The Limits of Ground-State Water Splitting on ZnO surfaces: A Density Functional Theory Study

Morales-Salvador, R.[a]; Bromley, S. T.[a,b]; Viñes, F.[a]; Catal. Today, 441, (2024)

[a]*Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, c/ Martí i Franquès 1, 08028 Barcelona, Spain*

[b]*Institució Catalana de Recerca i Estudis Avançats (ICREA), c/ Passeig Lluís Companys 23, 08010 Barcelona, Spain*

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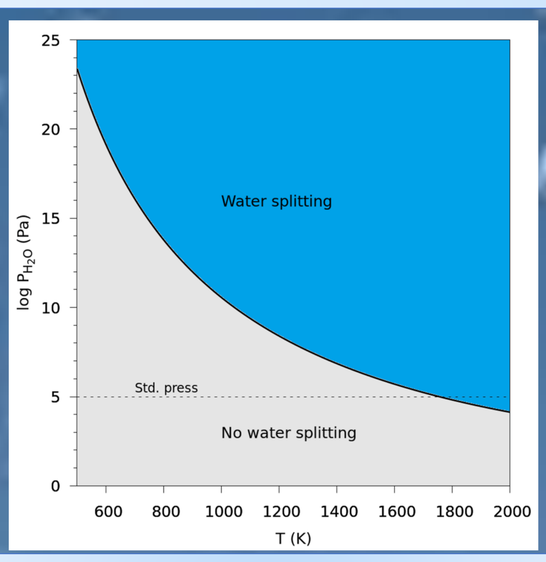
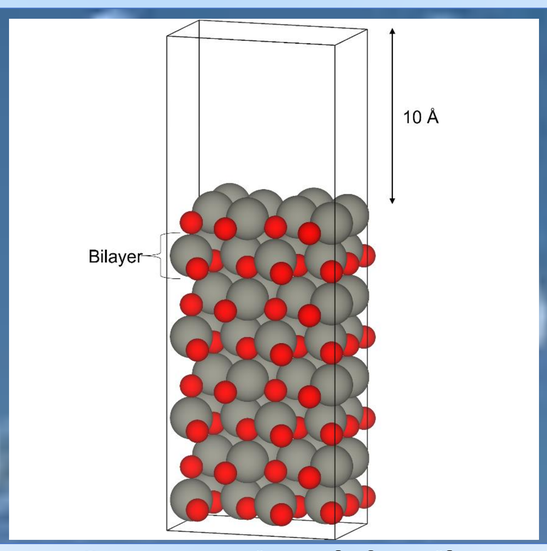
The water (H_2O) splitting reactions towards hydrogen (H_2) and oxygen (O_2) production in the ground state are here investigated on **(000$\bar{1}$), (0001), (10$\bar{1}$0) and (11$\bar{2}$0) ZnO catalyst surfaces,** by means of density functional theory simulations (dft). The **adsorption** and **co-adsorption** strengths and **elementary steps** energy **barriers** along the reaction path pinpoint the **key reaction limiting steps**.



$H_2O \rightarrow H_2 + ½\cdot O_2$

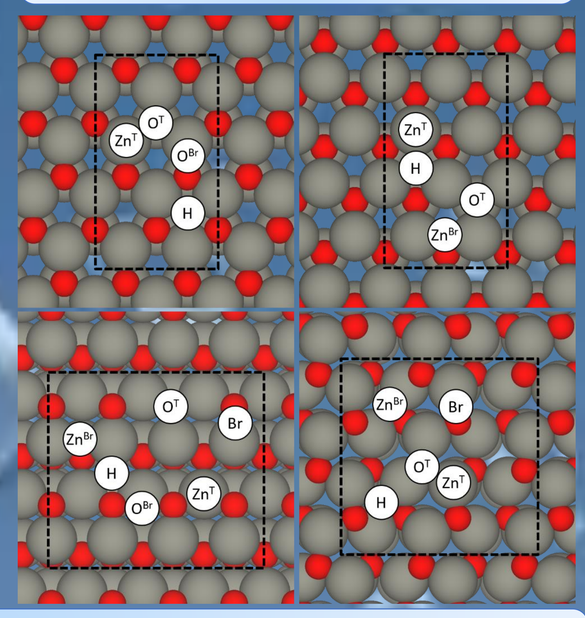
The **conditions** at which the **reaction** become **spontaneous** are **prohibitive.**



