Confinement of Mg−MgH$_2$ Systems into Carbon Nanotubes Changes Hydrogen Sorption Energetics

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The density functional theory (DFT) method was used to study the effect of nanoconfinement on the energetics of Mg−MgH$_2$ systems. Varying levels of loading of the Mg/MgH$_2$ particles into a (10,10) carbon nanotube were examined, and the corresponding energetics were computed. A clear trend was observed that, as the level of loading increases (increasing confinement), the net energy change in the hydrogen sorption/desorption processes decreases to a significant level when the loading approaches the maximum. The confinement was found not to depend on the tube length of the confining nanotubes.

Introduction

Modifying the energetics of a H-sorption system has been of a considerable interest.[1] Such modification is especially important for the categories of H-storage materials where relatively high reaction energetics becomes one of the hindrances in efficient/economical H-sorption/desorption processes in vehicle onboard applications. Magnesium happens to fall into a category of such materials. While it had been demonstrated[2] that, by reducing the metal into nanosized particles, the kinetics can be improved dramatically, the energetics was proven both experimentally[2−5] and theoretically[6] not to change significantly in going from the macro- to the nanoregime. Like kinetics, the energetics is one of the important factors that controls the temperature and pressure conditions in hydrogen sorption/desorption. This probably explains the U.S. Department of Energy's guideline of a range of 15−24 kJ/mol$_H$ of energy change in hydrogen sorption/desorption for onboard hydrogen storages. The enthalpy[7] of H-sorption/desorption of bulk Mg−MgH$_2$ systems is 76.15 ± 9.2 kJ/mol$_{H2}$ or 38.08 kJ/mol$_H$. Apparently, such a value is considerably higher than what is required. Is there a way to reduce this high (energetics) value? Furthermore, as it is known that reducing the metal into nanoparticles helps to improve the kinetics, is it possible somehow to improve the energetics, as well, when the metal is in nanosizes?

There have been experimental[8−10] and theoretical[11,12] evidence that carbon nanotubes are capable of altering the physical−chemical properties (e.g., the density of gaseous phases) of a material trapped inside the nanotubes. On the other hand, procedures have been developed in filling carbon nanotubes with solid phases.[13−16] What will happen then if we fill nanotubes with Mg/MgH$_2$? Will the energetics of hydrogen sorption/desorption be modified favorably when such processes happen in a confined environment inside a carbon nanotube?

It has been demonstrated[6] that the density functional theory (DFT) method can be used to reliably study the energetics of the Mg/MgH$_2$ systems. It will be a natural extension of the approach when used in attempts to address questions such as those stated previously.

Computation Details

The software package, Dmol3,[17] as available in Accelrys' MS Modeling (version 3.0) suite of programs, was used in all the DFT calculations. Setup parameters were the same as previously reported,[6] with the exception that convergence criteria of the geometry optimizations were set to coarse in the present work, corresponding to a maximum change of 10^{-4} Ha, 0.02 Ha/Å, and 0.05 Å in energy, force, and displacement, respectively.

Bulk DMol3-optimized Mg and MgH$_2$ structures[6] were used in building the Mg/MgH$_2$ nanoparticles. To establish a basis for calibration, the energetics of unconfined Mg/MgH$_2$ system of nanophases was calculated first, in addition to adopting the bulk calculated values[6] of the same system. For these nanophases, parallel calculations were performed with the structures of the phases both unrelaxed (as built based on the bulk unit cell) and relaxed (after full geometry optimization).

A section of a two-unit length of a (10,10) carbon nanotube (see, e.g, Rao et al.[18] for carbon nanotube nomenclature) of approximate dimensions of 1.2 nm (diameter) × 0.6 nm (length) was chosen as the host of nanoconfinement (Figure 1). Dangling bonds at both ends of the nanotube were pacified using hydrogen. These pacifying hydrogen atoms were geometry optimized while keeping the carbons of the nanotube fixed. The pacified nanotube, including all the pacifying hydrogen atoms, was subsequently held rigid throughout the project.

Unrelaxed segments of Mg/MgH$_2$ nanoparticles were manually introduced into the nanotube such that (a) the enclosure of the nanoparticle as defined by the van der Waals radii did not overlap with that of the nanotube and (b) the enclosure of the nanoparticle did not extend beyond the length of the nanotube (Figure 1). Geometry optimization was then performed, with the nanotube being held rigid, to allow the nanoparticles to relax in the confined environment.

