MgH₂ in Carbon Scaffolds: A Combined Experimental and Theoretical Investigation

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ABSTRACT: Understanding the thermodynamics of metal hydrides is crucial in order to employ them for reversible hydrogen storage. The use of a supporting nanoporous matrix for embedding the hydride can improve the kinetics of metal hydride reactions and even change the overall reaction path. In this study, density functional theory calculations were performed to understand the size effect of MgH₂ particles and changes in the physical and chemical properties of these nano-objects embedded in an amorphous carbon matrix. A stable amorphous carbon structure was successfully generated with two different approaches and further used as a template to construct the scaffold for nanophases of MgH₂. Using five different structure models, we have studied the physical and chemical changes of the nano-MgH₂ in this carbon scaffold. In addition, from small-angle neutron scattering studies, we could demonstrate experimentally that it is possible to incorporate such ultrasmall objects into the carbon scaffolds.

INTRODUCTION

Magnesium is an attractive element for hydrogen-storage applications because of its abundance, lightweight, low manufacture cost, and high hydrogen-storage capacity (7.66 wt %). Unfortunately, the use of magnesium hydride is hampered by relatively slow kinetics for hydrogen release and uptake. Moreover the thermodynamics is rather unfavorable, with the formation enthalpy of ∆Hₚ = −75 kJ/mol H₂ (i.e., MgH₂ must be heated to ca. 300 °C in order to release hydrogen at p(H₂) = 1 bar). Several factors hinder the rate of hydrogenation and dehydrogenation of the Mg/MgH₂ system. In order to use MgH₂ as an energy carrier in mobile applications, one has to find the possible ways to decrease the hydrogen desorption temperature. Numerous studies have been focused on improving the problematic sorption kinetics, including mechanical ball milling and chemical alloying. However, it is found that these methods can only improve the absorption and not the desorption kinetics, possibly because even the smallest particle sizes (20 nm) obtainable by these methods still primarily display bulk desorption characteristics. The hydrogenation/dehydrogenation kinetics can be effectively improved either by accreting Mg particles with transition metals such as Ti, V, and Nb (or their corresponding oxides) or by nanostructuring. Indeed, application of severe plastic deformation treatments (ball milling, equal channel angular pressing, and cold rolling) have not changed noticeably the thermodynamics of the Mg−H system. However, recently, the McPhy energy system has demonstrated that nanophases of Mg hydride with proper additives can store large quantities of hydrogen at low pressure within tens of minutes (for more details see ref 4).

From our theoretical simulations, we have found that most of the nanoparticles of complex hydrides have a critical particle size of the order ~2 nm (for more details see refs 5−7). It is difficult to prepare such nanoparticles from the available experimental techniques (such as ball milling, etc.). Alternatively, one can prepare/isolate such types of particles in porous scaffold structures. For example, recently Nielsen et al. synthesized nanoparticles of magnesium hydride through embedding them in nanoporous carbon aerogel scaffold materials in order to explore their kinetic properties of hydrogen uptake and release. The hydrogen-storage properties of nanoconfined MgH₂ were studied by Sievert’s measurements and thermal desorption spectroscopy, which clearly demonstrated that the dehydrogenation kinetics of the confined hydride depends on the pore size distribution of the scaffold material; that is, smaller pores mediated faster desorption rates, most likely due to the size reduction of the confined magnesium hydride.

