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Abstract

Prompted by the need for a self-supported, chemically stable, and functionally flexible catalytic nanoparticle system, we explore a system involving Pd clusters coated with a monolayer of polyhedral oligomeric silsesquioxane (POSS) cages. With an initial theoretical focus on hydrogen catalysis and sequestration in the Pd-POSS system, we report Density Functional Theory (DFT) results on POSS binding energies to the Pd(110) surface, hydrogen storing ability of POSS, and possible pathways of hydrogen radicals from the catalyst surface to unsaturated bonds away from the surface.

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Hydrogen build up in items such as electronics, heat-exchange equipment, vacuum maintenance, battery-operated devices etc. can potentially lead to explosive situations. As a preventive measure, scavenger molecules are designed to gather and store hydrogen in a variety of environments [1, 2]. Two of the most successful hydrogen scavengers so far have been 1,4-bis (phenylethynyl) benzene (DEB) and 1,4-diphenyl-butadiyne (DPB) [3]. Both are dialkyne, i.e., each molecule contains two triple bonds, and therefore can uptake four molecules of H_2. Prior to this uptake the H_2 molecules need to be broken down into H radicals. This step is usually achieved by catalysts, typically transition metal clusters placed on an inorganic (e.g., amorphous carbon or silica) support. Currently, however, there is a push for support-free design of such catalyst-scavenger systems, prompted by compatibility requirements with new materials. To this end we are exploring Pd nanoparticles coated with a monolayer of polyhedral oligomeric silsesquioxane (POSS) cages [4, 5]. The chemically diverse R-groups of such cages make them useful in multifunctional applications [6].

For usefulness of such a system in hydrogen catalysis and scavenging, several conditions need to be met: (1) the POSS-metal bonding should be strong and thermally stable; (2) it should be possible to place hydrogen-scavenging groups (like DPB or DEB) at several R-group positions of the POSS; (3) H-radicals formed at the metal surface should be able to find their way into the unsaturated bonds of the scavenger groups, many of which are not adjacent to the metal surface. Our experimental efforts are already addressing point (2) above through appropriate chemical synthesis steps [7]. However, points (1) and (3) could greatly benefit from insights gained through quantum chemical modeling, which could guide further design efforts.

In this Letter, we report a set of Density Functional theory (DFT) calculations to compare various modes of POSS binding to the Pd surface, i.e., through methyl groups, through linkers with amine end-groups, and through phenyl rings of hydrogen scavengers. Computed binding energies should help guide our experimental choice of a suitable binding mode of POSS to the Pd surface. If hydrogen scavenging is the primary aim, one would like to substitute most or all of the POSS R-groups by H-scavenging groups. Whether attached or not attached to POSS, typically most of the scavenger molecules are not directly adjacent to the metal surface, and we explore possible pathways in which H-radicals formed on the metal surface can find their way to the unsaturated bonds of such scavenging groups away from the surface. Finally, we investigate any hydrogen sequestering/storing capability that the hollow space of a POSS cage might possess.

Spin-polarized DFT calculations were performed using the code DMol^3 from Accelrys [8-11], which employs localized basis sets defined on a numerical grid. In our choice of settings the electronic wave functions are expanded in a double-numeric polarized (DNP) basis set, with the basis functions represented on a "medium" numerical grid and truncated at a real-space cutoff of 4.0 Å. The core electrons of the Pd atoms are represented by the Density-Functional Semi-core Pseudopotentials (DSPP) [11], while all other electrons are represented explicitly. A nonlocal DFT Hamiltonian is used with gradient-corrected exchange-correlation functional due to Perdew, Burke, and Ernzerhof (PBE) [12]. Calculations on the Pd (110) surface employ periodic supercells for which accurate Brillouin zone sampling was ensured by summing over a finite set of K-points chosen according to the Monkhorst-Pack scheme [13] with a grid spacing of 0.05 Å^{-1}. For certain reactions accurate transition state barriers are obtained by a generalized synchronous transit method [14].

