Key Ingredients for The Screening of Single Atom Catalysts for The Hydrogen Evolution Reaction: The Case of Titanium Nitride

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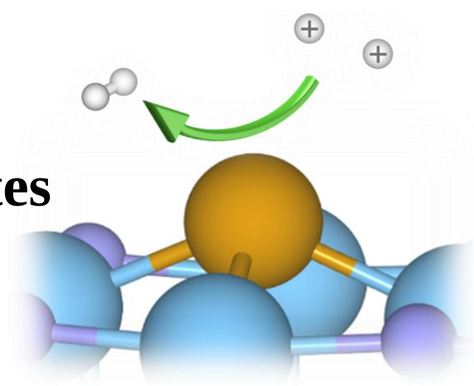
AIM OF THE STUDY

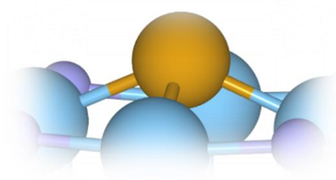
What are the **key ingredients** for the screening of **Single-Atom Catalysts** for the **HER** on **TM@TiN**?

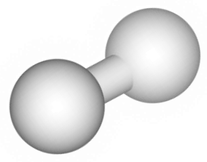
We expolred the role of:

Functional (PBE/PBE+*U*)
Unconventional intermediates (H_2-complexes)
Stability



COMPUTATIONAL FRAMEWORK





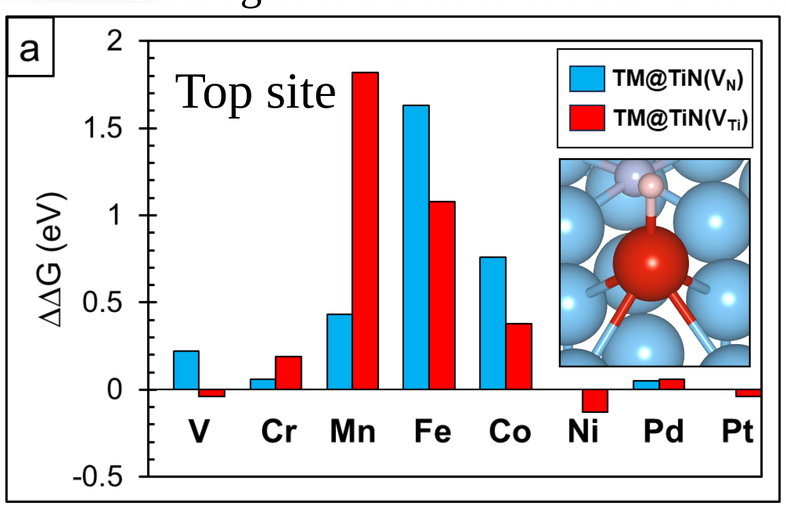
b-initio VASP ackage ienna imulation

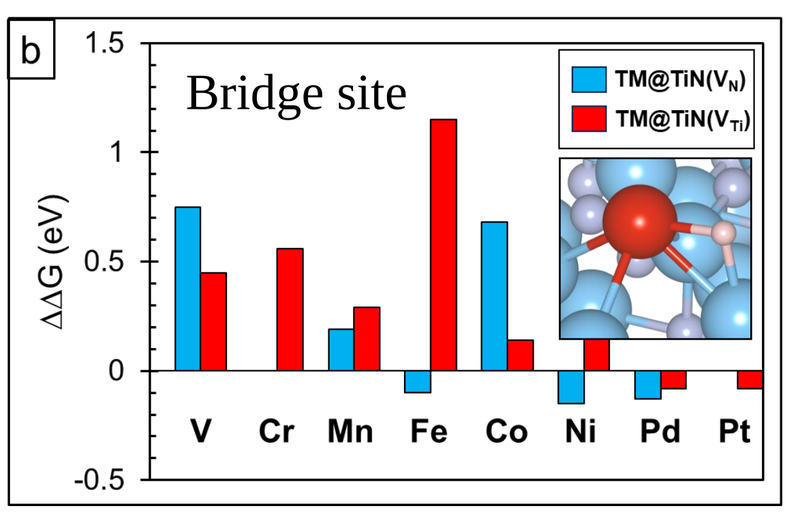
Computational Details

- **DFT+*U*** and **DFT** with PBE parametrization
- **PAW** pseudopotentials (core electrons) and valence electrons expanded on a set of **plane waves**
- The **Grimme's D3** scheme for dispersion forces

