Supporting Information For:

Reactivity of metal oxide clusters with hydrogen peroxide and water – A DFT study evaluating of the performance of different exchange-correlation functionals.

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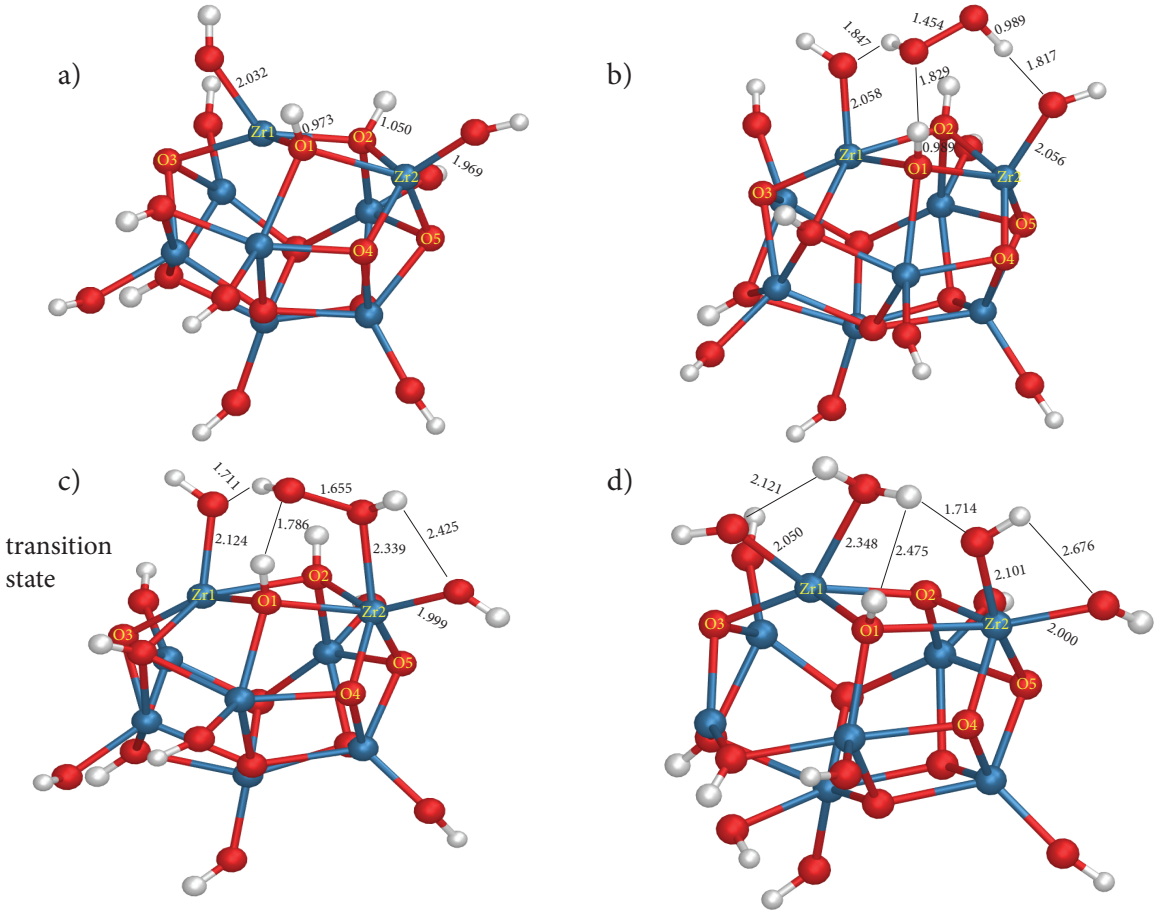

Figure S1. Optimized structures for the reaction of H_2O_2 with the surface of the m-$(ZrO_2)_8$ cluster: a) reactant, b) molecular adsorption of H_2O_2 onto the surface HO groups, c) transition-state for the cleavage of the O-O bond in H_2O_2, d) a stable product of the decomposition of H_2O_2. Bond distances given in Å.

Table S1. Mulliken charges of the Zr atoms directly involved in the bonding with 2HO radicals on the $(ZrO_2)_8$ cluster.

Geometry	*Zr1*	*Zr2*
Reactant	1.58378	1.91206
Product - 2HO$^{\bullet}$ adsorbed	1.84183	2.21459

Table S2. Mulliken charges of the Zr atoms on the $(ZrO_2)_2$ cluster.

Geometry	*Zr1*	*Zr2*
Reactant	1.93345	1.93778
Product - 2HO$^{\bullet}$ adsorbed	2.14270	2.15706

Table S3. Mulliken charges of the Ti atoms on the $(TiO_2)_2$ cluster.

Geometry	*Ti1*	*Ti2*
Reactant	1.66016	1.70011
Product - 2HO$^{\bullet}$ adsorbed	2.03994	1.95480

Table S4. Mulliken charges of the Y atoms on the $(Y_2O_3)_2$ cluster.

Geometry	*Y1*	*Y2*
Reactant	1.69991	1.35578
Product - 2HO$^{\bullet}$ adsorbed	2.13625	2.13777

Table S5. Vibrational frequencies (cm^{-1}) calculated in this work and literature experimental data.

Surface species	B3LYP/LACV3P++**	M06/LACV3P++**	Experimental[1]
HO terminal	3879 – 3763	3811 – 3795	3822 – 3743
HO bibridging	3754 – 3685	3763 – 3225	3755 – 3568
H_2O (H-O stretch)	3698 – 3154	3732 – 3225	—
H_2O (scissoring)	1628	1614	—
H_2O (rocking)	1037	1050	—

Table S6. Relative (to B3LYP) and total (s) computational time for a Single Point Energy calculation using the different functionals using the LACV3P**++ basis set. The geometry corresponds to the molecular adsorption of H_2O_2 onto the surface of a $(ZrO_2)_8$ cluster (Figure S1(b)).

Computation Time	B3LYP	PWPW91	PBE	PBE0	M06	M06-L
Relative to B3LYP	1	0.616	0.653	0.876	2.728	2.476
Total (s)	4615	2845	3015	4041	12590	11426
Number of SCF cycles	40	43	43	38	39	41
Relative to B3LYP (per SCF cycle)	1	0.573	0.608	0.922	2.798	2.415

1. S. T. Korhonen, M. Calatayud and A. O. I. Krause, *The Journal of Physical Chemistry C*, 2008, **112**, 6469-6476.