Single atoms on the regular surface

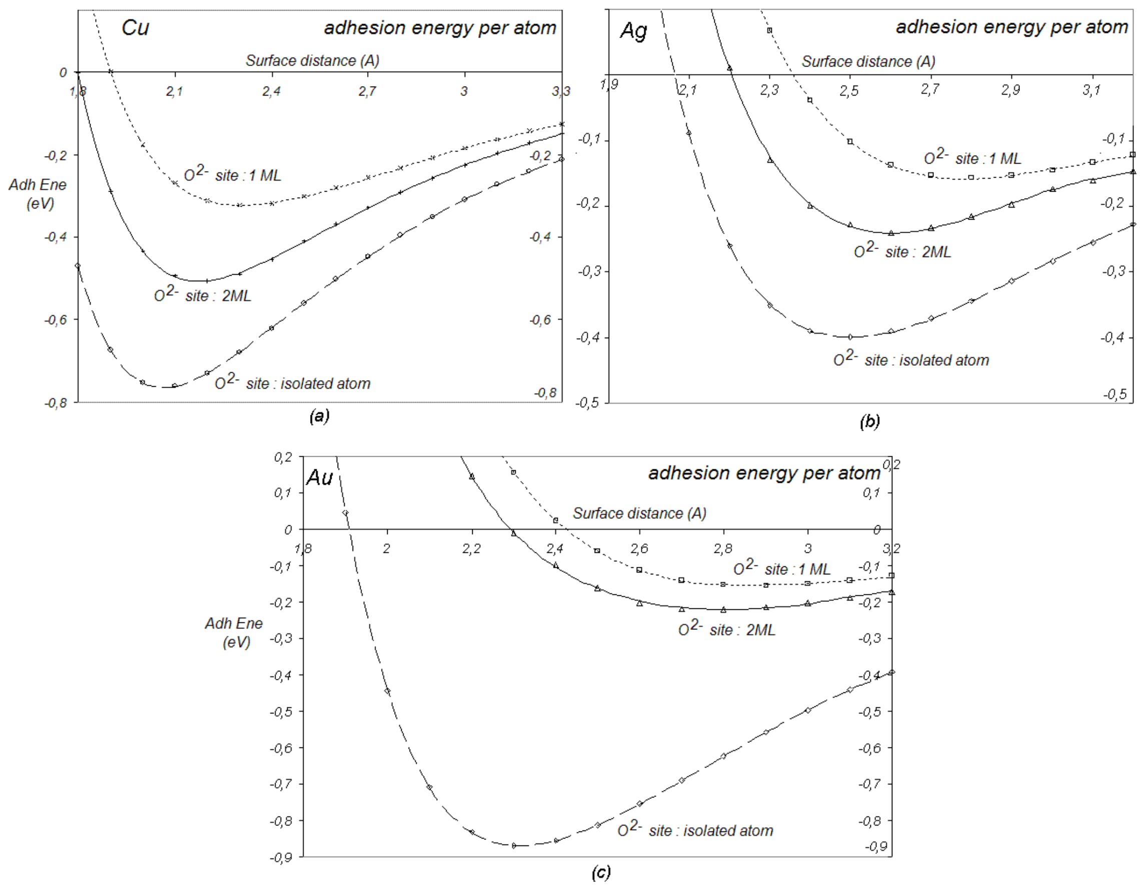
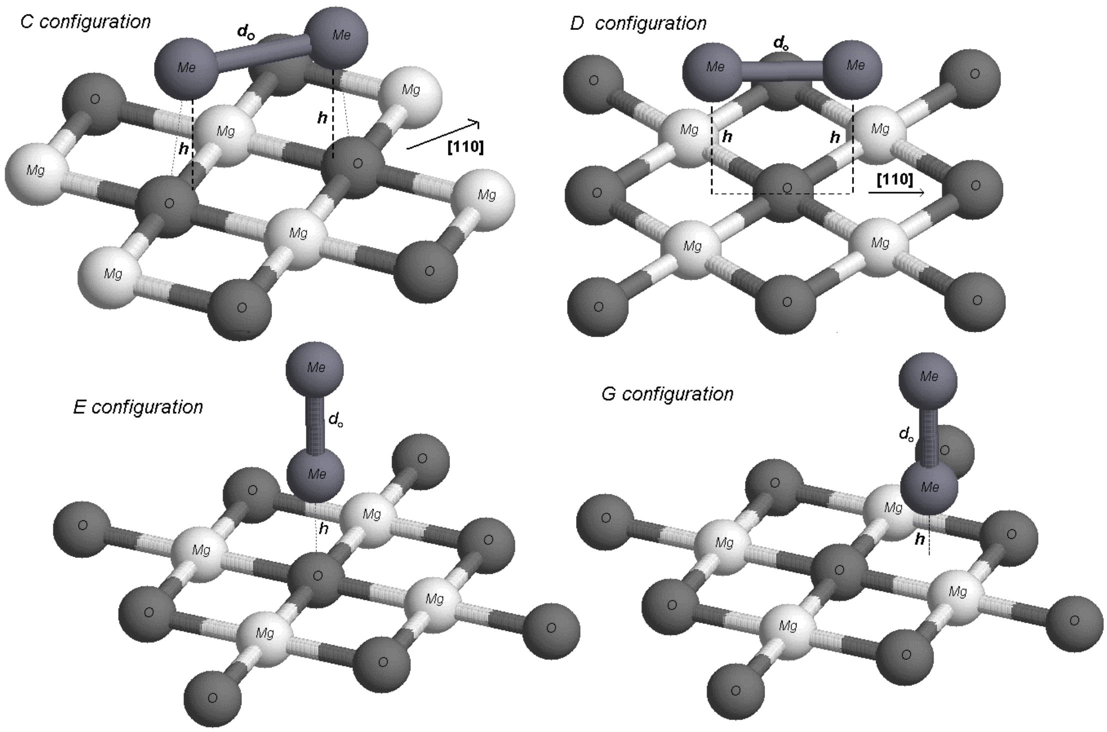


