Hydrogen Storage in Organometallic Structures Grafted on Silsesquioxanes

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Using density functional theory we show that a recently synthesized silsesquioxanes (SQ) nano complex $[RSiO_{3/2}]_n$ with R = $-C_5H_5$ provides a novel material for hydrogen storage. Grafting cyclopentadienyl on SQ totally changes its electronic structure and chemistry: cyclopentadienyl becomes a reactive site where a transition metal atom (e.g., Sc) can be doped to serve as an effective adsorption site for hydrogen molecules. This nano complex has the following advantages: (1) The storage capacity in the fully grafted case is 5 wt % where hydrogen is bound molecularly with a binding energy of about 0.6 eV/H_2 molecule. (2) The structure of SQ itself is stable. Our study shows for the first time that the functionalized SQ complexes can be an effective and practical material for hydrogen storage.

The success of a new hydrogen economy depends critically on our ability to find materials capable of not only storing hydrogen with large gravimetric and volumetric densities but also of operating at near ambient thermodynamic conditions. For the former, materials have to be lightweight; while for the latter, the bonding of hydrogen should be neither too weak (as in physisorption) nor too strong (as in atomic chemisorption). A novel form of bonding where hydrogen is bound molecularly with a binding energy in the range of 0.1 to 1.0 eV/H_2 is ideal both from the thermodynamics and kinetics points of view. Recently there has been considerable interest in exploiting this form of bonding in the design of hydrogen storage materials.[1−5]

Several authors have demonstrated computationally that a transition metal atom supported on isolated organic molecules such as cyclopentadiene (Cp) and C_{60} fullerenes can bind up to eight hydrogen atoms in nearly molecular form (H−H bond is stretched to about 0.83 Å) with an average binding energy of about 0.5 eV/H_2 molecule.[1−4] The origin of this bonding is due to the open d-shell nature of the transition metal atoms and has been discussed by Kubas and other authors more than a decade ago.[6,7] However, for practical applications these materials have to be stable. For example, transition metal atoms must not aggregate to form clusters and metal−organic complexes or metal-coated fullerenes must not coalesce, thus losing their individual structural identity. It has been recently demonstrated by Sun et al.[5] that transition metal atoms on a C_{60} surface would energetically prefer to cluster than remain isolated on the pentagonal faces as was assumed in the beginning. It has also been demonstrated[8] that this clustering of metal atoms can be avoided if C_{60} is doped with Li atoms instead of transition metal atoms. Although $Li_{12}C_{60}$ can adsorb up to 13 wt % hydrogen in nearly molecular form, the adsorption energy of hydrogen molecules is small and hydrogen can desorb at lower than ambient temperatures. The reason for this weak bonding is due to the mechanism that binds the hydrogen. Unlike the Kubas interaction, the transfer of electron from the Li atom to C_{60} leaves the metal atom in a cationic state and binds to hydrogen in nearly molecular form through a charge polarization mechanism.[9] Thus one must

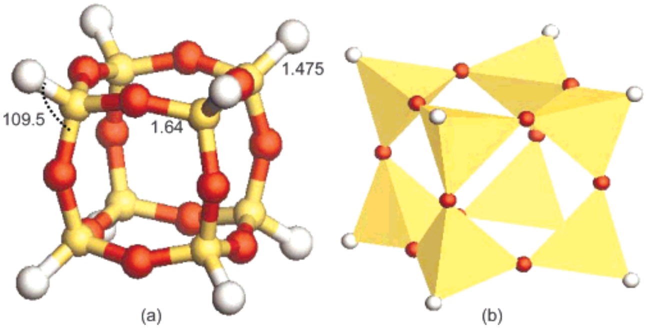

Figure 1. Geometry of (a) $H_8Si_8O_{12}$ and (b) its four-coordinated structure.

