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Direct oxidation of methane to methanol on Co embedded N-doped graphene: comparing the role of N$_2$O and O$_2$ as oxidants

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Graphical abstract
Highlights

- The CoN$_3$-G shows better catalytic activity toward adsorption of gas reactants and consequently methane oxidation.
- Methane converts to methanol on CoN$_3$-G via a two-step pathway, employing N$_2$O as an oxygen-donor.
- The C-H bond cleavage proceeds via the Eley-Rideal (ER) mechanism while other reactions proceed via the Langmuir-Hinshelwood (LH) mechanism.
- Methane dissociates actively on CoN$_3$-G results in the formation of ethane molecule in a C-C coupling reaction during the oxidation process.

Abstract

In this work, the effects of N-doping into the Co-doped single vacancy (Co-SV-G) and di-vacancy graphene flake (Co-dV-G) are investigated and compared toward direct oxidation of methane to methanol (DOMM) employing two different oxidants (N$_2$O and O$_2$) using density functional theory (DFT) calculation. We found that DOMM on CoN$_3$-G utilizing the N$_2$O molecule as oxygen-donor proceeds via a two-step reaction with low activation energies. In addition, we found that although CoN$_3$-G might be a good catalyst for methane conversion, it can also catalyze the oxidation of methanol to CO$_2$ and H$_2$O due to the required low activation barriers. Moreover, the adsorption behaviors of CH$_x$ (x=0-4) species and dehydrogenation of CH$_x$ (x=1-4) species on CoN$_3$-G are investigated. We concluded that CoN$_3$-G can be used as an efficient catalyst for DOMM and N$_2$O reduction at ambient conditions which may serve as a guide for fabricating effective C/N catalysts in energy-related devices.

Keywords: N-doped graphene, direct oxidation of methane, DFT, methanol, N$_2$O reduction, Co embedded graphene
1 Introduction

Traditional conversion of methane (CH\textsubscript{4}) to methanol (CH\textsubscript{3}OH) is performed by a two-step process in the industry under the harsh reaction conditions such as high temperature and pressure [1, 2]. Despite the fact that it is not a cost-effective procedure, there exists no industrial process capable of directly converting methane to methanol. In addition, N\textsubscript{2}O is known as an agricultural toxic gas which may also originate from other activities like wastewater treatments, or the combustion of fossil fuels and biomass. During the last century, it is found that the global warming of CH\textsubscript{4} and N\textsubscript{2}O are 28 and 265 times higher than CO\textsubscript{2}. Therefore, investigating the conversion of these gas molecules is of great interest. Direct synthesis of CH\textsubscript{3}OH from CH\textsubscript{4} at room temperature and pressure is a promising way for the industry. To date, many studies have been explored on the direct synthesis of methanol but none of them has proven cost-effective. Thus, it remains one of the considerable challenges in the sector of methane utilization due to the strong C–H bond energy and its chemical inertness of methane.

It is known that although noble metals like Ir, Pt, Rh and Ru [3-7] are highly active toward DRM and resistant to carbon formation, they are economically less attractive materials for large-scale industrial use due to their scarcity, high cost and toxicity [8]. Amongst different types of catalysts, single individual metal atoms anchored to graphene-based materials [9-11] are discovered as novel material not only because they minimize material usage to meet the goal of cost-effective catalysis, but also because they surpass conventional catalysts in terms of having a high specific activity with a significantly reduced amount of noble metals. Recently, single metal atoms doped into monolayer surfaces have been tested as catalysts for various reactions owing to their well-defined sites, unsaturated coordination environment, and high atom efficiency. Doping single-atoms into the graphene structure may be effective to improve its catalytic properties [12, 13]. Amongst an increasing number of single-atoms, most have been focusing on supporting noble metal atoms like Pt or Pd on metal oxide or metal surfaces [14, 15]. Dopants such as P [16], Si [17, 18], Fe [19, 20], Pt [21, 22], Pd [23, 24], Ni [25, 26] substitute with carbon atoms in the graphene sheet and can significantly enhance the properties of graphene sheet. On the other hands, tailoring the graphene sheet by introducing defects [27, 28] or heteroatoms (e.g., N, B, P) [29] into the structure of graphene sheet will speed up the catalytic reactions occurred on the surface [30, 31] and modulate the electronic properties of the catalyst [32-35].

It has been reported that N-doped graphene (N-G) [36] and transition metal-coordinated nitrogen-doped graphene (TMN-G) can enhance the chemical reactivity of graphene due to their low cost, high durability, and high catalytic activity. They are widely used in molecular sensors [37, 38], bio-sensing applications [39], metal-free oxygen reduction catalysis (ORR) [40, 41], CO oxidation reactions [42], and in lithium batteries [43-45]. The introduced N atoms modify the energy distribution of electronic states and thereby the local reactivity [46]. Three common N-doped configurations are observed in N-G, i. e., pyridinic, pyrrolic, and graphitic nitrogen [47, 48]. However, there are no investigations toward the differences of catalytic ability between different N defects. Recently, it was found that pyridinic-N can better anchor transition metal atoms in comparison to other types of N-G, due to their higher stability and catalytic activity toward various reactions [49, 50]. For instance, Yeager et al. [51] found that metal cations coordinated by pyridinic nitrogen-doped at the defective sites of graphitic carbon are the active sites for ORR in alkaline and acid electrolytes. Experimentally, graphene or carbonic structures containing nitrogen-coordinated transition metals can be easily synthesized [33, 52, 53]. Recently, Fei et al. [54] worked on the synthesis of nitrogen-enriched core-shell structured cobalt-carbon nanoparticles dispersed on graphene sheets, which can be used for hydrogen evolution reaction in both acidic and basic media. Wang et al. [55] found that Co embedded N-doped carbon nanotubes have high activity toward ORR and the oxygen evolution reaction (OER) in both alkaline and neutral
media due to their low cost and appropriate features to act as bifunctional catalysts for both the ORR and OER.

