

## Calcium-hydroxyl group complex for potential hydrogen storage media: A density functional theory study

Manh Cuong Nguyen, Moon-Hyun Cha, Keunsu Choi, Yealee Lee, and Jisoon Ihm\*

Department of Physics and Astronomy, FPRD, and Center for Theoretical Physics, Seoul National University, Seoul 151-747, Korea

(Received 12 December 2008; revised manuscript received 28 April 2009; published 26 June 2009)

Using density functional theory electronic structure calculations, we investigate the calcium-hydroxyl group complex for potential applications to the hydrogen storage at near ambient temperature and pressure. The Ca atom is bound to the hydroxyl group with a binding energy comparable to the cohesive energy of bulk Ca, and we find that each Ca atom binds up to seven H<sub>2</sub> molecules in the molecular form. Binding of an unexpectedly large number of H<sub>2</sub> molecules is attributed to the fact that *d* orbitals of Ca positive ions are downshifted and partially occupied, thereby validating the empirical 18-electron rule as in the transition metal atoms. The binding energy turns out to be  $\sim 0.1$  eV/H<sub>2</sub>, somewhat smaller than the requirement ( $\geq 0.2$  eV/H<sub>2</sub>) of the room-temperature application. We also show that an important bonding mechanism of H<sub>2</sub> molecules on Ca is the polarization, namely, the electric dipole moment of H<sub>2</sub> induced by the partially ionized Ca. Based on this result, the possibility of the organic material functionalized with hydroxyl groups for a hydrogen storage medium is discussed.

DOI: 10.1103/PhysRevB.79.233408

PACS number(s): 68.43.Bc, 71.15.Nc, 84.60.Ve, 73.22.-f

Hydrogen has been well known as a CO<sub>2</sub>-free alternative energy source. However, the major obstacles in using hydrogen energy at present, especially as fuels on board vehicles, are the safety and the efficiency in storing hydrogen at ambient temperature and pressure. Recently, people have paid much attention to transition metal (TM)-decorated organic systems.<sup>1-7</sup> In these systems, TM atoms can be bound to organic molecules through the Dewar-Chatt-Duncanson interaction<sup>8,9</sup> and then can bind hydrogen molecules in the molecular form via the Kubas interaction<sup>10</sup> with the binding energy between physisorption and chemisorption, i.e., in the desirable range for the hydrogen storage at ambient conditions. Many systems within this category were suggested by theoretical researchers with gravimetric and volumetric storage densities of hydrogen satisfying the U.S. Department of Energy goal by the year of 2010 (6 wt % and 45 g/l).<sup>11</sup> Although those systems may, if successfully synthesized, match the criteria of storing hydrogen, clustering of TM atoms occurs in reality and reduces the storage capacity drastically.<sup>12</sup> In order to avoid metal clustering, people suggested to decorate the background material with alkali or alkaline-earth metal atoms that have relatively small cohesive energy (1–2 eV),<sup>13,14</sup> hoping that the tendency toward cluster formation may be reduced. However, the overall stability of the alkali or alkali-earth decorated system is still not proven and the mechanism of bonding of early alkaline or early alkali-earth metal atoms with H<sub>2</sub> molecules is yet unclear.

In this study, we choose propane-1,3-diol as a representative organic system and show that the hydroxyl group added to organic systems can bind a Ca atom strongly and then the Ca atom can bind up to seven H<sub>2</sub> molecules in the molecular form. We also examine the bonding mechanism of H<sub>2</sub> molecules on this system. Unlike in the Kubas interaction in the TM where the electron donation and back donation give rise to the bonding, the polarization of H<sub>2</sub> molecules plays an important role in the present material system.

