Aromatic Clusters as Potential Hydrogen Storage Materials

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The scientific community is engrossed in the thought of a probable solution to the future energy crisis keeping in mind a better environment-friendly alternative. Although there are many such alternatives, the green hydrogen energy has occupied most of the brilliant minds due to its abundance and numerous production resources. For the advancement of hydrogen economy, Government agencies are funding pertinent research projects. There is an avalanche of molecular systems which are studied by several chemists for storing atomic and molecular hydrogens. The present review on molecular hydrogen storage focuses on all-metal and nonmetal aromatic clusters. In addition to the effect of aromaticity on hydrogen trapping potential of different molecular moieties, the importance of using the conceptual density functional theory based reactivity descriptors is also highlighted. Investigations from our group have been revealing the fact that several aromatic metal clusters, metal doped nonmetal clusters as well as pure nonmetal clusters can serve as potential molecular hydrogen trapping agents. Reported systems include $\text{N}_4\text{Li}_2$, $\text{N}_6\text{Ca}_2$ clusters, $\text{Mg}_n$, and $\text{Ca}_n$ ($n = 8–10$) cage-like moieties, $\text{B}_{12}\text{N}_{12}$ clathrate, transition metal doped ethylene complexes, $\text{M}_3^+$ ($\text{M} = \text{Li}, \text{Na}$) ions, $\text{E}_5\text{M}_2$ ($\text{E} = \text{Be}, \text{Mg}, \text{Al}; \text{M} = \text{Li}, \text{Na}, \text{K}$) clusters, $\text{Li}_2\text{Al}_5^-$ ions, Li decorated star-like molecules, $\text{B}_2\text{Li}_y$ ($y = 3–6$), Li-doped annular forms, Li-doped borazine derivatives, $\text{C}_{12}\text{N}_{12}$ Clusters ($\text{N}_4\text{C}_3\text{H}_{16}$)$_2\text{Li}_6$ and associated 3-D functional material, cucurbiturils, lithium–phosphorus double-helices. Ni bound $\text{C}_{12}\text{N}_{12}$ moieties are also reported recently.

Keywords: hydrogen storage, aromaticity, all-metal clusters, nonmetal clusters, conceptual density functional theory

1 INTRODUCTION

With the ever-increasing utilization of energy, whose primary source has been fossil fuels for so long, the rate of carbon dioxide concentration in the atmosphere is increasing at an alarming rate. With this level of energy demand, fossil fuels will soon be exhausted unless more and more clean fuels are adopted. As of 2019, the International Energy Agency (IEA, 2019) reports the world total energy consumption, of which oil source constitutes 40.4%, followed by 19.7% consumption of electricity, 16.4, 10.4, and 9.5% of natural gas, biofuels, and coal, respectively, and 3.6% constitute other sources of energy. Although 2020 has witnessed a significant reduction in global CO2 emissions (by 2.4 gigatons) and a decline in the usage of electricity owing to the industrial sector shutdown as a part of COVID-19 restrictions, we are far from reaching the goal of saving the world from collapsing due to over usage of non-renewable energy resources. On the bright side, more and more countries are announcing pledges towards attaining net-zero emissions by the year 2050. To achieve such goals,
more and more research projects are being undertaken to search for alternative reliable clean energy sources like hydrogen, nuclear, and efficiently harness the natural resources that we already have in the form of solar, hydro, and wind.

Hydrogen, as a fuel source, is ideal since we have an abundance of it, it causes no emission of harmful gases, and it has a much greater energy content per unit than fossil fuels (World Nuclear Association Website, 2016). The challenges that arise include the conversion of hydrogen from various sources like water and hydrocarbons to its free state, followed by its storage and transportation. The first challenge can be overcome by processes like electrolysis of water and steam reformation of small hydrocarbons, both of which have disadvantages of their own. While the former requires electricity, the latter produces CO₂ as a by-product. Between the two, the electrolysis process seems more preferable since it can be made eco-friendly by using solar, wind, and hydro electricity. Again, there is a downside of higher cost. After the production of free molecular hydrogen, it needs to be stored in an environment with high pressure and very low temperatures. A better way is to adsorb or entrap H₂ in materials that can be easily available, light weight, inexpensive, and can achieve high gravimetric and volumetric hydrogen storage density, and favourable thermodynamic parameters. The appropriate binding energy range depends on the type of hydrogen adsorption on the storage material. For physisorption, it is very small (in the milli-eV range), for chemisorption the value ranges between 2–4 eV, and for the type between physisorption and chemisorption, the binding energy ranges from 0.1 to 0.8 eV. Interaction energy that lies in between that of physisorption and chemisorption is ideal for a better reversible hydrogen storage material.