In the last few decades, researchers have been dedicated to the synthesis of cost-effective electrocatalysts using cheaper transition metals [56] in which, cobalt-based electrocatalysts show the most promising results [57]. As of any first-row transition metal (Ni, Fe, and Cu), cobalt is a cheap, environmentally friendly, and accessible metal in comparison with noble metals [58] and it can be introduced into the graphene lattice with no difficulties [10]. Recently, Fei et al. [54] worked on the synthesis of nitrogen-enriched core-shell structured cobalt-carbon nanoparticles dispersed on graphene sheets, which can be used for hydrogen evolution reaction in both acidic and basic media. In an experimental investigation, Jurković et al. [59] reported the plasma-activated methane partial oxidation reaction in a designed dielectric barrier discharge ionization reactor unit. They could produce valuable platform chemicals like methanol, formaldehyde, intermediate formic acid, acetic acid, and paraformaldehyde at room temperature and atmospheric pressure. Moreover, it is found that Co nanoparticles doped into carbon nanotube structures can decrease the local work function of the carbon surface because electrons transfer from cobalt to the surrounding carbon atoms, very easily [60]. Kattel et al. [61] investigated the ORR reaction pathway on M–N (M = Fe, Co, or Ni) catalytic clusters formed between pores in graphene supports. They found that O₂ molecule chemisorbs on CoN₄-graphene (CoN₄-G) and FeN₄-graphene (FeN₄-G) clusters but not on NiN₄-graphene (NiN₄-G) clusters. Therefore, the first two clusters were regarded as more active substrates toward ORR. The high stability is mainly attributed to the high conductivity of N-doped graphene and the embedded Co nanoparticles. N-doping increases the electron donor-acceptor properties of graphene and leads to the improvement of the conductance and interfacial electron transfer by doped Co nanoparticles [62]. Zhang et al. [49] calculated the activation barriers and thermodynamic properties of ORR on CoN₄-G. They demonstrated that CoN₄-G can enhance the ORR and resulted in the formation of two H₂O molecules. Kiefer et al. [63] reported that graphitic CoN₄ defects are stable at all potentials (U = 0-1.23 V) while CoN₂ defects are predicted to be unstable at high potentials. In addition, they predicted that the CoN₄ defect is the dominant in-plane graphitic defect in CoNₓ/C electrocatalysts.

Graphene nano-flakes and graphene nano-ribbons are promising graphene-based materials with a size controllable energy bandgap, which might be useful for various technological applications [64, 65]. They are important because of their potential for bottom-up fabrication of molecular devices, spintronic, and quantum dot technology [66]. They are cheap catalysts and being produced by a cheap method, they typically contain many defects. Because of the small size of graphene flakes they can be considered as a zero-dimensional form of graphene sheet showing different properties from graphene nanoribbons and bulk graphene. Such graphene flakes are promising for a variety of applications such as electronic and magnetic devices with different molecular sizes and shapes, and in light absorption in photovoltaics due to their edge structure and wide spectrum. They have unique electronic, magnetic, and optical properties since their bandgap can be modified. Moreover, the saturation of the zigzag edges of graphene flakes with different atoms (like H in our investigations) or molecular groups leads to a spin-polarized ground state with a non-zero total magnetic moment, an electronic energy gap, and spin density that strongly depends on the used atomic group to passivate the dangling bonds of the C atoms [67]. In this study, we have chosen to model such a graphene flake as a polyaromatic hydrocarbon molecule (PAH).

This article describes our efforts to develop a mechanism for methane conversion to methanol on a modified graphene flake. The modification of the graphene flake has been done in three steps, i. e., introducing a single vacancy (SV) and di-vacancy (dV) defect, doping the defective flake with nitrogen heteroatoms making pyridinic N-doping graphene flake (N₃- and N₄-G), and finally
introducing a single Co atom into the defective graphene flake lattice. Then, we investigated and compared the effect of nitrogen doping on the catalytic activity of the designed catalysts toward direct oxidation of CH$_4$ to CH$_3$OH using O$_2$ and N$_2$O as an oxidant. N$_2$O acts as an O-donor compound and gives us the ability to convert two pollutant gas simultaneously. The effects of using different oxidants have been studied in several investigations. For instance, Dasireddy et al. [68] studied the effects of oxidants (H$_2$O, N$_2$O, and O$_2$) on methane oxidation to methanol over the FePO$_4$ catalyst. They found that FePO$_4$ can actively convert methane to methanol using O$_2$ and N$_2$O oxidants.

It should be noted that although Ni or Cu metal surfaces would be most effective for C-H bond cleavage, the activity of an individual single Ni or Cu atoms doped graphene-like surfaces will vary toward the same reaction. For instance, in our previous investigation [69], single Ni and Si atoms were chosen to compare the catalytic activity of the tuned graphene flake toward the direct conversion of methane to methanol. Interestingly, we found that single Ni atom doped graphene flake (Ni-G) cannot actively catalyze methane oxidation while Si-doped graphene flakes (Si-G) showed a better catalytic activity thanks to the lower activation energies and more favourable thermodynamic properties. Therefore, we reasonably assume that depending on the investigated graphene nano-flake (with applying different tuning methods), the activity of an arbitrary doped single metal atom and consequently the whole tailored graphene nano-flake will change. Motivated by previous investigations, in this article, a single Co atom is chosen as a single metal atom due to its considerable activity for ORR and OER. Density functional theory (DFT) calculations are utilized in order to find the most energetically favourable substrate for the direct oxidation of methane to methanol. All the reactions take place at room temperature and then the catalytic performances of these carbon material catalysts were investigated. Moreover, the detailed surface interactions and reaction pathways that occurred on the interface of the substrate were also discussed.

2 Computational details

All structure optimizations and reaction pathway calculations are based on DFT using the Gaussian 16 package [70]. We employed the meta-GGA hybrid functional M06-2X [71] for geometry optimizations and frequency calculations. For carbon, nitrogen, hydrogen, and oxygen atoms the all-electron 6-31G$^*$ basis set is used. The Los Alamos National Laboratory [72] basis set of double-$\xi$ quality (LANL2DZ) used for Co atom. No significant spin contamination was found. To model the pristine graphene as a finite-size monolayer flake, a total of 85 carbon atoms were considered for all calculations. To minimize the boundary effect by dangling bonds, the edge atoms of the graphene flake are saturated by hydrogen. The binding/adsorption energy ($E_{\text{ads}}$) of each of the gas species involved in the reaction mechanism is characterized as:

$$E_{\text{bind/ads}} = E_{(AB)} - E_{(A)} - E_{(B)}$$

(1)

It is defined as the difference between the total energy of the optimized adsorbate-substrate system, $E_{(AB)}$, the sum of the total energy of the pure substrate, $E_{(A)}$, and the total energy of the optimized adsorbates or single metal atom in the gas phase, $E_{(B)}$. Moreover, the triplet state oxygen is considered for the adsorption configurations. The zero-point energy (ZPE) correction to the energy of adsorbed molecular species was calculated by:

$$ZPE = \sum \frac{1}{2} h \theta_i$$

(2)

where $h$ and $\theta_i$ are Planck’s constant and the frequency of the $i^{\text{th}}$ vibrational mode, respectively.