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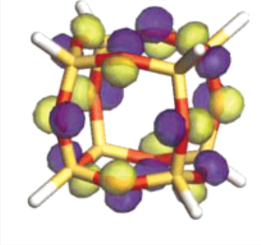
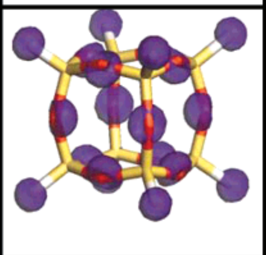
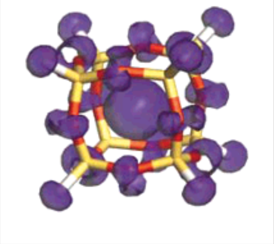
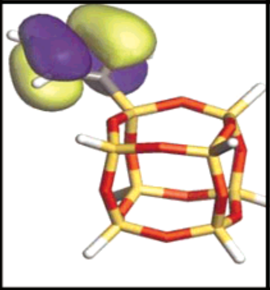
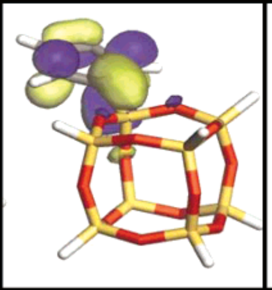
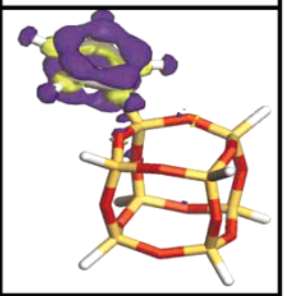
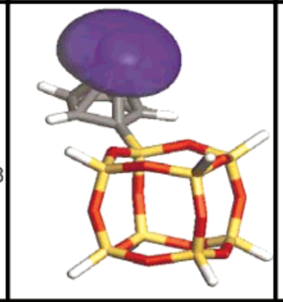
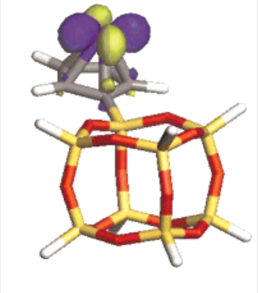
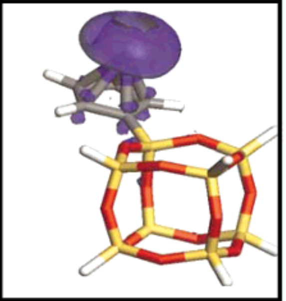
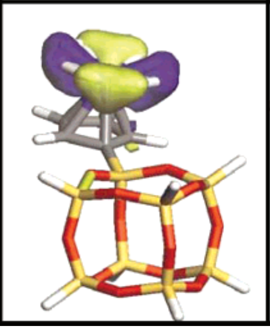
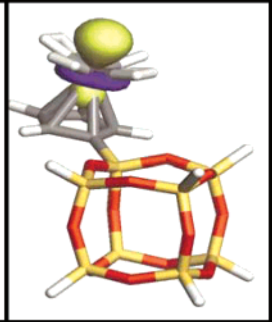
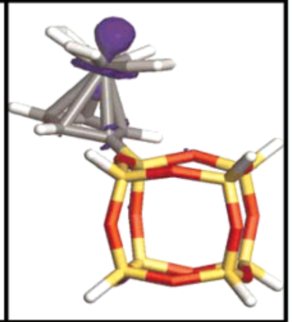
10.1021/cm0627948 CCC: $37.00

Table 1. Comparison of HOMO, LUMO, and Fukui Function

	HOMO	LUMO	Fukui
$H_8Si_{12}O_8$			
C_5H_4- $H_7Si_{12}O_8$			
ScC_5H_4- $H_7Si_{12}O_8$			
$4H_2$- ScC_5H_4- $H_7Si_{12}O_8$			

find ways where the synthesis routes would prevent transition metal atoms from clustering since these atoms bind hydrogen in nearly molecular form with a binding energy suitable for operation under ambient thermodynamic conditions.

