Do the Ni binding modes on C_{12}N_{12} cluster influence its H_{2} trapping capability?

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In order to introduce a new promising material for hydrogen storage application, Nickel (Ni) has been decorated on C_{12}N_{12} nano-cluster. Firstly, the binding mode of Ni on C_{12}N_{12} could be thought to be a bridge in between C, N (denoted as C-(μ-Ni)-N) or C, C (denoted as C-(μ-Ni)-C) or N, N (denoted as N-(μ-Ni)-N) resulting in three distinct geometries (abbreviated as X_{CN}, X_{CC}, and X_{NN} isomers, respectively). Owing to the variation in the bridging mode of Ni, the interacting properties with the hydrogen molecule are expected to be different. The spontaneity of formation of Ni-C_{12}N_{12} and 4Ni-C_{12}N_{12} in terms of ΔH_{f} of isodesmic reactions indicate the possibility of getting promising high-energy-density materials (HEDMs). Further, we have investigated whether Ni, being a 3d transition metal, can influence the aromatic behavior of C_{12}N_{12} nano-cluster. The binding energies and natural bond orbital (NBO) charges have been computed and energy decomposition analysis is carried out for Ni-C_{12}N_{12} isomers. Decoration of Ni on X_{CN} isomer releases slightly lower energy (~107.4 kcal/mol versus ~58.6 kcal/mol for X_{NN} and X_{CN} respectively). The hydrogen adsorption capacity of the strongest and the weakest Ni-bonded Ni-C_{12}N_{12} nano-clusters (X_{NN} and X_{CN} isomers, respectively) has also been investigated.

Introduction

The growth in population and the ever-increasing demand for urbanization is resulting in the depletion of fossil energy sources. The exploitation of fossil fuels is having numerous adverse effects on the planet and its environment since burning hydrocarbon deposits like oil, coal, etc. release carbon dioxide which is one of the main culprits in causing global warming. Currently, energy supply for running automobiles, power plants, household furnaces, etc. are mainly provided by burning fossil fuels. Hence it is high time for the scientific community to look for alternative eco-friendly energy sources. To that end, Hydrogen is turned out to be a clean and effective fuel owing to properties like lightweight, abundance in nature, recyclability, renewability, its combustion producing zero pollution, etc. [1-4] For example, a fuel-cell automobile running on hydrogen fuel will travel more distance than one running on an equal amount of gasoline. Despite such benefits, incorporating hydrogen as the major energy carrier into the world economy becomes challenging due to the high storage cost and limited large-scale transportation. Consequently, there has been a rise in interest and investments toward research and development on high capacity hydrogen storage materials. Desirable characteristics for suitable and efficient hydrogen storage materials include high volumetric and gravimetric densities, fast adsorption and desorption kinetics at ambient conditions, favorable enthalpies, recyclability, safety, and cost-effectiveness [5-7]. Several options are being extensively explored on that front, such as carbon-based materials (activated carbons, carbon nanotubes, nanofibers, fullerenes, templated porous carbons, etc.) [8-12], porous polymers [13], clathrate hydrates [14,15], zeolites [16-19], alumina, silica [20-23], metal-organic frameworks (MOFs) [24,25], covalent organic frameworks (COFs) [26,27], aerogels [28,29], alanates [30], boron nitride materials [31], Lithium-phosphorus double helix [32] and metal borohydrides [33]. Although research work is going on in all possible branches with the target of achieving hydrogen fuel as one of our reliable energy resources, we are yet to achieve hydrogen powered automobiles and instruments in a cost-effective manner. This failure stimulates the strong effort towards reaching the target for hydrogen storage established by bodies like DOE.