Natural bond orbital (NBO) analysis is used to measure the overlap population between two atoms. The formation energies ($E_f$) of Co-doped N embedded graphene flake are calculated by:
\[ E_t = E_{\text{substrate}} + a \mu_C - (E_{\text{pureG}} + b \mu_N + \mu_{\text{Co}}) \] (3)

the \( E_{\text{substrate}} \) represents the total energy of the doped graphene flake, \( \mu_C \) and \( \mu_N \) are the chemical potentials of the carbon and nitrogen atom, defined as the total energy per carbon atom in a pure graphene flake and the one-half of gaseous \( \text{N}_2 \) molecule, respectively. \( a \) (b) coefficients for \( \text{CoN}_3 \)-G and \( \text{CoN}_4 \)-G are 4(3) and 6(4), respectively. Finally, \( \mu_{\text{Co}} \) is the energy for isolated Co atom. Frontier Molecular Orbitals consist of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which play an important role in the chemical reactivity of the molecule. The location of the HOMO determines the ability of electron donation while the LUMO dictates the ability to accept an electron. The molecular orbital calculations were also performed for all adsorbents at the same level of theory. The electronic properties of the substrates were calculated using Multiwfn 3.3.9 [73]. Additionally, electron density difference [74] (EDD, \( \Delta \rho \)) for the adsorbed structures are also studied to understand the interaction between the substrate and adsorbate. It is defined as:

\[ \Delta \rho = \rho_C - \rho_A - \rho_S \] (4)

where \( \rho_C, \rho_A, \) and \( \rho_S \) are the electron charge densities of the adsorbed species on the substrate system, the free adsorbate, and the pristine graphene flake, respectively. In the EDD maps, the charge depletion and charge accumulation areas denoting as blue and red colors, respectively.

The thermodynamic properties of the reactions are calculated from the frequency calculations according to the following equations [75]:

\[ \Delta H = \sum (\varepsilon_0 + H_{\text{corr}}) \text{ products} - \sum (\varepsilon_0 + H_{\text{corr}}) \text{ reactants} \] (5)

\[ \Delta G = \sum (\varepsilon_0 + G_{\text{corr}}) \text{ products} - \sum (\varepsilon_0 + G_{\text{corr}}) \text{ reactants} \] (6)

\[ H_{\text{corr}} = E_{\text{tot}} + k_B T \] (7)

\[ G_{\text{corr}} = H_{\text{corr}} - T S_{\text{tot}} \] (8)

where \( \varepsilon_0 \) is the total electronic energy at \( T = 0 \) K and \( k_B \) is the Boltzmann constant. The internal thermal energy \( E_{\text{tot}} \) is obtained from translational \( (E_{\text{tr}}) \), rotational \( (E_{\text{rot}}) \), vibrational \( (E_{\text{vib}}) \), and electronic \( (E_{\text{el}}) \) energies, and \( S_{\text{tot}}, S_{\text{tr}}, S_{\text{rot}}, S_{\text{vib}}, S_{\text{el}} \) are the corresponding entropies. \( H_{\text{corr}} \) and \( G_{\text{corr}} \) refer to thermal corrections which should be added to \( \varepsilon_0 \) to obtain the enthalpy and Gibbs free energy, respectively. For all the reactions, the transition state (TS) located by analytical methods as defined in the default Gaussian 16 method. Vibrational frequency calculations performed for all the TS structures at the DFT-optimized geometries with the default Gaussian 16 algorithm having only one negative imaginary frequency. To characterize the nature of all transition state structures, the existence of the corresponding imaginary frequency along with intrinsic reaction coordinate (IRC) calculations was considered [76]. Reaction paths were followed for the ground state spin of the states for each reaction.

According to the NIST database, the oxidation of methane to methanol \( 2\text{CH}_4(g) + \text{O}_2(g) \rightarrow \) \( 2\text{CH}_3\text{OH}(g) \) is a thermodynamically favourable reaction, \( \Delta G_{298.15} = -2.32 \text{ eV} \) and \( \Delta H_{298.15} = -2.63 \text{ eV} \). The calculated thermodynamic results for this reaction using Gaussian16 also declare that it is a thermodynamically feasible reaction. \( \Delta G_{298.15} = -1.87 \text{ eV} \) and \( \Delta H_{298.15} = -2.20 \text{ eV} \), in order to diminish or reduce the existed difference between the calculated thermodynamic values by Gaussian and those we obtained from the NIST database, we investigated the thermodynamic properties of the reaction by applying various functional and basis sets. The obtained results are provided in Table S3. The best agreement with the NIST database data was found using the CBS-QB3 functional [77] with 6-311G** basis set, viz. \( \Delta G = -2.35 \text{ eV} \) and \( \Delta H = -2.66 \text{ eV} \), which is indeed very close to the database values.
3 Results and discussion

This work aims to investigate the catalytic activity of Co-SV-G, Co-dV-G, CoN$_3$-G, and CoN$_4$-G toward methane activation and conversion to methanol using N$_2$O and O$_2$ as an oxidant. In most cases, the methane oxidation reaction starts with C-H bond cleavage that is a challenge in heterogeneous catalysis, because of its great thermodynamic stability (435 kJ mol$^{-1}$) and strong tetrahedral bonds. Therefore, upon C-H bond cleavage, two different pathways with different intermediates can be identified for the H abstraction by oxygen: a radical and a non-radical process [78]. The possibility of the reaction to proceed via the Eley-Rideal (ER) and Langmuir-Hinshelwood (LH) mechanism is also investigated in detail.

3.1 Geometric and electronic properties of the substrates

Since the stability of doped graphene determines its usage in catalysis applications, an evaluation of the surface stability is required. The studied substrates are produced in three steps: (I) the creation of single vacancy graphene flake (SV-G) by removing one carbon atom (see Figure 1, labeled X)), and divacancy graphene flake (dV-G) by removing two carbon atoms, (labeled C3 and X)); (II) the replacement of three and four undercoordinated C atoms with N atoms to form the defective N$_3$-G and N$_4$-G, respectively; (III) incorporation of Co atom in the center of the SV-G, dV-G, N$_3$-G and N$_4$-G making Co-SV-G, Co-dV-G, CoN$_3$-G, and CoN$_4$-G, respectively. These substitutions were employed in similar theoretical studies [79-81]. Figure 1 shows the optimized configurations of each substrate. NBO charge analysis (q) of each substrate along with the calculated binding energy of Co atom into the vacancy sites, $E_{bind}$, energy gap ($E_g$), and the corresponding thermodynamic properties are listed in Table 1.

