Supplementary Information: First-Principles Investigation of Water Adsorption and Dissociation on the Al/Y-doped Mg (0001) Surface

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The reaction equation for the adsorption and dissociation process of water molecules on the Mg(0001) surface are as follow:

$$H_2O^* \rightarrow H^* + OH^* \tag{1}$$

The reaction energy of hydrolysis (ΔG_{dis}) is the energy required for water molecules to dissociate into H and OH (relative energy between the product and the reactant). It can reflect the trend of water molecule dissociation from a thermodynamic perspective. It can be calculated by using the following formula.

$$\begin{aligned}
\Delta G_{dis} &= \Delta G_{ads}^{\mathrm{H,OH}} - \Delta G_{ads}^{\mathrm{H_2O}} \\
&= (\Delta E_{ads}^{\mathrm{H,OH}} + \Delta E_{ZPE}^{\mathrm{H,OH}} - T\Delta S_{\mathrm{H,OH}}) - (\Delta E_{ads}^{\mathrm{H_2O}} + \Delta E_{ZPE}^{\mathrm{H_2O}} - T\Delta S_{\mathrm{H_2O}}) \\
&= (\Delta E_{ads}^{\mathrm{H,OH}} - \Delta E_{ads}^{\mathrm{H_2O}}) + (\Delta E_{ZPE}^{\mathrm{H,OH}} - \Delta E_{ZPE}^{\mathrm{H_2O}}) - (T\Delta S_{\mathrm{H,OH}} - T\Delta S_{\mathrm{H_2O}}) \\
&= (\Delta E_{ads}^{\mathrm{H,OH}} - \Delta E_{ads}^{\mathrm{H_2O}}) + (\Delta E_{ZPE}^{\mathrm{H,OH}} - \Delta E_{ZPE}^{\mathrm{H_2O}}) - T\Delta S_{dis} \\
&= \frac{1}{N}[(E_{slab+ads}^{\mathrm{H,OH}} - E_{slab} - NE_{ads}) - (E_{slab+ads}^{\mathrm{H_2O}} - E_{slab} - NE_{ads})] + \Delta E_{ZPE} - T\Delta S_{dis} \\
&= \frac{1}{N}(E_{slab+ads}^{\mathrm{H,OH}} - E_{slab+ads}^{\mathrm{H_2O}}) + \Delta E_{ZPE} - T\Delta S_{dis}
\end{aligned} \tag{2}$$

Here, $\Delta G_{ads}^{\mathrm{H_2O}}$ is the adsorption free energy of water molecules on the Mg(0001) surface. $\Delta G_{ads}^{\mathrm{H,OH}}$ is the adsorption free energy of dissociated H and OH on the Mg(0001) surface. $\Delta E_{ads}^{\mathrm{H_2O}}$ and $\Delta E_{ads}^{\mathrm{H,OH}}$ are the adsorption energies of water molecules and co-adsorbed H and OH calculated by first-principles methods, respectively. $\Delta E_{ZPE}^{\mathrm{H_2O}}$ is the change in zero-point energy of the system before and after adsorption of water molecules. $\Delta E_{ZPE}^{\mathrm{H,OH}}$ is the change in zero-point energy of the system before and after adsorption of H and OH. $E_{slab+ads}^{\mathrm{H_2O}}$ is the total energy of the Mg slab model with water molecule adsorption. $E_{slab+ads}^{\mathrm{H,OH}}$ is the total energy of the Mg slab model with H and OH adsorption. The variable N denotes the quantity of adsorbed atoms.

ΔS_{dis} is the entropy change of the water dissociation reaction process, which can be calculated using the following formula:

$$\begin{aligned}
\Delta S_{dis} &= \Delta S_{\mathrm{H,OH}} - \Delta S_{\mathrm{H_2O}} \\
&= S(\mathrm{H^*,OH^*}) - S(\mathrm{H_2O^*})
\end{aligned} \tag{3}$$

Here, based on vibration frequency analysis and statistical thermodynamic methods, we calculate the entropy values of H_2O^*, H^* and OH^*. $T\Delta S_{dis}$ during the hydrolysis reaction is -0.13 eV.

