

# High Hydrogen Capacity and Reversibility of K-Decorated Silicon Materials

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We have investigated the H<sub>2</sub> adsorption structures and binding energies of the metal (M)-doped (M = Li, Na, K, Mg, and Al) silicon complexes, M-Si<sub>19</sub>H<sub>11</sub> and M-Si<sub>24</sub>H<sub>12</sub>, using density functional calculations. Alkali metals are preferred as doping elements because the Mg-Si and Al-H<sub>2</sub> interactions are weak. The maximum numbers of H<sub>2</sub> molecules that can be adsorbed are four and five for M=Li and K, respectively. We propose that the K-decorated silicon material might be an effective hydrogen storage material with high hydrogen capacity and high reversibility.

**Key Words** : Alkali metal, Density functional calculation, Hydrogen storage, Potassium, Silicon

## Introduction

For more than a decade, hydrogen, as an alternative to traditional energy sources such as oil and natural gas, has been the focus of research and development efforts in all technologically advanced countries of the world. It is strongly believed that hydrogen can help address the growing demand for energy and thus slow down global climate change.<sup>1,2</sup> There are significant challenges in storing the large quantities of hydrogen that will be necessary in the hydrogen energy economy. The principal challenges in improving hydrogen storage technologies are increasing their efficiency, size, weight, capacity, and ultimately, their cost.<sup>3,4</sup> Currently available methods for storing and delivering hydrogen fuel include compressed hydrogen, liquefied hydrogen, metal hydride storage, and nanostructure storage. However, so far no material has been successful in combining the hydrogen storage capacity for *on-board* systems such as automotive engineering with the ability to reversibly adsorb and desorb hydrogen under proper kinetic and thermodynamic conditions.<sup>5-9</sup>

Despite the great progress of carbon-based nanostructures, including nanotubes,<sup>10,11</sup> fullerenes,<sup>12,13</sup> and nanoscrolls,<sup>14,15</sup> carbon materials are difficult for achieving a high adsorption capacity of hydrogen unless they have an extremely high specific surface. A solution to this problem is doping carbon-based porous materials, such as fullerene and carbon nanotube with metal atoms such as alkali metals, which opens a new strategy for hydrogen storage research. Doping carbon-based materials with some metals can enhance the hydrogen storage capacity significantly owing to the higher H<sub>2</sub> binding affinity of decorated atoms than that of pristine carbon-based materials.<sup>12,16</sup>

Compared with carbon, silicon has more electrons in the outer shells, which leads to higher polarizability and a stronger dispersion force. Accordingly, the silicon materials

exhibit a stronger *van der Waals* attraction to hydrogen than the corresponding carbon analogues. Many previous theoretical investigations have suggested the possibility of promising silicon materials and predicted their structures and properties for the development novel materials for hydrogen storage.<sup>17-23</sup>

In the present work, we evaluate the hydrogen storage capacity of metal-adsorbed silicon systems (metal=Li, Na, K, Mg, and Al) using quantum chemical calculations and propose relevant materials that satisfy both the high storage capacity and high reversibility required for hydrogen fuel storage.

## Computational Details

Calculations of the total energies and geometry optimization were performed with the generalized gradient approximation (GGA) of Perdew-Wang (PW91)<sup>24</sup> as implemented in the Gaussian03 package.<sup>25</sup> The 6-31G(d,p) basis sets were used. Geometry optimizations were carried out without any symmetry constraints.

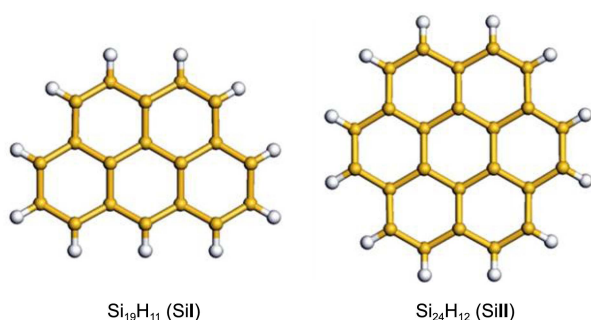
An exhaustive search for the lowest-energy structures was performed for each specific H<sub>2</sub> adsorption on the metal-decorated silicon complex. The binding energies ( $\Delta E_B$ ) of H<sub>2</sub> molecules adsorbed on the silicon complexes, Si<sub>19</sub>H<sub>11</sub> (SiI) and Si<sub>24</sub>H<sub>12</sub> (SiII), were evaluated by the formula,

$$\Delta E_B = (\text{energy of silicon material with } (n-1)\text{H}_2) + (\text{energy of H}_2) - (\text{energy of silicon material with } n\text{H}_2),$$

where a positive binding energy denotes a stable complex against the H<sub>2</sub> dissociation.