To study the influence of tube length over the nanoconfinement, two approaches were used (i.e., by incrementally increasing the tube length and by using a periodic boundary condition, respectively). In the first approach, while maintaining the fixed Mg/MgH$_2$ loadings, the length of the confining nanotube was incrementally increased. The otherwise identical procedure as outlined previously was used in calculating the corresponding energetics. In the second approach, the nanotube was placed

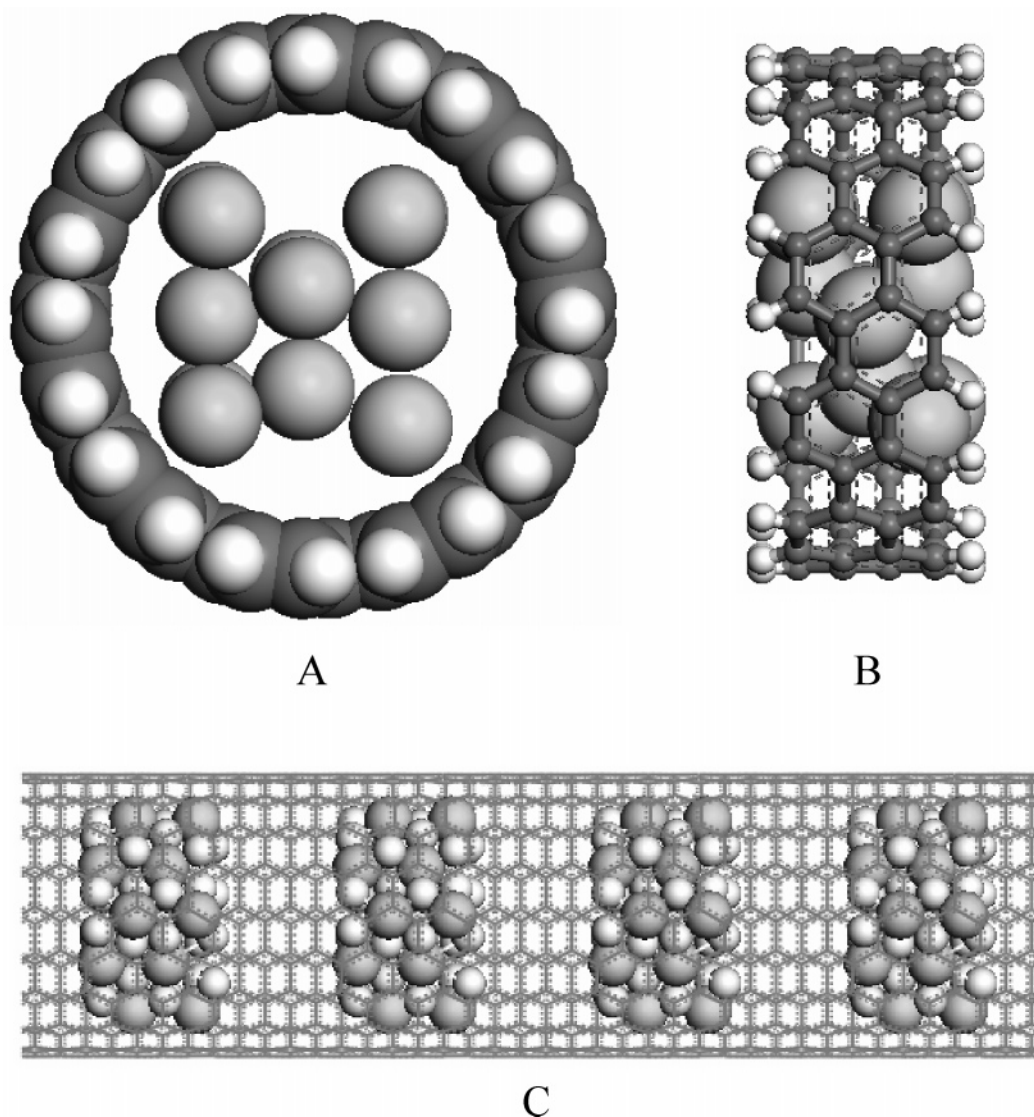* Corresponding author. Fax: (858) 799-5100. E-mail: jjl@accelrys.com.

