Supporting Information

First-principles assessment of the reactions of boric acid on NiO (001) and ZrO_2 ($\bar{1}11$) surfaces

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1. Calculated bulk properties of NiO and ZrO_2

Table S1 : Lattice parameter (a), magnetic moment (m), bulk modulus (B) and band gap ($\Delta\varepsilon$) of NiO.

	Present work	**Calc.** [S1]	**Exp.**
a (Å)	4.19	4.20	4.17[S2]
Magnetic moment m (μ_B)	1.68	1.72	1.67[S3], 1.77[S4]
B (GPa)	186.1	202.5	205[S2]
$\Delta\varepsilon$ (eV)	3.16	3.20	4.2[S2]

Table S2 : Structural properties of ZrO_2 (Monoclinic C_{2h}^5) in the Wyckoff coordinates: ±(x, y, z) and ±(x, 1/2 - y, 1/2 + z)

	Present work	**Calc.** [S5]	**Exp.** [S6]
a (Å)	5.199	5.192	5.150
b/a	1.013	1.012	1.012
c/a	1.032	1.032	1.032
γ (deg.)	99.23	99.23	99.23
x_{Zr}	0.277	0.277	0.276
y_{Zr}	0.044	0.042	0.040
z_{Zr}	0.210	0.210	0.209
x_{O1}	0.071	0.071	0.069
y_{O1}	0.336	0.336	0.342
z_{O1}	0.342	0.341	0.345
x_{O2}	0.449	0.448	0.451
y_{O2}	0.758	0.757	0.758
z_{O2}	0.479	0.479	0.479

2. Tilting of $B(OH)_3$ on NiO (001) surface

DFT calculations were performed to understand the orientation dependence of the boric acid molecule on the NiO (001) surface. Calculations were performed to explore angles in the range -90^0 to 90^0, from the normal to the surface. The interval was chosen to be 10^0. A plot showing the variation of adsorption energy with orientation is shown in Figure S1. Calculations show that, indeed for a molecule to orient at different angles to the normal, the energy penalty is quite small and the molecule can explore these

orientations at higher temperatures. The most stable orientation is seen around -20^0 from the normal.

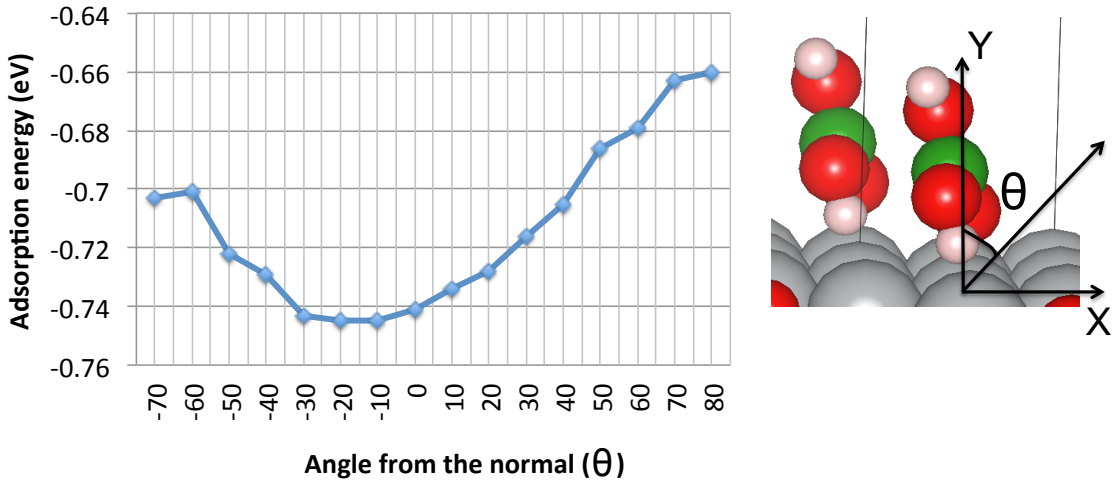

Figure S1 : Variation of the adsorption energy of $B(OH)_3$ on NiO (001) with orientation of the adsorbed molecule.

3. Additional adsorption configurations of $B(OH)_3$ on ZrO_2 ($\bar{1}11$)

Here, we present additional adsorption configurations of $B(OH)_3$ on ZrO_2 ($\bar{1}11$) as shown in Table S3. The molecular and dissociated adsorption configurations are seen to be metastable and hence are likely to be observed. In addition to the exothermic structure reported in the paper for the H_2O elimination reaction, several other structures were observed. However, these are found to be unfavorable with adsorption energy values of 0.46 and 1.75 eV.

Structure	**Adsorption mode**	**Adsorption energy (eV)**
O_5 ...(HO)B(OH)(HO)-Zr_2	Molecular (trans)	-0.68
Zr_1-(OH)B(OH)(HO)-Zr_3	Molecular (cis)	-0.70
Zr_2-OB(OH)(HO)-Zr_3 + O_6-H	Single O-H dissociated	-1.03
Zr_1-OB(OH)(HO)-Zr_3 + O_5-H	Single O-H dissociated	-1.50
Zr_2-OB(OH)O-Zr_3 + O_5-H + O_1-H	Double O-H dissociated	-1.24
Zr_2-OB(OH)O-Zr_3 + O_5-H + O_3-H	Double O-H dissociated	-1.41
Zr_3-OBO + O_5-H + H_2O	H_2O elimination	0.46
OB(OH)...O_5 + H_2O	H_2O elimination	1.75

Table S3 : Additional adsorption configurations, the corresponding adsorption mode and energy for $B(OH)_3$ on ZrO_2 ($\bar{1}11$).

References

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