## Results and Discussion

We selected the SiI (Si<sub>19</sub>H<sub>11</sub>) and SiII (Si<sub>24</sub>H<sub>12</sub>) as model systems (see Figure 1) for silicon hydrogen storage materials



**Figure 1.** Optimized structures of the  $\text{Si}_{19}\text{H}_{11}$  (SiI) and  $\text{Si}_{24}\text{H}_{12}$  (SiII).

such as silicon nanowires and silicon nanotubes. The metal-decorated silicon complex was formed with a SiI or SiII system and a single metal atom (Li, Na, K, Mg, and Al). We found that the metal atoms bind with the silicon systems in a  $\eta^6$  fashion. The binding energies of metal atoms are summarized in Table 1. The binding energies of the metal atoms vary significantly from the lowest for Mg to the highest for Al. The binding energies of the Li atom decorated on the center of SiI and SiII hexagon rings are 2.38 eV and 1.88 eV, respectively, which is larger than that of Li on carbon nanotubes, 1.64 eV, due to the dense electron cloud around the silicon rings. The binding energies of the K atom are 2.10 eV and 1.65 eV for SiI and SiII, respectively, which is  $\sim 0.2$  eV larger than those of the Na atom. The Mg atom seems to be a poor doping element because the binding energies of Mg with the silicon materials are low at about 1.0 eV lower than the K cases.

Table 2 lists the binding energies for consecutive adsorption of additional  $\text{H}_2$  species to the metal-decorated silicon complexes for metal elements along with the average binding energies ( $\Delta\bar{E}_B$ ). We found that all the metals bind with  $\text{H}_2$  molecules in a dihydrogen ( $\text{H}_2$ ) form, but not in a dihydride ( $2\text{H}$ ) form. Our calculations show that the binding energy of  $\text{H}_2$  on the undecorated system is 30 meV, which is similar to the reported values (30–40 meV) for undecorated silicon nanotubes.<sup>20</sup> Compared with the undecorated system, the binding energies of a  $\text{H}_2$  molecule on the alkali metal-decorated silicon complex are found to be 3–5 times larger. The enhanced binding is due to the charge transfer from the

**Table 1.** Calculated binding energy ( $\Delta E_n$ ) between metal atoms (metal=Li, Na, K, Mg, and Al) and silicon materials ( $\text{Si}_{19}\text{H}_{11}$ : SiI and  $\text{Si}_{24}\text{H}_{12}$ : SiII). Units are in eV

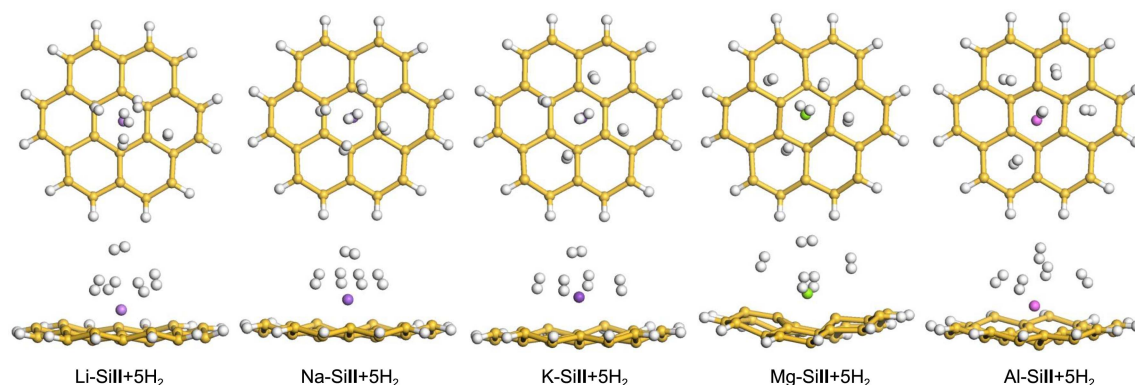
Silicon materials	Li	Na	K	Mg	Al
SiI	2.38	1.93	2.10	1.14	2.55
SiII	1.88	1.45	1.65	0.60	2.11

