Modelling the Interaction between Carboxylic Acids and Zinc Oxide: Insight into Degradation of ZnO Pigments

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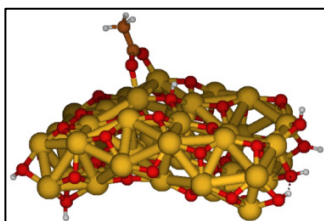
Supporting information

Figure S1. Optimized geometry of bridged bidentate adsorption configuration involving two different position of Zn centers in the adsorption.

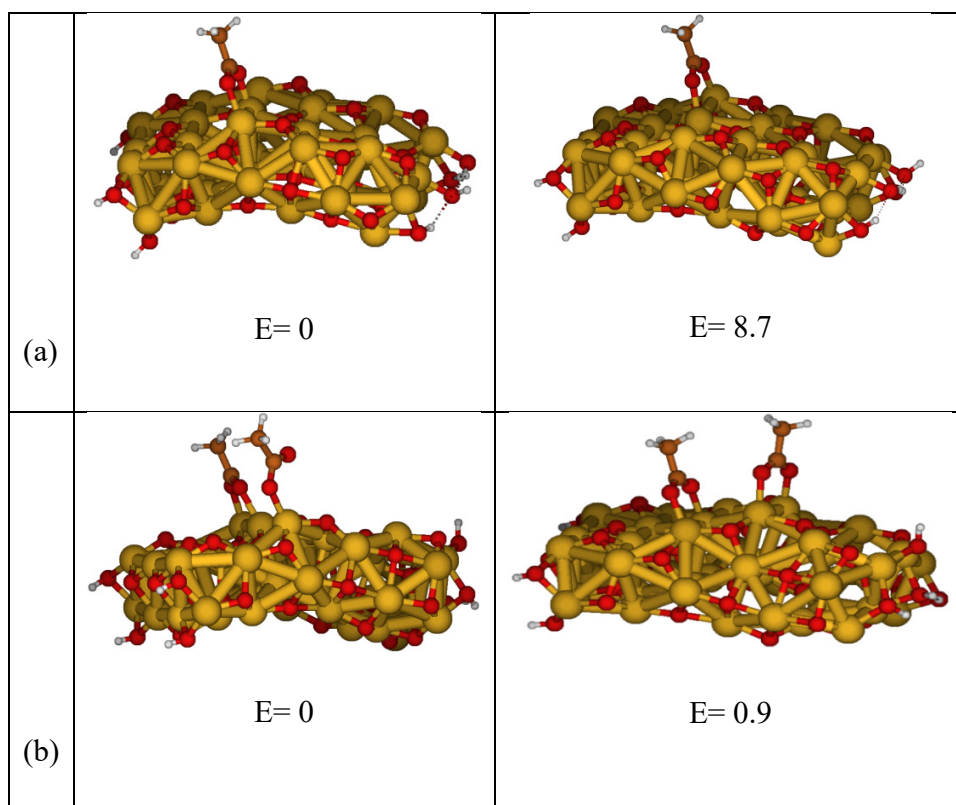|		
(a)	E= 0	E= 8.7
(b)	E= 0	E= 0.9

Figure S2. Optimized geometries of possible adsorption systems in low polarity medium, considering one acetate (a) or two acetates (b) on the surface, and the relative energy difference between the configurations in kcal/mol.
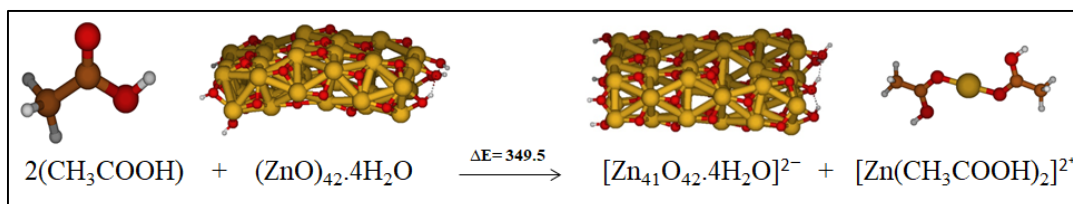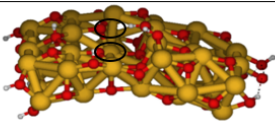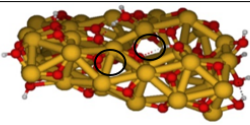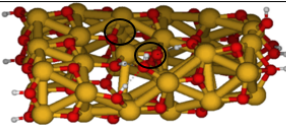

