Supporting Information

Theoretical study on the catalytic role of water in methanol steam reforming on PdZn(111)

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Table S1 Comparison of the adsorption energies of key species with and without co-adsorbed water

Species	E_{ads}[a] / eV	$E_{co\text{-}ads}$[b] / eV	ΔE_{ads}[c] / eV	d(O···H)[d] / Å
H_2O	–0.33	–0.95	–0.29	1.70
CH_3OH	–0.39	–0.99	–0.27	1.71
CH_3O	–2.32	–2.73	–0.08	1.49
H_2COOH	–2.09	–2.70	–0.28	1.75
HCOOH	–0.39	–0.89	–0.17	1.81
bi-HCOO	–2.73	–3.33	–0.27	1.80
mono-HCOO	–2.24	–2.84	–0.27	1.59

[a] The adsorption energy of separated key species. [b] The co-adsorption energy of key species and a water molecule. [c] $\Delta E_{ads} = E_{co\text{-}ads} - (E_{ads} + E_{ads(H_2O)})$, where $E_{ads(H_2O)}$ refers to the adsorption energy (–0.33 eV) of a separated H_2O. [d] The length of hydrogen bond between water and key species.

Table S2 Activation barriers (E_a) and reaction energies (ΔE) of the dehydrogenation of methanol and methoxyl at different water coverages

Elementary reaction	E_a / eV	ΔE / eV
$CH_3OH^* \rightarrow CH_3O^* + H^*$	1.27	0.15
$CH_3OH^* + H_2O^* \rightarrow CH_3O^* + H^* + H_2O^*$	0.86	0.29
$CH_3OH^* + 2H_2O^* \rightarrow CH_3O^* + H^* + 2H_2O^*$	0.91	0.37
$CH_3OH^* + 3H_2O^* \rightarrow CH_3O^* + H^* + 3H_2O^*$	0.89	0.42
$CH_3O^* \rightarrow HCHO^* + H^*$	1.41	1.18
$CH_3O^* + H_2O^* \rightarrow HCHO^* + H^* + H_2O^*$	1.16	0.60
$CH_3O^* + 2H_2O^* \rightarrow HCHO^* + H^* + 2H_2O^*$	1.01	0.49
$CH_3O^* + 3H_2O^* \rightarrow HCHO^* + H^* + 3H_2O^*$	1.16	0.61

Table S3 Activation barriers (E_a) and reaction energies (ΔE) of formaldehyde dehydrogenation with and without the assistance of water

Elementary reaction	E_a / eV	ΔE / eV
$HCHO^* \rightarrow HCO^* + H^*$	0.91	0.24
$HCHO^* + H_2O^* \rightarrow HCO^* + H^* + H_2O^*$	0.88	0.28
$HCHO^* + 2H_2O^* \rightarrow HCO^* + H^* + 2H_2O^*$	0.87	0.12