For pure graphene, we find a C-C bond length of 1.42 Å that is similar to the experimental value [82]. Working with a graphene flake, a bandgap is expected. We calculate an energy gap of $E_g = 2.66$ eV, which is used as a reference for comparing the geometry and electronic properties of doped configurations (see Table 1). These values are in good agreement with other theoretical and experimental studies [83-85]. In the graphene flake, a single carbon atom adsorbs with an adsorption energy of -7.23 eV into the single vacancy of graphene. One can see that in the SV-G, a five and nine-member ring (5-MR and 9-MR) are produced with C1-C2, C1-C3, and C2-C3 bond lengths of 1.76, 2.77, and 2.81 Å, respectively. By introducing a single Co atom into the SV-G configuration, the Co atom covalently binds to three surrounding carbon atoms of the vacancy site with equal Co-C bond lengths of 1.76 Å. These values are also in good agreement with previous studies (Co-C=1.79-1.90 Å) [86, 87]. Due to the larger atomic radius, the Co atom is pushed outward from the graphene plane in a tetrahedral-like configuration with respect to the neighbouring C atoms (see Figure 1), at a height of 1.29 Å above the graphene flake. This result is also in good agreement with other doped metal atoms into the graphene sheet [88, 89]. The calculated binding energy of the single Co atom into the SV-G is $E_{bind} = -4.52$ eV. To compare charge distributions in the Co-G structures, NBO charges are calculated for all obtained structures. In Co-G, a small charge of +0.25 e is transferred from the Co atom to the surrounding carbon atoms of the vacancy site making the neighbouring carbon atoms negatively charged (-0.30 e) with Co-C bonds of 1.78 Å.
In the dV-G, first, a 5-8-5 defect [90] is produced and then by introducing the Co atom into the vacancy site, Co-dV-G forms (see Figure 1) with low binding energy of $E_{\text{bind}} = -1.90$ eV. According to the NBO charge analysis, a charge of +0.65 e is transferred from the Co atom to the surrounding C atoms of the vacancy site leading to negatively charged C atoms (-0.85 e) with Co-C bond lengths of Co-C = 1.96 Å. If three or four surrounding C atoms of the SV-G or dV-G are substituted by three or four nitrogen atoms, a defective pyridinic $N_3$-G or $N_4$-G is created, respectively. According to the previous studies, the presence of pyridinic-N atoms around any defect sites might affect the electronic structure of graphene [89, 91]. The substitution of the vacancy C atoms by N atoms can considerably reduce the formation energy of the mono- or di-vacancy graphene sheet. The reason may refer to the vanishing of the existed dangling bonds in these systems. So, it is clear that the N embedded graphene structures are the dominant configurations. According to the NBO charge analysis, each nitrogen atom in $N_3$-G and $N_4$-G is negatively charged to -0.5 e showing that these negative sites are active enough to trap the Co atom making the CoN$_3$-G and CoN$_4$-G.

Table 1. The calculated NBO analysis (+ and – signs refer to the electron donation and acceptance), binding energy ($E_{\text{bond}}$), formation energy ($E_f$), energy gap ($E_g$), change of enthalpy ($\Delta H_{298}$), and change of Gibbs free energy ($\Delta G_{298}$) of pure graphene flake, Co-SV-G, Co-dV-G, CoN$_3$-G and CoN$_4$-G.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$q_{(Co/C \text{ or } N)}$</th>
<th>$E_{\text{bind}}$ (eV)</th>
<th>$E_f$ (eV)</th>
<th>$E_g$ (eV)</th>
<th>$\Delta H_{298}$ (eV)</th>
<th>$\Delta G_{298}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphene</td>
<td>+0.04</td>
<td>-7.23</td>
<td>-</td>
<td>2.66</td>
<td>-7.19</td>
<td>-7.23</td>
</tr>
<tr>
<td>Co-SV-G</td>
<td>+0.25 (-0.30)</td>
<td>-4.52</td>
<td>2.71</td>
<td>3.06</td>
<td>-4.47</td>
<td>-4.18</td>
</tr>
<tr>
<td>Co-dV-G</td>
<td>+0.65 (-0.85)</td>
<td>-1.90</td>
<td>3.31</td>
<td>1.78</td>
<td>-1.91</td>
<td>-1.65</td>
</tr>
<tr>
<td>CoN$_3$-G</td>
<td>+0.46 (-1.86)</td>
<td>-4.58</td>
<td>-0.95</td>
<td>2.48</td>
<td>-4.53</td>
<td>-4.21</td>
</tr>
<tr>
<td>CoN$_4$-G</td>
<td>+0.74 (-2.80)</td>
<td>-7.81</td>
<td>-3.47</td>
<td>3.20</td>
<td>-7.67</td>
<td>-7.28</td>
</tr>
</tbody>
</table>

In CoN$_3$-G, the Co atom and the surrounding three nitrogen atoms of the vacancy site are positively...
(0.46 e) and negatively (-1.86 e) charged, respectively. Therefore, the CoN₃ moiety is negatively charged by -1.4 e with the formation energy of Eₛ = -0.95 eV. Upon adsorption of a single Co atom into the defective N₂-G, the average bond length of Co-N is increased considerably to 2.02 Å, pushing the Co atom of the basal plane by 1.36 Å from the graphene flake surface. The calculated binding energy of Co on the N₁-G is Eₜₕₐₜ = -4.58 eV, which is higher than that of PdN₃-G (Eₜₕₐₜ = -3.19 eV) [92] and is quite close to that reported by Zhang et al. (Eₜₕₐₜ = -4.84 eV) [93].

In the defective N₄-G, Co-N₂/N₄ and Co-N₁/N₃ bond lengths are equal to 1.92 Å and 1.94 Å, respectively, in agreement with Orellana et al. study (Co-N =1.90 Å) [81]. In contrast to CoN₃-G, the Co adatom adsorbs in the pyridinic N₄-G and lies in the plane format by nitrogen atoms with the formation energy of Eₛ = -3.47 eV. The higher formation energy of CoN₄-G than CoN₃-G indicates that the Co atom can be more easily interact with the nitrogen atoms of the di-vacancy site than those in the single vacancy site. It adsorbs strongly into the N₄-G site with Eₜₕₐₜ = -7.81 eV. The high adsorption energy can be related to the additional valence electrons available from the substitutional N atoms that stabilize the unpaired electron of the coordinated C atom of the graphene flake. This results in a higher charge transfer (≈ 0.74 e) from the Co atom to the four nearest N atoms of the surface, which are all negatively charged by ≈ -2.8 e. Also, it is consistent with the high electronegativity of nitrogen atoms compared with that of carbon and Co atoms, such that the Co atom binds stronger with its neighbouring N and C atoms than those in CoN₃-G and Co-G, respectively.

The EDD of three stable substrates is shown in Figure S1 in the Supporting information. In Co-G, the charge is mostly accumulating on the surrounding C atoms while we found that the transferred electrons from Co atom and three neighbouring N atoms induce the charge redistribution at their interfaces. Also, as shown in Figure S1, the charges mainly accumulate on the N atoms illustrating that more electrons (>1.0 e) are transferred from Co dopant to the neighbouring N atoms leading to the enhancement of their interaction. Similar to CoN₃-G, in CoN₄-G the transferred charge from the Co atom to the four adjacent N atoms is high, and electrons dominantly accumulate on N atoms and around the Co-N bonds. These results indicate that the N₄-G could efficiently stabilize the embedded Co atom, which is stable enough to be used in the catalytic reactions.

