

# DFT Screening of Adsorption of Biodiesel Molecules on Aluminium and Stainless Steel Surfaces

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## Supplementary Material

### Bulk Oxides

Table S1: Calculated (VASP) versus experimental bulk structural parameters of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>.

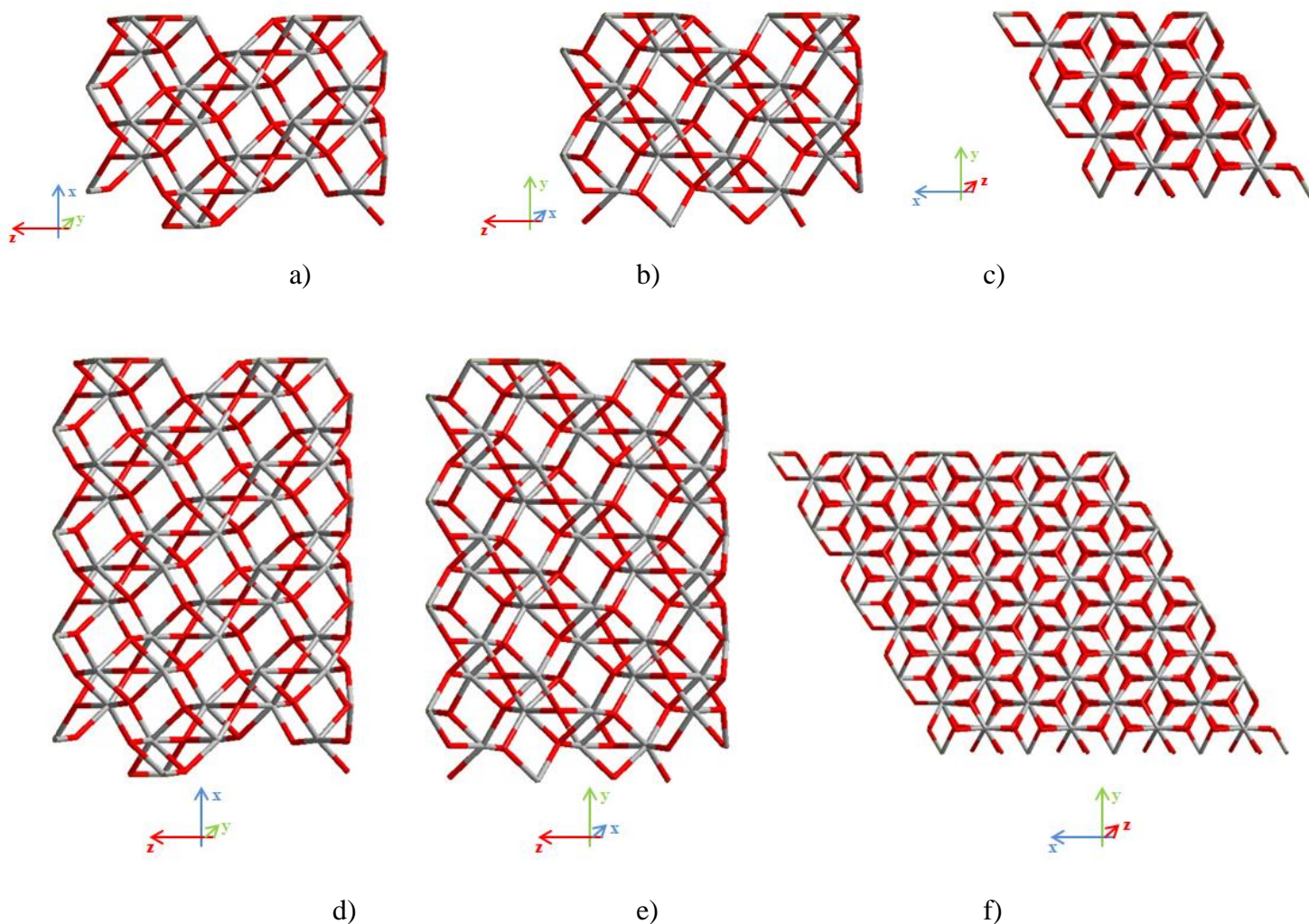
	Al <sub>2</sub> O <sub>3</sub>		Cr <sub>2</sub> O <sub>3</sub>	
	Experimental* [74]	Calc. Bulk (this work)	Experimental***	Calc. Bulk (this work)
<b>a = b (Å)</b>	4.759	4.780	4.95	5.07
<b>c (Å)</b>	12.993	13.047	13.57	13.85
<b>c/a (Å)</b>	2.730	2.729	2.74	2.73
<b>V (Å<sup>3</sup>)</b>	254.93	258.20	-	308.27
<b>Al-O<sub>1</sub> (Å)</b>	1.853**	1.861	-	2.055
<b>Al-O<sub>2</sub> (Å)</b>	1.974**	1.982	-	2.009

