Electronic Supplementary Information (ESI) for

Density functional theory based indicators to predict corrosion inhibition potential of ceramic oxides in harsh corrosive media

Anson Thomas,[a] Tuhin S. Khan,[b] and Puneet Gupta*[a]

[a] *Computational Catalysis Center, Department of Chemistry, Indian Institute of Technology, Roorkee, Uttarakhand - 247667, India. E-mail: puneet.gupta@cy.iitr.ac.in*
[b] *Light Stock Processing Division, CSIR-Indian Institute of Petroleum, Dehradun, Uttarakhand, 248005, India.*

Contents

S1 Pseudopotentials

Pseudopotentials used for the calculations with explicitly treated electrons are mentioned herewith. These have been obtained from the PSLibrary of Quantum ESPRESSO.[1,2]

Table S1 showing the pseudopotentials used for calculations

Pseudopotential	Atom	Explicitly treated electrons
Al.pbe-nl-kjpaw_psl.1.0.0.UPF	Al	$3s^2 3p^1$
Cl.pbe-nl-kjpaw_psl.1.0.0.UPF	Cl	$3s^2 3p^5$
Hf.pbe-spn-kjpaw_psl.1.0.0.UPF	Hf	$5s^2 5p^6 6s^2 5d^2$
O.pbe-nl-kjpaw_psl.1.0.0.UPF	O	$2s^2 2p^4$
S.pbe-nl-kjpaw_psl.1.0.0.UPF	S	$3s^2 3p^4$
Ti.pbe-spn-kjpaw_psl.1.0.0.UPF	Ti	$3s^2 3p^6 3s^2 3s^s$
Zr.pbe-spn-kjpaw_psl.1.0.0.UPF	Zr	$4s^2 4p^6 5s^2 4d^2$

S2 Energy Convergence

The ecutwfc (planewave kinetic energy cutoff) has been set to 200Ry and is sufficiently high to converge the energies of all the MO unit cells. The convergence is shown in the plot below.