We employed the density functional theory<sup>15</sup> electronic

structure calculations with the plane-wave total energy minimization.<sup>16</sup> The generalized gradient approximation (GGA) of Perdew *et al.*<sup>17</sup> was used in the calculation. We also presented, for comparison, the binding energy of H<sub>2</sub> molecules calculated within the local density approximation (LDA) described by Ceperley-Alder as parametrized by Perdew and Zunger.<sup>18</sup> The projector-augmented wave pseudopotential<sup>19,20</sup> calculations were performed by the VASP code<sup>21</sup> in optimizing the atomic structures. In analyzing the bonding mechanism, we used the PWSCF code<sup>22</sup> with the Vanderbilt ultrasoft pseudopotential<sup>23</sup> because the wave function (with positive and negative signs) and postprocessing codes were available only in the PWSCF code. The kinetic energy cutoffs were 350 eV and 40 Ry and the atomic positions are relaxed until the forces were reduced to within 0.01 eV/Å and 0.001 Ry/a.u. in calculations with VASP and PWSCF codes, respectively. We used the supercell method with the vacuum gap size of  $>10$  Å after the hydrogen adsorption so that the supercell size was  $22 \times 15 \times 15$  Å<sup>3</sup>. The H<sub>2</sub> binding energy was obtained by comparing the total energy of the system with and without the H<sub>2</sub> adsorption (fully relaxed, respectively). (That of Ca was also obtained in the same way.)

First, we consider the attachment of Ca to the hydroxyl group. Figures 1(a) and 1(b) show the propane-1,3-diol molecule and that with one Ca atom attached to the hydroxyl group. The binding energy of Ca is 1.73 eV and the distance between the O and the Ca atoms is 2.00 Å. This binding energy is much higher than the direct binding (without the

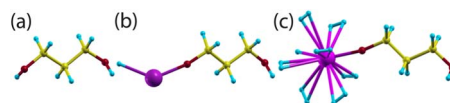


FIG. 1. (Color online) Atomic structures of (a) propane-1,3-diol, (b) propane-1,3-diol with one Ca atom added to the hydroxyl group, and (c) Ca-decorated propane-1,3-diol with seven H<sub>2</sub> molecules adsorbed on Ca.

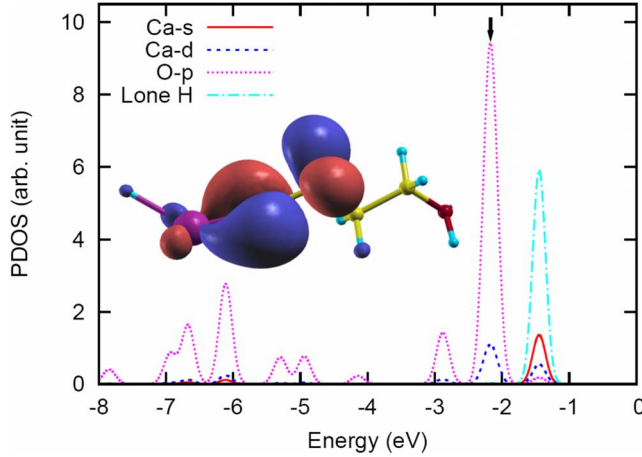


FIG. 2. (Color online) PDOS of the propane1,3-diol with one Ca added to the hydroxyl group as in Fig. 1(b). The inset is the eigenstate with the isovalue of  $0.001a_B^{-3/2}$  at the peak position (arrow) in the PDOS plot. Red and blue in the eigenstate indicate the plus and the minus signs of the wave function. The Fermi level is set to zero.

hydroxyl group in between) of Ca to a chain or a ring structure of carbons ( $\leq 1.0$  eV) and comparable with the cohesive energy of bulk Ca (1.84 eV). Since Ca atoms are preferentially bound to the functional group sites, we can control the number as well as the position of Ca atoms by our design of the functional group arrangement on the organic system, thereby avoiding metal clustering. Figure 2 shows the projected density of states (PDOS) of the system on the Ca and the O atoms. The inset is the eigenstate at the peak indicated by an arrow in the PDOS plot. We can see clearly that originally unoccupied  $d$  orbitals of an isolated Ca atom are involved in the bonding with the O atom. These  $d$  orbitals of the isolated Ca atom take part in bonding due to the downshift of the orbitals as a result of the ionization of the Ca atom. The Ca atom becomes a positive ion of  $+0.9642|e|$  according to the Lowdin analysis and the occupation of the  $d$  orbitals is  $0.6429e$ .

