

**Theoretical Insights into the Interaction of Oxygenated Organic Molecules
and Cobalt(II) Precursor with γ -Al₂O₃ Surfaces**

Supplementary Information

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S1: Complementary information on the adsorption modes

(b)

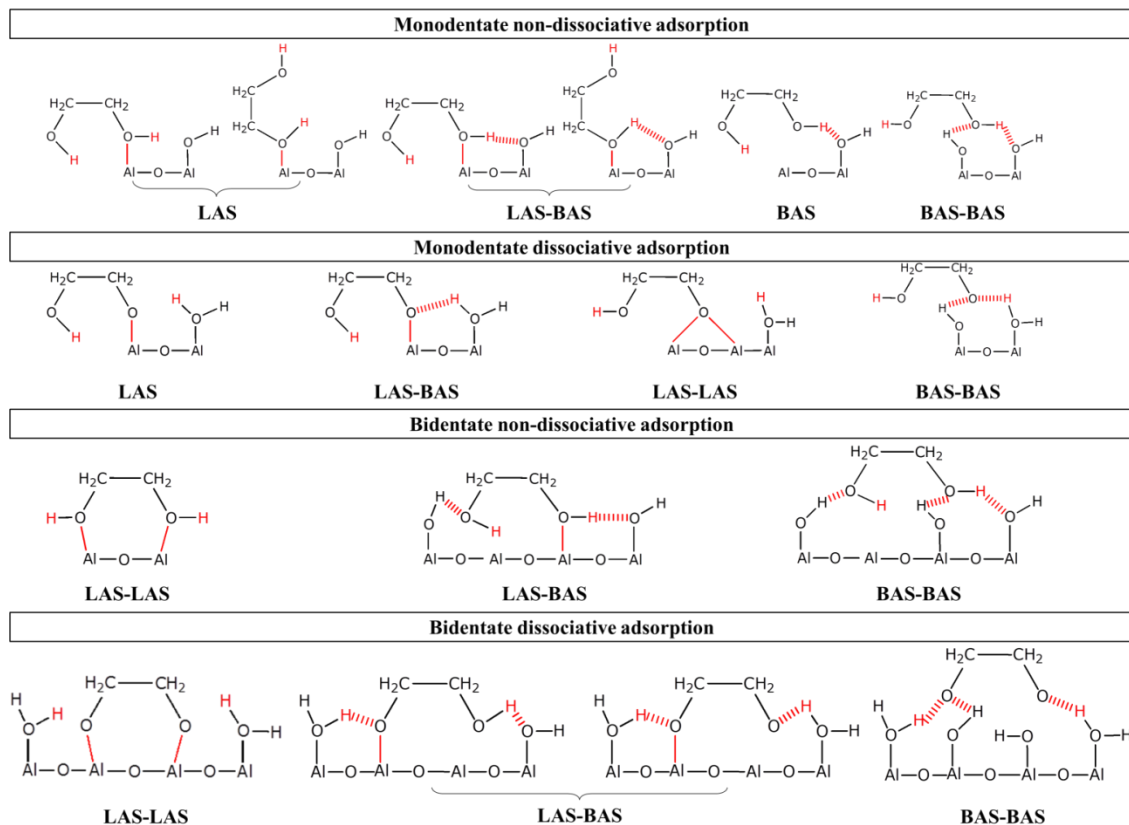


Figure S1.1. Schematic representation and denomination of the different initial adsorption modes of EG as a function of the adsorption mode (dissociative/non dissociative) and adsorption sites (LAS/BAS/LAS-LAS/BAS-BAS/LAS-BAS). Line code: Dashed red represent hydrogen bonds, plain red represent Al-O ionic-covalent bonding.

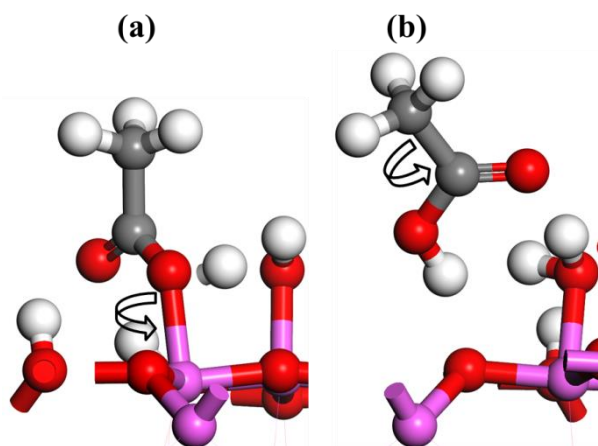


Figure S1.2. LAS (a) and BAS (b) adsorbed configurations for acetic acid on the (100) surface of γ -alumina. The arrows indicate the rotational movements of the molecule applied to create additional structures. Color code : pink (aluminum), red (oxygen), white (hydrogen), and grey (carbon).

