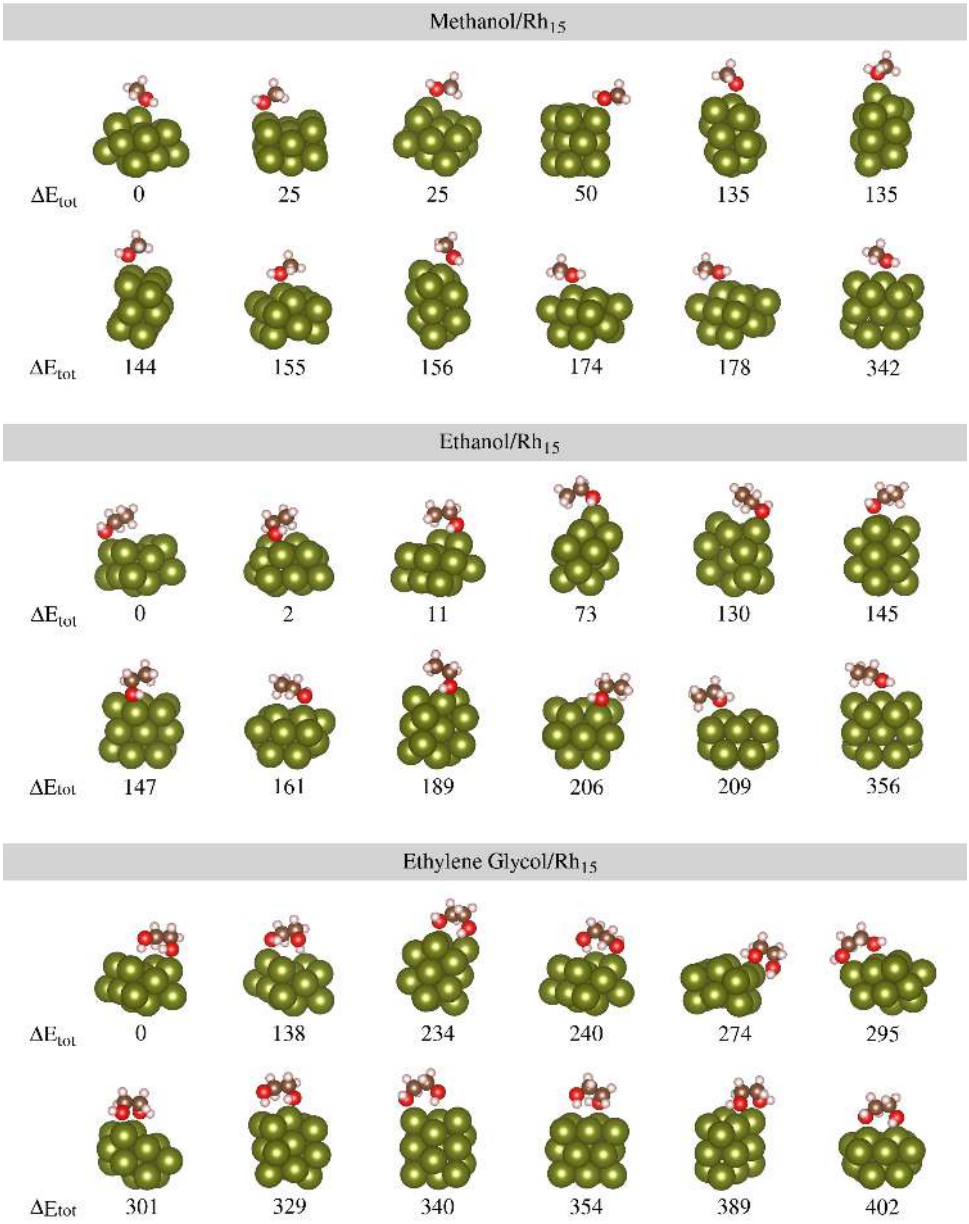

Figure S11: The Alcohols/Rh_{15} configurations and their relative energies in meV with respect to the lowest energy configuration.

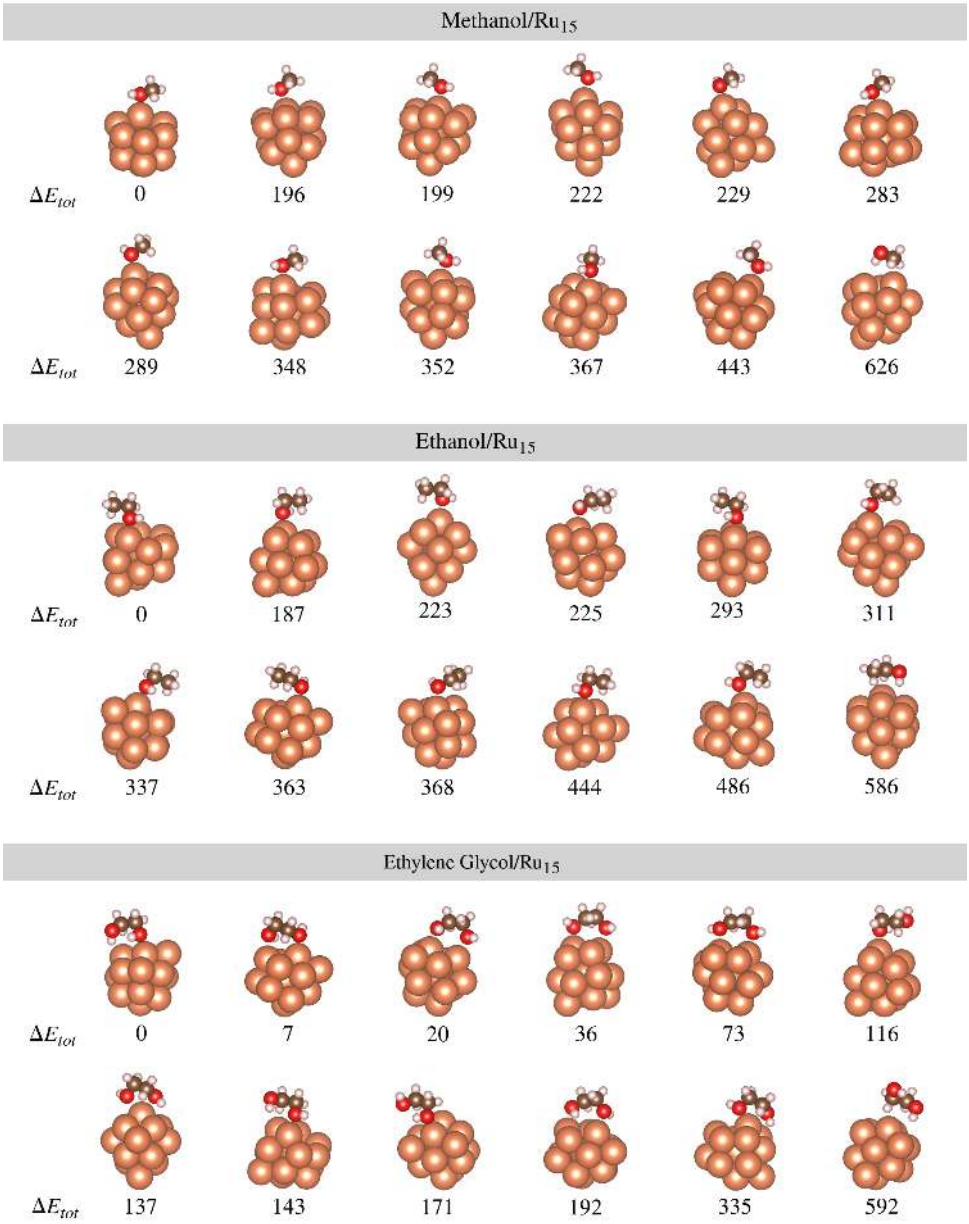

Figure S12: The Alcohols/Ru_{15} configurations and their relative energies in meV with respect to the lowest energy configuration.

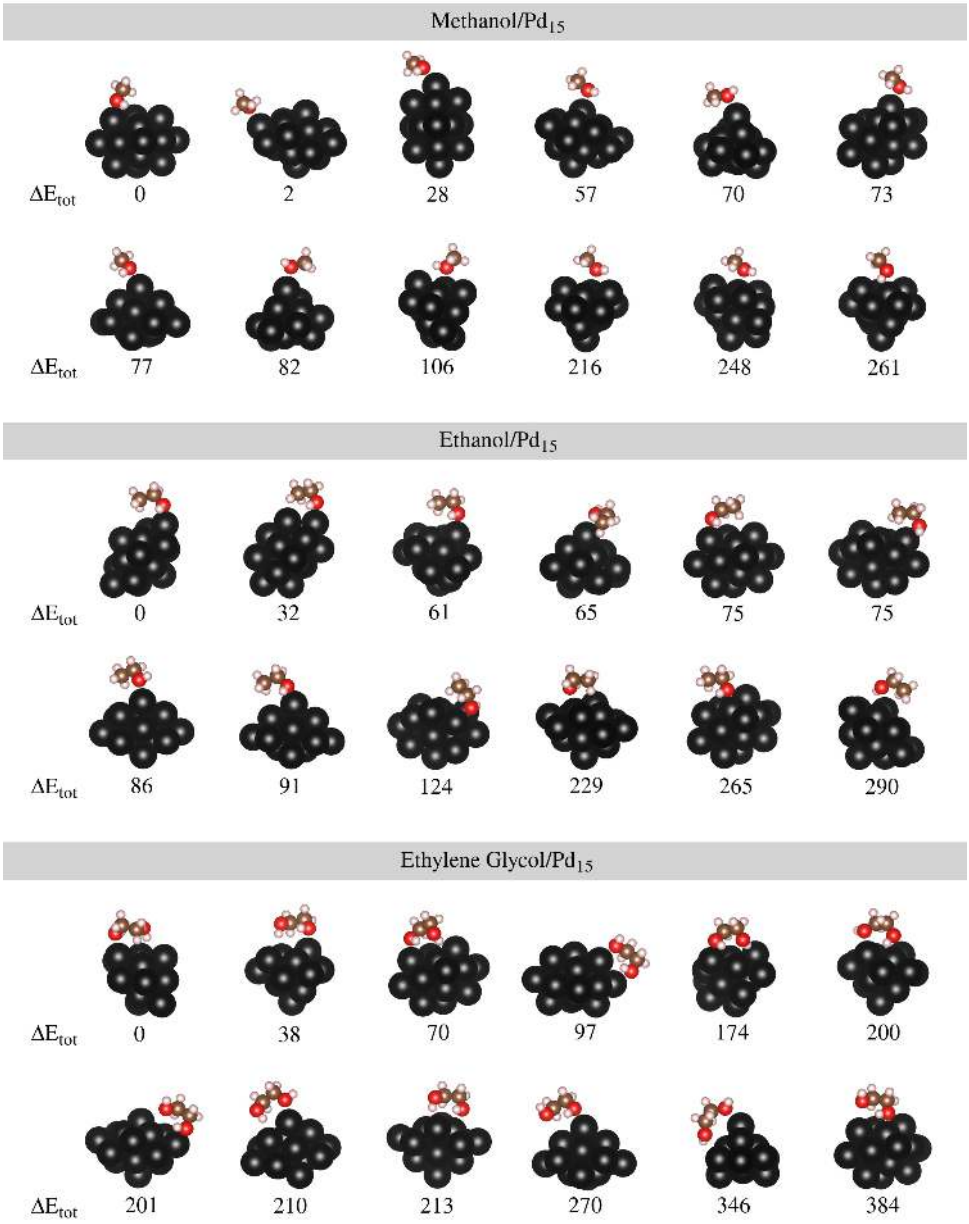

Figure S13: The Alcohols/Pd_{15} configurations and their relative energies in meV with respect to the lowest energy configuration.

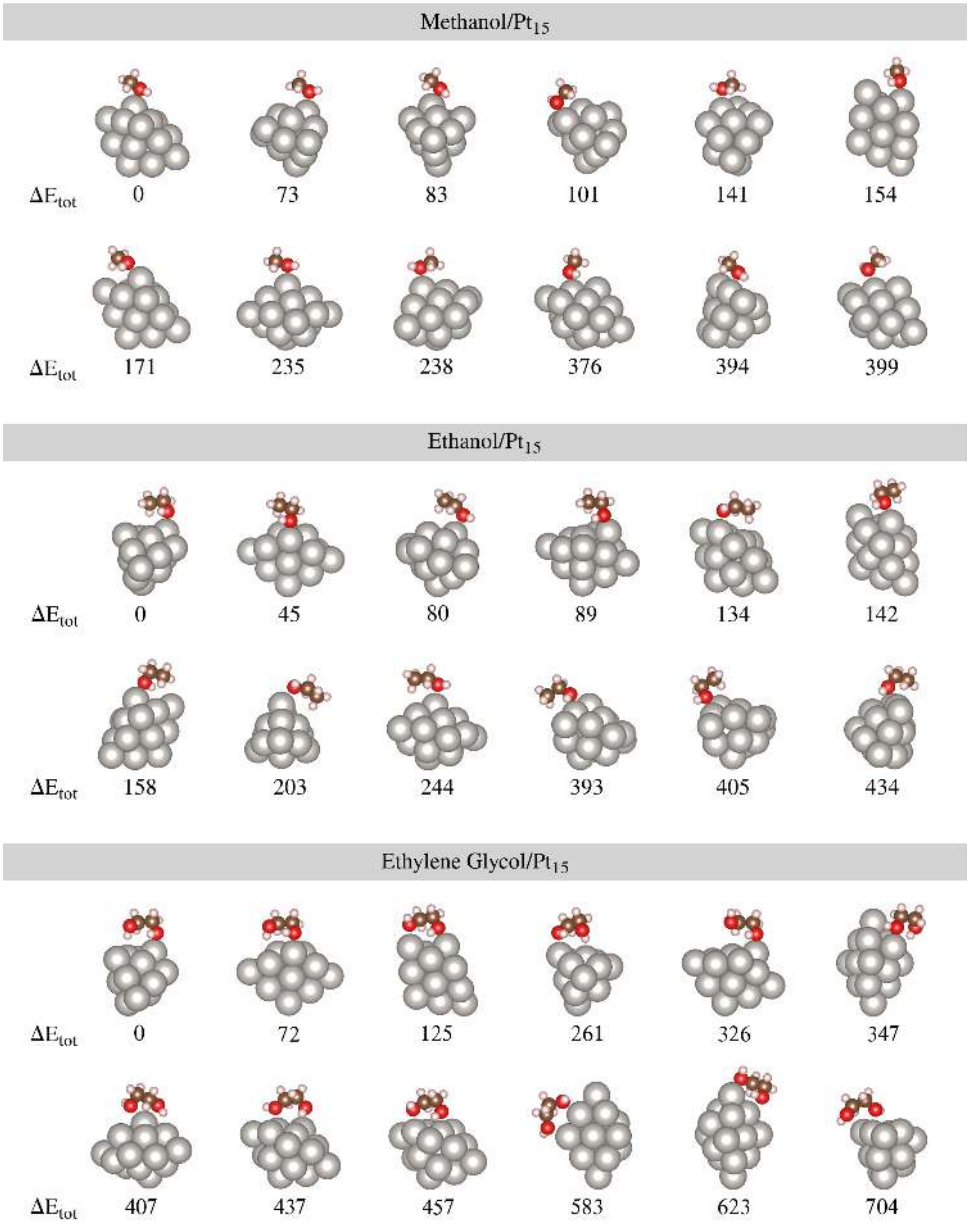

Figure S14: The Alcohols/Pt_{15} configurations and their relative energies in meV with respect to the lowest energy configuration.

