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Selective decomposition of hydrazine over metal free carbonaceous materials

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# Hydrazine selective decomposition over metal free carbonaceous materials

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## Abstract

Herein we report a combined experimental and computational investigation unravelling the hydrazine hydrate decomposition reaction on metal-free catalysts. The study focuses on commercial graphite and two different carbon nanofibers, Pyrolytically Stripped (CNF-PS) and High Heat-Treated (CNF-HHT), respectively treated at 700 and 3000 °C to increase their intrinsic defects. Raman spectroscopy demonstrated a correlation between the initial catalytic activity and the intrinsic defectiveness of the carbonaceous materials. The CNFs-PS higher defectivity ( $I_D/I_G = 1.54$ ) leads to the most performing metal-free catalyst, showing a hydrazine conversion of 94% after 6 hours of reaction and a selectivity to H<sub>2</sub> of the 89%. In addition, to unveil the role of NaOH CNFs-PS were also tested in absence of alkaline solution, showing a decreasing in the reaction rate. Density functional theory (DFT) demonstrated that the single vacancies (SV) present on the graphitic layer is the only active site promoting the hydrazine decomposition, whereas other defects such as double vacancy (DV) and Stone-Wales defects (SW) are unable to adsorb hydrazine fragments. Two symmetrical and one asymmetrical dehydrogenation pathways were found, in addition to an incomplete decomposition pathway forming N<sub>2</sub> and NH<sub>3</sub>. On the most stable hydrogen production pathway, the effect of the alkaline medium was elucidated through calculations concerning the diffusion and recombination of atomic hydrogen. Indeed, the presence of NaOH helps extracting H species without additional energetic barriers, as opposed to the calculations performed in polarizable continuum medium. Considering the initial hydrazine dissociative adsorption, the first step of the dehydrogenation pathway is the more favourable than the scission of the N-N bond, which lead to NH<sub>3</sub> as product. This first reaction step is crucial to define the reaction mechanisms and the computational results are in agreement with the experimental ones. Moreover, comparing two different hydrogen production pathways (with and without diffusion and recombination), we confirmed that the presence of sodium hydroxide in the experimental reaction environment can modify the energy gap between the two pathways, leading to an increased reaction rate and selectivity to H<sub>2</sub>.

**Keywords:** Hydrogen, Ammonia, Hydrazine decomposition, metal-free catalysts, carbon fibers.

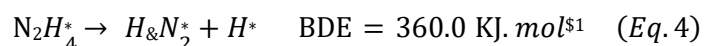
## Introduction

Green and sustainable sources of energy are essential to mitigate the environmental impact of fossil fuels and the rising energy demand. Hydrogen have been recognised as one of the most suitable alternative energy vectors due to its high energy and innocuous products upon utilisation [1]. Even though its benefits, hydrogen direct usage is inhibited by the scarcity of economically and safe hydrogen storage technologies [2]. Hence, alternative approaches to store and transport it [3–6], and materials that release hydrogen under mild condition, are urgently required [7].

Hydrazine ( $N_2H_4$ ) can be employed as hydrogen carrier because it is liquid at  $T < 114\text{ }^\circ\text{C}$  (1 atm) and can be easily transported [8–11]. In addition, it is a carbon-free fuel, hence avoiding undesired emissions, e.g.  $CO_2$ , and species damaging the catalysts as seen in CO poisoning Pt/C electrodes in proton exchange membrane fuel cells (PEMFCs) [12,13]. Currently, the  $N_2H_4$  exothermic decomposition is employed as a propellant in aerospace application, i.e., in rockets and artificial satellites [14,15].  $N_2H_4$  possesses an hydrogen content of 12.5 wt% [16] and decomposes into a mixture of ammonia, hydrogen and nitrogen in the presence of catalysts such as Shell 405 (30 wt % Ir/ $Al_2O_3$ ) [17,18].  $N_2H_4$  decomposition occurs into two different pathways [19–21]:



The first reaction (Eq. 1) represents the complete reforming pathway, where molecular hydrogen and nitrogen are produced. The second reaction (Eq. 2) is thermodynamically favoured and produces ammonia and nitrogen. The selectivity of the reaction can vary with the reaction conditions, such as pressure, temperature and catalyst presence [22–25]. In a typical hydrazine catalytic decomposition process on metal surfaces, the molecule adsorbs on catalyst surface (below marked with an asterisk) driving the N-N or the N-H cleavage. From a thermodynamic point of view, the cleavage of the N-N bond (Eq. 3) is favoured compared to the N-H bond dissociation energy (BDE, Eq. 4) [26,27]. Hence, the nature of the catalyst plays a crucial role in quenching the incomplete decomposition pathway (Eq. 2) and promoting the cleavage of N-H bond (Eq. 4).



Because of its hypergolic nature, the risk of explosion is one of the most serious problem related to handling hydrazine, especially in the presence of a metal that may catalyse its decomposition [28]. One solution can be the dilution of  $N_2H_4$  in inert gas such as argon [25] or in water, forming hydrous hydrazine ( $N_2H_4 \cdot H_2O$ ), which can be particularly important as a liquid hydrogen source [29]. Hydrous hydrazine still contains 7.9 wt % of hydrogen, avoiding all the issues related to  $H_2$  storage and transportation [7,30]. The development of a catalyst capable to exothermically react with  $N_2H_4 \cdot H_2O$  and selectively decompose it into hydrogen is key for a  $H_2$ -based economy [26,31]. In order to generate hydrogen in a controlled manner and on-demand, different supported [32–34] and unsupported metal NPs have been investigated [13,15,28]. At first, noble metals such as Ir [29,35] and Rh [10,36] performed well as reforming catalyst. Nevertheless, due to the cost and synergistic catalytic properties, Ni was introduced as second metal providing superior activity and selectivity [33,37–43].

The presence of NaOH in the hydrazine decomposition environment can favour its selective decomposition, suppressing the formation of NH<sub>3</sub>. In particular, Wang et al. have demonstrated that adding a 0.5 M solution of NaOH to unsupported Ni nanoparticles (NPs) can enhance the selectivity to H<sub>2</sub> from 64 % to 100 % [44]. In addition, Peng and co-workers have performed theoretical and experimental studies on Pt-Ni/C catalysts showing a strong dependence of the selectivity and reaction rate with the pH [45]. Indeed, the presence of OH<sup>-</sup> facilitates the N-H scission and promotes the H<sub>2</sub> and H<sub>2</sub>O formation [11,46].

Despite the excellent activity, selectivity and stability of metal-based catalysts [27,47–51], employing metals is raising reservations about the overall sustainability of hydrogen production reactions [52–54]. On the other hand, in the last few decades, carbon-based catalysts are attracting significant attention on replacing metal-based materials in heterogeneous catalysis. Different studies have demonstrated that metal-free carbon materials can be effective in gas phase reactions, in particular for alkenes and alkanes dehydrogenation [55–57], and in liquid phase reactions, i.e., oxidation of benzene [58] and alcohols [59,60], and reductions such as acetylene, carbon-carbon multiple bonds and functionalized benzenes [61,62].