In addition, ΔE_{ZPE} represents the change in zero-point energy during the hydrolysis reaction process. According to the water dissociation reaction in equation 1, ΔE_{ZPE} is the difference between the zero-point energy of adsorbed H and OH and the zero-point energy of adsorbed water molecules, with a value of -0.017 eV.

In summary, the reaction energy of hydrolysis after zero-point energy and entropy correction is as follows:

$$\begin{aligned}\Delta G_{dis} &= \frac{1}{N}(E_{slab+ads}^{\mathrm{H,OH}} - E_{slab+ads}^{\mathrm{H_2O}}) + \Delta E_{ZPE} - T\Delta S_{dis} \\ &= \frac{1}{N}(E_{slab+ads}^{\mathrm{H,OH}} - E_{slab+ads}^{\mathrm{H_2O}}) + 0.147\mathrm{eV}\end{aligned} \tag{4}$$

Currently, based on the CI-NEB data calculated above, we have obtained the minimum energy path (MEP) and corresponding atomic configuration for water molecules to dissociate into H and OH on the Al or Y doped Mg(0001) surface, as shown in Fig. S1 and Fig. S2, respectively. It can be seen that the energy barrier for water molecules to dissociate on Al or Y-doped Mg(0001) surface is lower than that on pure Mg(0001) surface, and the energy barrier observed on Y-doped Mg(0001) surface is relatively lower. This indicates that the dissociation reaction rate of water molecules on the Y-doped Mg(0001) surface is relatively fast, accompanied by exothermic reactions. In addition, the dissociated H and OH occupy stable adsorption sites with lower energy on the Y-doped Mg(0001) surface, indicating that Y doping has a higher thermodynamic driving force for the dissociation of water molecules on the Mg surface.

In summary, doping with Al or Y atoms promotes the dissociation of water molecules on the Mg(0001) surface，with Y doping having a stronger promoting effect.

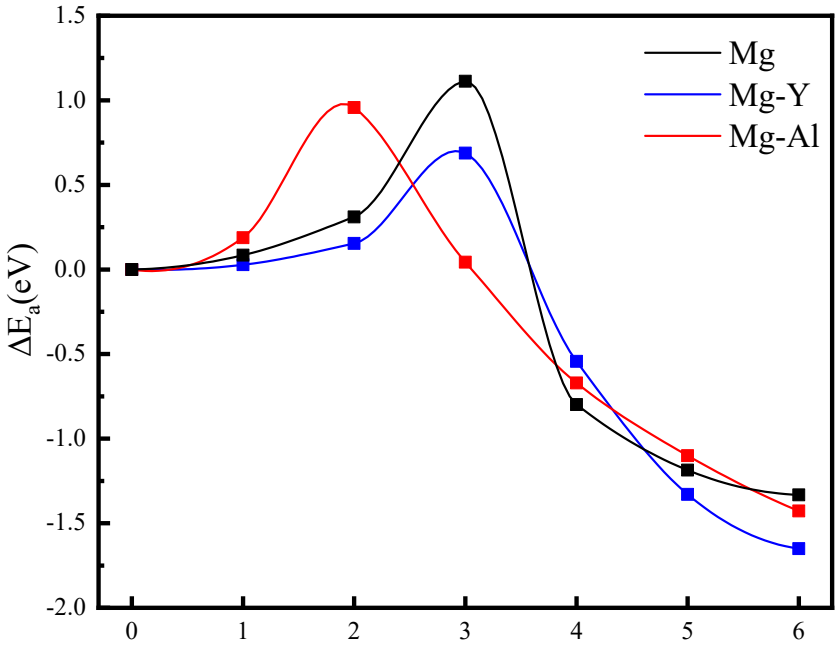

Fig. S1 The minimum energy path for hydrolysis dissociation into H and OH calculated based on density functional theory (DFT).