Hydrogen adsorption can occur via physisorption, chemisorption, and by virtue of Kabas interaction (Kubas, 2001) in the case of transition metals (TM) which is essentially the sequential electron donation from σ₂ to vacant d₅TM orbital, and a back donation from filled d₅TM to σ*₂. The H₂ storage capacity of a diverse range of molecular systems are explored like, nanomaterials based on carbon (Dresselhaus et al., 1999; Froudakis, 2002; Ding et al., 2001; Lochan and Head-Gordon, 2006; Ströbel et al., 2006; Xu et al., 2007), and aluminium nitride (Wang et al., 2009), Li-bound neutral and cationic Bₓ complexes (Bandaru et al., 2012), alkali-metal doped benzenoid systems (Srinivasu et al., 2009), polythiophene B N doped graphyne (Jana et al., 2018), clathrate-hydrate molecules (Chattaraj et al., 2011a), Boron–Li clusters (Wu et al., 2008; Yildirim and Güvenç, 2009), transition-metal doped BN systems (Shevlin and Guo, 2006), fullerene clusters (Peng et al., 2009), magnesium clusters (Wagemans et al., 2005), transition-metal coated boron buckyballs, BₓM (Wu et al., 2009), and metal–organic frameworks (MOFs) (Rosi et al., 2003; Dinca et al., 2006), trigonal, aromatic all-metal Li₃⁺ and Na₃⁺ systems as well as alkaline-earth metal (Mₓ,M = Mg, Ca; n = 8–10) cages (Giri et al., 2011a), transition-metal–ethylene complexes (Chakraborty et al., 2011) and cage-like BₓN₁₂₃ clusters (Giri et al., 2011b).

The aromatic stability of a compound can influence the hydrogen adsorbing power of the molecular motif as described on alkali metal doped hydrocarbons by Srinivasu et al. (2009). Others are discussed in this review. The concept of aromaticity is not yet completely unfolded. It started with being able to explain the reason behind the extra stability in some cyclic hydrocarbons following certain rules prescribed by Hückel, 1931a, Hükel, 1931b, Hückel, 1932. Thorn and Hoffman (1979) then contributed to explaining those of metallabenzene compounds. The accurate measurement of this behaviour is somewhat challenging in the sense that there is no “one-size-fits-all” concept here. Numerous descriptors can measure aromaticity using various techniques but they are highly system-dependent. In this report, we have described the influence of aromatic behaviour on the H₂ trapping potential of various all-metal and nonmetal systems where it is measured in terms of nucleus independent chemical shift (NICS) (Schleyer et al., 1996; Chen et al., 2005) values.

2 COMPUTATIONAL DETAILS

Computational chemistry packages, Gaussian 03 (Frisch et al., 2003) and Gaussian 09 (Frisch et al., 2009), are utilized to model the systems, followed by geometry optimization and frequency calculation. The levels of theory used in this study are MP2, MPW1K, M05–2X, M06, B3LYP, B3LYP-D3, ωB97X-D, and PBE0, with basis sets like 6-31G, 6–31+G(d), 6–311+G(d), 6–311+G(d,p), cc-pVDZ, and Def2-TZVP. The aromaticity is evaluated in terms of NICS values (Chen et al., 2005) at various distances from the molecular plane. Global and local reactivity descriptors like electronegativity (χ) (Parr et al., 1978), chemical hardness (η) (Parr and Pearson, 1983; Pearson, 1997) and electrophilicity index (ω) (Parr et al., 1999; Chattaraj and Roy, 2007; Chattaraj et al., 2011b) Fukui functions (fK) (Parr and Yang, 1984), atomic charges (qA), and dipolarity (ωD) (Chattaraj et al., 2003) derived from the Conceptual density functional theory (CDFT) help describe the molecular stability and reactivity. Following equations are followed for the calculation of the aforementioned descriptors:

\[ \mu = \left( \frac{\partial \mu}{\partial N} \right)_{v(r)} = -\chi \] (1)

\[ \mu = -\chi \approx -\frac{IP + EA}{2} \approx \frac{\varepsilon_{\text{HOMO}} + \varepsilon_{\text{LUMO}}}{2} \] (2)

\[ \eta = \left( \frac{\partial \mu}{\partial N} \right)_{v(r)} = \left( \frac{\partial^2 E}{\partial N^2} \right)_{v(r)} \approx IP - EA \] (3)