In this article, we suggest a novel approach to assemble transition metal Cp complexes that circumvent the above problems and yet can store hydrogen. This involves grafting of the metal−Cp complex on silsesquioxanes (SQ). Our study is based on spin-polarized calculations within density functional theory. The plane-wave basis set with the projector augmented plane-wave method, as implemented in theVienna ab initio simulation package (VASP),[10] is used. The exchange and correlation potential is taken into account using the PW91 form for the generalized gradient approximation. The geometries of all systems studied are optimized without symmetry constraint using a conjugate-gradient algorithm. We have used super cells with 12 Å vacuum spaces along *x*, *y*, and *z* directions for all the calculated structures. The Γ point is used to represent the Brillouin zone due to the large supercell. The energy cutoff was set to 400 eV, and the convergence in energy and force were 10^{-4} eV and 1×10^{-3} eV/Å, respectively. The accuracy of our numerical procedure was well tested for hydrogen-related systems in our previous papers.[5,8,11] For example, the calculated bond length and binding energy of H_2 are respectively 0.749 Å and 4.536 eV, which agree very well with experimental values of 0.741 Å and 4.533 eV.[12]

To validate our computational procedure we started with the Cp unit. When Sc atom is capped on a Cp ring, the binding energy is found to be 3.81 eV with a Sc−C bond length of 2.44 Å. This complex is able to bind up to four H_2 molecules with an average binding energy of 0.69 eV/H_2.

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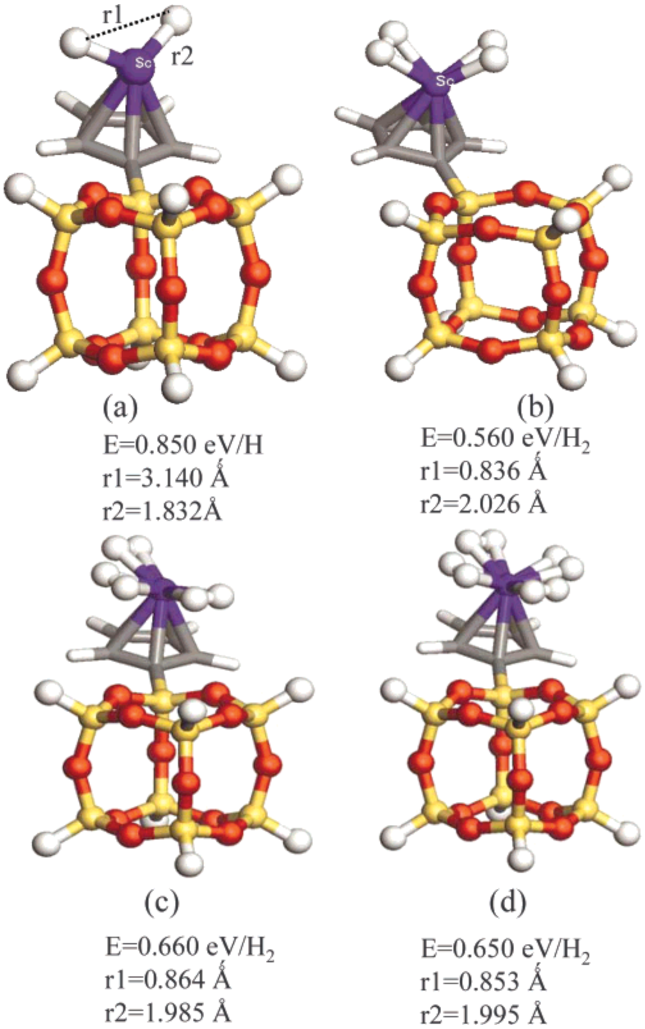


