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Features of interaction of adsorbed Cr and O atoms with hydrogen on the magnesium hydride surface

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Abstract. *In this paper, the first-principles study of the structural stability of the MgH_2, MgH_2–O, MgH_2–Cr, MgH_2–CrO systems was carried out to identify the features of influence of adsorbed chromium and oxygen atoms on the hydrogen binding energy with the magnesium hydride surface. It was revealed that the presence of oxygen prevents chromium from forming large clusters on the hydride surface. Chromium and oxygen atoms adsorbed on the surface of magnesium hydride weaken the Mg-H bonds potentially leading to the release of hydrogen at lower temperatures compared to pure MgH_2.*
Key words: *hydrogen desorption, magnesium hydride, surface, ab initio calculation.*

Introduction

Hydrogen energy is a promising candidate to replace traditional fossil fuels in terms of efficiency and ecology. From the hydrogen usage perspective, the effective, safe, technically and economically consistent hydrogen storage methods with high adsorption/desorption rate and capacity should be proposed. In terms of hydrogen transfer and storage, the use of solid-state hydrogen storage materials is considered to be the most efficient. Magnesium is the most promising material for this task due to its abundance (about 2.35% of the Earth's crustal mass), low density and sustainability. However, the application of magnesium-based alloys is limited by low cyclic stability and sorption/desorption rate, high sorption/desorption activation temperature and enthalpy (75 кJ/mol). To reduce these characteristics, magnesium is mixed with various catalytic additives and doped with transition metals [1]. Within the present work, the interaction of adsorbed chromium and oxygen atoms on the surface of magnesium hydride with hydrogen atoms is studied based on first principles. The structural stability of the MgH_2, MgH_2–O, MgH_2–Cr, MgH_2–CrO systems was studied to identify the features of influence of chromium and oxygen on the hydrogen binding energy with the magnesium hydride surface.

Research methods

The structural stability of the MgH_2, MgH_2–O, MgH_2–Cr, MgH_2–CrO systems was investigated theoretically based on first principles in order to reveal the characteristics of the hydrogen-chromium interaction on the surface of the magnesium hydride. Ab initio calculations were performed within the density functional theory using a projector augmented wave (PAW) method, implemented in the ABINIT code [2, 3]. The generalized gradient approximation in the form of Perdew, Burke, and Ernzerhof [4] was used to describe the exchange and correlation effects.

To perform the structural optimization and relaxation of the MgH_2, MgH_2–O, MgH_2–Cr, MgH_2–CrO systems, the supercell shown in Figure 6 was adopted. A 2×2×4 supercell was created to perform magnesium hydride (001) film and consists of 32 Mg atoms and 64 H atoms. The lattice parameters of $Mg_{32}H_{64}$ are a = 4.497 Å and c = 3.003 Å. The vacuum layer thickness was set to ~ 13.5 Å. The chromium and oxygen atoms were placed on only one surface of this film. Three non-equivalent symmetrical positions were chosen to deposit Cr or O atoms on the surface: bridge between H atoms (bridge(H)), bridge between Mg atoms (bridge (Mg)), and top position (Figure 1). In this case, the distance between Cr or O atoms is ~ 9 Å and the interaction between them is negligible. This allows us to claim that we study the interaction of a single Cr and O atom with the nearest hydrogen atoms of the considered surface. The chromium and oxygen atoms were initially placed

separately on the surface and then their combined effect was studied. The relaxation of the considered surface was carried out up to the fourth atomic layer and was deemed complete when the forces acting on the atoms became less than 2.5 meV/Å. For ease of discussion, the hydrogen atoms removed from the surface after adsorption of the Cr and O atoms were numbered. The k mesh grid was taken 8×8×3 and the cutoff energy for the plane wave basis was set to 700 eV.