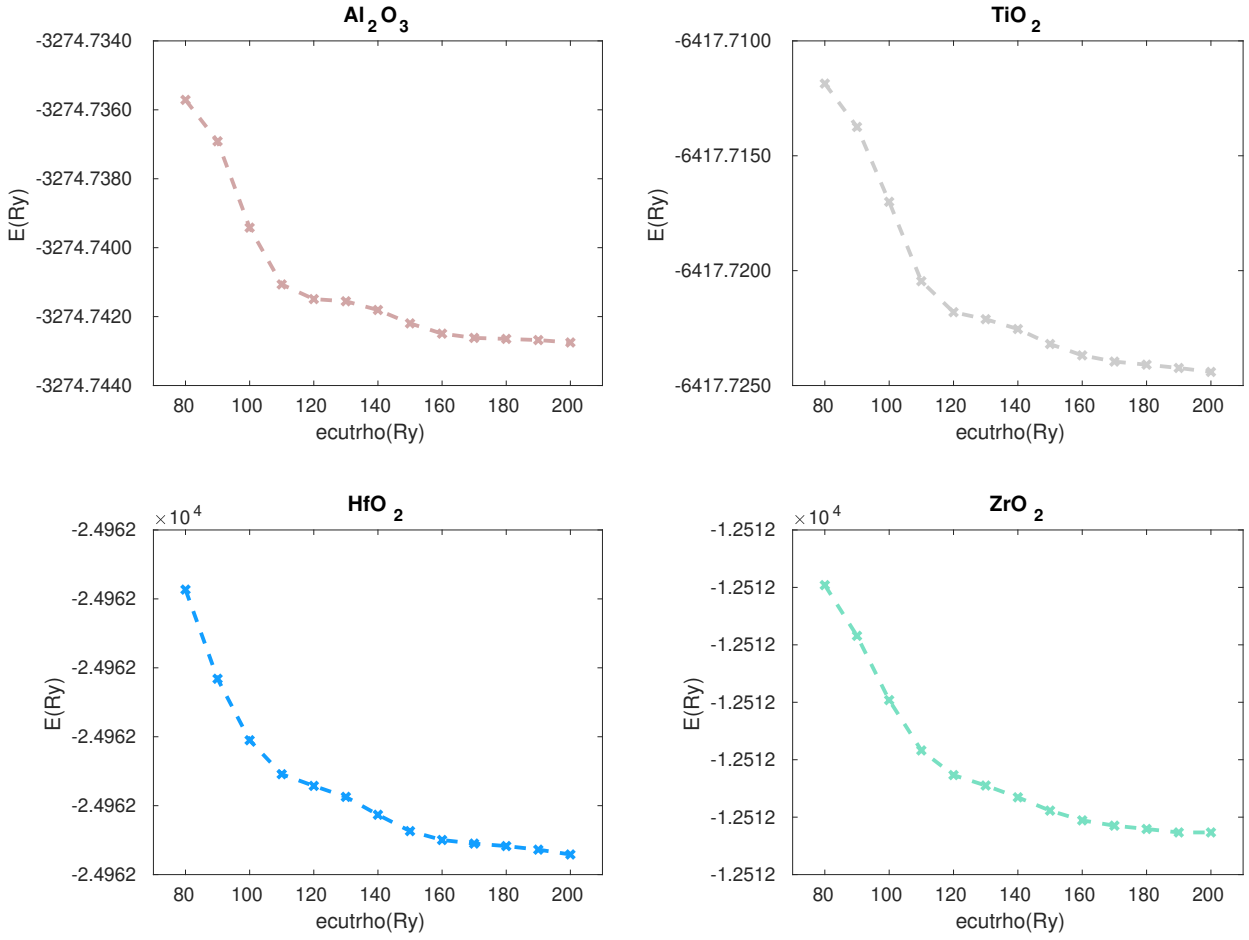


Figure S1 Graph showing energy convergence with respect to kinetic energy cutoff

S3 Charge Density Cutoff Convergence

The ecutrho (charge density cutoff) has been set to 1600Ry and is sufficiently high to converge the energies of all the MO unit cells. The convergence is shown in the plot below.

