



Article

Remarkable Single Atom Catalyst of Transition Metal (Fe, Co & Ni) Doped on C₂N Surface for Hydrogen Dissociation Reaction

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Abstract: Currently, hydrogen is recognized as the best alternative for fossil fuels because of its sustainable nature and environmentally friendly processing. In this study, hydrogen dissociation reaction is studied theoretically on the transition metal doped carbon nitride (C₂N) surface through single atom catalysis. Each TMs@C₂N complex is evaluated to obtain the most stable spin state for catalytic reaction. In addition, electronic properties (natural bond orbital NBO & frontier molecular orbital FMO) of the most stable spin state complex are further explored. During dissociation, hydrogen is primarily adsorbed on metal doped C₂N surface and then dissociated heterolytically between metal and nitrogen atom of C₂N surface. Results revealed that the Fe@C₂N surface is the most suitable catalyst for H₂ dissociation reaction with activation barrier of 0.36 eV compared with Ni@C₂N (0.40 eV) and Co@C₂N (0.45 eV) complexes. The activation barrier for H₂ dissociation reaction is quite low in case of Fe@C₂N surface, which is comparatively better than already reported noble metal catalysts.

Keywords: hydrogen dissociation reaction; hydrogen energy; C₂N surface; single atom catalyst; catalysis; transition metals



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1. Introduction

Catalysts are the backbone of many commercially available energy conversion and industrial processes [1]. Currently, catalytic technology is managing the production of approximately more than ten trillion dollars of goods annually in power, petroleum, food, and chemicals industries [2]. Noble metals have displayed exceptionally outstanding catalytic properties for energy conversion and production and have surpassed all other catalysts. Despite their wide-range use, there are some challenges associated with noble metals catalysts, such as their limited availability and high prices [3]. From economical perspective, the cost and scarcity of many promising catalytic metals such as palladium and platinum reduces their extensive use [4,5]. To deal with this problem effectively, many other catalysts are being considered with the motive of obtaining commercially viable economical catalyst with uncompromised catalytic efficiency.

The key goal of alternative approaches being considered is to reduce the quantity of these expensive noble metals while possibly improving or at least maintaining performance. Thus, in recent times, single atom catalysis (SAC) approach has been proposed, so that catalysis can be accomplished via single metal atom on a support surface [6–8]. Single atom catalysts usually include uniformly distributed catalyst on supports which act to stabilize these catalysts. With the passage of time, many synthetic procedures have been developed to prepare these catalysts. Novel techniques that are used to synthesize and characterize single atom catalyst are wet chemistry [9], atomic layer deposition [10] and

mass selected soft landing [11]. The catalytic efficiency of these catalysts is taking hold, but the understanding of these type of catalysts is still limited. Therefore, the study of supported single metal atom catalysis is of great interest [12].

Over the years, hydrogen has been recognized as the best alternative for fuels because of its sustainable nature and environment friendly processing [13]. Among chemical reactions being catalyzed in industries, hydrogen dissociation reaction is the most carried out process. It is a part of many important chemical reactions including production of ethylene from hydrogen-based energy fuel cells [14], and in Fischer-Tropsch process [15]. It is also part of famous Haber Bosch process for ammonia synthesis [16].

Previous studies have revealed that numerous noble metals such as Pt [17], Ru [18], Pd [19], Rh [20], and Au [21] have the potential to efficiently catalyze hydrogen dissociation reactions. However, these noble metals are very expensive and generally work at high temperature, which make them economically non-feasible [22]. Transition metals such as Mn, Fe, Ni, Co, Zn, and Cu etc. have gained much interest due to their relatively high abundance and low cost [23,24]. Replacing noble metals with a low-cost material is necessary for large-scale and practical application. On the contrary side, the carbon-based materials, organic frameworks [25], graphyne [26], graphene [27], graphitic carbon nitride (g-C₃N₄) [28], porous and other nanostructured materials have received considerable attention as adsorbent (support materials for catalyst) due to their promising H₂ storage capacities, large surface areas at low temperature and potential thermal and electronic properties [29,30]. Yan et al. investigated the Pd doped graphene surface for hydrogen dissociation reaction during the hydrogenation of 1,3-butadiene. They observed that dissociation of H₂ occurred over the Pd atom (for subsequent hydrogenation) with moderate energy barrier of 0.84 eV [31]. However, scientists are still trying to search and design more efficient catalysts that could offer more selectivity and economical way for hydrogen dissociation reaction.

Recently, a novel 2-D C₂N monolayer was synthesized experimentally by Mahmood et al. [32]. The special nitrogenated cavities in the C₂N monolayer are evenly distributed which serve as optimal site for capturing and holding single metal atom. The surface used is quite stable and employed in many research areas including sensors [33], storage materials [34], as support [35] and in drug delivery [36]. Furthermore, metal coordinated C₂N-based materials are also employed as catalyst in lithium sulfur batteries as well as in oxygen reduction [37,38]. Therefore, the C₂N sheet can be employed as a support for single metal atom similar to g-C₃N₄ and graphene [35]. 2D C₂N surface has been previously reported in literature to effectively catalyze several important reactions, for example H₂ evolution reaction, N₂ reduction, CO [39] and O₂ reduction reactions [40] due to rich nitrogen content and periodic porous structure [41–44].

Herein, we have investigated the hydrogen dissociation reaction through late transition metal (TM) atoms based single atom catalysis using density functional theory. In the current study, we mainly focus on the dissociation of H₂ on low-cost transition metals (TMs), for example Fe, Co and Ni supported on C₂N surface [45–47]. Being quite stable, C₂N surface stabilizes the single atom catalyst quite amazingly. In comparison to carbon-based surface, this surface also bears nitrogen which can play a good role in hydrogen dissociation reaction due to electronegativity difference with hydrogen and can tune the electronic properties of TMs [48,49].

