Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information

Hydrogen Storage on Metal Oxide Model Clusters with Density-Functional Methods and Reliable van der Waals Corrections

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Table S1: Sampling of adsorption sites for H_2 on the $(MgO)_6$ cluster and corresponding adsorption energies obtained at VWN level.

Site	E_{ads}/eV
$X^{\parallel}$	0.31
$X^{\perp}$	0.31
$Y^{\perp}$	0.16
$Y^{\parallel}$	$\rightarrow X^{\parallel}$
$XX_c^{\parallel}$	$\rightarrow X^{\parallel}$
$YY_c^{\parallel}$	$\rightarrow X^{\parallel}$
$XY_c^{\parallel}$	$\rightarrow X^{\parallel}$
$XY_c^{\perp}$	$\rightarrow X^{\parallel}$
$XX_h^{\parallel}$	$\rightarrow X^{\parallel}$
$YY_h^{\parallel}$	$\rightarrow X^{\parallel}$
$XY_h^{\parallel}$	$\rightarrow X^{\parallel}$
$XY_h^{\perp}$	$\rightarrow X^{\parallel}$
$Hollow_h^{\parallel}$	$\rightarrow X^{\parallel}$
$Hollow_h^{\perp}$	$\rightarrow X^{\parallel}$
$Hollow_c^{\perp}$	$\rightarrow X^{\parallel}$
Endo h-h	-2.00
Endo e-e	-2.00
$Endo^{\parallel}$	-2.01

Figure S1: Adsorption sites for H_2 on $(MgO)_6$. Hydrogen, oxygen, and magnesium atoms are depicted as white, red, and blue spheres, respectively.