$$2(CH_3COOH) \quad + \quad (ZnO)_{42}.4H_2O \quad \xrightarrow{\Delta E= 349.5} \quad [Zn_{41}O_{42}.4H_2O]^{2-} \quad + \quad [Zn(CH_3COOH)_2]^{2+}$$
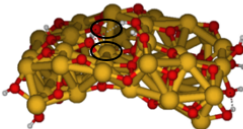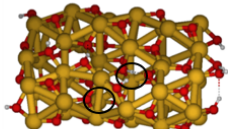
Figure S3. Investigated reactions in vauo considering the formation of a Zn complex with the two acetic acids coordinate to the metal and the ZnO surface deprotonated. The relative energy is reported in kcal/mol.

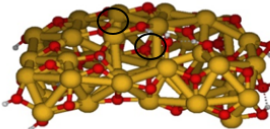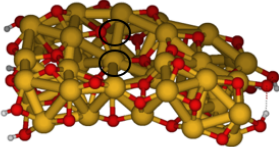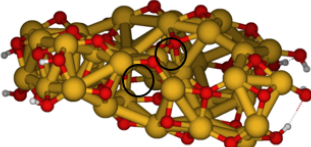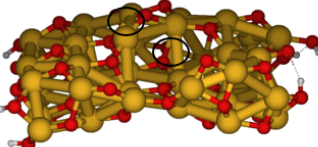| Zn(1-3)- extracted position	Zn(1-2)-extracted position	Zn(2-3)- extracted position
$E_{(vacuo)}= 41.7$	$E_{(vacuo)}=3.8$	$E_{(vacuo)}= 0$
$E_{(vacuo)}=7.5$	$E_{(vacuo)}=34.1$	$E_{(vacuo)}=10.3$

(**a**)

Zn(1-3)- extracted position	Zn(1-2)-extracted position	Zn(2-3)- extracted position
$E_{(vacuo)}= 0$	$E_{(vacuo)}=62$	$E_{(vacuo)}= 23$

(**b**)

Figure S4. (**a**). Optimized geometries of different positions for two released Zn ions from the surface of ZnO cluster leaving it protonated and the relative energy between these geometries in kcal/mol. (**b**) Optimized geometries of different positions for two released Zn ions from the surface of ZnO cluster leaving it deprotonated, and the relative energy between these geometries in kcal/mol.

ΔE (kcal/mol)	VACUUM	ε = 5	WATER
Reaction 1	−96.0	−60.3	−46.5
Reaction 2	−104.7	−38.9	−25.4
Reaction 3	−123.4	−87.2	−76.6
Reaction 4	−142.6	−63.5	−43.6

Table S1. Formation energies in kcal/mol for the investigated reactions reported in Figure 3 in vacuum and solution phases.

ΔE (kcal/mol)	VACUUM	ε = 5	WATER
Reaction 5	−40.2	−32.8	−29.1
Reaction 6	−38.3	11.4	27.8
Reaction 7	−95.1	−80.7	−75.1
Reaction 8	84.1	70.5	72.7

Table S2. Formation energies in kcal/mol for the investigated reactions corresponding to figure 5 in vacuum and solution phases.

ΔE (kcal/mol)	VACUUM	ε = 5	WATER
Reaction 1'	−97.1	−60.9	−48.6
Reaction 2'	−94.1	−39.1	−24.6
Reaction 3'	−134.0	−91.7	−69.0
Reaction 4'	−140.1	−64.0	−45.1

Table S3. Formation energies in kcal/mol for the investigated reactions corresponding to Figure 6 in vacuum and solution phases.

ΔE (kcal/mol)	VACUUM	ε = 5	WATER
Reaction 5'	−51.3	−38.1	−32.5
Reaction 6'	−35.5	10.8	27.0
Reaction 7'	−116.6	−91.7	−77.6
Reaction 8'	90.5	68.8	75.5

Table S4. Formation energies in kcal/mol for the investigated reactions corresponding to figure 7 in vacuum and solution phases.