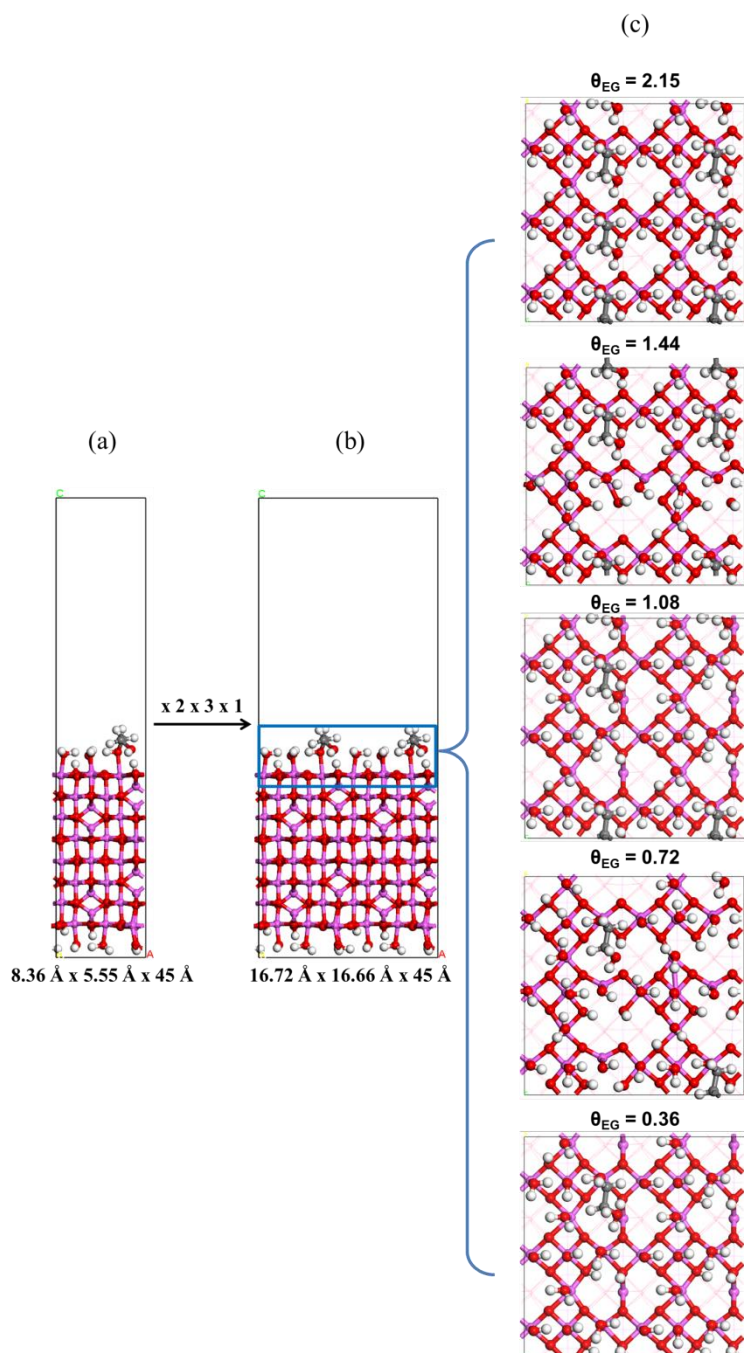


Figure S1.3. (a) Side view of the initial small simulation cell with one EG molecule adsorbed on one of the two surfaces of the (100) slab (thickness 20 Å, vacuum thickness 25 Å); (b) a and b vectors are respectively multiplied by 2 and 3 to create the larger simulation cell; (c) From top to bottom: top view of (b) with 6 EG molecules ($\theta_{EG} = 2.15$ molecules/nm²), 4 EG molecules ($\theta_{EG} = 1.44$), 3 EG molecules ($\theta_{EG} = 1.08$), 2 EG molecules ($\theta_{EG} = 0.72$), and 1 EG molecule ($\theta_{EG} = 0.36$). The last four were obtained after removing 2, 3, 4, and 5 molecules from (b). Each time one EG molecule is removed, the local environment is restored identical to that of the reference state of the (100) slab and the geometry of the resulting structure is optimized. A similar procedure is followed in the case of AA molecule. Color code: pink (aluminum), red (oxygen), white (hydrogen), and grey (carbon).