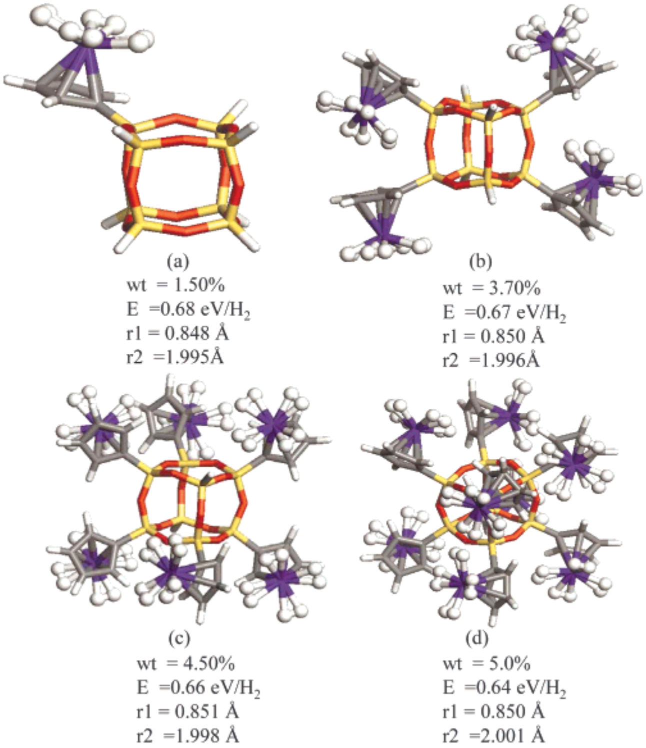
(a)
E=0.850 eV/H
r1=3.140 Å
r2=1.832Å

(b)
E=0.560 eV/H_2
r1=0.836 Å
r2=2.026 Å

(c)
E=0.660 eV/H_2
r1=0.864 Å
r2=1.985 Å

(d)
E=0.650 eV/H_2
r1=0.853 Å
r2=1.995 Å

Figure 2. Hydrogen adsorption on monografted structure. E is the adsorption energy, and r1 and r2 are the average distances of H−H and H−Sc.



(a)
wt = 1.50%
E =0.68 eV/H_2
r1 = 0.848 Å
r2 =1.995Å

(b)
wt = 3.70%
E =0.67 eV/H_2
r1 = 0.850 Å
r2 =1.996Å

(c)
wt = 4.50%
E =0.66 eV/H_2
r1 = 0.851 Å
r2 =1.998 Å

(d)
wt = 5.0%
E =0.64 eV/H_2
r1 = 0.850 Å
r2 =2.001 Å

Figure 3. Hydrogen adsorption in one- (a), four- (b), six- (c), and eight- (c) Sc−Cp-grafted structures. E is the average adsorption energy, r1 is the average hydrogen molecule bond length, and r2 is the average distance between H_2 and Sc.

The distance between H_2 and Sc is 1.995 Å. The adsorption of hydrogen was found to have little effect on the Cp geometry. All these results are in agreement with previous studies.[1]

Next we studied the assembly of the Sc−Cp complex by using SQ as a matrix which has the structural formula of $[RSiO_{3/2}]_n$. Here the functional group R can be H, alkyl, alkylene, aryl, arylene, or their organo-functional derivatives. The study of SQ and its derivatives has attracted great attention as they have applications in heat/abrasion resistant paints, coatings, cross-linking agents, fire retardants, viscosity modifiers, catalyst, polymer, porous materials, and biomedical materials.[13−15] In Figure 1, we show the geometry of $[HSiO_{3/2}]_8$, where the bond lengths of Si−O and Si−H are 1.640 and 1.475 Å, respectively, and the bond angle of H−Si−O is 109.5°, suggesting that all Si atoms are fully coordinated with sp^3 bonding.