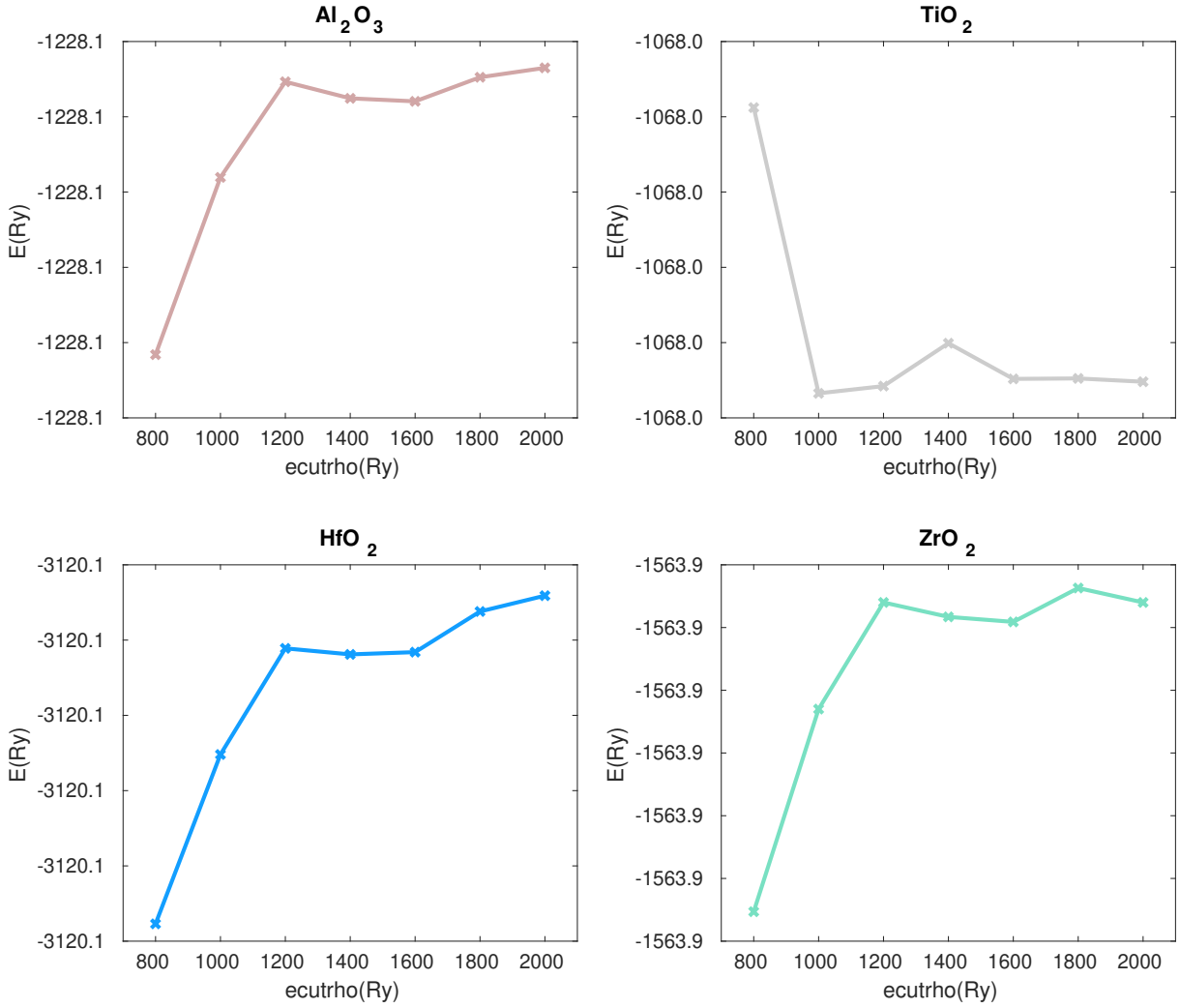


Figure S2 Graph showing energy convergence with respect to charge density cutoff

S4 Determination of most stable adsorption site

In order to determine the most stable adsorption site on the metal oxide surface, we considered all sites with high symmetry (top, bottom, and bridge) on the reconstructed MO slab. A Cl atom was placed on these sites, and their adsorption energies were computed. These energies have been shown in figure 1. The various adsorption sites are shown below.

S4.1 Al_2O_3

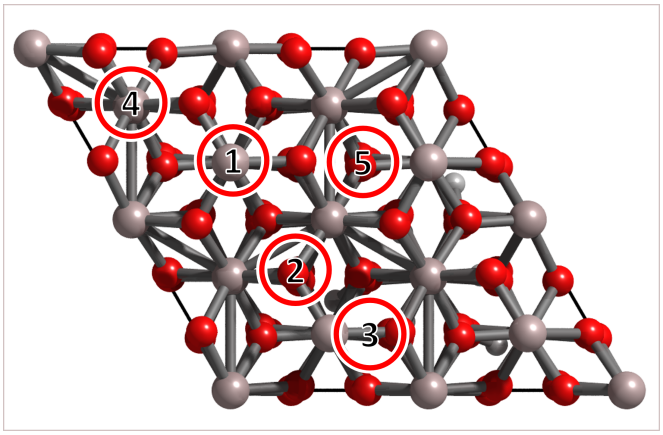
config1 Al-top

config2 O-top

config3 Hollow1 (on top of O of bottom layer)

config4 Hollow2 (on top of Al of bottom layer)

