Study of Si Surface Adsorption Towards Hydrogen Molecule

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Abstract. Recent approaches to address more efficient method on storing hydrogen by using adsorbent materials has been done. The hydrogen adsorption on silicon has been studied through molecular dynamics simulations and experiment by researchers. We conducted molecular dynamics simulation using a Lennard-Jones potential to demonstrate the hydrogen adsorption capability of silicon surface (001) and (111) with various temperature applied. The amount of hydrogen adsorbed by silicon surfaces are higher as entropy of the system decreases. Without considering entropy, Si (111) has higher adsorption capability due to its lower energy surface than Si (001).

Keywords: hydrogen storage; silicon; molecular dynamics simulation; Lennard-Jones potential; adsorption

1. Introduction

The availability of energy is decreasing as time goes by, transcendence of technology and human growth, it causes a dependency in energy sources. The energy that is a main source for supplying daily needs came from the fossil fuel. One of the energy sources that mostly used for life support is the energy from fossil fuel. Fuel energy has a big role to run various of daily needs such as industries and transportation. By that time, an alternative fuel is needed for the future energy demand when those fossil fuels become unavailable, more importantly for the transport sector. Among hydrogen appears to be the best choice due to the highest energy density per unit mass (120 MJ/kg), non-toxic molecule, colorless no environmental implications, so it is suitable to use as a fuel for motor vehicles. Even so, the using of hydrogen will be facing a problem in distribution and storing process due to its volatility [1].

To face the problem in the using of hydrogen, adsorption is the best method. Using that method, hydrogen will be saved in a porous material. Basically, gas adsorption happens because van der Waals’ force between gas molecules and adsorbent molecules that causes gas molecules trapped in a pore structure. One of the porous materials that can be used is using adsorption method in silicon. Silicon has a large surface and a big volume of pores, so it is suitable for hydrogen’s
storage media [1-2]. The advantage of using the technique of hydrogen storage using adsorption method is that it is more secure and cheaper in the application [2].

Adsorption of gases on the silicon surface has been studied. Adsorption properties of different types of gases in silicon studied by measuring pressure to identify decomposition products of the adsorbed gas. For the adsorption of hydrogen on silicon is quite a lot of study about it such as the terms of mechanisms, factors that affect, and the nature of adsorption. The H₂ desorption mechanism and H₂ interactions on the Si surface have been studied in. Factors that affect the adsorption of hydrogen on silicon have been widely explored. Temperature and pressure factors have been studied. The hydrogen atoms will adsorb prudentially on adatoms at low temperatures whereas the rest atoms are the first to become hydrogen terminated at elevated temperatures [3-4]. In another research, the amount of adsorption increases with the decreasing of the temperature and increasing of the pressure [3]. The effects of kinetic energy, dynamic lattice distortions, static lattice distortions, molecular vibrations, surface coverage and the angle of incidence of H₂ have been studied in [5].

The location and geometry of Si also affect this adsorption process. The properties of the respective lattice distortion is clear for Si (111)7×7. In this system to make lower the adsorption barrier, the backbonds of the silicon adatoms must be widely stretched in the transition state [6]. In another research the adsorption geometry changed from phase 2 x 1 monohydride to phase 1 x 1 dihydride with increased exposure to hydrogen [7]. From the difference in hydrogen chemisorption energy between the adsorption area on the terraces and at the steps of a vicinal Si (001) surface the equilibrium hydrogen position of the various surface sites can be derived [7-8]. Another factor like saturation of the atomic bonds between silicon atoms on this surface by hydrogen have been studied in [6]. In other paper a minor influence in adsorption is tunneling, molecular vibrations, and the structural details of surface. In enhancing the adsorption quantity, the structure of the silicon is modified as in nano-size. The combined ab-initio quantum mechanical calculations and Canonical Monte Carlo (CMC) simulations were developed to investigate the ability of hydrogen adsorption on silicon nanotubes. Studies on the configuration or structure of nanotubes of silicon and the structural and electronic properties of these nanostructures were also developed [8].

The hydrogen adsorption to the silicon surface that involved potential interaction between H₂-H₂ and Si-H₂ was considered as simple physical adsorption. Relatively low attractive force between adsorbate with adsorbent surfaces induced physical adsorption, so that adsorbate moved to another part of adsorbent surface [9]. In this study, we conducted molecular dynamics simulation towards the hydrogen interaction with Si (111) and Si (001) by Lennard-Jones function. The (001) and (111) Si surfaces are preferred due to its relatively feasible preparation with good quality characterization [10]. A research done by a simulation of molecular dynamics using a Lennard-Jones potential to demonstrate the hydrogen molecule adsorption capability of silicon surface with various temperature applied. The scope of the discussion in the present review is limited to recent advances in hydrogen storage using silicon adsorbents that have received significant attention from the hydrogen storage.
2. Materials and Methods

In this paper we study the gas adsorption of Si atoms using LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software. The arrangement of Si atoms was constructed using VMD (Visual Molecular Dynamics) software. The interaction of hydrogen molecule and silicon atom was estimated by simply employing Lennard-Jones function with potential parameter known. The intermolecular potential function of hydrogen molecule was also estimated with known parameter, while intramolecular interaction such as vibration and rotation activity and quantum effect of hydrogen were neglected [11].

| Atom | \( \sigma (\text{Å}) \) | \( \varepsilon (\text{kJ/mol}) \) |
|------|-----------------|-----------------|
| H    | 0               | 0               |
| Si   | 3.385           | 2.4522          |

Table 1. Parameter used to conduct Lennard-Jones interaction [12].