The development of recent synthesis techniques enables R in $[RSiO_{3/2}]_n$ to be any molecular or nano structural unit. For example, octaphenylsilsesquioxane ($(C_6H_5)_8Si_8O_{12}$) and the derivatives of octa(aminophenyl)silsesquioxane and octa(nitrophenyl)silsesquioxane have been synthesized and extensively studied in experiments.[16−25] Especially by derivatizing the phenyl group with atoms or molecules, the system can be functionalized. For instance, bromination of SQ results in $Br_8(C_6H_x)_8Si_8O_{12}$ structure.[21−23] Because of the special chemistry and functionalities of cyclopentadienyl, recently researchers are very much interested in grafting cyclopentadienyl on SQ structure[26−29] using hydrosilation or thermal methods. Bent and Gunko[28] successfully synthesized a hybrid structure of $[RSiO_{3/2}]_n$ with R = $-C_5H_5$ and n = 8 and 10 using hydrolytic condensation of the silicon organic precursors. This experimental advance in assembling Cp with SQ sheds new hope for using this material for hydrogen storage.

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To get a better understanding for the grafted complex, we begin first with the study of its electronic structure. In Table 1 we give the calculated highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and Fukui function $f(0)$[30] for $H_8Si_8O_{12}$, $C_5H_4-H_7Si_8O_{12}$, $Sc-C_5H_4-H_7Si_8O_{12}$, and $4H_2-Sc-C_5H_4-H_7Si_8O_{12}$. It is well known that HOMO and LUMO are the frontier orbitals playing important roles in reaction, while the Fukui function is a reactivity index which measures the propensity of a region in a structure to accept or donate electrons in a reaction. For the original $H_8Si_8O_{12}$, the HOMO is mainly located on O sites, while the LUMO and Fukui functions are on H and O sites. As one H is replaced by C_5H_4, we get a monografted complex of $C_5H_4-H_7Si_8O_{12}$. Now the electronic structures are completely changed, and HOMO, LUMO, and Fukui functions $f(0)$ are concentrated on the Cp ring making it the favored site for a transition metal atom to bind. When the Sc atom is introduced, the HOMO, LUMO, and Fukui function $f(0)$ become concentrated on the Sc site. This clearly indicates that Sc would become the preferable site for hydrogen adsorption. We find that Sc atom can adsorb four H_2 molecules in a nearly molecular state. The adsorption also changes the electronic structure. In $Sc-C_5H_4-H_7Si_8O_{12}$, the HOMO is mainly contributed by the 4s- and $3d_{zz}$-Sc, while the LUMO is from $3d_{xy}$-Sc. However, in $4H_2-Sc-C_5H_4-H_7Si_8O_{12}$, the HOMO is mainly from $3d_{xy}$-Sc, and LUMO is from $3d_{zz}$-Sc.

For more detailed information about hydrogen bonding in $Sc-C_5H_4-H_7Si_8O_{12}$ complexes, we show in Figure 2 the successive adsorption of one, two, three, and four hydrogen molecules. When one H_2 is introduced, it dissociates and binds atomically to Sc with a binding energy of 0.85 eV/H. The distance between these two H atoms is 3.14 Å, and they are 1.832 Å away from Sc. However, when two, three, and four H_2 molecules are successively introduced, they bind nearly molecularly and the adsorption energy ranges from 0.56 to 0.66 eV/H_2. Note that all the hydrogen molecules have elongated bond lengths ranging from 0.836 to 0.864 Å. This is very similar to what was discovered computationally in an isolated Sc−Cp complex.[1]

Next we go further from monografted to multigrafted structures as shown in Figure 3. When going from one to four, six, and eight grafted complexes, we found that each Sc can still adsorb up to four H_2 molecules, and the corresponding hydrogen storage capacity increases from 1.5 to 3.7, 4.5, and 5.0 wt %. However, the corresponding average adsorption energies (0.64, 0.65, 0.65, and 0.64 eV/H_2), the average distances between Sc and hydrogen molecules (1.995, 1.996, 1.998, and 2.001 Å), and the average H−H bond lengths (0.851, 0.850, 0.851. and 0.850 Å) remain relatively unchanged. Therefore, we can see that assembling Sc−Cp units by grafting SQ not only can prevent the clustering of Sc atoms but also can retain their favorable hydrogen adsorption energy. Especially, the storage weight percentage of 5 wt % is close to the target of 6 wt % set by DOE for 2010.