Hydrogen interaction with transition metals is very important in numerous chemical processes and fundamental aspect of many key reactions in different applications of chemical industries, especially when it comes to H_{2} storage and its purification [34,35]. Approaches made on hydrogen-storage by metal hydrides [36], different metal complexes and nanoparticles [37-41] including those of Fe [42], Ru [43], Ni [44-46], Pt [47], Pd [48] have been extensively studied and reported. Comprehensive studies performed by Ferrin et al. [49], Yarovsky et al. [50], and Jagliello et al. [51] on interaction
of hydrogen with seventeen different transition metals, on Al13 cluster, and porous carbons, respectively, have been very impactful in understanding the adsorption potential of hydrogen.

AlN nano-cages (spherical) and nanostructures have been found to be sufficiently capable of storing hydrogen, as reported by Guo et al. [52] and Wang et al. [53] respectively. In the recent past, theoreticians have reported some metal-doped and decorated nanostructures [54-59] along with their pure analogues for hydrogen storing purposes. Khurshid and his co-worker have carried out nickel adsorption on the surface of Al13P12 [60] and found four possible sites for nickel atom decoration. Furthermore, it was found that transition metal atom doping in nano-clusters, particularly Ti, V, Ni, and Pd were extensively used to increase the hydrogen storage potential of clusters [61] and also in the hydrogenation reaction.

In 2011, Chattaraj et al. have studied the hydrogen adsorption ability of B12N12 cluster [62]. Later on, Wen-Jie et al. in 2012 have investigated the hydrogen storage behavior of the Li-decorated B12N12 cluster using density functional theory [63]. Rad et al. have examined the hydrogen adsorption on Ni-decorated B12N12 nano-cages [64]. Carbon-based nanostructures are too inert to be used in most of the technological applications unless they are functionalized with heteroatoms. The existence of cyanogens nano-cluster (C12N12), has been verified in many theoretical as well as experimental studies [65-68]. In line with our research group’s quest, recently, the hydrogen storage efficacy and stability of this nano-cluster has been investigated by Chattaraj et al. [69] Now, the approach is being taken here to investigate the hydrogen storage potential of exohedrally doped, Ni atom(s) decorated C12N12 nanocluster which is quite natural and interesting. Out of the three ways of bridging modes of Ni, N-(μ-Ni)-N mode of binding (XNN), is found to be stronger than that in C-(μ-Ni)-N (XCN) and C-(μ-Ni)-C (XCC) reflected by the adsorption energy and the free energy change of adsorption. The polar nature of Ni-CN or Ni-NN bond and positive charge on Ni center can polarize and thereby interact and adsorb hydrogen (H2) molecules, thus resulting in efficient storage for molecular hydrogen.

Aromaticity is one of the well-known topics in chemistry by which one can fetch crucial information of a system [70]. Quantum mechanical approach helped in understanding and characterizing the aromaticity and stability of simple compounds with the Hückel’s (4n+2) π-electron rule [71-73]. The aromatic stabilization was then extended to heterocyclic compounds [74,75] and inorganic compounds, including metal clusters [71,72,76-89]. The impact of aromaticity on the geometrical and electronic structure, reactivity and magnetic properties of many molecular moieties helps us to observe it in an indirect manner. Due to the virtual and imprecise nature of aromaticity, numerous attempts have been developed to find out appropriate descriptors and indices like resonance energy (RE) [90], aromatic stabilization energy (ASE) [91], isomerization stabilization energy (ISE) [92], Julg index [93,94], harmonic-oscillator model of aromaticity (HOMA) [88] based on the equalization of bond lengths within the rings [95] Julg index [96], para-delocalization index (PDI) [97], Bird index [98-100], I

\[ I_{\text{ads}} = \frac{1}{n} \left( E_{\text{systems}} + nE_H \right) \]

\[ \Delta G_{\text{ads}} = \frac{1}{n} \left( G_{\text{systems}} + nG_H \right) \]

All these computations are done using Gaussian 09 program package [121].

The natural population analysis (NPA) [122,123] scheme is adopted to compute atomic charges (QNPA).

