Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Structure and stability of CaH_2 surfaces: on the possibility of electron-rich surfaces in metal hydrides for catalysis

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A. Structure of CaH_2

Figure S1 (A), (B) and (C) display different choices of CaH_2 unit cells where c-axis parallel to [001], [110], and [111] crystallographic orientations, respectively. These unit-cell structures make it convenient to create surfaces by axial scanning method. Slabs with all possible terminations can then be generated by axial scanning and cleaving the bulk crystal along [001], [110] and [111] crystallographic axes.

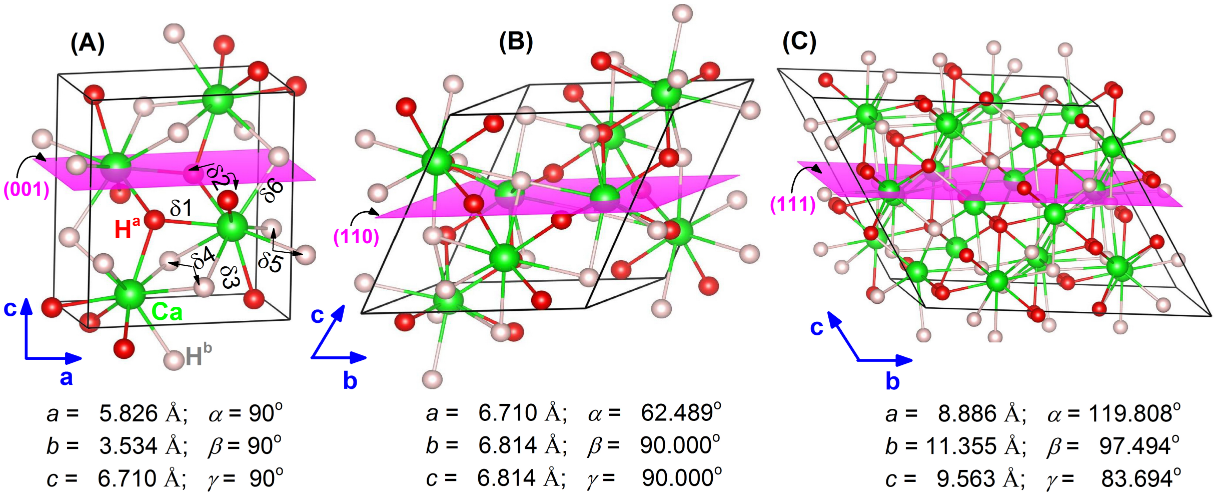


Figure S1: (A), (B) and (C) Different choices of cell of CaH_2 where c-axis parallel to [001], [110], and [111] crystallographic orientations, respectively. The shaded area indicate (001), (110), and (111) lattice planes, respectively. Sticks connecting a Ca to its nearest neighbor H atoms. Two sets of symmetrically inequivalent hydrogens are denoted by H^a and H^b. Ca-H^a bond lengths: $\delta 1 = 2.265\,Å$, $\delta 2 = 2.225\,Å$ (two bonds), and $\delta 3 = 2.267\,Å$; Ca-H^b bond lengths: $\delta 4 = 2.568\,Å$ (two bonds), $\delta 5 = 2.461\,Å$ (two bonds), and $\delta 6 = 2.391\,Å$.

B. Doubly-occupied vacancy band on a CaH_2 surface

To demonstrate that a surface vacancy can accommodate an additional electron transferred from a nearby H^-, we constructed (111) slabs with a neutral hydrogen vacancy and a Ne substitution for a surface hydrogen. As Ne is an inert gas element, the extra electron (otherwise transferred to the substituted H to form H^-) will be transferred to the vacancy site,