\[ \omega = \frac{\mu^2}{2\eta} \approx \frac{\chi^2}{2\eta} \] (4)

\[ f(r) = \left( \frac{\partial \mu}{\partial N} \right)_{v(r)} = \left( \frac{\partial \rho}{\partial N} \right)_{v(r)} \] (5)
\[ f_k = \left( \frac{\partial \rho}{\partial N} \right) \rho(r) \equiv p_k(N) - p_k(N - 1) \] for electrophilic attack \hfill (6a)

\[ f_k^* = \left( \frac{\partial \rho}{\partial N} \right) \rho(r) \equiv p_k(N + 1) - p_k(N) \] for nucleophilic attack \hfill (6b)

\[ f_k^0 = \left( \frac{\partial \rho}{\partial N} \right) \rho(r) \equiv \frac{1}{2} \left( p_k(N + 1) - p_k(N - 1) \right) \] for radical attack \hfill (6c)

\[ \omega^\alpha_k = \omega \cdot f_k^\alpha \] \hfill (7)

where \( E \) stands for total energy and \( N \) for a total number of electrons in the system, \( \varepsilon_{\text{HOMO}}, \varepsilon_{\text{LUMO}}, \text{IP}, \) and \( \text{EA} \) refer to highest occupied and lowest unoccupied molecular orbital energies, ionization potential, and electron affinity, respectively. \( \mu \) denotes chemical potential (Parr and Yang, 1989), \( \rho(r) \) denotes electron density, \( p_k \) stands for the electron population at the \( k \)th atomic site, and \( \alpha \) can be 0, +, or −, for radical, nucleophilic, and electrophilic attacks, respectively.

### 3 CASE STUDIES

#### 3.1 ALL-METAL Clusters

##### 3.1.1 Mg/\( \text{Ca}_n \) and Li/\( \text{Na}_3^+ \) Clusters

The hydrogen storage potential of magnesium and calcium cages (\( \text{Mg}_n \) and \( \text{Ca}_n; n = 8–10 \)) along with that of trigonal alkali-metal cationic clusters (\( \text{Li}_3^+ \) and \( \text{Na}_3^+ \)) were explored by Giri et al. (2011a) with a CDFT approach. The stability of \( \text{H}_2 \)-trapped \( \text{Mg}_n \) and \( \text{Ca}_n \) complexes increases with increase in \( n \). It is, however, interesting to discover that these bare cages could not be
stabilized i.e., before trapping the H\textsubscript{2} molecule within them. Again, in the cases of H\textsubscript{2}-bound Li\textsubscript{n}+ and Na\textsubscript{n}+ systems, the stability is found to increase with the increase in the number of bound H\textsubscript{2} molecules. Upon binding with the clusters, most of the H\textsubscript{2} retains their molecular identity, except in a few of the nH\textsubscript{2}Li\textsubscript{n}+ systems where one of the H\textsubscript{2} molecules dissociates and binds itself in the atomic form. This behaviour is also observed in the case of H\textsubscript{2}-trapped Ca\textsubscript{10} cage (Figure 1). The planarity of the Li\textsubscript{n}+ and Na\textsubscript{n}+ clusters remained intact in the H\textsubscript{2}-bound complexes. Further analysis of the changes in the CDFT based reactivity indices, viz., electronegativity (\(\chi\)) hardness (\(\eta\)) and electrophilicity (\(\omega\)), revealed a gradual decrease in the \(\omega\) values with an increase in the number of H\textsubscript{2} molecules.

The NICS (0, 1) values calculated for the top and bottom M\textsubscript{4} rings (M = Mg, Ca) of the H\textsubscript{2}-encapsulated Mg\textsubscript{n} and Ca\textsubscript{n} cages are found to be negative, indicating the existence of diatropic ring current at the said positions. Similarly, negative NICS\textsubscript{zz} (0) values for the poly-hydrogenated trigonal clusters also established the aromatic stability with gradual H\textsubscript{2} uptake. Further, from a thermodynamic point of view, the negative values of the reaction energy (\(\Delta E\textsubscript{B}\), kcal/mol) for the sequential H\textsubscript{2} binding on the Li\textsubscript{n}+ and Na\textsubscript{n}+ systems provide some theoretical justification towards their possible usage as hydrogen storage materials (Table 1).