Furthermore, by inspecting the electronic states of CoN₃-G and CoN₄-G near the Fermi level we can better understand the reason for having such large adsorption energies. One can see from Figure S2 that there are strong electron coupling between the 3d orbitals of Co atom and the 2p orbitals of N atoms around the Fermi level confirming the existence of covalent Co-N bond in the studied substrates. By doping Co atom into the vacancy site, Co atom pulls down the unoccupied localized anti-bonding states of N atoms near the Fermi level indicating that when Co atom adsorbs over the vacancy sites, those states are partially occupied. In addition, the incorporation of N atoms shifts the bandgap above the Fermi level gradually confirming the enhancement of electron (donor) concentration states. Similar electronic results are given by Li et al. [94] reporting that the pyridinic nitrogen act as an active catalyst toward ORR [95].

Finally, we evaluate the diffusion of Co atom to its nearest vacancy site in CoN₃-G and CoN₄-G. The stable configuration of CoN₃-G and CoN₄-G is chosen as the initial state (IS). The energy profile and the related stationary structures are depicted in Figure S3. Very high diffusion barriers required to diffuse the Co atom to the nearest hollow sites of the surface in both substrates. This confirms the Co atom is stable enough at the defective N₃-G and N₄-G sites that prevents the metal clustering problem. These results are in agreement with the experimental investigations indicating that the bonded Co atom cannot be easily migrated to other hollow sites of the nitrogen-doped graphene surface through the leaching process [96].
3.2 Adsorption of gas reactants on CoN$_3$-G and CoN$_4$-G

The accumulated charge on the active Co site increases the interaction of the substrate with the gas species by increasing the polarization of the gas molecule. This was also considered in recent studies for hydrogen storage purposes [97]. There are three different active sites on each substrate, Co, N, and C. Depending on which active site the gas reactant (CH$_4$, O$_2$, N$_2$O) adsorbs on, different adsorption configurations will be obtained. It should be noted that for each adsorbate various adsorption sites and different adsorption patterns (including side-on and end-on) are considered. Similar to earlier reports we found that each species tends to directly interact with the metal atom at the center of the vacancy site [81, 98, 99]. The corresponding geometric structures of adsorbed gas reactants on CoN$_3$-G, and CoN$_4$-G along with their EDD maps are shown in Figure 2. Additionally, the calculated E$_{ads}$, NBO charge analysis, and thermodynamic properties of the species are reported in Table 2.

Various spin multiplicities were considered for each configuration, i.e., singlet, doublet, triplet, and quadruplet. Our results reveal that as a function of progress of the reaction, the spin multiplicity changes either from singlet to triplet or from doublet to quadruplet, and vice versa. The dominant spin multiplicity of some species like OH, CH$_3$, CH$_2$, CH, O, O$_2$, and CH$_4$ on Co-N$_x$G and CoN$_x$-G is different. Therefore, the energetically more stable configurations are chosen for our calculations. In addition, the adsorption behaviour of CoN$_3$-G and CoN$_4$-G toward adsorption of the gas reactants and intermediates in different spin multiplicities were also been tested. For instance, investigating the O$_2$ dissociation on CoN$_3$-G considering singlet and triplet states, we chose the triplet multiplicity for the dissociation pathway not only because the configurations are energetically more stable but also because the calculated activation barrier is lower in the triplet state (2.76 eV) than in the singlet state (3.02 eV). A similar comparison was made for other configurations. Here, the energetically more favourable structures are reported.

One can see from Figure 2 that in complexes A and D, methane molecule adsorbs physically over the Co atom, at a distance of 2.46 Å and 3.00 Å and with an adsorption energy of E$_{ads}$ = -0.38 eV and E$_{ads}$ = -0.21 eV, respectively. The corresponding calculated charge transfer from methane to the surface in complexes A and D is 0.14 e and 0.07 e, respectively. These weak interactions are also apparent from their EDD map, showing almost no charge accumulation around the Co-C bond in the two complexes. Interestingly, adsorption of methane on CoN$_3$-G is exothermic while its adsorption on CoN$_4$-G is not spontaneous at room temperature (see Table 2).

![Figure 2](image-url)

**Figure 2.** The most plausible geometric structures of the gas reactants on CoN$_3$-G and CoN$_4$-G along with the corresponding EDD map. All distances are in Å.

In contrast to methane, the adsorption of O$_2$ on CoN$_3$-G is quite strong. In both complexes, the O$_2$
molecule tends to adopt a parallel position with the surface on the Co atom. In complex B, O\textsubscript{2} adsorbs on the Co atom makes a V shape with two Co-O bond length of 1.80 Å and large adsorption energy of E\textsubscript{ads} = -1.24 eV, which is lower than that on Pt\textsubscript{N\textsubscript{3}}-G (-1.89 eV) [100]. A charge of -0.46 e is transferred from the CoN\textsubscript{3}-G to the adsorbed O\textsubscript{2} molecule which makes the Co atom more positive (+0.71 e), leading to the stronger adsorption of O\textsubscript{2} on the CoN\textsubscript{3}-G surface and significant elongation of the O-O bond (1.40 Å). The EDD map of complex B correspondingly illustrates that the charge accumulation regions are mostly localized between the Co-O and O-O bonds. Furthermore, the higher reaction enthalpy for the formation of complex B shows that this substrate is more activated toward adsorption of O\textsubscript{2} molecule, ΔH\textsubscript{298.15} = -1.22 eV, and ΔG\textsubscript{298.15} = -0.72 eV.

Table 2. The calculated adsorption energy (E\textsubscript{ads}), NBO charge analysis (q) (+ and – signs refer to the electron donation and acceptance), change of enthalpy (ΔH\textsubscript{298.15}), and change of Gibbs free energy (ΔG\textsubscript{298.15}), of the gas reactants on CoN\textsubscript{3}-G and CoN\textsubscript{4}-G. All energies are in eV.

<table>
<thead>
<tr>
<th>Complex</th>
<th>E\textsubscript{ads} (eV)</th>
<th>q\textsubscript{Co/ads} (e)</th>
<th>ΔH\textsubscript{298.15} (eV)</th>
<th>ΔG\textsubscript{298.15} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoN\textsubscript{3}-G</td>
<td>-</td>
<td>+0.46</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>-0.38</td>
<td>+0.33/+0.14</td>
<td>-0.34</td>
<td>-0.02</td>
</tr>
<tr>
<td>B</td>
<td>-1.24</td>
<td>+0.71/-0.46</td>
<td>-1.22</td>
<td>-0.72</td>
</tr>
<tr>
<td>C</td>
<td>-0.02</td>
<td>+0.72/-0.51</td>
<td>0.01</td>
<td>0.36</td>
</tr>
<tr>
<td>O-CoN\textsubscript{3}-G</td>
<td>-2.93</td>
<td>+0.80/-0.52</td>
<td>-2.86</td>
<td>-2.48</td>
</tr>
<tr>
<td>CoN\textsubscript{4}-G</td>
<td>-</td>
<td>+0.74</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>-0.21</td>
<td>+0.68/+0.07</td>
<td>-0.16</td>
<td>0.11</td>
</tr>
<tr>
<td>E</td>
<td>-0.24</td>
<td>+0.72/+0.04</td>
<td>-0.20</td>
<td>0.16</td>
</tr>
</tbody>
</table>

