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

Supporting Information

DFT study of carbon monoxide adsorption onto hydroxylated α-Al_2O_3 (0001) surfaces.

Table SM1:

Structural and vibrational properties of free and adsorbed CO.

	Free CO	2 x 2	2 x 2	2 x 2	1 x 1
Adsorption site	--	Al_{1S}	Al_{1S} and Al_{4S}	Al_{1S} and Al_{3S}	--
coverage [%]	--	25	50	75	100
$r_{C\text{-}O}$ [Å]	1.154	1.149	1.150	1.151	1.152
$r_{Al\text{-}C}$ [Å]	--	2.148	2.160	2.170	2.183
$\nu_{C\text{-}O}$ [cm^{-1}]	2170	2226	2215	2203[15]	2200
$\Delta_{C\text{-}O}$ [cm^{-1}]		56	45	32	30
Adsorption energy [eV]	--	0.52	0.48	0.45	0.42

[15] An average value of the Al_{1S} and Al_{3S} is presented.

Table SM2:

Comparison of inter layer distances in Å of different water coverage is presented for adsorption sites in 1-4 configuration.

Inter layer spacing [Å]	Coverage [%]	Al_{1S}	Al_{2S}	Al_{3S}	Al_{4S}
Al_1/O_2	25	--	--	--	-0.211
Al_1/O_2	50	--	-0.102	--	-0.101
Al_1/O_2[16]	50	**0.683**	--	**0.683**	--
Al_1/O_2[17]	75	-0.147	**0.719**	**--**	**0.702**
Al_1/O_2[18]	75	-0.496	**--**	**--**	**--**
Al_1/O_2[19]	100	**0.537**	**0.537**	**0.537**	**0.537**
O_S/O_2[20, 16]	50	0.132	--	0.132	--
O_S/O_2[20,17]	75	0	0.126	--	0.134
O_S/O_2[20, 19]	100	0.184	0.184	0.184	0.184

16 Results of the (1 x 2) surface are represented, where water adsorbs in a linear fashion inflicting a 1-4 configuration on the occupied Al adsorption sites.

17 The 75 % coverage with water adsorption in 1-4 configuration with respect to two Al adsorption sites is presented.

18 The 75 % coverage with no water adsorption in 1-4 configuration is presented.

19 Results of the (1 x 1) surface are represented.

20 The relaxation of the protonated O being a nearest neighbour of the indicated Al adsorption site is given.

The subscript number indicates that layer number starting from the surface. The bold numbers represent lateral movement induced by OH at an adsorption site. Interlayer distances were computed by averaging over all atoms within one layer. The only exception to this is the O_S of O_S-H.

Table SM3:

Comparison of inter layer distances in Å of different water coverage is presented for adsorption sites not in 1-4 configuration.

Inter layer spacing [Å]	Coverage [%]	Al_{1S}	Al_{2S}	Al_{3S}	Al_{4S}
Al_1/O_2	25	0.112	**0.742**	0.125	--
Al_1/O_2	50	**0.755**	--	**0.755**	--
Al_1/O_2[21]	50	--	0.079	--	0.079
Al_1/O_2[22]	75	--	--	**0.747**	--
Al_1/O_2[23]	75	--	**0.778**	**0.782**	**0.782**
O_S/O_2[24]	25	0	0.100	0	0
O_S/O_2[24]	50	0.094	--	0.095	--
O_S/O_2[24, 22]	75	--	--	0.112	--
O_S/O_2[24, 23]	75	--	0.150	0.153	0.151

21 Results of a (1 x 2) cell are represented, where water adsorbs in a linear fashion inflicting a 1-4 configuration on the occupied Al adsorption sites.

22 The 75 % coverage with water adsorption in 1-4 configuration with respect to two Al adsorption sites is presented.

23 The 75 % coverage with no water adsorption in 1-4 configuration is presented.

24 The relaxation of the protonated O being a nearest neighbour of the indicated Al adsorption site is given.

The subscript number indicates that layer number starting from the surface. The bold numbers represent lateral movement induced by OH at an adsorption site. Interlayer distances were computed by averaging over all atoms within one layer. In case of the O_S-H adsorption site the averaging was done with respect to the non-protonated O_S counterparts.

Table SM4:

The influence of the 1-4 configuration with respect to structural and vibrational properties of CO and the adsorbed water molecules at total surface coverage of 50 % and 75 % are presented.

