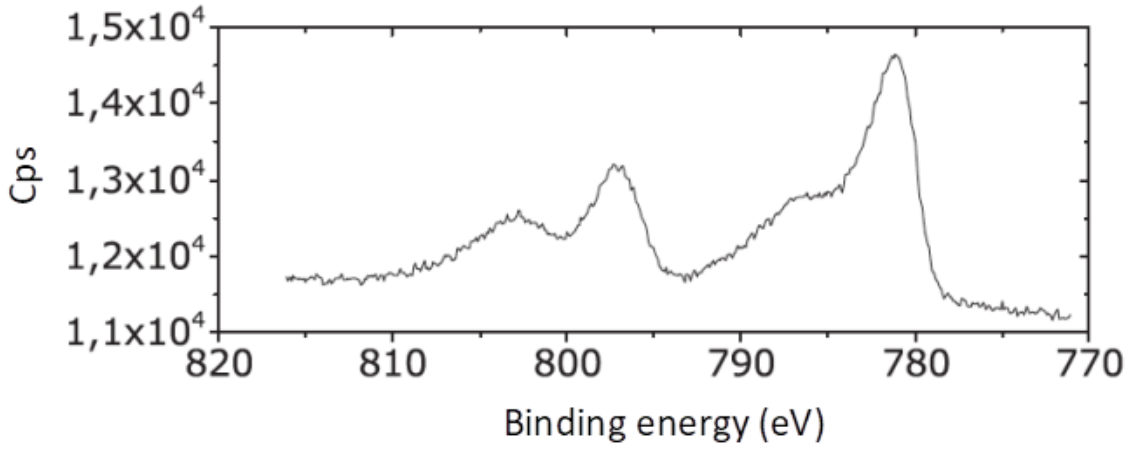

Figure S1. Example of an XPS spectrum in the Co2p region for Co(II)/α-Al_2O_3 on the R ($1\bar{1}02$) plane after 7 days of adsorption. The Co loading is 2.7 at.nm^{-2}.

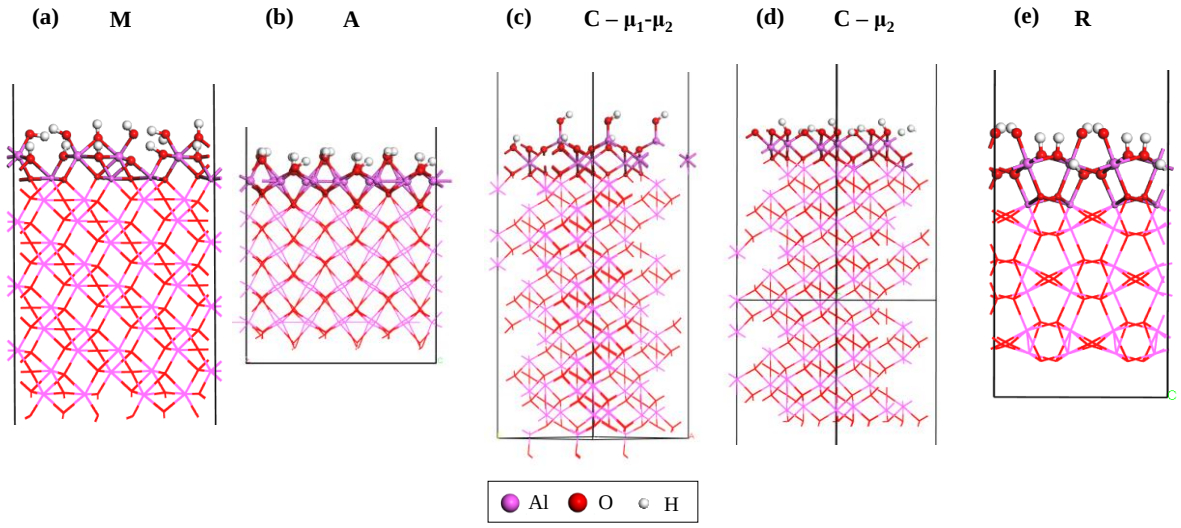

Figure S2. Side views of slabs used as surface models in the present work.