Figure 1. Crystalline Mg/MgH$_2$ particles confined in a carbon nanotube (pacified by hydrogen at the ends where needed). (A) Cross-sectional view. Atoms were represented in the closest-packing style (in van der Waals radii). (B) Longitudinal view of a model system where a periodic boundary condition was not used. (C) Supercell representation (four units shown here) of a model system when a periodic boundary condition was used. Atoms of the nanotube were represented in stick-and-ball style for clarity. Gray spheres: Mg atoms; dark gray spheres: C atoms; and off-white spheres: H atoms.

TABLE 1: Thermochemical Cycle Used in the Calculation of Enthalpy of Formation at 0 K of MgH$_2$ from Crystalline Mg and Gaseous Hydrogen When Confined in a Carbon Nanotube[a]

reaction	ΔH_C[b] (kJ/mol)
H (element) + H (element) → H$_2$ (gas)	−431.5
H (element) + H (element) + Mg (element) + ELEMENT (nanotube)[c] → MgH$_2$ (crystal) NANOTUBE[d]	−6338.6
Mg (element) + ELEMENT (nanotube) → Mg (crystal) NANOTUBE	−5828.2
Mg (crystal) + ELEMENT (nanotube) + H$_2$ (gas) → MgH$_2$ (crystal) NANOTUBE $\Delta H_f = -\Delta H_1 + \Delta H_2 - \Delta H_3$	−78.9

[a] The example values correspond to a system containing 12 Mg atoms. [b] ΔH_C: energy of formation, not corrected for zero-point vibration. [c] ELEMENT (nanotube) = shorthand for a list of elements (C, H) in the carbon nanotube used. [d] NANOTUBE = shorthand for the nanotube itself confining the Mg/MgH$_2$ nanoparticles.

into a unit cell such that (a) the tube length coincided with the *c*-axis and (b) the *a*- and *b*-axes were sufficiently large such that intertube interactions are minimized. In this approach, no H-capping was necessary. For the confined Mg/MgH$_2$ phases inside the nanotube, a sufficient cushion (vacuum) along the tube length was ensured to prevent strong interaction of the Mg/MgH$_2$ phases to their own periodic images.

For all systems, the DMol3 calculated binding energies, not corrected for zero-point energy (ZPE), were used as the raw data in the energetics calculations. The enthalpies obtained correspond to the values at 0 K without ZPE correction (see

the following discussion). For unconfined systems, a thermochemical cycle similar to the one previously reported[6] was used in the calculation of the energetics. For confined systems, a modified thermochemical cycle was used (Table 1).

Results and Discussion

Results from the DMol3 calculations are given in Tables 2 and 3. Values in Table 2 are strictly raw data, and the derived energetics of various systems were plotted in Figure 2. Values in Table 3 were calibrated to a per-Mg basis to accommodate the tabulation of the derived energetics that is not suitable for

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TABLE 2: Binding Energy at 0 K (E_B, Not Corrected for Zero-Point Enrgy) from DMol3 Calculations of Nanophase Mg and MgH$_2$, Respectively, without and with Nanoconfinement by the Carbon Nanotube

		Not confined	
		E_B (kJ/mol)	
formula	dimension (nm^3)[a]	unrelaxed	relaxed
	Mg		
Mg$_{16}$	0.4 × 0.8 × 0.5	−814.0	−833.7
Mg$_{24}$	0.7 × 0.8 × 0.5	−1526.3	−1559.3
Mg$_{32}$	0.9 × 0.8 × 0.5	−2242.0	−2289.4
Mg$_{40}$	1.2 × 0.8 × 0.5	−2962.6	−3069.0
Mg$_{48}$	1.5 × 0.8 × 0.5	−3684.1	−3818.0
Mg$_{56}$	1.8 × 0.8 × 0.5	−4405.8	−4558.3
	MgH$_2$		
Mg$_{16}$H$_{32}$	0.9 × 0.9 × 0.6	−7713.8	−8835.7
Mg$_{24}$H$_{48}$	0.9 × 0.9 × 0.9	−12361.4	−13595.5
Mg$_{32}$H$_{64}$	0.9 × 0.9 × 1.2	−17008.7	−18147.0
Mg$_{40}$H$_{80}$	0.9 × 0.9 × 1.5	−21653.7	−22899.4
Mg$_{48}$H$_{96}$	0.9 × 0.9 × 1.8	−26297.5	−27513.8
Mg$_{56}$H$_{112}$	0.9 × 0.9 × 2.1	−30940.8	−32208.6