Fig. 1 (a) displays an all-methyl POSS cage. The design flexibility with POSS lies in the fact that each of these methyl groups can be replaced with a specified functional group, thus making the system chemically versatile and multifunctional. For instance, one or more of the groups could be a linker chain that anchor it to the metal surface, and the remaining groups could be used for other purposes, e.g., hydrogen scavenging, polymer cross-linking, enhanced miscibility, reinforcement and so on [6, 15]. Fig. 1(b) displays DFT-optimized structures for an all-methyl POSS cage on a Pd(110) surface. The net binding energy of this structure is ~ 10 kcal/mol, with little charge transfer between the POSS and the metal. The binding energy to the metal surface could be enhanced by replacing a methyl group by a linker chain, e.g., the one shown in Fig. 1(c) that consists of a short alkane chain terminated by an electron-donor group like NH_2. The preferred binding mode is the one in which the lone-electron-pair orbitals of the N-atom face the metal surface. In such a mode, the linker donates ~ 0.3 electrons to the metal surface (by Mulliken analysis [16]) resulting in a large binding energy ~ 32 kcal/mol. The net binding of the POSS-linker system to the Pd surface (Fig. 1(d)) is ~ 40 kcal/mol, which is just a sum of the binding energies of the structures in Fig.

1(b) and 1(c). Even this binding is smaller than the binding energy of a DPB molecule with the Pd(110), which we previously computed to be ~ 66 kcal/mol [3] using the same DMol^3 parameters. Thus, a POSS-DPB system (schematically shown in Fig. 1(e), relaxed by classical force field) is expected to have a binding energy ~ 75 kcal/mol. Therefore, H-scavenger molecules like DEB or DPB can be used for the dual purpose of binding POSS particles to the Pd surface and scavenge for H radicals at the same time, and a separate design for a linker molecule may not be necessary.

Let us now turn to the hydrogen catalysis aspects of the Pd cluster. Table 1 recaps our previous results of H_2 dissociation into H radicals on the Pd(110) surface [3]: a H_2 molecule physisorbs exothermically with an energy gain of 9.4 kcal/mol, followed by the dissociation into two H radicals ($H\bullet$), which is also an exothermic process with an additional energy release of 7.1 kcal/mol. The dissociated H radicals possess high mobility on the Pd surface with a low migration barrier (~ 6 kcal/mol). With a scavenger molecule (DPB or DEB) physisorbed on the surface (as illustrated in Fig. 1(e)), the unsaturated bonds will gradually get saturated by the H radicals. As illustrated by calculations with an ethylene molecule, the insertion of the first H radical into an unsaturated bond (Fig. 2(a)) is actually an endothermic process, with an energy cost of $\Delta E \sim +19.7$ kcal/mol. However, the second radical insertion more than compensates with an energy release of ~ 45.0 kcal/mol, and the net process of a complete saturation of an unsaturated double bond by two H radicals is exothermic by $45.0 - 19.7 = 25.3$ kcal/mol, very close to the value we previously obtained for DPB [3].

The third row of Table 1 indicates that the energy of direct desorption of a H radical from the Pd surface is prohibitively large ~ 60.7 kcal/mol. However, our experiments [7] indicate that under high hydrogen pressure most of the scavenger molecules get saturated by hydrogen, even the ones that must reside at some distance from the Pd surface at the beginning of the reaction. This implies that either H radicals find their way from the metal surface to the unsaturated scavenger bonds away from the surface, or that non-reacted scavenger is transported at a reasonable rate toward the metal. The high energy cost we compute for desorption of hydrogen radical from the surface indicates that the former is not a likely process. Admittedly our calculations do not account for intrinsic quantum effects associated with the light H-nucleus [17, 18], which might effectively lower the barrier for radical desorption. The migration of H radicals away from the metal surface could also be enabled by one or more intermediate steps of lower energy barrier. For instance, the H radical can form an intermediate with the benzene ring (Fig. 2(b)) of the scavenger molecules. However, this process is endothermic as well, with an energy cost of ~ 35.5 kcal/mol. In addition, there needs to be a percolating pathway of benzene rings to enable longer range migration of H. In order to gain further insight we are experimentally studying the hydrogenation behavior of DPB physically blended with nanoscopic colloidal Pd supported on amorphous carbon. From limited data so far it appears that the extent of DPB hydrogenation depends on the reaction rate, which is a function of the applied hydrogen pressure. For sufficiently high rates (high hydrogen pressure) the reaction proceeds to a great extent, with around 90% of the DPB becoming H-saturated. Under low hydrogen pressure, on the other hand, the reaction rate is slow, and a much smaller fraction of DPB hydrogenates. A possible explanation could be that higher rates furnish adequate heat to drive the diffusion of unreacted scavenger that sits away from the catalyst down the DPB concentration gradient toward the catalyst.