An improvement in kinetics attributed to the nanoconfine-ment has also been demonstrated for NaAlH₄ infiltrated in mesoporous carbon or dispersed on carbon nanofibers. A similar kinetic effect was found for LiBH₄ infiltrated in mesoporous scaffolds. The reduced diffusion distances...
and increased surface areas for LiBH$_4$ were proposed to be responsible for the decrease as large as 75 °C in dehydrogenation temperature when the complex hydride was incorporated into aerogels and activated carbon.$^{15,16}$ Furthermore, an indication of the effect of nanoconfinement on the thermodynamic properties was proposed for NaAlH$_4$ infiltrated in activated carbon.$^{17}$ In the bulk phases, during the dehydrogenation of a complex hydride, such as NaAlH$_4$, the solid end products, NaH and Al, can separate and thereby reduce the complete rehydrogenation back to NaAlH$_4$. In contrast, the physical description of the nanocoﬁned system is complicated and not yet complete. However, it was suggested that the use of a nanoscale matrix embedded with the complex hydride could force the products to stay in close vicinity, thus enhancing the reversibility.$^{15,16,18}$ At the same time, the higher degree of disorder due to a larger contribution of phase boundaries to the overall volume is supposed to increase the entropy of the system, leading to a destabilization of the hydride.$^{18}$ The limited particle sizes also likely increase the contact area between the product decomposition phases, which can further improve the kinetics of the rehydrogenation reaction.$^{15,16,19}$ In the present study, we have investigated the changes in nano-objects of MgH$_2$ when they are embedded into the carbon scaffold. Nanoconfinement of the Mg/MgH$_2$ within carbon nanotubes was also investigated quantum mechanically by Liang and Kung.$^{20}$ They found that the loading level increases on increasing the confinement and the net energy change in the hydrogen sorption/desorption process decreases signiﬁcantly, when the loading approaches the maximum. The conﬁnement was found to be independent of length of the confining nanotubes.$^{20}$ To our knowledge, this is the ﬁrst theoretical work where MgH$_2$ nanoparticles were conﬁned into different types of carbon media/scaﬀold to study their changes in the physical and chemical properties. To the best of our knowledge, this is also the ﬁrst theoretical report on a scaﬀold material with experimental conﬁrmation on the nanosize of the conﬁned particles.

### MATERIALS AND METHODS

**Computational Details.** The quantum-mechanical calculations have been performed in the framework of density functional theory (DFT) using the generalized gradient approximation (GGA)$^{21,22}$ as implemented in the VASP code.$^{23,24}$ The interaction between the ion and the electron is described by the projector augmented wave method.$^{25,26}$ For the present calculations, we have used a plane-wave cutoff energy of 500 eV that gives well converged results with respect to the basis set. The k points were generated using the Monkhorst-Pack method with a grid size of $8 \times 8 \times 12$, and $8 \times 8 \times 1$, for the bulk and surfaces (structure models M1, M2, M3, M4, and M5; for more details about the structure models see the MgH2 with Amorphous Carbon section), respectively. Iterative relaxation of atomic positions was stopped when the change in total energy between successive steps was less than 1 meV/Å. Different sizes of the nanoclusters and nanowhiskers have been constructed from optimized bulk phases through different supercell sizes. The k points were generated using the Monkhorst-Pack method with a grid size of $1 \times 1 \times 1$ and $2 \times 2 \times 1$, for structural optimization for nanoclusters and nanowhiskers, respectively. During the nanoclusters/whisker construction, the MgH$_2$ stoichiometry was always maintained. For the nanowhisker construction, the vacuum is included only in the x and y directions. The vacuum thickness was considered wide enough to prevent whisker-to-whisker/cluster-to-cluster interactions, and we found that a width of 14 Å is sufﬁcient to ensure that the energy converged to less than 1 meV/atom.

To gauge the bond strength, we have used the bond overlap population (BOP) values calculated on the basis of the Mulliken population analysis implemented in the CASTEP$^{27}$ code. The Born effective charges in all the structure models of amorphous carbon (AC)–MgH$_2$ were calculated using density functional perturbation theory with an external electric field. For the CASTEP computation, we have used the optimized structures obtained from VASP as input, and the structure is again optimized with Norm-conserving pseudopotentials and the GGA exchange correlation functional proposed by PBE.$^{22}$

### RESULTS AND DISCUSSION

**Amorphous Structure Construction.** Carbon is an impressively versatile chemical element. As it is found in three distinct hybridizations, sp$^3$, sp$^2$, and sp, each with a well-defined local topology, this element can form a variety of different allotropes. For instance, the bulk hardness of diamond and the laminar softness of graphite can be tracked down to carbon sp$^3$ tetrahedron-like bonding and sp$^2$ planar configuration, respectively. Although these two materials exhibit quite distinctive physical and chemical properties, they represent only a small fraction of possible carbon solids. Noncrystalline carbon materials have a mixture of sp$^3$ and sp$^2$ hybridized C–C bonding and have lately received much attention due to their
many industrial applications. This class of material can be produced by chemical vapor deposition at a low cost.