### 3.1.2 Be\textsubscript{3}M\textsubscript{2}, Mg\textsubscript{3}M\textsubscript{2}, and Al\textsubscript{4}M\textsubscript{2} (M = Li, Na, K) Clusters

The aromaticity of all-metal Al\textsubscript{4}M\textsubscript{2} system was previously reported (both theoretically and experimentally) (Li et al., 2001), followed by that of Be\textsubscript{3}M\textsubscript{2} and Mg\textsubscript{3}M\textsubscript{2} systems (Kuznetsov and Boldyrev, 2004; Roy and Chattaraj, 2008; Giri et al., 2010). All these systems owe their aromatic behaviour to the presence of delocalized \(\pi\)-electrons. The motivation for using these systems with the alkali metal counterion M\textsuperscript{+} (M = Li, Na, and K) (Srinivasu et al., 2012) is backed by the logic that due to high polarization, the M centers will be highly electropositive and hence can serve as a suitable site for hydrogen adsorption. The optimized geometries of the systems under study are provided in Figure 2, and their hydrogen adsorbed structures are depicted in Figure 3. The positive charges carried by the M centers were found to be proportional to the difference in electronegativity values between the two types of metal species in the complex. This difference is lower in Mg\textsubscript{3}M\textsubscript{2} as compared to that in Be\textsubscript{3}M\textsubscript{2} and Al\textsubscript{4}M\textsubscript{2}, which causes a lower charge transfer from M to the Mg\textsubscript{3} ring compared to the others. This, in turn, results in poor H\textsubscript{2} adsorption in the Mg\textsubscript{3}M\textsubscript{2} complexes (interaction energy of \(-0.5\) kcal/mol per H\textsubscript{2}) compared to the same ranging between -1.8 to -3.1 and -2.7 to -3.2 kcal/mol per H\textsubscript{2} for Be\textsubscript{3}M\textsubscript{2} and Al\textsubscript{4}M\textsubscript{2}, respectively). Now, from the perspective of the alkali metals, a high ionic radius and low charge density (i.e., low ionic potential) on the potassium atom results in a very weak interaction with the K atom containing systems (as low as \(-0.6\) kcal/mol per H\textsubscript{2}). Both Be\textsubscript{3}Li\textsubscript{2} and Be\textsubscript{3}Na\textsubscript{2} are found to adsorb six hydrogen molecules each (three per alkali metal atom), whereas Al\textsubscript{4}Li\textsubscript{2} and Al\textsubscript{4}Na\textsubscript{2} are capable of binding eight molecules each (four H\textsubscript{2} per alkali metal atom). The gravimetric weight percentage of hydrogen adsorption for the

| TABLE 1 | Reaction energy in kcal/mol for the gradual hydrogen loading on Li\textsubscript{n}+ and Na\textsubscript{n}+ clusters (Adapted with permission from Springer Nature Customer Service Centre GmbH, Journal of Molecular Modeling (Giri et al., 2010)). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Reaction | \(\Delta E\textsubscript{B}\) |
| Li\textsubscript{3}+ + H\textsubscript{2} = H\textsubscript{2}Li\textsubscript{3}+ | -32.188 |
| H\textsubscript{2}Li\textsubscript{2}+ (a) + H\textsubscript{2} = H\textsubscript{2}Li\textsubscript{2}+ (a) | -3.677 |
| H\textsubscript{2}Li\textsubscript{2}+ (a) + H\textsubscript{2} = H\textsubscript{2}Li\textsubscript{2}+ (a) | -3.631 |
| H\textsubscript{2}Li\textsubscript{2}+ (a) + H\textsubscript{2} = H\textsubscript{2}Li\textsubscript{2}+ (a) | -3.584 |
| Li\textsubscript{3}+ + H\textsubscript{2} = H\textsubscript{2}Li\textsubscript{3}+ (b) | -2.508 |
| H\textsubscript{2}Li\textsubscript{2}+ (b) + H\textsubscript{2} = H\textsubscript{2}Li\textsubscript{2}+ (b) | -2.346 |
| H\textsubscript{2}Li\textsubscript{2}+ (b) + H\textsubscript{2} = H\textsubscript{2}Li\textsubscript{2}+ (b) | -2.168 |
| Na\textsubscript{3}+ + H\textsubscript{2} = H\textsubscript{2}Na\textsubscript{3}+ | -0.697 |
| H\textsubscript{2}Na\textsubscript{3}+ + H\textsubscript{2} = H\textsubscript{2}Na\textsubscript{3}+ | -0.839 |
| H\textsubscript{2}Na\textsubscript{3}+ + H\textsubscript{2} = H\textsubscript{2}Na\textsubscript{3}+ | -0.569 |
| H\textsubscript{2}Na\textsubscript{3}+ + H\textsubscript{2} = H\textsubscript{2}Na\textsubscript{3}+ | -0.200 |
| H\textsubscript{2}Na\textsubscript{3}+ + H\textsubscript{2} = H\textsubscript{2}Na\textsubscript{3}+ | -0.165 |
The former two are 22.64 and 14.12, those for Al4Li2 and Al4Na2 are 11.59 and 9.4, respectively. Evidently, Be3Li2 is preferred to Al4Li2 in terms of the gravimetric density, whereas with respect to the binding energy per H2 molecule, Al4Li2 is preferred as a better hydrogen storage material.