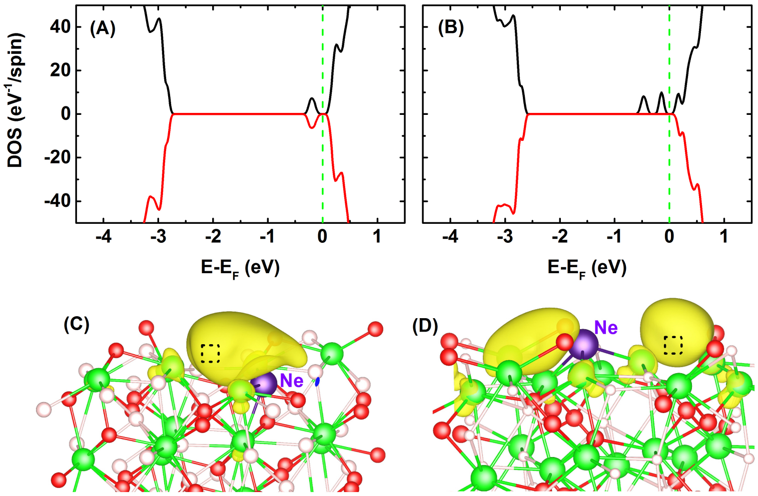


Figure S2: Total density of states (DOS) for a (111) slab containing a neutral hydrogen vacancy and a Ne substitution for a surface hydrogen nearby (A) and further from (B) the vacancy. (C) and (D) surfaces of the constant charge density for electrons occupying the gap states in (A) and (B), respectively. The dotted squares indicate positions of hydrogen vacancies.

form a new confined electron at a different site, or become delocalized. We found that when the Ne ion is close enough to the hydrogen vacancy, the extra electron is localized in the vacancy site and spin-paired with the vacancy-induced electron in the same vacancy band [Figure S2 (A) and (C)]. On the other hand, if the Ne is far enough from the vacancy, the extra electron is localized nearby the Ne and has the same spin as the vacancy-induced one [Figure S2 (B) and (D)]. The same conclusions have been reached when He, instead of Ne, was used as a substitute for the surface hydrogen.

C. Equation for Gibbs free energy of CaH_2 surface and boundary conditions

Gibbs free energy of surface – Consider a CaH_2 slab with N^s_{Ca} and N^s_{H} being the numbers of Ca and H, respectively. The Gibbs free energy of the surface is defined as,

$$\Omega^s = G^s_{slab} - N^s_{\mathrm{Ca}}\mu_{\mathrm{Ca}} - N^s_{\mathrm{H}}\mu_{\mathrm{H}} \tag{1}$$

where G^s_{slab} is Gibbs free energy of the CaH_2 slab and μ_{Ca} and μ_{H} are chemical potentials of Ca and H ions in the CaH_2 slab, respectively. If the surface is in equilibrium with bulk

CaH_2 reservoir, the sum of the chemical potentials is constrained to be equal to chemical potential $\mu_{\mathrm{CaH_2}}$ of the bulk CaH_2

$$\mu_{\mathrm{CaH_2}} = N^b_{\mathrm{Ca}}\mu_{\mathrm{Ca}} + N^b_{\mathrm{H}}\mu_{\mathrm{H}} \tag{2}$$

where N^b_{Ca} and N^b_{H} are the numbers of Ca and H, respectively, in the bulk. Therefore, using equation (2) we can eliminate μ_{Ca} in equation (1). Then the expression of Ω becomes

$$\Omega^s = G^s_{slab} - \frac{N^s_{\mathrm{Ca}}}{N^b_{\mathrm{Ca}}}\mu_{\mathrm{CaH_2}} - \left(N^s_{\mathrm{H}} - N^s_{\mathrm{Ca}}\frac{N^b_{\mathrm{H}}}{N^b_{\mathrm{Ca}}}\right)\mu_{\mathrm{H}} \tag{3}$$

Put

$$\Gamma^s_{\mathrm{Ca,H}} = N^s_{\mathrm{H}} - N^s_{\mathrm{Ca}}\frac{N^b_{\mathrm{H}}}{N^b_{\mathrm{Ca}}} \tag{4}$$