Finally, since POSS consists of nanoscopic cages, it is interesting to explore its endohedral hydrogen storage capabilities. The possibility of stabilization and trapping of H atoms by POSS cages has been discussed in the literature more than a decade ago [20]. Liquid solutions and organic substituents are known to play a significant role in stabilizing hydrogen radicals [4, 5]. However, as a first step for simplicity we base our analysis on an isolated all-methyl POSS cage. Table 2 describes a sequence of steps that can lead to the entrapment of H_2 inside a POSS cage, and the relevant DFT-optimized structures are illustrated in Fig. 3(a-d). As the first row of Table 2 indicates, a H radical weakly physisorbs onto the outside of the POSS cage (Fig. 3(a)). It can then potentially enter the cage through the nearest Si_4O_4 ring, leading to an endohedral hydrogen radical inside the POSS cage (denoted in Fig. 3 by the symbol H•@POSS). The process is mildly endothermic with an energy cost ΔE = 5.1 kcal/mol, and an energy barrier $\Delta E_{barrier}$ = 28.8 kcal/mol (corresponding to a de-trapping barrier $\Delta E_{detrapping}$ = 28.8-5.1=23.7 kcal/mol for a H• to diffuse out of the cage). It is interesting to compare the above numbers with previous B3LYP and MP2 results for an all-H POSS cage [21]: 6.2 kcal/mol and 2.2 kcal/mol respectively for ΔE, and 23.6 kcal/mol and 30.8 kcal/mol respectively for $\Delta E_{detrapping}$. Given that symmetric substitution of H by methyl groups do not alter results significantly [22], we conclude that our DFT results with DNP basis set and PBE functional is in excellent agreement with B3LYP results [21]. Being a light nucleus, the H radical could quantum mechanically tunnel through this barrier rapidly. Soon a dynamical equilibrium is expected to be established where the number of POSS cages with H radicals will depend on the overall concentration of H radicals in the surroundings. If it dynamically happens that a second H radical diffuses into a POSS cage with a H radical already present in it, a H_2 molecule forms spontaneously. Once the H_2 molecule forms, it is essentially stuck inside the cage because the barrier to diffuse out is rather high, 60.4 kcal/mol (which is 13 kcal/mol more than twice $\Delta E_{detrapping}$), as indicated in the 4th row of Table 2. If the concentration of hydrogen is high enough, additional H_2 molecules could similarly form in the same cage. We would like to note that all our arguments are based on T=0 calculations. At finite temperatures there could be thermally assisted processes, e.g., ring-opening vibrations [23] that could potentially lower the barriers mentioned above.