The stability of these hydrogenated systems is established in terms of higher energy gaps (5.17–6.40 eV) between their respective HOMO and LUMO. The variation in total energy ($E$), $\chi$, $\eta$, and $\omega$ also serve as good descriptors for judging the reactivity and stability of the molecular species. A uniform decrease in $E$, and decrease in $\omega$ values with increasing H2 adsorption describes the stabilization of the metal clusters upon hydrogenation. $\eta$ also shows a gradual increase in most of the cases. The aromaticity of Be3M2 and its hydrogenated species calculated in terms of NICS values at 0, 0.5, and 1 are highly negative and show very low variation with the number of H2 molecules loaded. For the Al4M2 cluster, however, most of the NICS values are found to be positive, even though it is an established fact that the Al42− species has aromatic stability. The variation of aromaticity with the number of adsorbed H2 molecule is also found to be quite random and significantly high. Clearly, NICS is not a good indicator for the Al4M2 clusters.

### 3.2 NON-METALLIC Aromatic Clusters

#### 3.2.1 Planar Molecular Stars

Several non-metallic aromatic/anti-aromatic clusters are also explored to understand the influence of aromaticity on their hydrogen adsorbing or trapping potential. Replacing the H atoms from planar hydrocarbon rings like C4H4, C5H5−, and C6H6 with Li atoms results in the formation of star-shaped molecular clusters since the Li atoms prefer to bind two adjacent C atoms via a bridging bond (Figure 4) (Giri et al., 2011c). The partial positive charges on the Li centers enable them to readily adsorb H2 molecules. Each Li atom in C4Li5− can efficiently bind with only one H2 (binding energy of $\sim$2.1 kcal/mol per H2), whereas those in the neutral clusters (i.e., in C4Li4 and C6Li6) can bind up to two H2 molecules with binding energies ranging within $\sim$2.5 to $\sim$3.3 kcal/mol per H2. A thorough analysis of the NICS-scan (0–5 Å) plots (Figure 5) for each of the studied species provides useful information regarding the variation in the degree of aromaticity/anti-aromaticity with gradual hydrogen loading. The antiaromatic nature of C4H4 is found to be enhanced in its lithium analogue. It further increases in the 4H2@C4Li4 system, followed by a decrease in 8H2@C4Li4, where the NICS (0) value falls below those of the parent moieties.
Since the C₄Li₄ species is more likely to exist in the 8H₂-bound form, it can be arguably stated that hydrogen adsorption on C₄Li₄ reduces its antiaromatic nature, which is favourable in terms of explaining the stability of these clusters.

In the case of the aromatic C₅H₅⁻ ring, lithiation increases its aromatic nature as evident from Figure 5B. The 5H₂-bound C₅Li₅⁻ complex follows the same trend as the parent moieties while moving from NICS (4) to NICS (1), i.e., they gradually decrease with decreasing distance from the ring center. However, unlike the parent moieties, 5H₂@C₅Li₅⁻ shows an unexpected rise in NICS (0) value rendering it anti-aromatic. Again, unlike in C₅⁻ species, the aromaticity reduces in the lithium analogue of C₆H₆ complex. Although all the species maintain their aromatic behaviour, the degree of aromaticity

\[\text{Figure 4: Optimized geometries of C}_n\text{H}_n (n = 4-6), \text{their Li analogues, and H}_2\text{ trapped C}_n\text{Li}_n (n = 4-6) \text{ systems at B3LYP/6-311+G (d,p) level of theory (Reproduced from Giri et al., 2011c with permission from the PCCP Owner Societies).}\]

\[\text{Figure 5: NICS-scan plots for the parent moieties, their Li analogues, and hydrogen loaded systems of (A) C}_4\text{Li}_4, (B) C}_5\text{H}_5^-, \text{and (C) C}_6\text{H}_6 \text{ species (Reproduced from Giri et al., 2011c with permission from the PCCP Owner Societies).}\]
initially decreases with hydrogen loading (i.e., in 6H₂@C₆H₆) with a final increase in the 12H₂@C₆H₆ species (Figure 5C). These plots provide ample evidence regarding the dominant π-ring current in the C₆ species compared to that in the C₅ complexes, which results in an enhanced H₂-trapping ability in the former.