A positive or negative value of $\Gamma^s_{\mathrm{Ca},H}$ indicates an excess or deficit, respectively, of H ions with respect to Ca ones in the CaH_2 slab. Therefore, a surface corresponding to positive, negative, or zero $\Gamma^s_{\mathrm{Ca},H}$ is said to be hydrogen-rich, hydrogen-poor, or stoichiometric, respectively. Substituting $\Gamma^v_{\mathrm{Ca,H}}$ into the equation (3), we obtain

$$\Omega^s = G^s_{slab} - \frac{N^s_{\mathrm{Ca}}}{N^b_{\mathrm{Ca}}}\mu_{\mathrm{CaH_2}} - \Gamma^s_{\mathrm{Ca,H}}\mu_{\mathrm{H}} \tag{5}$$

where we define

$$\mu_{\mathrm{H}} = \frac{1}{2}E(\mathrm{H_2}) + \Delta\mu_{\mathrm{H}} \tag{6}$$

where $\Delta\mu_{\mathrm{H}}$ is variation of chemical potential of hydrogen atom with respect to half an energy of the molecular hydrogen $E(\mathrm{H_2})$. Substituting equation (6) into (5), we obtain

$$\Omega^s = \phi^s - \Gamma^s_{\mathrm{H,Ca}}\Delta\mu_{\mathrm{H}} \tag{7}$$

where

$$\phi^s = G^s_{slab} - \frac{N^s_{\mathrm{Ca}}}{N^b_{\mathrm{Ca}}}\mu_{\mathrm{CaH_2}} - \frac{1}{2}\Gamma^s_{\mathrm{Ca,H}} E(\mathrm{H_2}) \tag{8}$$

The chemical potential $\mu_{\mathrm{CaH_2}}$ is nothing but the molar Gibbs free energy of the bulk $\mathrm{CaH_2}$

$$\mu_{\mathrm{CaH_2}} = g^b_{\mathrm{CaH_2}} \tag{9}$$

Therefore, equation (8) can be rewritten,

$$\phi^s = G^s_{slab} - \frac{N^s_{\mathrm{Ca}}}{N^b_{\mathrm{Ca}}} g^b_{\mathrm{CaH_2}} - \frac{1}{2}\Gamma^s_{\mathrm{Ca,H}} E(\mathrm{H_2}) \tag{10}$$

In general, we have

$$g^b_{\mathrm{CaH_2}} = E^{static}_{\mathrm{CaH_2}} + E^{phonon}_{\mathrm{CaH_2}} - TS_{\mathrm{CaH_2}} + pV_{\mathrm{CaH_2}} \tag{11}$$

where $E^{static}_{\mathrm{CaH_2}}$ and $E^{phonon}_{\mathrm{CaH_2}}$ are, respectively, static and vibrational components of the crystal energy; $S_{\mathrm{CaH_2}}$ is entropy; and $V_{\mathrm{CaH_2}}$ is volume; T and p are applied temperature and pressure of the system. Throughout the present work, we approximate the Gibbs free energy to the total energy obtained from *ab initio* calculation, *i.e.*,

$$g^b_{\mathrm{CaH_2}} \approx E^{tot}_{\mathrm{CaH_2}} \tag{12}$$

Similarly,

$$G^s_{slab} \approx E^{tot}_{slab} \tag{13}$$

Our estimation indicates that total contribution of the vibrational, entropic and mechanical terms is negligible. The above approximations result in an error of the order of 10^{-2} J/m^2 in $\mathrm{CaH_2}$ surface energy.

Boundary conditions – To make the $\mathrm{CaH_2}$ phase stable, precipitation of Ca metal and condensation of hydrogen ions into hydrogen gas should be prevented. These conditions can be expressed through relations of chemical potentials of the atomic constituents of CaH_2, *i.e.*, μ_{Ca} and μ_{H}, and the Gibbs free energies (*i.e.*, molar chemical potentials) of the undesired precipitated substances:

$$\text{(i)} \quad 2\mu_{\mathrm{H}} \leq g^b_{\mathrm{H}_2} \tag{14}$$

$$\text{(ii)} \quad \mu_{\mathrm{Ca}} \leq g^b_{\mathrm{Ca}} \tag{15}$$

From equation (6) and the approximations in equations (12) and (13), the condition (i) is equivalent to

$$\text{(i)} \quad \Delta\mu_{\mathrm{H}} \leq 0 \tag{16}$$

The upper bound $\Delta\mu_{\mathrm{H}} = 0$ is called hydrogen-rich limit.