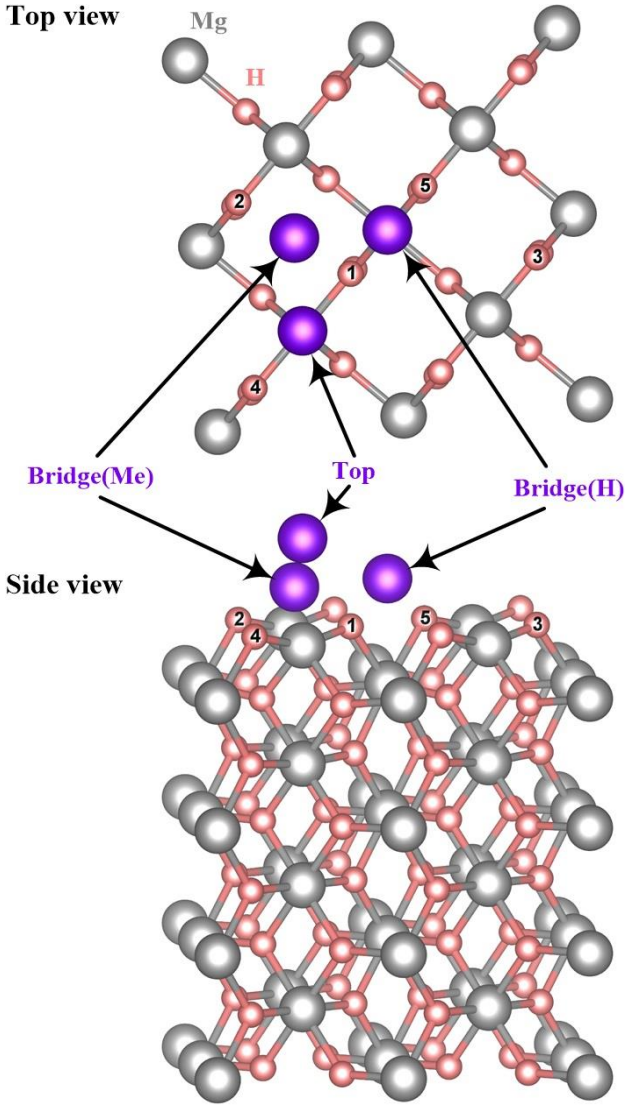

Fig. 1. Top view and side view of the MgH_2 film with a Cr or O atom adsorbed on the surface. The adsorption positions of the Cr or O atom are marked by purple spheres. The gray and pink spheres are magnesium and hydrogen atoms, respectively

To analyze the structural stability of the MgH_2, MgH_2-O, MgH_2-Cr, MgH_2-CrO systems the binding energies of hydrogen (E_H), chromium and oxygen (E_b) were calculated:

$$E_H = E_{tot}(Mg_{32}H_{64-z} - Cr_xO_y) + \frac{z}{2} \cdot E_{tot}(H_2) - E_{tot}(Mg_{32}H_{64} - Cr_xO_y), \quad (1)$$

$$E_b = E_{tot}(Mg_{32}H_{64-z}) + \frac{x}{2} \cdot E_{tot}(Cr_2) + \frac{y}{2} \cdot E_{tot}(O_2) - E_{tot}(Mg_{32}H_{64-z} - Cr_xO_y). \quad (2)$$

Here $E_{tot}(Mg_{32}H_{64-z}–Cr_xO_y)$, $E_{tot}(Mg_{32}H_{64}–Cr_xO_y)$ and $E_{tot}(Mg_{32}H_{64-z})$ are the total energies of the $Mg_{32}H_{64-z}$ and $Mg_{32}H_{64}$ films with x Cr atoms and y O atoms adsorbed on their surface (x or y equals 1 or 0) and the clean $Mg_{32}H_{64-z}$ film; z is the number of removed hydrogen atoms in the $Mg_{32}H_{64-z}–Cr_xO_y$ and $Mg_{32}H_{64-z}$ supercells (z equals 2, 1 or 0); $E_{tot}(Cr_2)$ is the total energy of pure chromium (the total energy of 2 Cr atoms in the BCC unit cell); $E_{tot}(H_2)$ and $E_{tot}(O_2)$ are the total energies of the hydrogen and oxygen molecules, respectively.

Oxygen and chromium atoms were adsorbed at all the non-equivalent positions (marked purple in Figure 1) on the surface of the $Mg_{32}H_{64}$ film. The calculated chromium and oxygen binding energies (E_b) are presented in Table 1. The positive (O) and negative (Cr) values of the binding energy indicate whether the configuration is stable. The latter indicates that the chromium atoms tend to form large clusters on the MgH_2 surface. However, the formation of the Cr–O complex leads to the positive value of their binding energy. This means that oxygen increases the binding energy of the chromium atom adsorbed on the MgH_2(001) surface. Analysis of the calculation results showed that near the adsorbed chromium atom there is a noticeable weakening of the bond of hydrogen atoms with magnesium, but the desorption of a hydrogen molecule near chromium requires significantly more energy (2.173 eV) than on a clean magnesium hydride surface (1.501 eV). The oxygen atom forms a strong chemical bond with the nearest hydrogen atoms. However, the desorption of a hydrogen molecule near oxygen requires 0.472 eV. The mutual influence of adsorbed Cr and O atoms on the binding energy of H to the surface was also studied. Regardless of the location of chromium and oxygen relative to each other, in the $Mg_{32}H_{64-z}$–$Cr^{bridge(Mg)}O^{sub(H)}$ and $Mg_{32}H_{64-z}$–$Cr^{bridge(Mg)}O^{topCr}$ configurations the hydrogen atoms closest to the Cr–O complex have a binding energy of 0.657 eV and 0.127 eV, respectively, which is significantly lower than on the clean magnesium hydride surface (1.293 eV).

Table 1

The binding energy of Cr and O atoms with the magnesium hydride surface

System	Positions	E_b, eV	
$Mg_{32}H_{64}$–O	bridge(H)	1.874	
	bridge(Mg)	1.965	
	top* (sub(H))	4.777	
$Mg_{32}H_{64}$–Cr	bridge(H)	-5.650	
	bridge(Mg)	-5.292	
	top	-7.404	
$Mg_{32}H_{64}$–CrO	O in sub(H) and Cr in bridge(Mg)	1.272	
	O above Cr in bridge(Mg)	1.885	

Conclusion

The first-principles study of the features of the interaction of chromium and oxygen atoms adsorbed on the surface of magnesium hydride with hydrogen atoms was carried out. It was found that the presence of the Cr–O complexes on the magnesium hydride surface leads to a decrease in the hydrogen sorption/desorption characteristics due to the decrease in the hydrogen binding energy. Oxygen was shown to prevent chromium atoms from forming large clusters on the magnesium hydride surface.

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