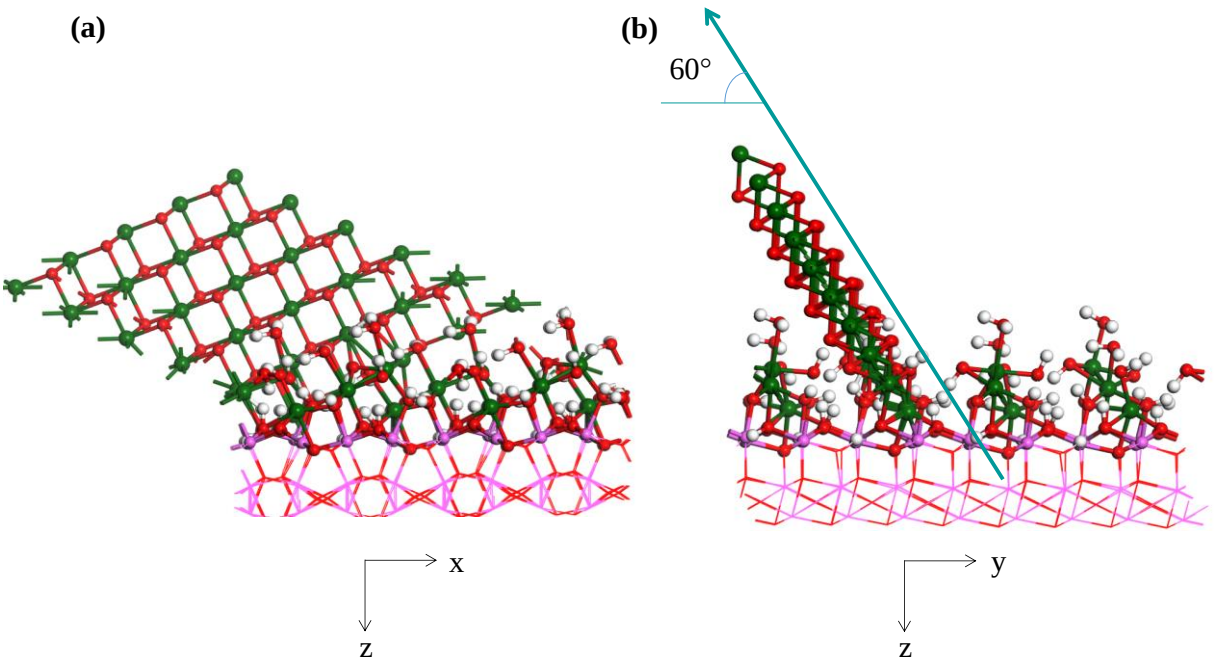

Figure S3. Side views of the R orientation with the surface deposit at θ_{Co} = 5.97 nm^{-2}, plus a layer of cobalt hydroxide grown in the direction given by the surface deposit symmetry. The hydrogen atoms of the hydroxide layer are not depicted. The cobalt hydroxide – alumina composite system is not optimized. Co: green, O: red, H: white, Al: purple.

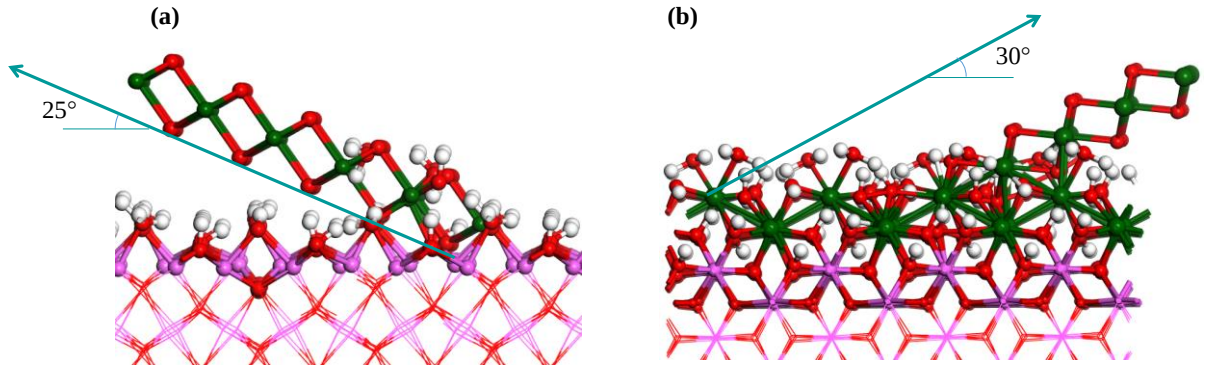

Figure S4. Side views of the (a) A orientation, (b) M orientation with the surface deposit at maximal investigated coverage, plus a layer of cobalt hydroxide grown in the direction given by the surface deposit symmetry. The hydrogen atoms of the hydroxide layer are not depicted. The cobalt hydroxide – alumina composite system is not optimized. Co: green, O: red, H: white, Al: purple.

Table S1. EXAFS Fitting results for Co(II)/α-Al2O3 on the R ($1\bar{1}02$) plane with different adsorption time and sample polarization with respect to the X-ray beam.