		Confined in carbon nanotube	
		E_B (kJ/mol)	
formula	dimension (nm^3)[a]	before confinement	after confinement[b]
	Mg		
Mg$_{12}$	0.4 × 0.5 × 0.5	−554.3	−69937.9
Mg$_{14}$	0.4 × 0.6 × 0.5	−629.8	−70159.5
Mg$_{15}$	0.4 × 0.8 × 0.5	−696.9	−70238.9
Mg$_{18}$	0.4 × 1.0 × 0.5	−918.6	−70646.8
	MgH$_2$		
Mg$_{12}$H$_{24}$	0.9 × 0.6 × 0.5	−6792.3	−76063.0
Mg$_{14}$H$_{28}$	0.9 × 0.7 × 0.5	−7965.5	−77164.5
Mg$_{15}$H$_{30}$	0.9 × 0.8 × 0.5	−8534.9	−77706.9
Mg$_{18}$H$_{36}$	1.0 × 0.9 × 0.5	−10263.7	−79288.8

[a] Approximate dimensions before structure relaxation, along directions that are closest to orthogonal to each other. Distances are measured between the cores of the outmost atoms. [b] Contribution from all elements in both the confining nanotube and the Mg/MgH$_2$ phases (actual values used in the thermochemical cycle similar to that in Table 1, after proper calibration). Binding energy of an empty nanotube (as used in the present study) is −69196.5 kJ/mol.

TABLE 3: Binding Energy at 0 K (Not Corrected for Zero-Point Energy) and the Derived Enthalpy of H-Sorption of the Mg$_{18}$ Particle as a Function of Tube Length of the Confining Nanotube[a]

	tube length[b]			
	2	4	5	periodic
	Binding Energy (kJ/mol)			
Mg$_{18}$	−3924.8	−7302.4	−9005.3	−8544.5
Mg$_{18}$H$_{36}$	−4404.9	−7781.0	−9484.2	−9024.8
	Enthalpy of H-sorption (kJ/ mol)			
	−48.6	−47.1	−47.4	−48.8

[a] All energy values calibrated to a per-Mg basis. [b] Represented by the number of repeating units (∼0.3 nm in length) along the tube length.

plotting. As mentioned earlier, the energetics data do not contain ZPE corrections, and as a result, the energetics was not projected to room temperature where standard energetics data are usually reported. It is true that the ZPE correction can be significant for certain systems even at 0 K.[19] However, for the Mg−MgH$_2$ systems, it has been shown[6] that ZPE corrections are relatively insignificant. More importantly, the present work compares systems that are very similar in structural configurations both before−and after their chemical reactions (hydrogen sorption/ desorption). The fact that an identical thermochemical cycle can be used for all data points in a particular Mg−MgH$_2$ series (e.g., unrelaxed, unconfined Mg−MgH$_2$ nanosystems) leads to a
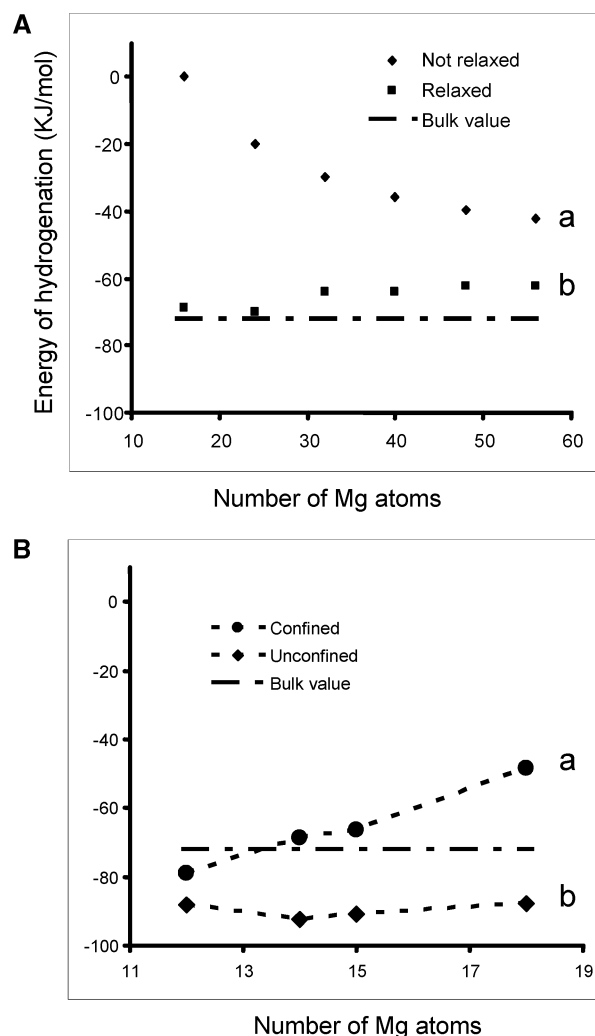