FIGURE 6 | Optimized geometries of (A) maximum H₂-loaded Li⁺/F⁻-doped annular systems, (B) 3D molecular star-like systems, C₅Li₇⁺ and its Si and Ge analogues (Reproduced from (A) Giri et al., 2011c, and (B) Pan et al., 2012 with permission from the PCCP Owner Societies).
3.2.2 Li-Doped Annular Systems and 3D Molecular Stars
The H2 binding ability of a series of lithium ion complexed hydrocarbons (Li\(^+\) above and below the planar ring), viz., C\(_6\)H\(_{8}\), C\(_9\)H\(_{9}\), and C\(_{14}\)H\(_{10}\) are explored in the same study (Giri et al., 2011c), along with that of an F\(^-\) ion stabilized tropylium complex. Each Li atom in these systems can store up to four H2 molecules (Figure 6A). The same is true for the C\(_6\)H\(_{8}\)F system, even though, unlike the Li\(^+\)-complexed hydrocarbons, C\(_6\)H\(_{7}\)\(^+\) loses its planarity and hence aromaticity on complexation with F\(^-\). Other 3D molecular star-like systems like C\(_3\)Li\(_7\)\(^+\) (\(\pi\)-aromatic and \(\sigma\)-nonaromatic) and its Si analogue (\(\sigma\)- and \(\pi\)-aromatic) can bind up to a maximum of 21 H2 molecules (three per Li center) with a gravimetric wt% of 28.0 and 18.3, respectively (Pan et al., 2012; Perez-peralta et al., 2011; Tiznado et al., 2009) (Figure 6B). The Ge analogue has a maximum capacity of 19 H2 molecules with 9.3 wt% of H2 (Contreas et al., 2013). It is a well-known fact that temperature and pressure can act as tuning parameters in various adsorption/desorption processes. An interesting study performed on a series of Li clusters (BLi\(_n\)\(^+\), O\(_2\)Li\(_n\)\(^+\), N\(_2\)Li\(_n\)\(^+\), B\(_2\)Li\(_n\)\(^+\), OL\(_2\)Li\(_n\)\(^+\), C\(_2\)Li\(_n\)\(^+\), F\(_2\)Li\(_n\)\(^+\), and FLi\(_2\)\(^+\)) was reported by Pan et al. (2012) where they have achieved enhanced interaction between Li and H2 by applying an external electric field. By gradually varying the field in the range 0.001–0.005 au, the negative \(\Delta E\) value increases indicating improved interaction.