	(2 x 2)	**(2 x 2)**	**(2 x 2)**	**(2 x 2)**
H_2O coverage [%]	25	25	50	50
CO coverage [%]	25	25	25	25
Species in 1-4 configuration	free adsorption site	CO	OH	CO
	A	B	C	D
$r_{C\text{-}O}$ [Å]	1.148	1.148	1.148	1.147
$r_{Al\text{-}C}$ [Å]	2.161	2.175	2.164	2.170
$r_{Al\text{-}OH}$ [Å]	1.731	1.735	1.730[25]	1.730
$r_{O\text{-}H}$ [Å]	0.971	0.972	0.971[25]	0.971
$r_{Os\text{-}H}$ [Å]	0.985	0.982	0.984[25]	0.984
$\nu_{C\text{-}O}$ [cm^{-1}]	2225	2232	2233	2240
$\Delta_{C\text{-}O}$ [cm^{-1}]	55	62	63	70
$\nu_{O\text{-}H}$ [cm^{-1}]	3936	3925	3935	3914
$\nu_{Os\text{-}H}$ [cm^{-1}]	3696	3740	3698	3733
CO adsorbtion energy [eV]	0.57	0.44	0.51	0.52

[25] Average values are presented.

Table SM5:

The influence of the 1-4 configuration with respect to structural and vibrational properties of CO and the adsorbed water molecules at total surface coverage of 100 %.

	(1 x 2)	**(1 x 2)**	**(2 x 2)**
H_2O coverage [%]	50	50	75
CO coverage [%]	50	50	25
Species in 1-4 configuration	OH	CO	CO/ OH
	E	F	G
$r_{C\text{-}O}$ [Å]	1.149	1.150	1.147
$r_{Al\text{-}C}$ [Å]	2.167	2.195	2.177
$r_{Al\text{-}OH}$ [Å]	1.738	1.737	1.728[26,27] 1.732[28]
$r_{O\text{-}H}$ [Å]	0.971	0.972	0.972[26,27] 0.973[28]
$r_{Os\text{-}H}$ [Å]	0.984	0.982	0.984[26,27] 0.982[28]
$\nu_{C\text{-}O}$ [cm^{-1}]	2227	2225	2242
$\Delta_{C\text{-}O}$ [cm^{-1}]	57	52	72
$\nu_{O\text{-}H}$ [cm^{-1}]	3922	3915	3921[26,27] 3914[28]
$\nu_{Os\text{-}H}$ [cm^{-1}]	3683	3720	3701[26,27] 3747[28]
CO adsorbtion energy [eV]	0.51	0.44	0.48

[26] Average values are presented.
[27] Al-OH adsorption site in 1-4 position is presented.
[28] Al-OH adsorption site inflicting 1-4 position upon CO adsorption is presented.

Table SM6:

Comparison of inter layer distance in Å with respect to the CO adsorption site in 1-4 configuration (Al CO 1-4) and the CO site which is not in 1-4 configuration (Al CO) are given. In addition the OH adsorption site (Al OH Inflicting 1-4) inflicting a 1-4 arrangement onto adsorption sites of OH (Al OH 1-4), CO or the free Al adsorption site (Al Free 1-4) as well as the free adsorption site not in 1-4 configuration are shown.

Inter layer spacing [Å]	Coverage H_2O/CO[%]	Al CO 1-4	Al CO	Al OH 1-4	Al OH Inflicting 1-4	Al Free 1-4	Al Free
Al_1/O_2	A 25/25	--	0.364	--	0.748	-0.342	0.093
Al_1/O_2	B 25/25	0.301	--	--	0.728	--	0.046[32]
Al_1/O_2	C 50/25		0.344	0.694	0.693	--	0.030
Al_1/O_2	D 50/25	0.312	--	0.732 [30,31]	0.732[30]	-0.337	--
Al_1/O_2	E 50/50[29]	--	0.279	0.651	0.651	--	--
Al_1/O_2	F 50/50[29]	0.233	--	--	0.655	--	--
Al_1/O_2	G 75/25	0.295	--	0.681[32]	0.712	--	--

[29] Results of a 1x2 super cell are represented.

[30] This Al adsorption site is inflicting 1-4 configuration upon CO.

[31] This Al adsorption site is inflicting 1-4 configuration upon the free Al adsorption site.

[32] An average value of the two equivalent adsorption site is presented.

The subscript number indicates the layer number starting from the surface. Interlayer distances were computed by averaging over all atoms within one layer.

Table SM7:

Comparison of inter layer distance in Å of the O_S adsorption site in 1-2 position with respect to the OH adsorption site inflicting a 1-4 arrangement (Al O_S-H inflicting 1-4) to CO another OH or the free Al adsorption are shown. In addition the O_S site in 1-2 arrangement to its OH adsorption site which is in 1-4 configuration (Al O_S-H 1-4), caused by a linear adsorption of water is presented. Interlayer distances were computed by averaging over all atoms within one layer. In case of the O_S-H adsorption site the averaging was done with respect to the none protonated O_S counterparts.