After attaching Ca to the hydroxyl group, we supply  $H_2$  molecules to the system and the Ca atom can adsorb up to seven  $H_2$  molecules in the molecular form with the binding energy of 0.099 eV/ $H_2$  molecule (Table I). The atomic structure in the case of seven  $H_2$  molecule adsorption is shown in Fig. 1(c). We note that the maximum number ( $N_m$ ) of  $H_2$  molecule adsorption obtained here from the *ab initio* calculations is consistent with the so-called 18-electron rule.<sup>3</sup> According to this empirical rule,  $N_m = [(18 - N_v - N_b)/2]$ , where the rounding-off symbol  $[ ]$  means that  $[X]$  is the largest

TABLE I. Average binding energy of  $H_2$  molecules (in eV) for variable number of  $H_2$  molecules adsorbed on Ca-decorated propane1,3-diol as shown in Fig. 1. Both GGA and LDA results are presented.

No. of $H_2$	1	2	3	4	5	6	7
GGA	0.094	0.098	0.116	0.128	0.114	0.106	0.099
LDA	0.256	0.339	0.361	0.369	0.324	0.316	0.307

integer not exceeding a real number  $X$ ,  $N_v$  is the number of valence electrons, and  $N_b$  is the number of chemical bonding of the Ca.  $N_m$  is 7 here as  $N_v^{Ca}=2$  and  $N_b=2$ . This rule certainly requires the availability of the  $d$  orbitals (the number 18 comes from the availability of  $2s$ ,  $6p$ , and  $10d$  orbitals) and usually holds only for TM atoms having some occupied  $d$  orbitals. However, Ca is positively ionized in the present situation and the originally high-lying unoccupied  $d$  orbitals are downshifted and partially occupied. Some unoccupied  $d$  orbitals are close to the highest occupied molecular orbital level as well. Such a modified environment explains the somewhat unexpected validity of the 18-electron rule. Since Ca has less  $N_v$  than any other TM atoms (e.g.,  $N_v^{Ti}=4$  and  $N_v^{Fe}=8$ ), Ca has a great advantage in achieving large  $N_m$ . On the other hand, the average binding energy ( $\sim 0.1$  eV) is a little bit too small compared with the ideal binding energy for the room-temperature storage (0.2–0.4 eV). Much larger binding energies obtained using the LDA method are also presented for comparison, but it is widely accepted that the LDA gives a too strong binding energy in situations similar to the present case and the true binding energy should be closer to the GGA than to the LDA result. It is known that the GGA is unable to produce the dispersion (van der Waals) interaction energy adequately. One possible way to give a rough correction to this deficiency is to add simply a typical value of this interaction energy (typically  $\sim 50$  meV) to the obtained binding energies. On the other hand, as pointed out in a previous study,<sup>5</sup> we need to subtract the zero-point energy of the adsorbed  $H_2$  to obtain the true (dynamic) binding energy of  $H_2$  molecules. Our calculations using the Born approximation with a harmonic-potential-surface fit show that the correction to the binding energy from the zero-point vibration is about 25 meV ( $\sim 25\%$  of the binding energy), which is consistent with the empirical value suggested in Ref. 5. The correction from the van der Waals interaction energy and that of the zero-point energy have opposite signs and will result in a small net increase ( $\sim 25$  meV) in the binding energy. In all cases of different numbers of  $H_2$  adsorption, adsorbed  $H_2$  molecules, are always in the molecular form with the H-H distance of 0.761–0.782 Å, which is  $<4\%$  stretched from the calculated value (0.752 Å) of the isolated  $H_2$  molecule. The binding energy per  $H_2$  molecule varies for different numbers of  $H_2$  adsorption with the trend that it increases with the increasing number of adsorbed  $H_2$  molecules from 1 and reaches the highest value of 0.128 eV for four  $H_2$  molecule adsorption and then decreases afterward. This trend is also observed for the binding energy calculated within the LDA.