Figure 2. Hydrogen sorption energy at 0 K of crystalline Mg nanoparticles as a function of particle size (represented by the number of Mg atoms in the particles). (A) Mg/MgH$_2$ systems without nanoconfinement by the carbon nanotube. Data series a: Mg/MgH$_2$ systems with structures not relaxed from those of the bulk. Data series b: Mg/MgH$_2$ systems with structures fully relaxed. (B) Mg/MgH$_2$ systems confined in the carbon nanotube (data series a) with reference to the same systems not confined (data series b).

reasonable assumption that, should the ZPE correction become significant in a series of data points, the ZPE corrections should largely cancel each other out in a comparison of data points in the same series. Therefore, the derived energetics trends in each given series should represent a close approximation of the respective true trends at 0 K.

Confinement Mechanism. It may not be immediately apparent that two mechanisms were used in the present work to model the nanoconfinement, namely, molecular and periodic. In the molecular approach, an individual nanotube of a given tube length was considered explicitly. Nanoconfinement was realized through the interactions calculated exhaustively between the atoms of the nanotube and the Mg/MgH$_2$ crystallites placed inside the nanotube. As a result, the model systems (Mg/MgH$_2$ confined inside the nanotubes) considered in this approach corresponded to systems of finite dimensions (in particular, of a finite tube length of the confining nanotube) of varying sizes.

In the second approach of using periodic boundary conditions (PBC), confinement within the unit cell (the actual model system used in the calculations) was similar to that as in the molecular approach. However, there was a second, more important dimension in such calculations−the interaction between the

confined Mg/MgH$_2$ phases and their periodic images. Because of the periodic nature, the model system was essentially replicated in all three dimensions to infinity. Therefore, the system modeled corresponds to infinitely extending nanotubes (with the Mg/MgH$_2$ phases inside) that are sufficiently separated by vacuum from each other (Figure 1C). One constraint in this approach is in filling the nanotubes with the Mg/MgH$_2$ phases. Ideally, each such nanotube should be filled solid along the tube length by the Mg/MgH$_2$ phases to achieve maximum loading. While this is conceptually possible if a long nanotube is considered explicitly (as in the molecular approach discussed previously), it will be computationally intractable due to the almost extreme size of the model system needing to be used. The situation will, however, be very different when a periodic boundary condition is used. The difficulty lies in the fact that both the nanotube and the Mg/MgH$_2$ phases are crystalline and that there is a significant lattice mismatch between the crystalline phases. To be able to use the periodic boundary condition, motifs of the nanotube and the Mg/MgH$_2$ phases, respectively, need to be found that share identical periodicity along the tube length. That means that huge supercells need to be built that become intractable in the quantum-mechanics-based calculations.

As described in the Computational Details, the compromise was to construct the unit cell based on the nanotube's periodicity and patch by vacuum space the lattice mismatch between the Mg- or MgH$_2$–crystallites inside the nanotube and the nanotube motif. It is important to keep in mind that a sufficient vacuum (cushion) in such a case is essential. Because of the periodic nature, the Mg- or MgH$_2$–crystallites will interact with their own periodic images. While the energies of such interactions can be excluded easily from the confinement energies through the thermochemical cycle, the effect of such interactions on the structural configuration of the crystallites in relation to the nanotube will be complicated. In fact, interactions between nanocrystallites as a function of particle size and particle separation can well be a separate research topic in its own right.

Unconfined Systems. In the unconfined Mg–MgH$_2$ systems, when unrelaxed structurally, the net change in energy decreases as the number of Mg atoms decreases in the system, approaching the point of zero energy change (data series a, Figure 2A). Note here that the actual crossing point at zero energy change may be offset by a small amount depending on the ZPE corrections. Nevertheless, the trend points to an interesting aspect of the Mg–MgH$_2$ nanosystems: if the structures of the solid phases (Mg and MgH$_2$, respectively) can be confined as close to those of the bulk structures as possible, significant reduction of the net energy change in the hydrogen sorption/desorption processes can be achieved. As we can see later, this observation bears implications in cases where nanoconfinement is in place.