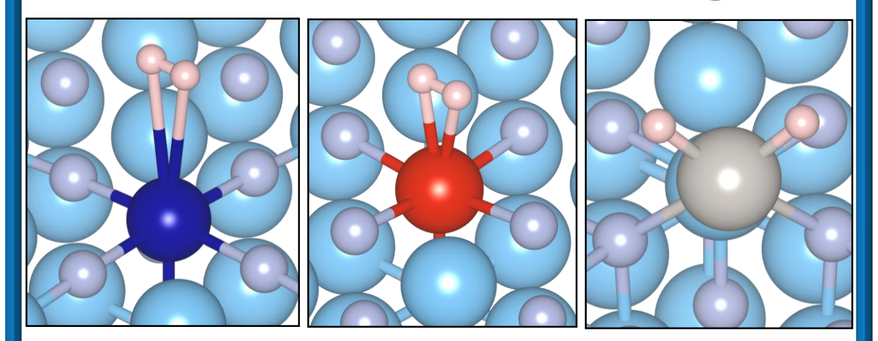
FUNCTIONAL

Deviation of Gibbs free energy of adsorption of **H*** calculated with PBE against the same at PBE+*U* level

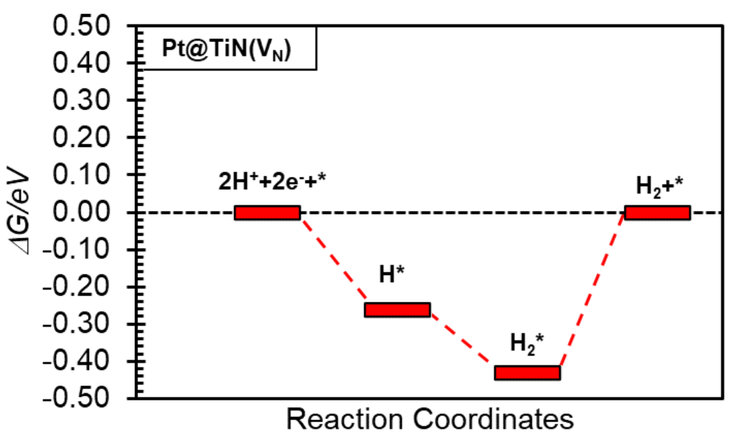




UNCONVENTIONAL INTERMEDIATES



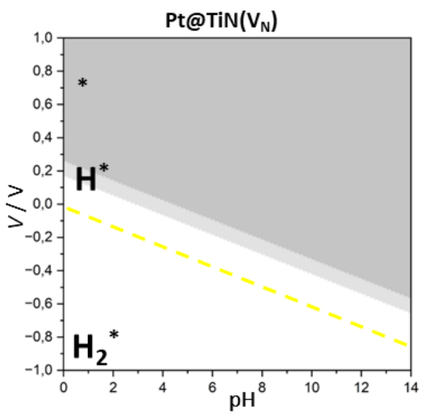
H_{2phys} H_2* H*H*



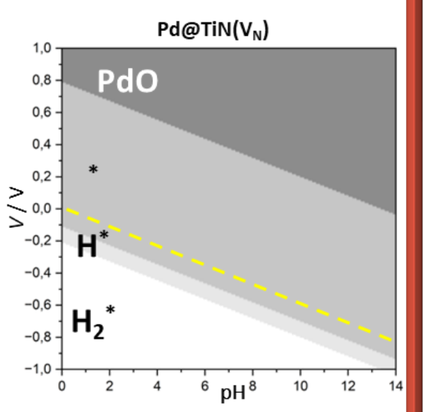
The number of **potential candidates** is reduced to **6**

STABILITY

Pourbaix Diagrams



In line with experiments



Only **2** candidates result **stable** in **HER working conditions**

CONCLUSIONS

We observed the need to go beyond the standard PBE functional and introduce a self-interaction corrected method. Then, we included in the model dihydrogen and dihydride complexes, these species form and strongly affect the energy profile, and thus the prediction of the catalytic activity. Finally, we addressed another important aspect in the activity of a catalyst: we considered the stability of the SACs against dissolution in working conditions of pH and voltage. Once both unconventional intermediates and stability issues are considered, the number of potentially active catalyst is considerably reduced. This provides another example of the complex chemistry of SACs.

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