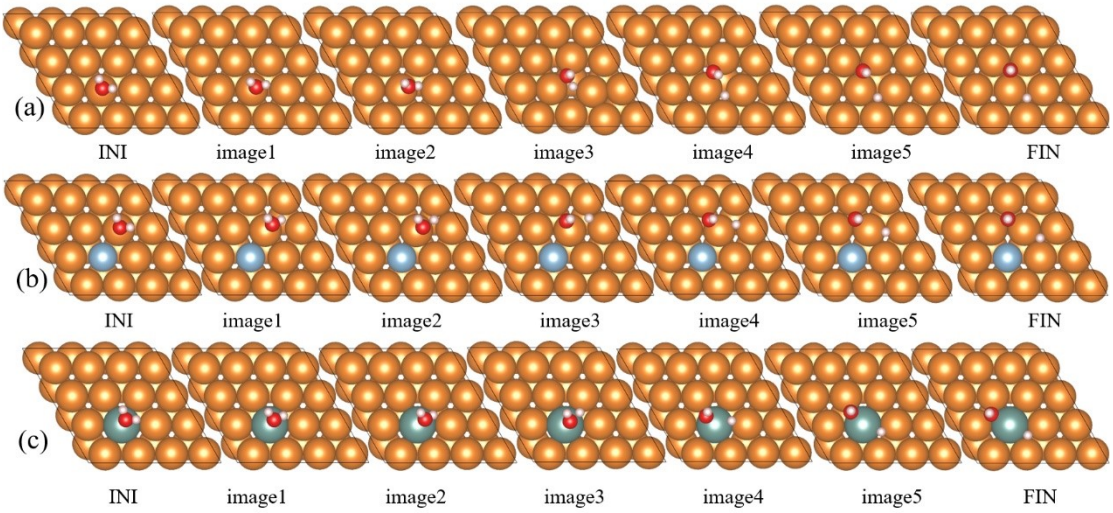

Fig. S2 Top views of the minimum energy path configurations for H_2O dissociation on the Al or Y-doped Mg (0001) surface. (a) On the pure Mg(0001) surface; (b) On the Al-doped Mg(0001) surface; (c) On the Y-doped pure Mg(0001) surface.

We established a model for the reactants and products of formula (3), as shown in Fig. S3. Due to the lowest adsorption free energy of water molecules on the first nearest neighbor TOP (II) site of Al-doped Mg (0001) surface, We assumed that the second water molecule still adsorbed at the TOP site of the first nearest neighbor of the Al atom and dissociated at the FCC and HCP sites surrounding that site, as shown in Fig. S3(a). On Y doped Mg (0001) surface, we assumed that the second water molecule adsorbed at the TOP site of the second nearest neighbor of the Y atom with relatively low adsorption free energy, and dissociated at the FCC and HCP sites around this site, as shown in Fig. S3(b). In this model, the OH was believed to remain at its adsorption site during the binding of two H atoms. After optimizing the reactants and products in Fig.S3, the adsorption free energy for H_2 generation on the Al or Y-doped Mg (0001) surfaces was obtained, as shown in Table S1.

The results indicated that the Gibbs free energy of H_2 generation on the Al-doped Mg (0001) surface was $\Delta G_{H_2} = -0.387\ eV$. On the Y-doped Mg (0001) surface, the Gibbs free energy of H_2 generation was $\Delta G_{H_2} = 0.083\ eV$. This difference was mainly due to the lower electronegativity of Y, which resulted in a higher absolute value of the adsorption free energy $|\Delta G_{H^*}|$ of H atoms [5]. The stronger adsorption effect hindered the desorption and generation of H_2, thus suppressing the overall hydrogen evolution reaction(HER).

It is worth noting that after water molecules dissociate into H and OH on the Mg surface, the subsequent hydrogen evolution stage may not occur through the Tafel reaction but through the Heyrovsky reaction, and the Tafel reaction may also occur at other sites. Nevertheless, our computational results have confirmed thermodynamically that the generation of H_2 on both doped surfaces is possible.