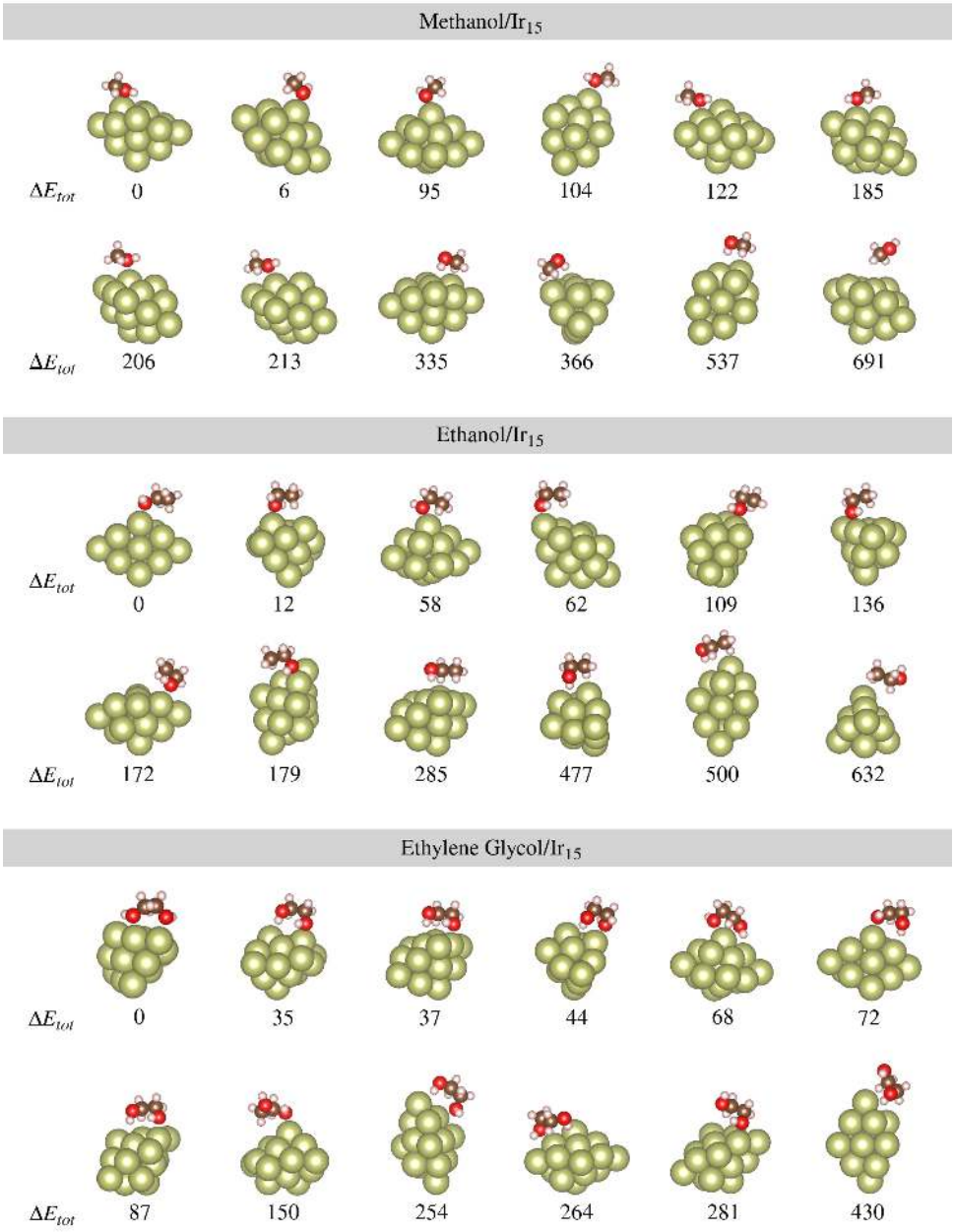

Figure S15: The Alcohols/Ir_{15} configurations and their relative energies in meV with respect to the lowest energy configuration.

Table S4: Energetic, geometric and electronic properties of the systems selected by *k-means* clustering algorithm: relative total energy, ΔE_{tot} (in meV), adsorption energy, E_{ad} (in eV), interaction energy, E_{int} (in eV), total magnetic moment, m_{tot} (in μ_B), change in average effective coordination number of the TM_{15}, ΔECN_{av} (in %), change in average weighted bond length of the TM_{15}, Δd_{av} (in %), shorter distances between the C, O, H (only that closer) atoms and a TM in the nanocluster, d_{C_1-TM}, d_{C_2-TM}, d_{O_1-TM}, d_{O_2-TM} and d_{H-TM} (Å) and change in the molecule charge, Q^{Mol} (in e).

System	ΔE_{tot}	$\lvert E_{ad}\rvert$	$\lvert E_{int}\rvert$	m_{tot}	ΔECN_{av}	Δd_{av}	d_{C_1-TM}	d_{C_2-TM}	d_{O_1-TM}	d_{O_2-TM}	d_{H-TM}	Q^{Mol}
CH_3OH/Fe_{15}	481	0.30	0.30	48	0.02	0.03	3.53	-	3.42	-	2.68	−0.10
CH_3OH/Fe_{15}	191	0.58	0.65	48	−0.18	0.24	3.15	-	2.22	-	2.66	0.01
CH_3OH/Fe_{15}	41	0.74	0.83	48	−0.22	0.36	3.11	-	2.20	-	2.55	0.02
CH_3OH/Fe_{15}	0	0.78	0.82	48	−0.05	−0.06	3.07	-	2.08	-	2.51	0.03
C_2H_5OH/Fe_{15}	512	0.34	0.35	48	0.05	0.03	3.53	3.39	3.50	-	2.49	−0.10
C_2H_5OH/Fe_{15}	198	0.66	0.74	48	−0.20	0.23	3.19	3.61	2.22	-	2.68	0.00
C_2H_5OH/Fe_{15}	26	0.83	0.93	48	−0.18	0.38	3.11	3.49	2.20	-	2.56	0.00
C_2H_5OH/Fe_{15}	0	0.86	0.89	48	−0.04	−0.05	3.10	3.64	2.08	-	2.53	0.03
$(CH_2OH)_2/Fe_{15}$	831	0.05	0.19	48	0.11	0.01	4.41	3.34	3.61	3.96	2.23	−0.03
$(CH_2OH)_2/Fe_{15}$	135	0.74	0.98	48	−0.12	0.33	3.22	3.38	2.25	2.27	2.74	0.02
$(CH_2OH)_2/Fe_{15}$	24	0.85	0.90	48	−0.05	−0.07	3.08	3.61	2.08	4.05	2.51	0.02
$(CH_2OH)_2/Fe_{15}$	0	0.88	1.07	48	−0.15	0.36	3.31	3.49	2.21	3.38	2.43	−0.09
CH_3OH/Co_{15}	241	0.60	0.68	27	−0.01	−0.18	3.03	-	2.03	-	2.46	0.05
CH_3OH/Co_{15}	150	0.69	0.73	29	−0.46	−0.03	3.00	-	2.08	-	2.58	0.02
CH_3OH/Co_{15}	123	0.72	0.74	29	0.00	0.04	3.05	-	2.07	-	2.52	0.04
CH_3OH/Co_{15}	0	0.84	0.87	29	−0.22	−0.02	3.03	-	2.03	-	2.51	0.06
C_2H_5OH/Co_{15}	453	0.46	0.50	29	−0.09	−0.03	3.35	2.98	3.51	-	2.54	−0.07
C_2H_5OH/Co_{15}	225	0.69	0.77	27	−0.03	−0.19	3.04	3.44	2.02	-	2.46	0.05
C_2H_5OH/Co_{15}	90	0.83	0.86	29	−0.07	0.02	3.06	3.69	2.05	-	2.56	0.03
C_2H_5OH/Co_{15}	0	0.92	0.95	29	−0.24	−0.01	3.07	3.44	2.03	-	2.51	0.05
$(CH_2OH)_2/Co_{15}$	334	0.69	0.83	29	−0.05	0.07	3.22	3.89	2.13	3.09	2.45	−0.06
$(CH_2OH)_2/Co_{15}$	84	0.94	1.06	29	0.03	0.03	3.20	3.36	2.05	3.44	2.43	−0.04
$(CH_2OH)_2/Co_{15}$	84	0.94	1.10	27	0.00	−0.12	3.01	3.16	2.10	2.12	2.25	0.02

Continuation of Table 5

System	ΔE_{tot}	$\lvert E_{ad}\rvert$	$\lvert E_{int}\rvert$	m_{tot}	$\Delta\mathrm{ECN}_{av}$	Δd_{av}	d_{C_1-TM}	d_{C_2-TM}	d_{O_1-TM}	d_{O_2-TM}	d_{H-TM}	Q^{Mol}
$(CH_2OH)_2/Co_{15}$	0	1.02	1.10	29	−0.19	0.00	3.07	3.20	2.04	3.34	2.40	−0.01
CH_3OH/Ni_{15}	279	0.49	0.58	12	−0.71	0.30	3.03	-	2.11	-	2.45	0.03
CH_3OH/Ni_{15}	83	0.68	0.76	12	−0.06	0.13	2.97	-	2.05	-	2.44	0.04
CH_3OH/Ni_{15}	59	0.71	0.76	12	−0.12	0.45	3.00	-	2.06	-	2.60	0.05
CH_3OH/Ni_{15}	0	0.77	0.81	12	−0.26	0.18	2.98	-	2.05	-	2.32	0.02
C_2H_5OH/Ni_{15}	302	0.57	0.66	12	−0.78	0.46	3.11	3.55	2.13	-	2.41	0.01
C_2H_5OH/Ni_{15}	130	0.74	0.91	12	−0.44	0.69	3.19	3.43	2.16	-	2.37	0.00
C_2H_5OH/Ni_{15}	104	0.77	0.85	12	−0.08	0.16	3.03	3.34	2.05	-	2.46	0.04
C_2H_5OH/Ni_{15}	0	0.87	0.90	12	−0.02	0.08	3.01	3.48	2.03	-	2.49	0.04
$(CH_2OH)_2/Ni_{15}$	154	0.73	0.86	12	−0.09	0.17	3.11	3.56	2.05	3.34	2.46	−0.02
$(CH_2OH)_2/Ni_{15}$	19	0.87	0.90	12	−0.01	0.08	3.00	3.50	2.04	3.98	2.47	0.04
$(CH_2OH)_2/Ni_{15}$	12	0.87	0.99	12	0.00	0.23	3.14	3.33	2.02	3.31	2.47	−0.02
$(CH_2OH)_2/Ni_{15}$	0	0.88	1.09	12	−0.73	0.71	3.19	3.13	2.20	2.26	2.35	0.00
CH_3OH/Cu_{15}	351	0.35	0.36	1	0.06	0.00	3.34	-	3.33	-	2.61	−0.08
CH_3OH/Cu_{15}	252	0.47	0.51	1	0.35	0.13	3.08	-	2.15	-	2.58	0.01
CH_3OH/Cu_{15}	92	0.61	0.63	1	−0.24	−0.04	2.94	-	2.07	-	2.57	0.05
CH_3OH/Cu_{15}	0	0.70	0.73	1	0.18	0.033	2.96	-	2.07	-	2.58	0.04
C_2H_5OH/Cu_{15}	247	0.56	0.60	1	0.33	0.13	3.08	3.48	2.14	-	2.53	0.01
C_2H_5OH/Cu_{15}	171	0.63	0.67	1	0.75	0.15	3.02	3.61	2.09	-	2.65	0.03
C_2H_5OH/Cu_{15}	99	0.70	0.73	1	−0.29	−0.05	2.95	3.38	2.48	-	2.58	0.04
C_2H_5OH/Cu_{15}	0	0.80	0.85	1	0.36	0.04	3.01	3.57	2.06	-	2.58	0.03
$(CH_2OH)_2/Cu_{15}$	370	0.58	0.93	1	1.73	0.17	3.14	3.14	2.24	2.28	2.44	0.02
$(CH_2OH)_2/Cu_{15}$	142	0.81	0.97	1	0.95	0.22	3.12	3.27	2.18	2.19	2.56	0.00
$(CH_2OH)_2/Cu_{15}$	118	0.83	0.88	1	0.39	0.05	2.98	3.53	2.06	4.14	2.53	0.03
$(CH_2OH)_2/Cu_{15}$	0	0.95	1.05	1	1.09	0.11	3.08	3.39	2.08	3.31	2.39	−0.01
CH_3OH/Ru_{15}	352	0.12	0.53	2	−0.14	−0.03	2.57	-	3.38	-	2.16	−0.03
CH_3OH/Ru_{15}	283	0.55	0.87	4	−2.66	−0.59	3.18	-	2.21	-	2.59	0.04

