Molecular Dynamics Simulation of Hydrogen Adsorption on Silica

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Abstract. Hydrogen is one of the future energy because it is environmentally friendly. However, there still some problem in the storage method of hydrogen. In its development, there are many candidates that are still in research as a hydrogen storage medium. Also in several studies, it was found that Silicon based material is a promising candidate. In this study we conduct the effect of various pressure to the adsorption of hydrogen on Silica with molecular dynamics simulation using Lennard-Jones potential. The simulations indicate that Silica has a good hydrogen storage capability where pressure and time affect the amount of hydrogen adsorbed.

1. Introduction

In recent years, there has been many research carried out with the concept of green energy because this is a way to save our environment. In addition, fossil based energies diminish their existence, so that an alternative energy is needed to replace these kind of resources. One of the renewable energy that get attention by researchers is hydrogen. Hydrogen characteristic is friendly for the environment. The hydrogen reaction does not produce CO₂ as a side product [1]. Hydrogen also has the highest energy density of any hydrogen based fuel [2]. With this character, currently hydrogen has been developed for fuel cell applications in vehicles, mobile and other portable applications [3,4]. But there are still some challenges in storing hydrogen. As we know, hydrogen can explode when get a contact with air and the way to store it is very difficult [2].

In its development, there are many ways to store this hydrogen. Adsorption becomes an interesting method and continues to be developed when compared to other methods such as physical storage as compressed gas and cryogenic liquid hydrogen [5-8]. The advantage of using the adsorption method were it take cheaper cost, the use of operating pressure lower and the storage system design is not complex [9]. Beside the method, the materials that use as an storage medium must be considered. They must have a high surface areas and usually is porous materials. So far, hydrogen storage medium were carbon nanotubes, graphite, graphene, metal organic frameworks and many more [10-12]. Beside that, silicon based material usually used as a storage material such as silicon surface, silicon nanotube, and zeolites [13-15].

Silica is also a silicon based material with porous and can be a promising candidate as a hydrogen storage media. Silica has a good thermal stability, harmless and inexpensive. The properties like thermal stability is needed because in some hydrogen storage mediumit is constrained in its applications as an automotive applications whereas at room temperature and moderate pressure can not store the amount of hydrogen is needed [16]. Therefore silica can be a solution for that problem. Beside that silica has high surface area. In this work, we want to study the effect of various pressure in adsorption of hydrogen on silica by using molecular dynamics.

2. Experimental Methods

In this study, we performed simulations using LAMMPS. The hydrogen molecules were modeled in round particles and amorphous silica was build by the inorganic builders in the VMD. All interactions that occur in this process were defined using the lennard jones equation. The LJ parameters used in this study are shown in Table 1. The placement of amorphous silica particles is carried out regularly in
all parts of the cube wall. Whereas for the placement of the hydrogen is done randomly but remains close together. The results obtained will be in the form of weight percent. The simulation results that carried out on LAMMPS, it can be visualized to see how many atoms are adsorbed on silica.

Table 1. Lennard-Jones Interaction Parameter [17].

| Atom | 𝜎(Å) | 𝜖(kJ/mol) |
|------|------|-----------|
| H    | 0    | 0         |
| Si   | 3.385| 2.4522    |
| O    | 3.17 | 0.6503    |

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

(1)

Cross parameter that used to identify the pair coefficient of different atom, which each particle is termed as i and j is know with Lorentz-Berthelot mixing function.

\[ \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \]  

(2)

\[ \sigma_{ij} = \frac{(\sigma_i + \sigma_j)}{2} \]  

(3)

In this study, the simulation conditions was set in fix temperature and some variations in pressure. The temperature was set in 273 K with the variation of the pressure is 1 atm, 2 atm, 4 atm, 6 atm, 8 atm, and 10 atm. In this study we just set one kind of temperature because above 273 K, the atom motion will randomized. So it still difficult for us to capture the interaction. The hydrogen storage capacity in silica can be calculated with equation 4.

\[ \rho_w = \frac{N_{H} \cdot m_{H}}{N_{Si} \cdot m_{Si} + N_{O} \cdot m_{O} + N_{H} \cdot m_{H}}. \]  

(4)

N are the number of atoms or molecule while m are atomic relative masses. In this simulation, the pressure variations that we use are calculated by the modification of ideal gas equation. So that the amount of hydrogen needed at the specific pressure can be known.

\[ (P + a \left( \frac{n}{V_{m}} \right)^2 ) (V_{m} - n \cdot b) = nRT \]  

(5)

a and b in this equation represent van der Waals coefficient for hydrogen, while \( V_{m} \) is volume of a hydrogen molecule and R is universal gas constant [18].

3. Result and Discussion

This simulation made in different pressure conditions with fixed temperature at 273 K. Amount of pressure that we observed in this hydrogen adsorption was 1 atm, 2 atm, 4 atm, 6 atm, 8 atm, and 10 atm. The amount of hydrogen in the initial conditions of each pressure varies according to equation 5. From equation 5, we can calculated the amount of hydrogen for initial condition where the result was in table 2. The hydrogen concentration were calculated in different pressure at each 10000 time step. The total running time in each simulation is 200000. The capacity of silica in adsorbing hydrogen in this simulation is shown in table 3. We also take an value in each pressure at the same time step to know the trend at each pressure that were given in table 4. The results were also plotted in figure 2 and 3.
Table 2. Initial hydrogen molecules amount in various pressure.

| Pressure | 1 atm | 2 atm | 4 atm | 6 atm | 8 atm | 10 atm |
|----------|-------|-------|-------|-------|-------|--------|
| Amount of Molecules | 7 | 15 | 30 | 44 | 59 | 74 |