Figure 1: curves of the adhesion energy for the absorption of isolated atoms, 1 ML and 2 ML in the case of Cu (a), Ag (b) and Au (c)

Adatoms		*O site*	*Mg site*	*Hollow site*
Cu	E_{adh} (eV)	0.76	0.26	0.43
	d_o (Å)	2.1	2.8	2.3
Ag	E_{adh} (eV)	0.40	0.22	0.32
	d_o (Å)	2.5	2.9	2.6
Au	E_{adh} (eV)	0.87	0.49	0.67
	d_o (Å)	2.3	2.7	2.4

Table 1: Interactions and distances characterizing the isolated atoms absorption on the regular MgO (100)surface

Dimers on the regular surface



. Figure 2: dimers configurations on the regular (100) MgO surface

		C	*D*	*E*	*G*
Cu_2	*d_0 (Å)*	*2.31*	*2.27*	*2.26*	*2.26*
	h (Å)	*2.49*	*2.02*	*2.16*	*2.16*
Ag_2	*d_0 (Å)*	*2.61*	*2.58*	*2.59*	*2.59*
	h (Å)	*2.79*	*2.35*	*2.41*	*2.41*
Au_2	*d_0 (Å)*	*2.56*	*2.51*	*2.53*	*2.53*
	h (Å)	*2.63*	*2.18*	*2.31*	*2.31*

Table 2: geometrical parameters characterizing the geometrical configurations shown in Figure 2

	Cu_2	*Ag_2*	*Au_2*
Binding Energy (eV)	*2.09*	*1.72*	*2.33*
Equilibrium Bond length (Å)	*2.25*	*2.59*	*2.52*

Table 3a: characteristics of the coinage metal dimers in the gas-phase

		C	*D*	*E*	*G*
Cu_2	E_{int} (eV)	2.96	2.40	3.24	2.66
	E_{adh} (eV)	0.89	0.32	1.15	0.57
	ΔE_{met} (eV)	0.02	0.01	0.00	0.00
Ag_2	E_{int} (eV)	2.18	2.00	2.39	2.14
	E_{adh} (eV)	0.46	0.28	0.68	0.43
	ΔE_{met} (eV)	0.00	0.00	0.01	0.01
Au_2	E_{int} (eV)	2.92	2.88	3.75	3.14
	E_{adh} (eV)	0.61	0.56	1.42	0.81
	ΔE_{met} (eV)	0.02	0.01	0.00	0.00