2. Computational Methodology

In this study, M06-2X/6-31G(d,p) is used for the optimization of all the structures using Gaussian09 software. M06-2X is a long-range functional which is well reported to estimate non-covalent interaction energies and barrier heights [50]. Benchmark studies show that M06-2X functional perform better for interactions of stacked system. M06-2X also shows better performance when interactions of TMs are studied with other systems [51].

TMs show various spin states, therefore, each of these metal complexes were optimized at various spin states to obtain the most stable spins state. The electronic config-

urations of Fe, Co and Ni are $[\text{Ar}] 3d6^4s^2$, $[\text{Ar}] 3d6^7s^2$ and $[\text{Ar}] 3d6^8s^2$, respectively. In case of Fe and Ni doped C_2N , singlet, triplet, quintet, and septet spin states were considered, and the most stable spin states are septet and triplet for Fe and Ni, respectively (see Table S1 of Supplementary Material). For Co doped C_2N , doublet, quartet, sextet, and octet spin states were optimized in search of the most thermodynamically stable spin state of metal doped C_2N . Among the optimized spin states, doublet is the most stable in case of $\text{Co@C}_2\text{N}$ complex. The interactions energies of these complexes were based on the stable spin states. Hydrogen dissociation reaction was also performed on the most stable spin state metals.

Interaction energies are calculated for the most stable geometries of studied complexes by using the following expression:

$$E_{\text{int}} = E_{\text{T.M@C}_2\text{N}} - (E_{\text{C}_2\text{N}} + E_{\text{T.M}}) \quad (1)$$

Here, $E_{\text{T.M@C}_2\text{N}}$, $E_{\text{C}_2\text{N}}$ and $E_{\text{T.M}}$ are interaction energies of $\text{T.Ms@C}_2\text{N}$ complexes, bare C_2N surface and TMs, respectively.

For hydrogen dissociation, primary step is adsorption of hydrogen on metal doped C_2N surface. The adsorption energy of hydrogen doped catalyst is calculated through following equation:

$$E_{\text{ads.}} = E_{\text{H}_2\text{@C}_2\text{N-M}} - (E_{\text{M@C}_2\text{N}} + E_{\text{H}_2}) \quad (2)$$

Here, $E_{\text{H}_2\text{@C}_2\text{N-M}}$, $E_{\text{M@C}_2\text{N}}$ and E_{H_2} represent the energies of the hybrid structures of hydrogen adsorbed complexes, metal@ C_2N , and H_2 , respectively.

For calculation of activation barrier and energy of reaction, Equations (3) and (4) were used, respectively.

$$E_a = E_{\text{TS}} - E_{\text{Reactant}} \quad (3)$$

$$\Delta E_R = E_{\text{Product}} - E_{\text{Reactant}} \quad (4)$$

In Equation (3), the E_a represents activation barrier and E_{TS} represents the energy of transition states. Whereas in Equation (4), the E_R shows energy of reaction.

3. Results and Discussion

Geometries and Electronic Properties

The optimized structure of C_2N consists of hexagonal unit cell (see Figure 1). The C-N bond length is 1.32 Å whereas for C-C bond length is 1.46 Å in the benzene ring and 1.42 Å in the pyrazine ring. The observed C-N-C bond angle is 116.73°. All of these bonding parameters are comparable with already reported in the literature [52].

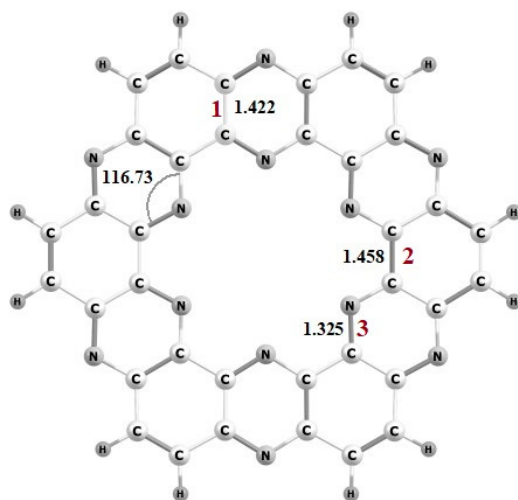


Figure 1. Optimized structure of C_2N surface.

For each TM being considered, we have studied various spin states in order to obtain thermodynamically the stable spin state. The most stable spin state geometries are reported in the main manuscript (see Figure 2), while least stable $M@C_2N$ complexes are given in Supplementary Information (Figure S1). While the interaction energy values for studied $TM@C_2N$ clusters are reported in Table 1.