This system, if used as is, requires somewhat low temperature for operation because of the weak binding. For example, at 77 K, the store capacity is 15.2 wt % (seven  $H_2$ 's are fully adsorbed). However, at  $-50$  °C (typical hydrogen mass-storage temperature at the fuel station) and 100 atm, our calculation using the grand partition function shows that it is reduced to 8.9% (approximately four  $H_2$ 's are adsorbed) and it becomes essentially zero at room temperature. The practicality of the low temperature storage on board vehicles (requirement of cooling systems, etc.) is a challenging task to be studied further in the future. In addition, it may be necessary to search for other atomic species or modify structural designs so as to increase the binding energy.

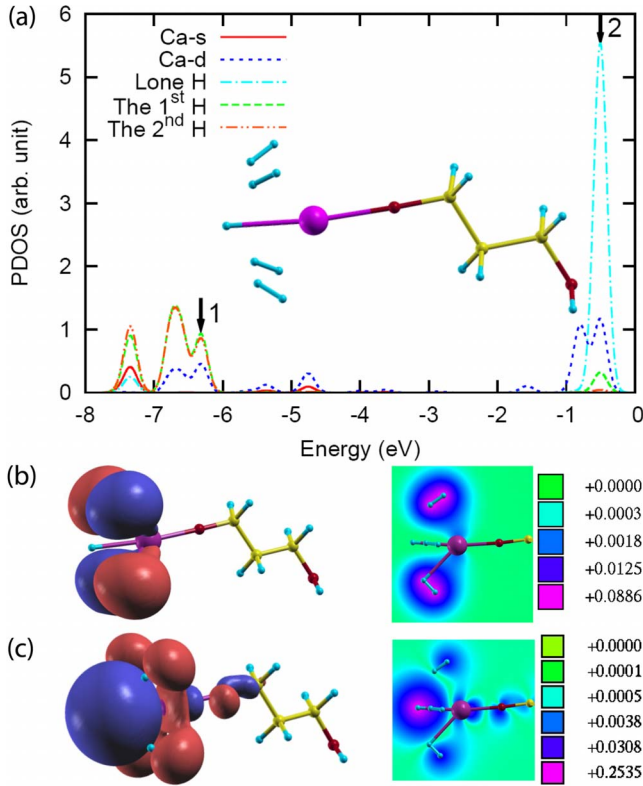


FIG. 3. (Color online) (a) PDOS of the inset atomic structure on the Ca atom, the lone H atom, and a  $H_2$  molecule. The Fermi level is set to zero. The inset is the relaxed atomic structure of the system. Eigenstates corresponding to peaks 1 and 2 in (a) are shown in (b) and (c), respectively. The wave function with the isovalue of  $0.0004a_B^{-3/2}$  and the integrated density of states with the energy window of 0.4 eV are plotted in each case. Red and blue in the eigenstates indicate the plus and the minus signs of the wave function.

Next, in order to analyze the bonding mechanism of  $H_2$  molecules on the system, we investigate in detail the atomic and electronic structures in the case of the highest  $H_2$  bind energy (as well as the highest geometric symmetry), which is the four  $H_2$  molecule adsorption. In this case, the configuration of four hydrogen molecules is square symmetric and tilted a little toward the lone H atom, as shown in the inset of Fig. 3. The O, Ca, and lone H atoms are aligned almost linearly so that we can regard the environment around the Ca atom as nearly octahedral. Thus,  $d$  orbitals of the Ca atom will mainly be split into  $e_g$  ( $d_{x^2-y^2}$  and  $d_{3z^2-r^2}$ ) and  $t_{2g}$  ( $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$ ) orbitals. We also show in Fig. 3(a) the PDOS on the Ca atom, the lone H atom, and a  $H_2$  molecule. In Figs. 3(b) and 3(c), we show the eigenstate and the integrated local density of states (ILDOS) at two peaks indicated by 1 and 2 in the PDOS plot. The isovalue of the eigenstates is  $0.0004a_B^{-3/2}$  and the energy window of the ILDOS is 0.4 eV.