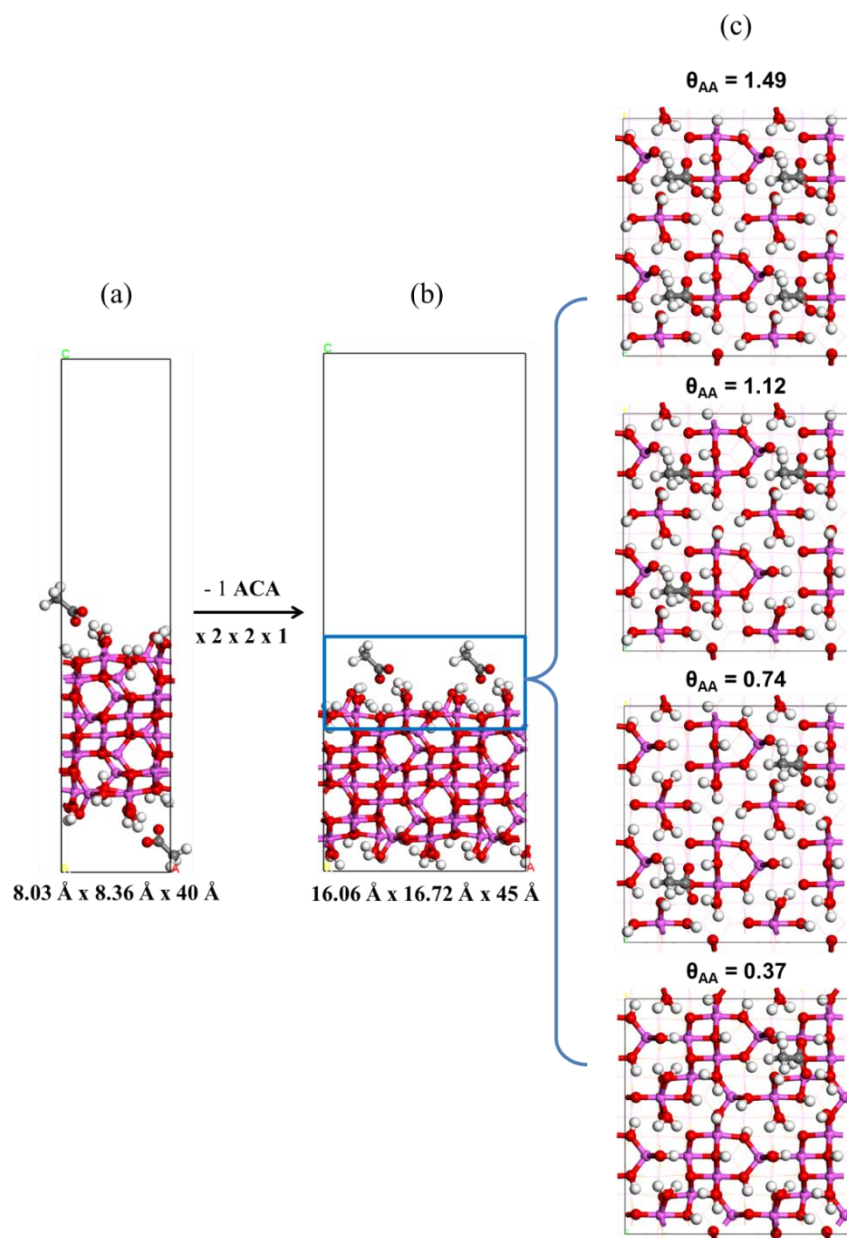


Figure S1.4. (a) Side view of the initial small simulation cell with two AA molecules adsorbed on the two surfaces of the (110) slab (slab thickness 15 Å, vacuum thickness 25 Å) in the same adsorption configuration. One AA molecule is then removed from (a) and the surface hydroxyls are adjusted to look like the reference state before adsorption (similar procedure for AA on (100) slab); (b) a and b vectors are respectively multiplied by 2 to create the larger simulation cell; (c) From top to bottom: top view of (b) with 4 AA molecules ($\theta_{AA} = 1.49$ molecule/nm²), 3 AA molecules ($\theta_{AA} = 1.12$), 2 AA molecules ($\theta_{AA} = 0.74$), and 1 AA molecule ($\theta_{AA} = 0.37$). The last three were obtained after removing 1, 2, and 3 molecules from (b). Each time one AA molecule is removed, the local environment is restored identical to that of the reference state of the (110) slab and the resulting structure is geometry optimized. A similar procedure is followed in the case of EG molecule. Color code is as follows: pink (aluminum), red (oxygen), white (hydrogen), and grey (carbon).