In summary, through spin-polarized gradient-corrected DFT calculations we have explored various aspects of a Pd-POSS system, especially as it pertains to hydrogen scavenging and storage. We find that one could simply utilize the benzene rings of DPB or DEB hydrogen scavenger molecules to bind the POSS to the Pd surface, and a separate linker group, e.g., the commonly used alkyl-amine system may not be necessary. We also find that even if the scavenger is physisorbed on the metal surface, the insertion of the first H-radical into an unsaturated bond is an endothermic process with an energy cost of ~ 20 kcal/mol. However, the net process of insertion of first and second H radicals is an exothermic process with a net energy gain of ~ 25 kcal/mol. The H radical can move freely on the Pd surface, but has a very high desorption barrier (~ 60 kcal/mol) from the surface. Given the experimental observation that even the scavenger molecules away from the metal surface get H-saturated over time, we speculate that either the H radical uses one or more intermediate states to reach these unsaturated bonds, or thermal convection of scavenger molecules brings non-reacted unsaturated bonds to the catalyst surface. Experiments to shed more light on the actual mechanism are currently underway. Finally, we explore the possibility of hydrogen storage inside the POSS cage. We show that a H radical weakly binds to the outside of a POSS cage, and then can enter the cage through the nearest Si_4O_4 ring with an energy barrier of ~ 29 kcal/mol. If a second H radical enters the cage while the first one is still inside, a H_2 molecule forms spontaneously. Interestingly a H_2 molecule inside the POSS cage is 16.5 kcal/mol less stable than an H_2 outside the cage. This is essentially because each H atom is 5.1 kcal/mol less stable inside the cage (see row 2 of Table 2) and there is an additional energy cost of 6.3 kcal/mol due to either of the H-atoms in the H_2@POSS structure not being at the center of the cage. Even then, once formed, the H_2 molecule is essentially stuck inside because the barrier to diffuse out is large, ~ 60.4 kcal/mol. The work presented here should be interpreted as a theoretical first step. In a real system the structures and mechanisms are expected to be more complicated due to the effects of solvent, functional substituents, and temperature.

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Table 1. Energetics of various processes relevant to the uptake of H radicals from Pd(110) surface. $\Delta E > 0$ (< 0) indicates endothermic (exothermic) process.

Process	Description	ΔE (kcal/mol)
$H_2 + Pd \rightarrow H_2/Pd$	Physisorption of H_2 molecule on Pd surface	-9.4
$H_2/Pd \rightarrow 2\, H\bullet/Pd$	Dissociation of H_2 molecule into H radicals ($H\bullet$)	-7.1
$H\bullet/Pd \rightarrow H\bullet + Pd$	Direct desorption of H radical from Pd surface	+60.7
$H\bullet/Pd + C_2H_4 \rightarrow Pd + C_2H_5\bullet$	Uptake of a $H\bullet$ on Pd surface by an adjacent unsaturated bond (see Fig. 2(a))	+19.7
$H\bullet/Pd + C_2H_5 \rightarrow Pd + C_2H_6$	Uptake of a second $H\bullet$ on Pd surface by a partially saturated bond (product of the previous step)	-45.0
$H\bullet/Pd + C_6H_6 \rightarrow Pd + C_6H_7\bullet$	Uptake of a $H\bullet$ on Pd surface by an adjacent benzene ring (see Fig. 2(b))	+35.5
$C_6H_7\bullet \rightarrow C_6H_6 + H\bullet$	Desorption of $H\bullet$ from $C_6H_7\bullet$	+25.2

Table 2. Sequence of steps leading to hydrogen storage inside an all-methyl POSS cage (see Fig. 3). Energy change (ΔE) and the activation barrier ($\Delta E_{barrier}$) for each step are indicated.

Step	Description	ΔE (kcal/mol)	$\Delta E_{barrier}$ (kcal/mol)
H• + POSS → H•/POSS	Physisorption of H radical (H•) to outside of POSS	-0.2	0.0
H•/POSS → H•@POSS	H• enters the POSS cage through a Si_4O_4 ring	+5.1	28.8*
H• + H•@POSS → H_2@POSS	A second H• enters the POSS cage to form a H_2 molecule inside the cage	-94.0	28.8
H_2@POSS → H_2/POSS	The H_2 molecule diffuses out of the POSS cage through a Si_4O_4 ring	-16.5	60.4