**Table 2.** Calculated binding energy ( $\Delta E_n$ ) by successive additions of  $\text{H}_2$  molecules to metal-decorated silicon materials ( $\text{Si}_{19}\text{H}_{11}$ : SiI,  $\text{Si}_{24}\text{H}_{12}$ : SiII)

Unit	Metal	$\Delta E_n$ (meV)					$\Delta\bar{E}_B$ (meV)
		$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	
SiI	Li	<b>150</b>	76	68	46	38	<b>76</b>
	Na	93	103	76	84	46	<b>80</b>
	K	<b>87</b>	<b>84</b>	<b>87</b>	<b>73</b>	<b>68</b>	<b>80</b>
	Mg	90	46	38	63	41	56
	Al	38	33	44	35	38	38
Unit	Metal	$\Delta E_n$ (meV)					$\Delta\bar{E}_B$ (meV)
		$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	
SiII	Li	<b>150</b>	84	63	49	35	<b>76</b>
	Na	93	101	73	90	22	<b>76</b>
	K	<b>60</b>	<b>87</b>	<b>101</b>	<b>84</b>	<b>68</b>	<b>80</b>
	Mg	38	90	41	44	38	50
	Al	41	38	22	30	60	38

metal atoms and silicon materials. A local dipole can subsequently be formed on a metal-decorated silicon system, which can then induce a dipole on the molecular hydrogen. The charge-induced dipole interactions reinforce the adsorption energy between the decorated systems and the hydrogen molecules.

The first  $\text{H}_2$  molecules ( $n=1$ ) bind with the Li-decorated silicon complexes ( $\text{H}_2 \cdots \text{Li-Si}_x\text{H}_y$ ) with binding energies of 150 meV for both SiI and SiII. After the first  $\text{H}_2$  molecule binds to Li, the binding energies between the  $\text{H}_2$  molecule and the Li-decorated silicon complexes gradually decrease to 38 meV (SiI) and 35 meV (SiII) for the fifth  $\text{H}_2$  binding energies. On the other hand, it is notable that K-decorated silicon systems show similar binding energies from the



**Figure 2.** Optimized structures of the maximum number of  $\text{H}_2$  adsorbed on the metal-decorated SiII complexes (metal=Li, Na, K, Mg, and Al).

first to the fifth  $H_2$  molecule adsorbed on the SiI and SiII complexes, indicating the higher reversibility of K-decorated silicon materials with respect to Li-decorated silicon materials. In this regard, Na shows poorer reversibility than K. The enhancement of reversibility from Li to K can be attributed to the different size of alkali metals. The ionic (covalent) radii are 0.60 (1.34) Å and 1.33 (1.96) Å for Li and K, respectively. As a doping element, the Al atom seems irrelevant, because its binding energies with  $H_2$  molecules are weak ( $\Delta E_B$  values of 38 meV for both the SiI and SiII cases) compared with those of undecorated silicon materials.

Figure 2 shows the optimized structures of metal-decorated SiII complexes (metal=Li, Na, K, Mg, and Al) in interaction with five  $H_2$  molecules. The distances between the Li atom and the five  $H_2$  molecules vary significantly from 2.3 Å to 4.3 Å, whereas the K atom adsorbs up to five  $H_2$  molecules on the SiII complex within a similar distance, 3.1–3.2 Å. The distances between the Al-decorated SiII system and the  $H_2$  molecules are somewhat longer (3.7–4.2 Å) than other metal atoms, reflecting a weaker interaction with  $H_2$  molecules than other metal-decorated complexes (see Table 2).

### Conclusions

Alkali metals are preferred candidates as doping elements because the Mg-Si and Al- $H_2$  interactions are weak. The maximum numbers of  $H_2$  molecules that can be adsorbed are four and five for M=Li and K, respectively. We propose that K-decorated silicon material might be an effective hydrogen storage material with high hydrogen capacity and high reversibility.

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