Computational details

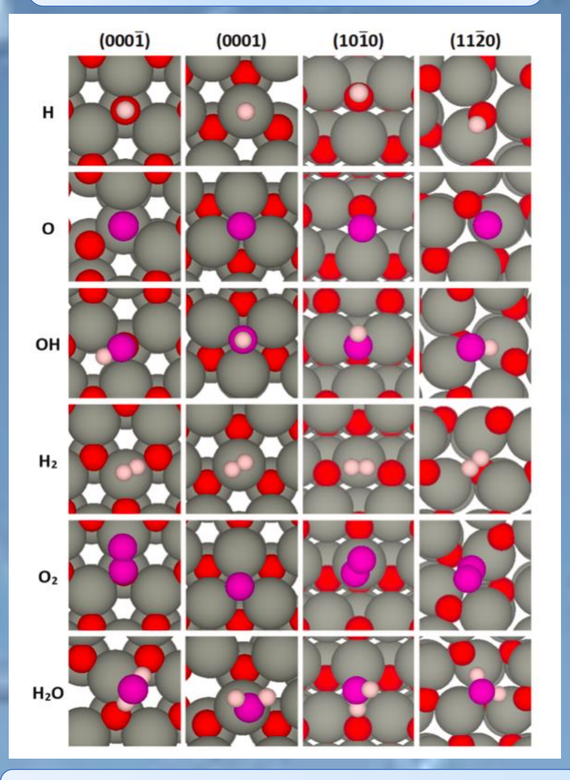
- (2×2) or (4x2) supercell model
- Code: VASP
- Functional: PBE and PBE-D3 correction

Sampled high symmetry sites

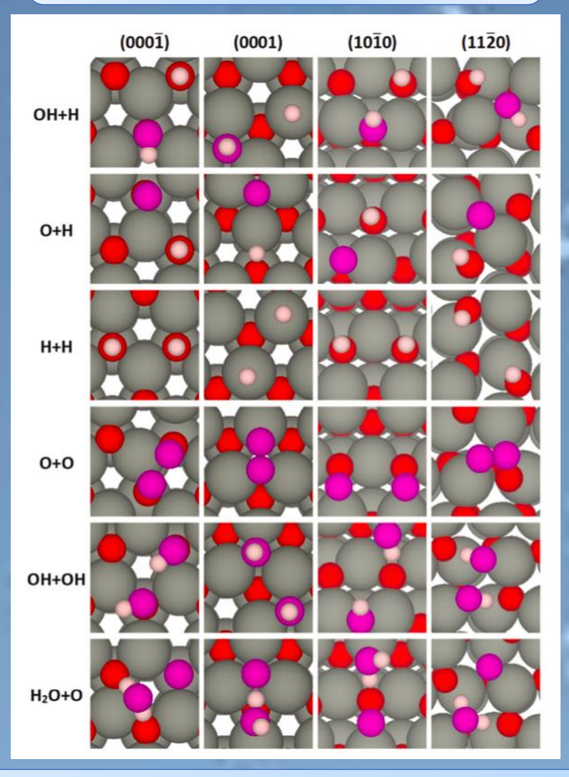


Adsorption landscape (most stable adsorption sites)