Table 3b: energies of the coinage dimers absorbed on the regular surface

Trimers on the regular surface

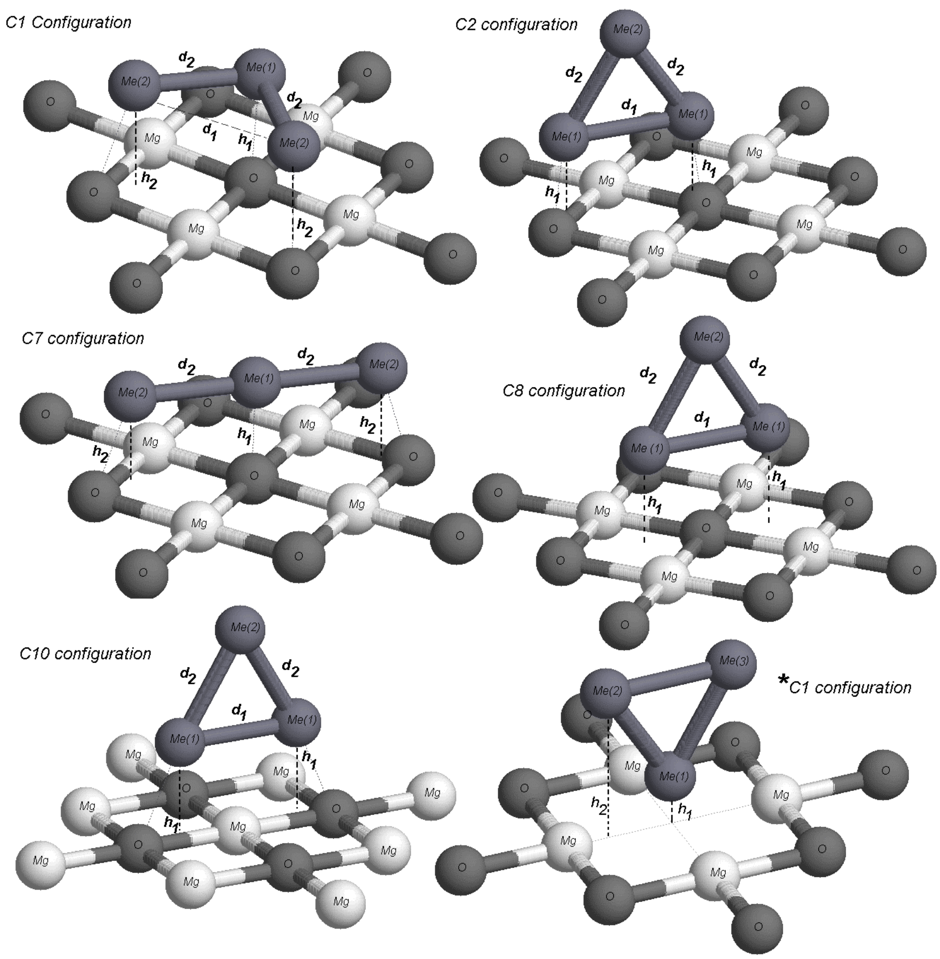


Figure 3: trimers configurations on the regular surface. The last configuration on the right correspond to the relaxation of the Au trimer on the F_s vacancy

	Cu_3	Ag_3	Au_3
Binding Energy (eV)	*3.40*	*2.59*	*3.60*
Bond length d_1 *(Å)*	*2.61*	*3.09*	*2.90*
Bond length d_2 *(Å)*	*2.32*	*2.66*	*2.61*

Table 4a: binding energies and geometrical parameters of the coinage metal trimers in the gas-phase