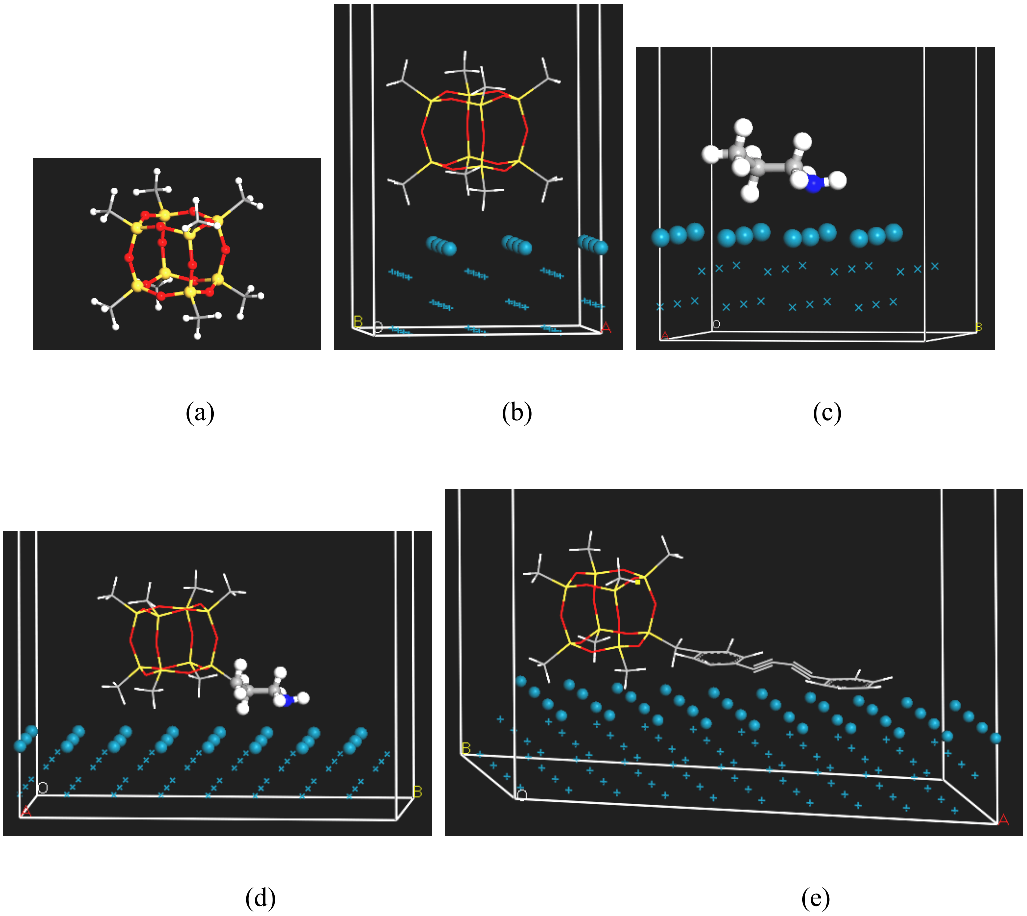
*The de-trapping barrier, i.e. barrier for a H• to diffuse out of a cage is = 28.8 – 5.1 = 23.7 kcal/mol.

Figure Captions:

Fig. 1. (a) Structure of an all-methyl POSS-cage; (b)-(e) binding of various complexes to the Pd(110) surface: (b) POSS; (c) alkyl-amine linker; (d) POSS + alkyl-amine linker; (e) POSS + DPB scavenger. Color scheme (online): C (grey), O (red), N (dark blue), H (white), Si (yellow), Pd (light blue).

Fig. 2. Intermediates formed by partial saturation of an ethylene and benzene by a H radical: (a) C_2H_5; (b) C_6H_7. The ethylene double bond is just a simple representation of a scavenger unsaturated bond, while benzene is a part of the structure of both DPB and DEB scavengers [3].