3.2.3 Lithium Doped Boron Hydrides
A discussion on hydrogen storage warrants the inclusion of boron hydrides. Metal borohydrides like LiBH\(_4\) and NaBH\(_4\) are reported to be good hydrogen storage materials (Kojima et al., 2002; Züttel et al., 2003; Liang et al., 2010). The effect of aromaticity on the structural preference of both neutral and ionic boron hydrides with the general formula B\(_x\)H\(_{y}\) ( \(n = 3–9\)) was reported by Korkin et al. (1995). A similar study (Bandaru et al., 2012) was performed on several boron-lithium complexes with the general formula B\(_x\)Li\(_y\) ( \(x = 2–6; y = 1, 2\)) where the cationic species show a higher H2 binding capacity than their neutral counterparts owing to the greater net positive charge on the Li centers in the former. Among various boron hydrides, B\(_3\)H\(_3\)\(^2-\) can be considered as the iso-electronic boron-analogue of the aromatic cyclopropenium ion (Garratt, 1986; Minkin et al., 1994). A theoretical study on B\(_3\)H\(_3\)\(^2-\) and its various Li doped species performed by Pan et al. (2011) investigates the H2 storage process via an interaction that lies somewhere between physisorption and chemisorption. The aromaticity of these systems is evident from the negative values of NICS (0) (ranging within −3.32–29.38) and NICS (1) (varies from −7.48 to −17.91). The parent moiety itself is capable of adsorbing a maximum of 11 H2 molecules. Here, the importance of the dispersion interaction is clearly reflected from the interaction energy values obtained before and after including the dispersion corrected terms in the theoretical calculations. For example, the interaction energy per H2 molecule in the maximum H2-loaded systems ranges within −1.2–1.9 kcal/mol, which changes to a range of −2.6–5.6 kcal/mol after dispersion correction. Although judging by parameters like the H2 binding capacity, and gravimetric wt% of H2, the B\(_3\)H\(_3\)\(^2-\) system seems to be a preferable choice, it is yet to be experimentally realized. In that regard, B\(_3\) (\(\mu\)-Li)\(_3\)H\(_3\)\(^+\) species is a better alternative with high aromatic stability. The H2 molecules are mostly bound by weak interaction and most of the adsorption process shown here is energetic in nature. Thus an optimal condition for these processes to be feasible would be that of high pressure (P) and low temperature (T). A T-P phase diagram (Figure 7) for the adsorption of 6 H2 molecules on B\(_3\) (\(\mu\)-Li)\(_3\)H\(_3\)\(^+\) reveals the anti-aromatic \(\pi\)-aromatic and \(\sigma\)-antiaromatic and \(\sigma\)-aromatic natures, respectively. The NICS-scan plots of all four systems are provided in Figure 8 where it can be clearly seen that the NICS variation of N\(_6\)\(^2-\) follows a similar trend as that of the benzene, whereas this is not the case for N\(_4\)\(^2-\) and cyclobutadiene. The otherwise antiaromatic N\(_4\)\(^2-\) ring shows aromaticity at a distance of 1 Å above the molecular plane, and gradually decreases away from the ring. Thus, a positive NICS (0) value and a negative NICS (1) value makes it \(\sigma\)-antiaromatic and \(\pi\)-aromatic. These anionic clusters are stabilized by complexation with lithium and calcium counterions to form N\(_4\)Li\(_2\) and N\(_6\)Ca\(_2\) (optimized structures provided in Figure 9). Each Li center is found to bind with...
FIGURE 8 | NICS-scan plots for $N_6^{4+}$, benzene (Bz), $N_4^{2-}$, and Cyclobutadiene (Cb) (Reprinted from Duley et al., 2011 with permission from Elsevier. Copyright © 2011 Elsevier B.V.).

FIGURE 9 | Optimized geometries of $N_6Ca_2$, $N_4Li_2$, and their respective maximum hydrogen loaded systems at B3LYP/6-31G(d) level of theory (Reproduced from Duley et al., 2011 with permission from Elsevier. Copyright © 2011 Elsevier B.V.).
up to four H$_2$ ($\Delta E = -1.2$ kcal/mol) and each Ca center adsorbs up to six H$_2$ molecules ($\Delta E = -1.3$ kcal/mol).

3.2.5 C$_{12}$N$_{12}$, B$_{12}$N$_{12}$, and Ni-Decorated C$_{12}$N$_{12}$ Cages

C$_{12}$N$_{12}$ cage can have three possible isomers, viz., C$_{12}$N$_{12}$-A, C$_{12}$N$_{12}$-B, and C$_{12}$N$_{12}$-C with the optimized structures having D$_{6d}$, C$_3$, and C$_2$ point group symmetries, respectively (Figure 10A) (Mondal et al., 2013). Unlike isomers A and B, C is an open cage structure and hence is the most stable of the lot. Although the NICS (0) for all the isomers are found to be negative, isomers A and B do not obey the Spherical Aromaticity rule $[(2N+1)^2 \pi$-electrons], and isomer C does not follow the Open-Shell Spherical Aromaticity rule $[[2N^2 + 2N + 1] \pi$-electrons]. Although, the hydrogen may be expected to bind at three possible sites: N, C, and bridging C and N, the minimum energy structures are obtained only for the N-site adsorption. All the isomers are capable to bind 12 H$_2$ molecules providing a gravimetric wt% of 7.2 (Figure 10B). These clusters can have potential applications as high energy density materials (HEDMs) since they have high heat of formation values ($\Delta H_{0}^{f}$). These $\Delta H_{0}^{f}$ values (1747.759, 1758.442, and 1813.864 kcal/mol for isomers A, B, and C, respectively) are calculated using the following isodesmic reaction:

$$\text{C}_{12}\text{N}_{12} + 12\text{H}_2\text{C} = \text{CH}_2 + 3\text{NH}_3 \rightarrow 9\text{C}_4\text{H}_4\text{NH} + 3\text{H}_2\text{N} - \text{NH}_2$$