		C1	***C2***	***C7***	***C8***	***C10***
Cu_3	E_{int} *(eV)*	*4.50*	*5.00*	*4.47*	*4.02*	*4.85*
	E_{adh} *(eV)*	*1.29*	*1.60*	*1.38*	*0.65*	*1.62*
	ΔE_{met} *(eV)*	*0.19*	*0.00*	*0.31*	*0.04*	*0.17*
Ag_3	E_{int} *(eV)*	*3.27*	*3.51*	*3.33*	*3.20*	*3.45*
	E_{adh} *(eV)*	*0.72*	*0.92*	*0.80*	*0.67*	*0.90*
	ΔE_{met} *(eV)*	*0.04*	*0.00*	*0.06*	*0.06*	*0.04*
Au_3	E_{int} *(eV)*	-	*5.15*	-	*5.19*	*5.28*
	E_{adh} *(eV)*	-	*1.56*	-	*1.60*	*1.76*
	ΔE_{met} *(eV)*	-	*0.00*	-	*0.00*	*0.08*

Table 4b: energies corresponding to the absorption of coinage metal trimers on the regular surface

		C1	***C2***	***C7***	***C8***	***C10***
Cu_3	d_1 *(Å)*	*3.77*	*2.61*	*4.84*	*2.82*	*3.50*
	d_2 *(Å)*	*2.37*	*2.33*	*2.42*	*2.32*	*2.36*
	h_1 *(Å)*	*2.25*	*2.10*	*2.20*	*2.37*	*2.06.*
	h_2 *(Å)*	*2.17*	-	*2.12*	-	-
Ag_3	d_1 *(Å)*	*4.33*	*3.08*	*5.32*	*3.74*	*4.00*
	d_2 *(Å)*	*2.69*	*2.66*	*2.70*	*2.65*	*2.66*
	h_1 *(Å)*	*2.73*	*2.43*	*2.98*	*2.71*	*2.51*
	h_2 *(Å)*	*2.67*	-	*2.55*	-	-
Au_3	d_1 *(Å)*	*3.38*	*2.91*	*4.25*	-	-
	d_2 *(Å)*	*2.60*	*2.62*	*2.60*	-	-
	h_1 *(Å)*	*4.26*	*2.32*	*3.81*	-	-
	h_2 *(Å)*	*2.29*	-	*2.30*	-	-

Table 5: values of the geometric parameters reported in Figure 3

Extended depositions on the regular surface

		1 ML			2 ML		
		O site	*Mg site*	*Hollow site*	*O site*	*Mg site*	*Hollow site*
Cu	E_{int} (eV)	1.95	1.67	1.75	2.75	2.52	2.57
	E_{adh} (eV)	0.32	0.045	0.13	0.50	0.041	0.15
	h_1 (Å)	2.3	3.4	2.7	2.2	3.4	2.6
	h_2 (Å)	-	-	-	3.4	4.6	3.8
Ag	E_{int} (eV)	1.80	1.67	1.72	2.12	2.03	2.05
	E_{adh} (eV)	0.16	0.036	0.083	0.24	0.066	0.10
	h_1 (Å)	2.8	3.4	3.0	2.6	3.9	2.9
	h_2 (Å)	-	-	-	4.6	5.9	4.9
Au	E_{int} (eV)	2.26	2.20	2.24	2.66	2.59	2.62
	E_{adh} (eV)	0.15	0.095	0.13	0.22	0.084	0.15
	h_1 (Å)	2.9	3.1	2.9	2.8	3.3	2.9
	h_2 (Å)	-	-	-	4.8	5.3	4.9

Table 6: results for the absorption of 1 and 2 ML on the regular surface; h_1 and h_2 respectively correspond to the height of the first and of the second metal layer on the MgO surface

Single adatoms on the F_s defect

Adatoms	***Cu***	***Ag***	***Au***
$E_{adh} = E_{int}$ (eV)	1.76	1.59	3.04
h_o (Å)	1.80	2.00	1.81

Table 7: adatoms absorbed atop the F_s vacancy

Dimers on the Fs defect

We studied the absorption of the coinage metals dimer by choosing the same configurations used in the case of absorption on the regular surface, but neglecting the G geometry