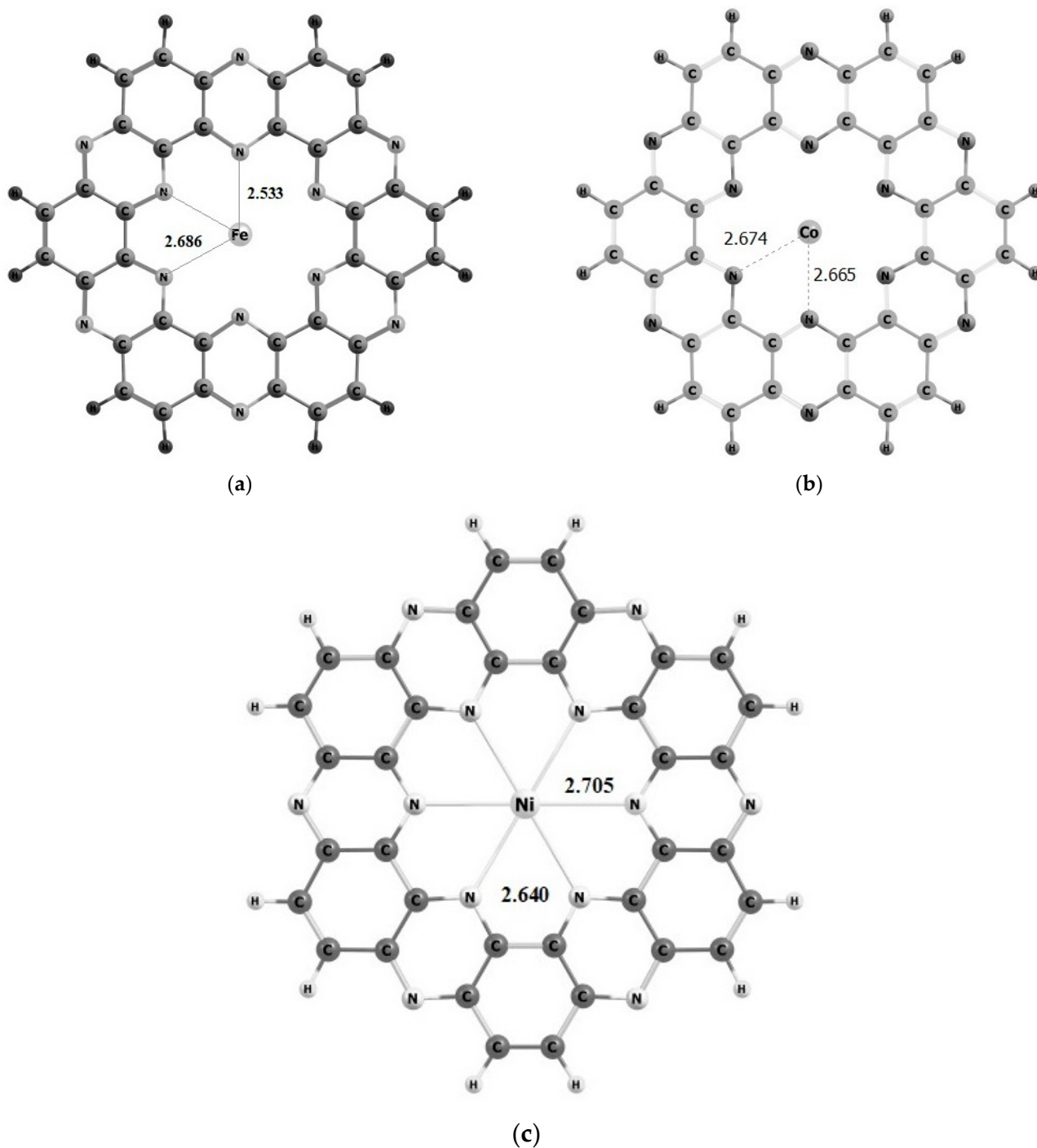


Figure 2. Geometries of (a) iron, (b) cobalt and (c) nickel doped C_2N complexes.

Table 1. Interaction energy of metal doped C₂N surface (eV), M-N distance (Å) between the metal atom and the neighboring nitrogen (N) atoms, charge transfer between the adsorbed metal atom and surface (e[−]) and the HOMO-LUMO energy gap (eV) of M@C₂N complexes.

M@C ₂ N	E _{int}	M-N	NBO	HOMO	LUMO	E _{H-L}
Fe@C ₂ N	−3.19	2.53, 2.69	1.43	−4.84	−2.29	2.56
Co@C ₂ N	−1.42	2.66, 2.67	0.92	−7.27	−2.15	5.11
Ni@C ₂ N	−2.51	2.64, 2.71	0.74	−4.08	−2.59	1.50
C ₂ N	–	–	–	−7.59	−1.99	5.61

Optimized structure of Fe@C₂N cluster is presented in Figure 2a. Fe atom binds with neighboring nitrogen atoms. The stabilization or adsorption energy in case of Fe@C₂N cluster is −3.19 eV. The geometry of Co@C₂N surface is given in Figure 2b, Co shows interaction with neighboring nitrogen atoms and the calculated stabilization energy is −1.42 eV, whereas adsorption of Ni atom over C₂N surface resulted in the interaction energy of −2.51 eV (Figure 2c). The highest interaction energy value is observed in case of Fe@C₂N among all studied M@C₂N clusters, which is attributed to least interaction distance between Fe and N atoms of C₂N surface. The bonding distance between Fe and nitrogen atoms of C₂N is 2.53 Å, as compared to 2.64 Å and 2.66 Å for Ni@C₂N and Co@C₂N, respectively. Furthermore, it is observed in studied complexes that as the number of unpaired electrons (d-orbital of TMs) decreases, decrease in their interaction energy is observed. Moreover, no distortion is observed in M@C₂N clusters upon adsorption of TMs (Fe, Ni & Co) due to fused rings of benzene and pyrazine. In addition, no change in bond lengths of C-N and C-C are observed upon adsorption of TMs on C₂N surface.

4. HOMO-LUMO and DOS Analysis

HOMO-LUMO analysis and DOS spectra have been investigated to fully understand the corresponding changes in electronic properties. The charge transfer results and the HOMO-LUMO energy gap of metal doped C₂N complexes are reported in Table 1. Density of states graphs are presented in Figure 3, which show the formation of new states causes the change in H-L gap. In the DOS graph of Ni doped on C₂N, the formation of new HOMO states also confirms the change in H-L energy gap.