Combining experimental and DFT studies, we reported the activity of metal-free carbon catalysts in the generation of H<sub>2</sub> from formic acid [63]. In particular, we demonstrated that defects, especially single vacancies, are active in the formic acid dehydrogenation reaction even in the presence of oxygen groups, i.e., alcohols and carbonyls. Similar investigations including a wide range of carbon dopants proved the same results on ammonia reforming [64]. For the best of our knowledge, the decomposition of hydrazine on a metal-free carbon-based catalyst has been reported only on g-Si<sub>3</sub>C, which is able to adsorb N<sub>2</sub>H<sub>4</sub> in its *anti*-configuration and decompose it following pathways different to those on metal surfaces [65].

In the present work, different carbonaceous materials, i.e., graphite and two different types of carbon nanofibers differing in graphitization degree (PR24-PS and PR24-HHT), were employed in the liquid phase hydrazine decomposition reaction. A systematic density functional theory (DFT) study on N<sub>2</sub>H<sub>4</sub> adsorption and decomposition was employed to understand the role of the defects in this process, paving the pathway to the development of new and efficient carbo-catalysts.

## EXPERIMENTAL METHOD

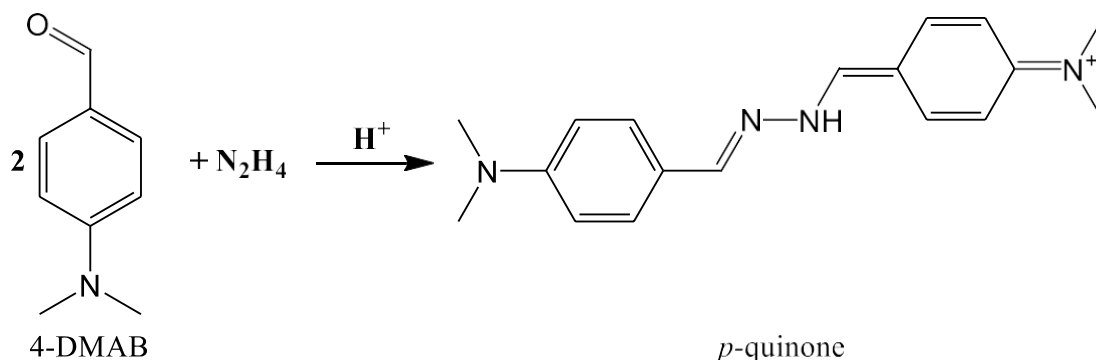
**Materials and chemicals:** CNFs PR24-PS and PR24-HHT were purchased from the Applied Science Company. These nanofibers were prepared with different post-treatment temperature, in order to remove polyaromatic carbon layers covering their external surface. The thermal treatments were performed at 700 and 3000 °C for PR24-PS and PR24-HHT, respectively. Graphite was obtained from Johnson Matthey. N<sub>2</sub>H<sub>4</sub> · H<sub>2</sub>O (98 %), sodium hydroxide (NaOH, ≥98 %), hydrochloric acid (HCl, 37 % wt) and 4-dimethylaminobenzaldehyde (4-DMAB, 98 %) were acquired from Sigma-Aldrich.

**Catalytic tests:** Liquid phase NH<sub>2</sub>NH<sub>2</sub> · H<sub>2</sub>O decomposition was performed at a constant reaction temperature of 50 °C using a 50 mL three-necked round bottom flask, with one of the flask's neck connected with a burette employed for gas volume analyses.

Typically, the required amount of catalyst (hydrous hydrazine/catalyst weight ratio 15.7/1) was added in the reactor, where 16.0 mL of a 0.5 M NaOH aqueous solution was placed and heated at the desired temperature. Once the solution reached the desired temperature, 600 μL of a 3.3 M hydrous hydrazine aqueous solution was inserted and the final mixture was stirred at 1400 rpm using a magnetic stirrer.

**Product analyses:** Hydrous hydrazine conversion was analysed using a Jasco V-730 Spectrophotometer, using a 1 cm quartz cell. The conversion was calculated according to the equation  $\text{mol}_{\text{in}} - \text{mol}_{\text{out}} / (\text{mol}_{\text{in}} \times 100)$ ,

where  $\text{mol}_{\text{in}}$  and  $\text{mol}_{\text{out}}$  are the initial and the remaining moles, respectively. The analytical method was based on the reaction of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  with 4-dimethylaminobenzaldehyde (4-DMAB) in dilute hydrochloric acid (Scheme 1). The substrate quantitatively reacts with 4-DMAB to give a *p*-quinone structure that adsorb at 456 nm [66,67]. The concentration was calculated using the Beer-Lambert equation.



Scheme 1: Reaction of 4-DMAB and hydrazine to give the yellow *p*-quinone

The volume of gas produced was measured using the water displacement method. The gaseous products released were allowed to pass to a trap containing a 0.05 M HCl aqueous solution to ensure the removal of  $\text{NH}_3$ , if any, and volumetrically monitored employing the burette. Using this method, the volume measured was only due to  $\text{N}_2$  and  $\text{H}_2$  molecules, enabling us to evaluate  $n(\text{N}_2+\text{H}_2)$ . The selectivity to hydrogen ( $x$ ) was then calculated according to Eq. 5:



Considering the molar ratio  $n(\text{N}_2+\text{H}_2) / n(\text{N}_2\text{H}_4)$  ( $\lambda$ ),  $x$  can be evaluated as Eq. 6:

$$x = \frac{\lambda - 1}{2} \quad (\text{Eq.6})$$

**Catalyst characterization:** Carbon samples were characterized by ICP-OES and Raman spectroscopy.

Raman spectroscopy was executed using a Horiba LabRam HR Evolution micro-Raman spectrometer equipped with a green solid-state laser (532 nm) focused through a 100× objective, giving a spatial resolution of approximately 1  $\mu\text{m}$ . The micro-Raman system was set with 300 lines per mm grating; the spectrum was collected with a final laser power of about 0.1 mW. The sample surface was measured through a hand-held power meter. Spectra were calibrated using the 520.7  $\text{cm}^{-1}$  line of a silicon wafer. The sample was scanned at an attenuation time of 300 s and 2 scans were performed giving a spectrum.

The presence of possible residual metal was analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a PerkinElmer Optima 8000 emission spectrometer.