Single species



Co-adsorptions

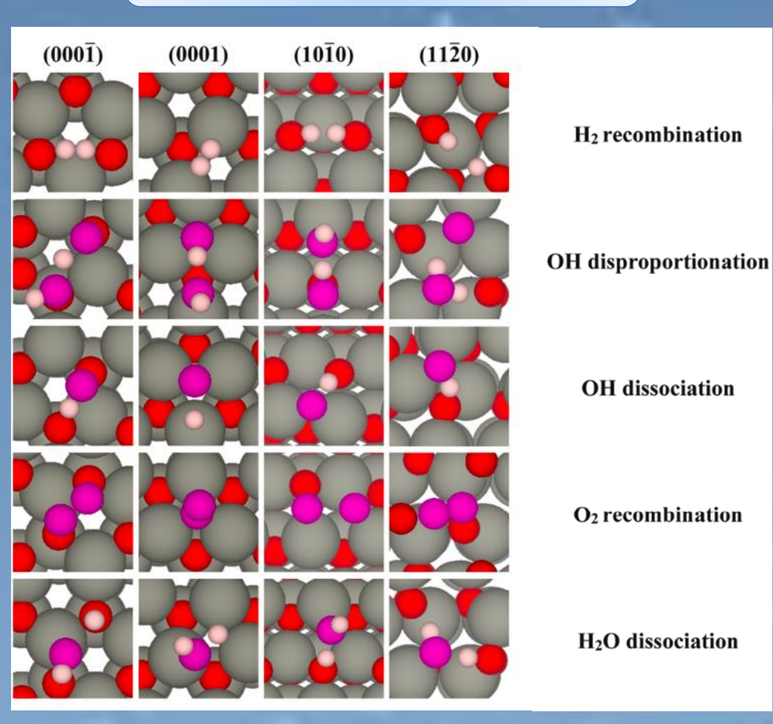


Reaction mechanism

1. $H_2O + * \rightarrow H_2O*$
2. $H_2O* + * \rightarrow OH* + H*$
3. $OH* + * \rightarrow O* + H*$
4. $H* \rightarrow H_2* + *$
5. $H_2* \rightarrow H_2 + *$
6. $2\cdot O* \rightarrow O_2* + *$
7. $O_2* \rightarrow O_2 + *$
8. $2\cdot OH* \rightarrow H_2O* + O*$

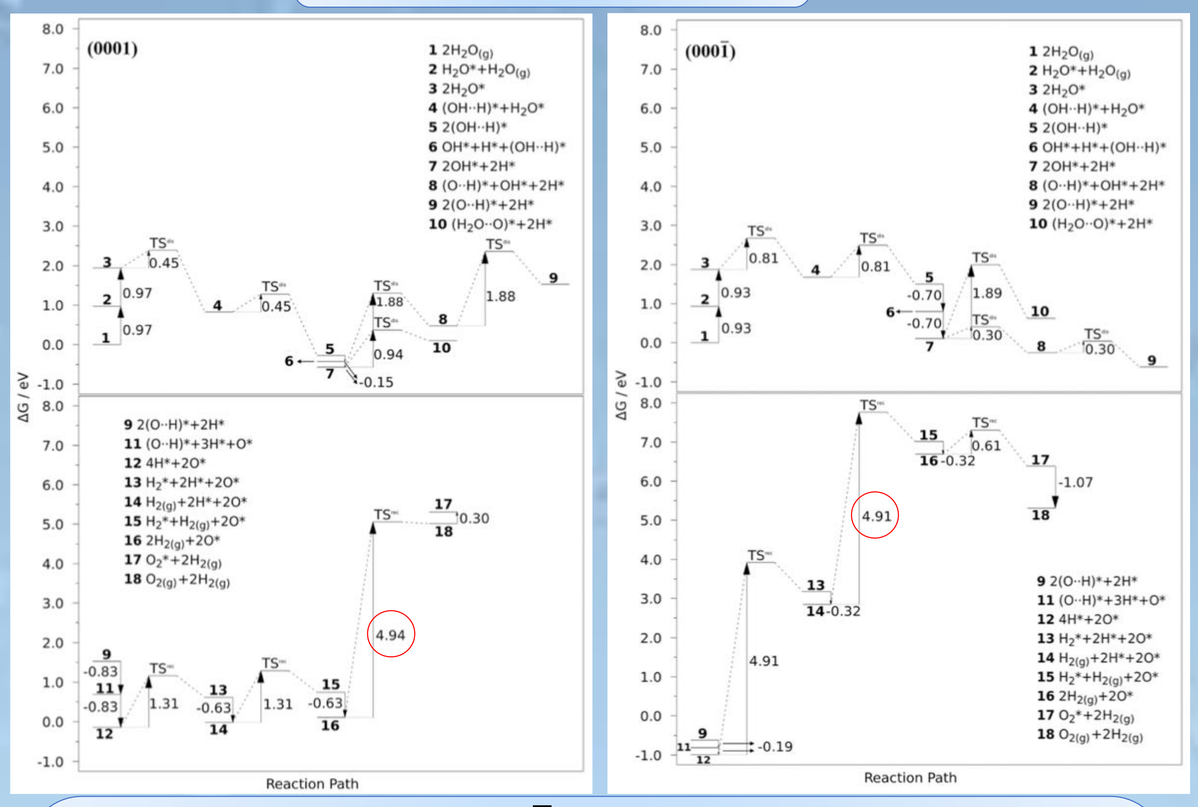
For each reaction step, the TSs have been gained