In experimental studies, the complex hydrides are typically incorporated/dispersed into either mesoporous carbon, carbon nanofibers, aerogels, or activated carbon matrices that may or may not have any three-dimensional periodic structural arrangements. Activated carbon fibers are carbon sorbents with a narrow and uniform pore size distribution. They are utilized as supports for catalysts and electrical materials due to their microporosity with high specific surface cyclic effects. Simulations on such carbon forms are very challenging, because of the large number of atoms as well as lack of information on the starting structures for the simulations. In the present study, we have assumed that all these media (either mesoporous carbon, carbon nanofibers, aerogels, or activated carbon) are amorphous structures and that the pore sizes are directly related to the density of the amorphous structures. Hence, we have constructed several amorphous carbon structures with varying densities using two different amorphous construction methods (see the following section for more details). These starting structures are optimized with the VASP code, and the resultant structure models are further used to construct the nano-MgH2 embedded structures.

In our first approach, the amorphous carbon structures (hereafter referred to as AC1) were obtained by a liquid quench within a Metropolis Monte Carlo scheme (MC scheme). At each MC step, each atom is given a random displacement, and the resulting change in total energy ($\Delta E$) of the system is calculated. This new position is accepted with a probability

$$\exp\left(\frac{-\Delta E}{k_B T}\right),$$

where $k_B$ is the Boltzmann constant and $T$ is the temperature in kelvin. We have melted a 128 atoms cubic cell at a density of 3 g cm$^{-3}$ and at a temperature of 5000 $^\circ$C (method I) using the Monte Carlo technique by exploiting the Tersoff potential with the cutoff distance set at 2.45 Å to correctly locate the second-neighbor coordination shell of the tetrahedral amorphous carbon structure. The amorphous carbon structures were obtained by cooling (exponentially along the MC steps) the hot carbon from 5000 $^\circ$C down to a temperature of 1040 $^\circ$C. In our second approach (method II), for the amorphous structure construction (hereafter referred as AC2; the number of atoms and density are the same as for AC1; i.e., 128 atoms cubic cell at a density of 3 g cm$^{-3}$), we have used the familiar concept of rotational states combined with the stepwise nature of the chain construction process implemented in the Materials studio 5.0 package, in which at each step, we have selected a continuation of the chain from a series of candidates according to a set of probabilities. During this process, we have used the following three steps: (1) rotational states are chosen according to a pair wise interdependent RIS model; (2) a single-chain backbone bond and its pendant atoms are added to the system; and (3) the set of probabilities comprises the modified conditional probabilities for the allowed states of the added bond. In this approach, the number and location of minima in the bond's torsional potential are first noted. Next, the height of the barrier between states is examined to decide whether adjacent states are mutually accessible. If the factor

$$\exp\left(-\frac{\text{barrier height}}{RT}\right)$$

where $R$ is the gas constant and $T$ is the temperature] exceeds 0.00005, the states are considered to communicate, and the full set of torsional potential minima is used to define allowed states.

Such constructed amorphous carbon structures were further used as a starting point for the vicarious DFT calculations. The unit-cell volume and shape as well as atomic positions were relaxed simultaneously in a series of calculations made with progressively increasing precision. A final high accuracy calculation of the total energy was performed after completion of the relaxations with respect to k-point convergence and plane-wave cutoff. The optimized final structures of AC1 (density 2.85 cm$^{-3}$) and AC2 (density 2.78 cm$^{-3}$) are shown in Figure 1a and b, respectively. In these two optimized amorphous structure models from the above-mentioned methods, the majority of the C atoms are tetrahedrally coordinated with the neighboring C atom in the matrix. The calculated C–C distances versus the number of bonds (pair distribution function, PDF; see Figure 1) for the AC1 and AC2 models indicate that the PDF values were scattered between 1.35 and 1.65 Å in AC1 while the corresponding values in AC2 vary from 1.34 to 1.72 Å. This type of structural arrangement is expected in nano and amorphous phases with no three-dimensional crystallinity owing to reduction in coordination number of the atoms. It may be noted that the C–C distance in graphite is 1.42 Å and that for diamond is 1.54 Å. The presently constructed models cover these values indicating they have both sp$^3$ and sp$^2$ hybridized C–C bonds in their structures. In order to understand the electronic structure and structural