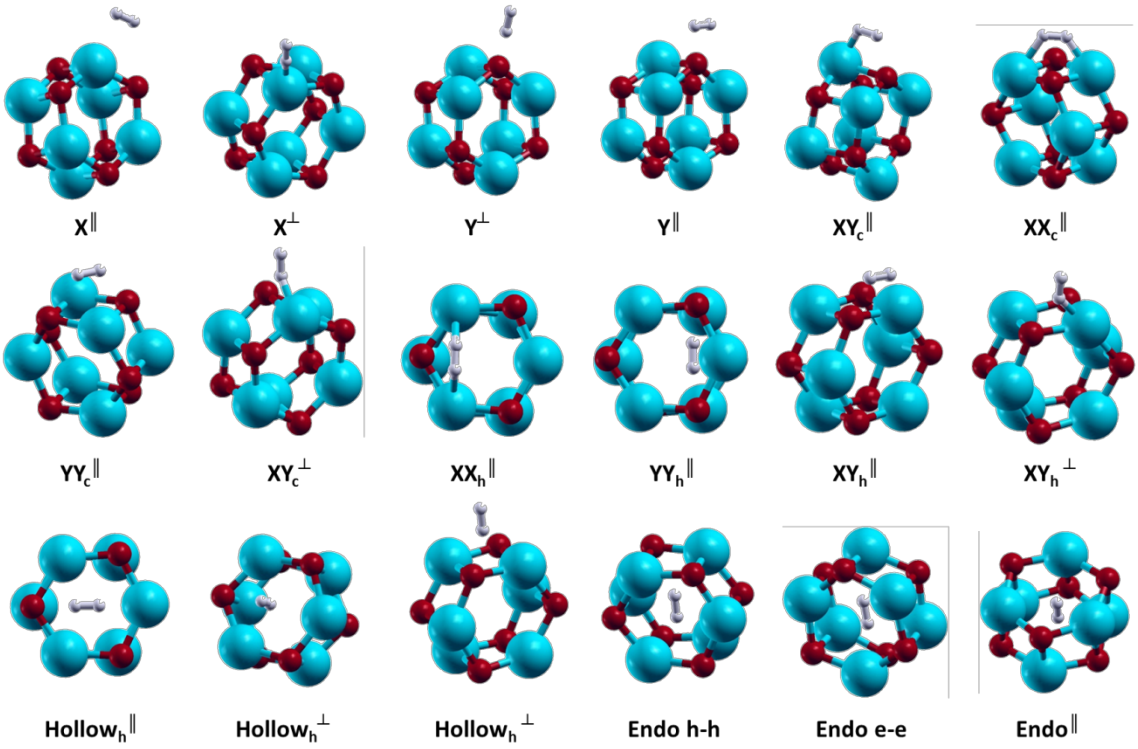

Table S2: Most stable adsorption sites and corresponding adsorption energies of a hydrogen molecule adsorbed on different $(XY)_6$ clusters as obtained from VWN calculations. *d*(H-X/Y) is the closest distance of one atom of the hydrogen molecule and the nearest cluster ion. The H_2 molecular bond length is shown as *d*(H-H).

Cluster	Site	E_{ads} eV	*d*(H-X/Y) Å	*d*(H-H) Å
$(ZnO)_6$	$X^{\parallel}$	0.38	1.89	0.79
	$X^{\perp}$	0.36	1.91	0.79
$(BeO)_6$	$X^{\parallel}$	0.36	1.74	0.78
	$X^{\perp}$	0.34	1.74	0.78
$(MgO)_6$	$X^{\parallel}$	0.31	2.10	0.81
	$X^{\perp}$	0.31	2.00	0.81
$(BaO)_6$	$Y^{\perp}$	0.28	1.79	0.82
$(BN)_6$	$X^{\parallel}$	0.24	1.70	0.79
$(ZnS)_6$	$X^{\parallel}$	0.25	2.04	0.79
	$X^{\perp}$	0.24	2.04	0.79
$(CdS)_6$	$X^{\parallel}$	0.19	2.34	0.78
	$X^{\perp}$	0.19	2.33	0.78
$(ZnSe)_6$	$X^{\parallel}$	0.22	2.06	0.79
	$X^{\perp}$	0.21	2.07	0.78
$(CdSe)_6$	$X^{\parallel}$	0.17	2.47	0.78
	$X^{\perp}$	0.17	2.38	0.78
$(NaI)_6$	$X^{\perp}$	0.14	2.44	0.78
	$X^{\parallel}$	0.12	2.37	0.77
$(LiF)_6$	$X^{\perp}$	0.15	1.99	0.77
	$X^{\parallel}$	0.12	2.05	0.77

Figure S2: Adsorption energy profiles of a hydrogen molecule on a $X^{\parallel}$ site for $(BeO)_6$ and $(ZnO)_6$, and on a $Y^{\perp}$ site for the $(BaO)_6$ cluster, for different vdW corrections due to Grimme (D3) and Ortmann (O) with standard and ionic parameters (indicated by a star) compared to CCSD(T) reference values.

