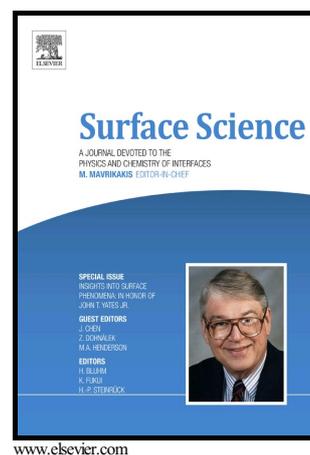# Author's Accepted Manuscript

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Phenol Dissociation on Pristine and Defective Graphene

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Abstract

Phenol ($C_6H_5O–H$) dissociation on both pristine and defective graphene sheets in terms of associated enthalpic requirements of the reaction channels was investigated. Here, we considered three common types of defective graphene, namely, Stone-Wales, monovacancy and divacancy configurations. Theoretical results demonstrate that, graphene with monovacancy creates C atoms with dangling bond (unpaired valence electron), which remains particularly useful for spontaneous dissociation of phenol into phenoxy (C_6H_5O) and hydrogen (H) atom. The reactions studied herein appear barrierless with reaction exothermicity as high as 2.2 eV. Our study offers fundamental insights into another potential application of defective graphene sheets.

Keywords: density functional theory (DFT), nudged elastic band (NEB), graphene, phenol, phenoxy, Stone-Wales, vacancy defects

1. Introduction

Phenol (C_6H_5OH), a planar aromatic compound with singular hydroxyl group (OH), has ubiquitous industrial and pharmaceutical applications. It widely serves in the production of

plastics, dyes, resins, nylon, throat sprays, aspirin and other important commodities [1,2]. These applications have led to various phenolic-based pollutants wastes (e.g. dioxin [3]) that constitute negative impacts on public health and the environment alike. As a solution, adsorption processes stand out in providing a viable clean-up treatment for this matter due to their relatively simple implementation [4]. Moreover in theory, ultrathin nanomaterials, such as graphene, exhibit remarkable properties to assist the adsorption procedure. Graphene represents a two-dimensional sheet of pure sp^2-hybridised carbon atoms, arranged in a flat single-atomic-layer hexagonal lattice, and for a decade now, it has gained significant recognition within the scientific community as a result of its excellent electronic, mechanical, optical and chemical properties[5]. Due to its delocalized π-electron system, which can form strong interactions with various chemical species; graphene display remarkable properties towards adsorption of various pollutants as experimentally proven in case of pharmaceutical pollutants [6], reactive black 5 (RB5) [7], and methylene blue [8] and many other water and gaseous pollutants [9].

The weakest bond in phenol is the hydroxyl's O-H bond amounting to nearly 4.0 eV. However, O/H radical pool could readily abstracts the hydroxyl' H atom affording a phenoxy radical [10]. On the other hand, the saturated bonds in pristine graphene renders it relatively inert. Nonetheless, the material is capable of forming weak interlayer bonds (as in graphite)[11], strong multi-functional bonds (as in graphene oxide)[12] and various covalent bonds with halogens (as in fluorographene)[13] and other pure elements[14–17]. In relations to phenol-graphene interaction, phenolic materials have been used to adsorb epoxy (−O−) or hydroxyl (−OH) in graphene oxide to synthesize graphene [18,19]. For the reverse process, Luz et al. reported from their experiment that, phenol adsorbed weakly on graphene in a graphite-like interaction [4]. An experiment by Huang et al. suggested the application of defective oxygenated graphene to attract water molecules for humidity sensor[20].

Computational simulation by Hernandez et al.[2] revealed that pristine graphene-phenol interaction is weak (0.1 eV). However, by doping graphene with Al, the graphene-Al-phenol interaction becomes stronger (2.6 eV). Another simulations by Avila et al. [21] show that pristine graphene and B-doped-graphene exhibit weak interaction with phenol; while Al- and Ga-doped-graphene exhibit strong interaction. In another related study, Kang calculated that dioxin is effectively adsorbed by Ca-doped graphene, with binding energy of 3.0 eV[22].