**Computational method:** Periodic plane-wave density functional theory (DFT) calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) [68,69]. The generalized gradient approximation from the revised Perdew-Burke-Ernzerhof approximation (RPBE) [70] has been used to take into account the correlation-exchange electronic contributions, with a kinetic energy cutoff of 500 eV chosen for the expansion of the Kohn–Sham valence states plane-waves [71]. All the calculations includes the long-range dispersion correction approach by Grimme – DFT-D3 methods [72,73], an improvement on pure DFT to evaluate molecular interactions[74–77]. We also included the implicit solvation model as implemented in VASPsol [78,79], where solvent is considered as a polarizable continuum dielectric bath. The optimization thresholds for electronic and ionic forces relaxation were respectively  $10^{-5}$  eV and 0.02 eV/Å. For Brillouin

zone sampling, a  $\Gamma$ -centered k-point mesh generated through Monkhorst–Pack method of dimensions  $5 \times 5 \times 1$  in order to avoid Pulay stress [80]. To improve the convergence of the Brillouin-zone, a first order Methfessel–Paxton method has been used with an energetic width value of 0.2 eV. All carbon-based materials were modeled starting from a single layer slab of a  $6 \times 6$  pristine graphene supercell and introduced different defects: single vacancy (SV), double vacancy (DV) and three different Stone Wales defects (SW1, SW2, SW3) [63]. The supercell is in a hexagonal crystalline system with unit cell vectors  $a$  and  $b$  lying in surface plane and perpendicular to  $c$  axis. Both,  $a$  and  $b$ , were optimized at 14.8 Å, in well agreement with experimental values obtained by Transmission Electron Aberration-corrected Microscope (TEAM) [81]. We introduced a polarizable continuum dielectric bath of  $\sim 16$  Å perpendicular to the C-surface in order to avoid spurious periodic interactions with periodic images. Computational characterization of the surfaces was performed using the Bader analysis as implemented by Henkelmann et al. [82]. A fast convergence of charges with respect to the Fast Fourier Transform grid was obtained employing the Grid Method by Yu [83], which quadratically converges charge values with respect to mesh size. A grid of  $370 \times 370 \times 390$  points was applied in order to optimize memory usage and precision of the calculations. These values were obtained converging two equivalent carbon charges in pristine graphene. Charge density local curvatures, local accumulations and depletions were evaluated to disclose the ability of every inequivalent surface site to adsorb and decompose hydrazine. The optimized parameters obtained from the Grid method were employed in a Laplacian topological analysis [84]. The AIM-UC Bader Analysis Toolkit implemented by David Vega et al. [85] was applied on a total electron density obtained combining the valence charge data and the core charges, resulting in Laplacian of charge density map, which allowed to analyze Bond Critical Points (BCP). Before adsorbing the hydrazine molecule, a systematic study on all possible active sites was performed using  $\text{NH}_3$  as a probe molecule and considering both dissociative and non-dissociative adsorption modes. The molecular adsorption energy ( $E_{\text{ADS}}$ ) was defined as the difference between the combined system and the isolated species. The reaction energy ( $E_{\text{R}}$ ) of each  $\text{N}_2\text{H}_4$  dissociation elementary step was described as the total energy difference between the final (final adsorbate/C) and the initial states (initial adsorbate/C). Hydrogen diffusion calculations were performed on the single vacancy (SV) system, which proved to be the most active defect in this study. A hydrogen atom was placed in the desired position where only its  $z$  coordinate could relax during the optimization calculation. Later on, all carbon atoms were allowed to relax except two of them sufficiently far from the active site to avoid rotations or translations of the considered surface as a whole [86]. The hydrogen diffusion energy ( $E_{\text{D}}$ ) was calculated as the energy difference between atomic hydrogen within the vacancy, in the most stable configuration, and diffused atomic hydrogen structures.

## RESULTS

Different carbonaceous materials, i.e., CNFs-PS, CNFs-HHT and graphite were employed as catalysts for the hydrous hydrazine reforming reaction. ICP-OES analysis was employed to ensure the absence of possible metallic impurities. The reaction conditions were optimized to assess the reaction kinetic regime and to establish the correct amount of catalyst to be used. The optimum conditions were at 50 °C and 1400 rpm, using 600  $\mu\text{L}$  of a hydrazine solution 3.3 M in 16 mL of NaOH 0.5 M and a  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ :catalyst weight ratio of 15.7:1. To ensure reproducibility, all the experiments were repeated three times. Figure 1 shows the different kinetic profiles for 6 h of reaction. CNFs-PS exhibited the highest conversion at 6 h (94 %), whereas CNFs-HHT and graphite showed similar conversion (71 % and 65 %, respectively) (Table 1, column 4). On the most active material, CNFs-PS,  $\text{H}_2$  selectivity was calculated using water displacement method and 89 % selectivity for the complete hydrazine decomposition reaction was determined.

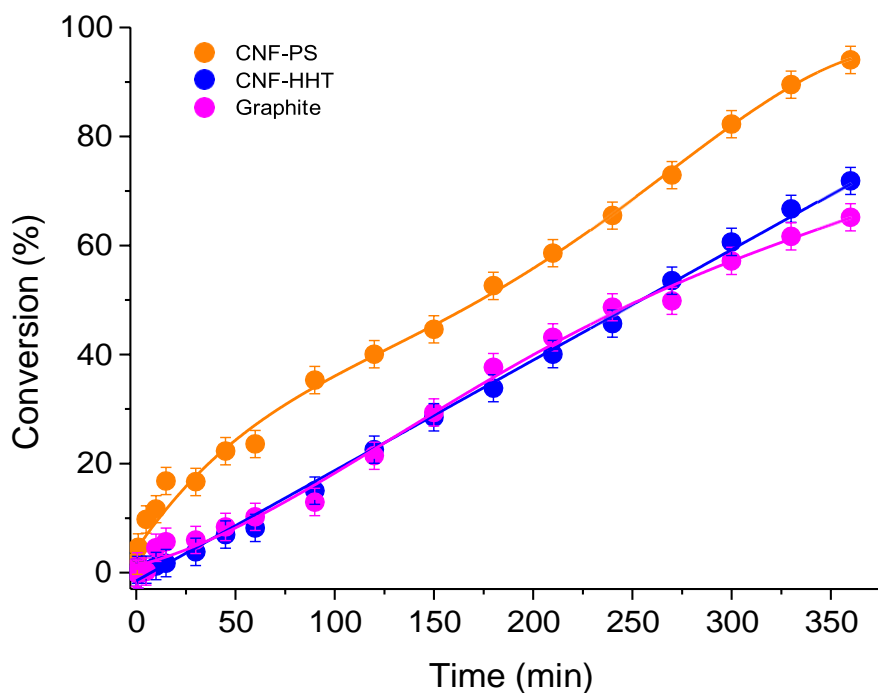


Figure 1 Conversion trend for the hydrazine decomposition reaction for the different carbonaceous materials: Graphite (violet), CNFs PR24-PS (orange) and PR24-HHT (blue). All the tests were performed at 50 °C and 1400 rpm, using 600  $\mu$ L of a hydrazine solution 3.3 M in 16 mL of NaOH 0.5 M and a  $N_2H_4 \cdot H_2O$ :catalyst weight ratio of 15.7:1.

In order to rationalize these results in terms of structural properties, we characterized all the catalysts using Raman spectroscopy. It allowed us to investigate the graphitization degree of carbon materials measuring the two bands at around  $1600\text{ cm}^{-1}$  (G band) and  $1350\text{ cm}^{-1}$  (D band) [87]. The G band is generated by the C=C stretching vibrations in the graphite lattice, and it is related to structurally ordered graphite domains. The D band corresponds to the  $A_{1g}$  mode, which is forbidden according to the selection rules in graphite, but active in the presence of structural defects or in plane substitutional heteroatoms [87]. All carbon materials studied in this work present both D and G Raman bands with the following  $I_D/I_G$  ratio: CNF-PS (1.54) > Graphite (0.20) > CNFs-HHT (0.11) (Figure S1 and Table 1).