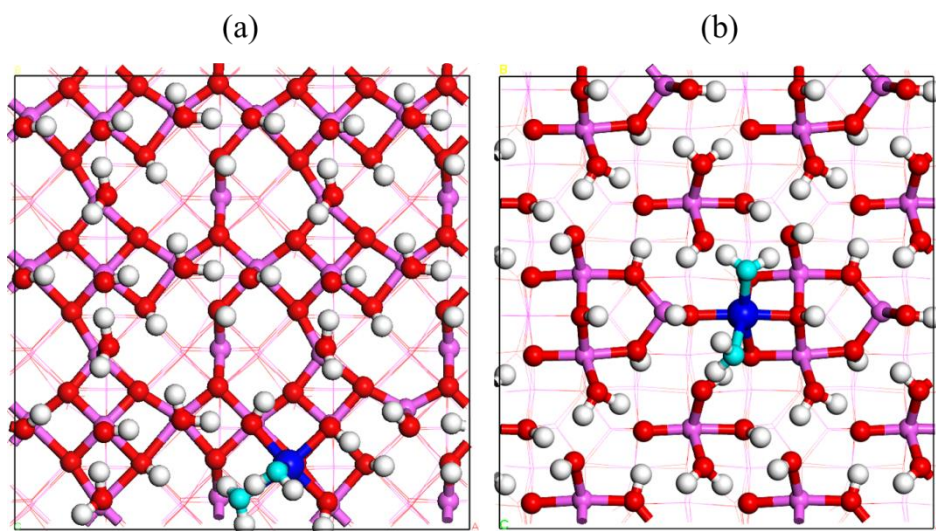


Figure S1.5. Top views of the cobalt adsorbed configurations on (a) (100) and (b) (110) slabs. The main difference between Larmier's results and ours is that our geometry optimizations were carried out using the PBE+D functional (instead of PBE only), and for the reference (110) slab a significant redistribution of the surface hydroxyl groups appeared, giving a more stable reference (110) slab compared to that of Ref. ¹. All this contributed to diminish the energy difference between the reference slab and the slab with adsorbed species, and hence a lower free energy of adsorption on the (110) surface than on the (100) surface. Color code: pink (aluminum), red (surface oxygen atoms), cyan (oxygen of the H₂O groups attached to cobalt), white (hydrogen atoms), and blue (cobalt).

S2: Complementary molecular views of AA and EG adsorption configurations

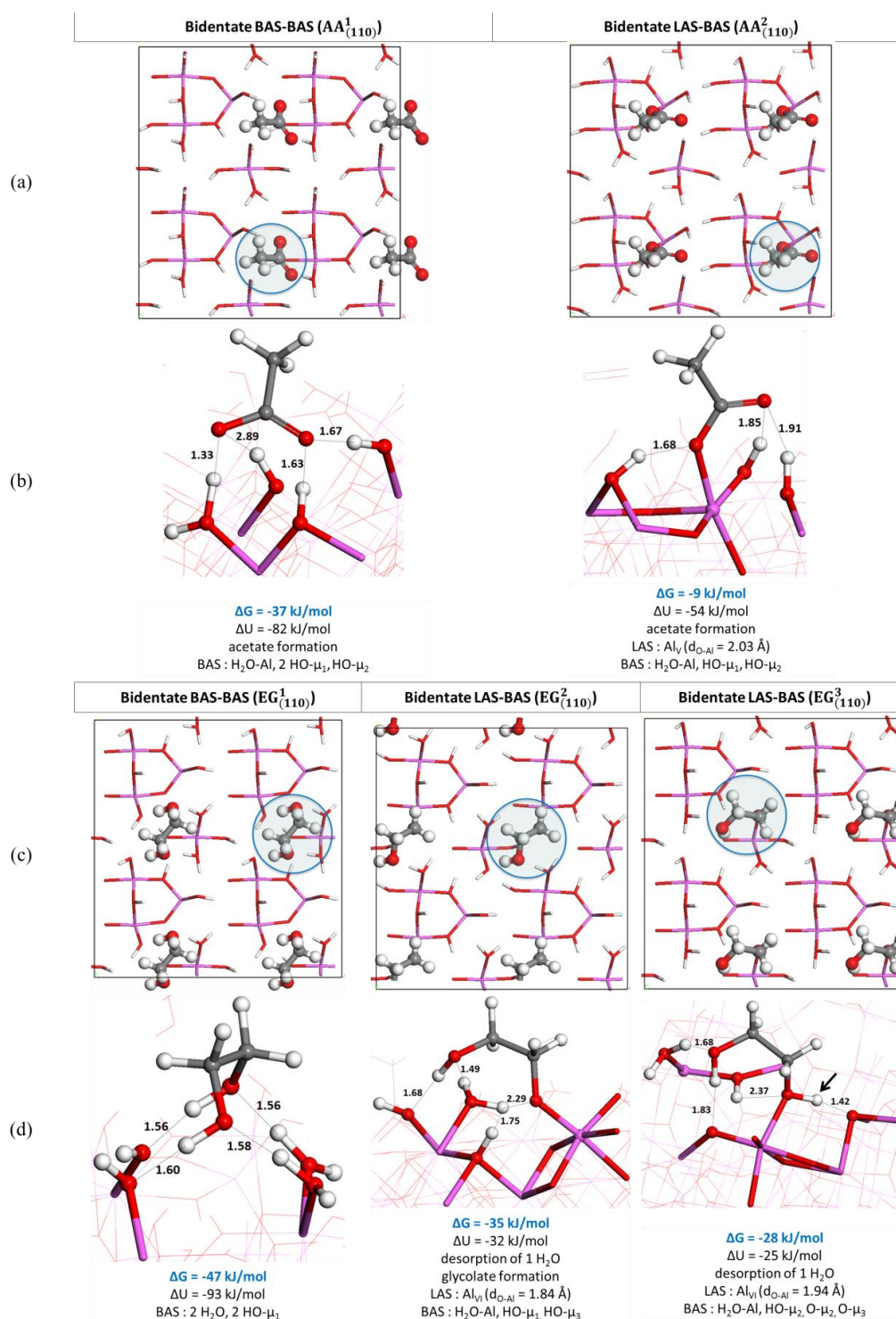


Figure S2.1. Molecular views of the most favorable adsorption configurations of AA and EG on the (110) surface in the large cells and highest adsorption coverage considered in this work ($\theta_{(110)} = 1.49 \text{ molecules/nm}^2$). Top views of the (a) AA molecules and (c) EG molecules adsorbed on the surface. The blue circles represent a hypothetical van der Waals sphere around the molecules. Surface interacting sites around one AA molecule (b) and one EG molecule (d).