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Indeed, elemental doping certainly presents an opportunity to strengthen the interaction between phenol and graphene, and as such, the primary objective of this work is to investigate the interaction between phenol and undoped defective graphene. This is motivated by the work of Hassan et al. [23] and Sanyal et al. [24] in which the former reported in their simulation that, undoped defective graphene lowers its interaction with benzene (C_6H_6) as compared to the pristine graphene. However Sanyal et al.'s showed that, the 585 divacancy assists the molecular adsorption on graphene by breaking the adsorbate's bonds that subsequently saturate the dangling bonds on the divacancy sites. Hence, the contrast conclusions remain open to further investigation.

During the fabrications of nanomaterials such as graphene, defects are unavoidable. Therefore, the importance of defective graphene has attracted significant number of studies[25–28]. In the view of its application in supercapacitor electrodes, Wood and co-workers reported in their theoretical study that, defects in graphene enable increasing capacitance by several fold [29]. Basically, three types of graphene defects exist, i.e. dislocation, vacancy, and combined dislocation and vacancy (Figure 1). In the dislocation defects, the C atoms form a non-hexagonal network, i.e. Stone-Wales[26], whereas, vacancy defects are characterised by loss of C atom, i.e. monovacancy. Also, in some other cases, vacancy defect is followed by dramatic atomic dislocations, i.e. 555777 divacancy. There are unlimited combinations of these types of defects. As such, only three common defects have been selected in this study; Stone-Wales, monovacancy and divacancy[28] whereby Stone-Wales defect is a 90° rotated C–C bond in graphene.

Figure 1.

Despite of Sanyal et al.'s hint on the molecular adsorption on graphene with vacancy, it does not provide the detail of its reaction pathways. In this work, we deploy density functional theory (DFT) [30], to investigate the chemical interaction of phenol with both pristine and undoped defective graphene. We explore the enthalpic requirements of the reaction channels, as well as charge transfer analyses. Result presented herein provides more insight into adsorption treatment of phenol-like waste substances by defective ultrathin graphene sheets.

2. Methods

VASP code [31] was used in all structural relaxation and energy calculations. The details include the plane wave DFT, with spin-polarized PAW-GGA functional[32], Grimme[33] van der Waals correction, and a Gaussian smearing. The reaction paths/transition energies were calculated using the nudged elastic band (NEB) method[34]. All calculations uses plane wave cut off energy of 500 eV, energy tolerance of 0.1 meV and atomic force tolerance of 0.02 eV/Å. The reaction modellings employ a monolayer pristine/defective graphene with the size of 5×5 supercell, and an adequate spacing to avoid adsorbate-adsorbate interaction. We have applied this theoretical approach in our recent studies on elemental adsorption on graphene [10].

Countless orientation possibilities exist in the phenol−graphene interaction, but in this work, we chose an orientation suggested by Hernandez et al.[2], i.e. phenol was dropped onto the pristine/defective graphene with C−O bond oriented perpendicularly to the surfaces. Our theoretical calculation proceeds in five steps. First and foremost, we calculate the gas-phase dissociation energies of phenol into different radical products, i.e. C_6H_5O + H, C_6H_5 + OH, C_6H_5 + O + H, according Equation (1).

$$E_{dissociation} = \left(\sum E_{radicals} \right) - E_{phenol} \tag{1}$$

Then, we assess the stability of defective graphene sheets. For this purpose, we have selected the pristine graphene, graphene with Stone-Wales defect, asymmetric monovacancy [35] , and 555777 divacancy[36], as shown in Figure 1. The asymmetric monovacancy has one dangling bond and it appear relatively more stable than the symmetric monovacancy with three dangling bonds. Whilst in divacancy, 555777 structure eliminates all the dangling bond and results in better stability. Moreover, Haldar et al. also showed that 555777 structure is more stable than 585 structure [36]. The dangling bonds for both the radicals and the surfaces are expected to play a role in the reaction channels. In the third step, we optimise the reacting species, i.e., phenol on pristine/defective graphene, with a separating distance of 10 Å such that they do not interact with each other (Figure 2a). Afterwards, we optimise the products by selectively placing phenol in tight proximity to the surface of the

pristine/defective graphene (Figure 2b).   Although are unlimited possible product configurations, as shown in Figure 3, the hollow site has been selected based on the assumption that, the combined reactivity of surrounding carbon atoms will preferentially support the dissociation of OH bond in phenol. Subsequent to obtaining the most favorable product configurations, the last step was to calculate its reaction paths using the NEB method [34].

