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Influence of a transition metal atom on the geometry and electronic structure of Mg and Mg–H clusters

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ABSTRACT

We report on the study of $(MgH_2)_n + M$ complexes ($M = Ti$ or Ni) carried out within the framework of the cluster density functional theory (DFT) method. The influence of such transition metal atoms on the cluster geometry and electronic structure is discussed considering the stability of MgH_2 hydride.

1. Introduction

MgH_2 is one of the most promising materials for hydrogen storage. However, its rather slow hydrogen absorption and desorption kinetics and high dissociation temperature essentially limit its application in the field. Nevertheless mixing Mg or MgH_2 with small amount of transition metals or other additives as e.g. oxides remarkably accelerates the hydrogenation kinetics [1–4]. Our previous theoretical study of new ordered Mg_7MH_{16} and Mg_6MH_{16} magnesium hydrides carried out by band FLAPW method confirmed the ability of *ab initio* method to describe and predict the destabilizing role of transition metal atoms in the parent structure of the magnesium dihydride [5]. Nevertheless, calculations on bulk systems do not allow to simulate imperfect structures without considering supercells. If we need to study the influence of a few percents, then we face a large supercells (up to several hundred atoms) and the calculations cannot be achieved in reasonable time. From this point of view the cluster approach can be considered as a powerful tool for studying effects of atomic substitution. The cluster DFT calculations of MgH_2–M systems (with M = Sc to Zn) made in Ref. [6] to study the catalytic activity of 3*d* transition metals on the Mg–H dissociation of magnesium dihydride showed that among 3*d* transition metals, Sc and Ni displayed the highest catalytic activity. However, it contraries to experimental data obtained in Ref. [4], according to which Ti exhibits better catalytic activity then Ni.

In this contribution, we aim to improve the cluster model of MgH_2–M systems proposed in Ref. [6], where magnesium dihydride was simulated by the linear molecule MgH_2. We expand cluster size up to 13 formula units of MgH_2 and focus on Mg_3M, Mg_3MH_8 and $Mg_{11}M_2H_{26}$ cluster systems, as substitutional cases of Mg_4, Mg_4H_8 and $Mg_{13}H_{26}$ clusters, where one or two Mg atoms were substituted by Ti or Ni. So, we intend to investigate the impact of these alloying elements on stability of magnesium dihydride and on hydrogen sorption in it.

2. Computational details

To calculate the total energy and electronic structure we use the density functional theory (DFT) based on the hybrid Becke-type three parameters exchange functional [7] paired with the gradient corrected Lee, Yang, and Parr correlation functional (B3LYP) [8,9]. All calculations are carried out using GAUSSIAN 03 code [10].

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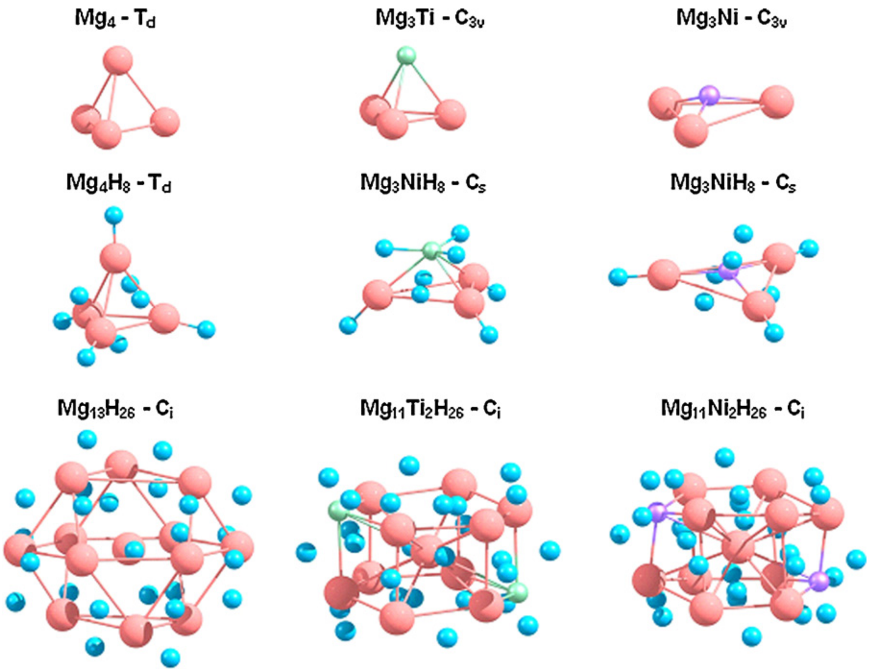