Transition states

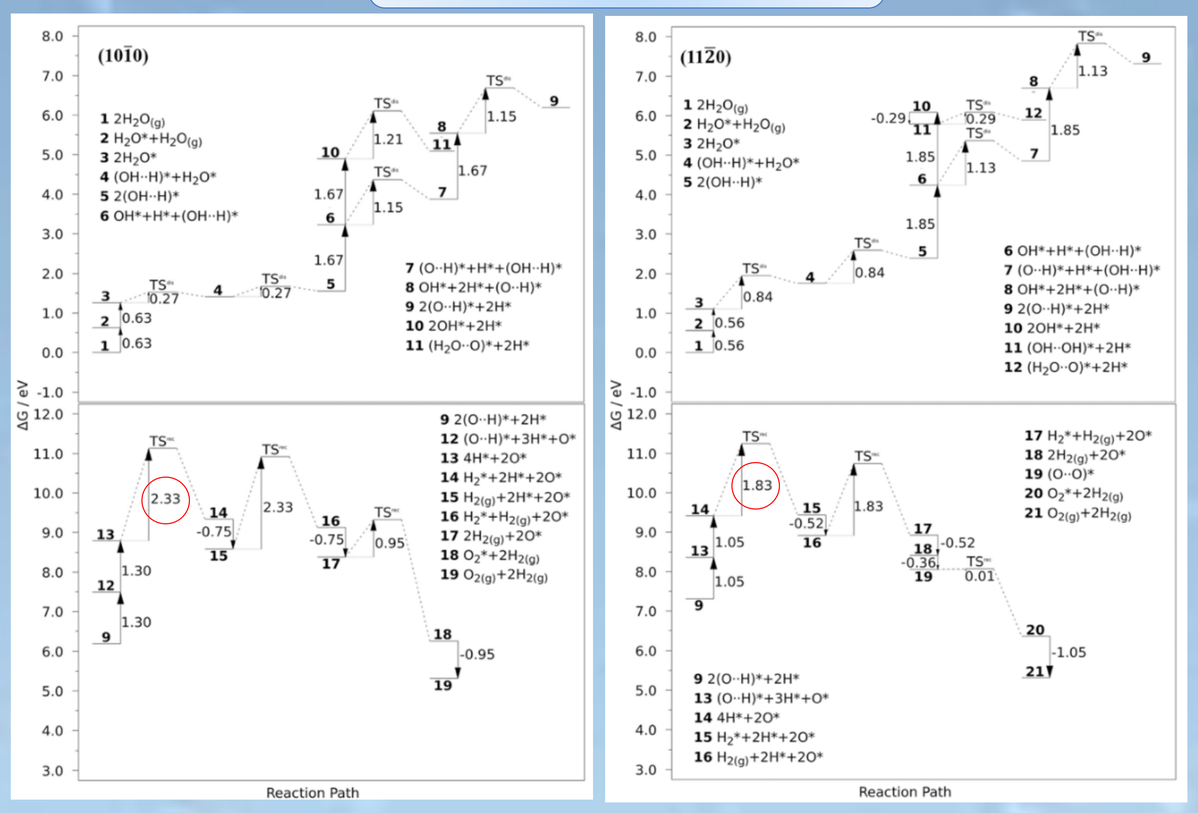


Reaction energy profiles

Polar surfaces



Non-Polar surfaces



Pronounce activity of **(000$\bar{1}$)** and **(0001)** surfaces towards **H** and **O adatoms**, respectively. In principle making **H_2** and **O_2 generation** steps, on them the **difficult reactions** with barriers* of 4.94 and 4.91 eV, respectively.

*The employed polar surface models feature artificial metallic surface states, which could be a source of error our results. For more information, check the tests carried out.

H_2 formation is the **rate limiting step**, with barriers of 2.33 and 1.83 eV **(10$\bar{1}$0)** and **(11$\bar{2}$0)** surfaces.

CONCLUSIONS

- The **(11$\bar{2}$0)** surface is found to be the one with a **smoother reaction profile**.
- **H_2 formation** is found to be the **reaction** steps **to be improved** on **(000$\bar{1}$)**, **(10$\bar{1}$0)**, and **(11$\bar{2}$0)** surfaces
- **O_2 formation** on **(0001)** surface is the rate limiting step.

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