The trend (data series b, Figure 2A) in the unconfined, but structurally relaxed, Mg–MgH$_2$ nanosystems is very different: there does not seem to be a variation in the net change of energy in the hydrogen sorption/desorption processes as a function of particle size (represented by the number of Mg atoms in each respective nanoparticle). This finding agrees with the experimental results[2−5] and with previous theoretical calculations on thin-film Mg/MgH$_2$ systems[6] that the energetics does not change when Mg metal is reduced into nanosizes. Note here that there is about 10 kJ/mol$_{H2}$ difference in the energy values between that of the bulk and the average value of the nanoparticles. While within the experimental error range[7] and therefore may not be noticeable in experimental determinations, such an offset could also arise from the omission of ZPE correction in the present work that should be significantly larger in the nanophases as observed previously.[6] Further work accounting for ZPE corrections should clear up the ambiguity.

Confined Systems. It is challenging to achieve maximum confinement without experimentally or theoretically growing MgH$_2$ into the nanotube. We again, rather than relying on a single point of maximum confinement, resorted to observing the trend in net energetics changes of the Mg−MgH$_2$ systems filled into the nanotube, through incrementally increasing the percentage of the filled cavity (increasing the number of Mg atoms of the confined particles) of the nanotube. Note that the Mg/MgH$_2$ phases are free to grow in any direction and therefore grow, in particular, against the walls of the nanotube. Therefore, the confinement will be felt stronger and stronger as the MgH$_2$ loading approaches the maximum, without really reaching the point of maximum loading. Also, the relatively open systems (no restraints at the openings of the nanotubes) provided a mechanism that, should the nanotube become overloaded, the excess portions of the Mg/MgH$_2$ phases can spill out through the tube openings. It should be noticed here that, after full geometry optimizations, we did not see the Mg/MgH$_2$ phases extruding beyond the perimeters of the confining nanotubes, indicating no overfill in any of the nanoconfined samples studied.

Data series a in Figure 2B shows the net energetics changes in H-sorption in the Mg−MgH$_2$ systems confined in a (10,10) nanotube, as a function of increasing confinement (represented by the increasing number of Mg atoms in the confined phases). This data series was contrasted to data series b where the nanoconfinement was removed while the structures of the Mg/MgH$_2$ phases were fully relaxed. Again, when the Mg/MgH$_2$ phases were not confined and fully relaxed (data series b, Figure 2B), the energetics of H-sorption/desorption remained invariant with respect to the particle sizes (represented by the number of Mg atoms in the particles). Note, however, that there is a difference of ∼20 kJ/mol$_{H2}$ in the energetics between the data series b in Figure 2B and data series b in Figure 2A. An important difference between the two sets of samples in the two data series, respectively, is that, in Figure 2A, all samples correspond to integral numbers of unit cells (multiples of the Mg$_2$/Mg$_2$H$_4$ units) of the Mg/MgH2 systems, whereas in Figure 2B, all samples correspond to nonintegral multiples of the Mg/MgH$_2$ unit cells (Mg/MgH$_2$ atoms added to the systems did not form multiples of the Mg$_2$/Mg$_2$H$_4$ units) to meet the needs of incremental loading of the Mg/MgH$_2$ phases. Similar dependency of physical−chemical[6] and structural[20] properties over the exact correspondence of the sample contents to the integral multiples of the unit cell contents of the materials had been observed elsewhere. Further investigations on such dependence may yield important insight into surface engineering of nanoparticles.

A clear trend (data series a in Figure 2B) is apparent that, as the confinement increases, the energy change decreases. When the loading is light (corresponding to 12 Mg atoms in this particular case), the energy change is similar to those in the unconfined and fully structurally relaxed Mg−MgH$_2$ systems. However, as the loading gradually increased (stronger confinement), the energy change decreased steadily, passing the point where the value is reduced by half.