Similarly, we have

$$\text{(ii)} \quad \Delta\mu_{\mathrm{Ca}} \leq 0 \tag{17}$$

From equation (2), we have

$$g^b_{\mathrm{CaH}_2} = N^b_{\mathrm{Ca}}(g^b_{\mathrm{Ca}} + \Delta\mu_{\mathrm{Ca}}) + N^b_{\mathrm{H}}(\frac{1}{2}E(\mathrm{H}_2) + \Delta\mu_{\mathrm{H}}) \tag{18}$$

or

$$\Delta g^b_{\mathrm{CaH}_2} = N^b_{\mathrm{Ca}}\Delta\mu_{\mathrm{Ca}} + N^b_{\mathrm{H}}\Delta\mu_{\mathrm{H}} \tag{19}$$

where

$$\Delta g^b_{\mathrm{CaH}_2} = g^b_{\mathrm{CaH}_2} - N^b_{\mathrm{Ca}}g^b_{\mathrm{Ca}} - \frac{1}{2}N^b_{\mathrm{H}}E(\mathrm{H}_2) \tag{20}$$

From the approximation in (12)

$$\Delta g^b_{\mathrm{CaH}_2} \approx E^{tot}_{\mathrm{CaH}_2} - N^b_{\mathrm{Ca}}E^{tot}_{\mathrm{Ca}} - \frac{1}{2}N^b_{\mathrm{H}}E(\mathrm{H}_2) \tag{21}$$

where E^{tot}_{Ca} is total energy per Ca atom.

From equations (17) and (19), we have

$$\text{(ii)} \quad \Delta\mu_{\mathrm{H}} \geq \frac{1}{N^b_{\mathrm{H}}}\Delta g^b_{\mathrm{CaH_2}} \tag{22}$$

The lower bound $\Delta\mu_{\mathrm{H}} = \Delta g^b_{\mathrm{CaH_2}}/N^b_{\mathrm{H}}$ is called the hydrogen-poor limit. From *ab initio* calculations, $E^{tot}_{\mathrm{Ca}} = -2.000$ eV and $E(\mathrm{H_2}) = -6.770$ eV. For a 8×8 bulk supercell, in which $N^b_{\mathrm{Ca}} = 32$ and $N^b_{\mathrm{H}} = 64$, total energy calculation gave $E^{tot}_{\mathrm{CaH_2}} = -334.402$ eV. Therefore, the hydrogen-poor limit is $\Delta\mu_{\mathrm{H}} = -0.840$ eV. From (16) and the calculation above, the range of $\Delta\mu_{\mathrm{H}}$ is

$$-0.840 \leq \Delta\mu_{\mathrm{H}} \leq 0 \quad \text{(in eV)} \tag{23}$$

D. Temperature and pressure dependence of chemical potential of hydrogen in $\mathrm{CaH_2}$ slabs

In this part, we present the calculation of variation of chemical potential of hydrogen, $\Delta\mu_{\mathrm{H}}$, in the $\mathrm{CaH_2}$ slab as a function of temperature and pressure.

We start from the Maxwell's relation

$$\left(\frac{\partial\mu_{\mathrm{H}}}{\partial p_{\mathrm{H_2}}}\right)_T = \frac{k_B T}{2}\frac{1}{p_{\mathrm{H_2}}} \tag{24}$$

Its solution takes the form

$$\mu_{\mathrm{H}}(T, p_{\mathrm{H_2}}) = \mu_{\mathrm{H}}(T, p^{\mathrm{o}}_{\mathrm{H_2}}) + \frac{k_B T}{2} ln \frac{p_{\mathrm{H_2}}}{p^{\mathrm{o}}_{\mathrm{H_2}}} \tag{25}$$

where standard state pressure $p^{\mathrm{o}}_{\mathrm{H_2}} = 0.1$ MPa and k_B is Boltzmann's constant. We rewrite equation (25) as

$$\mu_{\mathrm{H}}(T, p_{\mathrm{H_2}}) = \mu_{\mathrm{H}}(0\mathrm{K}, p^{\mathrm{o}}_{\mathrm{H_2}}) + \left[\mu_{\mathrm{H}}(T, p^{\mathrm{o}}_{\mathrm{H_2}}) - \mu_{\mathrm{H}}(0\mathrm{K}, p^{\mathrm{o}}_{\mathrm{H_2}})\right] + \frac{k_B T}{2} ln \frac{p_{\mathrm{H_2}}}{p^{\mathrm{o}}_{\mathrm{H_2}}} \tag{26}$$