\* C. B. Alcock Crystallographic data on minerals, *CRC Handbook of Chemistry and Physics*, D. R. Lide CRC Press, Boca Raton, FL, 2003–2004, pp. 4–158

\*\* R. E. Newnham and Y. M. de Haan, *Z. Kristallogr.*, 1962, **117**, 235

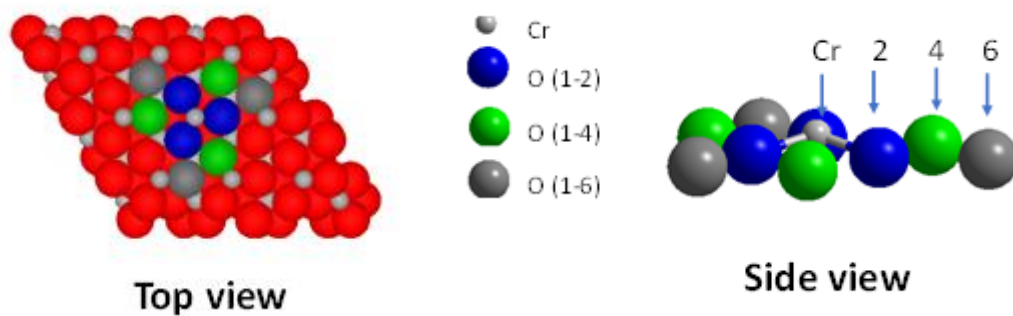
\*\*\* L. Finger and R. Hazen, *J. Appl. Phys.*, 1980, **51**, 5362

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Fig. S1: Slabs retained for the (0001) surfaces: a-c) 2x2 cell d-f): 4x4 cell; Grey: Al, Cr; red: O.



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Fig. S2: Nomenclature for adsorption and dissociation of protic molecules at corundum  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  (0001) surfaces. Top-view of  $\text{Al}_2\text{O}_3$  or  $\text{Cr}_2\text{O}_3$  with a metal cation (grey) in the center of 3 oxygen atoms (blue). If the metal (Cr/Al) ion is considered at position 1, the blue (oxygen) atoms are at position 2, and the green (oxygen) at position 4.

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**Table S2: Energy, ZPE contribution, Free energy and Entropy contributions of the free molecules**

Molecule	E <sub>scf</sub> (Hartree)	E <sub>scf</sub> +E <sub>ZPE</sub> (Hartree)	G (Hartree)	S <sub>tot</sub> (cal/K.mol)	S <sub>trans</sub> (cal/K.mol)	S <sub>rot</sub> (cal/K.mol)	S <sub>vib</sub> (cal/K.mol)
acetaldehyde	-153.876859	-153.821654	-153.846587	62.655	37.273	21.639	3.744
propane	-119.180682	-119.077698	-119.102701	64.139	37.275	21.311	5.552
oxirane	-272.396586	-272.246204	-272.279686	90.230	39.306	26.871	22.676
ethanol	-155.088116	-155.008371	-155.033746	64.412	37.406	22.313	4.692
toluene	-271.636042	-271.508696	-271.539283	79.441	39.471	26.976	12.993
acetic-acid	-229.156429	-229.094737	-229.121837	68.594	38.196	23.846	6.551
benzene	-232.308544	-232.208393	-232.235852	69.026	38.979	25.650	4.397
hexanoate	-424.518409	-424.339466	-424.37731	104.663	40.456	29.879	34.328
methylacrylate	-306.541456	-306.446748	-306.477494	80.689	39.270	26.595	14.824
acetone	-193.213023	-193.129901	-193.159299	75.383	38.096	24.147	13.139
methylpropionate	-307.779509	-307.661807	-307.693263	83.600	39.339	26.780	17.481

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The desorption temperatures were calculated using the thermodynamic corrections of the molecules in the gas phase (G16 calculations), while for the systems “slab+molecule” only the electronic energies were used. Upon considering the general desorption reaction:

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Slab-Molecule = slab + molecule(gas)

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At thermal equilibrium we can write that

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$$\Delta G_{\text{desorp}} = \Delta H_{\text{desorp}} - T\Delta S_{\text{desorp}} = 0$$

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We now make 3 key assumptions:

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1)  $\Delta H_{\text{desorp}} \approx \Delta E_{\text{desorp}}$ . In other words, the corrections (zero-point energy, translational, rotational and vibration internal energies and PV corrections) are equal for reactant and product.