Figure 2.

Figure 3.

Charge transfers from the (dissociated) phenol to the surfaces (or vice versa) have also been estimated using Bader analysis[37].

3. Results and discussion

Figure 4 illustrates the dissociation energies of phenol into different radical products. Severance of O–H bond in phenol requires the least energy of 4.0 eV, while the dissociation of phenol into three radical parts (phenyl (C_6H_5), O and H) necessitates the highest energy of 9.9 eV. This Figure also shows that oxygen has a role of lowering the dissociation energy, hence phenol is expected to be more reactive than benzene.

Figure 4.

From Figure 1, the most stable surfaces are cases (a), (b), (c) and (d). Thus, we employ these four surfaces in the subsequent calculations. The trend in Figure 4 concurs with the fact that aromatic C-H bonds are significantly stronger than O-H bonds (4.8 eV versus 3.9 eV) [38]. There are four reactant configurations, i.e. phenol on pristine graphene, Stone-Wales, asymmetric monovacancy and 555777 divacancy. However, there are fourteen product configurations (Figure 3), and the calculated results for the products are listed in Table 1.

Table 1.

As seen in Table 1, cases 1Va and 1Vb respectively incur high reaction exothermicity of 2.1 and 2.2 eV, large charge transfers of 0.75 and 0.49 electron, dissociate phenol into C_6H_5O + H, and also adsorb the C_6H_5O and the H. All other cases relatively show low reaction exothermicity (between 0.2 and 0.5 eV), negligible charge transfers (0.01−0.02 electron) and significant separations between phenol and the surfaces (1.86–2.37 Å). Thus 1Va and 1Vb cases are chemisorption processes, while others are physisorption processes. Furthermore, it is easy to show that the chemisorption conditions rely on: (1) the presence of dangling bond on the surface, (2) the proximity of the dangling bond with the adsorbate, and (3) the assistance of C atom(s) adjoining the C atom with the dangling bond. These three conditions are fulfilled in 1Va and 1Vb cases. The low reaction energies of other cases are the result of no dangling bond on the surfaces, and thus are physisorption processes which is dominated by van der Waals force.

Adsorbing phenol using defective graphene with dangling bonds may not effective in a competitive environment in which the concentration of phenol is negligible compared with other species. So we compared adsorption of phenol with the analogous process encountered for water a molecule with an OH group. Sanfelix and Darling have calculated water dissociation into OH + H onto asymmetric monovacancy graphene and reported a barrier energy of ≈ 0.47 eV and reaction energy of ≈ −3.4 eV [39]. The reaction energy of water is higher to that of phenol (–2.1 or –2.2 eV). As such, there might be an adsorption competition between phenol and water, with the decisive route being determined by the transition energy requirements. Therefore, we performed transition states calculation for 1Va case, and as shown in Figure 5, the reaction occurs without a barrier. A reaction coordinate for the 1Vb case is expected to be similar to the 1Va case. So in this dissociation process, when compared to H atom in water, the C_6H_5 ring in phenol eliminates the barrier energy and also reduces the overall exothermicity of the reaction. This implies that, the C_6H_5O radical is attached more weakly to the monovacancy graphene than hydroxyl radical.

Figure 5.

In Figure 6, the spontaneous dissociation of phenol can be explained using the equivalency of the three asymmetric monovacancy configurations. Robertson et al. suggested that the

bonding in monovacancy graphene might oscillate among atoms B−C (Figure 6a), atoms A−C (Figure 6b), and atoms A−B (Figure 6c)[35]. Averaging this oscillation results in a symmetric monovacancy image (Figure 6d), as seen in the aberration-corrected transmission electron microscopy (AC-TEM) characterizations.