Table 1: Raman characteristics of the carbon catalyst, their initial catalytic activity (15 minutes of reaction) and final conversion towards hydrazine decomposition (6 h).

	Raman $I_D/I_G$	Activity at 15 min ( $\text{mg}^{-1}\text{min}^{-1}$ ) * $10^2$	Conversion at 6 h (%)
Graphite	0.20	6.0	65
CNFs-PS	1.54	18	94
CNFs-HHT	0.11	1.9	71

To unveil the effect of NaOH in the reaction environment, the most active material (i.e. CNFs-PS) was tested at the same experimental conditions, but with distilled water as solvent, i.e. pH=7. From the comparison between the reaction profiles showed in Figure 2, it appears clear that the presence of NaOH affects not only the selectivity of the reaction, but also its kinetics [11,46]. Indeed, the catalyst tested at the same conditions with NaOH exhibited about 70% of hydrous hydrazine conversion at 4 h of reaction, while the same material tested in water presented a 15 % conversion.

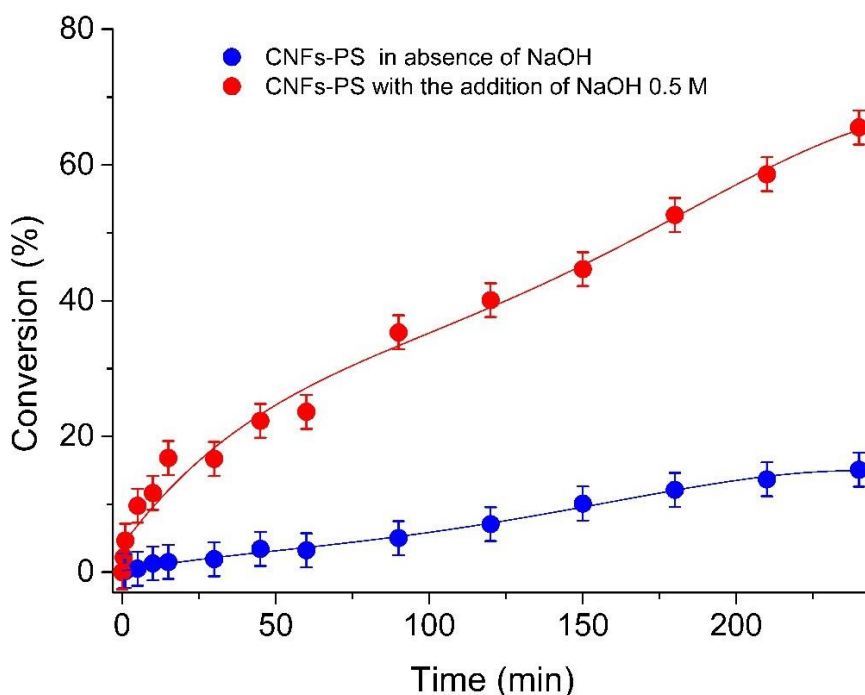


Figure 2 Comparison of conversion trend for hydrazine decomposition in a different reaction environment. Alkaline aqueous solvent, red solid line, and distilled water, blue solid line. All the tests were performed at 50 °C and 1400 rpm, using 600  $\mu\text{L}$  of a hydrazine solution 3.3 M in 16 mL of solvent (NaOH 0.5 M for red profile, distilled water for the blue one) and a  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ :catalyst weight ratio of 15.7:1.

Systematic DFT simulations were performed to elucidate the roles of carbon defects in hydrazine activation and decomposition. Six different graphitic surfaces were modelled: pristine graphite (PG), single vacancy (SV), double vacancy (DV) and three different Stone-Wales defects (SW, VSW1, VSW2), represented in Figure S1. Prior to proceed with the adsorptions, we performed an evaluation of charge density at Bond Critical Points (BCP)[88] to estimate the potential active sites of the different optimized surfaces (Figure S1). As previously shown, only sites presenting distortions in the graphene  $\pi$ -system are able to interact favourably with adsorbates [64]. The obtained electron densities measured on the defects are summarised in Table 2. It was observed that only SV and DV are potential catalysts candidates to bind  $\text{N}_2\text{H}_4$  as these two structures contain dangling C-atoms lacking electron density [63]. This result, underling the localization of the catalytic site on both SV and DV.

Table 2: Charge density at Bond Critical Points of the potential active sites.

Surface Site	$\rho(\vec{r}_{BCP}) / \frac{e^3}{\text{\AA}^3}$
PG	2.03
SV	0.587
DV	0.974 and 0.979
SW	1.863 - 2.589

VSW1	1.628 - 2.156
VSW2	1.602 - 2.134

We validated the assumptions regarding the active sites by using ammonia ( $\text{NH}_3$ ) as a probe molecule. It was brought near non-equivalent active sites and the system relaxed. In line with previous studies, the graphitic areas possess an inactive  $\pi$ -conjugation, not sensitive to adsorption of molecules [64,89–91]. Only single vacancies showed a favourable (exothermic) interaction with ammonia, indicating that a  $\rho(\vec{r}_{BCP})$  smaller than  $0.6 \frac{e}{\text{\AA}^3}$  defines the active sites on carbon surfaces. Combining the Laplacian of charge density analysis and the performed tests with  $\text{NH}_3$ , we were able to identify  $\text{C}_3$ ,  $\text{C}_{3'}$  and  $\text{C}_7$  in the single vacancy system as possible active sites (Figure 3). Then, hydrazine was placed and relaxed on such sites with different initial orientations. We also investigated the molecule dissociative adsorption [92,93], i.e., breaking the N-H or N-N bonds while forming a new one with the surface similar to previous works on metal surfaces.

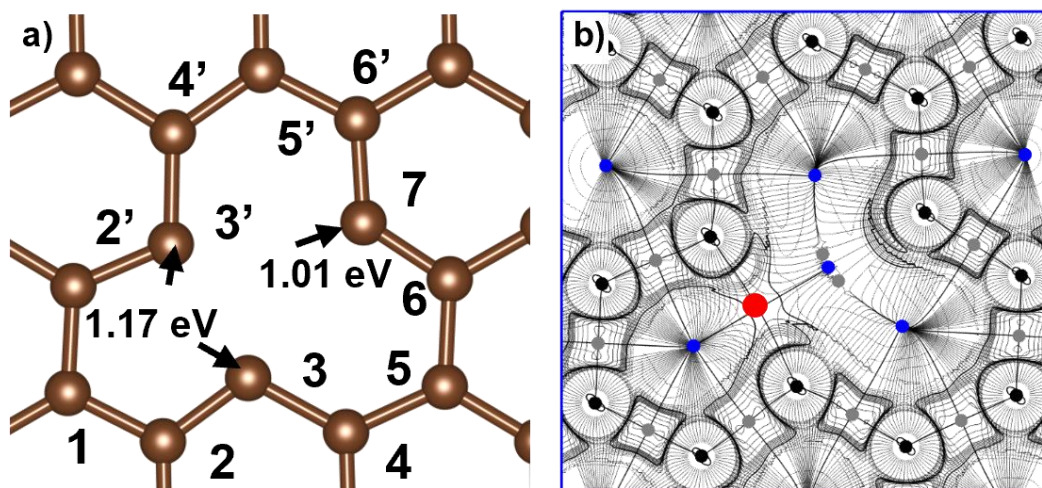


Figure 3 Single vacancy representation. a) Individuated active sites and  $\text{NH}_3$  relative adsorption energies. b) Charge-density Laplacian analysis iso-surfaces plot; Red circle indicates the evaluation site for  $\rho(\vec{r}_{BCP})$ , black circles indicate nuclear charge density maxima, grey Bond Critical Points and blue Ring Critical Points.