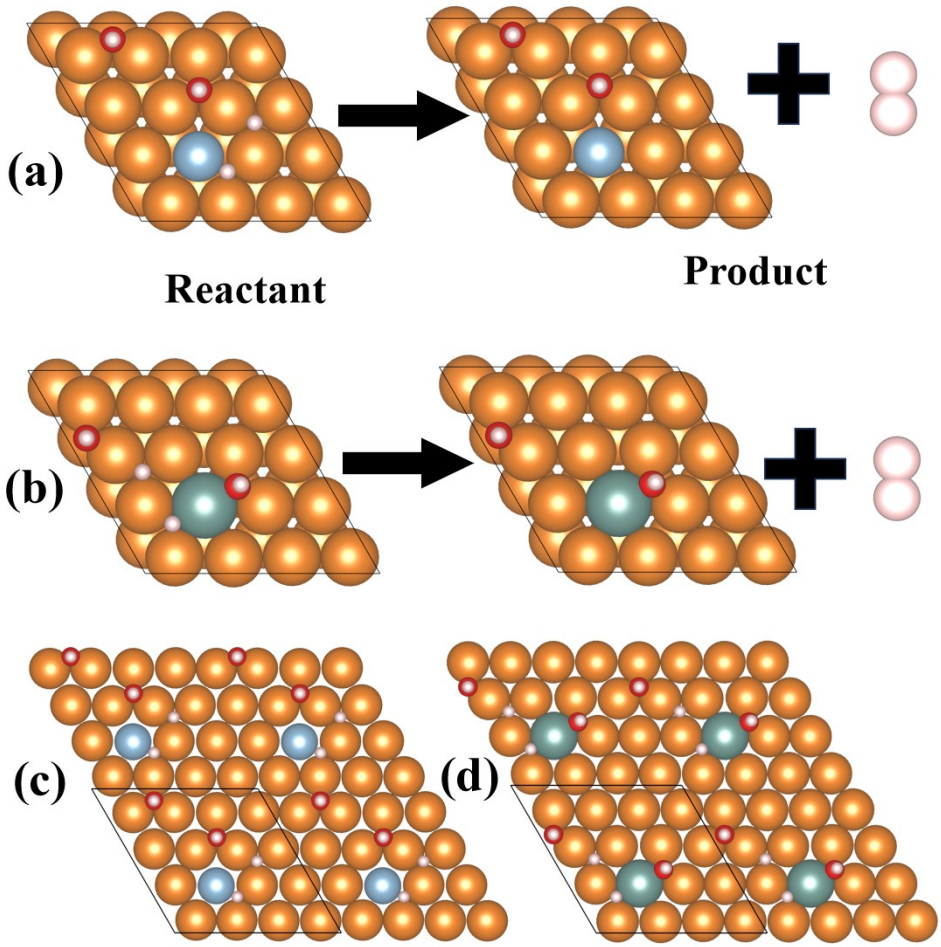

Fig. S3 Structural optimization model of reactants and products for the Tafel reaction of H and OH dissociated from water molecules on the Al or Y-doped Mg (0001) surface. (a) on the Al-doped Mg (0001) surface; (b) on the Y-doped Mg (0001) surface; (c) The dissociation model of 2 × 2 water molecules on the Al-doped Mg (0001) surface; (d) The dissociation model of 2 × 2 water molecules on the Y-doped Mg (0001) surface

Table S1 Calculated energy and thermodynamic quantities of $Mg(OH)_2$ and H_2 formation on the Al or Y doped Mg (0001) surface.

System	$E_{Mg(OH_{ad})_2(H_{ad})_2}$ (eV)	$E_{Mg(OH_{ad})_2}$ (eV)	E_{H_2} (eV)	ΔE(eV)	TΔS(eV)	ΔG_{H_2} (eV)
Mg-1Al	-168.746	-161.983	-6.75	0.013	0.4	-0.387
Mg-1Y	-172.038	-164.805	-6.75	0.483	0.4	0.083