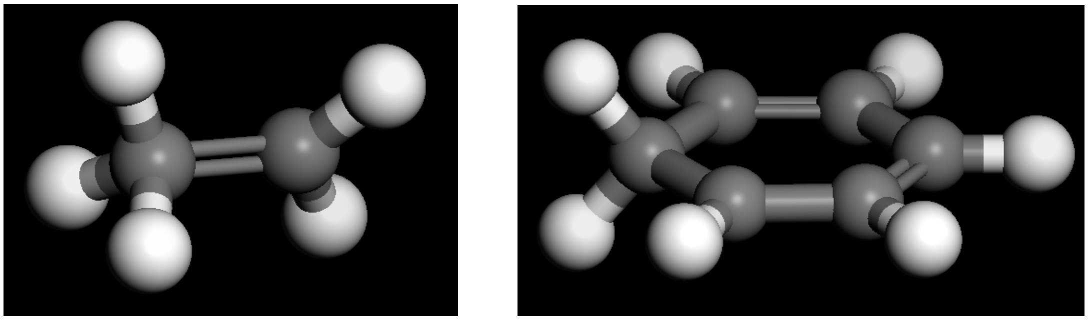
Fig. 3. Pictorial representation of various steps of a simple scheme in which a H_2 molecule can get stored inside an all-methyl POSS cage: (a) $H\bullet$/POSS; (b) $H\bullet$ @POSS; (c) $H\bullet$ + $H\bullet$ @POSS; (d) H_2 @POSS. The "@" symbol denotes an "endohedral" species. Energetics and barriers of various steps are listed in Table 2. Color scheme (online): C (grey), O (red), H (white), Si (yellow).



(a) (b) (c)

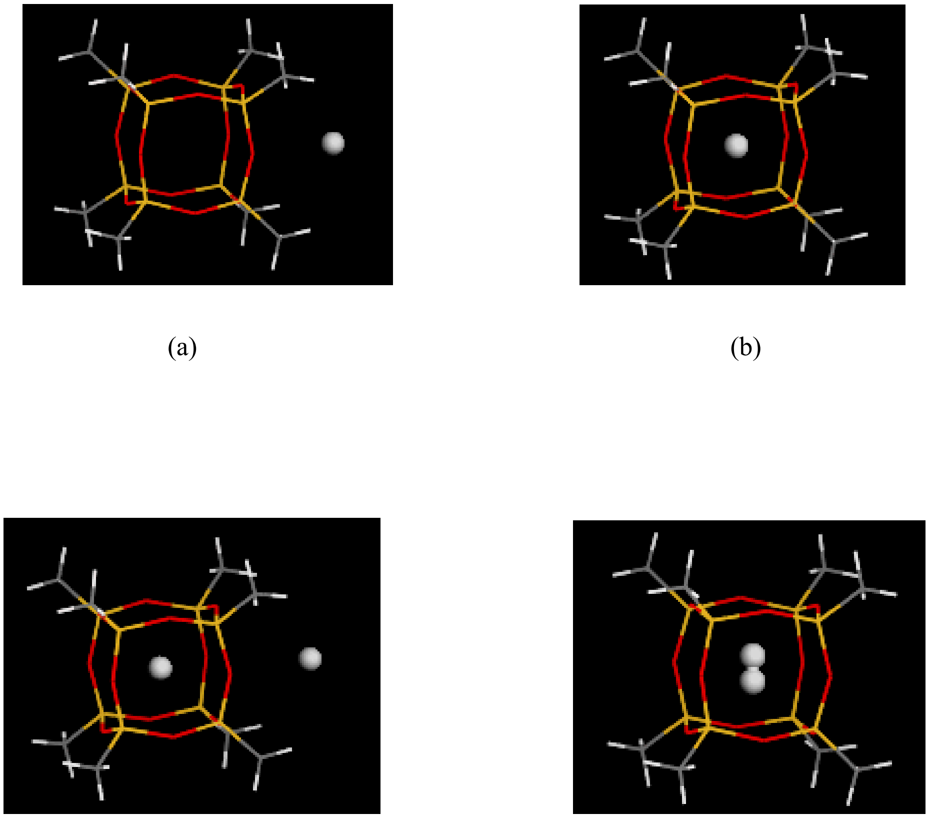
(d) (e)

Figure 1



(a) (b)

Figure 2



(a) (b)

(c) (d)

Figure 3