\[
U = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right) \tag{1}
\]

Here, \( \sigma \) is length parameter of Lennard-Jones potential and \( r \) is distance between two molecules. Cross parameter of different pair, termed as i and j particles formulated using Lorentz-Berthelot mixing function. The simulation ran with probabilistic concept, a system composed of interacting atoms which are given initial coordinates and orientations as a set. The successive random displacement of the atoms generated the initial set.

\[
\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \tag{2}
\]

\[
\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{3}
\]

Temperature was set to 248K, 273 K, and 298 K for silicon surface adsorption towards hydrogen molecule which is higher than temperature of nitrogen in liquid state. Temperature condition was set to be higher than 77 K was based on its feasibility as hydrogen storage utilization [13]. Nevertheless, the critical temperature where hydrogen can be liquefied is 33.19 K and considered as safe to be stored and transported. The gravimetric storage capacity \( \rho_w \) of Si calculated as the amount of hydrogen adsorbed where \( N \) are number of atoms or molecule and \( m \) are atomic relative masses.

\[
\rho_w = \frac{N_{H} m_{H}}{N_{Si} m_{Si} + N_{H} m_{H}} \tag{4}
\]

Formulation to determine the amount of hydrogen input on certain pressure condition defined in van der Waals equation state which are modification of ideal gas law:

\[
(P + a \left( \frac{n}{V_m} \right)^2)(V_m - n\,b) = nRT \tag{5}
\]
where \( a \left( 2.44 \times 10^{-7} \text{ m}^6 \cdot \text{atm/mol}^2 \right) \) and \( b \left( 2.661 \times 10^{-5} \text{ m}^3/\text{mol} \right) \) represent van der Waals coefficient for hydrogen, \( V_m \) is volume of a hydrogen molecule (\( \text{ m}^3/\text{molecule} \)), \( R \) is universal gas constant (8.314 J/mol.K) [14].

3. Results and Discussion

The initial condition were 60 hydrogen atoms (30 molecules) which were placed outside of Si surface. This initial pressure condition represents roughly 8 atm. The simulations run in molecular time scale of (10000, 25000, 50000 and 100000). In this molecular simulation, one-time step represents roughly 1 femtosecond. The results were given in table (1), (2) and (3) for the temperature of 248 K, 273 K and 298 K respectively. The results were also plotted in figure 1 (a) and (b) for surface of Si (001) and Si (111).

| Si Surface | Number of Atoms Adsorbed per Run | Timestep |
|------------|---------------------------------|----------|
|            |                                 | 10000    | 25000    | 50000    | 100000   |
| Si (111)   |                                 | 6        | 9        | 17       | 32       |
| wt%        | 0.06652                          | 0.09978  | 0.18847  | 0.35477  |
| Si (001)   |                                 | 6        | 10       | 14       | 29       |
| wt%        | 0.07236                          | 0.1206   | 0.16884  | 0.34973  |

Table 2. Number of hydrogen atoms adsorbed at 248 K.

| Si Surface | Number of Atoms Adsorbed per Run | Timestep |
|------------|---------------------------------|----------|
|            |                                 | 10000    | 25000    | 50000    | 100000   |
| Si (111)   |                                 | 6        | 10       | 17       | 30       |
| wt%        | 0.06652                          | 0.11086  | 0.18847  | 0.33259  |
| Si (001)   |                                 | 4        | 10       | 14       | 26       |
| wt%        | 0.04824                          | 0.1206   | 0.16884  | 0.31356  |

Table 3. Number of hydrogen atoms adsorbed at 273 K.

| Si Surface | Number of Atoms Adsorbed per Run | Timestep |
|------------|---------------------------------|----------|
|            |                                 | 10000    | 25000    | 50000    | 100000   |
| Si (111)   |                                 | 6        | 9        | 15       | 29       |
| wt%        | 0.06652                          | 0.09978  | 0.1663   | 0.32151  |
| Si (001)   |                                 | 3        | 10       | 14       | 24       |
| wt%        | 0.03618                          | 0.1206   | 0.16884  | 0.28944  |

Table 4. Number of hydrogen atoms adsorbed at 298 K.
From the results, the hydrogen adsorption is temperature dependent. As the temperature increases, the hydrogen adsorption decreases according to statistical thermodynamics of adsorption that prefers adsorption at lower temperature. Physical adsorption is done in exothermic condition, so it worked better at lower temperature as heat is liberated and entropy of the system decreases due to its decreased microstate number and freedom of hydrogen molecules movement [15]. This shows that our simulation is in accordance with the real phenomena. This curve shows saturation of adsorption which is usually demonstrated in BET (Brunauer, Emmett and Teller) adsorption measurement. Our results also showed that the Si surface (111) has higher adsorption capacity in comparison with Si surface (001). This result is related to the stability of (111) surface in comparison with (001) surface. Surface energy as thermodynamic property of Si indicate which surface indices has relatively better stability between each Si atoms [16]. Without considering entropy, Lu et al., has shown that the Si (111) surface has lower energy in comparison with the surface of (001) which lead to more hydrogens can be adsorbed physically without disturbed by Si-Si interaction [17].

4. Conclusions.

In this simulation, we had successfully calculated hydrogen adsorption of Si surface of (001) and (111) using LAMMPS and VMD as builder. We demonstrated that Si surface of (111) has higher adsorption capability in comparison with Si surface of (001) due to the lower surface energy and condition which has lower temperature, silicon tend to adsorb more hydrogen as entropy of the system decreases. In general, our simulations capture the real phenomenon of hydrogen adsorption; saturation and the temperature dependence of hydrogen adsorption.

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