		C	***D***	***E***		***C***	***D***	***E***
Cu_2	d_0 (Å)	2.33	2.33	2.34	E_{int} (eV)	4.13	2.74	4.16
	h_1 (Å)	1.55	2.24	1.68	E_{adh} (eV)	2.05	0.66	2.09
	h_2 (Å)	2.86	2.24	4.02	ΔE_{met} (eV)	0.01	0.01	0.02
Ag_2	d_0 (Å)	2.65	2.62	2.64	E_{int} (eV)	3.59	2.16	3.62
	h_1 (Å)	1.80	2.43	1.82	E_{adh} (eV)	1.89	0.44	1.92
	h_2 (Å)	3.91	2.43	4.46	ΔE_{met} (eV)	0.01	0.00	0.01
Au_2	d_0 (Å)	2.59	2.59	2.59	E_{int} (eV)	-	4.14	6.05
	h_1 (Å)	1.60	2.29	1.60	E_{adh} (eV)	-	1.84	3.75
	h_2 (Å)	4.19	2.29	4.19	ΔE_{met} (eV)	-	0.03	0.03

Table 8: dimer geometries and interaction energies of the coinage dimers on the F_s defect

Trimers on the F_s defect

The chosen configurations are similar to the C1, C2 and C7 considered in the case of absorption on the regular surface (see Fig 3): in the C1 configuration we put the F_s vacancy under the central metal atom; in the C2 configuration we put the vacancy under one of the atoms at the base of the cluster triangle and in the case of the L configurations we put the vacancy under the central metal atom of the linear trimer (L2) or under one of the two lateral atoms (L1).

	Cu_3				Ag_3				Au_3			
	C1	**C2**	**L1**	**L2**	**C1**	**C2**	**L1**	**L2**	**C1**	**C2**	**L1**	**L2**
d_{1-2} (Å)	2.38	2.58	2.47	2.35	2.67	2.97	2.73	2.67	2.73	2.80	2.67	2.63
d_{2-3} (Å)	2.45	2.36	2.37	4.46	4.79	2.73	2.71	5.09	2.69	2.69	2.62	4.71
d_{1-3} (Å)	2.38	2.40	4.80	2.35	2.67	2.70	5.30	2.67	2.73	2.69	4.68	2.63
h_1 (Å)	1.49	1.68	1.91	1.81	1.92	1.80	1.92	1.98	1.56	1.57	1.66	1.75
h_2 (Å)	2.56	2.17	2.48	2.54	2.82	2.67	3.04	2.80	3.94	2.85	3.37	2.92
h_3 (Å)	2.56	3.90	2.43	2.54	2.82	4.40	2.92	2.80	3.94	4.25	2.65	2.92

Table 9: geometric parameters for the coinage trimers absorbed on the F_s vacancy. The atom labeled 1 is the one absorbed atop the vacancy

		C1	**C2**	**L1**	**L2**
Cu_3	E_{int} (eV)	6.07	6.12	5.58	5.65
	E_{adh} (eV)	2.70	2.75	2.48	2.46
	ΔE_{met} (eV)	0.035	0.026	0.308	0.205
Ag_3	E_{int} (eV)	4.52	4.96	4.78	4.58
	E_{adh} (eV)	1.95	2.39	2.25	2.03
	ΔE_{met} (eV)	0.025	0.016	0.067	0.043
Au_3	E_{int} (eV)	7.78	7.80	7.70	7.31
	E_{adh} (eV)	4.22	4.24	4.09	3.67
	ΔE_{met} (eV)	0.040	0.036	0.009	0.04

Table 10: energies involved in the trimers absorption on the F_s vacancy

Extended depositions on the F_s defect

	1 ML			2 ML		
	Cu	**Ag**	**Au**	**Cu**	**Ag**	**Au**
$< E_{int} >$ (eV)	2.14	1.99	2.72	2.84	2.25	2.85
$< E_{adh} >$ (eV)	0.54	0.41	0.84	0.68	0.47	0.79
$< \Delta E_{met} >$ (eV)	0.03	0.06	0.20	0.005	0.01	0.09
h_1 (Å)*	1.79	2.00	1.71	1.83	2.31	1.80
h_2 (Å)**	2.41	2.84	2.90	2.17	2.74	2.69
h_3 (Å)***	2.54	2.96	2.99	2.18	2.77	2.73