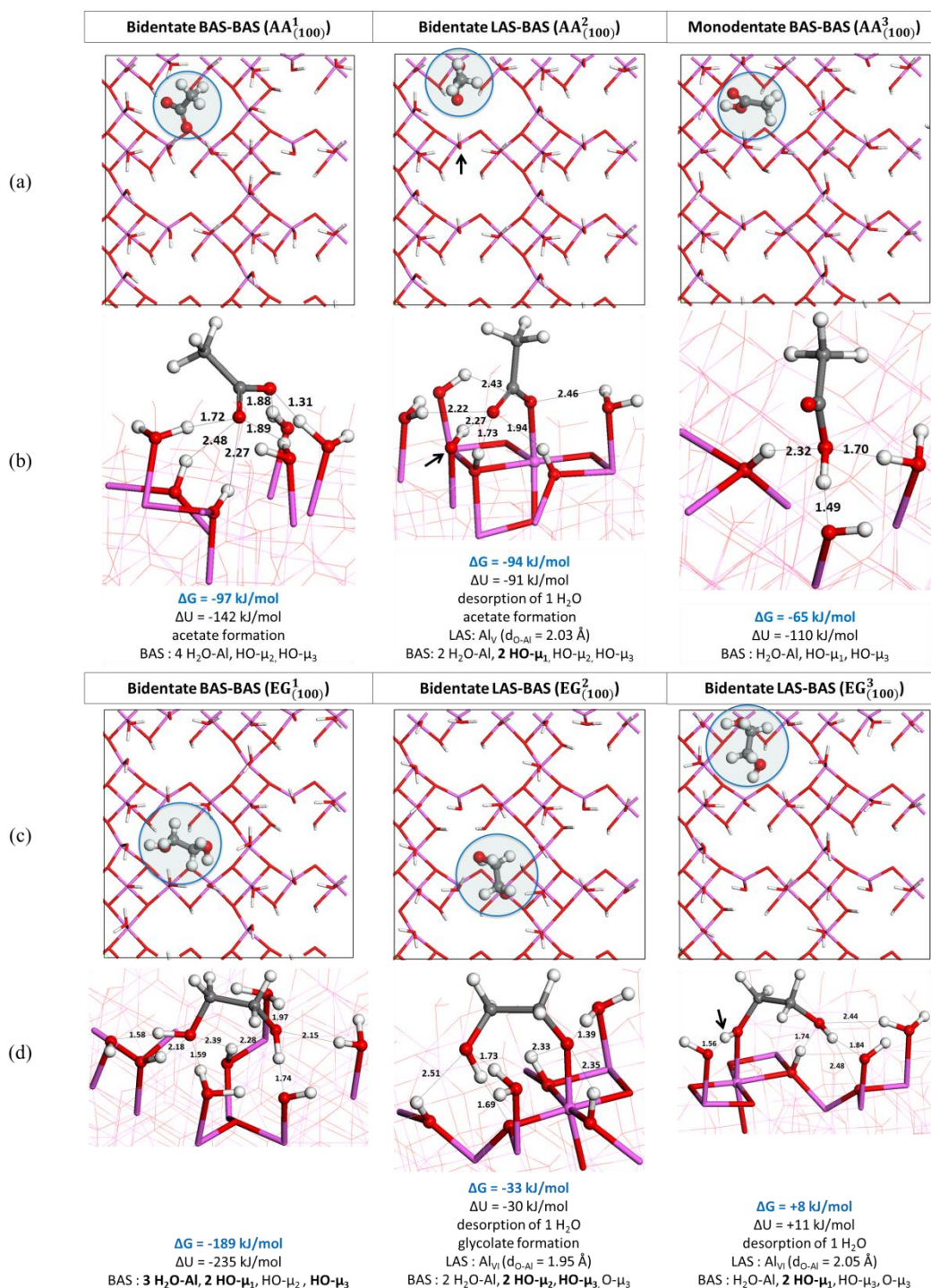


Figure S2.2. Molecular views of the most favorable adsorption configurations of AA and EG on the (100) surface in the large cells and lowest adsorption coverage considered in this work ($\theta_{(100)} = 0.36 \text{ molecules/nm}^2$). Top views of AA molecules (a) and EG molecules (c) adsorbed on the surface. The circles represent a hypothetic van der Waals sphere around the molecules. Surface interacting sites around one AA molecule (b) and one EG molecule (d).