Fig. 1. Optimized geometries of Mg_3M, Mg_3MH_8 and $Mg_{11}M_2H_{26}$ clusters.

We use 6-311 basis set of primitive Gaussian functions to expand the cluster orbitals. Self-consistency of calculations is considered achieved when the total energies have converged by 0.1 mRy. All cluster characteristics calculated and presented further are obtained for the clusters with optimized geometry.

3. Results and discussion

First of all we studied metallic Mg_4 and Mg_3M clusters. As it was shown theoretically [11], magnesium clusters Mg_n possess various isomer forms, and their number increases dramatically with cluster size. For $n = 4$ the lowest energy state is a regular tetrahedron (T_d symmetry), as shown in Fig. 1, with Mg–Mg distance equal to 3.24 Å, that is close to the value obtained previously [11–13]. To follow the effect of a 3*d* transition metal atom on the cluster geometry one of magnesium atoms is substituted by Ti or Ni. This immediately reduces the symmetry of the cluster to C_{3v}. However, for Mg_3Ti, the geometry changes are not very significant. The tetrahedron becomes slightly distorted and more compact with interatomic distances about 3 Å. The distances are listed in Table 1. The impact of Ni on the cluster geometry is more pronounced. The Ni atom is found almost in the plane formed by the three magnesium atoms, as it is shown in Fig. 1, that makes the Mg–Mg distance increase up to 4.057 Å.

Further, to simulate the magnesium dihydride, we have calculated the Mg_4H_8 cluster. Addition of eight hydrogen atoms to the Mg_4 cluster does not break its symmetry. The distance between magnesium atoms slightly decreases, a comparison made to the non-hydrogenated cluster. There are two types of hydrogen atoms situated on the C_3 axis which connects the Mg atom and the center of a tetrahedron face. The shortest Mg–H distance between Mg and outward hydrogen atom is 1.7 Å.

Table 1
Total energy, the HOMO–LUMO gap and interatomic distances for calculated clusters.

Cluster	Symmetry	E_{tot} (Ry)	E_g (eV)	Distances (Å)			
				Mg–Mg	Mg–H	Mg–M	M–H
Mg_4	T_d	−1600.775967	2.97	3.2359			
Mg_3Ti	D_{3h}	−2899.193802	1.32	3.0090		2.9439	
Mg_3Ni	D_{3h}	−4216.982290	1.85	4.0567		2.3935	
Mg_4H_8	T_d	−1610.331068	6.00	3.0859	1.6996		
					1.9930		
Mg_3TiH_8	C_s	−2908.985433	2.72	3.3702	1.6990	2.7652	1.7909
				3.9827	1.7079	2.7759	1.8257
							1.8346
Mg_3NiH_8	C_s	−4226.6669078	4.44	3.8282	1.6931	2.3721	1.5229
				4.2746	1.9703	2.4296	1.5248
							1.7624
$Mg_{13}H_{26}$	C_i	−5203.9806764	4.67	2.9457[a]	1.7983[a]		
$Mg_{11}Ti_2H_{26}$	C_i	−7789.6840582	2.40	2.8137[a]	1.8265[a]	2.7412[a]	1.7958[a]
$Mg_{11}Ni_2H_{26}$	C_i	−10412.5346126	3.43	2.9055[a]	1.8055[a]	2.4544[a]	1.4530[a]

[a] Only the shortest distances are given.