The least stable  $\text{N}_2\text{H}_4$  adsorption configuration is the anti-single linked (*a*-*SL*) configuration where hydrazine bonded  $\text{C}_3$  (Figure 4a). When the molecule is bonded to two active sites in a bridge configuration, it may adopt the cis-bridged (*cB*-*N*) configuration driving the N-H dissociation (Figure 4b) or the cis-bridged (*cB*-*H*) structure resulting in the N-N bond scission (Figure 4c). It can be seen from the adsorption energies inserted in Figure 4 that the resulting stability increases following the sequence *a*-*SL* < *cB*-*N* < *cB*-*H*. Zheng et al. investigated the same adsorption process on metal-free  $\text{SiC}_3$  siligraphene resulting in the following stability sequence: *cis*- $\text{N}_2\text{H}_4$  < *gauche*- $\text{N}_2\text{H}_4$  < *anti*- $\text{N}_2\text{H}_4$  [65]. In addition, mechanistic studies performed on metal surfaces, such as Ir [94], Cu [95], Ni [96–98] and Pt [99], are consistent with the siligraphene trends. In our study, a *gauche* adsorbed configuration was not obtained from structural optimizations, which shows C behaves differently to  $\text{SiC}_3$  siligraphene and metals. Unlike in these studies, the different adsorption modes on defective graphene are driven by the lack of electron density. Hence, the *a*-*SL* structure only saturates one dangling carbon atom showing a weak adsorption energy ( $E_{\text{ADS}} = -0.78 \text{ eV}$ ), whereas when two or more

dangling bonds are saturated (cB-N and cB-H, respectively), the species are more strongly bonded to the surface.

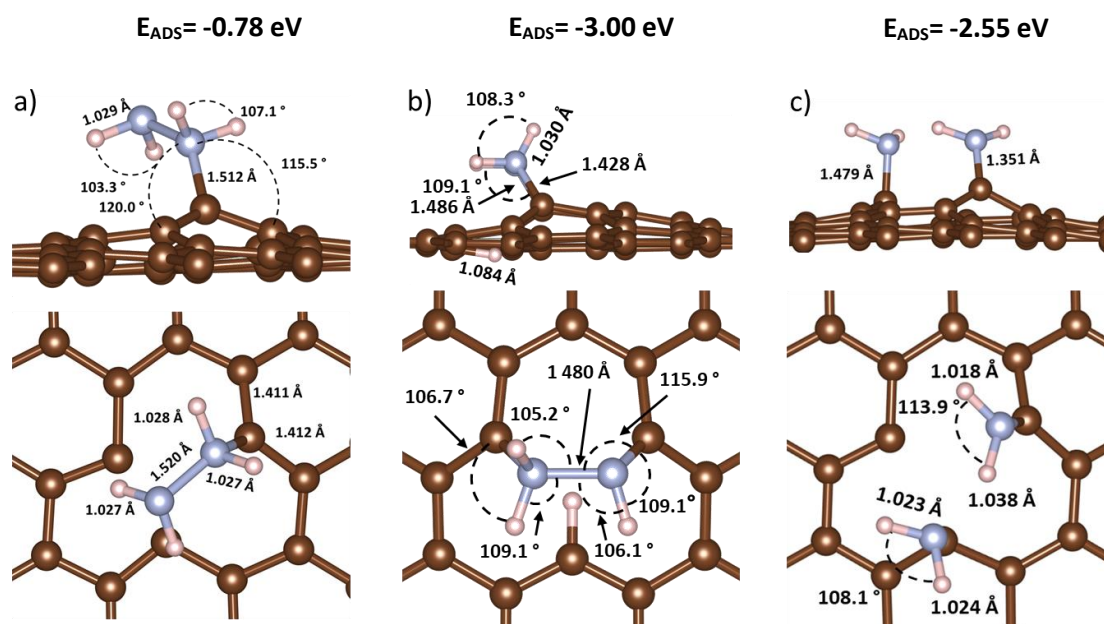


Figure 4: Top and side view of the most favourable Hydrazine configurations: a) a-SL b) cB-N c) cB-H. Inset are the adsorption energies ( $E_{\text{ADS}}$ ) and the main distances (Å) and angles (°) of interest. Carbon atom is labelled in brown, nitrogen in blue and hydrogen in white.

We considered two symmetric and one asymmetric dehydrogenations, and incomplete decomposition pathways based on previous reports [19–21]. However, only the most stable routes to the formation of  $\text{H}_2$  and  $\text{NH}_3$  was analysed in detail. The cB-H was the most stable adsorption configuration and the first step for the complete hydrazine reforming (Eq. 1), whereas the cB-N was the first step towards an incomplete hydrazine decomposition (Eq. 2) (Figure 4b and c). The difference in energy between the N-H and the N-N dissociative adsorptions indicated that the hydrogen production pathway was the preferable one ( $\Delta E_{(\text{NN-NH})} = 0.450 \text{ eV}$ ). Indeed, once the N-H bond was broken and a  $\text{C}_3\text{-H}$  was formed leading towards the hydrogen production.

To proceed with dehydrogenation reaction mechanisms, we could consider a negligible activation energy for the migration of the dissociated H adatoms similar to the spill on metal catalysts [100]. However, the SV is a point defect, and the active site is isolated from adjacent dangling bonds. Thus, two different hydrogen production pathways were tested (Figure 5). The first one, SWC-Decomposition (Symmetric non-directional solvent Complete decomposition, Figure 5), simulated the absence of an alkaline aqueous medium and the H species needed to overcome a non-negligible diffusion energy barrier to free the active site. Hence, we investigated the H migration along three different paths (Figure S3) in similar fashion to previous studies [101–103]. For the most favourable migration pathway (Figure S4), we obtained a diffusion energy barrier of ( $E_{\text{D}}$ ) 3.48 eV in polarizable continuum background, which did not provide a realistic directional solvation in aqueous solutions [102] (Figure S5). According to our simulations, two H atoms occupying nearest neighbour dangling carbon sites had an endothermic reaction energy ( $E_{\text{R}} = 2.90 \text{ eV}$ ) to form  $\text{H}_2$  (Figure S6). However, the experiments were performed in solution, which surrounded  $\text{H}^*$  with an arranged (dipole) solvation shell promoting the H diffusion through the solution as well as the  $\text{H}_2$  evolution through the Heyrovsky mechanism [104]. Thus, we considered the desorption from  $\text{C}_3$  (Figure 3) negligible in comparison with the energy