Sample	**Contribution**	**N**	**R (Å)**	**σ^2 (x10^{-3} Å^2)**	**ΔE° (eV)**	**R factor (%)**
Co(II)/R($1\bar{1}02$) 6 days paral.	Co-O	5.7	2.08	13.3	-0.6	1.1
	Co-Co	5.8	3.17	14.4	2.4	
Co(II)/R($1\bar{1}02$) 6 days perp.	Co-O	4.4	2.06	13.3	-0.7	1.4
	Co-Co	1.1	3.12	15.9	-1.0	
Co(II)/R($1\bar{1}02$) 1 h paral.	Co-O	5.8	2.05	14.5	-3.8	1.6
	Co-Co	3.6	3.18	14.6	3.1	
Co(II)/R($1\bar{1}02$) 1 h perp.	Co-O	4.1	2.08	14.0	1.5	3
	Co-Co	0.8	3.18	8.0	-6.5	
Co(II)/R($1\bar{1}02$) 1 h wash paral.	Co-O	6.0	2.04	15.5	-4.4	1.9
	Co-Co	3.8	3.19	14.1	4.0	
Co(II)/R($1\bar{1}02$) 1 h wash perp.	Co-O	3.8	2.09	14.0	-0.8	2.3
	Co-Co	1.3	3.17	13.4	-9.6	

Table S2. Structure analysis performed on the basis of the optimized geometries by DFT for the surface deposits, for the highest stable coverage simulated. CN: coordination number. Distances are averaged on all the measured distances, with a cutoff distance of 3 Å for Co-O and Co-Al. For Co-Co, a cutoff distance of 4 Å was used, and three bond length domains distinguished for the averaging: d < 3 Å or 3 Å < d < 3.5 Å or 3.5 Å < d < 4 Å. Notably, the CN remains lower that 6 for Co-Co, due to the fact that the formation of a full cobalt hydroxide layer supported on alumina was not modeled.

Surface	**Coverage (nm^{-2})**	**Co-O**		**Co-Al**		**Co-Co**	
		d (Å)	**CN**	**d (Å)**	**CN**	**d (Å)**	**CN**
R	5.97	2.10	5.3	2.85	1.3	2.52 - -	1.3 - -
A	5.60	2.07	5	2.89	0.7	2.53 3.16 -	1.3 1.3 -
M	16.18	2.07	4.7	2.91	0.6	2.57 3.26 3.67	3.5 1.3 1.7
C – μ_1-μ_2	14.19	2.20	5.9	2.83	2.4	2.45 3.22 3.65	0.6 1.7 0.9

Table S3. EXAFS Fitting results for Co(II)/α-Al_2O_3 on the R ($1\bar{1}02$), A($11\bar{2}0$) and M($10\bar{1}0$) planes for long adsorption times (6 days) and different sample polarization with respect to the X-ray beam.

Sample	**Contribution**	**N**	**R (Å)**	**σ^2 (x10^{-3} Å^2)**	**ΔE° (eV)**	**R factor (%)**
Co(II)/R($1\bar{1}02$) 6 days paral.	Co-O	5.7	2.08	13.3	-0.6	1.1
	Co-Co	5.8	3.17	14.4	2.4	
Co(II)/R($1\bar{1}02$) 6 days perp.	Co-O	4.4	2.06	13.3	-0.7	1.4
	Co-Co	1.1	3.12	15.9	-1.0	
Co(II)/A($11\bar{2}0$) 6 days paral.	Co-O	5.8	2.08	13.6	-2.0	0.8
	Co-Co	5.5	3.14	14.8	0.9	
Co(II)/A($11\bar{2}0$) 6 days perp.	Co-O	4.6	2.08	15.8	2.0	4.5
	Co-Co	1.3	3.17	14.0	2.0	
Co(II)/M($10\bar{1}0$) 6 days paral.	Co-O	5.8	2.08	13.1	-1.4	1.4
	Co-Co	5.8	3.14	13.6	-1.8	
Co(II)/M($10\bar{1}0$) 6 days perp.	Co-O	5.5	2.04	17.1	-1.2	0.8
	Co-Co	1.1	3.09	17.3	-1.3	

Table S4. EXAFS Fitting results for Co(II)/α-Al_2O_3 on the C(0001) plane for different adsorption times (1 hour, 1 day, 6 days) for a parallel polarization with respect to the X-ray beam.

Sample	**Contribution**	**N**	**R (Å)**	**σ^2 (x10^{-3} Å^2)**	**ΔE° (eV)**	**R factor (%)**
Co(II)/C(0001) 6 days paral.	Co-O	6.6	2.03	18.3	-4.5	0.6
	Co-Co	2.4	2.90	18.3	-4.5	
Co(II)/C(0001) 1 day paral.	Co-O	7.2	2.11	13.2	-0.6	2.3
	Co-Co	4.0	3.89	13.2	-0.6	
Co(II)/C(0001) 1 h paral.	Co-O	6.4	2.09	12.9	-2.2	2.4
	Co-Co	6.2	3.17	15.0	-3.0	
Co(II)/C(0001) 1 h wash paral.	Co-O	5.8	2.11	12.8	-0.8	1.6
	Co-Co	4.1	3.21	5.9	-0.7	