

## Gravimetric storage capacity of Hydrogen on $C_{24}H_{12}$ Coronene and its Si substituted at 298 K, a Monte Carlo Simulation

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**ABSTRACT:** In this study, the radial distribution and gravimetric storage capacities of hydrogen on coronene ( $C_{24}H_{12}$ ) and its Si substituted forms,  $C_{24}H_{12-n}Si_nH_{12}$  ( $n= 4-24$ ), have been investigated at 298 K and 0.1 MPa (standard situation) using (N,V,T) Monte Carlo simulation by Lennard-Jones (LJ) 12-6 potential. The results show that the increase of number of silicon substitution doesn't have any effect on the value of Radial Distribution Function (RDF) of  $H_2$ . Also, the symmetric silicon substituted structures have more RDF than asymmetric types. The magnitude of hydrogen radial distribution on the surface of  $C_6Si_{18}H_{12}$  is larger than other structures. The maximum value of radial distribution, gravimetric storage capacity and weight percent of hydrogen storage under identical temperature and pressure conditions are 0.0434, 0.0612 and %6.12 for  $C_6Si_{18}H_{12}$  structure at 0.73Å. On the basis of results, the coronene with 18Si can be suggested as a choice for hydrogen container compared with other its Si substituted forms.

**Keywords:** Coronene, Silicon, Gravimetric Storage Capacity, Hydrogen, Radial distribution, Symmetry

### INTRODUCTION

The use of hydrogen as fuel for cars in the future is discussed. Pure hydrogen may be the final destination in the evolution of fuel usage from coal to petroleum to natural gas, which has followed a trail of increasing hydrogen content (Zhou, 2005). A major bottleneck for the hydrogen vehicle is the problem of hydrogen storage. Hydrogen has the highest energy per unit mass but occupies a large volume. Even in liquid form, the energy density of hydrogen is only 8.4 MJ/L, compared to 34.2 MJ/L for gasoline. Hydrogen has been recognized as an ideal energy carrier with heating value three

times higher than petroleum (Moriarty and Honnery, 2009). The energy conversion and storage systems require a rather complex combination of materials that can selectively promote an adsorption process with efficiencies close to the thermodynamic limit (Bisquert, 2011). Recently, considerable attention has been driven to porous materials such as clathrates, zeolites, carbon nanotubes, fullerenes and coronene as possible materials for hydrogen storage (Jena, 2011). Coronene,  $C_{24}H_{12}$  (or superbene) is a yellow polycyclic aromatic hydrocarbon comprising six peri-fused benzene rings that dissolves in such solvents as benzene, toluene, and di-

chloromethane, Fig. 1-a (Fetzer, 2000, Micha, *et al.*, 2006). Coronene and a series of coronene-derived graphitic nanoribbons were synthesized by Talyzin *et al* at 2012 (Talyzin, *et al.*, 2011, Fujihara, *et al.*, 2012, De Aguiar, *et al.*, 2014) and enthalpies of formation for these compounds was studied by Thomas (Allison, *et al.*, 2015, Thomas, 2015). The properties of silicon substituted of nano carbon structures have motivated a number of studies in recent years on SiC structures (Melinon, *et al.*, 2007, Ray, *et al.*, 2006).

### SIMULATION DETAILS

In this work, the radial distribution of hydrogen on coronene ( $C_{24}H_{12}$ ) and its Si substituted forms,  $C_{24}H_{12}$ ,  $C_{24-n}Si_nH_{12}$  ( $n=4-24$ ), Fig. 1, have been investigated at 298 K and 0.1 MPa using (N,V,T) Monte Carlo simulation by Lennard-Jones (LJ) 12-6 potential ( $\phi_{LJ(r)}$ ),

Eq.1 (13 Cheng, *et al.*, 2004).