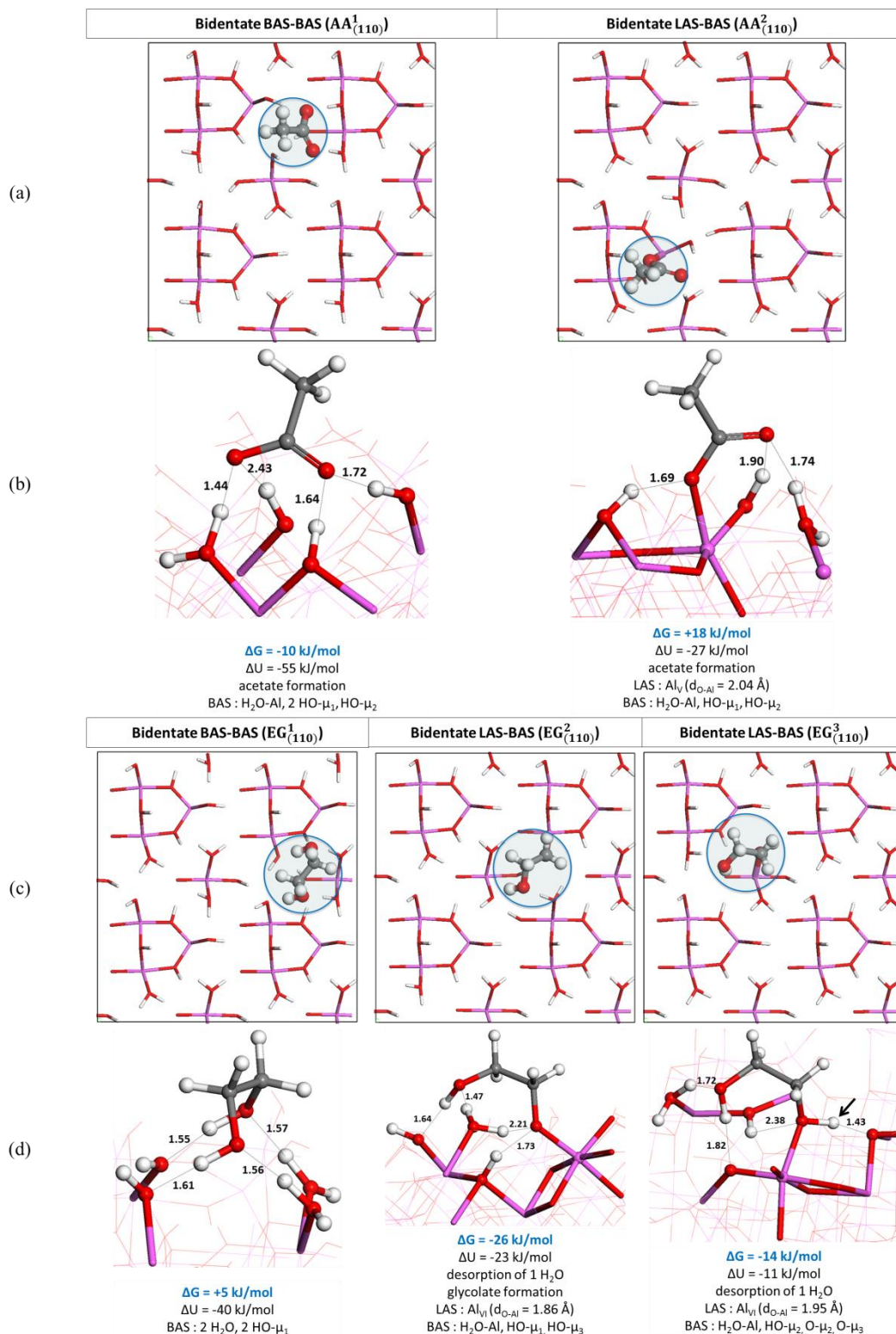


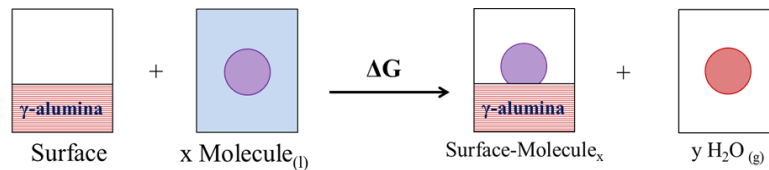
Figure S2.3. Molecular views of the most favorable adsorption configurations of AA and EG on the (110) surface in the large cells and lowest adsorption coverage considered in this work ($\theta_{(110)} = 0.37 \text{ molecules/nm}^2$). Top views of AA molecules (a) and EG molecules (c) adsorbed on the surface. The circles represent a hypothetical van der Waals sphere around the molecules. Surface interacting sites around one AA molecule (b) and one EG molecule (d).

S3: Calculation of the adsorption free energies

The following general assumptions were made for the calculation of the free energies of adsorption:

- Vibrational contributions to adsorption energy for reactants and products are similar and need not to be taken into account.
- Both molecules and the cobalt complex lose 1/3 of their rotational and translational degrees of freedom upon transfer from vacuum to water.
- The translational and rotational degrees of freedom of the molecules and cobalt complex in the liquid phase are converted into bound motions after adsorption.