![Figure 1](https://example.com/figure1.png)

Figure 1. Optimised amorphous carbon structure obtained from method I (a) and II (b; see text for more details). The pair distribution functions are shown as a function of distance in Å for the amorphous carbon obtained from the two methods (see text).
the well scattered C–C bond-length values, the calculated density of states for both phases is well dispersed. From Figure 2, it is evident that both structure models have finite electrons at the Fermi level ($E_F$) having metallic character. Further, the $E_F$ is exactly at the pseudogap (a deep valley at/near to the $E_F$). A strong correlation has often been emphasized between the position of the pseudogap and structural stability.\textsuperscript{35–38} It has been demonstrated in intermetallics both experimentally and theoretically that the material is found to be more stable in a particular structure if the filling of the bonding states is maximum. For the most stable structures, there is enough room to accommodate all the valence electrons into the bonding states so as to bring the $E_F$ to the pseudogap thus making the antibonding states fully empty. In other words, the stable structure is often characterized by a low $N(E_F)$.\textsuperscript{37,39–42} From this point of view, the considered two models are stable, both methods give a similar result, and AC2 is lower in energy.

However, the calculated total energy difference between these two models is 0.00013 eV/atom. Hence, we have used the AC2 structure as the scaffold matrix in our present study.

**Nanoclusters of MgH$_2$.** α-MgH$_2$ crystallizes in a TiO$_2$ rutile-type structure at ambient pressure and low temperatures.\textsuperscript{43,44} At higher temperatures and pressures, it transforms into several other polymorphs.\textsuperscript{45–50} In this study, we have concentrated mainly on the ambient condition α-MgH$_2$ phase. As the interatomic distances in the nanophases are different than those in the corresponding bulk materials, different physical and chemical properties could be expected compared to the bulk materials. Upon decreasing the particle size below a certain range (critical particle size), a large fraction of the atoms become exposed to the surface, and the total energy starts to deviate from its constant value. In order to identify the critical particle size, we have calculated the total energy as a function of the cluster size for MgH$_2$ as shown in Figure 3. From this figure, it is evident that, if the cluster size decreases, the total energy becomes more positive. In particular, there is a steep increase in the total energy when the size of the MgH$_2$ cluster is below ~1 nm. Furthermore, the positive change in the total energy for the nanoparticles suggest that there will be modifications in the thermodynamical properties and in particular the hydrogen sorption temperature is expected to be reduced in the nanophases compared to the bulk materials. The reason is that the surface-to-volume ratio increases upon decreasing the cluster size. Since the surface atoms have lower coordination (generally found to occupy the less stable top and bridge sites) than that in bulk materials, the average number of bonds between constituents is lower for smaller clusters. This could explain why the decomposition temperature for nanoparticles is usually lower than that in bulk materials. If one compares the variation in total energy with particle size for MgH$_2$ and that with the combination of nanoparticles of Mg with H$_2$ molecules (see Figure 3), the nanoparticles of MgH$_2$ are energetically unstable below 1 nm compared to the corresponding decomposed phases (i.e., nanoparticles of Mg with remaining H$_2$ gas). This is opposite to the conclusion we reached on nanoparticles of AlH$_3$ and borohydrides, where below the critical particle size, these nanoparticles will be more stable than the corresponding decomposed phases.\textsuperscript{51} Therefore, the present result suggests that one can destabilize nanoparticles of MgH$_2$ below 1 nm size. In order to substantiate this observation, we have calculated the formation energy ($\Delta H$) as a function of particle size using the following equation:

$$\Delta H = E_{\text{MgH}_2\text{(nano)}} - [E_{\text{Mg\text{(nano)}}} + E_{\text{H}_2\text{(mol)}}]$$