Energy decomposition analysis (EDA) was carried out at the revPBE-D3 [124,125]/TZ2P//ωB97X-D/Def 2-TZVP level using ADF 2013.01 program package [126, 127] and the scalar relativistic effects are considered for the heavy elements using the zeroth-order regular
approximation (ZORA) [128]. The total interaction energy ($\Delta E_{\text{int}}$) between two fragments in EDA can be represented as the summation of three attractive energy terms, viz., the electrostatic interaction energy ($\Delta V_{\text{elstat}}$), orbital interaction energy ($\Delta E_{\text{orb}}$), dispersion interaction energy ($\Delta E_{\text{disp}}$), and one repulsive energy term, namely, Pauli repulsion energy ($\Delta E_{\text{Pauli}}$).

Therefore, $\Delta E_{\text{int}}$ can be written as,

$$\Delta E_{\text{int}} = \Delta E_{\text{Pauli}} + \Delta V_{\text{elstat}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}}$$

In order to calculate NICS, a ghost or dummy atom (Bq) is considered at the geometric center of the Ni-C$_{12}$N$_{12}$ cages (denoted by NICS(0)). A normal NMR calculation suggests the chemical shifts for all atoms, including the ghost atom under consideration. According to NICS definition, we have reported the NICS$_{\text{iso}}$ values as negative on multiplying by -1. The negative NICS indices suggest the molecular system(s) is/are aromatic while positive value(s) suggest anti-aromatic character of the system(s). NMR shielding tensors are computed in G09 program with the Gauge-Independent Atomic Orbital (GIAO) method in ppm unit. NICS(0) is considered as a gauge of the $\sigma$$^+$$\pi$-electron delocalization.

**Results and discussion**

**Structure, stability and reactivity**

We have taken cyanogen clathrates which are made up of CN linkages encircling twelve units to form C$_{12}$N$_{12}$ nano-clusters. Out of the three reported isomers [69], the most symmetric isomer is considered here for Ni decoration and H$_2$ storage purposes since it is reported to be capable of possessing maximum H$_2$ adsorption capacity. In the present study, we have investigated the stability of Ni-decorated C$_{12}$N$_{12}$ clusters with different possible bridging modes of Ni viz, N-(μ-Ni)-N, C-(μ-Ni)-C and C-(μ-Ni)-N which are abbreviated as X$_{NN}$, X$_{CC}$, and X$_{CN}$, respectively. The optimized geometries of all the studied clusters are depicted in Fig. 1 and Fig. 2. The binding energy ($E_b$, kcal/mol), free energy change ($\Delta G_b$, kcal/mol) for the formation of Ni-decorated C$_{12}$N$_{12}$ clusters along with the natural charge at Ni center ($q_{\text{Ni}}$, |e|), and the energy gap ($\Delta E_{\text{H-L}}$, eV) between highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) computed at oB97X-D/Def2-TZVP level are provided in Table 1. It is clear from Table 1 that the binding energy of Ni with C$_{12}$N$_{12}$ cluster in X$_{NN}$ isomer is higher than those of the other two modes, namely, X$_{CC}$ and X$_{CN}$ (least one). So, we have extended the doping process in X$_{NN}$ isomer up to a maximum of four Ni atoms (see Fig. 2). Further, the change in the HOMO-LUMO energy gap ($\Delta E_{\text{H-L}}$, eV) on Ni bound clusters is investigated in order to observe the change in reactivity since $\Delta E_{\text{H-L}}$ is often used as a reactivity indicator. Due to Ni binding, the $\Delta E_{\text{H-L}}$ decreases and it reaches the lowest in the case of X$_{CN}$ isomer and the highest for X$_{CC}$ suggesting the highest reactivity in case of C-(μ-Ni)-N bridging mode. The natural charge on the Ni center in X$_{CN}$, X$_{CC}$, and X$_{NN}$ isomers vary within 0.53–0.81|e| where Ni in X$_{NN}$ isomer acquires the highest positive charge (due to the coordination of two more electronegative N atoms) indicating that this isomer can be used as the best potential material for hydrogen storage purpose. The natural charge on the Ni center in both of the X$_{CN}$ and X$_{CC}$ isomers are the same and they attain the least value. On decorating more Ni atoms i.e., maximum up to four, the natural charge on Ni gradually decreases as observed from Table 1, and reactivity also increases which is reflected in $\Delta E_{\text{H-L}}$, accordingly.
Table 1. The binding energy ($E_b$, kcal/mol), free energy change ($\Delta G$, kcal/mol) (per Ni molecule), natural charge at Ni center ($q_{Ni}$, $\mu$), HOMO-LUMO energy gap ($\Delta E_{H-L}$, eV) at the ωB97X-D/Def2-TZVP level.