Acetic Acid and ethylene glycol



For a given surface coverage value (θ) the molecule adsorption free energy data presented in our work for AA and EG molecules are calculated based on the reaction above,

and using the following equations : $\Delta G = \Delta U + \Delta G^{trans} + \Delta G^{rot}$

(E3.1)

With

$$\Delta U = \frac{(E_{Surface-Molecule_x}^{el} + yE_{H_2O}^{el} - E_{Surface}^{el} - xE_{Molecule}^{el})}{x} \quad (E3.1a)$$

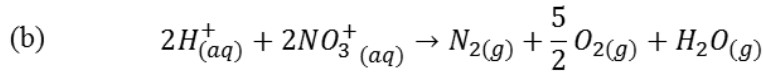
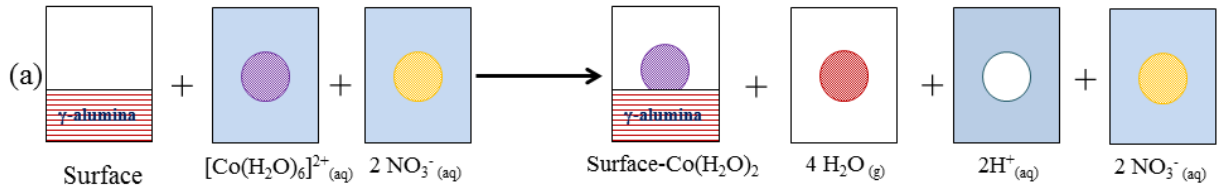
$$\Delta G^{trans} = \frac{(yG_{H_2O}^{trans} - xG_{Molecule}^{trans})}{x} \quad (E3.1b)$$

$$\Delta G^{rot} = \frac{(yG_{H_2O}^{rot} - xG_{Molecule}^{rot})}{x} \quad (E3.1c)$$

In this approach, we assume that the vibrational contribution from surface and molecule cancel out.

Cobalt

For cobalt, we only considered the adsorption of a single cobalt atom initially in the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complex, following the chemical reactions in Figure 5 of the main text.



The mathematical equations used for calculating the adsorption free energy of the overall process (Co(II) adsorption and counter-ion decomposition) are:

$$\Delta U = \left(E_{Surface-[Co(H_2O)_2]}^{el} + 5 E_{H_2O}^{el} + E_{N_2}^{el} + \frac{5}{2} E_{O_2}^{el} - E_{Surface}^{el} - E_{[Co(H_2O)_6]^{2+}}^{el} - 2 E_{NO_3^-}^{el} \right) \quad (E3.1d)$$

$$\Delta G^{trans} = \left(5G_{H_2O}^{trans} + G_{N_2}^{trans} + \frac{5}{2} G_{O_2}^{trans} - G_{[Co(H_2O)_6]^{2+}}^{trans} - 2G_{NO_3^-}^{trans} \right) \quad (E3.1e)$$

$$\Delta G^{rot} = \left(5G_{H_2O}^{rot} + G_{N_2}^{rot} + \frac{5}{2} G_{O_2}^{rot} - G_{[Co(H_2O)_6]^{2+}}^{rot} - 2G_{NO_3^-}^{rot} \right) \quad (E3.1f)$$

In equations above the E^{el} terms term denotes the electronic energies obtained from our DFT geometry optimizations. The G^{rot} and G^{trans} terms are evaluated according to:

$$G^i = H^i - TS^i \quad i = trans, rot \quad (E3.1g)$$

The H^{trans} , H^{rot} , S^{trans} and S^{rot} terms are the translational and rotational enthalpies and entropies that were evaluated in gas phase with the BIOVIA Materials Studio DMol³ program. In the liquid phase these values are equal to 2/3 of the gas phase values, as we assume that 1/3 of the rotational and translational motions are lost upon solvation.

S4: Extrapolation of the energetic data of Larmier et al.¹

The free energies that we calculated and present in this work are the cumulative adsorption free energies averaged over the number of adsorbed species. For cobalt, this is done using Equations E3.1 d-f above, with only one species adsorbed on each of the two studied surfaces. However Larmier et al. provide incremental adsorption free energies (one cobalt complex adsorbed successively) calculated using Equation S3.4 of the supplementary electronic materials in their paper. If we consider that all the electronic, translational and rotational components are known we can rewrite that equation using only the G values as follows :

$$\Delta G_y^{incremental} = G_{Surface-[Co(H_2O)_2]_y} + (n_y - n_{y-1})G_{H_2O} - G_{Surface-[Co(H_2O)_2]_{y-1}} - G_{[Co(OH)(H_2O)_2]} \quad (E S4.1)$$

The cumulative free energies for the adsorption of y and $y-1$ cobalt complexes are calculated respectively as :

$$\Delta G_y^{cumulative} = G_{Surface-[Co(H_2O)_2]_y} + n_y G_{H_2O} - G_{Surface} - y G_{[Co(OH)(H_2O)_2]} \quad (E S4.2)$$

$$\Delta G_{y-1}^{cumulative} = G_{Surface-[Co(H_2O)_2]_{y-1}} + n_{y-1} G_{H_2O} - G_{Surface} - (y-1) G_{[Co(OH)(H_2O)_2]} \quad (E S4.3)$$

From this we deduce that

$$\Delta G_y^{incremental} = \Delta G_y^{cumulative} - \Delta G_{y-1}^{cumulative} \quad (E S4.3)$$

Since the adsorption free energy of the first cobalt complex is known, we can use that value and the incremental values provided in Ref. ¹ to calculate the cumulative adsorption free energies, averaged with respect to the number of adsorbed cobalt complexes as follows:

$$\Delta G_y^{cumulative} = \frac{\Delta G_y^{incremental} + \Delta G_{y-1}^{cumulative}}{y} \quad (E S4.4)$$