Continuation of Table 5

System	ΔE_{tot}	$\lvert E_{ad}\rvert$	$\lvert E_{int}\rvert$	m_{tot}	$\Delta\mathrm{ECN}_{av}$	Δd_{av}	d_{C_1-TM}	d_{C_2-TM}	d_{O_1-TM}	d_{O_2-TM}	d_{H-TM}	Q^{Mol}
CH_3OH/Ru_{15}	196	0.46	0.94	2	0.05	0.06	3.25	-	2.25	-	2.63	0.03
CH_3OH/Ru_{15}	0	0.75	0.97	4	−10.03	−1.60	3.18	-	2.21	-	2.60	0.06
C_2H_5OH/Ru_{15}	586	0.23	0.48	2	0.18	0.05	3.13	3.39	3.61	-	2.11	−0.04
C_2H_5OH/Ru_{15}	337	0.48	0.91	6	−1.98	−0.38	3.28	3.79	2.22	-	2.62	0.04
C_2H_5OH/Ru_{15}	187	0.63	1.09	2	0.53	−0.04	3.17	3.63	2.18	-	2.65	0.07
C_2H_5OH/Ru_{15}	0	0.81	1.06	4	−9.94	−1.60	3.22	3.52	2.21	-	2.53	0.05
$(CH_2OH)_2/Ru_{15}$	143	0.58	1.06	2	−6.83	−1.21	3.30	3.21	2.19	3.86	2.14	0.06
$(CH_2OH)_2/Ru_{15}$	20	0.70	1.33	2	−0.04	0.09	3.29	3.51	2.27	2.36	2.64	0.06
$(CH_2OH)_2/Ru_{15}$	7	0.72	1.24	4	−3.28	−0.56	3.22	3.48	2.25	2.36	2.43	0.01
$(CH_2OH)_2/Ru_{15}$	0	0.72	1.04	2	−0.14	0.06	3.30	3.48	2.24	3.63	2.59	−0.03
CH_3OH/Rh_{15}	342	0.36	0.41	11	−0.05	−0.22	3.30	-	2.34	-	2.57	0.03
CH_3OH/Rh_{15}	144	0.52	0.60	9	−0.07	−0.31	3.14	-	2.20	-	2.53	0.06
CH_3OH/Rh_{15}	50	0.65	0.70	11	−0.34	−0.29	3.19	-	2.23	-	2.49	0.07
CH_3OH/Rh_{15}	0	0.70	0.79	9	−0.28	−0.32	3.16	-	2.20	-	2.49	0.06
C_2H_5OH/Rh_{15}	356	0.44	0.51	11	−0.07	−0.21	3.32	3.27	2.36	-	2.55	0.04
C_2H_5OH/Rh_{15}	206	0.59	0.68	9	0.01	−0.30	3.18	3.57	2.21	-	2.54	0.07
C_2H_5OH/Rh_{15}	73	0.72	0.78	11	−0.33	−0.30	3.21	3.42	2.22	-	2.51	0.07
C_2H_5OH/Rh_{15}	0	0.80	0.90	9	−0.20	−0.30	3.18	3.73	2.19	-	2.68	0.06
$(CH_2OH)_2/Rh_{15}$	402	0.66	0.90	9	−0.76	−0.25	3.26	3.46	2.27	2.35	2.44	0.07
$(CH_2OH)_2/Rh_{15}$	295	0.76	1.06	9	0.04	−0.20	3.15	3.30	2.24	2.24	2.48	0.11
$(CH_2OH)_2/Rh_{15}$	234	0.82	0.96	11	−0.34	−0.25	3.23	3.51	2.27	2.48	2.45	0.05
$(CH_2OH)_2/Rh_{15}$	0	1.06	1.22	9	−0.19	−0.27	3.22	3.32	2.20	3.54	2.51	0.02
CH_3OH/Pd_{15}	106	0.48	0.50	8	−0.18	−0.04	3.25	-	2.33	-	2.59	0.05
CH_3OH/Pd_{15}	70	0.51	0.53	8	−0.18	0.04	3.19	-	2.33	-	2.83	0.06
CH_3OH/Pd_{15}	2	0.58	0.59	8	0.03	0.03	3.20	-	2.28	-	2.59	0.07
CH_3OH/Pd_{15}	0	0.58	0.61	8	−0.13	−0.11	3.26	-	2.29	-	2.50	0.05
C_2H_5OH/Pd_{15}	265	0.40	0.43	8	−0.04	0.09	3.40	3.51	2.42	-	2.74	0.04

Continuation of Table 5

System	ΔE_{tot}	$\lvert E_{ad}\rvert$	$\lvert E_{int}\rvert$	m_{tot}	$\Delta\mathrm{ECN}_{av}$	Δd_{av}	d_{C_1-TM}	d_{C_2-TM}	d_{O_1-TM}	d_{O_2-TM}	d_{H-TM}	Q^{Mol}
C_2H_5OH/Pd_{15}	124	0.54	0.57	8	−0.22	−0.04	3.33	3.67	2.32	-	2.61	0.04
C_2H_5OH/Pd_{15}	65	0.60	0.63	8	−0.14	0.06	3.25	3.48	2.32	-	2.72	0.06
C_2H_5OH/Pd_{15}	0	0.67	0.68	8	0.09	0.06	3.26	3.53	2.28	-	2.60	0.07
$(CH_2OH)_2/Pd_{15}$	346	0.49	0.71	8	−0.04	0.07	3.29	3.56	2.33	2.63	2.60	0.07
$(CH_2OH)_2/Pd_{15}$	210	0.63	0.74	8	−0.08	0.08	3.37	3.37	2.31	3.29	2.36	0.01
$(CH_2OH)_2/Pd_{15}$	38	0.80	0.88	8	−0.18	−0.04	3.25	3.51	2.28	3.29	2.35	0.02
$(CH_2OH)_2/Pd_{15}$	0	0.84	0.90	8	−0.04	0.03	3.26	3.45	2.31	3.32	2.51	0.00
CH_3OH/Ag_{15}	45	0.32	0.33	1	−0.02	0.01	3.48	-	2.59	-	2.73	0.00
CH_3OH/Ag_{15}	31	0.33	0.34	1	−0.08	0.01	3.43	-	2.55	-	2.74	0.00
CH_3OH/Ag_{15}	18	0.35	0.36	1	−0.03	0.02	3.40	-	2.55	-	2.83	0.01
CH_3OH/Ag_{15}	0	0.36	0.37	1	0.09	−0.02	3.33	-	2.47	-	2.85	0.03
C_2H_5OH/Ag_{15}	46	0.38	0.40	1	−0.02	−0.02	3.36	3.91	2.49	-	2.97	0.02
C_2H_5OH/Ag_{15}	42	0.39	0.40	1	−0.07	0.00	3.38	3.79	2.52	-	2.83	0.01
C_2H_5OH/Ag_{15}	24	0.40	0.42	1	0.00	−0.01	3.42	3.73	2.53	-	2.84	0.01
C_2H_5OH/Ag_{15}	0	0.43	0.44	1	0.07	−0.02	3.28	3.75	2.48	-	2.91	0.02
$(CH_2OH)_2/Ag_{15}$	256	0.30	0.45	1	0.05	−0.02	3.32	3.79	2.50	4.70	2.91	0.02
$(CH_2OH)_2/Ag_{15}$	162	0.39	0.42	1	−0.03	−0.01	3.34	3.88	2.51	4.52	2.95	0.02
$(CH_2OH)_2/Ag_{15}$	90	0.47	0.51	1	−0.06	0.01	3.42	3.75	2.58	2.77	2.81	0.00
$(CH_2OH)_2/Ag_{15}$	0	0.56	0.61	1	0.02	−0.03	3.42	3.77	2.48	3.32	2.64	−0.01
CH_3OH/Os_{15}	730	0.35	0.37	2	−0.32	0.02	3.67	-	3.82	-	2.90	−0.06
CH_3OH/Os_{15}	296	0.78	1.12	4	−2.57	−0.06	3.20	-	2.32	-	2.64	0.06
CH_3OH/Os_{15}	63	1.02	1.21	0	−0.56	−0.01	3.12	-	2.14	-	2.65	0.11
CH_3OH/Os_{15}	0	1.08	1.14	4	−0.53	0.03	3.10	-	2.15	-	2.53	0.10
C_2H_5OH/Os_{15}	809	0.39	0.49	0	−0.69	0.00	3.71	3.15	3.77	-	2.14	−0.03
C_2H_5OH/Os_{15}	305	0.89	1.17	4	−1.40	−0.04	3.20	3.68	2.13	-	2.61	0.08
C_2H_5OH/Os_{15}	64	1.13	1.26	2	−0.35	−0.01	3.13	3.69	2.11	-	2.64	0.12
C_2H_5OH/Os_{15}	0	1.20	1.29	4	−0.56	0.02	3.16	3.45	2.15	-	2.54	0.10

Continuation of Table 5

System	ΔE_{tot}	$\lvert E_{ad}\rvert$	$\lvert E_{int}\rvert$	m_{tot}	$\Delta\mathrm{ECN}_{av}$	Δd_{av}	d_{C_1-TM}	d_{C_2-TM}	d_{O_1-TM}	d_{O_2-TM}	d_{H-TM}	Q^{Mol}
$(CH_2OH)_2/Os_{15}$	280	0.97	1.29	2	−1.57	−0.08	3.18	3.66	2.14	4.06	2.58	0.08
$(CH_2OH)_2/Os_{15}$	195	1.05	1.37	2	0.34	0.10	3.20	3.48	2.14	3.65	2.49	0.06
$(CH_2OH)_2/Os_{15}$	51	1.20	1.39	2	0.03	0.08	3.22	3.67	2.17	3.64	2.66	0.05
$(CH_2OH)_2/Os_{15}$	0	1.25	1.42	4	−0.55	0.07	3.20	3.56	2.20	3.72	2.57	0.02
CH_3OH/Ir_{15}	335	0.49	0.64	1	−0.62	−0.02	2.85	-	3.33	-	1.92	0.05
CH_3OH/Ir_{15}	122	0.70	0.81	3	−1.15	−0.04	3.21	-	2.24	-	2.60	0.09
CH_3OH/Ir_{15}	6	0.82	0.94	3	−0.76	−0.04	3.23	-	2.20	-	2.73	0.09
CH_3OH/Ir_{15}	0	0.82	0.99	3	1.12	0.24	3.16	-	2.17	-	2.49	0.08
C_2H_5OH/Ir_{15}	285	0.58	0.68	3	−0.60	−0.02	3.05	3.43	3.36	-	1.98	0.06
C_2H_5OH/Ir_{15}	109	0.76	0.89	3	−1.19	−0.04	3.26	3.51	2.24	-	2.60	0.09
C_2H_5OH/Ir_{15}	12	0.86	0.96	1	−0.39	−0.03	3.22	3.81	2.14	-	2.55	0.11
C_2H_5OH/Ir_{15}	0	0.87	1.01	1	−0.74	−0.05	3.22	3.93	2.19	-	2.72	0.10
$(CH_2OH)_2/Ir_{15}$	254	0.73	0.94	1	−1.13	−0.02	3.39	3.50	2.25	3.30	2.33	0.03
$(CH_2OH)_2/Ir_{15}$	68	0.91	1.31	1	−1.35	0.00	3.20	3.10	2.28	2.42	2.54	0.12
$(CH_2OH)_2/Ir_{15}$	35	0.98	1.23	3	−1.34	−0.01	3.22	3.07	2.23	3.38	2.06	0.07
$(CH_2OH)_2/Ir_{15}$	0	1.02	1.36	3	−0.78	0.00	3.17	3.33	2.24	2.35	2.50	0.13
CH_3OH/Pt_{15}	141	0.77	0.80	2	0.27	0.10	3.17	-	2.28	-	2.68	0.10
CH_3OH/Pt_{15}	83	0.83	1.01	2	2.75	0.29	3.08	-	2.18	-	2.48	0.12
CH_3OH/Pt_{15}	73	0.84	0.95	0	0.43	0.05	3.15	-	2.22	-	2.67	0.12
CH_3OH/Pt_{15}	0	0.91	1.06	2	2.28	0.26	3.10	-	2.19	-	2.51	0.12
C_2H_5OH/Pt_{15}	393	0.61	0.69	2	0.14	0.15	3.20	3.39	2.29	-	2.56	0.11
C_2H_5OH/Pt_{15}	89	0.91	1.12	2	2.98	0.33	3.13	3.64	2.17	-	2.52	0.13
C_2H_5OH/Pt_{15}	45	0.95	1.09	0	0.42	0.04	3.19	3.58	2.21	-	2.55	0.12
C_2H_5OH/Pt_{15}	0	1.00	1.16	2	2.38	0.27	3.20	3.51	2.18	-	2.51	0.12
$(CH_2OH)_2/Pt_{15}$	407	0.78	1.01	2	−0.92	−0.07	3.31	3.18	2.40	2.54	2.45	0.11
$(CH_2OH)_2/Pt_{15}$	125	1.06	1.29	2	0.87	0.11	3.31	3.21	2.26	2.34	2.53	0.13
$(CH_2OH)_2/Pt_{15}$	72	1.12	1.36	0	0.45	0.07	3.16	3.41	3.16	3.68	2.41	0.10

Continuation of Table 5

System	ΔE_{tot}	$\lvert E_{ad}\rvert$	$\lvert E_{int}\rvert$	m_{tot}	$\Delta\mathrm{ECN}_{av}$	Δd_{av}	d_{C_1-TM}	d_{C_2-TM}	d_{O_1-TM}	d_{O_2-TM}	d_{H-TM}	Q^{Mol}
$(CH_2OH)_2/Pt_{15}$	0	1.19	1.40	2	2.40	0.28	3.17	3.45	2.18	3.39	2.44	0.08
CH_3OH/Au_{15}	119	0.29	0.32	1	−0.38	0.05	3.23	-	3.17	-	2.18	0.03
CH_3OH/Au_{15}	29	0.38	0.61	1	−6.38	−0.41	3.32	-	2.38	-	2.66	0.08
CH_3OH/Au_{15}	11	0.40	0.42	1	−0.28	0.01	3.25	-	2.46	-	2.97	0.07
CH_3OH/Au_{15}	0	0.41	0.46	1	−0.70	0.06	3.34	-	2.44	-	2.73	0.07
C_2H_5OH/Au_{15}	27	0.46	0.52	1	−0.68	0.079	3.46	3.75	2.44	-	2.72	0.07
C_2H_5OH/Au_{15}	24	0.46	0.67	1	−5.85	−0.37	3.36	3.52	2.38	-	2.71	0.09
C_2H_5OH/Au_{15}	6	0.48	0.50	1	−0.12	0.01	3.29	3.76	2.47	-	2.97	0.07
C_2H_5OH/Au_{15}	0	0.49	0.54	1	−0.77	0.07	3.33	3.64	2.42	-	2.71	0.08
$(CH_2OH)_2/Au_{15}$	310	0.29	0.56	1	−6.09	−0.38	3.31	3.75	2.44	4.61	2.77	0.08
$(CH_2OH)_2/Au_{15}$	118	0.48	0.53	1	−0.41	0.07	3.17	3.76	3.13	3.49	2.10	0.04
$(CH_2OH)_2/Au_{15}$	42	0.56	0.84	1	−5.86	−0.36	3.42	3.63	2.42	2.70	2.62	0.10
$(CH_2OH)_2/Au_{15}$	0	0.60	0.71	1	−0.84	0.05	3.38	3.57	2.45	3.53	2.66	0.05