where, $E_{\text{MgH}_2\text{(nano)}}$ and $E_{\text{Mg\text{(nano)}}}$ are the total energy of the MgH$_2$ and Mg nanoclusters, respectively. $E_{\text{H}_2\text{(mol)}}$ refers to the total energy of the hydrogen molecule. The calculated $\Delta H$ value for the bulk α-MgH$_2$ phase is $-73.5$ kJ/mol. This result is in good agreement with the experimental value for the bulk phase (varies from $-74.4 \pm 0.4$ to $-76.2 \pm 9.2$ kJ/mol).\textsuperscript{52,53} The calculated $\Delta H$ as a function of the particle size (see Table 1) is also displayed in Figure 3 where the critical particle size is found to be 2.2 nm and the corresponding $\Delta H$ value is $-73.4$ kJ/mol, which is closer to that of the bulk phase. A recent study\textsuperscript{54} by Liang found that, as thickness of the film decreases, the enthalpy also decreases, to a value of 5 kJ/mol for a two unit-cell depth compared to that of the bulk phase. The present
Table 1. Calculated Formation Energy (ΔH) as a Function of Particle Size for the Nanoparticles of MgH2

<table>
<thead>
<tr>
<th>particle size (nm)</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>49.46</td>
</tr>
<tr>
<td>0.6</td>
<td>31.39</td>
</tr>
<tr>
<td>0.83</td>
<td>−4.938</td>
</tr>
<tr>
<td>1.1</td>
<td>−53.04</td>
</tr>
<tr>
<td>1.3</td>
<td>−67.01</td>
</tr>
<tr>
<td>1.6</td>
<td>−71.82</td>
</tr>
<tr>
<td>2.2</td>
<td>−73.43</td>
</tr>
<tr>
<td>2.8</td>
<td>−73.46</td>
</tr>
</tbody>
</table>

*For calculation method, see eq 1.*

results for MgH2 nanoclusters provide a useful way to compare our methods to other approaches and to consider the strengths and limitations of our calculations. Possibly, the most direct comparison we can make with experimental data is via the experiments of Li et al., who examined hydrogen evolution from MgH2 nanowires of radii 20, 45, and 80 nm.55 In these experiments, no noticeable difference in the temperatures associated with H2 evolution was observed between the nanowires of different radii, although the thinner nanowires had better reaction kinetics. From Figure 3, it is evident that, when the particle size is sufficiently small (below ca. 1.6 nm), the formation energy of the system becomes much more positive and the system can be highly unstable compared to the decomposed phases (i.e., nano Mg + H2). This clearly indicates that, when the particle size becomes continuously smaller, the system becomes highly unstable. For practical applications, it is anticipated that the ΔH value should be around −40 kJ/mol, and from this point of view, the nanoparticles of MgH2 with size below 1.6 nm get special attention. However, it is a challenging task to make bare nanoparticles of MgH2 by existing experimental techniques. Even if this could be achieved, the particles may agglomerate and form larger entities that will not exhibit the expected size effect anymore. This can be overcome if one encapsulates such nanoparticles in nanoporous scaffold materials, because the physical and chemical properties of such nanoparticles may change due to the interface effect. It is also important to note that the experimental characterization of such scaffold materials is a very challenging task. From the stability of the nanoparticles of MgH2, one can anticipate that the scaffolded nano-objects may have a fundamental structural framework that is different from that of bulk material. It should be noted that the recent work by Zhao-Karger et al.28 demonstrated that one can alter the thermodynamic and kinetic properties of MgH2 by infiltrating them into a microporous scaffold. In this study, MgH2 nanoparticles were formed by direct hydrogenation of Bu2Mg inside the pores of a carbon scaffold, and the authors found that the activation energy for the dehydrogenation was lowered by 52 kJ/mol compared with that of the bulk material. Similarly, a significantly reduced reaction enthalpy of 63.8 ± 0.5 kJ/mol and entropy of 117.2 ± 0.8 J/mol were found for the nanocoated system.

**Evaluation of Particle Size in the Scaffold Material.** In order to identify the particle size and the effective infiltration of the prepared MgD2/ACF25 composite, we performed SANS on bulk MgD2, the composite MgD2/ACF25, and the scaffold ACF25 alone. As any particles of bigger size would affect the low-q range, not visible in our SANS data, they are not considered here. When the scattering data satisfy the condition of qr ≫ 1, where r is the particle size, the scattered intensity I(q) can be well approximated as proportional to q−α. The power-law scattering exponent α can thus be evaluated from a plot of log(I) versus log |q|. The composite material, MgD2/ACF25, and the scaffold alone follow the same behavior at low-medium q (see Figure 4), whereas a clear difference in slope behavior becomes evident at q values higher than approximately 0.18 Å−1. These values correspond with material deposited in very small pores (<a few nm).