Upon adsorption of metal atoms, the energy gap (E_{H-L}) is significantly reduced. Least reduction in energy gap is observed in case of Co@C₂N complex which is from 5.61 eV to 5.11 eV. However, a significant decrease in energy gap is observed for Fe@C₂N and Ni@C₂N complexes as compared to bare C₂N surface i.e., E_{H-L} values are 2.56 eV and 1.50 eV, respectively. The change in electronic parameters is confirmed through DOS analysis which clearly shows the formation of new states. Thus, it also explains the significant lowering of HOMO-LUMO energy gap in Fe@C₂N and Ni@C₂N complexes.

In case of Ni@C₂N complex, potential decrease in H-L gap is observed due to increase in HOMO and decrease in LUMO energies as compared to bare C₂N surface. Same type of observations is observed from TDOS spectra of Ni@C₂N due to increase in HOMO energy and decrease in LUMO energy.

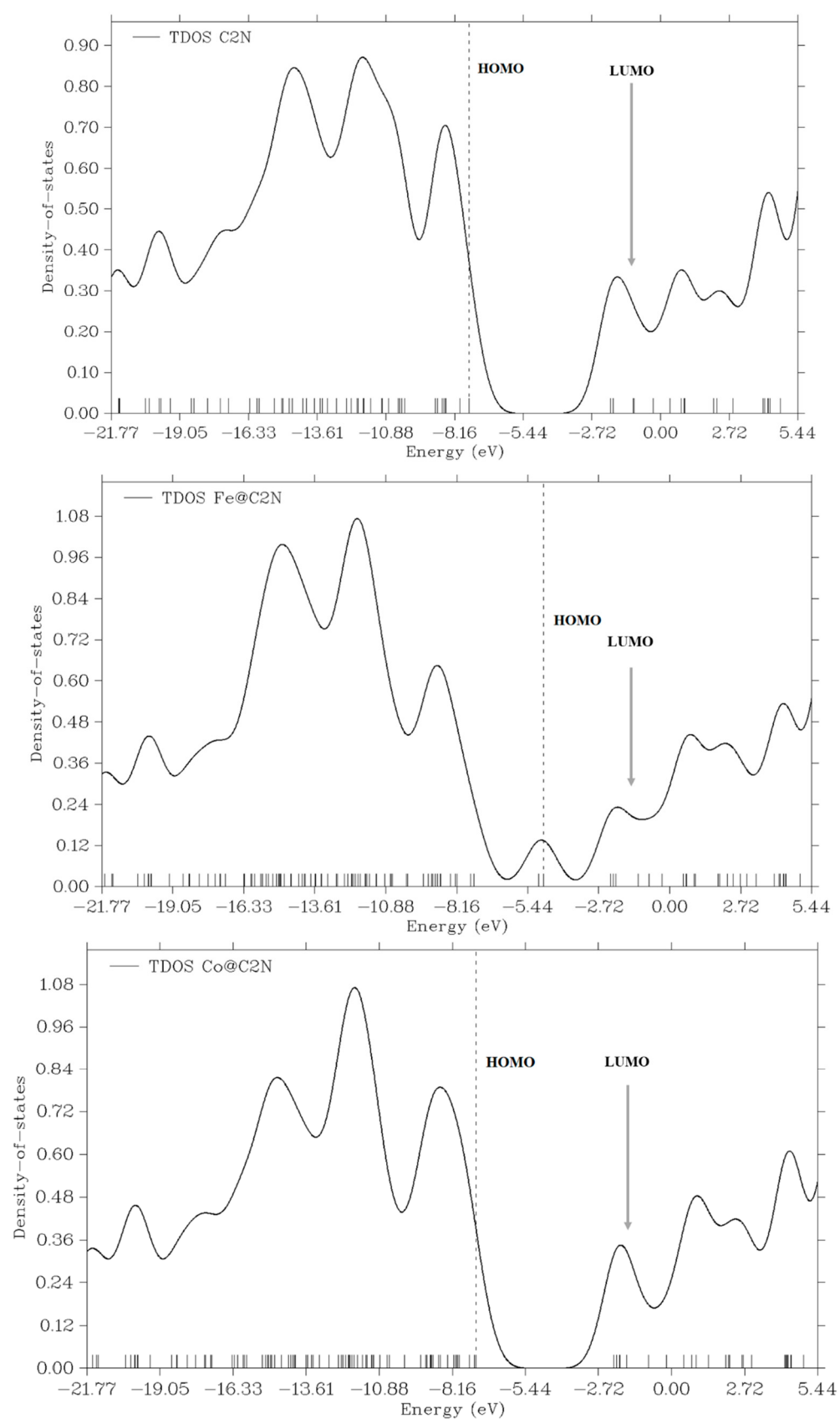


Figure 3. Cont.