Table 11: 1 and 2 ML absorbed on the Fs vacancy. * distance of the metal atom atop the vacancy; ** distance of the metal atom atop an O ions at 2.97 Å far from the vacancy; *** distance of the metal atom atop an O ions at 4.21 Å far from the vacancy

Single atoms on the double vacancy

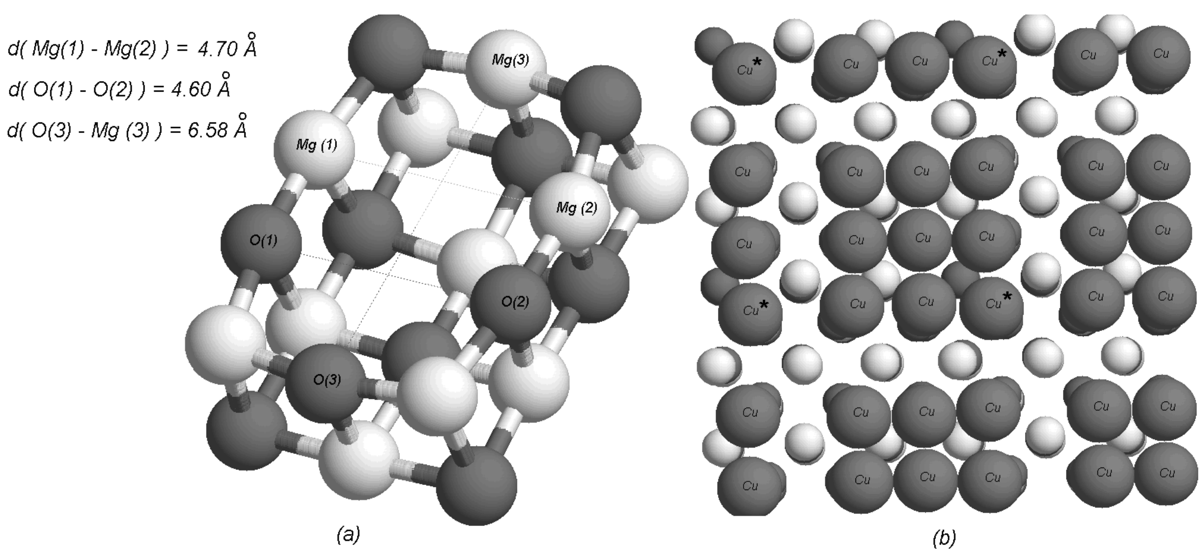


Figure 4: (a) the relaxed geometry of the oxide surface around the divacancy (b) the Cu_9 island formation; the Cu* atoms are the ones absorbed upon the vacancy

Adatoms	***Cu***	***Ag***	***Au***
E_{int} *(eV)*	*2.83*	*1.95*	*2.34*
E_{adh} *(eV)*	*3.94*	*2.47*	*2.90*
ΔE_{MgO} *(eV)*	*1.11*	*0.522*	*0.568*
ΔE_{relax} *(eV)*	*0.778*	*0.454*	*0.481*
h_o *(Å)*	*0.189*	*0.547*	*0.501*
Dist. from Mg site (Å)	*0.176*	*0.585*	*0.781*

Table 12: interaction energies and characteristic distances of the isolated adatoms on the double vacancy

Dimers on the double vacancy

Whatever the starting configuration, all the coinage metal dimers relaxed to a configuration with the two atoms of the molecule atop the two empty sites of the vacancy.