<table>
<thead>
<tr>
<th>Systems</th>
<th>$E_b$ per Ni</th>
<th>$\Delta G$ per Ni</th>
<th>$q_{Ni}$</th>
<th>$\Delta E_{H-L}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>{12}$N$</em>{12}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-C$<em>{12}$N$</em>{12}$ (X$_{CN}$)</td>
<td>-58.6</td>
<td>-50.7</td>
<td>0.53</td>
<td>6.0</td>
</tr>
<tr>
<td>Ni-C$<em>{12}$N$</em>{12}$ (X$_{CN}$)</td>
<td>-79.6</td>
<td>-71.0</td>
<td>0.53</td>
<td>7.1</td>
</tr>
<tr>
<td>Ni-C$<em>{12}$N$</em>{12}$ (X$_{NC}$)</td>
<td>-107.4</td>
<td>-98.1</td>
<td>0.81</td>
<td>6.7</td>
</tr>
</tbody>
</table>

2Ni-C$_{12}$N$_{12}$ (Ni-X$_{CN}$) | -102.3 | -93.1 | 0.80 | 6.7 |
3Ni-C$_{12}$N$_{12}$ (2Ni-X$_{CN}$) | -101.0 | -91.9 | 0.78-0.79 | 6.5 |
4Ni-C$_{12}$N$_{12}$ (3Ni-X$_{CN}$) | -96.8 | -87.8 | 0.77 | 6.4 |

In order to prepare Ni decorated C$_{12}$N$_{12}$ clusters, we must study the thermodynamics of their formation, which we have carried out in terms of isodesmic reaction. The dependence of their aromatic behavior on the extent of Ni doping on C$_{12}$N$_{12}$ cluster is also investigated by evaluating their corresponding NICS(0) values.

A) Isodesmic reaction

To analyze the spontaneity of formation of Ni-C$_{12}$N$_{12}$ (X$_{CN}$) and 4Ni-C$_{12}$N$_{12}$ (3Ni-X$_{CN}$), the heat of formation (Δ$H^o$) of isodesmic reactions are useful. Heat of formation (Δ$H^o$) of Ni-C$_{12}$N$_{12}$ and 4Ni-C$_{12}$N$_{12}$ are first calculated using theoretically computed enthalpies of Ni-C$_{12}$N$_{12}$, C, N, Ni and 4Ni-C$_{12}$N$_{12}$ at ωB97X-D/Def2-TZVP level of theory:

$$
\Delta H^o_{\text{(Ni-C$_{12}$N$_{12}$)}} = H_{\text{(Ni-C$_{12}$N$_{12}$)}} - \{12H_C + 12H_N + H_{Ni}\}
$$

$$
\Delta H^o_{\text{(4Ni-C$_{12}$N$_{12}$)}} = H_{\text{(4Ni-C$_{12}$N$_{12}$)}} - \{12H_C + 12H_N + 4H_{Ni}\}
$$

Then, we have carried out in terms of the bare C$_{12}$N$_{12}$, and minimum energy configuration for the corresponding NICS(0) values of ethylene, ammonia, hydrazine, nickel, and pyrrole [129,130] to calculate the Δ$H^o$ of the following isodesmic reactions.