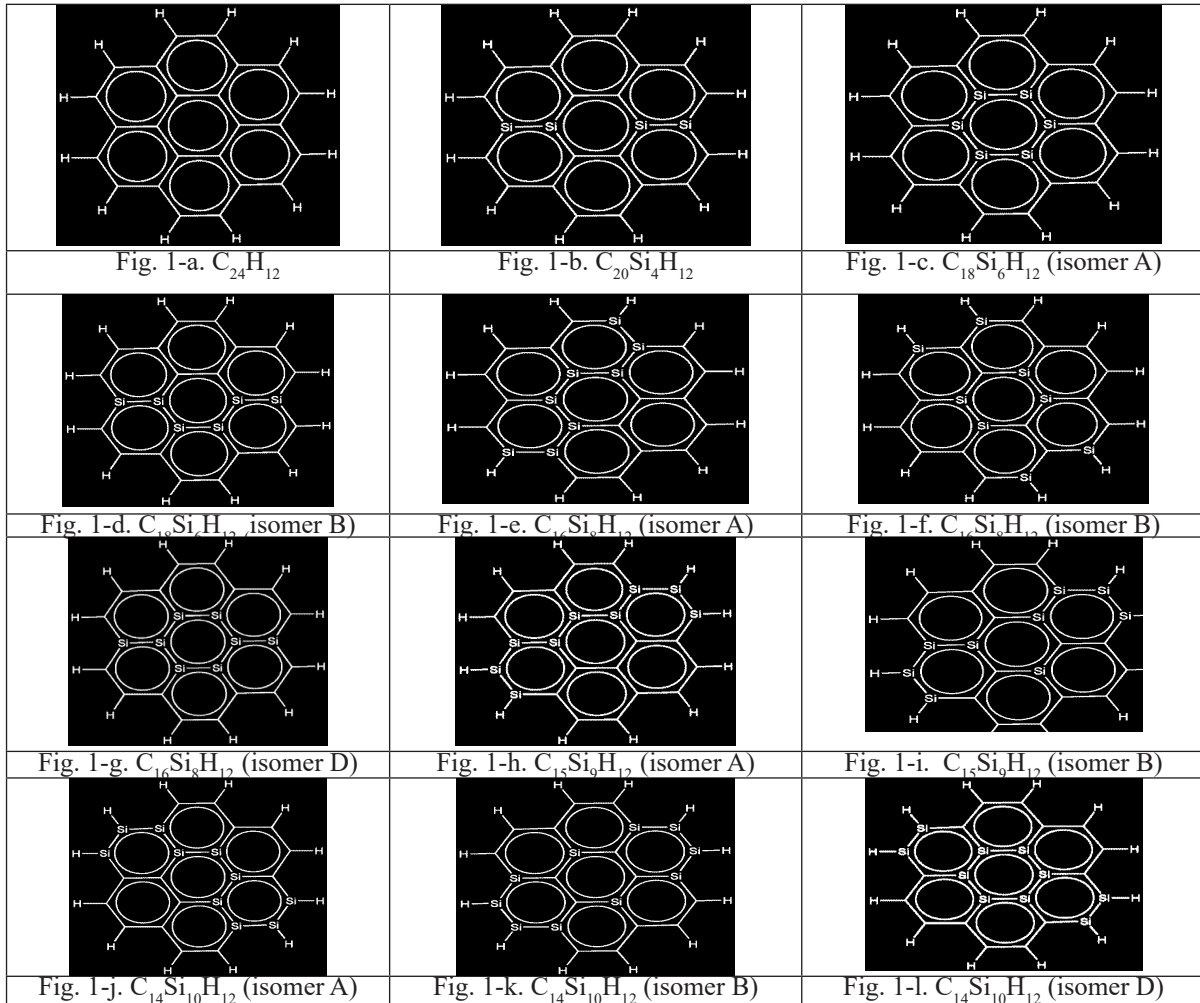
$$\phi_{LJ(r)} = 4\epsilon_{gc} \left[ \left( \frac{\sigma_{gc}}{r} \right)^{12} - \left( \frac{\sigma_{gc}}{r} \right)^6 \right] \quad (1)$$

Where  $r$  is the distance between gas molecules and surface atoms in the coronene structures,  $\sigma_{gc}$  denotes the LJ gas- coronene collision diameter, and  $\epsilon_{gc}$  is the LJ gas-carbon potential well depth. The Lennard-Jones parameters for the interaction between the gas and coronene surfaces were calculated using the Eq. 2, 3 (Lithoxoos, *et al.*, 2008).