The slope parameter α has a value well below 3.0 (ca. 1.3) in the high-q range. This shows that the particle sizes are so small that the material has a mass fractal behavior even at the shortest length scale accessible in our experiments, that is, around 1 nm. Figure 5 shows the size distribution obtained by means of an indirect Fourier transform of the excess scattering, that is, of the data obtained by subtracting the scaffold scattering from the composite scattering. As commented in our recent paper,50 one should show some caution here, since there are cross-correlation terms that may not be nulled out upon subtraction. However, this curve, with its main peak around 10 Å (1 nm),
confirms the small sizes of the MgD₂ particles when they are integrated into the scaffold.

As an independent check of the average particle size, we also performed a Guinier regression in the high-q region (above \(q \approx 0.1 \text{ Å}^{-1}\)), where the “knee” in the composite data is a clear indication of a characteristic size in this size range. This resulted in a radius of gyration for the MgD₂ particles just below 1 nm (9.7 Å), see Figure 6. The SANS data therefore seem to confirm that the nanoinfiltration of MgD₂ was successful. The very small size measured for the confined MgD₂ is likely to be the reason for the observed destabilization effect.\(^45\)

**MgH₂ with Amorphous Carbon.** As mentioned previously, there is no unique way to describe the starting structure models for amorphous carbon. Therefore, in the present theoretical study, we constructed different types of amorphous carbon models with altered density (corresponding to different pore size), see Figure 7. From the optimized AC2, we have constructed various types of models named M1 (overlayers of MgH₂ on AC substrate layers where the nanoparticles stand on the surface of the carbon media), M2 (MgH₂ layers arranged between two AC layers, also called sandwich/multilayer model, which corresponds to nano-MgH₂ trapped between the carbon sheets), M3 (MgH₂ nanoparticles inserted into a carbon scaffold; this situation corresponds to nanoparticles of MgH₂ trapped inside a carbon cave), M4 (similar to the M3 model, but the cave is also closed by AC layers), and M5 (where a MgH₂ nanowire is placed into the carbon scaffold matrix; this situation corresponds to needle shape of MgH₂ trapped in a carbon cave). It may be noted that, as we have used a periodic boundary condition and no vacuum was introduced in the M5 model along z direction, the length of the nanowire is infinite.

All the above-mentioned models are constructed from the optimized \(\alpha\)-MgH₂ structures (i.e., M1 and M2, nanoclusters and nanowire configurations) and the relaxed carbon scaffolds with specific density as described in the Amorphous Structure Construction section. For more details about the nanophase construction see ref 5.

Layers of AC have been constructed by cleaving the bulk phase that was earlier fully relaxed with respect to stress and strain. We have earlier shown that the (101) slab of \(\alpha\)-MgH₂ has the lowest surface energy\(^5\), and therefore, the layer is constructed from this surface. All atoms in such created slabs have been allowed to relax by minimization of the forces acting on them. In the structure models M1 (\(a = 12.18, b = 8.33, c = 18.49 \text{ Å (28.496 Å with vacuum)}\)) and M2 (\(a = 12.18, b = 8.33, c = 26.35 \text{ (36.35 Å with vacuum)}\)), each slab is separated from its neighbors by a vacuum of 10 Å thickness. The thickness of a slab is usually expressed in terms of number of atomic layers, where a layer is defined as an integer number of MgH₂ formula units and is thus stoichiometric. For the structure models M3 and M4, the optimized 1.5 nm nanocluster was inserted into the carbon scaffold, and the calculations were done with the periodic model (i.e., no vacuum space was introduced in the model). Similarly, for the M5 structure model, we have used our previously reported 1.4 nm nanowire.\(^5\) In order to prevent possible direct reaction/interaction (because of the unsaturated broken C bonds) between the AC and MgH₂, we have saturated all open bonds in the cleaved layers and scaffolds of AC by H atoms. The passivation of carbon surface dangling bonds with hydrogen does not correspond to a real situation. However, it is worth noting that MgH₂ nanoparticles are formed by direct hydrogenation of Bu₄Mg inside the pores of a carbon scaffold. Such a procedure could result in a saturation of carbon dangling bonds by hydrogen simultaneously with MgH₂ synthesis. The numbers of broken bonds in M1, M2, M3, M4, and M5 models are 6, 12, 10, 16, and 11, respectively, and corresponding supplementary H atoms are added. Hence, the total number of atoms involved in the M1, M2, M3, M4, and M5 models are 239 (128 C, 35 Mg, 76 H), 373 (256 C, 35 Mg, 70 H, and 12 UBBH) atoms involved in this model; M3: MgH₂ in the carbon scaffold (386 (280 C, 32 Mg, H 64, 10 UBBH) atoms involved in this model); M4: MgH₂ nanoparticle (embedded nanoparticle size is 1.5 nm) is placed in the closed scaffolds (424 (304 C, 32 Mg, 64 H, and 14 UBBH) atoms involved in this model); and M5: MgH₂ nanowire (diameter is 1.5 nm, and length of the wire is infinite length) in the carbon scaffold (386 (294 C, 27 Mg, 54 H, and 11 UBBH) atoms involved in this model). Vacuum around the structures is removed in the illustration for better visibility.