The O\textsubscript{2} molecule adopts an end-on configuration on CoN\textsubscript{3}-G at a distance of O-Co = 1.95 Å. it adsorbs weakly on the CoN\textsubscript{4}-G surface with a low adsorption energy E\textsubscript{ads} = -0.24 eV, which can be due to the stronger binding energy of Co-N (-7.81 eV) (see Table 1). The obtained adsorption energy value is somewhat lower than the value reported by Feng et al. (E\textsubscript{ads} = -0.85 eV) [101]. FeN\textsubscript{4}-G (E\textsubscript{ads} = -0.98 eV) and MnN\textsubscript{4}-G (E\textsubscript{ads} = -0.35 eV) [102, 103]. Consistent with the weak interaction, a negligible charge of +0.04 e is transferred from the surface to the adsorbed O\textsubscript{2} molecule. In the EDD map, the blue color areas around the Co-O bond confirm the weak interaction of O\textsubscript{2} with the surface. However, the formation of complex E is exothermic ΔH\textsubscript{298.15} = -0.20 eV and endergonic ΔG\textsubscript{298.15} = 0.16 eV.

Since the interaction of O\textsubscript{2} with CoN\textsubscript{3}-G is stronger than that on CoN\textsubscript{4}-G, we also evaluated the dissociation of O\textsubscript{2} on CoN\textsubscript{3}-G (to confirm the stability of the adsorbed structure toward oxygen dissociation. To find the energy profile of the O\textsubscript{2} decomposition, we started with the most stable adsorption configuration of O\textsubscript{2} on CoN\textsubscript{3}-G (complex B) as IS and shown in Figure S4. Passing via the TS structure, the final state (FS) is obtained in which two individual O atoms are dissociatively adsorbed on Co and C atom of the surface. The formed O-Co and O-C bond lengths are 1.62 Å and 1.37 Å, respectively. The calculated activation barrier for the O\textsubscript{2} dissociation on CoN\textsubscript{3}-G is calculated to be E\textsubscript{act} = 2.76 eV and the reaction is endothermic, ΔH\textsubscript{298.15} = 1.23 eV, and endergonic ΔG\textsubscript{298.15} = 1.20 eV. The large decomposition barrier of O\textsubscript{2} on CoN\textsubscript{3}-G confirms the stability of the adsorbed O\textsubscript{2} molecule over the surface and its low tendency to dissociate over the CoN\textsubscript{3}-G surface.

According to above discussions and previous investigations [100, 104], we conclude that amongst the studied substrates, CoN\textsubscript{3}-G is more active toward adsorption of gas reactants, especially O\textsubscript{2} molecule, and therefore is more favourable for methane conversion reaction which is in good agreement with Kattel et al. work [29]. The higher adsorption energy of O\textsubscript{2} molecule than methane reveals that the reactive Co sites will be dominantly covered by the O\textsubscript{2} when exposed to a CH\textsubscript{4}/O\textsubscript{2} mixture as the reaction gas. However, the co-adsorption of CH\textsubscript{4} and O\textsubscript{2} on CoN\textsubscript{3}-G (E\textsubscript{ads} = -1.66 eV) is
stronger than the sum of the individual adsorption of CH\textsubscript{4} or O\textsubscript{2} on CoN\textsubscript{3}-G (see Table 2). Therefore, we propose that all the reaction pathways start with the co-adsorption configuration of CH\textsubscript{4} and O\textsubscript{2} on the surface.

Recent theoretical studies [105-107] reported that the N\textsubscript{2}O molecule attaches to metal-embedded nanostructures via different configurations. It may adsorb via a linear parallel position with the surface, a [3+2]- or [2+2]-cycloaddition configuration. Here, on CoN\textsubscript{3}-G, the N\textsubscript{2}O molecule adsorbs weakly, E\textsubscript{ads} = -0.02 eV, via its O and N atoms with the Co atom of the surface while the N–N–O angle decreases from 180° in the gas phase to 123.37° in the adsorbed form (configuration C, Figure 2). Interestingly, upon the adsorption of N\textsubscript{2}O on the surface, it immediately dissociates to N\textsubscript{2}(g) and atomic O\textsuperscript{*} molecule above active Co site (see Figure S5). The reaction is barrierless and thermodynamically favourable at room temperature (ΔH\textsubscript{298.15} = -2.35 eV, ΔG\textsubscript{298.15} = -2.43 eV). It is shown that in the final state the atomic O\textsuperscript{*} adsorbs chemically on Co atom with Co-O bond length of 1.81 Å and E\textsubscript{ads} = -1.49 eV.

We also studied the effect of the substrate size on the adsorption behaviour of the gas species on CoN\textsubscript{3}-G. To achieve this, a larger graphene flake with 110 carbon and 28 hydrogen atoms (with about 1.5 times larger surface area) is considered as pure graphene flake. All the configurations are optimized using different spin multiplicities, singlet, doublet, triplet, and quadruplet. Amongst those configurations, the energetically more favourable configurations have been chosen as the main structures. The calculated adsorption energy of the Co atom into the pyridinic-N\textsubscript{3} graphene flake along with the adsorption energies of the gas reactants on CoN\textsubscript{3}-G are listed in Table S4.

Our results show that by increasing the size of the graphene flake the geometry of the structures do not change while the adsorption energy of O\textsubscript{2}, CH\textsubscript{4}, and N\textsubscript{2}O increases by almost 50%, 3.3%, and 36%, respectively. Nevertheless, we also find that in spite of this increase in adsorption energy, increasing the size of the graphene flake has no significant effect on the general concepts of the used catalyst toward the gas reactants. Indeed, we still find that the O\textsubscript{2} molecule pre-adsorbs on the active Co site of the surface while methane physisorbs on the CoN\textsubscript{3}-G flake. Moreover, the dissociation of N\textsubscript{2}O molecule to N\textsubscript{2} + O\textsuperscript{*} proceeds via a negligible barrier energy proposing that still the N\textsubscript{2}O molecule is the more favourable oxidant for methane oxidation. Since increasing the size of the graphene-flake did not change either the overall adsorption behaviour of the catalyst or even their corresponding charge transfer, to avoid expensive calculations, we continued using the smaller-sized graphene-flake.