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad (2)$$

$$\sigma_{ij} = \frac{(\sigma_i + \sigma_j)}{2} \quad (3)$$

We considered these parameters for Si-C, C-C,  $H_2-H_2$ , C- $H_2$  and Si- $H_2$  pairs (Darkrim, *et al.*, 1998, Lee, *et*



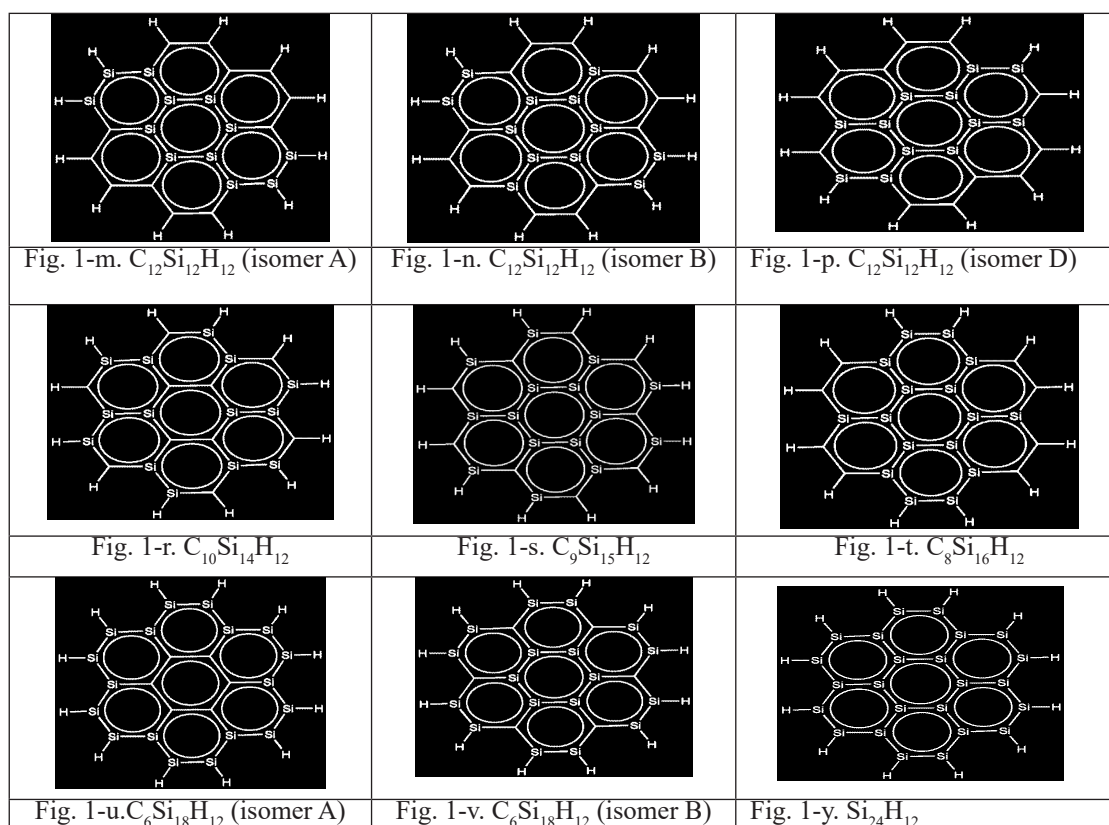


Fig. 1. Coronene (C<sub>24</sub>H<sub>12</sub>) and its Si substituted C<sub>24-n</sub>Si<sub>n</sub>H<sub>12</sub> (n= 4-24) forms

*al.*, 2000, Levesque, *et al.*, 2002, Dimitrakakis, *et al.*, 2008). In our simulations, periodic boundary conditions are imposed in all directions. A cubic simulation box (50.0 Å, 50.0 Å, 50.0 Å) contains one coronene structure and H<sub>2</sub> molecules. The cutoff length in evaluating the LJ potential is set to 2.5 Å on all coronene structures. For every calculation, 10<sup>7</sup> configurations are generated. The initial configurations are discarded to guarantee equilibration, whereas the remaining configurations are used as the average of the desired ensemble properties. The aim of present work is presentation and comparison of gravimetric storage capacity (absolute value adsorption per mass of adsorbent, ρ<sub>w</sub>) and radial distribution function (RDF) parameters for

the structures. The gravimetric storage capacities on the basis of hydrogen absorption are comparable for all structures. The gravimetric storage capacity, ρ<sub>w</sub>, was calculated by Eq. 4.

$$\rho_w = \frac{N_{\text{gas}} m_{\text{gas}}}{N_{\text{gas}} m_{\text{gas}} + N_c m_c + N_{\text{hetero}} m_{\text{hetero}}} \quad (4)$$

Where N<sub>gas</sub>, N<sub>c</sub> and N<sub>hetero</sub> are the number of gas molecules outside the coronene structure up to 2.5 Å, number of carbon atoms in the simulation box and number of heteroatom (Si), and m<sub>gas</sub>, m<sub>c</sub> and m<sub>hetero</sub> (g. mol<sup>-1</sup>) are the corresponding molar mass, respectively (Rafati, *et al.*, 2010).