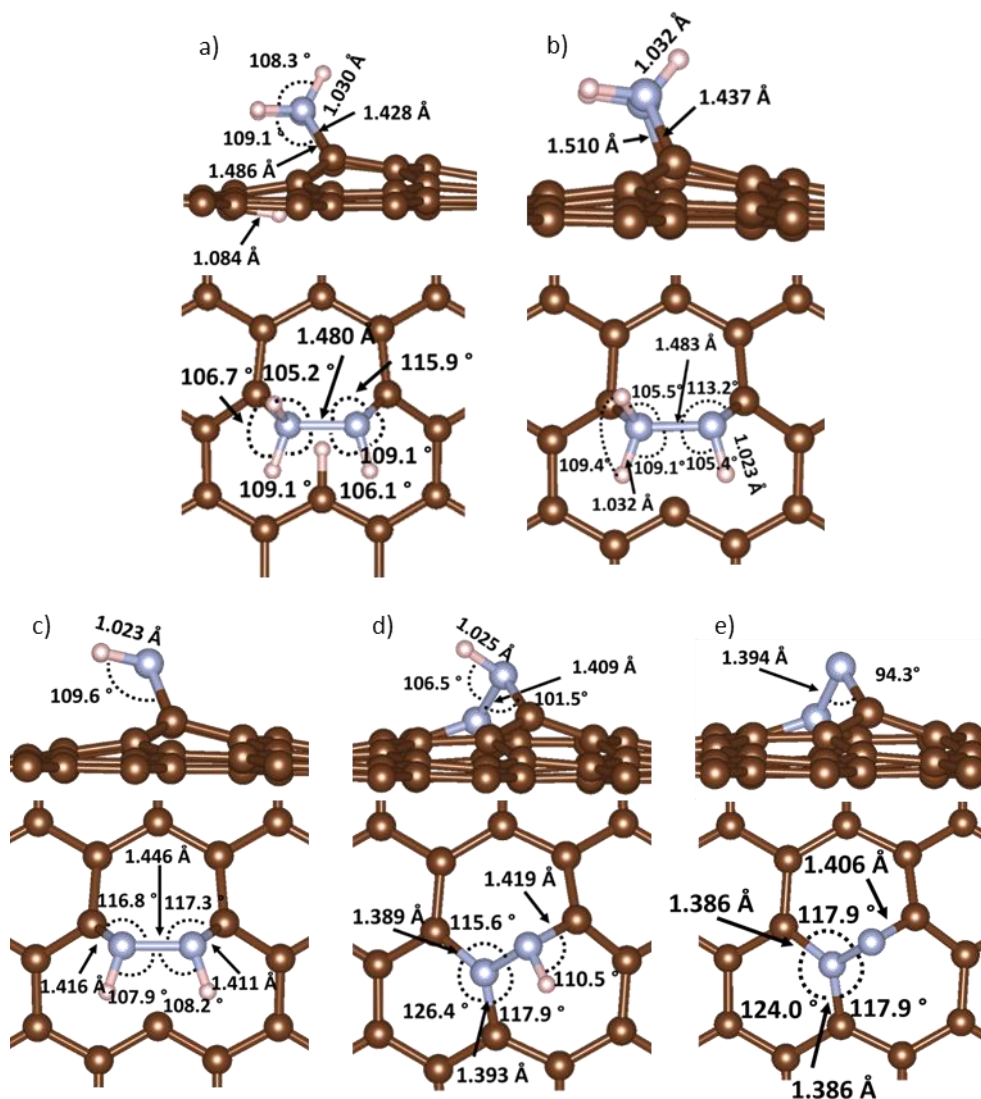
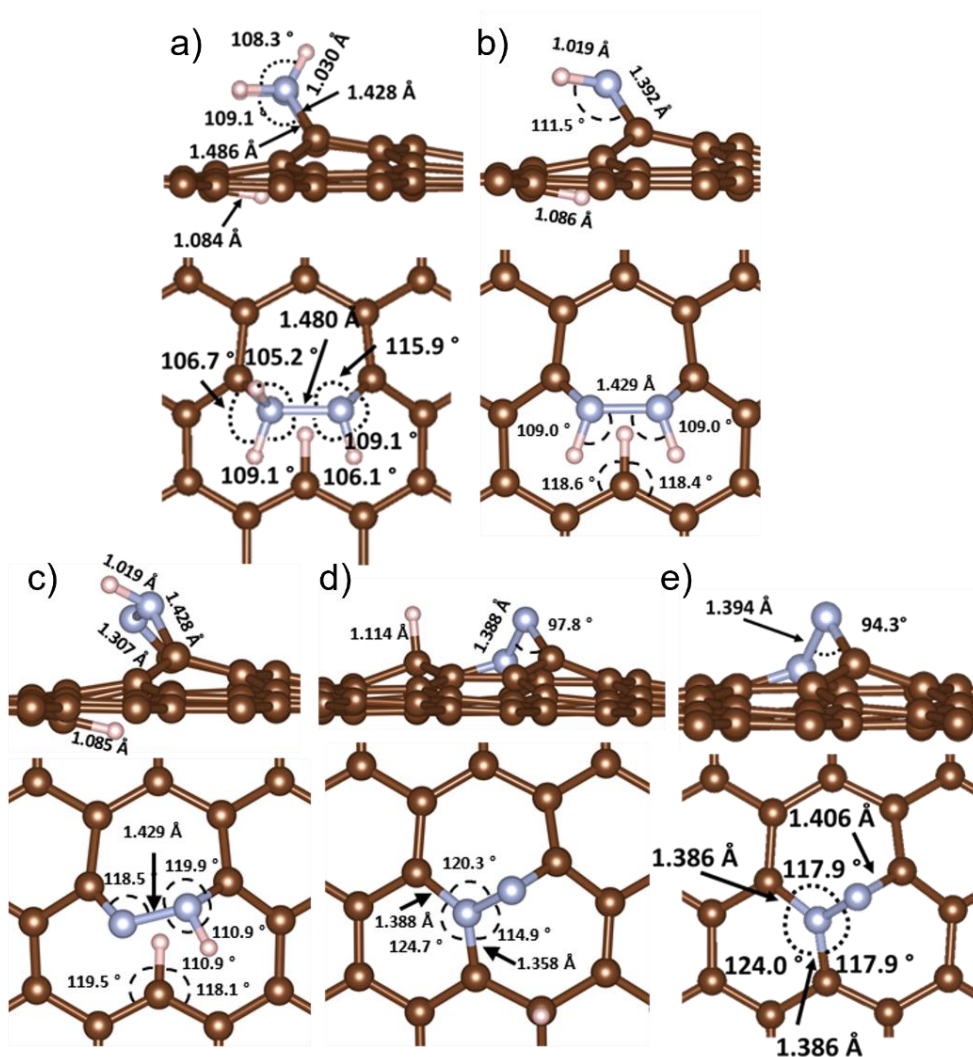


Figure 6: Top and side view of the most favourable hydrazine configurations for  $H_2$  production in water: a) Dissociative adsorption step  $N^*H_2N^*H + H^*$ , b) Hydrogen diffusion step  $N^*H_2N^*H + H^{**}$ , c) second dehydrogenation step and  $H_2$  evolution,  $N^*HN^*H$ , d) third dehydrogenation step with diffusion,  $N^*N^*H + H^{**}$  and e) last dehydrogenation step,  $H_2$  and  $N_2$  evolution,  $N^*N^*$ . Inset, distances (Å) and angles ( $^\circ$ ) of interest. Carbon atoms are labelled in brown, nitrogen in blue and hydrogen in white.