Oxygen in the $\mathrm{CaH_2}$ slab is in equilibrium with $\mathrm{H_2}$ gas. Therefore,

$$\mu_{\mathrm{H}}(T,p_{\mathrm{H_2}})=\frac{1}{2}\mu_{\mathrm{H_2}}(T,p_{\mathrm{H_2}})=\frac{1}{2}G^{m}_{\mathrm{H_2}}(T,p_{\mathrm{H_2}}) \tag{27}$$

where $G^{m}_{\mathrm{H_2}}(T,p_{\mathrm{H_2}})$ is molar Gibbs free energy of $\mathrm{H_2}$ gas. Then the terms enclosed in [..] in equation (26) can be rewritten

$$\begin{aligned}\mu_{\mathrm{H}}(T,p^{\mathrm{o}}_{\mathrm{H_2}})-\mu_{\mathrm{H}}(0\mathrm{K},p^{\mathrm{o}}_{\mathrm{H_2}}) &= \frac{1}{2}\left[G^{m}_{\mathrm{H_2}}(T,p^{\mathrm{o}}_{\mathrm{H_2}})-G^{m}_{\mathrm{H_2}}(0\mathrm{K},p^{\mathrm{o}}_{\mathrm{H_2}})\right]\\ &\equiv \frac{1}{2}\Delta G^{m}_{\mathrm{H_2}}(T,p^{\mathrm{o}}_{\mathrm{H_2}}) \qquad (28)\end{aligned}$$

Using the relation $G=H-TS$, where H and S are enthalpy and entropy, respectively, we obtain

$$\begin{aligned}\Delta G^{m}_{\mathrm{H_2}}(T,p^{\mathrm{o}}_{\mathrm{H_2}}) = &\quad \left[H^{m}_{\mathrm{H_2}}(T,p^{\mathrm{o}}_{\mathrm{H_2}})-H^{m}_{\mathrm{H_2}}(T_R,p^{\mathrm{o}}_{\mathrm{H_2}})\right]\\ &- \left[H^{m}_{\mathrm{H_2}}(0\mathrm{K},p^{\mathrm{o}}_{\mathrm{H_2}})-H^{m}_{\mathrm{H_2}}(T_R,p^{\mathrm{o}}_{\mathrm{H_2}})\right]\\ &- TS^{m}_{\mathrm{H_2}}(T,p^{\mathrm{o}}_{\mathrm{H_2}}) \qquad (29)\end{aligned}$$

Equation (29) can then be separated as

$$\begin{aligned}A &= \left[H^{m}_{\mathrm{H_2}}(T,p^{\mathrm{o}}_{\mathrm{H_2}})-H^{m}_{\mathrm{H_2}}(T_R,p^{\mathrm{o}}_{\mathrm{H_2}})\right] \qquad (30)\\ B &= \left[H^{m}_{\mathrm{H_2}}(0\mathrm{K},p^{\mathrm{o}}_{\mathrm{H_2}})-H^{m}_{\mathrm{H_2}}(T_R,p^{\mathrm{o}}_{\mathrm{H_2}})\right] \qquad (31)\\ C &= TS^{m}_{\mathrm{H_2}}(T,p^{\mathrm{o}}_{\mathrm{H_2}}) \qquad (32)\end{aligned}$$

The A, B, and C values can be determined from thermodynamic tables.[1]

From the equation (6), (26), (28), and the approximation $\frac{1}{2}E(\mathrm{H_2})=\mu_{\mathrm{H}}(0\mathrm{K},p^{\mathrm{o}}_{\mathrm{H_2}})$ we obtain the equation determining the variation of chemical potential of oxygen, $\Delta\mu_{\mathrm{H}}$, in