## RESULTS AND DISCUSSION

The radial distribution of H<sub>2</sub> on C<sub>24</sub>H<sub>12</sub> and C<sub>24-n</sub>Si<sub>n</sub>H<sub>12</sub> (n= 4-24) coronene structures at 298 K and 0.1 MPa of pressure are studied by (N,V,T) Monte Carlo Molecular simulation and fitted by the Lennard-Jones potential equation.

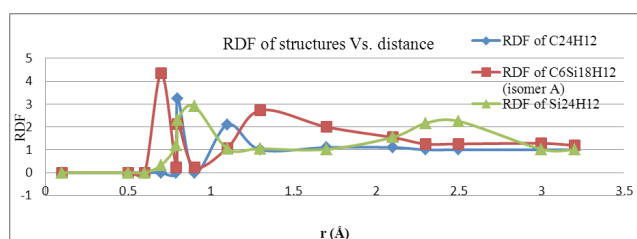


Fig. 2. RDF of C<sub>24</sub>H<sub>12</sub>, C<sub>6</sub>Si<sub>18</sub>H<sub>12</sub> (isomer A) and Si<sub>24</sub>H<sub>12</sub>

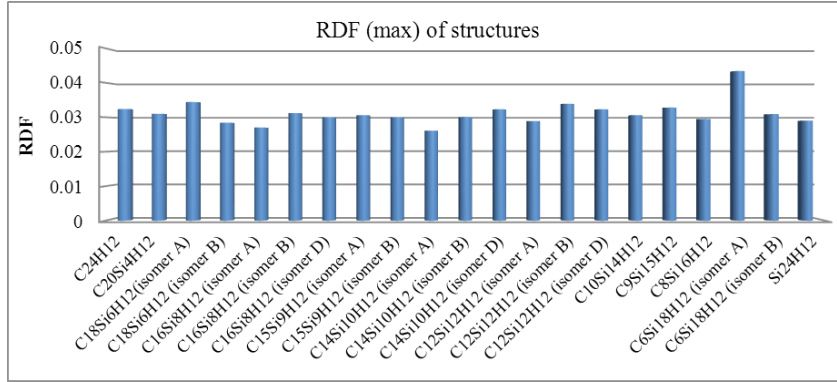


Fig. 3. The values of RDF (max) of structures

In the present work we have considered the Si substituted forms of coronene with different number and different position of Si atoms. We have investigated the effect of number, position of Si substitution and symmetry of structure on the radial distribution of H<sub>2</sub>. Therefore, the structures of  $C_{24-n}Si_nH_{12}$  ( $n=6, 8, 9, 10, 12, 18$ ) have been considered at symmetry and asymmetry forms. Because of numerousness of structures, RDF of only three samples,  $C_{24}H_{12}$ ,  $C_6Si_{18}H_{12}$  (isomer A) and  $Si_{24}H_{12}$  with respect to  $r$  (Å) at 298 K are shown at Fig. 2. The maximum of RDF for structures

are shown at Fig. 3. Comparison of RDF (max) of isomer structures of  $C_{24-n}Si_nH_{12}$  ( $n=6, 8, 9, 10, 12, 18$ ) at Fig. 3 and Table 1, show that the symmetric structures have more RDF (max) value with respect to asymmetric type. As an example,  $C_{18}Si_6H_{12}$  (isomer A), (Fig. 1-c), with RDF (max) equal to 0.0344 is more symmetric than  $C_{18}Si_6H_{12}$  (isomer B) with 0.0284 of RDF (Fig. 1-d). The RDF (max) of  $C_{14}Si_{10}H_{12}$  (isomer D) (0.0323),  $C_{12}Si_{12}H_{12}$  (isomer D) (0.0323) and  $C_9Si_{15}H_{12}$  (0.0328) are almost equal to RDF (max) of  $C_{24}H_{12}$  coronene (0.0324). The RDF (max) of  $C_{18}Si_6H_{12}$  (iso-

Table 1: RDF (max),  $r$  (distance between gas and surface of coronene at RDF (max)), Gravimetric storage capacity ( $\rho_w$ ) and weight percent of hydrogen storage for structures at 298 K and 0.1 MPa