	Cu_2	Ag_2	Au_2		Cu_2	Ag_2	Au_2
d_o *(Å)*	*2.43*	*2.68*	*2.69*	E_{int} *(eV)*	*5.51*	*4.23*	*5.21*
h_1 *(Å)**	*0.191*	*0.525*	*0.467*	E_{adh} *(eV)*	*4.56*	*3.21*	*3.89*
h_2 *(Å)***	*1.59*	*2.10*	*2.04*	ΔE_{met} *(eV)*	*0.11*	*0.02*	*0.12*
$r_{1\text{-}Mg}$ *(Å)*	*0.089*	*0.276*	*0.370*	ΔE_{MgO} *(eV)*	*1.03*	*0.68*	*0.89*
$r_{2\text{-}O}$ *(Å)*	*0.028*	*0.336*	*0.442*	ΔE_{relax} *(eV)*	*0.86*	*0.60*	*0.73*

Table 13: coinage dimers on the double vacancy; * height of the atom atop the Mg^{2+} empty site; ** height of the atom atop the O^{2-} empty site

Trimers on the double vacancy

we chose the starting geometries of the coinage trimers with two metal atoms on top of the two sites of the vacancy and the third metal atom (A) atop the other two, not in direct contact with the surface; (B) atop the O^{2-}(2) ion at the border of the cavity and (C) atop the O^{2-}(3) ion at the border of the cavity (see Figure 4a for the nomenclature of the surface sites).

	Cu₃			***Ag₃***			***Au₃***	
	A	***B***	***C***	***A***	***B***	***C***	***A***	***B***
d_{1-2} (Å)	*2.49*	*2.44*	*2.39*	*2.68*	*2.70*	*2.66*	*2.63*	*2.64*
d_{2-3} (Å)	*2.47*	*2.61*	*2.70*	*2.76*	*2.82*	*2.88*	*2.65*	*2.61*
d_{1-3} (Å)	*2.38*	*2.39*	*4.04*	*2.80*	*2.79*	*4.50*	*2.81*	*2.91*
h_1 (Å)*	*0.217*	*0.255*	*0.309*	*0.789*	*0.808*	*0.766*	*1.13*	*1.15*
h_2 (Å)**	*1.56*	*1.67*	*1.68*	*2.17*	*2.17*	*2.12*	*1.82*	*1.84*
h_3 (Å)	*2.68*	*2.05*	*2.05*	*3.55*	*2.92*	*2.65*	*3.73*	*3.10*

Table 14: coinage trimers geometries on the double vacancy; * height of the atom atop the Mg^{2+} empty site; ** height of the atom atop the O^{2-} empty site

	Cu₃			***Ag₃***			***Au₃***	
	A	***B***	***C***	***A***	***B***	***C***	***A***	***B***
E_{int} (eV)	*6.90*	*7.09*	*6.57*	*5.19*	*5.20*	*4.81*	*6.74*	*6.82*
E_{adh} (eV)	*4.65*	*5.00*	*4.94*	*3.23*	*3.28*	*3.10*	*4.11*	*4.26*
ΔE_{met} (eV)	*0.06*	*0.07*	*0.46*	*0.03*	*0.02*	*0.14*	*0.01*	*0.005*
ΔE_{MgO} (eV)	*1.09*	*1.24*	*1.32*	*0.60*	*0.65*	*0.74*	*0.96*	*1.03*

Table 15: energies for the trimers on the double vacancy

Extended deposition on the double vacancy

	1 ML			*2 ML*		
	Cu	***Ag***	***Au***	***Cu***	***Ag***	***Au***
$< E_{int} >$ (eV)	*2.19*	*1.81*	*2.31*	*2.85*	*2.18*	*2.73*
$< E_{adh} >$ (eV)	*0.47*	*0.25*	*0.31*	*0.78*	*0.32*	*0.50*
$< \Delta E_{met} >$ (eV)	*-0.17*	*0.05*	*0.02*	*-0.02*	*-0.03*	*0.02*
ΔE_{MgO} (eV)	*0.70*	*0.29*	*0.67*	*1.37*	*0.67*	*1.00*

Table 16: 1 and 2 ML absorbed on the double vacancy. * distance of the metal atom atop the vacancy; ** distance of the metal atom atop an O ions at 2.97 Å far from the vacancy; *** distance of the metal atom atop an O ions at 4.21 Å far from the vacancy