Ni-C$_{12}$N$_{12}$ + 12H$_2$C=CH$_2$ + 3NH$_3$ → 9C$_6$H$_4$NH + 3H$_2$N-NH$_2$ + Ni

4Ni-C$_{12}$N$_{12}$ + 12H$_2$C=CH$_2$ + 3NH$_3$ → 9C$_6$H$_4$NH + 3H$_2$N-NH$_2$ + 4Ni

Calculated Δ$H^o$ values are 4239.470 and 4520.528 kcal/mol for Ni-C$_{12}$N$_{12}$ and 4Ni-C$_{12}$N$_{12}$ isomers, respectively, suggesting the formation of the latter to be slightly more spontaneous.

B) Aromaticity of Ni-C$_{12}$N$_{12}$ cluster

NMR analysis of the bare C$_{12}$N$_{12}$ cluster and Ni-decorated cluster have been done to describe aromatic stability by measuring NICS(0) values. A negative NICS(0) value for the bare C$_{12}$N$_{12}$ cluster supports the existence of its aromatic behavior. The decoration of Ni atom(s), maximum up to four, brings a significant change in the aromaticity. The NICS(0) value of C$_{12}$N$_{12}$ cluster is -3.937 ppm computed at the center of the cage using ωB97X-D/Def2-TZVP level of theory. All the NICS(0) data are presented in Table 2. NICS(0) value in case of the different bridging modes of Ni is different. It shows maximum value in the case of X$_{NN}$ isomer, almost three times of that in the bare C$_{12}$N$_{12}$ and minimum in case of X$_{CN}$ isomer indicating the highest aromatic behavior of X$_{CN}$ isomer compared to other two isomers (X$_{CN}$ and X$_{CC}$). The aromatic stabilization increases almost four times than that of the bare C$_{12}$N$_{12}$ on a maximum of four Ni atoms decoration on the X$_{NN}$ isomer.

Table 2. Nucleus Independent Chemical Shift (NICS(0), ppm) values computed at ωB97X-D/Def2-TZVP level.

<table>
<thead>
<tr>
<th>Systems</th>
<th>NICS(0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>{12}$N$</em>{12}$</td>
<td>-3.937</td>
</tr>
<tr>
<td>Ni-C$<em>{12}$N$</em>{12}$(X$_{CN}$)</td>
<td>-4.578</td>
</tr>
<tr>
<td>Ni-C$<em>{12}$N$</em>{12}$(X$_{CC}$)</td>
<td>-4.691</td>
</tr>
<tr>
<td>Ni-C$<em>{12}$N$</em>{12}$(X$_{NC}$)</td>
<td>-11.536</td>
</tr>
</tbody>
</table>

2Ni-C$_{12}$N$_{12}$(Ni-X$_{CN}$) | -12.095 |
3Ni-C$_{12}$N$_{12}$(2Ni-X$_{CN}$) | -13.700 |
4Ni-C$_{12}$N$_{12}$(3Ni-X$_{CN}$) | -14.852 |

Hydrogen storage capacity

Inspired by the Ni-decorated BN nano-cluster by a prior report [64] where Ni shows superior performance for H$_2$ storage, we have chosen the exohedral decoration of Ni ad-atoms on C$_{12}$N$_{12}$. Due to such molecular modeling, positive charges developed on Ni atoms make it suitable for H$_2$ trapping. The optimized geometries the H$_2$ adsorbed configurations are given in Fig. 3. In the free state, the H-H bond distance of the H$_2$ molecule is 0.744 Å. In case of the exohedral doping of single Ni atom in C- (μ-Ni)-N binding mode with C$_{12}$N$_{12}$ cluster, adsorbing up to three H$_2$ molecules, the corresponding H-H bond lengths range from 0.767 to 0.820 Å, while those for N-(μ-Ni)-N binding mode lies within 0.748-0.780 Å (see the Fig. 2).

![Fig. 3. Optimized structures of H$_2$ trapped single Ni bound C$_{12}$N$_{12}$ cluster at the ωB97X-D/Def2-TZVP level.](image-url)
The adsorption energy ($E_{ads}$, kcal/mol), adsorption free energy change ($\Delta G_{ads}$, kcal/mol) per H$_2$ molecule, natural charge at Ni center ($q_{Ni}$, [e]), and HOMO-LUMO energy gap ($\Delta E_{elstat}$, eV) computed at the ωB97X-D/Def2-TZVP level.

