Electronic Supplementary Information

for

A first-principle study of the tuning effect of Fe_2O_3 cluster on the dehydrogenation properties of $LiBH_4$(001) surface

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Section S1. Model and calculating considerations

The optimized bulk $LiBH_4$ was used as a basis for constructing surface slab of $LiBH_4$. The surface model of $LiBH_4$ (001) surface studied here was a 2×2×1 supercell slab consisting of six layers of $LiBH_4$ formula units and had a total number of 144 atoms (24 $LiBH_4$ formula units). Fe_2O_3 cluster was placed at different positions and directions on $LiBH_4$ (001) surface to generate the optimized lowest-energy structures. The static total energy and electronic properties calculations were performed based on the optimized lowest-energy structures geometries. The method to calculate hydrogen removal energy is that we firstly remove one H atom out from the optimized Fe_2O_3 cluster doped $LiBH_4$ (001) surface and then optimize the H atom removed structures. The difference of total energy between the H atom removed and unremoved optimized structures is defined as hydrogen removal energy.

Section S2. Density of state of Fe2-$B2H_4^-$ subject

The states of H6 *s*, B2 *p*, and Fe2 *d* orbitals are all smaller than those of H1, B1, and Fe1 atoms, which demonstrates the hybridizations of H6 *s*, B2 *p*, and Fe2 *d* orbitals is weaker than the hybridizations of H1 *s*, B1 *p*, and Fe1 *d* orbitals. Thus, it is no doubt that the interaction between Fe2 and $B2H_4^-$ unit is weaker than the interaction between Fe1 and $B1H_4^-$ units. A new peak arise at -1.75 eV due to the coupling effect of the spin-unrestricted Fe *d* orbitals. However, the peaks at -1.75 eV in the partial DOSs of H6 and B2 atoms are smaller than those of H1 and B1 atoms, which also verifies that the interaction between Fe2 and $B2H_4^-$ unit is weaker than the interaction between Fe1 and $B1H_4^-$ units.

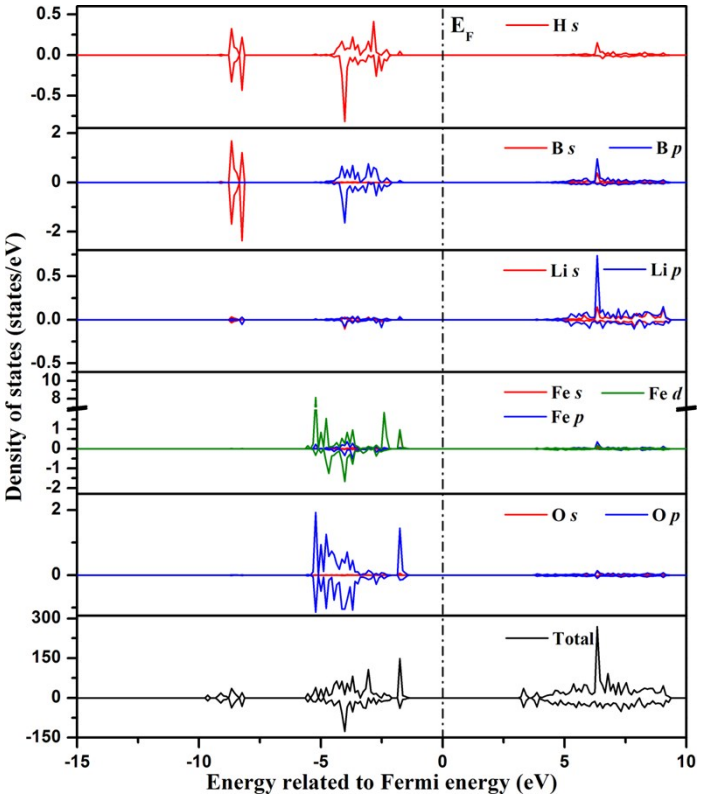

Figure S1: The calculated total and partial density of states for Fe_2O_3 cluster doped $LiBH_4$ (001) surface. The selected atoms are H6, B2, Li2, Fe2, and O3 atoms (labeled in Fig. 1b), respectively.

Section S3. Hydrogen removal energy

Hydrogen removal energy is successfully used to explain the bond strength of X-H in the complex hydrogen storage materials. In order to sturdy the doping of Fe_2O_3 cluster on the bond strength of B-H bonds in $LiBH_4$ (001) surface, we calculate hydrogen removal energies of these H atoms in the top two layer of Fe_2O_3 cluster doped $LiBH_4$ (001) surface. The studied H atoms are labeled in Fig. S2, and the calculated results are listed in Table S1.

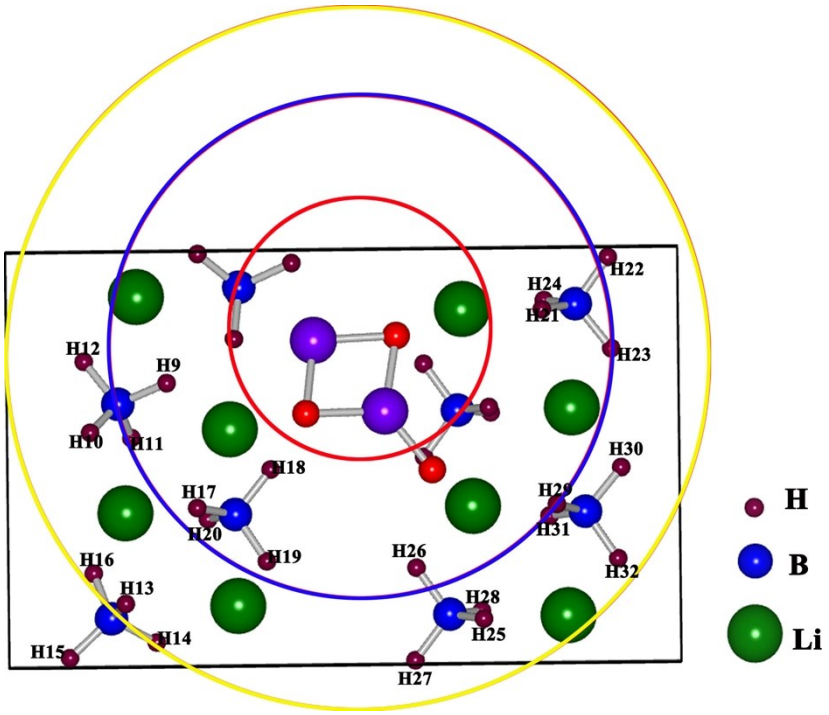

Figure S2: Top view of the top two layers of the optimized structure of Fe_2O_3 cluster doped $LiBH_4$ (001) surface.

Table S1 The calculated hydrogen removal energy for these specific H atoms (labeled in Fig. S2).

H atom	Removal energy (eV)	H atom	Removal energy (eV)	H atom	Removal energy (eV)
H9	0.05	H17	0.65	H25	0.24
H10	0.05	H18	0.15	H26	0.25
H11	2.33	H19	0.11	H27	0.32
H12	0.07	H20	0.13	H28	0.16
H13	2.27	H21	0.24	H29	0.09
H14	2.25	H22	0.16	H30	0.17
H15	2.27	H23	0.28	H31	0.38
H16	2.25	H24	0.15	H32	0.05