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2) Upon adsorption of the organic molecule, the entropic contributions for translation and rotation become zero. Thus

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$$\Delta S_{\text{desorption}}^{\text{transl.}} = S_{\text{molecule gazphase}}^{\text{transl.}} - S_{\text{molecule adsorbed}}^{\text{transl.}} = S_{\text{molecule gazphase}}^{\text{transl.}} - 0$$

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And

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$$\Delta S_{\text{desorption}}^{\text{rot.}} = S_{\text{molecule gazphase}}^{\text{rot.}} - S_{\text{molecule adsorbed}}^{\text{rot.}} = S_{\text{molecule gazphase}}^{\text{rot.}} - 0$$

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3) Entropic contributions from the vibrations modes of the organic molecules remain constant upon adsorption so  $\Delta S_{\text{desorp}}^{\text{vib}} = 0$

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These 3 assumptions allow us to write:

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$$\Delta G_{\text{desorp}} = \Delta H_{\text{desorp}} - T_{\text{desorp}}\Delta S_{\text{desorp}} = 0$$

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$$\Delta H_{\text{desorp}} = T_{\text{desorp}}\Delta S_{\text{desorp}} = \Delta E_{\text{desorp}}^{\text{electronic}} = T_{\text{desorp}}(\Delta S_{\text{desorp}}^{\text{transl.}} + \Delta S_{\text{desorp}}^{\text{rot.}} + \Delta S_{\text{desorp}}^{\text{vib.}})$$

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931 Solving for  $T_{\text{desorp}}$ :

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$$T_{\text{desorp}} = \frac{\Delta E_{\text{desorp}}^{\text{electronic}}}{\Delta S_{\text{desorp}}^{\text{transl.}} + \Delta S_{\text{desorp}}^{\text{rot.}} + \Delta S_{\text{desorp}}^{\text{vib.}}} = \frac{\Delta E_{\text{desorp}}^{\text{electronic}}}{S_{\text{mol. gazphase}}^{\text{transl.}} + S_{\text{mol. gazphase}}^{\text{rot.}} + 0}$$

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935 Consequently, we avoid the time-consuming vibrational frequencies calculations for the systems in which  
936 the organic molecule is adsorbed on the slab.

937 *Since the entropy itself is a function of temperature, one cannot solve directly the equation:*

938  $T_{\text{desorb}} = -\Delta E_{\text{ads}} / (S_{\text{trans}} + S_{\text{rot}})$ . Therefore, we:

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940 1) Calculate the entropic contributions at intervals of 10 degrees between  $T = 0$  and  $T = 500$  K using the  
941 Freqchk utility of Gaussian 16.

942 2) Calculate  $T_{\text{desorb}}$  at each of those temperatures using the above-mentioned equation.

943 3) Apply a 3<sup>rd</sup> degree polynomial curve fitting to the graph where  $(T_{\text{desorption}} - T)$  is plotted against  $T$ .

944 4) Use Microsoft Excel's build-in "Goal Seek" module to find where  $(T_{\text{desorption}} - T) = 0$ .

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948 In **Table S3** below, we report the intramolecular bonds of each compound that presented the highest distortion  
949 from the consequent adsorption above the dry  $\alpha$ -(0001)  $\text{Al}_2\text{O}_3$ . We chose to report the values related to the  
950 adsorption on dry  $\alpha$ -alumina since in our study this substrate was observed to be the most reactive, thus the  
951 one that could provide the highest variations between the pre and post-adsorption conditions. We can notice  
952 that the general trend confirms the weak impact of surface on the intramolecular distortion, at the exception  
953 of the dissociated case of the acetic acid, where indeed we see a  $\Delta_{\text{O-H}} = 0.44 \text{ \AA}$ , which confirms the proton  
954 transfer from the molecule towards the surface oxygen atom (**Fig.2**).

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957 **Table S3: Intramolecular bonds presenting the highest distortion after adsorption of each molecule on dry  $\alpha$ -(0001)  $\text{Al}_2\text{O}_3$**

Molecules	MAX $\Delta d_{\text{mol}}$ (Ads - Gas) [Angstrom]	Intramol. Bond
Acetic acid (Diss. Ads)	<b>0.44</b>	O-H
Ethanol	0.05	C-O
Acetaldehyde	0.03	C-C
Acetone	0.03	C-C
Benzene	0.01	C=C
Toluene	0.01	C-C
Methyl Acrylate	0.03	C=O
Methyl-3T-Hexenoate	0.03	C=O
Methyl propionate	0.04	C=O
2Ethyl-3methyl-oxirane	0.04	C-O
N-propane	0.00	-

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