Influence of the Length of the Confining Nanotube. The H-sorption energetics of fixed Mg/MgH$_2$ loading (corresponding to 18 Mg atoms) but varying tube length of the confining nanotubes is given in the last row of Table 3. Such an exercise serves two (correlated) purposes: (a) to map out the longitudinal component, if any, of the confinement and (b) to rule out the potential complication of portions of the confined phases (unnoticeably) extruding beyond the perimeter of the confining nanotube.

As is apparent in Table 3, the energetics appeared to remain unchanged as the tube length of the confining nanotube

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increased. The introduction of the periodic boundary condition brought about the extreme condition where the nanotube was infinitely extending (of infinite length), carrying along with it uniform pockets of the Mg/MgH₂ phases. Yet, no significant change in the sorption/desorption energetics was observed in this extreme case. Therefore, we can safely conclude that the tube length does not play a role in the confinement.

Implication on Practical Systems. The plausibility of confining the Mg/MgH₂ systems into carbon nanotubes and the subsequent H-sorption/desorption reactions is yet to be demonstrated by experimental studies. Energetics data obtained so far suggest that the reaction characteristics of the nanoconfined Mg/MgH₂ systems inherit those of the unconfined systems. At low loading (Figure 2B, corresponding to 12 Mg atoms in the systems considered in the present study), the H-sorption/desorption reaction carries an identical signature of energetics of the completely unconfined Mg/MgH₂ system. As the loading level increases, the corresponding energetics changes, but only gradually (Figure 2B). Therefore, from the energetics point of view, H-sorption/desorption of Mg confined into carbon nanotubes can be considered as reactions perturbed from those of the unconfined system. Of course, the exact reaction pathways can still be very different, even after experimental verification of such confined systems. Key variables may include transporting hydrogen molecules to the solid/gas interface, dissociation of hydrogen molecules, and migration of the dissociated hydrogen species along/through the interfaces and within the Mg lattice (with/without reconstructive lattice relaxations). It is very encouraging to note that the presence of a minor alkaline species such as Li⁺ that comes with a carbon nanotube has proven to be capable of greatly enhancing the formation of metal hydride inside a carbon nanotube.[21] Therefore, the nanotube confined Mg/MgH₂ systems can benefit significantly from such catalytic mechanisms should the systems be found to suffer from sluggish/difficult forward/reverse (hydrogen sorption/desorption) reactions.

Aside from the carbon nanotube-confined Mg/MgH₂ systems, it is helpful to keep in mind that Mg and carbon nanotubes used in the present study can be considered prototype materials—a similar nanoconfinement effect can very well be important elsewhere. There had already been experimental demonstrations that nanoconfinement does change many aspects of the H-sorption/desorption processes. One[22] such example is the controlled hydrogen release of ammonia borane (NH₃BH₃) when confined in a mesoporous medium, SBA-15. It was observed that, when confined in the mesopores of SBA-15, ammonia borane gave an increased rate of H₂ release, modified polymeric products in the course of hydrogen release, and minimally formed borazine. The same research group had also been using computational methods to examine the thermochemistry[23] of unconfined ammonia borane and related materials. It will be interesting to see the thermochemistry of the meso-confined systems in regard to the individual reactions, most probably computationally.

One other category of potential H-storage materials that may benefit from nanoconfinement is the complex hydrides AMH₄ (A = Li, Na, K and M = B, Al, Ga). Its representative materials, NaAlH₄, show two-step dehydrogenation,[24] one at near-ambient temperature and the other at approximately 110 °C, apparently a function of thermochemistry in the different steps. Other members of the category, such as LiBH₄, while containing as high as 18.5 wt % hydrogen, are thermochemically so stable that they require extreme temperature conditions to dehydrog-

enize. It will therefore be useful to examine their thermochemistry in nanophases and to see the effect of nanoconfinement in, for example, the newly discovered metal−organic framework materials.[25]

Conclusions

When the structures of the unconfined nanoparticles of Mg/MgH₂ are fully relaxed, the energetics does not change as a function of particle size of the nanoparticles. However, the energetics tends to change significantly and favorably when the structures of the Mg/MgH₂ nanoparticles can be maintained as close to those of the bulk structures as possible. When confined into a (10,10) carbon nanotube, the Mg−MgH₂ system tends to yield a favorable modification of the energetics, reducing the net energy change in a hydrogen sorption/desorption process by as much as half the bulk value when the loading of the Mg/MgH₂ nanoparticles approaches the maximum. It appeared that such confinement is independent of the tube length of the confining nanotube.

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