Inter layer spacing [Å]	Coverage H_2O/CO[%]	Al O_S-H inflicting 1-4	Al O_S-H 1-4
O_S/O_2	A 25/25	--	0.089
O_S/O_2	B 25/25	0.094	--
O_S/O_2	C 50/25	0.104	0.116[34]
O_S/O_2	D 50/25	0.091	0.107
O_S/O_2	E 50/50[33]	--	0.120
O_S/O_2	F 50/50[33]	0.101	--
O_S/O_2	G 75/25	0.118[35]	0.089

33 Results of a (1 **x** 2) surface are represented.

34 Nearest neighbour to the free adsorption site.

35 An average value of the two equivalent adsorption site is presented.

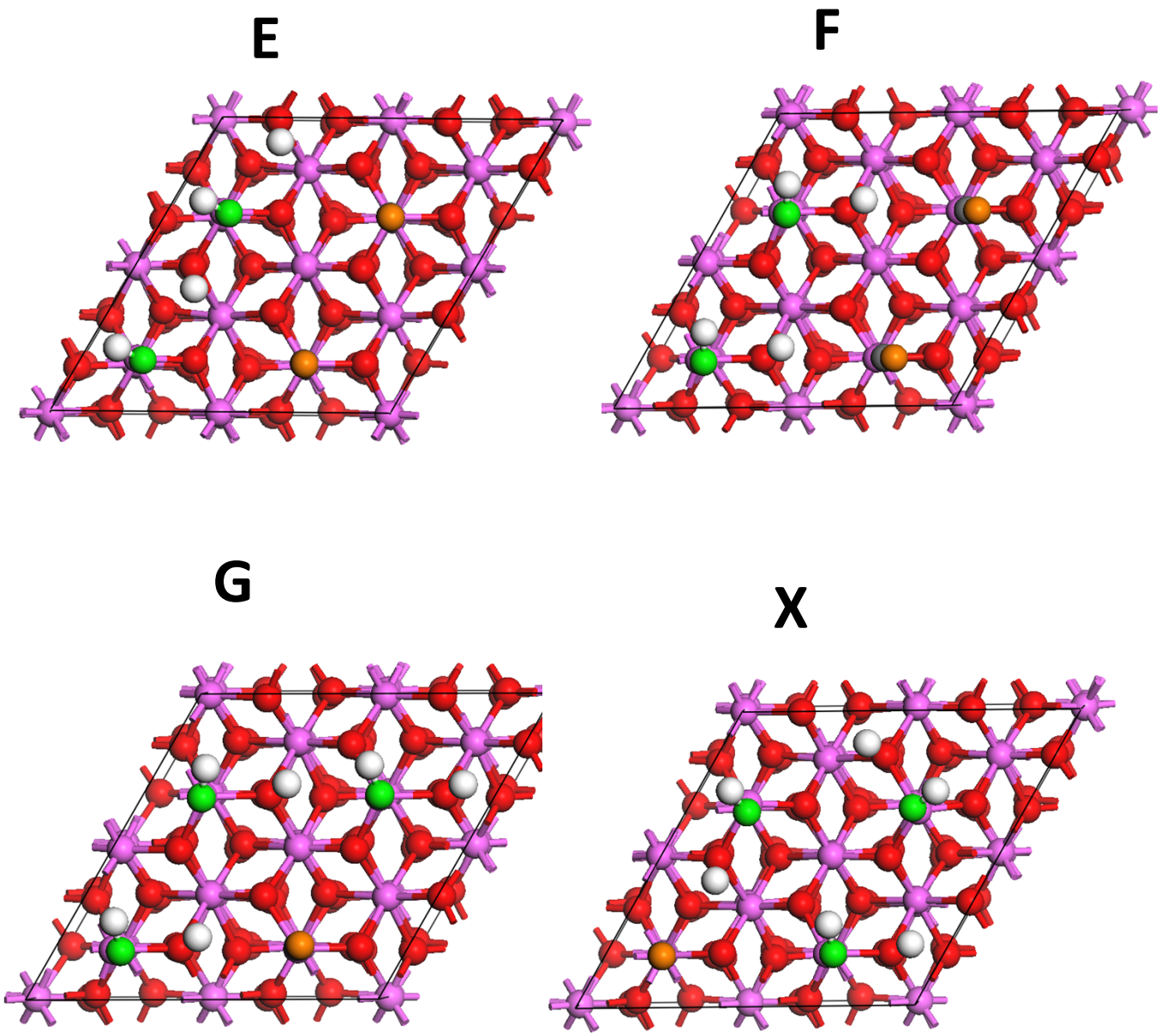

Figure SM 1:

(E) 50 % hydroxylation 50 % CO coverage, 1-4 inflicted on the OH adsorption site.
(F) 50 % hydroxylation 50 % CO coverage, 1-4 inflicted on the CO adsorption site.
(G) 75 % hydroxylation 25 % CO coverage, 1-4 inflicted on the CO and the OH adsorption sites.
(X) 75 % hydroxylation 25 % CO coverage, 1-4 inflicted three times on the CO adsorption site.