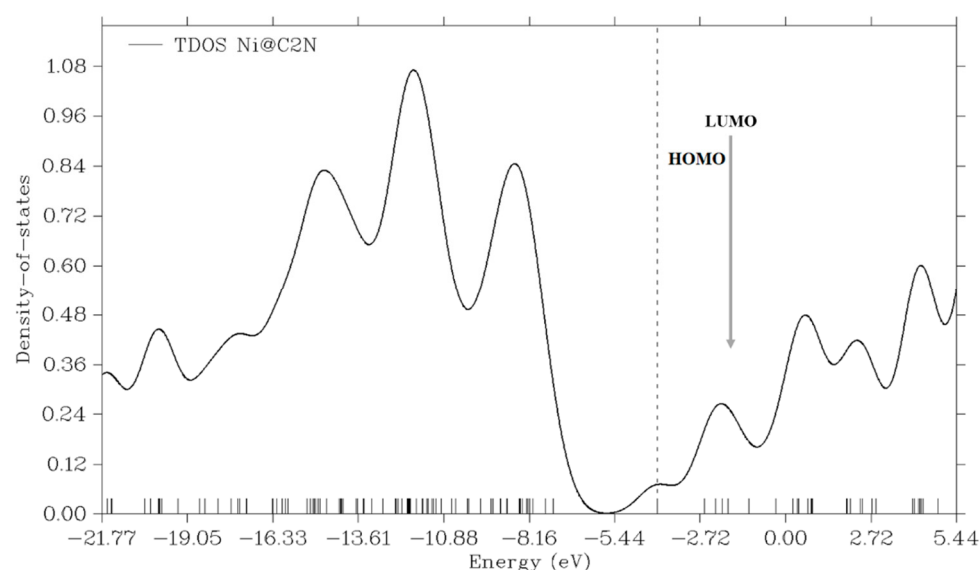


Figure 3. DOS analysis of bare C₂N surface and metal doped C₂N surface.

5. Natural Bond Orbital (NBO) Analysis

NBO analysis was performed on studied TM doped C₂N clusters to investigate the transfer of charge between C₂N surface and TM atoms. The values of NBO charges are reported in Table 1. The adsorption of Fe on C₂N surface resulted in a net charge of $1.43e^-$ on Fe atom. The appearance of positive charge ($1.43e^-$) on the Fe atom upon adsorption over C₂N represents the electron recipient character of C₂N and electropositive nature of Fe in the most stable geometry of Fe@C₂N complex. Similarly, in case of Co and Ni dopants, the NBO charges observed are $0.92e^-$ and $0.74e^-$, respectively. In both Co@C₂N and Ni@C₂N complexes, the positive sign of charge transfer indicates that charge is shifting towards C₂N surface from TMs, revealing the electropositive character of studied TMs. Highest charge transfer is observed in case of Fe@C₂N complex, which reveals the strong interaction among Fe atom and C₂N support through a charge transfer from Fe atom to C₂N surface [53].

NBO analysis reveals that TMs adsorbed on C₂N surface showed electropositive character due to their metallic behavior and electron rich C₂N surface. Highest charge transfer is observed in case of Fe, which verify its high interaction energy with C₂N surface. However, in case of Co@C₂N and Ni@C₂N complexes NBO charges observed are $0.92e^-$ and $0.74e^-$, respectively.

6. Hydrogen Dissociation Reaction on Iron Doped C₂N Surface

The reaction started with adsorption of H₂ molecule on C₂N surface (Figure 4). The hydrogen molecule is adsorbed at iron with adsorption energy of -1.35 eV. The metal atom (Fe1) shows interaction with both hydrogen atoms marked as H2 and H3 with interaction distances of 2.06 Å and 2.07 Å, respectively. Initially H-H bond length of isolated H₂ is 0.75 Å. After adsorption, the hydrogen dissociation proceeds. In the transition state, H-H bond length increases from 0.75 Å to 0.93 Å and the Metal-Hydrogen bond length decreases to 1.78 Å in transition state. Single imaginary frequency confirms that the transition state is located on Fe@C₂N (see Table S2 for more details). In the product, the Fe-H bond length is 1.67 Å and N-H bond length is 1.03 Å. The activation barrier for this hydrogen dissociation reaction occurring on Fe@C₂N is 0.36 eV, while the enthalpy of reaction is -0.05 eV, as mentioned in Table 2.