### 3.3 Conversion of methane to methanol on monolayer CoN\textsubscript{3}-G

The energy landscapes for CH\textsubscript{x} (x=0-4) adsorption and CH\textsubscript{x} (x=1-4) dehydrogenation over CoN\textsubscript{3}-G along with the most probable C-C coupling reaction are explained and shown in the Supporting information. There are two different mechanisms for C-H bond cleavage, a surface-stabilized or a radical-like mechanism [78, 108]. In the first mechanism, the carbon atom of methane molecule partially interacts with the catalyst, while in the radical-like mechanism there is no binding or interaction with the catalyst. It is known that the radical-like pathway is the more probable route for single-atom catalysts [109] due to the lower concentrations of the active sites on these substrates making them promising candidates for direct methane to methanol oxidation [110]. We propose two different pathways for the direct conversion of CH\textsubscript{4} to CH\textsubscript{3}OH on CoN\textsubscript{3}-G using N\textsubscript{2}O and O\textsubscript{2} as an oxidant. N\textsubscript{2}O acts as an O-donor compound that provides atomic oxygen to oxidize methane to methanol. Depending on the oxidation agent, the formed intermediates, and subsequently, the reaction pathways are different. The formed intermediates are a combination of "OH, CH\textsuperscript{3}O*, *OOH, and CH\textsubscript{3}O". The schematic reaction mechanisms of oxidation routes are shown in Scheme 1. Most of the reactions
proceed via the LH mechanism.

Scheme 1. Proposed reaction pathways on CoN₃-G. The values in parentheses refer to the energy barriers and enthalpy of the reaction. All the energy values are in eV.

3.3.1 Methane to methanol oxidation by N₂O

Upon desorption of N₂, the remained atomic oxygen reacts with methane to form methanol. This pathway goes through the formation of CH₃⁺ and OH⁻ intermediate species. The related stationary structures along with the preferential potential energy pathways are shown in Figure 3. The calculated reaction heats and the corresponding barriers are summarized in Table 3.

In pathway I, the oxidation reaction starts with co-adsorption of O⁻ and CH₄ named as IS-1. Hydrogen abstraction with oxygen occurs passing via a low energy barrier of $E_{act} = 0.83$ eV results in the formation of CH₃⁺ and OH⁻ intermediate species on top of the Co site (MS-1) that is in good agreement with Yuan et al. work ($E_{act} = 0.7$ eV) [106]. Then, the combination of CH₃⁺ and OH⁻ species produces the methanol molecule on CoN₃-G surface. The required energy barrier of this reaction is $E_{act} = 0.91$ eV. According to the thermodynamic results, all the reactions are exothermic and exergonic (see Table 3). Due to the higher activation energy of the reaction MS-1→P-1, we propose it to be the rate-limiting step.
Figure 3. The optimized stationary points for the methane oxidation on CoN$_3$-G along with the corresponding energy profile of methane conversion by N$_2$O. All distances are in Å.

Table 3. The calculated forward and backward energy barrier ($E_{\text{act-f}}$, $E_{\text{act-b}}$), change of enthalpy ($\Delta H_{298.15}$), and change of Gibbs free energy ($\Delta G_{298.15}$) of the proposed pathway I for methane oxidation reaction on CoN$_3$-G.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_{\text{act-f}}$ (eV)</th>
<th>$E_{\text{act-b}}$ (eV)</th>
<th>$\Delta H_{298}$ (eV)</th>
<th>$\Delta G_{298}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O(g) $\rightarrow$ N$_2$(g) + O$^*$</td>
<td>0.00</td>
<td>2.27</td>
<td>-2.35</td>
<td>-2.43</td>
</tr>
<tr>
<td>CH$_4$(g) + O$^<em>$ $\rightarrow$CH$_3^</em>$ + OH$^*$</td>
<td>0.83</td>
<td>1.15</td>
<td>-0.32</td>
<td>-0.30</td>
</tr>
<tr>
<td>CH$_3^<em>$ + OH$^</em>$ $\rightarrow$ CH$_3$OH(g) + *</td>
<td>0.91</td>
<td>1.19</td>
<td>-0.28</td>
<td>-0.28</td>
</tr>
</tbody>
</table>

3.3.2 Methane to methanol oxidation by O$_2$

The proposed pathway II starts with the coadsorption of O$_2$ and CH$_4$ at a distance of H-O$_2$ = 2.40 Å above the surface (Figure 4, IS-2). Interestingly, we found that the C-H and Co-O cleavage of methane and adsorbed atomic O$^*$ has the highest barrier energies of $E_{\text{act}}$ = 1.73 eV and $E_{\text{act}}$ = 2.19 eV, respectively, which inhibited the formation of methanol. In both first and second reaction of methane with oxygen, breaking of the C–H bond occurs concurrently with the formation of an O-H bond and Co-C bond on CoN$_3$-G, and a further elongation of the O–O bond to 1.97 Å. The formation of the first CH$_3$OH occurs with the introduction of the second methane to the system through reaction IS-3$\rightarrow$P-2. Although the activation of the second CH$_4$ requires $\sim$0.46 eV more energy, it is more exergonic (see Table 4). The second CH$_3$OH is formed upon the association of the CH$_3^*$ and OH$^*$ species with a reasonable energy barrier of 0.91 eV. Finally, upon the desorption of the second CH$_3$OH, $E_{\text{des}} = 0.57$ eV, the catalytic cycle is closed. As CH$_4$ is only physisorbed at Co active site and then reacts with preadsorbed O$_2$, the methane conversion mechanism in all the reactions can be described as an ER mechanism, except the reaction MS-1$\rightarrow$ P-1 that proceeds via the LH mechanism. The rate-limiting step is the formation of P-2 which is related to the second C-H and Co-O bond cleavage.
We also investigated the other possibilities of methanol formation on CoN$_3$-G by the formation of other intermediates. We found two other possible pathways (labeled as pathways II(a) and II(b)) that goes via the formation and recombination of CH$_3^*$, O*, OH*, and CH$_3$O* species on CoN$_3$-G. The related potential energy profile is shown in Figure S8. The calculated activation energies and thermodynamic values are listed in Table 4. One can see from Figure S8 that in Pathway II(a) and II(b) the reaction MS-2 $\rightarrow$ MS-3 (formation of CH$_3$O* and OH*) and P-2 $\rightarrow$ P-3 requires high energy barrier of $E_{\text{act}}$ = 2.27 eV and $E_{\text{act}}$ = 2.59 eV, respectively. Therefore, we estimate that the possibility of methane conversion to methanol via pathways II(a) and II(b) is very low.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>E$_{\text{act}}$ (eV)</th>
<th>$\Delta H_{298.15}$ (eV)</th>
<th>$\Delta G_{298.15}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pathway II</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_2$(g) + * $\rightarrow$ 2O*</td>
<td>0.00</td>
<td>-1.22</td>
<td>-0.72</td>
</tr>
<tr>
<td>CH$_4$(g) + 2O* $\rightarrow$ CH$_3^*$ + *OOH</td>
<td>1.73</td>
<td>1.23</td>
<td>1.38</td>
</tr>
<tr>
<td>CH$_4$(g) + CH$_3^*$ + <em>OOH $\rightarrow$ CH$_3$OH(g) + CH$_3^</em>$ + *OH</td>
<td>2.19</td>
<td>-2.63</td>
<td>-2.52</td>
</tr>
<tr>
<td>CH$_3^*$ + *OH $\rightarrow$ CH$_3$OH(g) + *</td>
<td>0.91</td>
<td>-0.28</td>
<td>-0.28</td>
</tr>
<tr>
<td><strong>Pathways II(a) and II(b)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3^*$ + <em>OOH $\rightarrow$ CH$_3$O</em> + *OH</td>
<td>2.27</td>
<td>-2.88</td>
<td>-2.97</td>
</tr>
<tr>
<td>CH$_4$(g) + CH$_3$O* + <em>OH $\rightarrow$ CH$_3$OH(g) + CH$_3^</em>$ + *OH</td>
<td>1.61</td>
<td>-0.20</td>
<td>-0.20</td>
</tr>
<tr>
<td>CH$_3$OH(g) + CH$_3^*$ + *OH $\rightarrow$ 2CH$_3$OH(g) + *</td>
<td>2.59</td>
<td>-0.54</td>
<td>-0.47</td>
</tr>
</tbody>
</table>