config5 Al-O bridge



S4.2 TiO_2

config1 Ti-top

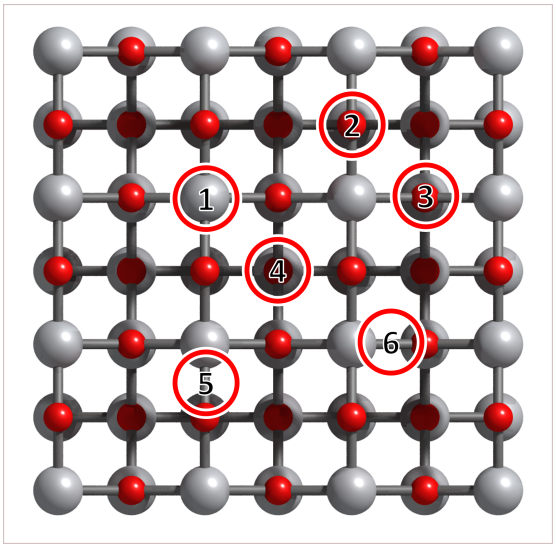
config2 O1-top

config3 O2-top

config4 Hollow

config5 Ti-O1 bridge

config6 Ti-O2 bridge



S4.3 HfO_2

config1 Hf1-top

config2 Hf2-top

config3 O1-top

config4 O2-top

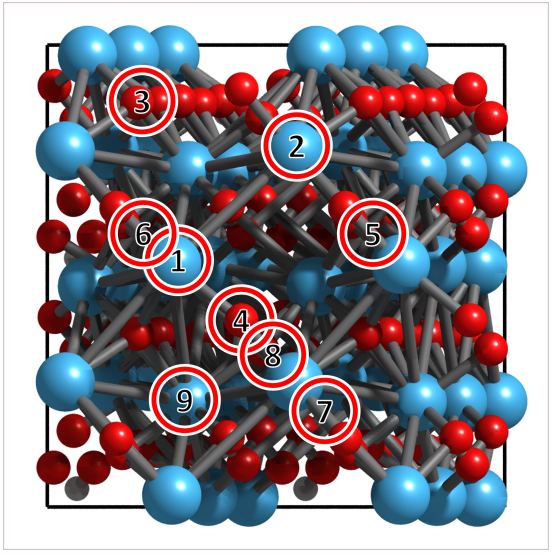
config5 Hf1-O1 bridge

config6 Hf1-O2 bridge

config7 Hf2-O1 bridge

config8 Hf2-O2 bridge

config9 Hollow



S4.4 ZrO_2

config1 Zr1-top

config2 Zr2-top

config3 O1-top

config4 O2-top

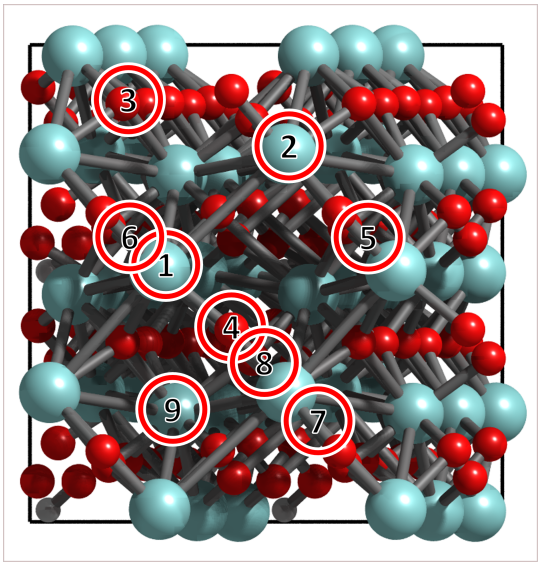
config5 Zr1-O1 bridge

config6 Zr1-O2 bridge

config7 Zr2-O1 bridge

config8 Zr2-O2 bridge

config9 Hollow



Following the adsorption calculations, we calculated the adsorption energies and these have been plotted below. The configuration with highest E(ads) is used for all calculations.