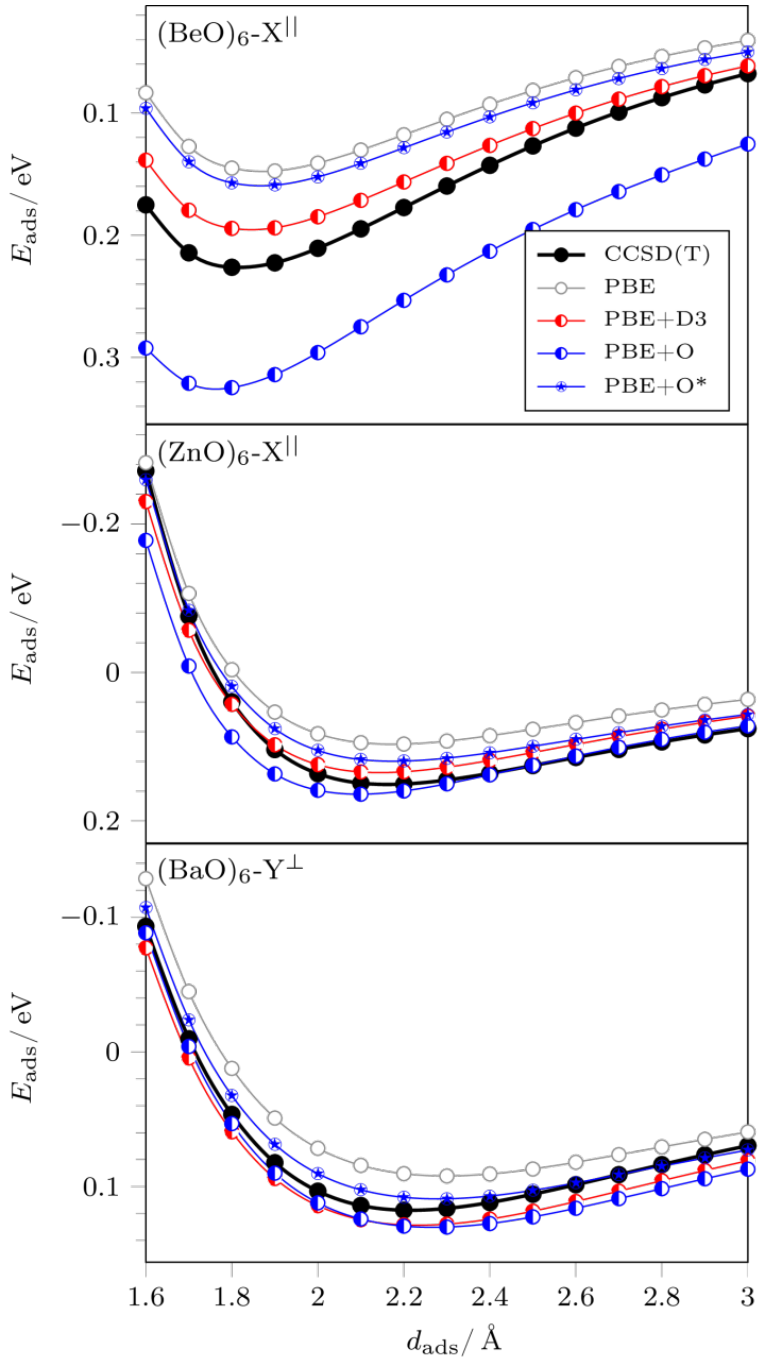

Table S3: Sampling of adsorption sites for atomic hydrogen on $(XO)_6$ clusters (X = Be, Mg, Ba, Zn) and corresponding adsorption energies as obtained at VWN level.

Site	$(ZnO)_6$ E_{ads}/eV	$(BeO)_6$ E_{ads}/eV	$(MgO)_6$ E_{ads}/eV	$(BaO)_6$ E_{ads}/eV
Y	0.53	$\rightarrow XY_c$	-0.08	0.30
X	-1.20	$\rightarrow XY_c$	-2.00	-2.08
XY_h	$\rightarrow$Y	-2.04	$\rightarrow$Y	$\rightarrow$Y
XX_h	-1.72	$\rightarrow XY_h$	$\rightarrow$Y	$\rightarrow$Y
YY_h	$\rightarrow$Y	$\rightarrow XY_h$	$\rightarrow$Y	$\rightarrow$Endo
XY_c	$\rightarrow$Y	-1.97	$\rightarrow$Y	$\rightarrow$Y
$Hollow_h$	$\rightarrow XX_h$	-2.32	-1.86	$\rightarrow$Y
$Hollow_c$	$\rightarrow$X	$\rightarrow XY_c$	$\rightarrow$Y	$\rightarrow$Y
Endo	-2.49	-4.24	-2.10	-1.69

Figure S3: Adsorption sites for atomic hydrogen on $(MgO)_6$. Hydrogen, oxygen, and magnesium atoms are depicted as white, red, and blue spheres, respectively.