Table 3. Hydrogen Concentration at 273 K.

| Time Step | 1 atm | 2 atm | 4 atm | 6 atm | 8 atm | 10 atm |
|-----------|-------|-------|-------|-------|-------|--------|
| 10000     | 0.000777932 | 0.00155567 | 0.0031106 | 0.0051106 | 0.00777303 | 0 |
| 20000     | 0.00155586 | 0.0031106 | 0.0062219 | 0.0124368 | 0.0248737 | 0.0310921 |
| 30000     | 0.00311173 | 0.0062226 | 0.012439 | 0.0248737 | 0.0497474 | 0.0628505 |
| 40000     | 0.0062226 | 0.0124368 | 0.0248737 | 0.0497474 | 0.0994948 | 0.1317010 |
| 50000     | 0.0124368 | 0.0248737 | 0.0497474 | 0.0994948 | 0.1989896 | 0.2634020 |
| 60000     | 0.0248737 | 0.0497474 | 0.0994948 | 0.1989896 | 0.3979792 | 0.5268040 |
| 70000     | 0.0497474 | 0.0994948 | 0.1989896 | 0.3979792 | 0.7959584 | 1.0536060 |
| 80000     | 0.0994948 | 0.1989896 | 0.3979792 | 0.7959584 | 1.5919168 | 2.1072120 |
| 90000     | 0.1989896 | 0.3979792 | 0.7959584 | 1.5919168 | 3.1838336 | 4.2144240 |
| 100000    | 0.3979792 | 0.7959584 | 1.5919168 | 3.1838336 | 6.3676672 | 8.4288480 |
| 110000    | 0.7959584 | 1.5919168 | 3.1838336 | 6.3676672 | 12.7353344 | 16.8576960 |
| 120000    | 1.5919168 | 3.1838336 | 6.3676672 | 12.7353344 | 25.4706688 | 33.7153920 |
| 130000    | 3.1838336 | 6.3676672 | 12.7353344 | 25.4706688 | 50.9413376 | 67.4307840 |
| 140000    | 6.3676672 | 12.7353344 | 25.4706688 | 50.9413376 | 101.8826752 | 134.8615680 |
| 150000    | 12.7353344 | 25.4706688 | 50.9413376 | 101.8826752 | 203.7653504 | 269.7231360 |
| 160000    | 25.4706688 | 50.9413376 | 101.8826752 | 203.7653504 | 407.5307008 | 539.4462720 |
| 170000    | 50.9413376 | 101.8826752 | 203.7653504 | 407.5307008 | 815.0614016 | 1078.8925440 |
| 180000    | 101.8826752 | 203.7653504 | 407.5307008 | 815.0614016 | 1630.1228032 | 2157.7850880 |
| 190000    | 203.7653504 | 407.5307008 | 815.0614016 | 1630.1228032 | 3260.2456064 | 4315.5701760 |
| 200000    | 407.5307008 | 815.0614016 | 1630.1228032 | 3260.2456064 | 6520.4912128 | 8631.1403520 |

Table 4. Hydrogen Concentration at 273 in 170000 Timestep.

| Pressure | 1 atm | 2 atm | 4 atm | 6 atm | 8 atm | 10 atm |
|----------|-------|-------|-------|-------|-------|--------|
| Hydrogen Concentration (Wt %) | 0.00311173 | 0.0046670 | 0.0139978 | 0.0217696 | 0.0295375 | 0.0341933 |

In Table 2 we can see that the amount of initial hydrogen molecules will increase by the increasing of pressure. This is in accordance with theory of ideal gas equation. The value in table 3. Indicates that at 10 atm the hydrogen concentration become higher.
Figure 1. The hydrogen adsorption in 170000 time step at (a) 1 atm, (b) 2 atm, (c) 4 atm, (d) 6 atm, (e) 8 atm, (f) 10 atm.
Figure 2. The hydrogen molecules adsorption at 273 K.

Figure 3. The hydrogen concentration adsorption at 273 K in 170000 time step.

We can see the figure 1. show the mechanism of hydrogen adsorption in 170000 time step at various pressure figure 1. The red atom represented hydrogen. Silica molecules were shown by the blue and white atoms, where silicon was blue and the white atom was oxygen. From figure 2, it is shown that the hydrogen adsorption is pressure dependent. As the pressure increases, the hydrogen adsorption will also increases. This is in accordance with another literature that prefers adsorption at high pressure [19, 20]. It also can be seen that with increasing of the running time, the hydrogen concentration that can be adsorbed increases. This graph indicates the amount of adsorption hydrogen in silica will be stable in some running time. The adsorption become saturated in some point because the material has maximum capacity to adsorb gas or fluid depending on the interaction between them. In this simulation at all pressure the hydrogen concentration will stable at 180000 time step. From Figure 3 we can know the optimum hydrogen concentration that can be adsorbed with various pressure occurs at the 1700000 running time. We can see that from table 4 that the greatest hydrogen concentration in silica was in 10 atm with 0.0341933 Wt %. This results shows that this simulation can describe the real phenomena of hydrogen adsorption. This simulation can also demonstrated the BET (Brunauer, Emmett and Teller) adsorption measurement.
4. Conclusion
We had successfully obtained the value of hydrogen concentration in hydrogen adsorption on silica using LAMMPS, VMD as builder and Ovito as visualizer. From the result we can say that silica is one of promising candidates for hydrogen storage. We observed that pressure has a good effect in hydrogen adsorption. When pressure increases, the hydrogen concentration adsorption becomes higher. Our simulation also visualizes the real mechanism of hydrogen adsorption by demonstrating time dependence of adsorption, saturation and the pressure dependence of adsorption.

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