<table>
<thead>
<tr>
<th>Systems</th>
<th>$E_{ads}$ per H$_2$</th>
<th>$\Delta G_{ads}$ per H$_2$</th>
<th>$q_{Ni}$</th>
<th>$\Delta E_{elstat}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$<em>2$···X$</em>{CN}$</td>
<td>-23.3</td>
<td>-13.1</td>
<td>0.27</td>
<td>6.2</td>
</tr>
<tr>
<td>2H$<em>2$···X$</em>{CN}$</td>
<td>-15.4</td>
<td>-5.2</td>
<td>0.12</td>
<td>6.2</td>
</tr>
<tr>
<td>3H$<em>2$···X$</em>{CN}$</td>
<td>-11.9</td>
<td>-1.7</td>
<td>-0.21</td>
<td>6.2</td>
</tr>
<tr>
<td>H$<em>2$···X$</em>{NN}$</td>
<td>-39.2</td>
<td>-28.9</td>
<td>0.62</td>
<td>6.6</td>
</tr>
<tr>
<td>2H$<em>2$···X$</em>{NN}$</td>
<td>-22.9</td>
<td>-13.0</td>
<td>0.46</td>
<td>6.9</td>
</tr>
<tr>
<td>3H$<em>2$···X$</em>{NN}$</td>
<td>-16.0</td>
<td>-6.6</td>
<td>0.44</td>
<td>6.9</td>
</tr>
<tr>
<td>H$<em>2$···3Ni-X$</em>{NN}$</td>
<td>-11.4</td>
<td>-1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4H$<em>2$···3Ni-X$</em>{NN}$</td>
<td>-11.4</td>
<td>-1.4</td>
<td>0.56</td>
<td>6.1</td>
</tr>
<tr>
<td>8H$<em>2$···3Ni-X$</em>{NN}$</td>
<td>-8.1</td>
<td>1.6</td>
<td>0.41</td>
<td>6.4</td>
</tr>
</tbody>
</table>

The adsorption energy ($E_{ads}$, kcal/mol), adsorption free energy change ($\Delta G_{ads}$, kcal/mol) per H$_2$ molecule, natural charge at Ni center ($q_{Ni}$, [e]), and HOMO-LUMO energy gap ($\Delta E_{elstat}$, eV) of adsorbed H$_2$ are provided in Table 3 computed using the same level of theory. We have computed the hydrogen adsorption energy and free energy per H$_2$ for the lowest and highest binding cases, i.e., X$_{CN}$ and X$_{NN}$ isomers, respectively. In all the cases, the negative values of adsorption free energy suggest an exergonic nature or the spontaneity of the process at room temperature (298 K) except in the case of 3Ni-X$_{NN}$ which is endergonic by 1.6 kcal/mol and would be feasible at lower temperatures. Owing to the highest positive natural charge on Ni center in X$_{NN}$ isomers (0.81[e]), it will polarize the H$_2$ molecule(s) maximum and accordingly this isomer can be considered as the best candidate for potential hydrogen storage material. We have investigated the improvement in H$_2$ storing capability in four Ni-doped C$_{12}$N$_{12}$ clusters (see Table 1 and Fig. 4).