Figure 7. Considered structure models (after the relaxation) in this study. M1: overlayers of MgH₂ in amorphous carbon (AC) substrate (239 (128 C, 35 Mg, 70 H, and 6 unsaturated broken bonds are saturated by H atoms; UBBH) atoms involved in this model); M2: AC—MgH₂—AC (sandwich/multilayer; 373 (256 C, 35 Mg, 70 H, and 12 UBBH) atoms involved in this model); M3: MgH₂ in the carbon scaffold (386 (280 C, 32 Mg, H 64, 10 UBBH) atoms involved in this model); M4: MgH₂ nanoparticle (embedded nanoparticle size is 1.5 nm) is placed in the closed scaffolds (424 (304 C, 32 Mg, 64 H, and 14 UBBH) atoms involved in this model); and M5: MgH₂ nanowire (diameter is 1.5 nm, and length of the wire is infinite length) in the carbon scaffold (386 (294 C, 27 Mg, 54 H, and 11 UBBH) atoms involved in this model). Vacuum around the structures is removed in the illustration for better visibility.
In all these structure models, the calculated Mg–H distances versus number of bonds (see Figure 8) for the optimized models indicate that the values were scattered compared to those in the corresponding bulk phase (Mg–H distance in the bulk phase is 1.95 Å). In particular, a number of Mg–H bonds have longer bond distances than that in the corresponding bulk material. This type of structural arrangement is expected in nano and amorphous phases without three-dimensional crystallinity, owing to reduction in coordination number of atoms. It should be noted that, in all these structure models, the initial MgH₂ structure is completely rearranged even in the central region. In general, we found that the inner part of the nanowhisker/nanoclusters has almost the same H–Mg–H atomic arrangement as that in the bulk α-MgH₂ phase.57 This finding clearly indicates that the scaffold materials are having different atomic arrangement than that of the free nanophasic materials and hence one can expect the thermodynamic behavior of scaffolds to be different from that in the bulk and nanophases. The atomic arrangement of these nano-objects in the scaffold materials is close to that of an amorphous structure. A similar situation is also present in scaffolded NaAlH₄.17 It is important to recall that recent work by Lohstroh et al.57 found that cycled material consisting of NaAlH₄ nanoconfined in activated carbon showed equilibrium sorption properties considerably different from those of Ti-doped and ball-milled material. The solubility of hydrogen was greatly enhanced, and the two-step behavior vanished.19 This is the first experimental evidence that thermodynamic effects may also be observed in such systems. It is a challenging task for experimentalists to identify any rearrangement in the structure when particles are incorporated into scaffold materials. In these situations, simulations can be helpful in order to understand and explain such unusual behaviors, and our pair distribution analysis shows that the atomic distribution in the scaffolded MgH₂ is similar to that of the amorphous state.