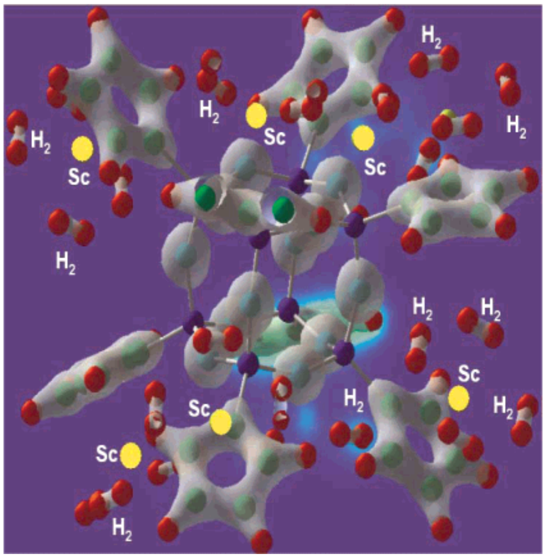

Figure 4. Charge density distribution of molecular hydrogen adsorption in Sc−Cp complex grafted on SQ.

In the following we focus on the discussions of the fully grafted complex in Figure 3d, where the average distance between the linking C in Cp ring and the linking Si in SiO cage (Si−C bond length) is 1.842 Å. Grafting the Cp ring makes the SiO cage expand only slightly with the Si−O bond length changing from 1.640 to 1.645 Å. To study the energetics of the fully grafted structure, we consider the following formation process,

$$H_8Si_8O_{12} + 8[Sc-C_5H_5] \rightarrow 8[C_5H_4-Sc]-Si_8O_{12} + 8H_2$$

Using the total energies of individual components in the above reaction, we found that this process is exothermic with the formation energy of −1.6 eV. This suggests that this formation process is energetically favorable.

In Figure 4, we present the iso-surface plot of charge density for the fully grafted complex of Figure 3d. The covalent bonding features in H_2 and in the Cp ring as well as the ionic feature between Si and O are evident. In fact, using Wigner−Seitz cell method for charge partitioning, we found that each Si, O, and Sc atom carries an average charge of +0.50 e, −0.29 e, and + 0.28 e, respectively. Due to the polarization interactions between Sc and H_2, each H_2 molecule is slightly negatively charged (−0.03 e).

As we have seen in the above, the grafting of Cp on SQ provides a novel and efficient way for storing hydrogen in molecular form. Readers may ask the following question: Because metal-containing silsesquioxanes have been widely studied,[31,33] where Si can be replaced by metal atoms including alkali, alkaline earth, and transition metal, can we also store hydrogen by just using Sc-containing SQ without Cp grafting? To answer this, we have carried out further calculations. When one Si in SQ is substituted by a Sc atom (Figure 5a), and initially three H_2 molecules are introduced

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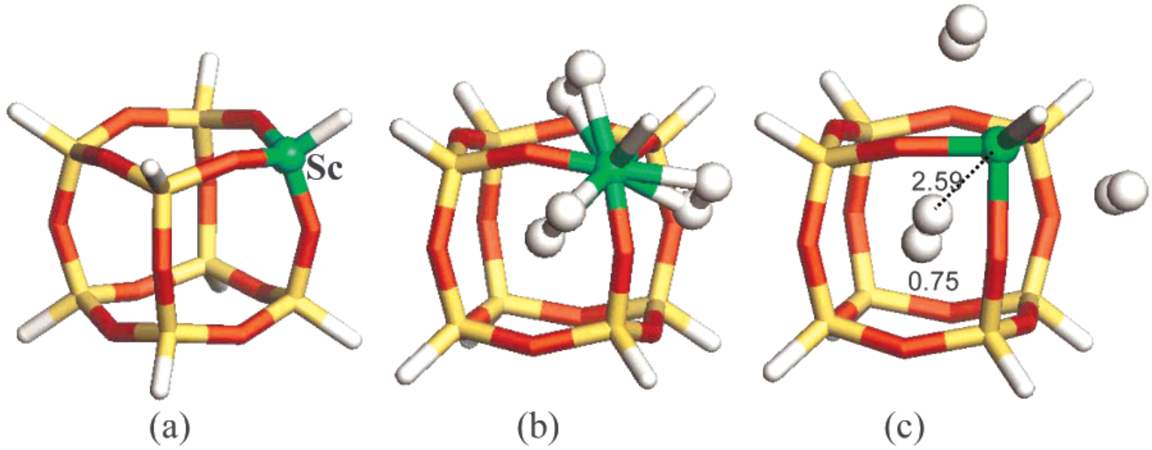