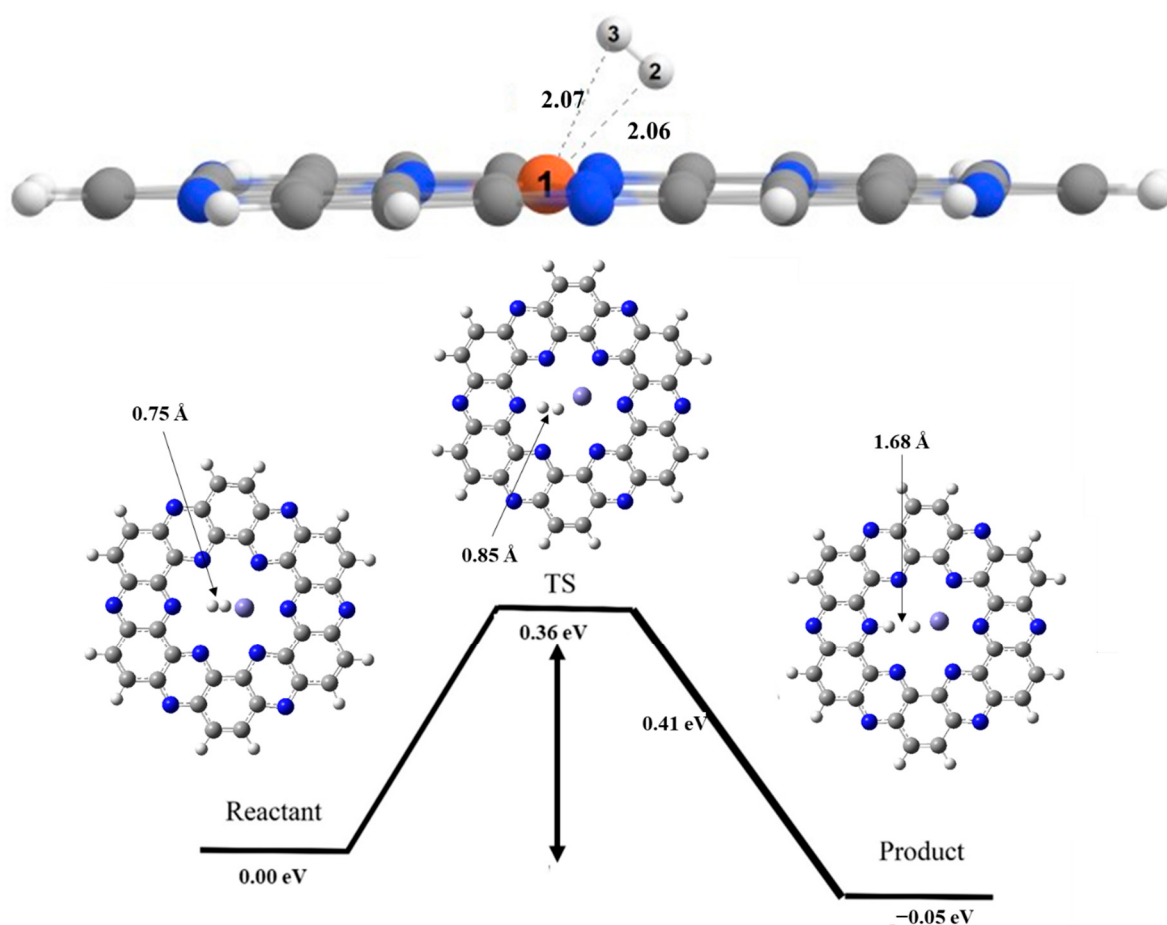


Figure 4. Potential energy surface diagram of H_2 dissociation on $Fe@C_2N$ for reactant, transition state and product. Where, grey color is for carbon, white for hydrogen, blue for nitrogen and cobalt blue for iron atom.

Table 2. H_2 dissociation energies at $M@C_2N$ clusters in eV and calculated bond lengths of H—H bond and M—H bonds, here E_a (eV), ΔE (eV) and B.L. (Å) represent activation energy barrier, energy of reaction and bond length (Å), respectively.

Reaction Energies		$Fe@C_2N$	$Co@C_2N$	$Ni@C_2N$
E_a		0.36	0.45	0.40
ΔE		−0.05	−0.08	0.23
H—H Bond length	B.L _R	0.76	0.75	0.76
	B.L _{TS}	0.93	0.85	0.84
	B.L _P	1.68	1.80	1.84
Ni—H Bond length	B.L _R	2.06	1.83	1.89
	B.L _{TS}	1.78	1.76	1.75
	B.L _P	1.67	1.60	1.56

In case of Fe doped C_2N catalyst, the activation barrier reduced significantly, which show higher catalytic activity of Fe doped C_2N catalyst. Iron possesses greater number of unpaired electrons (d-orbital), which are responsible for higher catalytic efficiency of $Fe@C_2N$ complex.

7. Hydrogen Dissociation Reaction on Cobalt Doped C₂N Surface

In the first step, H₂ molecule is adsorbed over the C₂N surface (Figure 5). The stabilization energy observed for the adsorption of hydrogen molecule at cobalt site is -1.93 eV, which is higher than the value observed for adsorption at Fe site (-1.35 eV). Optimized geometry of H₂ molecules over Co@C₂N surface reveals that H₂ is bit tilted. Initially, the interaction distances of Co atom with H2 and H3 atoms of reactant molecule are 1.83 Å and 1.92 Å, respectively (see Figure 5). Then, hydrogen dissociation proceeds through a transition state, where H—H bond length increases from 0.76 Å to 0.85 Å and the Co—H bond length is decreased to 1.76 Å. At final step, the Co—H and N—H bond lengths observed are 1.60 Å and 1.03 Å, respectively. The activation barrier for hydrogen dissociation reaction occurring on Co@C₂N surface is 0.45 eV, and the enthalpy of reaction is -0.08 eV (see Table 2).