## SAC $H_2$ production

The presence of NaOH as alkaline medium (SAC) led to a more favourable dehydrogenation pathway (Figure 5). **Error! Reference source not found.** shows the SAC-Decomposition mechanism where, in each step, the dangling bonds were completely saturated increasing its stability. The dissociative adsorption step (Figure 7a) was followed by a further hydrogen extraction (**Error! Reference source not found.**b,  $E_R = -0.491$  eV) due to the interaction with  $OH^-$  ions, which presented an exothermic behaviour. Differently from the SWC, the formation of a  $C_3-H$  bond influenced both structures and energies ( $\Delta E_{SWC-SAC} = 3.810$  eV, Figure 6b and **Error! Reference source not found.**b). The N-H and C-N bonds were more contracted, in particular the C-N bonds respectively by 0.018 and 0.045 Å, while the N-H bonds by 0.004 and 0.013 Å. In the subsequent step (**Error! Reference source not found.**c,  $E_R = 0.525$  eV), further dehydrogenation was performed with the *in-situ* evolution of a molecular hydrogen specie. The C-N bond related to the bare N centre contracted by 0.085 Å, while either N-N or N-H bonds did not show any variation. Moreover, it is possible to observe that the bare N centre tilted towards the  $C_3-H$ . Overall, the step is slightly endothermic, due to the breakage of the N-H bond. Subsequently (**Error! Reference source not found.**d), the bare N centre bonded to  $C_3$  and a scission of the N-H bond occurred and the atomic H bonded to a non-active C atom ( $E_R = +1.377$  eV). Indeed,

from **Error! Reference source not found.** it is possible to observe that the structure was deformed in order to bond the H atoms. The structure of the last dehydrogenation step (**Error! Reference source not found.**) was completely equivalent to the one described in the SWC mechanism (Figure 6e). Nonetheless, from the energetic point view, the difference was mainly related to H<sub>2</sub> evolution. Indeed, in the SWC mechanism it was necessary to overcome the energetic barrier deriving from the in-vacancy recombination of two diffused H atoms ( $E_R = 2.900$  eV, Figure S6). Here, the hydrogen evolution did not require any recombination, leading to an exothermic step ( $E_R = -0.937$  eV). In the last step, N<sub>2</sub> evolution was endothermic and required overcoming an energetic barrier of 2.328 eV.



**Figure 7** Top and side view of the most favourable hydrazine configurations for H<sub>2</sub> production in presence of aqueous NaOH: a) Dissociative adsorption step  $N^*H_2N^*H + H^*$ , b) Dehydrogenation step:  $N^*HN^*H + H^*$ , c) second dehydrogenation step and H<sub>2</sub> evolution,  $N^*N^*H + H^*$ , d) third dehydrogenation step,  $N^*N^* + H^*$  and e) last dehydrogenation step, H<sub>2</sub> and N<sub>2</sub> evolution,  $N^*N^*$ . Inset, distances (Å) and angles (°) of interest. Carbon atoms are labelled in brown, nitrogen in blue and hydrogen in white.

## NH<sub>3</sub> production

The first step of NH<sub>3</sub> production (Figure 8a) involved the breakage of N-N bond upon adsorption, forming the cB-N structure ( $E_{ADS} = -2.55$  eV). The two adsorbed NH<sub>2</sub> lied on the dangling carbons with sp<sup>3</sup>-like configuration. The following elementary step consisted in a hydrogen transfer, involving the two N\*H<sub>2</sub>, followed by the NH<sub>3</sub> evolution. As can be seen from the structure in Figure 6b, the remaining N\*H tilted toward vacancy centre. A contraction of the free dangling carbons (C<sub>3</sub>-C<sub>3</sub>) distance is then observed, leading to a slightly endothermic process ( $E_R = +0.018$  eV). To close the catalytic cycle, a subsequent hydrazine

adsorption bridging between the available active sites was considered (Figure 6c). The initial N\*H took two hydrogen atoms from the second N<sub>2</sub>H<sub>4</sub> in a concerted mechanism upon its adsorption, leading to the formation of HN\*N\*H + N\*H<sub>3</sub>. This step showed an overall exothermic energy ( $E_R = -0.019$  eV), along with the following NH<sub>3</sub> exothermic evolution process, leading HN\*N\*H on the SV (Figure 6d,  $E_R = -0.35$  eV). In the subsequent elementary step, a third hydrazine could exothermically co-adsorb on the under-coordinated carbon sites C<sub>7</sub> ( $E_R = -0.163$  eV, Figure 8e). In this position, the third hydrazine molecule interacted with an H of the adsorbed HN\*N\*H yielding a NH<sub>3</sub> molecule (Figure 8e). The structure obtained is energetically favourable ( $E_R = -3.33$  eV, Figure 8f) and the H-free N bridged between two carbon sites with a sp<sup>2</sup> hybridization. Instead, the C<sub>7</sub> atom was saturated connecting two N atom, showing a conventional sp<sup>3</sup> geometry. The interaction between N\*H<sub>2</sub> and the H located on the bridged HN\*N\* led to the evolution of the last NH<sub>3</sub> (Figure 8f,  $E_R = -0.05$  eV). The resulting N<sub>2</sub> was anchored on the carbon lattice ( $E_R = +2.32$  eV) analogously to the SAC hydrogen production pathway.