Table S5: Percentage changes in bond lengths, Δd_0 (%), from the molecules in the methanol, ethanol and ethylene glycol adsorbed on the $3d$, $4d$, $5d$ TM_{15} clusters.

d_0	Δd_0															
	Methanol/Fe_{15}				Methanol/Co_{15}				Methanol/Ni_{15}				Methanol/Cu_{15}			
O−H	0.48	0.63	0.48	1.63	0.37	0.29	0.53	0.52	1.44	0.27	0.50	0.72	0.29	0.41	0.56	1.41
C−O	1.54	1.64	1.51	−0.18	1.76	1.45	1.95	1.72	1.75	1.73	1.48	1.25	1.76	1.83	1.32	−0.60
C−H	−0.29	−0.21	−0.25	0.42	−0.73	−0.63	−0.65	−0.65	−0.18	−0.65	−0.28	−0.11	−0.55	−0.62	−0.23	1.01
C−H	−0.65	−0.32	−0.26	0.37	−0.36	−0.19	−0.26	−0.29	−0.63	−0.33	−0.63	−0.50	−0.23	−0.31	−0.22	−0.30
C−H	−0.29	−0.66	−0.63	−0.35	−0.34	−0.22	−0.25	−0.24	−0.23	−0.31	−0.28	−0.19	−0.26	−0.35	−0.47	0.23
	Ethanol/Fe_{15}				Ethanol/Co_{15}				Ethanol/Ni_{15}				Ethanol/Cu_{15}			
O−H	1.47	1.52	1.42	2.63	1.36	1.38	1.53	2.72	1.48	1.39	2.72	1.69	1.32	1.37	1.28	1.54
C−O	1.59	1.73	1.45	−0.71	1.83	1.45	1.74	−1.11	1.77	1.69	1.30	1.16	1.75	1.80	1.33	1.10
C−C	−0.50	−0.68	−0.37	0.18	−0.38	−0.46	−0.43	0.22	−0.40	−0.70	−0.22	−0.74	−0.48	−0.32	−0.38	−0.32
C−H	−0.35	−0.07	0.03	−0.10	−0.10	0.00	−0.01	0.00	−0.39	0.01	−0.31	0.42	0.00	0.02	0.02	−0.15
C−H	−0.08	0.17	−0.36	0.61	−0.39	−0.25	−0.32	0.61	0.05	0.06	0.03	0.05	−0.10	−0.34	−0.12	0.06

Continuation of Table S5

d_0	Δd_0															
C–H	0.04	0.21	0.27	0.64	−0.11	0.13	−0.08	1.95	0.19	−0.23	−0.08	0.28	0.02	0.05	−0.18	0.25
C–H	−0.12	−0.29	−0.14	−0.28	0.02	−0.02	0.04	−0.21	−0.17	0.09	−0.10	−0.29	0.18	−0.06	−0.03	−0.09
C–H	−0.23	−0.29	−0.07	−0.12	−0.10	−0.15	−0.16	−0.12	−0.05	−0.21	0.10	−0.26	−0.12	−0.15	0.01	−0.22
	Ethylene Glycol/Fe_{15}				Ethylene Glycol/Co_{15}				Ethylene Glycol/Ni_{15}				Ethylene Glycol/Cu_{15}			
O–H	1.24	1.24	0.27	−0.15	0.57	0.48	−0.01	0.66	1.88	−0.05	1.10	0.36	1.11	1.22	0.47	0.13
O–H	0.01	0.01	0.19	−0.04	1.73	1.94	2.13	1.98	1.29	1.53	0.03	1.96	1.53	0.10	1.78	0.13
C–O	1.31	1.31	0.76	−0.14	2.24	1.80	2.20	1.33	1.14	1.85	1.42	1.66	1.44	1.40	0.83	1.11
C–O	0.21	0.21	0.77	−0.89	−0.74	1.23	−1.23	−1.19	0.80	−1.01	0.22	−1.27	−0.32	0.39	0.66	1.51
C–C	0.00	0.00	−0.29	−0.48	0.15	−0.43	−0.09	0.11	−0.42	−0.15	−0.08	0.07	0.19	−0.03	−0.09	0.85
C–H	0.06	0.06	−0.06	0.30	−0.29	−0.04	−0.20	−0.02	−0.14	0.05	0.08	−0.36	−0.16	0.01	0.04	0.04
C–H	−0.42	−0.42	−0.28	0.16	−0.40	0.23	−0.08	−0.30	−0.42	−0.17	−0.45	−0.10	−0.47	−0.25	−0.04	−0.14
C–H	−0.03	0.10	0.09	1.76	−0.09	−0.21	0.60	−0.07	0.07	0.65	0.28	0.71	−0.06	0.12	0.10	0.47
C–H	0.10	−0.03	0.17	0.35	0.42	−0.41	−0.09	0.64	0.35	−0.02	−0.07	−0.12	0.27	−0.10	−0.20	−0.14
	Methanol/Ru_{15}				Methanol/Rh_{15}				Methanol/Pd_{15}				Methanol/Ag_{15}			
O–H	0.51	0.54	0.86	1.68	1.03	0.94	0.89	0.75	1.04	0.41	0.23	0.70	0.31	0.38	0.65	0.66
C–O	1.89	1.37	1.64	−1.84	1.51	1.59	1.42	1.01	1.19	1.35	1.38	1.04	1.01	0.73	0.82	0.63
C–H	−0.24	−0.16	−0.26	3.15	−0.19	−0.33	−0.66	−0.10	−0.06	−0.21	−0.18	−0.21	−0.10	−0.01	−0.14	−0.10
C–H	−0.21	−0.71	−0.66	2.23	−0.62	−0.21	−0.21	−0.57	−0.21	−0.67	−0.62	−0.62	−0.55	−0.53	−0.51	−0.56
C–H	−0.63	−0.29	−0.25	−0.34	−0.20	−0.61	−0.18	−0.18	−0.66	−0.23	−0.14	−0.13	−0.18	−0.10	0.03	0.22
	Ethanol/Ru_{15}				Ethanol/Rh_{15}				Ethanol/Pd_{15}				Ethanol/Ag_{15}			
O–H	1.39	1.50	1.56	2.77	1.33	1.80	1.66	1.78	1.44	1.18	1.71	1.44	1.23	1.22	1.25	1.23
C–O	2.13	2.23	1.47	−2.39	1.75	1.58	1.45	0.89	1.27	1.54	0.87	0.52	0.80	0.59	0.88	0.55
C–C	−0.78	−0.51	−0.44	−0.19	−0.49	−0.27	−0.62	−0.66	−0.31	−0.64	−0.27	−0.26	−0.17	−0.48	−0.53	−0.28
C–H	−0.01	−0.05	0.04	4.34	−0.21	0.02	0.07	0.11	−0.32	0.06	0.15	0.24	0.13	0.17	0.16	0.16
C–H	−0.02	−0.38	−0.39	−0.15	0.00	−0.35	0.06	0.24	0.14	0.06	−0.27	−0.17	−0.11	0.29	0.37	−0.12
C–H	−0.28	−0.13	−0.03	−0.27	0.04	−0.10	−0.29	−0.30	−0.01	−0.30	0.15	−0.15	−0.04	−0.28	−0.25	0.03
C–H	0.62	−0.09	−0.16	1.15	−0.13	−0.11	0.50	−0.34	−0.13	−0.18	−0.07	−0.01	−0.20	−0.22	−0.25	−0.18
C–H	−0.32	−0.10	−0.07	−0.19	−0.05	−0.03	−0.26	1.36	−0.12	0.27	−0.07	0.27	−0.03	−0.10	−0.05	−0.07
	Ethylene Glycol/Ru_{15}				Ethylene Glycol/Rh_{15}				Ethylene Glycol/Pd_{15}				Ethylene Glycol/Ag_{15}			
O–H	1.25	0.17	0.50	0.18	1.34	0.28	1.01	0.27	0.98	1.16	−0.11	0.13	1.00	0.20	0.77	−0.09
O–H	1.47	2.33	0.10	0.56	1.99	2.12	0.22	1.36	1.82	1.80	1.89	0.71	0.86	0.77	0.13	0.08

Continuation of Table S5

d_0	Δd_0															
C–O	1.14	1.13	0.97	2.08	1.31	1.03	1.25	0.95	1.11	1.00	1.61	1.61	0.72	0.70	0.39	1.16
C–O	−0.21	0.50	1.09	−1.85	−0.97	0.12	1.84	0.40	−0.21	−0.11	−0.85	0.32	0.02	−0.31	0.31	−0.41
C–C	0.38	−0.05	−0.62	−0.22	0.18	0.10	−0.27	−0.36	0.10	0.31	−0.10	0.12	0.16	0.00	−0.01	−0.63
C–H	−0.45	−0.08	−0.08	−0.05	−0.09	0.10	0.06	−0.32	−0.43	−0.47	−0.03	−0.08	−0.39	0.08	−0.11	−0.06
C–H	−0.04	−0.02	−0.17	−0.24	−0.46	−0.29	−0.07	0.09	0.06	0.01	−0.06	−0.16	0.09	−0.21	0.29	0.23
C–H	0.76	−0.26	0.14	2.68	1.70	0.29	−0.09	−0.19	0.40	0.15	0.33	0.07	0.18	0.43	0.06	0.50
C–H	−0.17	0.13	0.02	−0.28	−0.05	−0.15	−0.18	0.22	0.10	−0.03	−0.05	0.12	0.11	−0.21	−0.10	0.35
	Methanol/Os_{15}				Methanol/Ir_{15}				Methanol/Pt_{15}				Methanol/Au_{15}			
O–H	1.06	0.48	1.27	1.04	1.98	0.27	0.90	1.97	0.99	0.34	1.64	0.29	0.56	0.21	0.98	0.63
C–O	2.44	2.29	2.16	−0.86	1.67	2.07	1.63	−2.76	1.89	2.02	1.94	1.76	1.13	1.21	1.14	−0.90
C–H	−0.77	−0.44	−0.23	0.68	−0.19	−0.66	−0.27	−0.14	−0.31	−0.73	−0.65	−0.58	−0.13	−0.58	−0.63	2.63
C–H	−0.36	−0.69	−0.35	0.74	−0.28	−0.37	−0.72	6.80	−0.74	−0.33	−0.32	−0.24	−0.65	−0.23	0.14	−0.08
C–H	−0.46	−0.46	−0.72	−0.36	−0.72	−0.35	−0.30	−0.31	−0.24	−0.30	−0.35	−0.22	−0.22	−0.25	−0.25	−0.47
	Ethanol/Os_{15}				Ethanol/Ir_{15}				Ethanol/Pt_{15}				Ethanol/Au_{15}			
O–H	1.89	1.58	1.48	2.14	1.39	2.13	1.77	2.75	1.89	1.36	2.41	2.23	1.52	1.29	1.58	1.68
C–O	3.10	3.22	2.68	−1.26	2.34	2.04	1.86	−3.11	1.93	2.12	2.12	1.29	1.06	1.04	1.18	0.92
C–C	−0.96	−0.74	−0.66	0.16	−0.64	−0.57	−0.70	−0.25	−0.48	−0.58	−0.48	−0.29	−0.63	−0.27	−0.63	−0.23
C–H	−0.09	−0.47	−0.09	0.91	−0.10	−0.02	−0.05	−0.06	0.02	−0.39	−0.05	0.09	0.08	0.09	0.05	0.14
C–H	−0.18	−0.22	−0.15	−0.03	−0.30	−0.43	0.03	6.25	−0.37	−0.04	−0.32	−0.30	0.16	−0.20	0.20	−0.30
C–H	−0.36	−0.06	−0.15	−0.47	−0.02	−0.06	−0.26	−0.26	−0.11	−0.15	−0.11	−0.10	−0.28	0.02	−0.25	−0.04
C–H	−0.28	−0.21	−0.11	−0.12	−0.21	0.00	−0.01	0.59	−0.17	−0.02	−0.10	0.05	−0.30	−0.13	−0.24	−0.03
C–H	0.10	−0.11	−0.09	2.63	−0.10	−0.20	−0.24	−0.20	−0.11	0.48	−0.11	−0.14	−0.07	−0.03	0.10	−0.11
	Ethylene Glycol/Os_{15}				Ethylene Glycol/Ir_{15}				Ethylene Glycol/Pt_{15}				Ethylene Glycol/Au_{15}			
O–H	2.04	0.36	0.97	1.30	1.64	1.55	0.17	0.31	1.31	1.86	2.04	0.10	0.88	0.63	1.00	0.35
O–H	1.70	1.33	1.49	−0.04	0.40	2.80	1.66	2.82	1.88	0.97	0.28	2.08	0.87	1.06	0.91	−0.12
C–O	2.37	2.71	2.46	2.53	1.82	1.54	1.73	2.34	1.78	1.76	0.74	1.10	0.89	1.12	−0.13	1.33
C–O	−0.02	−1.27	−1.12	0.33	1.30	−1.85	0.67	−1.31	−0.41	0.12	1.42	0.31	−0.30	0.09	−1.60	−0.41
C–C	0.65	0.22	0.38	−0.24	0.10	0.34	−0.68	−0.06	0.11	0.72	−0.22	−0.47	0.13	−0.24	0.25	−0.76
C–H	−0.66	−0.23	−0.54	−0.30	−0.13	−0.50	−0.18	−0.13	−0.15	−0.61	−0.37	−0.09	−0.40	0.06	3.73	−0.15
C–H	−0.31	−0.44	−0.28	−0.10	0.11	−0.14	−0.25	−0.27	−0.53	−0.12	0.23	−0.11	0.00	0.12	−0.23	0.12
C–H	0.00	0.52	1.14	−0.10	−0.46	3.71	−0.07	0.59	0.01	0.78	−0.03	0.02	0.06	0.04	0.17	0.35