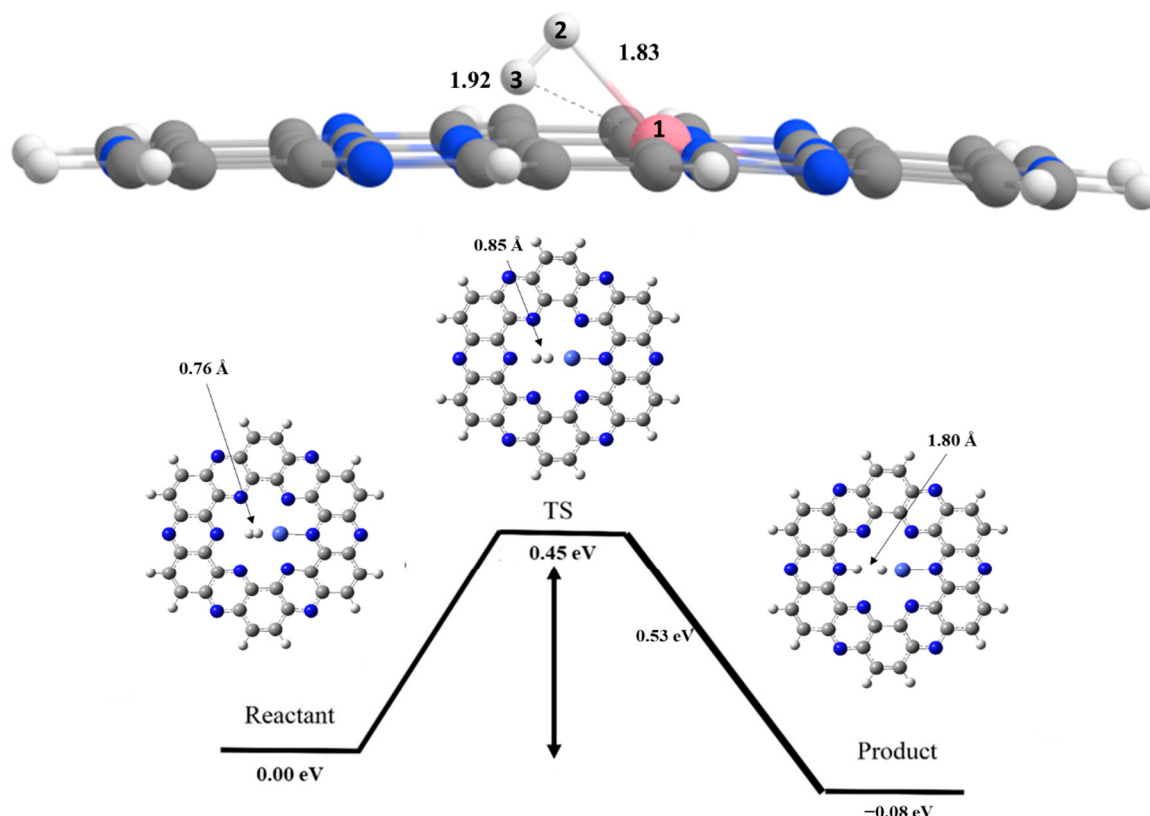


Figure 5. Potential energy surface diagram of H₂ dissociation on Co@C₂N for reactant, transition state and product. Where, grey color is for carbon, white for hydrogen, blue for nitrogen and cobalt blue for cobalt atom.

In case of Co@C₂N complex, the activation barrier of 0.45 eV is observed for hydrogen dissociation, which is comparatively higher as compared to Fe@C₂N complex (0.36 eV). The higher potential barrier for Co@C₂N catalyst is due to less unpaired electrons (d-orbital) in TM (Co).

8. Hydrogen Dissociation Reaction on Nickel Doped C₂N Surface

H₂ molecule is also adsorbed on Nickel of Ni@C₂N surface with the adsorption energy of -2.02 eV (see Figure 6). In optimized geometry, reactant hydrogen molecule is oriented almost parallel over the C₂N surface. The bond distances between nickel atom of Ni@C₂N and, H2 and H3 atoms of molecule are 1.90 Å and 1.89 Å, respectively, whereas the H—H bond length is 0.76 Å. At transition state, H—H bond length increases from 0.76 Å to 0.84 Å and the Ni—H bond length is decreased from 1.89 Å to 1.75 Å. Finally at product side, the Ni—H bond length gets further reduced to 1.56 Å, whereas N—H bond length is 1.03 Å. In

case of Ni@C₂N cluster, the activation barrier for hydrogen dissociation reaction is 0.40 eV (Table 2), while the enthalpy of reaction is 0.23 eV.