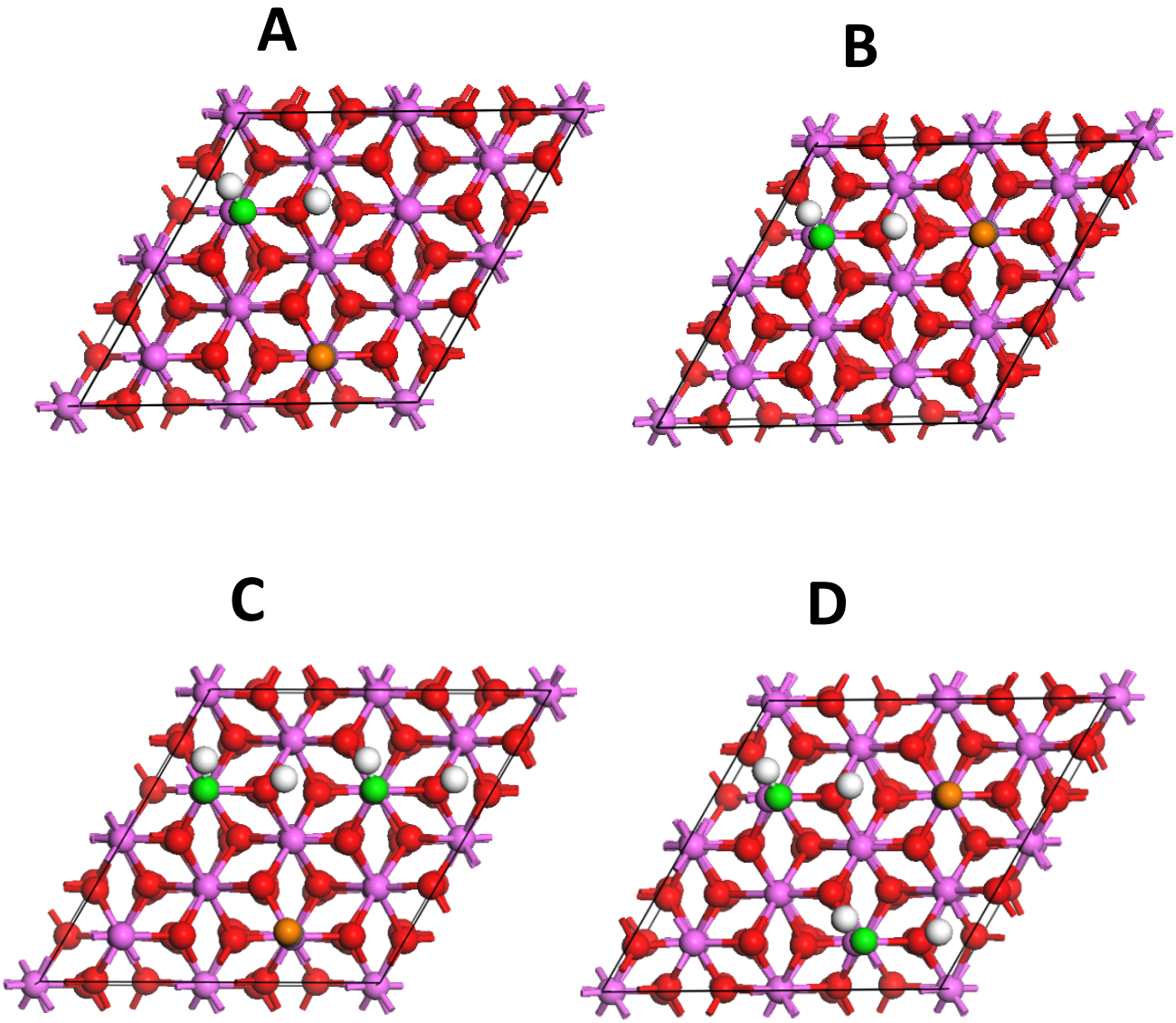

Figure SM 2:
(A) 25 % hydroxylation, 1-4 inflicted on the free Al adsorption site.
(B) 25 % hydroxylation, 1-4 inflicted on the CO adsorption site.
(C) 50 % hydroxylation, 1-4 inflicted on two OH adsorption sites.
(D) 50 % hydroxylation, 1-4 inflicted on the CO and the free adsorption site. All results are on the 25% CO coverage.