Continuation of Table S5

d_0	Δd_0															
C−H	−0.22	−0.05	−0.14	−0.09	−0.09	−0.10	0.01	−0.11	0.12	−0.23	−0.08	0.09	0.27	−0.25	−0.21	0.50

6 Geometric Parameters of the Adsorbed Systems

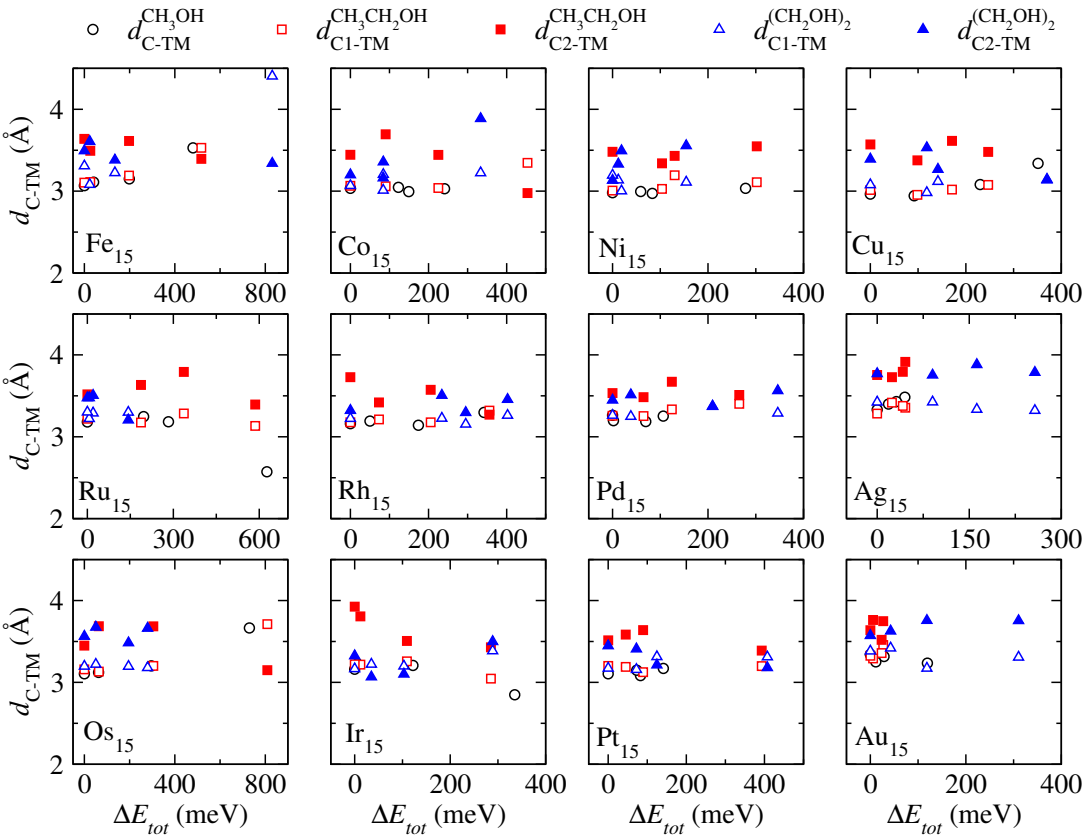

Figure S16: The C−TM distances (in Å) in the adsorbed systems.

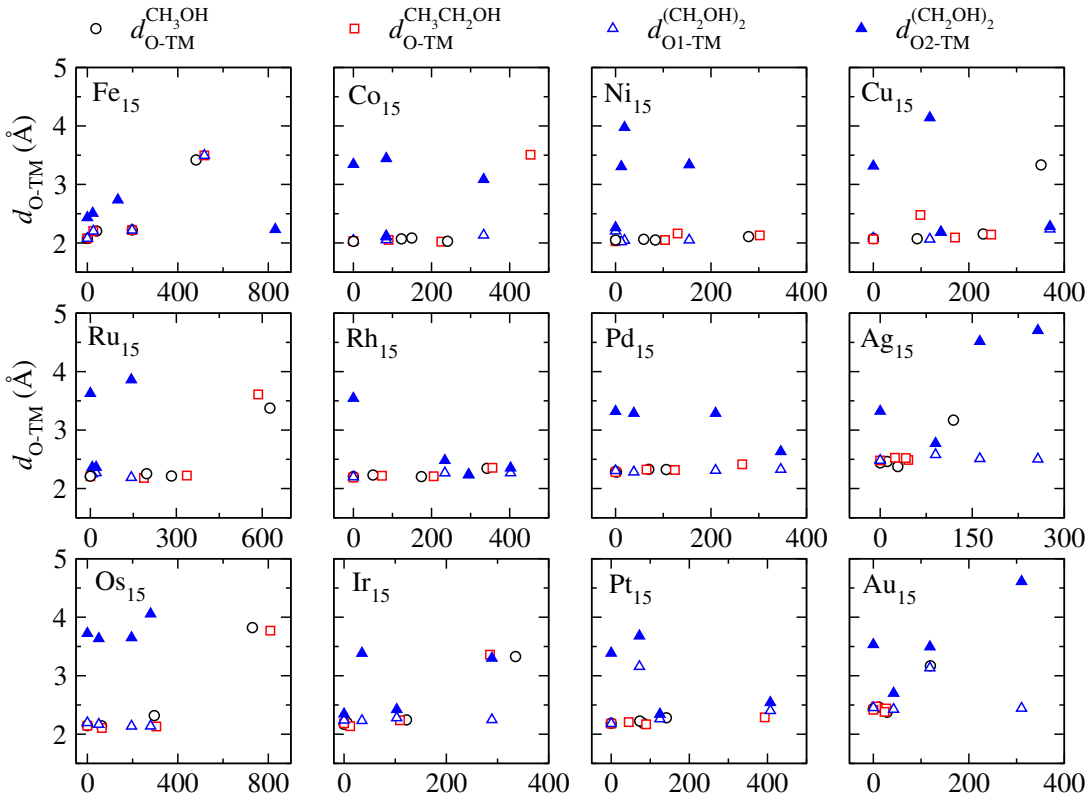

Figure S17: The O–TM distances (in Å) in the adsorbed systems.

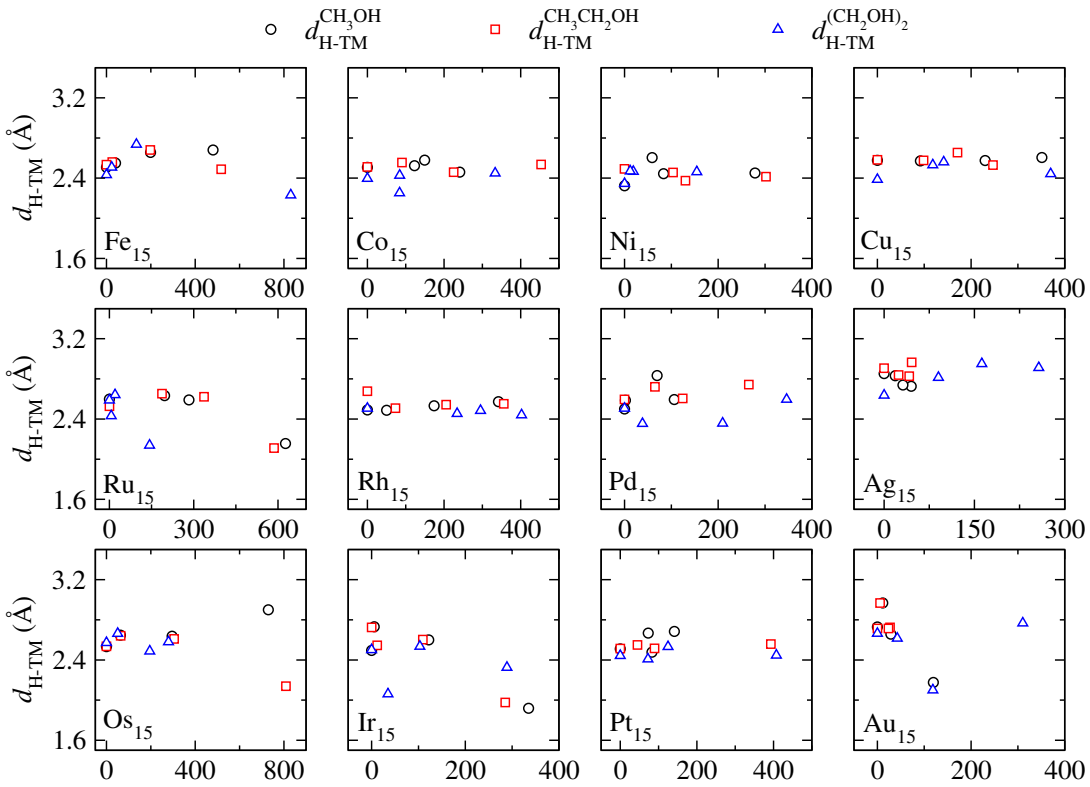

Figure S18: The closest H–TM distance (in Å) in the adsorbed systems.

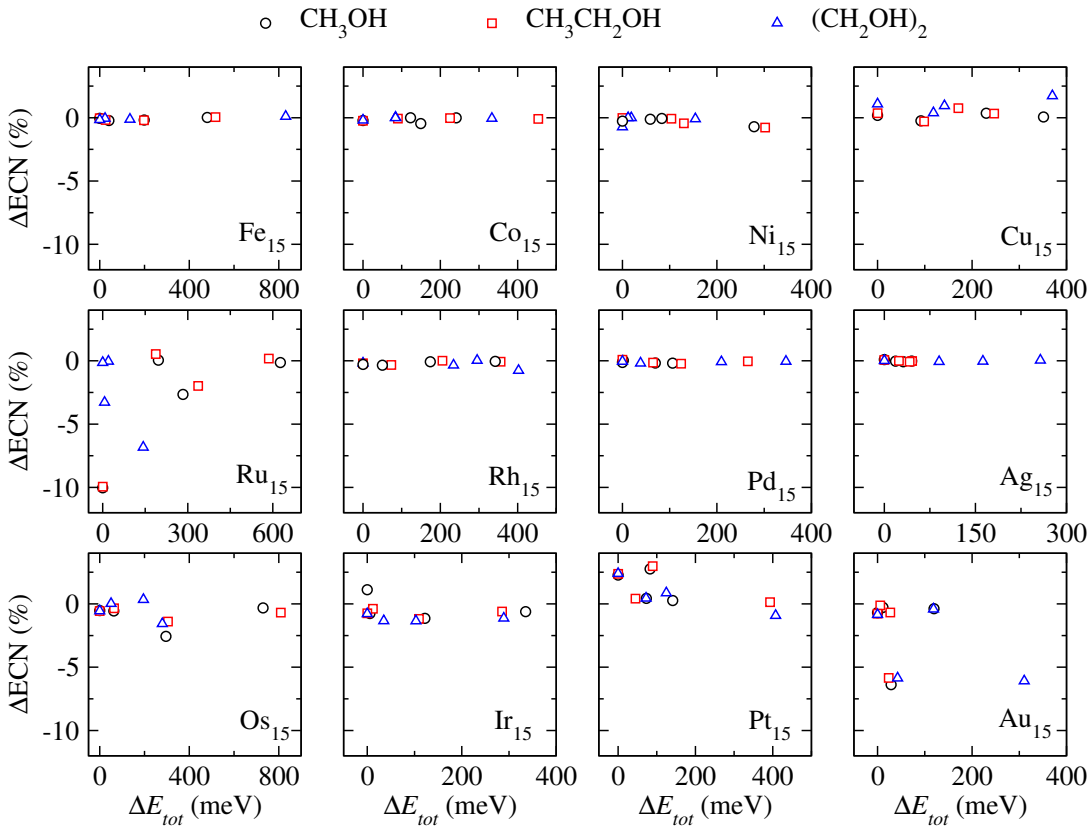

Figure S19: Percentage change in the ECN_{av} of the TM_{15} clusters due the adsorption of the methanol, ethanol and ethylene glycol.

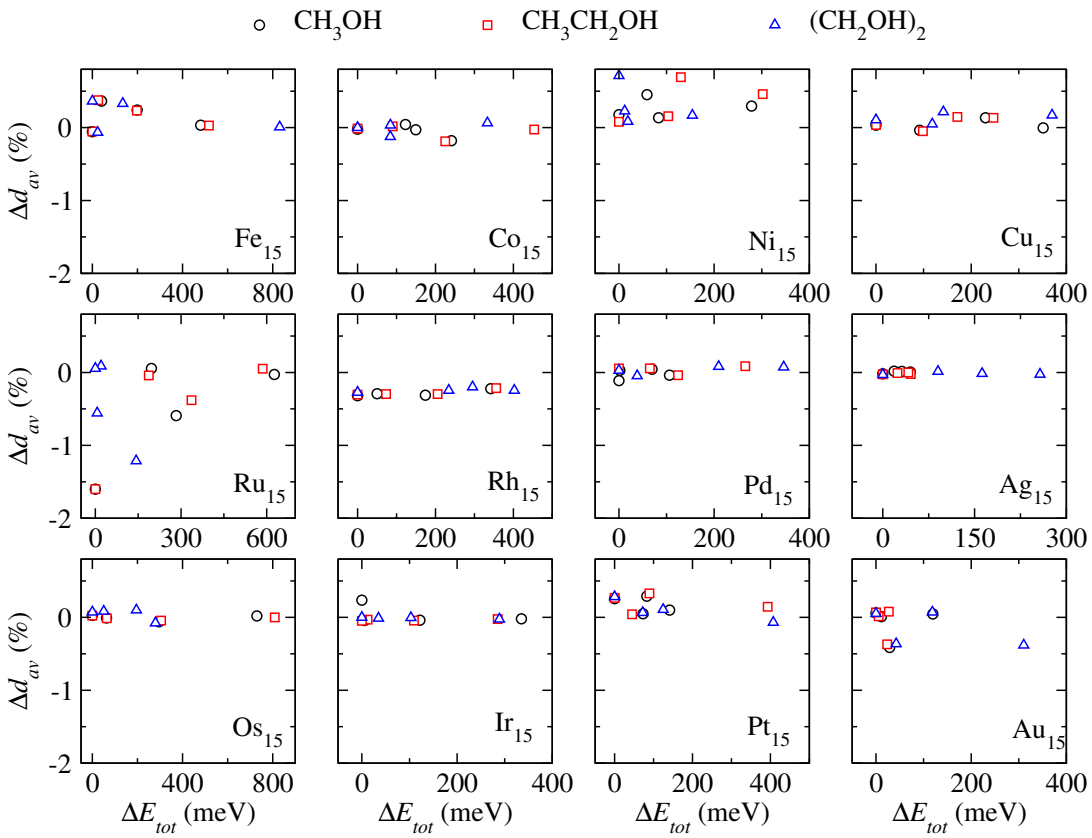

Figure S20: Percentage change in the d_{av} of the TM_{15} clusters due the adsorption of the methanol, ethanol and ethylene glycol.