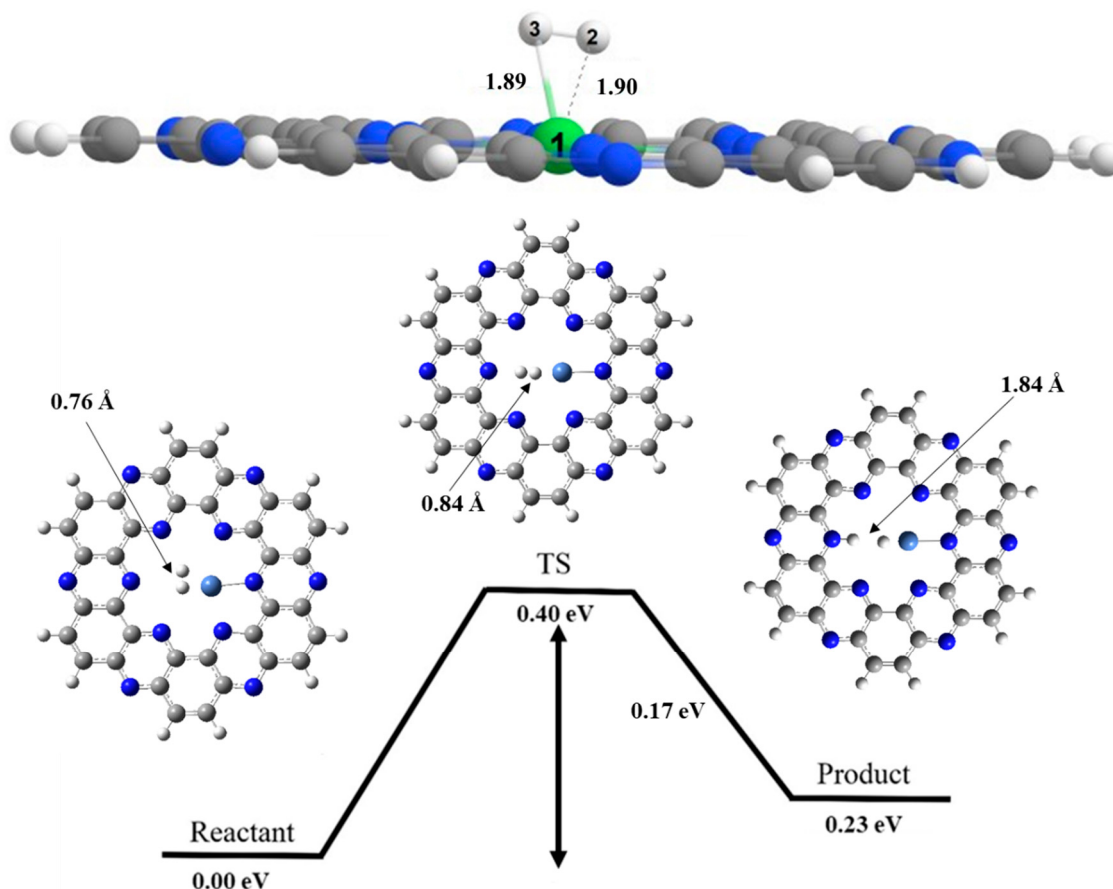


Figure 6. Potential energy surface diagram of H₂ dissociation on Ni@C₂N for reactant, transition state and product. Where, grey color is for carbon, white for hydrogen, blue for nitrogen and cobalt blue for nickel atom.

The hydrogen dissociation barrier in Ni@C₂N complex is 0.40 eV. The observed value of activation barrier in this case is lower than Co@C₂N catalyst and greater than the Fe@C₂N catalyst.

Overall, the order activation barrier observed for studied catalysts is Fe@C₂N < Ni@C₂N < Co@C₂N. The observed trend is quite similar with the trend of TMs doped Al₂O₃ reported by Yang et al. [54] for the oxidation of CO by single atom catalysis.

For comparison, the activation barrier of hydrogen dissociation in our work and some other surfaces are reported in Table 3. Our results show good agreement with already reported values of dissociation barrier using noble TMs. In our case, the lowest hydrogen dissociation barrier is observed for Fe@C₂N catalyst (0.36 eV), and the value is much better than the reported value of Au/TiO₂ complex (0.54 eV). Our results are in accordance with the already reported values of dissociation barriers obtained on different surfaces doped with noble TMs. In our case, Fe-incorporated C₂N surface displays the smallest activated barrier (0.36 eV), which is due to the presence of strong interaction between the metal d orbitals and molecular orbital of H₂.

Table 3. Comparison of current activation barrier of hydrogen dissociation with already reported values over different Surfaces.

Surfaces	Dissociation Barrier	References
Ni adsorbed $\text{Mg}_{17}\text{Al}_{12}$ surface	$\text{Mg}_{16}\text{NiAl}_{12}$ 0.82 eV $\text{Mg}_{15}\text{Ni}_2\text{Al}_{12}$ 0.53 eV	[55]
Ti doped Mg Surface	0.35 eV	[56]
Au/ TiO_2	0.54 eV	[57]
Mg_9Rh cluster	0.63 eV	[58]
$\text{Fe@C}_2\text{N}$	0.36 eV	This work
$\text{Co@C}_2\text{N}$	0.45 eV	–
$\text{Ni@C}_2\text{N}$	0.40 eV	–

9. Conclusions

Herein, we have theoretically investigated the hydrogen dissociation reaction on TMs doped C_2N surface through single atom catalysis. Single atom catalysis provides better efficiency and stability in heterogeneous catalysis. Stable spin states of $\text{TMs@C}_2\text{N}$ complexes evaluated for catalytic hydrogen dissociation reaction. Electronic properties (NBO, FMO) of the most stable spin state of $\text{TMs@C}_2\text{N}$ complexes are further explored. NBO analysis reveals the electropositive character of TMs, thus, significant charge transfer is observed between TMs and C_2N surface. Hydrogen molecule, primarily adsorbed on metal doped C_2N surface during dissociation and then heterolytically dissociated between metal and nitrogen atom of C_2N surface. The mechanistic pathway of hydrogen dissociation reaction shows that $\text{Fe@C}_2\text{N}$ complex is the most suitable catalyst for hydrogen dissociation reaction with activation barrier of 0.36 eV compared to $\text{Ni@C}_2\text{N}$ (0.40 eV) and $\text{Co@C}_2\text{N}$ (0.45 eV) complexes. Our results indicate that the studied $\text{TMs@C}_2\text{N}$ complexes significantly decrease in the activation barrier, which speaks volumes about their success. However, the highest reduction in activation barrier is observed in the case of $\text{Fe@C}_2\text{N}$ complex, thus can act as a promising catalyst for hydrogen dissociation reaction in single atom catalysis.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano13010029/s1>, Figure S1: Optimized geometries of studied $\text{M@C}_2\text{N}$ complexes at various possible spin states at M06-2X/6-31G(d,p) level of theory. Where grey color is for carbon, light grey for hydrogen, blue for nitrogen, orange for nickel, purple for iron and cobalt blue for cobalt atom; Table S1: Relative stabilities of studied $\text{M@C}_2\text{N}$ complexes at various possible spin states (all values are in eV). Table S2: Energies and lowest vibrational frequencies of reactants, products, and transition states over designed $\text{M@C}_2\text{N}$ catalysts.

Author Contributions: Conceptualization, K.A. and M.Y.; methodology, A.B.S. and S.S.; software, M.Y.; validation, M.Y.; investigation, A.B.S., S.S. and M.Y.; resources, K.A., H.H.H. and N.S.S.; writing—original draft preparation, A.B.S. and S.S.; writing—review and editing, K.A., M.Y. and N.S.S.; supervision, K.A. and M.Y.; project administration, K.A., H.H.H. and N.S.S.; funding acquisition, K.A., H.H.H. and N.S.S. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

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