Structure	RDF (max)	$r$ (Å)	$\rho_w$	wt%
$C_{24}H_{12}$	0.0324	0.79	0.0490	4.90
$C_{20}Si_4H_{12}$	0.0310	0.73	0.0481	4.81
$C_{18}Si_6H_{12}$ (isomer A)	0.0344	0.75	0.0395	3.95
$C_{18}Si_6H_{12}$ (isomer B)	0.0284	0.73	0.0331	3.31
$C_{16}Si_8H_{12}$ (isomer A)	0.0270	0.71	0.0452	4.52
$C_{16}Si_8H_{12}$ (isomer B)	0.0312	0.73	0.0593	5.93
$C_{16}Si_8H_{12}$ (isomer D)	0.0300	0.73	0.0512	5.12
$C_{15}Si_9H_{12}$ (isomer A)	0.0306	0.71	0.0402	4.02
$C_{15}Si_9H_{12}$ (isomer B)	0.0300	0.73	0.0363	3.63
$C_{14}Si_{10}H_{12}$ (isomer A)	0.0261	0.73	0.0397	3.97
$C_{14}Si_{10}H_{12}$ (isomer B)	0.0301	0.75	0.0463	4.63
$C_{14}Si_{10}H_{12}$ (isomer D)	0.0323	0.73	0.0484	4.84
$C_{12}Si_{12}H_{12}$ (isomer A)	0.0289	0.73	0.0305	3.05
$C_{12}Si_{12}H_{12}$ (isomer B)	0.0339	0.73	0.0537	5.37
$C_{12}Si_{12}H_{12}$ (isomer D)	0.0323	0.73	0.0550	5.55
$C_{10}Si_{14}H_{12}$	0.0306	0.73	0.0542	5.42
$C_9Si_{15}H_{12}$	0.0328	0.73	0.0586	5.86
$C_8Si_{16}H_{12}$	0.0295	0.73	0.0420	4.20
$C_6Si_{18}H_{12}$ (isomer A)	0.0434	0.73	0.0612	6.12
$C_6Si_{18}H_{12}$ (isomer B)	0.0309	0.75	0.0599	5.99
$Si_{24}H_{12}$	0.0290	0.90	0.0502	5.02

mer A) (0.0344),  $C_{12}Si_{12}H_{12}$  (isomer B) (0.0339), and  $C_6Si_{18}H_{12}$  (isomer A) (0.0434) are more than  $C_{24}H_{12}$  coronene (0.0324).

The structures of  $C_{20}Si_4H_{12}$ ,  $C_{18}Si_6H_{12}$  (isomer B),  $C_{16}Si_8H_{12}$  (isomers A, B, D),  $C_{15}Si_9H_{12}$  (isomers A, B),  $C_{14}Si_{10}H_{12}$  (isomers A, B),  $C_{12}Si_{12}H_{12}$  (isomer A),  $C_{10}Si_{14}H_{12}$ ,  $C_8Si_{16}H_{12}$ ,  $C_6Si_{18}H_{12}$  (isomer B) and  $Si_{24}H_{12}$  have less RDF (max) than  $C_{24}H_{12}$ . Fig. 3 shows that the maximum RDF for  $C_6Si_{18}H_{12}$  (isomer A) is more than the others. The maximum value of radial distribution under identical temperature and pressure conditions is 0.0434 for  $C_6Si_{18}H_{12}$  (isomer A) (Fig. 1-u) structure at 0.73Å. Table 1 shows that the calculated form of gravimetric storage capacity ( $\rho_w$ ) for  $C_6Si_{18}H_{12}$  (isomer A) at 298 K and 0.1 MPa of pressure is bigger than other structures. The values of gravimetric storage capacity and weight percent of hydrogen storage are obtained for  $C_6Si_{18}H_{12}$  (isomer A), are 0.0612 and %6.12, respectively. The U.S. Department of Energy (DOE) is proposed the 6.5 wt% H<sub>2</sub> / kg system (wt% is weight percent) for hydrogen storage at 2005-2010 (Bouza, *et al.*, 2004).

## CONCLUSIONS

In this work, the RDF,  $\rho_w$  and %wt of hydrogen on  $C_{24}H_{12}$  coronene and its silicon substituted structures have been investigated. The main aim of this study is to investigate the effect of number and position of silicon substitution on radial distribution function (RDF) and gravimetric storage capacity ( $\rho_w$ ) of hydrogen. The results show that the symmetric silicon substituted structures have more RDF than asymmetric types. The increase of number of silicon substitution doesn't have any effect on the value of RDF. The maximum value of radial distribution,  $\rho_w$  and %wt are 0.0434, 0.0612 and %6.12 for  $C_6Si_{18}H_{12}$  (isomer A) (Fig. 1-u) structure at 0.73Å.

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