Figure 5. (a) Sc-containing SQ complex formed by replacing one Si with Sc; (b) initial and (c) final structures showing hydrogen adsorption.

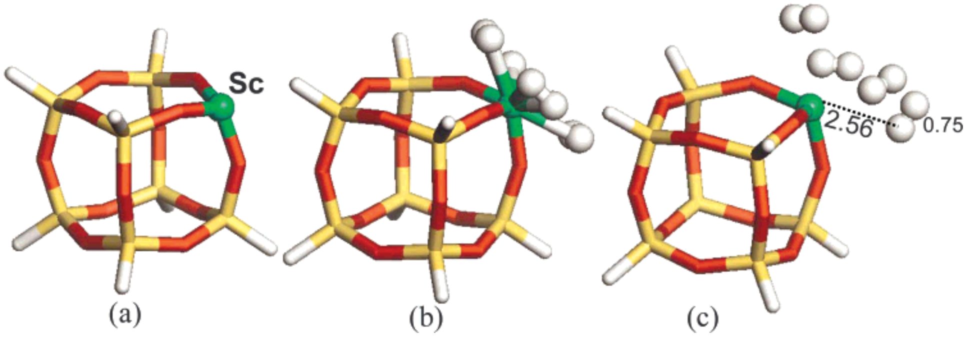

Figure 6. (a) Sc-containing SQ complex formed by replacing −SiH with Sc; (b) initial and (c) final structures showing hydrogen adsorption.

around the Sc site (Figure 5b), we found, after full optimization, that hydrogen molecules could not be bound to the Sc site. The distance between H_2 and Sc became 2.50 Å, and hydrogen molecules are almost in their free state with a bond length of 0.75 Å. Similar situations have also been found when one −SiH group is replaced with a Sc atom as shown in Figure 6a. Initially we put four H_2 molecules near that Sc site (Figure 6b), but in the final optimized configuration, all the hydrogen molecules moved away from the Sc site to a distance of 2.56 Å. The bond lengths of the hydrogen molecules are 0.75 Å which are very close to 0.749 Å in the free state. Therefore, metal-containing silsesquioxanes without Cp grafting cannot be used for hydrogen storage.

It should be noted that due to the large number of atoms in the systems we have studied, we could not carry out frequency calculations to correct for zero-point energy, which leads to over-binding for hydrogen molecules with the substrate. However, it has been found that in dihydrides of TiH_2 and VH_2 the over-binding is typically about 20 kJ/mol H_2.[34] When this correction is taken into account, the absorption energy of H_2 is around 0.45 eV/H_2. Fortunately, this binding energy is large enough for the storage material to operate at near ambient conditions, and neglect of zero-point energy corrections in our calculations will not change our main conclusions.

In summary, we show that SQ provides a stable, flexible matrix where Sc−Cp units can be grafted for storing hydrogen in nearly molecular form. In this way, the clustering problem found in Sc-coated C_{60} fullerene can be avoided while keeping the strength of the hydrogen binding within the desirable Kubas interaction regime. Furthermore, the system can store hydrogen molecularly with a gravimetric density of 5 wt %. These conclusions obtained using Sc as an example may also be applied to other transition metal systems. We hope that our study together with the recent synthesis of the C_5H_5 grafted SQ by Bent and Gunko[28] will stimulate further interest in the synthesis of these materials by doping with transition metals.

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