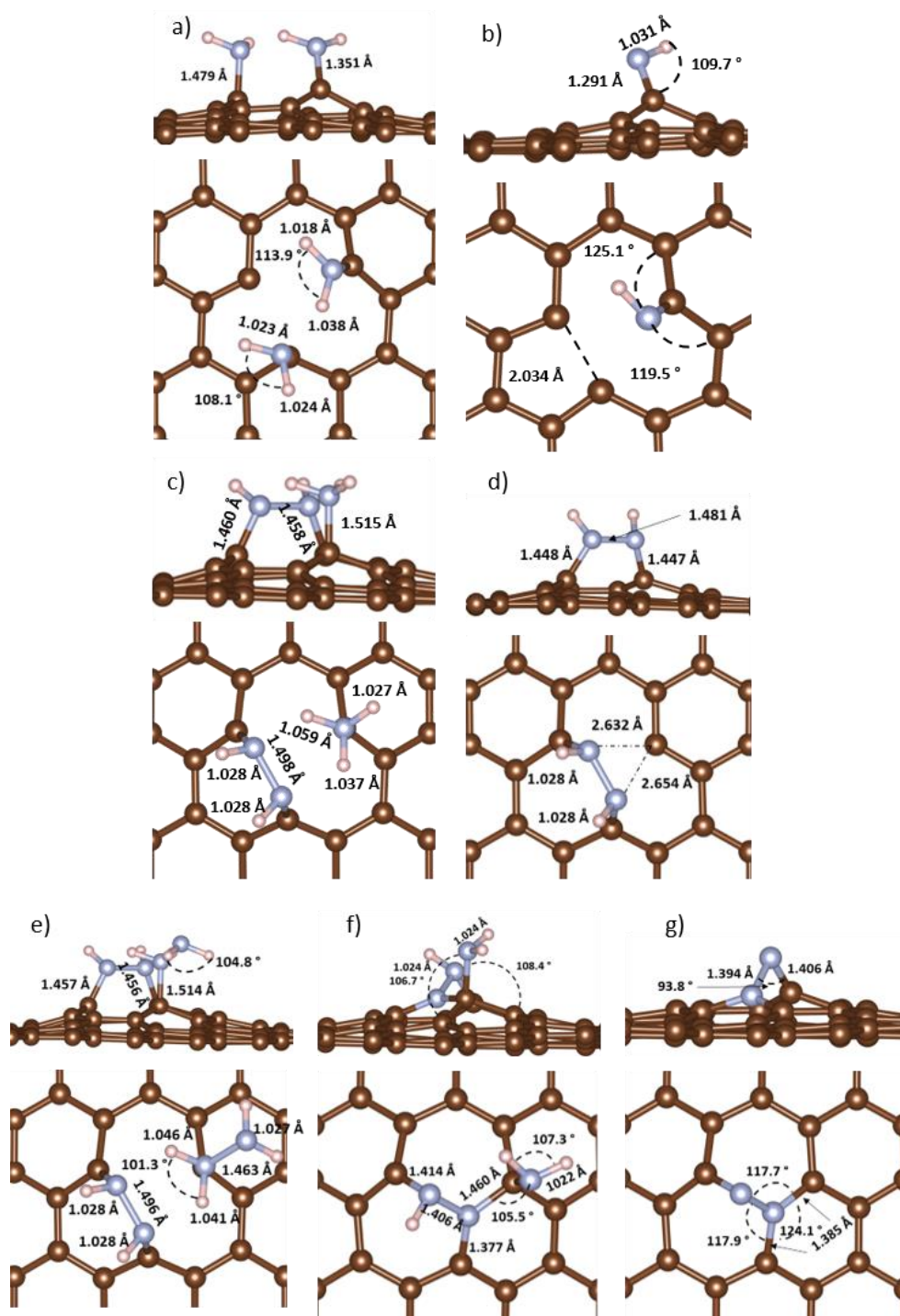


Figure 8 Top and side view of the most favourable Hydrazine configurations for  $\text{NH}_3$  production: a) N-N bond breakage step,  $2 \text{ N}^* \text{H}_2$ , b) First  $\text{NH}_3$  evolution step,  $\text{N}^* \text{H}$ , c) Second Hydrazine adsorption step,  $\text{N}^* \text{HN}^* \text{H} + \text{N}^* \text{H}_3$ , d) Second  $\text{NH}_3$  evolution step,  $\text{N}^* \text{HN}^* \text{H}$ , e) Third Hydrazine linkage step,  $\text{N}^* \text{HN}^* \text{H} + \text{N}^* \text{H}_2 \text{NH}_2$ , f) Third  $\text{NH}_3$  evolution step,  $\text{N}^* \text{HN}^* + \text{N}^* \text{H}_2$  and g) Fourth  $\text{NH}_3$  and  $\text{N}_2$  evolution step,  $\text{N}^* \text{N}^*$ . Inset, distances (Å) and angles ( $^\circ$ ) of interest. Carbon atom is labelled in brown, nitrogen in blue and hydrogen in white.

## CONCLUSIONS

In this study, different metal-free carbonaceous materials, i.e. CNFs PS, CNFs HHT and graphite were tested in hydrazine hydrate decomposition reaction for the first time. In addition, a systematic density functional

theory (DFT) study on  $N_2H_4$  adsorption and decomposition mechanism was then employed to understand the role of the defects paving the pathway to the development of new and efficient carbocatalysts to be used in this reaction. A conversion of 94 %, 71 % and 65 % was observed after 6 h of reaction for CNFs PS, CNFs HHT and graphite, respectively. For the best of our knowledge, this is the first work reported in literature which shows the ability of metal-free carbonaceous materials to decompose hydrazine hydrate. Moreover, a selectivity for  $H_2$  of the 89 % at 97 % of conversion was found testing CNFs-PS. The materials were also analysed using ICP and Raman spectroscopy. A correlation between the numbers of defects present in the catalysts and the initial activity of the hydrazine decomposition reaction was found. In particular, initial activity increases increasing the number of defects, i.e. CNFs-PS > CNFs-HHT > graphite. Correlating the  $I_D/I_G$  ratio obtained by Raman spectroscopy and the initial activity, a linear correlation was found ( $R^2 = 0.981$ ). In addition, CNFs PS were also tested in absence of alkaline medium to understand the effect of NaOH. The catalyst showed a conversion (15 % conversion at 4 h) lower than in presence of NaOH (94 % conversion at 4 h

In order to understand the effect of the defects on the decomposition of hydrazine, different surfaces were modelled using DFT calculation, i.e. pristine graphene, single and double vacancies, and different Stone–Wales defects. According to our previous studies, only SV showed an exothermic adsorption energy to our substrate, indicating that it is the only defect which participates in the reaction. Two symmetrical and one asymmetrical dehydrogenation pathways were found, but only the most favourable (symmetric hydrazine dehydrogenation) was considered in our discussion. On the most stable hydrogen production pathway, the effect of the alkaline medium was elucidated through calculations concerning the diffusion and recombination of atomic hydrogen. Indeed, the presence of NaOH helps extracting H species without additional energetic barriers, as opposed to the calculations performed in polarizable continuum medium. In addition, an incomplete decomposition pathway forming  $N_2$  and  $NH_3$  was studied and compared with the dehydrogenation one. Considering the initial dissociative adsorption, the first step of the dehydrogenation pathway is the more favourable (dissociation of the N-H bond, -3.00 eV) than the scission of the N-N bond (-2.55 eV) which lead to  $NH_3$  as product. This first reaction step is crucial to define the reaction mechanisms and the computational results fully agree with the ones obtained in the experiments. Moreover, comparing two different hydrogen production pathways (with and without diffusion and recombination), we confirmed that the presence of sodium hydroxide in the experimental reaction environment can modify the energy gap between the two pathways, leading to a selectivity to  $H_2$  near 90 %. Overall, this work provides a complete insight of hydrazine decomposition over intrinsic elementary defects of metal-free carbonaceous catalysts. Finally, these results can be used as a raw model for the synthesis of carbocatalysts with enhanced features for the liquid phase hydrazine decomposition reaction, focusing on widening the  $\Delta E_{NN-NH}$  energy gap.

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