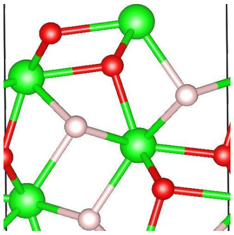
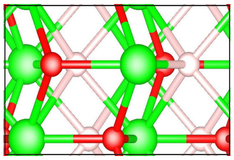
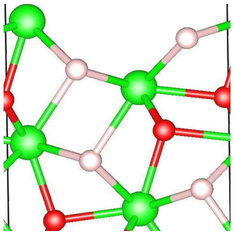
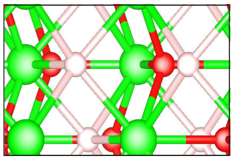
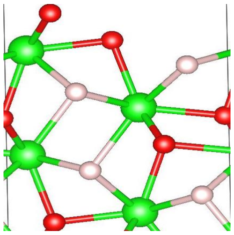
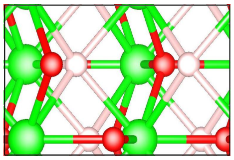
CaH_2 slab with temperate and oxygen pressure.

$$\Delta\mu_{\mathrm{H}}(T,p_{\mathrm{H}_2}) = \frac{1}{2}\left[\Delta G^{m}_{\mathrm{H}_2}(T,p^{o}_{\mathrm{H}_2}) + k_B T ln \frac{p_{\mathrm{H}_2}}{p^{o}_{\mathrm{H}_2}}\right] \tag{33}$$

E. Surface nomenclature

In this section, we explain surface nomenclature and show atomic structures of (001), (110) and (111) surfaces. Symmetric slabs with all possible terminations were generated by axial scanning and cleaving the bulk crystal along [001], [110] and [111] crystallographic axes.

Table S1: Surface nomenclature for (001)CaH_2. Positive, negative, or zero $\Gamma^{s}_{\mathrm{Ca},H}$ indicates a hydrogen-rich (-r), hydrogen-poor (-p), or stoichiometric (-s) surface, respectively.

Name	Surface structure		$\Gamma^{s}_{\mathrm{Ca},H}$	Explanation
	Side view	Top view		
$\mathrm{CaH}^a - p$			-2	The top most layer is Ca; the subsurface layer is $\mathbf{H}^a$.
$\mathrm{CaH}^b - p$			-2	The top most layer is Ca; the subsurface layer is $\mathbf{H}^b$.
$\mathrm{H}^a - r$			2	The top most layer is $\mathbf{H}^a$; the subsurface layer is also $\mathbf{H}^a$.

. . . continued (001)CaH_2

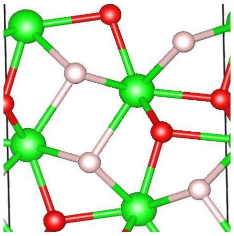
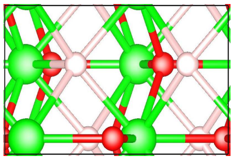
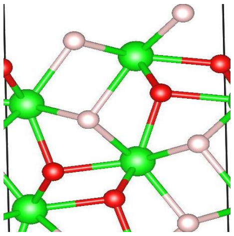
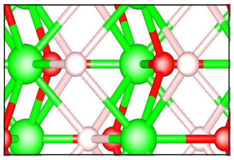
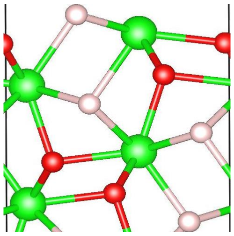
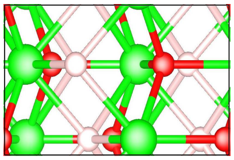
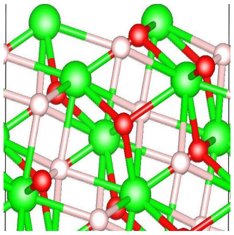
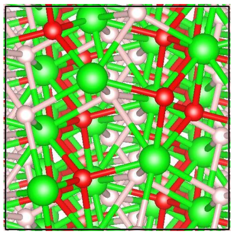
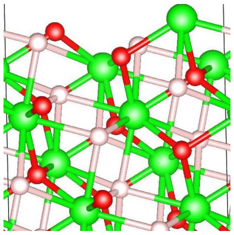
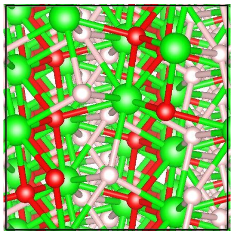
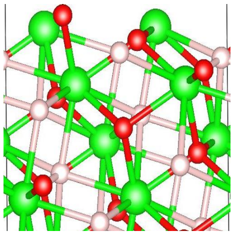
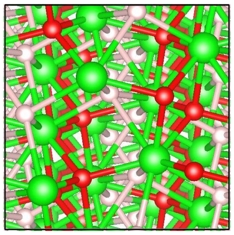
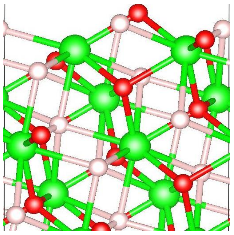
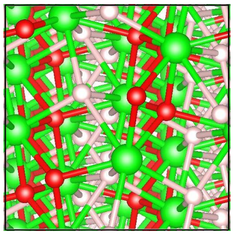
Name	Surface structure		$\Gamma^{s}_{\mathrm{Ca},H}$	Explanation
	Side view	Top view		
$H^a - s$			0	The top most layer is **H^a**; the subsurface layer is **Ca**.
$H^b - r$			2	The top most layer is **H^b**; the subsurface layer is also **H^b**.
$H^b - s$			0	The top most layer is **H^b**; the subsurface layer is **Ca**.