The adsorption energies ($E_{ads}$) per H$_2$ molecule has been calculated as:

$$E_{ads} = \frac{1}{n} [E(nH_2 \cdots X_{CN/NN}) - (E(X_{CN/NN}) + E(nH_2))]$$

$$E_{ads} = \frac{1}{n} [E(nH_2 \cdots 3X_{NN}) - (E(3X_{NN}) + E(nH_2))]$$

Each Ni atom in 3Ni-X$_{NN}$ isomer binds a maximum of two H$_2$ molecules with binding energy ranging from -8.1 to -11.4 kcal/mol. The natural charge on Ni atom gets lowered on gradual H$_2$ loading, suggesting the charge transfer from the Ni center(s) of the Ni-C$_{12}$N$_{12}$ nano-cluster to the anti-bonding orbital of H$_2$. Similarly, the decrease in $E_{ads}$ and $G_{ads}$ values with an increase in the loaded number of H$_2$ molecules is noted. The reactivity change on H$_2$ adsorption of Ni-C$_{12}$N$_{12}$ nano-clusters is reflected in their HOMO-LUMO energy gap ($\Delta E_{elstat}$, eV). In our studied cases, X$_{CN}$ isomer shows that the reactivity decreases on H$_2$ loading and remains almost the same as we load a maximum of up to three H$_2$ molecules. In case of X$_{NN}$ the reactivity decreases as we load 2-3 H$_2$ molecules but for a single H$_2$ case, a slight increase is observed.

Energy decomposition analysis

Further, we have examined the interaction energy ($\Delta E_{int}$) and the contribution of energy terms towards total interaction which are responsible for stabilizing the H$_2$···Ni-C$_{12}$N$_{12}$ interaction. EDA is carried out considering H$_2$ molecule(s) as one fragment and the Ni-C$_{12}$N$_{12}$ cluster as another (see Table 4). It is evident from the energy values per H$_2$ molecule that the electrostatic and orbital interactions are the primary contributors to the interaction energy, the contribution from the former being 50.5–57.8% while that from the latter is 41.0–48.0% of the total attractive energy. On the other hand, the dispersion interaction is almost negligible (ca. 1.1–5.7% of the total attraction).

Table 4. EDA results of H$_2$ bound Ni-decorated Ni-C$_{12}$N$_{12}$ and 4Ni-C$_{12}$N$_{12}$ clusters at the revPBE-D3/TZ2P/ωB97X-D/Def2-TZVP level. All energy values reported here are per H$_2$ in kcal/mol. The values in parentheses are percentage contribution toward the total attraction, $\Delta E_{int} + \Delta E_{elstat} + \Delta E_{orb}$.

<table>
<thead>
<tr>
<th>Systems</th>
<th>$\Delta E_{int}$</th>
<th>$\Delta E_{elstat}$</th>
<th>$\Delta E_{orb}$</th>
<th>$\Delta E_{total}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$<em>2$···X$</em>{CN}$</td>
<td>-24.9</td>
<td>-59.8</td>
<td>-48.9(57.8)</td>
<td>-101.2</td>
</tr>
<tr>
<td>2H$<em>2$···X$</em>{CN}$</td>
<td>-15.7</td>
<td>-62.4</td>
<td>-43.1(55.2)</td>
<td>-100.1</td>
</tr>
<tr>
<td>3H$<em>2$···X$</em>{CN}$</td>
<td>-13.6</td>
<td>-69.9</td>
<td>-42.0(50.5)</td>
<td>-101.5</td>
</tr>
<tr>
<td>H$<em>2$···X$</em>{NN}$</td>
<td>-10.7</td>
<td>-49.3</td>
<td>-33.2(55.4)</td>
<td>-84.0(52.1)</td>
</tr>
<tr>
<td>2H$<em>2$···X$</em>{NN}$</td>
<td>-7.6</td>
<td>-41.7</td>
<td>-26.6(53.9)</td>
<td>-67.9(51.9)</td>
</tr>
<tr>
<td>3H$<em>2$···X$</em>{NN}$</td>
<td>-4.0</td>
<td>-29.6</td>
<td>-18.5(51.9)</td>
<td>-52.1(42.3)</td>
</tr>
<tr>
<td>H$<em>2$···3Ni-X$</em>{NN}$</td>
<td>-44.9</td>
<td>213.0</td>
<td>-144.2(55.9)</td>
<td>-108.5(42.1)</td>
</tr>
<tr>
<td>8H$<em>2$···3Ni-X$</em>{NN}$</td>
<td>-30.2</td>
<td>164.0</td>
<td>-104.1(53.9)</td>
<td>-164.5(43.5)</td>
</tr>
</tbody>
</table>

Fig. 4. Optimized structures of nH$_2$···3Ni-X$_{NN}$ (n=1, 4, 8) at the ωB97X-D/Def2-TZVP level.