7 Energetic properties off the adsorbed systems

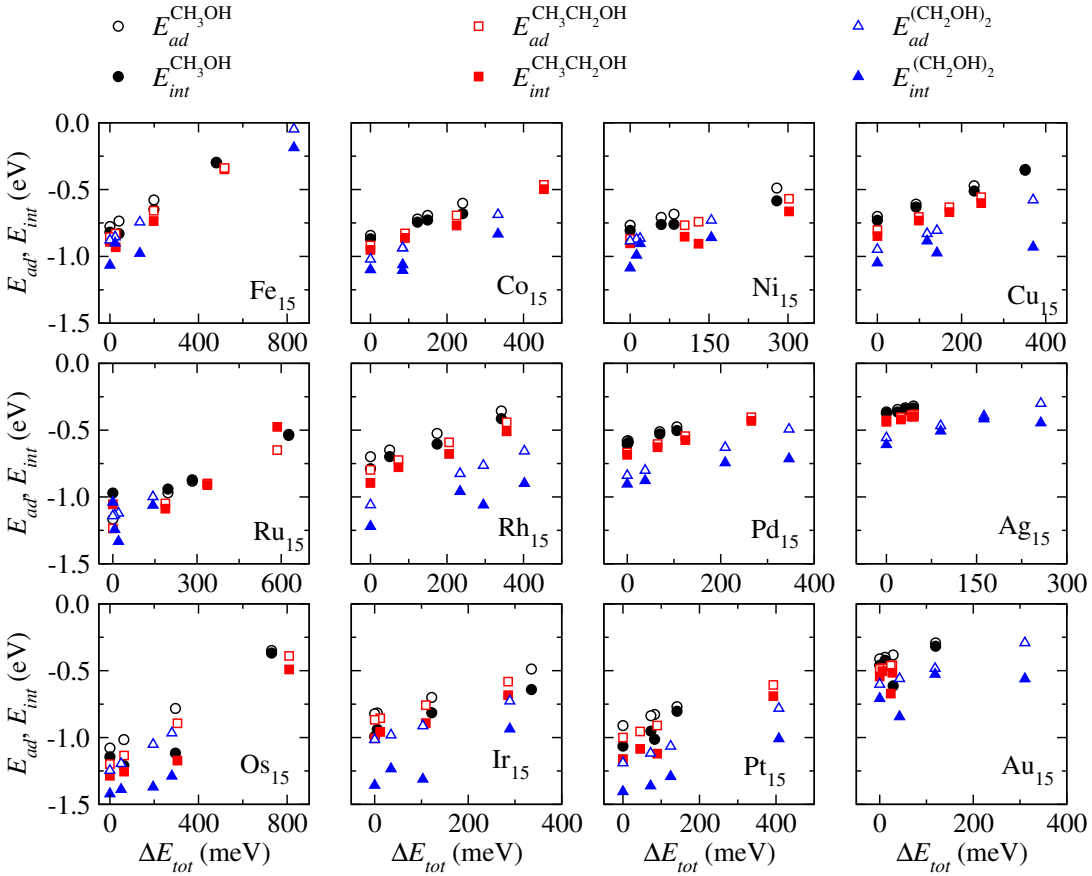

Figure S21: Adsorption and interacting energies for the methanol, ethanol and ethylene glycol on TM_{15} clusters

8 Electronic and charges properties of the adsorbed systems

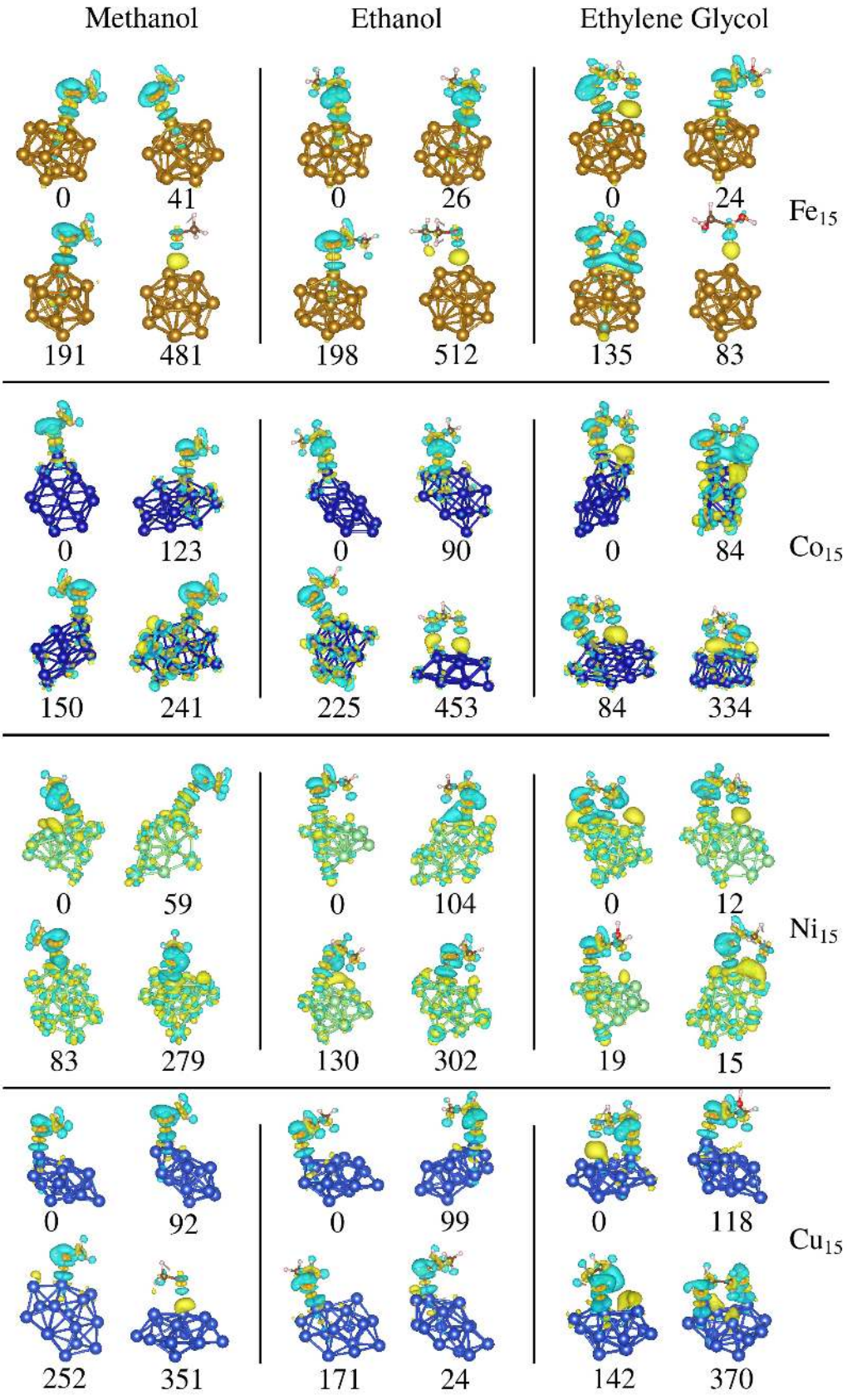

Figure S22: Isosurfaces of the electron density difference for the methanol, ethanol and ethylene glycol on 3*d* TM_{15} clusters

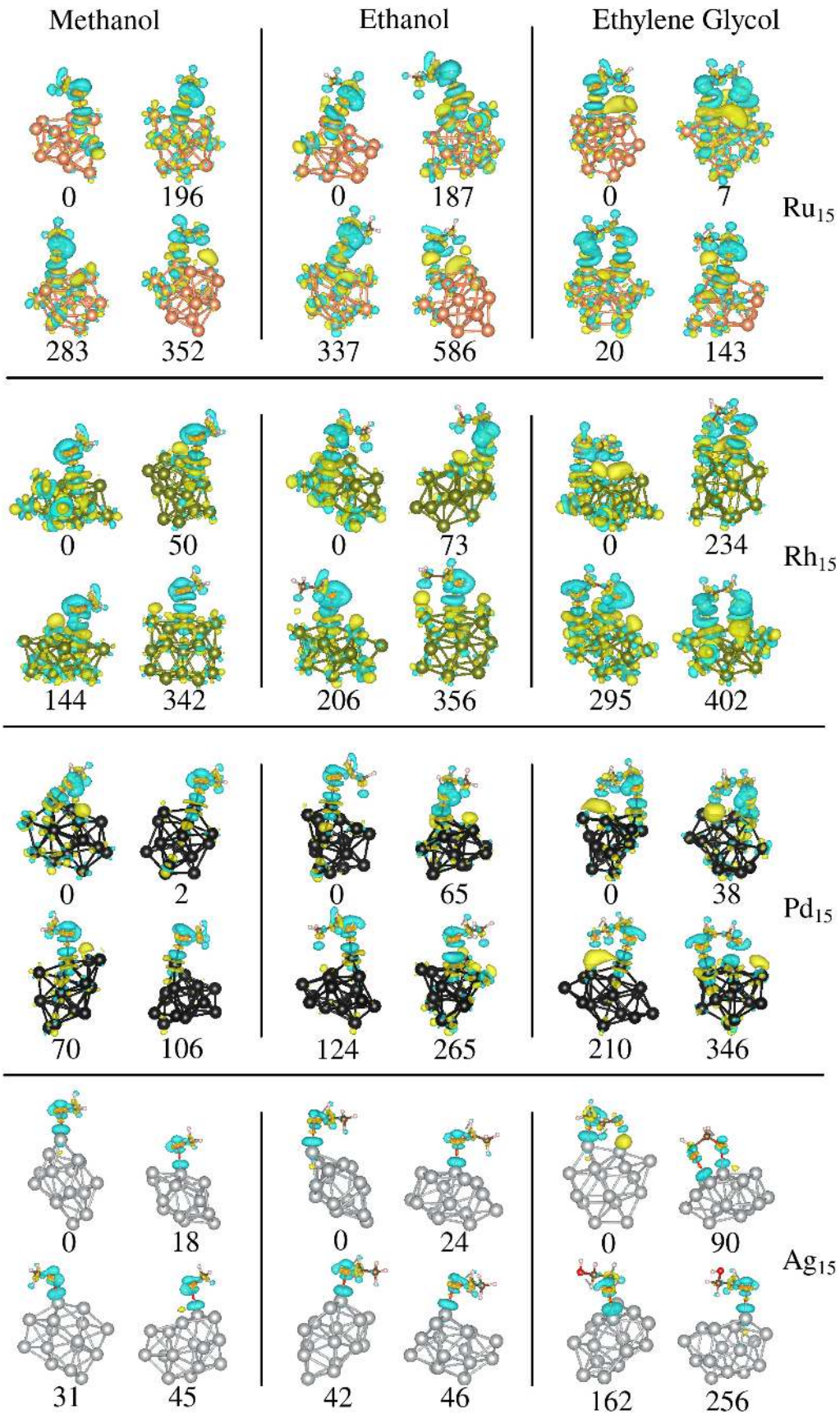

Figure S23: Isosurfaces of the electron density difference for the methanol, ethanol and ethylene glycol on 4*d* TM_{15} clusters

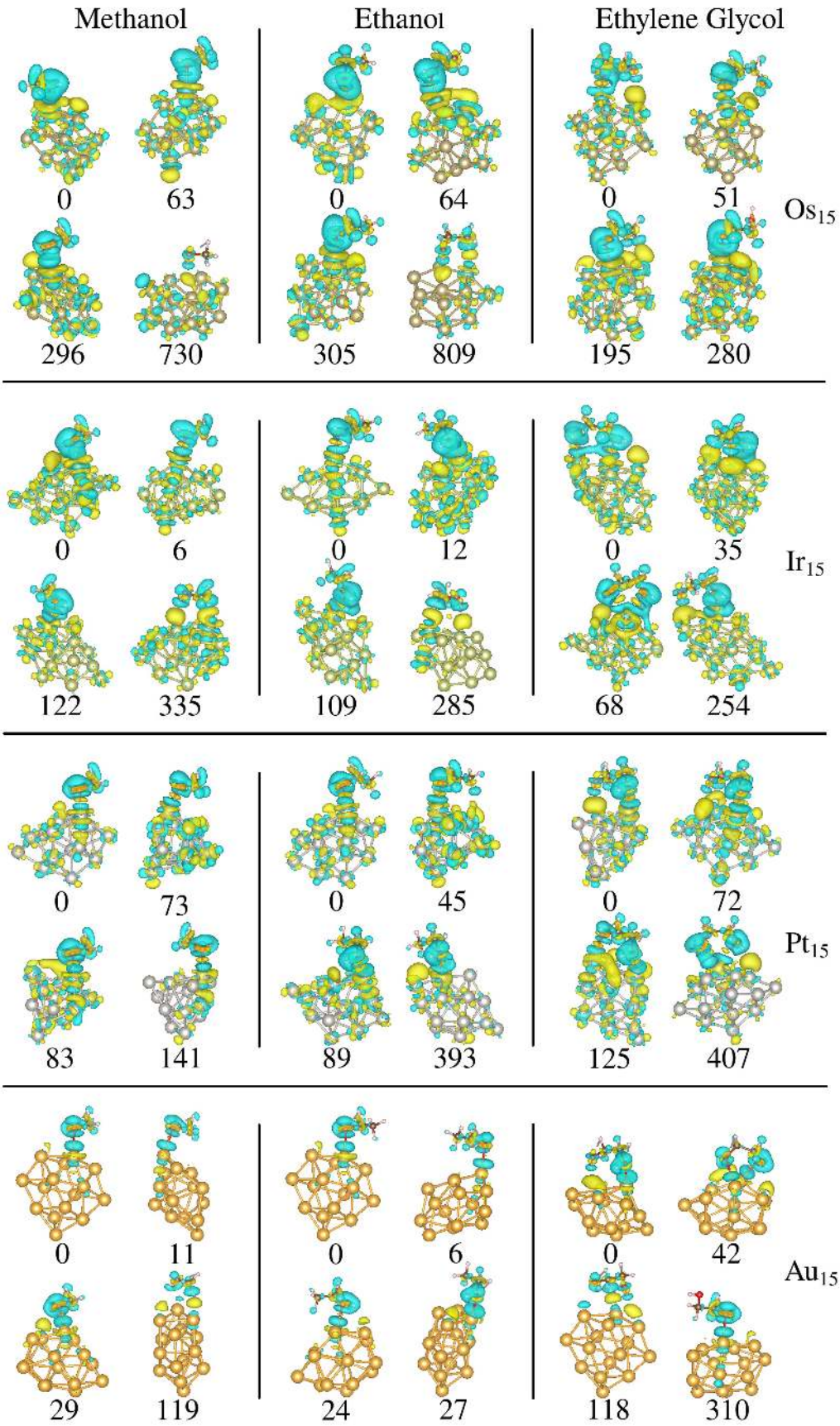

Figure S24: Isosurfaces of the electron density difference for the methanol, ethanol and ethylene glycol on 5*d* TM_{15} clusters