Table S2: Surface nomenclature for (110)CaH_2. Positive, negative, or zero $\Gamma^{s}_{\mathbf{Ca},H}$ indicates a hydrogen-rich (-r), hydrogen-poor (-p), or stoichiometric (-s) surface, respectively.

Name	Surface structure		$\Gamma^{s}_{\mathrm{Ca},H}$	Explanation
	Side view	Top view		
Ca$-p$			-4	The top most layer is Ca.
Ca$-s$			0	The top most layer is Ca of lower concentration.
H$^a - p$			-2	The top most layer is **H**^{a}; the subsurface layer is Ca.
H$^a - r$			4	The top most layer is **H**^{a}; the subsurface layer is **H**^{b}.

. . . continued (110)CaH_2

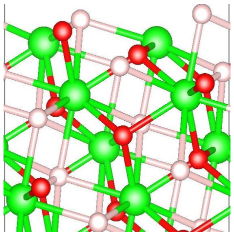
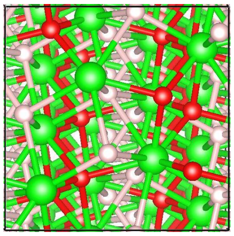
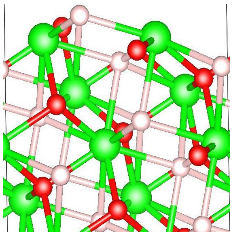
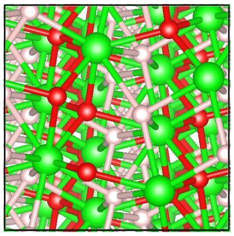
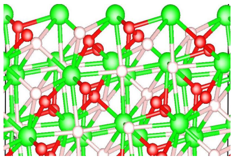
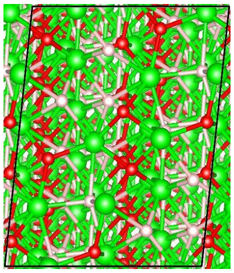
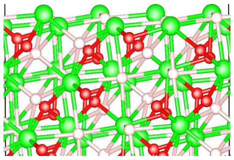
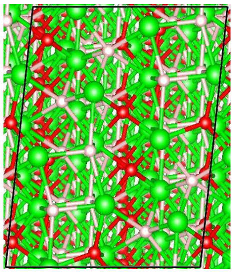
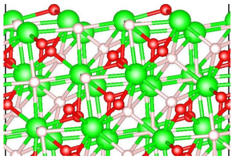
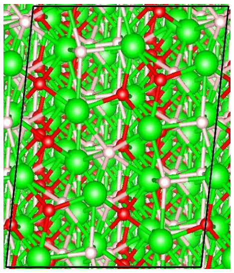
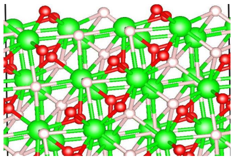
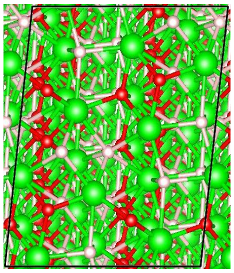
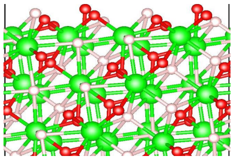
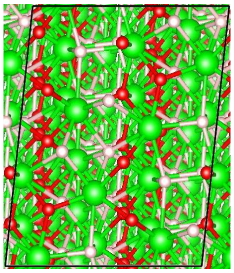
Name	Surface structure		$\Gamma^{s}_{\mathrm{Ca},H}$	Explanation
	Side view	Top view		
$H^b - r$			2	The top most layer is **H^b**; the subsurface layer is also **H^b**.
$H^b - s$			0	The top most layer is **H^b**; the subsurface layer is **H^a**.