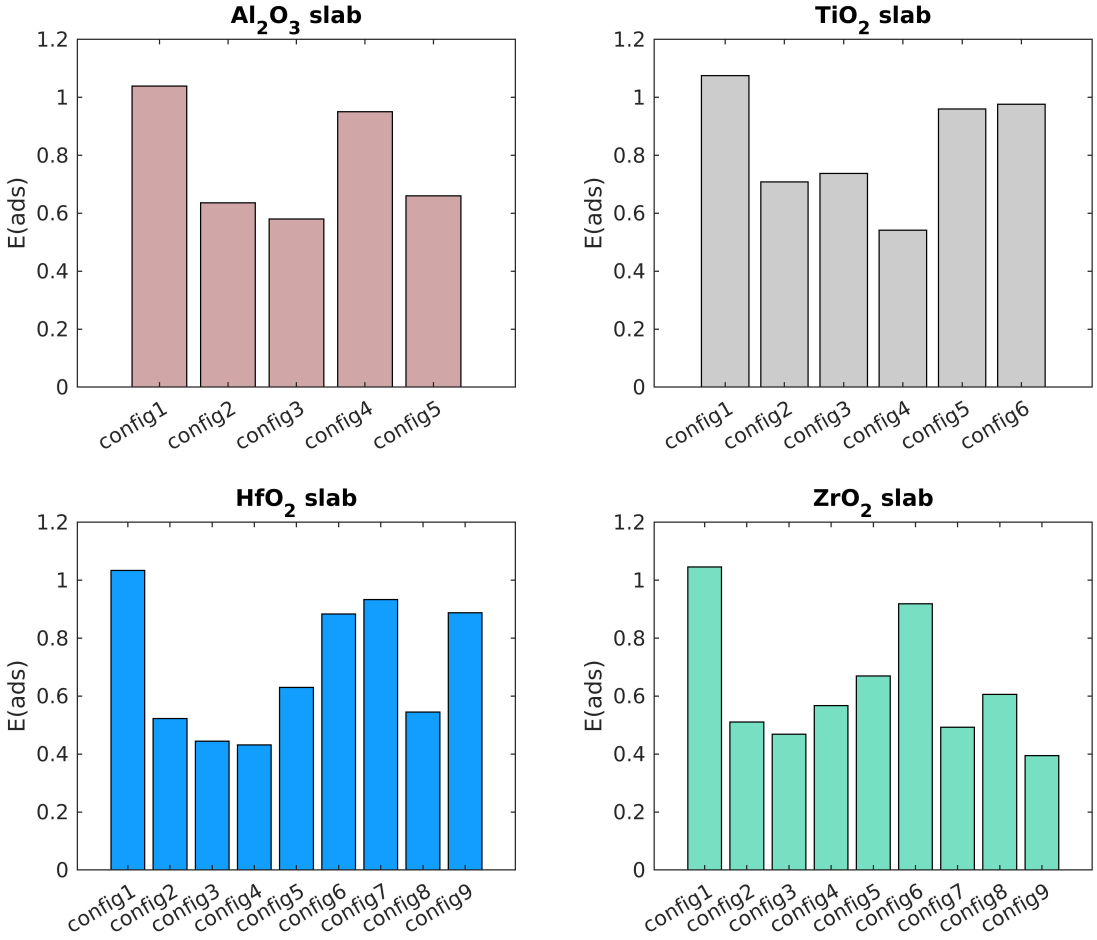


Fig. 1 Graph showing *E(ads)* for determining the most stable adsorption site

S5 Adsorption Energy Values

The adsorption energy values calculated using Eq. 1 in the main text have been given below.

Adatom	α-Al_2O_3	TiO_2	m$-HfO_2$	m$-ZrO_2$
Cl	-3.23	-2.46	-2.12	-2.07
S	-1.84	-4.35	-5.44	-5.22
O	-3.02	-3.86	-4.19	-3.91

S6 Bader charges on adsorbate atom

Adatom	α-Al_2O_3	TiO_2	m$-HfO_2$	m$-ZrO_2$
Cl	-0.76	-0.31	-0.51	-0.51
S	-0.40	0.16	-0.06	-0.02
O	-0.66	-0.62	-0.92	-0.90

S7 Distance of the adsorbate atoms from the topmost layer of MOs (in Å)

Adatom	α-Al_2O_3	TiO_2	m$-HfO_2$	m$-ZrO_2$
Cl	2.81	1.45	1.09	1.00
S	2.83	1.39	0.59	0.60
O	2.39	1.27	0.26	0.19

These distances have been calculated using the xyz2tab tool developed by Sebastian Dechert.[3]

S8 References

1 A. Dal Corso, *Comput. Mater. Sci.*, 2014, **95**, 337–350.

2 A. Corso, *pslibrary | A library of ultrasoft and PAW pseudopotentials*, `https://dalcorso.github.io/pslibrary/`.

3 S. Dechert, *xyz2tab*, `https://github.com/radi0sus/xyz2tab`, 2016.