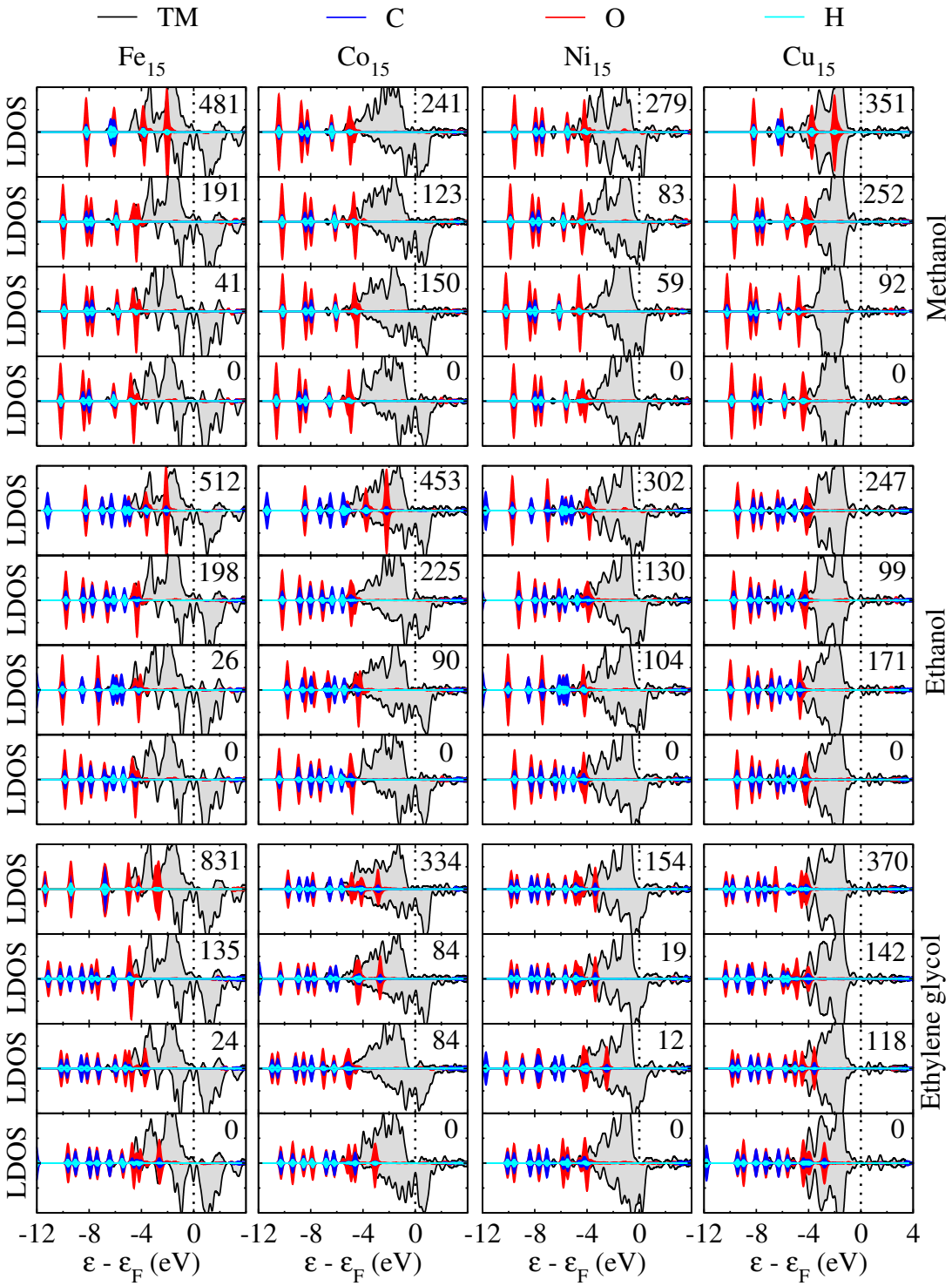

Figure S25: Density of states per atom for alcohols and the average density of states for 3*d*-TM atoms that interact with the molecules in the adsorbed systems.

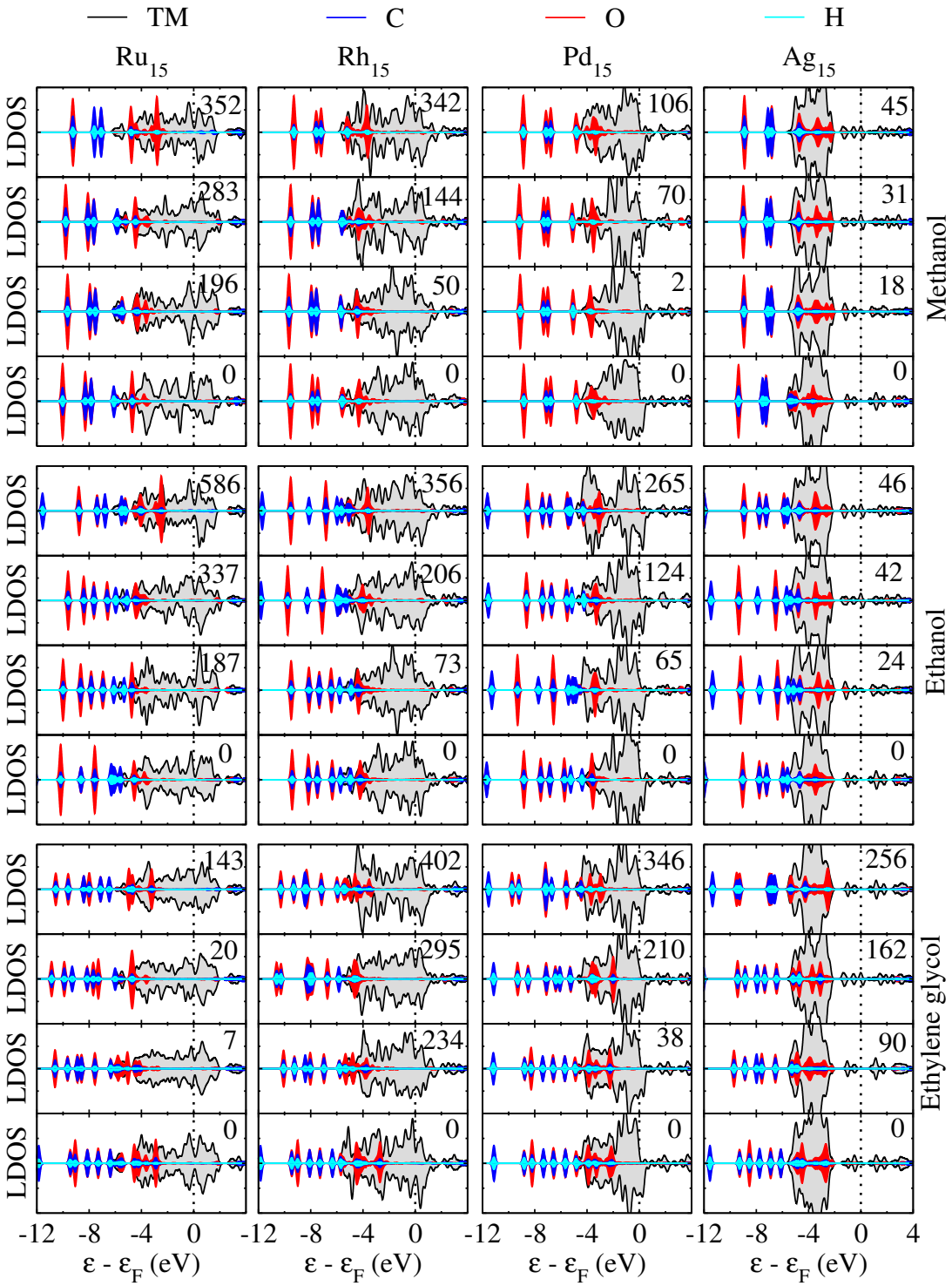

Figure S26: Density of states per atom for alcohols and the average density of states for 4*d*-TM atoms that interact with the molecules in the adsorbed systems.

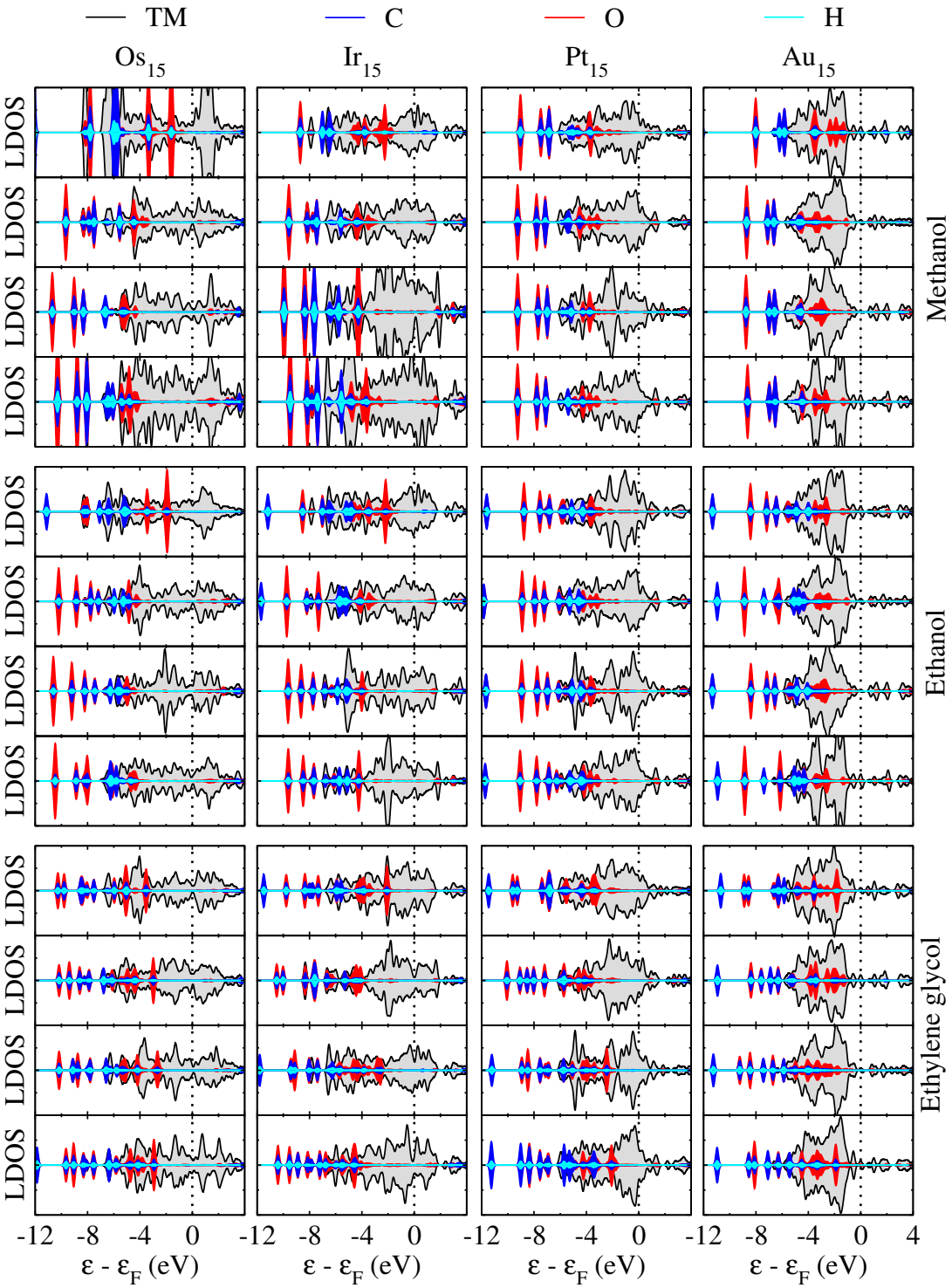

Figure S27: Density of states per atom for alcohols and the average density of states for 5*d*-TM atoms that interact with the molecules in the adsorbed systems.