The eigenstate at peak 1 is a hybridized state of the Ca  $d_{x^2-y^2}$  orbital with  $\sigma$  orbitals of four  $H_2$  molecules and this hybridization is usually called the donation channel in the Kubas model.<sup>10</sup> In this donation channel, filled  $\sigma$  orbitals of  $H_2$  molecules donate electrons to the empty  $d_{x^2-y^2}$  orbital of the Ca atom. The ILDOS at peak 1 shows clearly the

symmetry between two H atoms of a  $H_2$  molecule, which confirms that this is really the  $\sigma$  bonding orbital of the  $H_2$  molecule. It is in contrast to the case of the TM atom<sup>24</sup> where the Kubas interaction unambiguously exists with both donation and back-donation channels. In the back-donation channel in the TM- $H_2$  hybridization, the  $d$  orbitals give back electrons to  $\sigma^*$  ( $\sigma$ -antibonding) orbitals of  $H_2$  molecules leading to significant (10–20%) stretching of the H-H bond length. In the present case of the Ca bonding, we do not find the back-donation channel and the stretching of  $H_2$  molecules is very small ( $<4\%$ ) as mentioned above. On the other hand, we find another bonding mechanism between the Ca atom and  $H_2$  molecules at peak 2. In this bonding mechanism, there is a small overlap of  $d_{z^2}$  orbital of Ca with only one of the two H atoms (the atom farther from the lone H) of each  $H_2$  molecule as demonstrated in the ILDOS where a weak link between the Ca atom and the  $H_2$  molecule is present. The amplitude of the eigenstate at the other H atom (the atom nearer to the lone H) of each  $H_2$  molecule is practically zero, as can be seen in the ILDOS. The PDOS of this second H atom is almost zero at peak 2 while that of the first H atom is significant comparing to other peaks at different energy levels. The difference in the charge occupation between two constituting H atoms in  $H_2$  indicates that there occurs a polarization of  $H_2$  molecules and the Lowdin analysis confirms this polarization. The average difference in the charge between two H atoms in  $H_2$  is  $0.0452e$ . Admittedly, in Lowdin analysis as well as in any other charge analyses, it is difficult to assign electrons clearly to a particular atom and the value obtained from a charge analysis has to be accepted with caution. Another quantity that has a more precise and quantitative meaning, as long as the total charge is neutral, is the dipole moment because we can calculate charge distribution accurately.

To calculate the dipole moment of four polarized  $H_2$  molecules, we first define the charge distribution of a particular  $H_2$  molecule as the difference in total charge between the above atomic structure with four  $H_2$  molecule adsorption and the atomic structure with one less  $H_2$  molecule (i.e., three  $H_2$  molecules attached). From this charge difference distribution we calculate the dipole moment by postprocessing code of the PWSCF code.<sup>22</sup> The average dipole moment per  $H_2$  for the four adsorbed  $H_2$  molecules is  $0.262ea_B$  (0.667 Debye), which is quite substantial. There are other methods to calculate the dipole moment, which give approximately the same result. From this dipole moment we can estimate roughly the contribution of the polarization to the binding energy. We assume the polarized  $H_2$  molecules as point dipoles and the Ca, the lone H, and the O atoms as point charges of  $0.8355|e|$ ,  $-0.4184|e|$ , and  $-0.5546|e|$  obtained from the Lowdin analysis, respectively. The interaction energy of these dipoles in the electric field generated by the Ca, the lone H, and the O ions is subtracted from the scalar product of the dipole and the field. The angles between the dipole and the electric field generated by the Ca, the lone H, and the O ions are  $101^\circ$ ,  $24^\circ$ , and  $106^\circ$ , respectively, and the interaction energy per dipole is  $-0.068$  eV, which is  $\sim 50\%$  of the binding energy. The  $H_2$ -Ca and the  $H_2$ -O angles are close to  $90^\circ$  ( $101^\circ$  and  $106^\circ$ ) so that the contributions to the dipole energy are small whereas the  $H_2$ -H angle is small (i.e., tending to lie

in parallel) and provides a major contribution. Although our estimation is rather rough, we can conclude that, at least, the polarization contributes to the binding energy of the same order of magnitude as the hybridization. To reiterate, the donation channel and the polarization play equally important roles in the bonding mechanism of  $H_2$  molecules to the Ca-decorated system, unlike in the TM-decorated case.