The minimum energy H$_2$ loaded or relaxed structures of 3Ni-X$_{NN}$ (having D$_{2d}$ point group symmetry) on the potential energy surface (PES) are shown in Fig. 4. The single H$_2$ molecule adsorption on 3Ni-X$_{NN}$ is found to align in two different ways, i) side-on orientation and ii) end-on orientation. In the case of side-on orientation, the H-H distance is elongated more than that in the latter and partial dissociation is observed therein. The adsorption free energy values for all the H$_2$ binding processes are negative which indicates that the adsorption processes are exergonic in nature and these processes are thermodynamically spontaneous except for the maximum H$_2$ loaded case, where slight cryogenic temperature is required when the unfavorable T∆S term exceeds the favorable ∆H term giving positive value for ∆G$_{ads}$ term. A
step-by-step flow diagram of the entire process, starting from $\text{C}_12\text{Ni}_2$ to $\text{H}_2\cdots\text{Ni-Ni}$, is depicted in Fig. 5 along with the corresponding values of formation energy.

Fig. 5. Formation energies ($F_a$, kcal/mol) of the shown processes at the oB97X-D/Def2-TZVP level.

Conclusion

Using DFT calculations, it has been observed that the systematic decoration of Ni in a different mode of bridging on $\text{C}_12\text{Ni}_2$ nano-cluster can tune the $\text{H}_2$ storage capacity. The calculated binding energy and free energy change of adsorption infer that the structures of Ni-$\text{C}_12\text{Ni}_2$ and $\text{H}_2\cdots\text{Ni-C}_12\text{Ni}_2$ are thermodynamically feasible. NPA charge calculation indicates that the polar nature of Ni-C or Ni-N bonds are responsible for $\text{H}_2$ interaction as well as their partial dissociation on adsorption. It has been found that a positively charged Ni atom on C$_{12}$Ni$_2$ and H$_2$Ni$_2$ are thermodynamically feasible. NPA charge calculation indicates that the polar nature of Ni-C or Ni-N bonds are responsible for $\text{H}_2$ interaction as well as their partial dissociation on adsorption. It has been found that a positively charged Ni atom on C$_{12}$Ni$_2$ can adsorb up to three H$_2$ molecules. The average adsorption energies of H$_2$ molecules have been found to be within the range (11.9-23.3 kcal/mol for C-($\mu$-Ni)-N bridge case versus 16.0-39.2 kcal/mol for the N-($\mu$-Ni)-N case). The organization of four Ni in the N, Ni bridging mode gives a new thermodynamically stable geometry ($D_{2d}$ point group) that is potent for $\text{H}_2$ storage as well. Aromatization increases on Ni doping in a symmetric and systematic fashion surrounding the C$_{12}$Ni$_2$ cluster.

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Conflicts of interest

The authors declare that they have no conflict of interests regarding the publication of this article, financial, and/or otherwise.

Keywords

Nickel decorated C$_{12}$Ni$_2$ structure and stability, isodesmic reaction, aromaticity, H$_2$ storage.

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References

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Graphical Abstract

Ni-decorated polycyanogen clusters, $\text{C}_{12}\text{N}_{12}$, exhibiting three different isomeric forms, are promising high-energy-density materials for Hydrogen storage. Gas-phase heat of formation suggests the spontaneous formation of the Ni-decorated $\text{C}_{12}\text{N}_{12}$ cluster. Systematic Ni decoration enhances the aromaticity of the $\text{C}_{12}\text{N}_{12}$ cluster. Interaction energy between $\text{H}_2$ and Ni-decorated $\text{C}_{12}\text{N}_{12}$ cluster mainly originates from the electrostatic and orbital interactions.