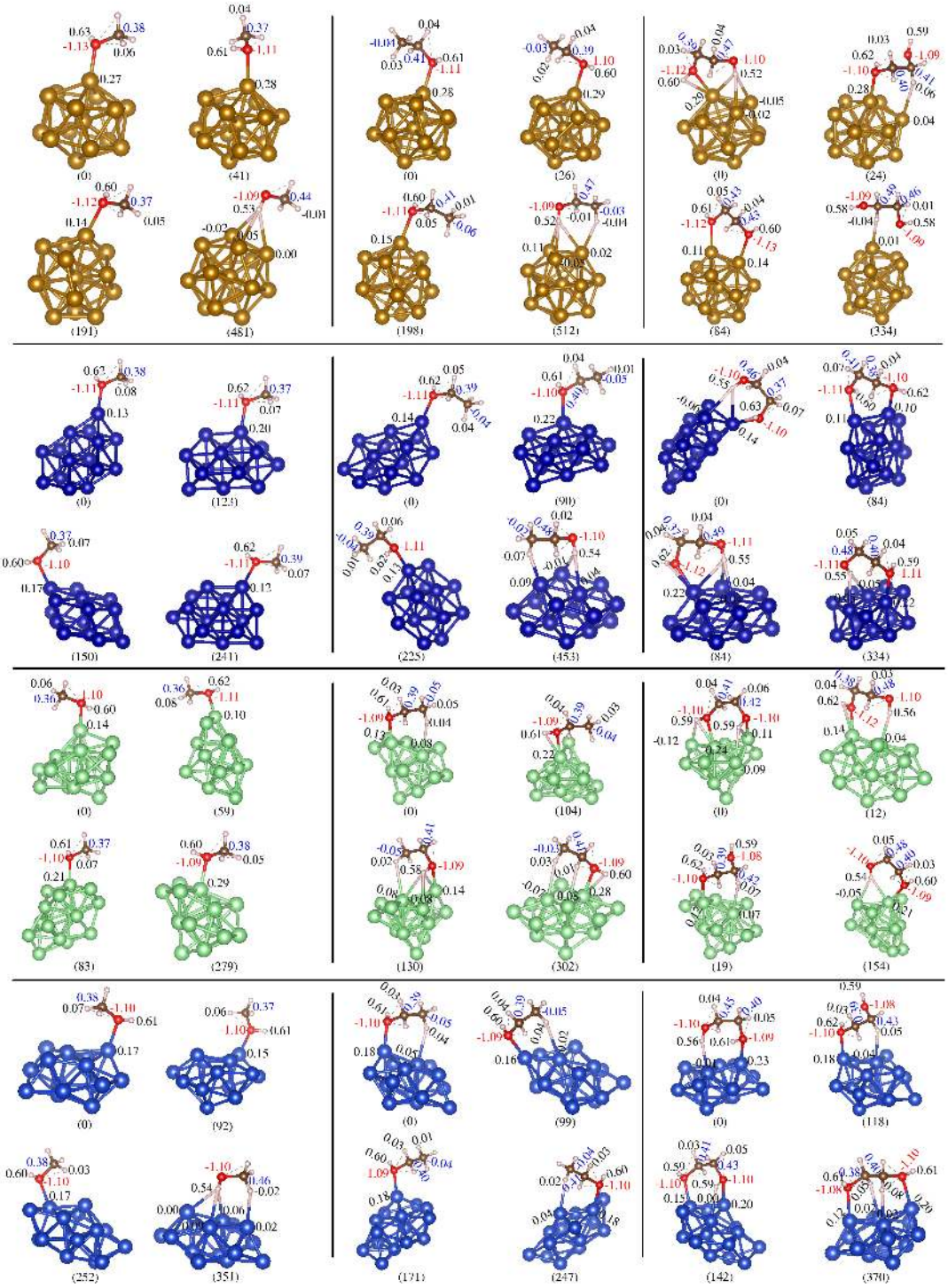

Figure S28: for alcohol/$TM_{15}{}^{3d}$ adsorbed systems.

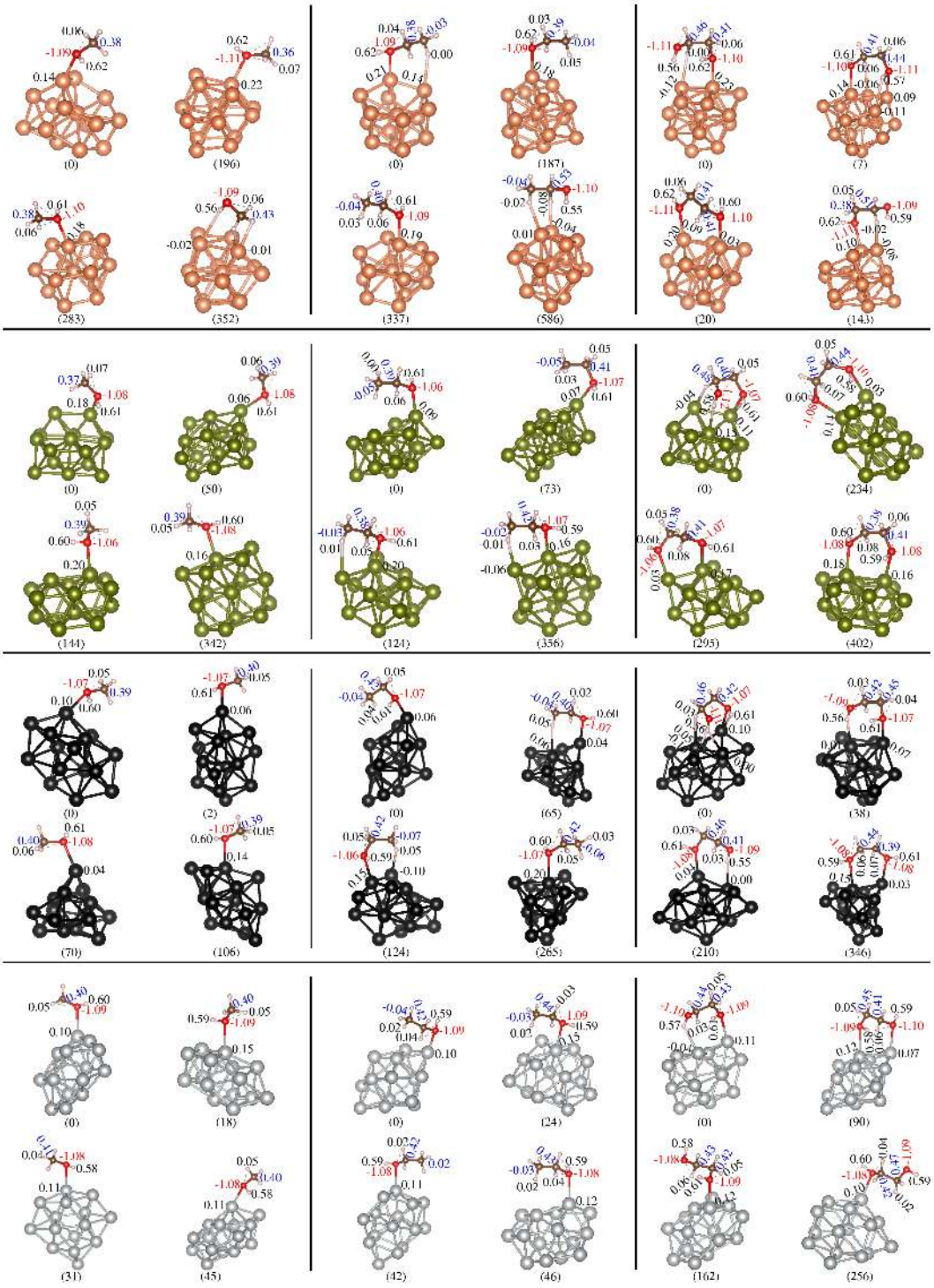

Figure S29: for alcohol/$TM_{15}{}^{4d}$ adsorbed systems.

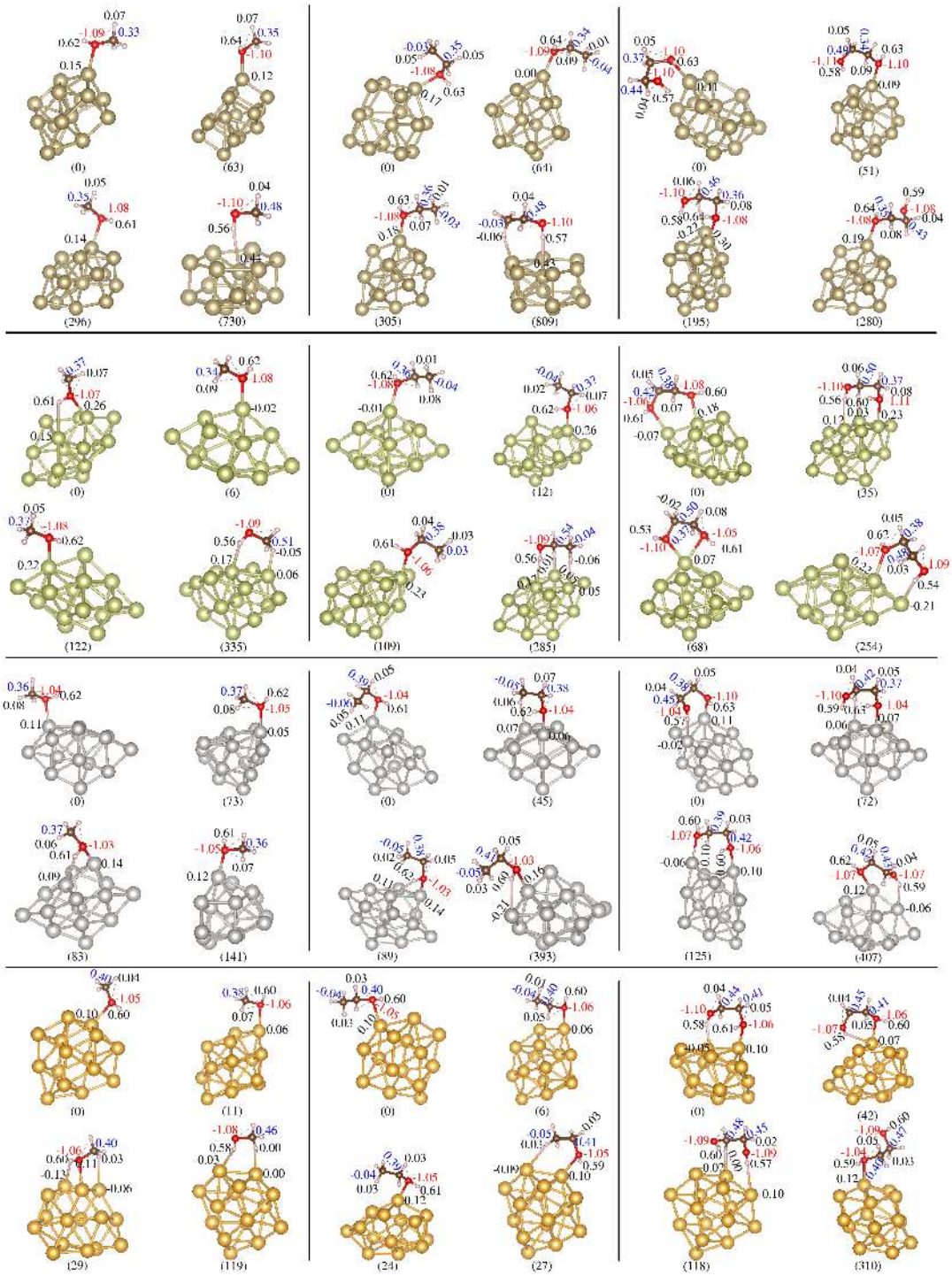

Figure S30: for alcohol/$TM_{15}{}^{5d}$ adsorbed systems.

9 Linear Regression

Table S6: Coefficients, w_i, and relative importancies $\left(RR_i = \frac{|w_i|}{\sum_i |w_i|}\right)$ for the linear regressions of adsorption energy ($E_{ad} = \sum_i w_i x_i + b$), where b is the constant in the decision function also known as bias), for each one of the alcohols. As x_i are unit-less (because of standard scaling), w_i and b are in eV. *RR* is unit-less by definition. R^2 is the standard coefficient of determination.

	Methanol		Ethanol		Ethylene Glycol	
	Absolute	*RR* (%)	Absolute	*RR*(%)	Absolute	*RR* (%)
Coef. for d_{O1-TM}	0.153 104	33.12	0.221 039	37.20	0.116 320	25.00
Coef. for d_{O2-TM}	-	-	-	-	−0.019 855	4.27
Coef. for d_{H1-TM}	0.018 889	4.09	−0.023 093	3.89	0.029 998	6.45
Coef. for d_{H2-TM}	-	-	-	-	0.020 738	4.46
Coef. for θ_{O1H1}	−0.051 143	11.06	−0.074 934	12.61	0.053 663	11.53
Coef. for θ_{O2H2}	-	-	-	-	0.007 550	1.62
Coef. for θ_{cm}	0.003 967	0.86	−0.005 880	0.99	0.004 282	0.92
Coef. for Total Charge	0.012 726	2.75	0.083 563	14.06	0.064 786	13.92
Coef. for TM group	0.024 036	5.20	0.013 159	2.21	0.093 733	20.14
Coef. for TM period	−0.104 532	22.61	−0.074 724	12.58	−0.032 098	6.90
Coef. for TM val. elec.	−0.038 846	8.40	−0.036 415	6.13	0.018 393	3.95
Coef. for TM electronegativity	0.055 089	11.92	0.061 330	10.32	−0.003 888	0.84
Constants in decision function	−0.563 772	-	−0.629 883	-	−0.740 960	-
R^2	0.6847	-	0.7131	-	0.7434	-

Table S7: Number of samples observed in each of the groups classified by *k-means* using bond lengths between metal and hydroxyl atoms, discriminated by metallic specie.

	Ethylene Glycol			Ethanol			Methanol		
TM_{15}	O_1-TM+H^O-TM	$O-TM+O-TM$	$O-TM$	$O-TM$	H^O-TM	$H^{-CH3}-TM$	$O-TM$	H^O-TM	$H^{-CH3}-TM$
Ag	6	2	4	12	0	0	12	0	0
Co	7	3	2	11	1	0	12	0	0
Cu	7	2	3	11	1	0	11	1	0
Ni	6	4	2	11	1	0	11	1	0
Os	10	1	1	10	2	0	11	1	0
Pt	4	7	1	12	0	0	12	0	0
Ag	6	2	4	12	0	0	12	0	0
Fe	4	4	4	11	1	0	11	1	0
Pt	4	7	1	12	0	0	12	0	0
Rh	6	6	0	12	0	0	12	0	0
Au	5	5	2	11	1	0	11	1	0
Ir	7	2	3	8	3	1	8	3	1
Total	72	45	27	133	10	1	135	8	1