In fact, to produce methanol, the most favourable pathway is pathway I, in which methane oxidation reaction is catalyzed by atomic oxygen, which is donated to the system by dissociative adsorption of N$_2$O over CoN$_3$-G. It proceeds via the LH mechanism and all the reactions are thermodynamically favourable. Therefore, we propose that CoN$_3$-G can actively convert methane to methanol using N$_2$O as an oxidant agent thanks to the lower activation barriers.

One of the greatest challenges in the catalysts which are used for methane oxidation to methanol is that they can even better cleave the O-H bond of the formed methanol which leads to its overoxidation to CO$_2$ and H$_2$O. Thus, we tested the activity of CoN$_3$-G toward the over-oxidation of methanol. Since
the investigation of the complete over-oxidation process is not the main focus of this paper, only the primary reactions of methanol over-oxidation to CO$_2$ and H$_2$O on CoN$_3$-G were calculated. Our results reveal that methanol oxidation goes through two different routes: (i) O-H bond cleavage, reaction IS-5→MS-4 (ii) C-H bond cleavage IS-5→MS-5 (see Figure 5). We found that the over-oxidation of methanol via reaction pathway IS-5→MS-4 is more probable to proceed than reaction IS-5→MS-5. In IS-5 the methanol molecule adsorbs on Co atom of CoN$_3$-G with adsorption energy of $E_{\text{ads}} = -1.77$ eV. The H abstraction by introduced atomic oxygen to the system occurs via the cleavage of the O-H bond with a low energy barrier of $E_{\text{act}} = 0.23$ eV. This reaction is exothermic and exergonic ($\Delta H_{298.15} = -0.25$ eV, $\Delta G_{298.15} = -0.23$ eV). In the next step, H is abstracted from the C atom via TS-9 to form H$_2$O while H$_2$CO adsorbs over CoN$_3$-G with Co-O bond length of 1.31 Å (see Figure 5, P-4) and energy barrier of $E_{\text{act}} = 0.56$ eV.

In pathway (ii), the C-H bond cleavage requires overcoming a higher energy barrier, $E_{\text{act}} = 1.29$ eV, than that of O-H cleavage. In addition, the corresponding reaction is not thermodynamically favourable at ambient conditions ($\Delta H_{298.15} = 0.57$ eV, $\Delta G_{298.15} = 0.51$ eV). These initial calculations for the probability of methanol over-oxidation indicate that although CoN$_3$-G could better catalyze methane conversion to methanol, it might also oxidize the produced methanol molecule to CO$_2$ and H$_2$O or other intermediates with low activation barriers. In practice, this can affect the conversion percentage of methane to methanol.

![Figure 5. The optimized stationary points for methanol over-oxidation on CoN$_3$-G. All distances are in Å](image)

4 Conclusions

In summary, the geometric stability and catalytic activity of Co-SV-G, Co-dV-G, CoN$_3$-G, and CoN$_4$-G toward adsorption of gas reactants are studied in detail employing DFT calculations. Studying the geometric, electronic, and thermodynamic properties of all optimized structures showed that amongst other modified graphene flakes, CoN$_3$-G and CoN$_4$-G are energetically more stable than other substrates. Investigating the adsorption behavior of CoN$_3$-G and CoN$_4$-G toward the gas reactants indicated that CoN$_3$-G has a higher tendency for the adsorption of methane and oxygen. Therefore, we chose CoN$_3$-G as for methane-to-methanol oxidation. Two powerful oxidants are used for catalyzing methane oxidation, viz. O$_2$ and N$_2$O. N$_2$O adsorbs dissociatively on CoN$_3$-G providing atomic oxygen for methane oxidation. Oxidation of methane using N$_2$O proceeds via two steps on CoN$_3$-G with considerably lower energy barriers while using O$_2$ as oxidant proceeds through a pathway with higher activation barriers. All the C-H bond cleavage reactions proceed through the ER mechanism and
followed by the LH mechanism.

One of the greatest challenges in methane oxidation processes is the over-oxidation of methanol to CO₂ and H₂O or other intermediates. According to our calculations, the dominant pathway for methanol over-oxidation on CoN₃-G occurs through two main routes, viz. the O-H bond cleavage route with low energy barriers of E_{act} = 0.23 eV and E_{act} = 0.56 eV, and the C-H bond cleavage route with a higher barrier of E_{act} = 1.29 eV. Thus, we propose that CoN₃-G might be a good catalyst for methane conversion but it can also catalyze the oxidation of methanol to CO₂ and H₂O or other intermediates due to the required low activation barriers. In practice, this can affect the conversion percentage of methane to methanol.

Investigating the adsorption (CHₓ, x=0-4) and dehydrogenation (CHₓ, x=1-4) process of methane on CoN₃-G indicated that the adsorption energy of CH₄, CH₃, CH₂, CH, and C on CoN₃-G increases by reducing the number of hydrogen atoms. In the dehydrogenation process, all pathways start from the C-H scission (CHₓ → CHₓ₋₁ + H) and dehydrogenation of methane to methyl showed the lower energy barrier of 1.10 eV. This makes the C-C coupling of the two-methyl group to ethane easier passing via an energy barrier of 0.45 eV. To the best of our knowledge, this is the first report on the direct oxidation of methane-to-methanol on CoN₃-G using different oxidants. We believe our findings may open a new way to design such heteroatom doped graphene-based single-atom catalysts to eliminate toxic molecules, which are harmful to the environment.

Credit Author statement
Parisa Nematollahi: Investigation, calculations, methodology, analyzing the data, writing, original draft preparation, problem solving, visualization: plotting and designing the Figures, reviewing and editing.
Erik Neyts: Reviewing and editing.

5 Conflicts of interest
There are no conflicts to declare.

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