In conclusion, we have suggested a method to insert Ca in the hydrogen storage system via the hydroxyl group. In this way, we can bind Ca atoms strongly to the hydroxyl group and then adsorb  $H_2$  molecules on Ca atoms. Since Ca atoms are bound preferentially to the hydroxyl group sites, we can design organic systems such that hydroxyl groups are located at desired positions and disperse Ca atoms on these sites without clustering. The maximum gravimetric storage capacity can be very high (15.2% for the propane-1,3-diol with two

Ca decoration at two hydroxyl groups). However, the binding energy of the  $H_2$  molecule is rather small ( $\sim 0.1$  eV) and we may need either a low temperature for the hydrogen storage or a further change in the atomic species or structures to increase the binding energy. We also explain the bonding mechanism of  $H_2$  molecules on the Ca-hydroxyl complex, in which the polarization of  $H_2$  molecules, as well as the Ca- $H_2$  hybridization, plays an important role.

We acknowledge the support of the KOSEF grant funded by the Korea Government MEST (Center for Nanotubes and Nanostructured Composites), the Korean Government MOE-HRD, Basic Research Fund No. KRF-2006-341-C000015, and the Hanwha Chemical Co. Computations were performed through the support of KISTI.

\*jihm@snu.ac.kr

<sup>1</sup>Y. Zhao, Y. H. Kim, A. C. Dillon, M. J. Heben, and S. B. Zhang, *Phys. Rev. Lett.* **94**, 155504 (2005).

<sup>2</sup>T. Yildirim and S. Ciraci, *Phys. Rev. Lett.* **94**, 175501 (2005).

<sup>3</sup>B. Kiran, A. K. Kandalam, and P. Jena, *J. Chem. Phys.* **124**, 224703 (2006).

<sup>4</sup>E. Durgun, S. Ciraci, W. Zhou, and T. Yildirim, *Phys. Rev. Lett.* **97**, 226102 (2006).

<sup>5</sup>H. Lee, W. I. Choi, and J. Ihm, *Phys. Rev. Lett.* **97**, 056104 (2006).

<sup>6</sup>P. F. Weck and T. J. D. Kumar, *J. Chem. Phys.* **126**, 094703 (2007).

<sup>7</sup>E. Durgun, Y.-R. Jang, and S. Ciraci, *Phys. Rev. B* **76**, 073413 (2007).

<sup>8</sup>J. Chatt and L. A. Duncanson, *J. Chem. Soc.* (1953) 2939.

<sup>9</sup>M. J. S. Dewar, *Nature (London)* **156**, 784 (1945).

<sup>10</sup>G. J. Kubas, *J. Organomet. Chem.* **635**, 37 (2001).

<sup>11</sup><http://www.eere.energy.gov/hydrogenandfuelcells/mypp/>.

<sup>12</sup>Q. Sun, Q. Wang, P. Jena, and Y. Kawazoe, *J. Am. Chem. Soc.*

**127**, 14582 (2005).

<sup>13</sup>Q. Sun, P. Jena, Q. Wang, and M. Marquez, *J. Am. Chem. Soc.* **128**, 9741 (2006).

<sup>14</sup>M. Yoon, S. Yang, C. Hicke, E. Wang, D. Geohegan, and Z. Zhang, *Phys. Rev. Lett.* **100**, 206806 (2008).

<sup>15</sup>W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).

<sup>16</sup>J. Ihm, A. Zunger, and M. L. Cohen, *J. Phys. C* **12**, 4409 (1979).

<sup>17</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

<sup>18</sup>J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).

<sup>19</sup>P. E. Blochl, *Phys. Rev. B* **50**, 17953 (1994).

<sup>20</sup>G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).

<sup>21</sup><http://cms.mpi.univie.ac.at/vasp/>.

<sup>22</sup><http://www.pwscf.org/>.

<sup>23</sup>D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).

<sup>24</sup>M. C. Nguyen, H. Lee, and J. Ihm, *Solid State Commun.* **147**, 419 (2008).