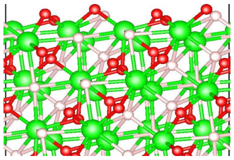
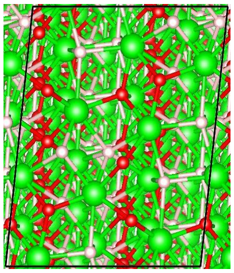
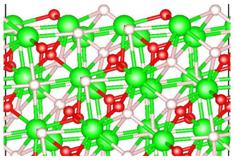
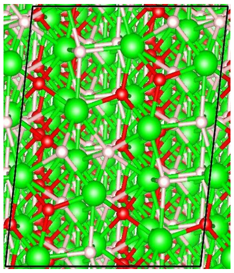
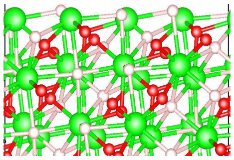
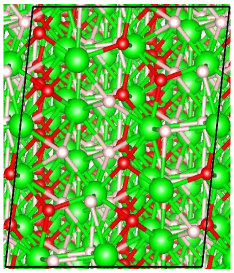
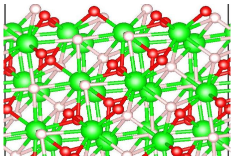
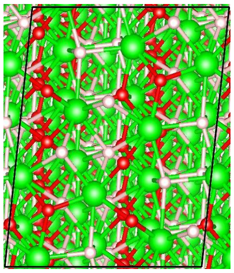
Table S3: Surface nomenclature for (111)CaH_2. Positive, negative, or zero $\Gamma^{s}_{\mathrm{Ca},H}$ indicates a hydrogen-rich (-*r*), hydrogen-poor (-*p*), or stoichiometric (-*s*) surface, respectively.

Name	Surface structure		$\Gamma^{s}_{\mathrm{Ca},H}$	Explanation
	Side view	Top view		
$CaH^a - p$			-4	The top most layer is Ca; the subsurface layer is **H^a**.

…continued (111)$\mathrm{CaH_2}$

Name	Surface structure		$\Gamma^{s}_{\mathrm{Ca},H}$	Explanation
	Side view	Top view		
$\mathrm{CaH}^b - p$			-12	The top most layer is **Ca**; the subsurface layer is **H^b**.
$\mathrm{H}^a - p$			-8	The top most layer is **H^a**; the subsurface layer is **Ca**.
$\mathrm{H}^a - s$			0	The top most layer is **H^a**; the subsurface layers are **H^b**, **H^a**, and **Ca**, in that order.
$\alpha{-}\mathrm{H}^a - r$			12	The top most layer is **H^a**; the subsurface layers are **H^b**, **H^a**, and **H^a**, in that order.

. . . continued (111)CaH_2

Name	Surface structure		$\Gamma^{s}_{\mathrm{Ca},H}$	Explanation
	Side view	Top view		
β–$H^a - r$			4	The top most layer is **H**^{a}; the subsurface layers are **H**^{a}, **H**^{b}, and **H**^{a}, in that order.
$H^b - p$			-4	The top most layer is **H**^{b}; the subsurface layers are **H**^{a} and **Ca**.
α–$H^b - r$			4	The top most layer is **H**^{b}; the subsurface layer is **Ca**.
β–$H^b - r$			8	The top most layer is **H**^{b}; the next two subsurface layers are **H**^{a}.

References

(1) *JANAF Thermochemical Tables*, 3rd edition, by M. W. Chase, Jr., C. A. Davies,1. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, published by Am. Chem. Soc. and Am. Inst. Phys. for NBS (now NIST), Washington, DC (1986).