In order to substantiate this observation, we have calculated the H site energy (HSE; ΔE) in these nanophases. The H site energy is calculated in the following manner:

\[
\Delta E = \left( E_{\text{Hvac}} + \frac{1}{2} E_{\text{Hmol}} \right) - (E_{\text{nano}})
\]

where \( E_{\text{Hvac}} \) and \( E_{\text{nano}} \) refer to the energy of the nano-object/models with and without a H vacancy and \( E_{\text{Hmol}} \) is the total energy of a free H₂ molecule. In all these studied models, H is situated in four different chemical environments: the center of the model (H1), adjacent to the center (H2), near the interface (H3), and at the interface (H4), see Figure 9. The calculated

![Figure 9. Hydrogen sites used to calculate the hydrogen site energies are marked as H1 (center of the sandwich; 20 kJ/mol), H2 (adjacent to the center; 43.10 kJ/mol), H3 (near to the interface; 80.43 kJ/mol), and H4 (at the interface; 108.4 kJ/mol). The corresponding value for the bulk MgH₂ phase is 83 kJ/mol. Total number of atoms involved in this model is 373 (256 C, 35 Mg, 70 H, and 12 UBBH). The structure is magnified two times along the x axis for better view.](image)

![Table 2. Calculated Bond Overlap Population (BOP) and Hydrogen-Site Energy (in kJ/mol) for the Bulk and M1–M5](image)
the inner part of the nano-object. In contrast, in the scaffolded materials, removal of H from the center of the material is much easier than from other lattice sites. This clearly indicates that the scaffolded materials behave differently from the free nanophases as well as from bulk materials. In all these studied systems, the HSE value of H1 is always lower than that in H2, H3, and H4, and the magnitude of the HSE values vary in the following sequence H1 < H2 < H3 < H4. The calculated higher HSE value for the H4 site indicates that the C/MgH2 interface plays a significant role on the decomposition process.

In order to obtain a better understanding of the bonding interaction between the constituents, the bond overlap population (BOP) values were calculated on the basis of Mulliken population analysis. The BOP values can provide useful information about the character of the bonding interaction between atoms. A high BOP value indicates a strong covalent bond, while a low BOP value indicates an ionic interaction. For the practical use of MgH2 as hydrogen-storage materials, the Mg–H bonds should be weakened. The calculated BOP values for the studied structure models are listed in Table 2. Similar to the HSE values, the calculated BOP values are also scattered in a wide range (see Table 2 and Figure 10). Due to the ionic interaction, the calculated BOP value for the bulk phase is 0.64, which is much smaller than that of B–H in borohydrides. The calculated BOP value for the different pairs of the Mg–H bonds in the M2 structure model is displayed in Figure 10. The BOP values in Figure 10 clearly show that the Mg–H bonds are considerably weakened in some pairs and much stronger in some other pairs compared with that in the bulk phase. This finding clearly indicates that the interaction between the Mg–H pairs is changed considerably when they are in different parts of the structure (i.e., the bond strength is reduced in the central part of the structure than at the interface). This finding is consistent with the HSE study, where the HSE values vary from 22 to 108 kJ/mol (in the M2 model) depending upon the position of hydrogen. A similar observation was found in the rest of the structure models considered in the present study. The role of particle and pore sizes on the changes in the hydrogen desorption process in the carbon scaffolds are under investigation. The results will be published in a forthcoming article.

## CONCLUSIONS

In summary, we have systematically studied changes in formation energy with respect to the size of a MgH2 particle. We have predicted that the critical particle size for the MgH2 nanocluster is less than 2.2 nm. The calculated formation energy as a function of particle size revealed that the nanoparticles of MgH2 are more unstable than the corresponding decomposed phases. From experimental SANS studies, we have demonstrated that it is possible to incorporate nano-objects into the carbon scaffolds. Stable amorphous carbon structures have been successfully generated with two different approaches and have been used as a template to construct the scaffold MgH2 material. Using five different structure models, we studied the physical and chemical changes in the scaffold MgH2 materials. The calculated hydrogen-site energy as well as bond overlap analysis revealed that the bonding interactions in the inner part of the scaffold materials are considerably weaker than those at the AC/MgH2 interface. As a result, one can expect that the removal of hydrogen from the center of the scaffold is easier than that from the bulk or from the interface of the scaffold.

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