

Supporting information

1) Atomic positions and supercell description

The clusters in this work were obtained according to the bulk crystallographic symmetry $Fm\bar{3}m$ (SG 225) for Pd_{13} and $P4_2/mmc$ (SG 131) for $Pd_{13}O_{12}$. As the structure of Fe_3O_4 (001) is concerned, our starting point is the ($\sqrt{2} \times \sqrt{2}$) $R45^\circ$ configuration, for which top layers were then relaxed to allowed the reconstruction based on the chemical environment. Below are the coordinates for $Pd_{13}/Fe_3O_4(001)$ supercell atoms, in angstrom units.

Fe	1.053535228	1.053535228	11.143658431
Fe	5.245143750	1.049028750	15.245143750
Fe	1.049028750	5.245143750	15.245143750
Fe	5.244518703	5.244518703	11.150836810
Fe	7.343201250	3.147086250	13.147086250
Fe	7.331089580	7.331089580	17.419930957
Fe	3.140939262	3.140939262	17.376468306
Fe	3.147086250	7.343201250	13.147086250
Fe	4.196115000	4.196115000	14.196115000
Fe	2.048702018	6.241968592	10.105437190
Fe	6.294172500	0.000000000	12.098057500
Fe	0.000000000	2.098057500	16.294172500
Fe	4.251282759	0.055697820	10.103315596
Fe	2.098057500	2.098057500	14.196115000
Fe	6.294172500	4.196115000	16.294172500
Fe	0.000000000	6.294172500	12.098057500
Fe	0.055697820	4.251282759	10.103315596
Fe	6.294172500	6.294172500	14.196115000
Fe	2.098057500	0.000000000	16.294172500
Fe	4.196115000	2.098057500	12.098057500
Fe	0.000000000	0.000000000	14.196115000
Fe	6.241968592	2.048702018	10.105437190
Fe	2.098057500	4.196115000	12.098057500
Fe	4.196115000	6.294172500	16.294172500
Fe	2.017920816	6.351570839	18.425496938
Fe	4.235388729	0.004316324	18.399348839
Fe	0.004316324	4.235388729	18.399348839
Fe	6.351570839	2.017920816	18.425496938
O	2.138675893	2.138675893	12.138675893
O	4.155496607	8.351611607	16.334790893
O	8.351611607	6.334790893	14.155496607
O	6.439008411	4.159291208	18.272043219
O	0.040618393	4.236733393	12.057439107
O	6.253554107	6.253554107	16.253554107
O	4.308222647	1.988981752	10.023434537
O	2.057439107	0.040618393	14.236733393
O	2.138675893	6.334790893	16.334790893

O	4.155496607	4.155496607	12.138675893
O	8.260235601	2.307399521	18.309402380
O	6.334790893	8.351611607	14.155496607
O	0.040618393	0.040618393	16.253554107
O	6.253554107	2.057439107	12.057439107
O	4.236733393	6.253554107	14.236733393
O	1.988981752	4.308222647	10.023434537
O	6.334790893	2.138675893	16.334790893
O	8.351611607	8.351611607	12.138675893
O	4.159291208	6.439008411	18.272043219
O	2.138675893	4.155496607	14.155496607
O	4.236733393	4.236733393	16.253554107
O	2.057439107	6.253554107	12.057439107
O	0.040618393	2.057439107	14.236733393
O	6.184463893	0.115348898	10.022122792
O	6.334790893	6.334790893	12.138675893
O	8.351611607	4.155496607	16.334790893
O	4.155496607	2.138675893	14.155496607
O	2.307399521	8.260235601	18.309402380
O	4.236733393	0.040618393	12.057439107
O	2.057439107	2.057439107	16.253554107
O	0.115348898	6.184463893	10.022122792
O	6.253554107	4.236733393	14.236733393
O	4.275469940	1.967900923	18.344346634
O	1.967900923	4.275469940	18.344346634
O	6.200501181	0.080302043	18.390402544
O	0.080302043	6.200501181	18.390402544
Pd	4.349902315	2.033952917	20.415561338
Pd	2.033952917	4.349902285	20.415561338
Pd	4.215695966	4.215695966	22.013800905
Pd	2.278682111	2.278682111	22.138339960
Pd	4.263084387	2.321073381	23.917924631
Pd	2.321073381	4.263084387	23.917924631
Pd	4.118528613	6.251922665	20.282856460
Pd	2.305964943	6.295393872	22.198544390
Pd	4.288268382	6.181118067	23.924628634
Pd	6.251922665	4.118528613	20.282856460
Pd	6.295393872	2.305964943	22.198544390
Pd	6.181118067	4.288268382	23.924628634
Pd	6.156019718	6.156019718	22.019388291

2) Discarding the Hubbard correction in the study

The mean charge transfer for $\text{Fe}_3\text{O}_4(001)$ from GGA calculations is $-0.057e$, compared to $-0.062e$ from GGA+U, both with the same distribution over different palladium atoms. It should be pointed out that calculations on clean magnetite surfaces were found accurate without the Hubbard correction. We

have checked that the charge transfer process is not significantly affected by the U as shown below in the Table below.

On top Pd atom # in Pd13 cluster	Charge transfer per atom for Pd13/Fe3O4(001) without the U	Charge transfer per atom for Pd13/Fe3O4(001) with the U
1	-0.2057	-0.1934
2	-0.2057	-0.1934
3	0.0483	0.0584
4	-0.0314	-0.0326
5	0.0266	0.0006
6	0.0266	0.0006
7	-0.1937	-0.1825
8	-0.03	-0.0359
9	0.0328	0.0077
10	-0.1937	-0.1825
11	-0.03	-0.0359
12	0.0328	0.0077
13	-0.0297	-0.028
Mean value	-0.057907692	-0.062246154

3) Charge transfer enhancement for Pd₁₃O₁₂/Fe₃O₄

Although the adsorption energy is positive for Pd₁₃O₁₂/Fe₃O₄, making the structure not favorable, the charge transfer process is enhanced as shown in the following table (in units of e).

System	Fe ₃ O ₄ (001)	All surface atom	Only surface Fe-ions	On-top cluster
Pd ₁₃ /Fe ₃ O ₄	+0.598	+0.557	-0.103	-0.752
Pd ₁₃ O ₁₂ /Fe ₃ O ₄	+2.018	+4.115	+0.259	-8.265

Even if the interaction is stronger with Pd₁₃O₁₂ and the charge accumulation in the lower layers of the cluster is higher as shown in the Table below.

Fe-ion index	Fe ₃ O ₄ (001) with Pd ₁₃	Fe ₃ O ₄ (001) with Pd ₁₃ O ₁₂
Fe1	-0.0273	0.0333
Fe2	-0.0273	0.0300
Fe3	-0.0242	0.0977
Fe4	-0.0242	0.0989