The Ni-decorated analogue (Jana et al., 2020) of the cage can have three possible binding modes: bridging between C and N (denoted as X$_{CN}$ isomer), between 2 C atoms (X$_{CC}$ isomer), or between 2 N atoms (X$_{NN}$ isomer) (Figure 11A). Higher numbers of Ni decoration (up to four) in the N-(μ-Ni)-N bridging mode reveals the variation in aromaticity and H$_2$-binding potential with the number of Ni atoms (Figure 11B). The reason for selecting N-(μ-Ni)-N bridging mode for this purpose is the highest amount of positive charge on the Ni center of the X$_{NN}$ isomer. The isodesmic reactions used to determine the $\Delta H_{0}^{f}$ of Ni-C$_{12}$N$_{12}$ (4,239.470 kcal/mol) and 4Ni-C$_{12}$N$_{12}$ (4,520.528 kcal/mol) are as follows:

$$\text{Ni} + \text{C}_{12}\text{N}_{12} + 12\text{H}_2\text{C} = \text{CH}_2 + 3\text{NH}_3 \rightarrow 9\text{C}_4\text{H}_4\text{NH} + 3\text{H}_2\text{N} - \text{NH}_2 + \text{Ni}$$

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

Each Ni center on C$_{12}$N$_{12}$ is capable to adsorb up to three H$_2$ molecules (Figure 11C). In the single Ni-doped clusters, the aromaticity increases in the order X$_{CN} < X_{CC} < X_{NN}$, and in the case of multiple Ni-doping, the aromaticity increases uniformly with the number of Ni atoms.

The boron analogue of the C$_{12}$N$_{12}$ cage, i.e., B$_{12}$N$_{12}$ can trap hydrogen both endohedrally and exohedrally (Giri et al., 2011b). A total of 12 hydrogen molecules can be adsorbed in this cage system, the interaction energy per H$_2$ molecule...
varies from \(-11.5\) to \(-12\) kcal/mol. The change in the reactivity descriptors with the gradual hydrogen uptake validates the CDFT based electronic structure principles. The aromaticity in terms of NICS (0) values of all the \(n\)H\(_2@\)B\(_{12}\)N\(_{12}\) \((n = 0–12)\) species are plotted and presented in Figure 12. It is evident that among all the hydrogen-loaded species, the four, eight, and twelve numbers of H\(_2\) loaded clusters have high aromatic stability.

In this report, we have described the influence of aromatic behaviour on the H\(_2\) trapping potential of various all-metal and nonmetal systems where it is measured in terms of nucleus independent chemical shift (NICS) values. The effect of aromaticity is not uniform throughout all systems. In some systems, the variation of aromaticity with the number of adsorbed H\(_2\) molecule is quite uniform and systemic, like in the cases of C\(_4\)Li\(_4\), C\(_5\)Li\(_5^-\), and C\(_6\)Li\(_6\) rings, N\(_4\)\(^2-\) and N\(_6\)\(^-\) rings, the \(n\)Ni-decorated C\(_{12}\)N\(_{12}\) clusters. While for others, like that in the Al\(_2\)M\(_2\) clusters, it is found to be quite random and significantly high. It deserves a careful scrutiny.

4 CONCLUSION

In this review, we have covered several case studies predicting all-metal and non-metal aromatic clusters with potential applications in hydrogen storage and highlighted the effect of aromaticity on the hydrogen uptake potential. The aromatic stabilization present in these clusters enables them to be applicable as promising building blocks for nanomaterials. The NICS-scan plots turn out to be very helpful in understanding the degree and trend in the variation of the aromatic/anti-aromatic nature. The presence of an electropositive center in the molecular clusters provides a
suitable site for the H$_2$ molecules to undergo a dipole–induced dipole interaction for adsorption. Temperature and pressure are good tuning parameters in controlling the adsorption/desorption process. In this context, a T-P phase diagram can provide proper guidance as to which temperature and pressure range could be ideal to undergo a favourable adsorption process. We have also highlighted the use of external electric fields in tuning the H$_2$ loading and release processes and hence overall improving the H$_2$ trapping capacity of the cluster in question. For future research, the search for chemical frameworks with large surface area and high porosity can be made for better reversible hydrogen storage via physisorption having interaction energy closer to that of chemisorption, with a target of improving the gravimetric and volumetric storage capacity, favourable rates of adsorption and desorption, operating temperatures, and thermal conductivity. Molecular frameworks offering higher surface area to volume ratio can increase volumetric capacity. The binding energies can be increased by tuning the pore volume, and the thermal conductivity can be improved with the help of new and developed heat exchangers.

**AUTHOR CONTRIBUTIONS**

PC came up with the concept and design of the review, wrote the abstract, reviewed the final manuscript. RP contributed towards the literature survey, writing the manuscript. All authors contributed to manuscript revision, read, and approved the submitted version.

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