The substitution of one Mg atom by Ti or Ni changes dramatically the cluster geometry. The clusters become flatter (more pronounced for Mg_3NiH_8), the symmetry reduces to C_s, and the 3*d* atom is coordinated by five H atoms. When substituting Ti to Mg the metal–hydrogen distances do not change noticeably (see Table 1), whereas for the Mg_3NiH_8 cluster, the Ni–H distances are markedly reduced to about 1.52 Å.

Furthermore we have studied $Mg_{13}H_{26}$ and $Mg_{11}M_2H_{26}$ clusters. The starting geometry is constructed from a fragment of the Mg_7TiH_{16} hydride, whose crystal structure was optimized in our previous bulk DFT calculations [5]. During the calculation the symmetry of the clusters was kept C_i. Their optimized geometries are shown in Fig. 1 as well. Because of a large number of interatomic distances, only the shortest are listed in Table 1. As it is seen, the Mg–Mg distances decrease, whereas the Mg–H distances increase upon cluster expansion. As compared to $Mg_{13}H_{26}$ the Mg–H bond lengths are shorter in $Mg_{11}Ti_2H_{26}$ and longer in $Mg_{11}Ni_2H_{26}$. Besides, the Ni–H bonds are shorter than the Ti–H ones.

The other characteristic related to the cluster stability is the energy gap E_g between the highest occupied and the lowest unoccupied molecular orbitals (the HOMO–LUMO gap). In Table 1 we listed the HOMO–LUMO gap for all calculated clusters. For the Mg_4H_8 cluster the calculated gap is ~6.0 eV, that is much larger than 4.2–4.3 eV found for the bulk MgH_2 hydrides [14]. However, for the bigger cluster $Mg_{13}H_{26}$, that contains thirteen MgH_2 formula units, the calculated gap is 4.44 eV that is very close to the value in bulk material. Substitution of Mg by 3*d* metal decreases the HOMO–LUMO gap. This is in fair agreement with our previous bulk calculations of Mg_7MH_{16} and Mg_6MH_{16} hydrides [5], for which a transition metal *d*-band occurs in the middle of a rather large gap and the Fermi level falls in this *d*-band. From the present calculations, the lowest energy gap (2.40 eV) is found for the $Mg_{11}Ti_2H_{26}$ cluster. The $Mg_{11}Ni_2H_{26}$ cluster has the HOMO–LUMO energy gap of 3.43 eV.

This fact, together with the results of interatomic distances analysis, allows us to conclude that substitution of Ti to Mg destabilizes more the Mg–Ti based clusters then those formed by substitution of Ni to Mg. This is in fair agreement with experimental investigations of MgH_2–M (M = Ti, V, Mn, Fe, Ni) nanocomposites prepared by mechanical milling, which lead to demonstrate that titanium and vanadium are better so-called "catalysts" than Ni for hydrogen absorption and desorption processes [4]. The small clusters with rigid Mg–H angle bonds as calculated earlier (see Ref. [6]) do not describe so well the MgH_2–M systems. According to the present calculations, typically the bigger clusters, such as $Mg_{11}M_2H_{26}$, should be considered as well on the bases used in Ref. [6].

4. Conclusion

Within the framework of cluster approach, we have studied the influence of Ti and Ni atoms on the stability of the magnesium dihydride. The $Mg_{n-1}M$, $Mg_{n-1}MH_{2n}$ and $Mg_{n-2}M_2H_{2n}$ ($n = 4$ and 13; M = Mg, Ti and Ni) clusters have been studied. It has been found that the substitution of Ti or Ni to Mg dramatically changes the geometry of studied clusters. In the view of both interatomic distances and HOMO–LUMO gap, the role of Ti in destabilization of MgH_2 looks much more promising, that is in fair agreement with experimental investigation on the catalytic activity of various transition metal additives in nanostructured MgH_2 when prepared by mechanical milling [4]. This demonstrates the pertinence DFT methods to describe, and further to predict so-called "catalytic" effects of specific additives on hydrogen sorption rate in magnesium dihydride.

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