S5: Complementary data on the adsorption competition of $\text{Co}(\text{H}_2\text{O})_2$ complexe, AA and EG on the (110) alumina surface

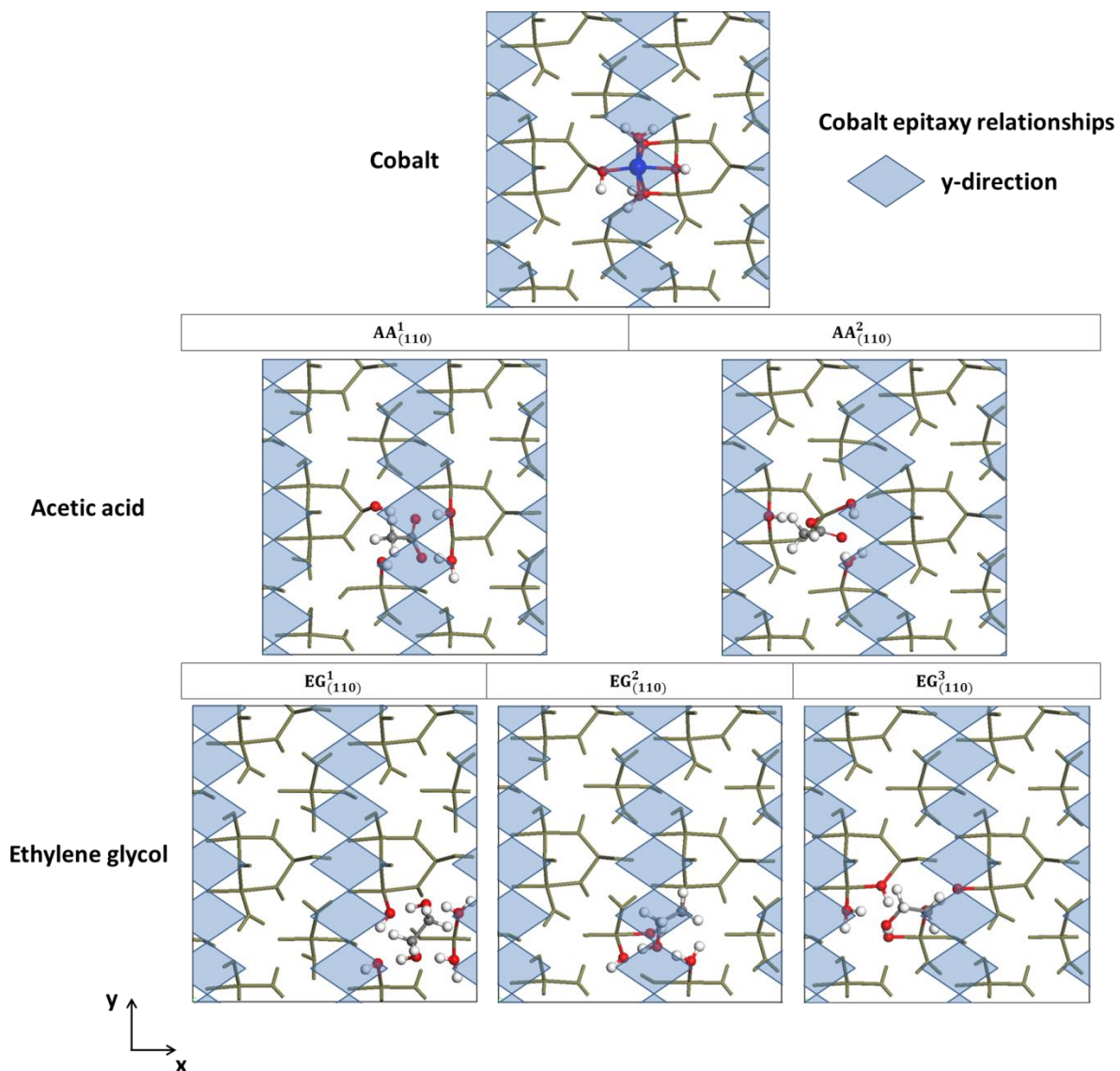


Figure S5.1. Top views of the (110) surface showing the location of the adsorbed species (Cobalt, acetic acid, and ethylene glycol). The blue losanges represent schematically the epitaxial interaction of Co complexes according to the schemes proposed in Ref.¹ The lowest surface coverage (0.37 species per nm²) correspond to one losange for Cobalt or to the single molecule represented. The higher coverage (4.44 Co atoms per nm²) correspond to the complete region mapped by losanges. Color code: grey (carbon), red (oxygen), white (hydrogen), and blue (cobalt), dark green colors (all alumina surface atoms).

References

(1) Larmier, K.; Chizallet, C.; Raybaud, P. Tuning the Metal–Support Interaction by Structural Recognition of Cobalt-Based Catalyst Precursors. *Angew. Chem. Int. Ed.* **2015**, *54*, 6824–6827.