Figure 6.

The dissociation mechanism for the 1Va case is shown in Figure 7. Initially, the bond length of B−C is relatively shorter than that of A−B and A−C (reaction coordinate 7). As H atom approaches atom B, the surface rearranges the A−B−C bonding configurations, and results in a comparatively shorter A−C bond length (reaction coordinate 8). Lastly, the O atom attaches to atom A in reaction coordinate 9. It is surmised that in other cases, O atom may be attached to both atom A and C to saturate the dangling bond.

Figure 7.

Defective graphene with dangling bond is less stable than the ones without dangling bond. So our asymmetric monovacancy case is less favorable than Stone-Wales or even-numbered vacancy cases [40]. This can be quantified using energy per carbon atom. Energy/carbon atom for pristine graphene, Stone-Wales, monovacancy and divacancy are −9.29, −9.18, −9.13 and −9.16 eV/atom. At room temperature (300 K), their distributions are determined using Maxwell-Boltzmann statistics as 97.7%, 1.5%, 0.2% and 0.6%. This is certainly a drawback for our phenol dissociation process but such findings are useful for researchers focusing on surface design of nanoporous (activated) carbon for treatment of organics-laden wastewater. This is because defective graphene sheets are essentially the building blocks for porous carbon materials with eclectic porous structures.

In spite of the fact that monovacancy graphene appears effective in dissociating phenol into radical fragments, the practical applications may be somewhat challenging. The following questions are potential, as well as prospective for future studies. (1) Reusability of vacancy sites: effective elutriating and/or desorption methods are needed to remove the dissociated fragments from exhausted vacancy sites. This may include thermal treatments, redox recycling and chemical stripping. However, the stability of the vacancy sites in such

conditions must be critically considered. (2) Competition concern: besides water, the relative role of other compound with hydroxyl group requires further scrutiny. Strong attachment of adsorbents into graphene might facilitate their oxidative decomposition for instance. It is worthwhile mentioning in this regard that highly re-usable reduced graphene coated with ZnO for pollutants adsorptions has been synthesised [41]. Underlying factors for re-usability comprise mechanical, photolytic and thermal stability of the graphene composite.

4. Conclusions

Pristine graphene, graphene with Stone-Wales defect and divacancy graphene are not usually considered for dissociating phenol, due to their lack of dangling bond. However, graphene with asymmetric monovacancy is able to spontaneously dissociate phenol into phenoxy and an H atom, and also adsorb them. The process is assisted by the conditions of a dangling bond at the surface, the proximity of the O–H bond at this dangling bond, and the assistance of the nearby C atoms at the surface. It involves spontaneous bond rearrangement of the three equivalent asymmetric monovacancy configurations at the surface

Acknowledgements

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Table 1. Phenol adsorption on hollow site of graphene surfaces: G, SW, 1V and 2V signify pristine graphene, Stone-Wales, monovacancy and divacancy, respectively.

Case[1]	Reaction energy (eV)	Phenol height[2] (Å)	Charge transfer[3] (electron)	Phenol dissociated into C_6H_5O + H
Ga	-0.2	2.21	0.02	No
Gb	-0.2	2.18	0.02	No
SWa	-0.3	1.98	0.01	No
SWb	-0.3	1.88	0.02	No
SWc	-0.5	1.86	0.02	No
SWd	-0.4	1.92	0.01	No
1Va	-2.1	–	0.75	Yes
1Vb	-2.2	–	0.49	Yes
1Vc	-0.2	2.20	0.02	No
1Vd	-0.2	2.21	0.02	No
2Va	-0.2	2.27	0.02	No
2Vb	-0.2	2.22	0.01	No
2Vc	-0.2	2.26	0.02	No
2Vd	-0.2	2.37	0.01	No

[1] refer to Figure 3
[2] the distance between the bottommost H atom in phenol and the average height of C atoms at the surface
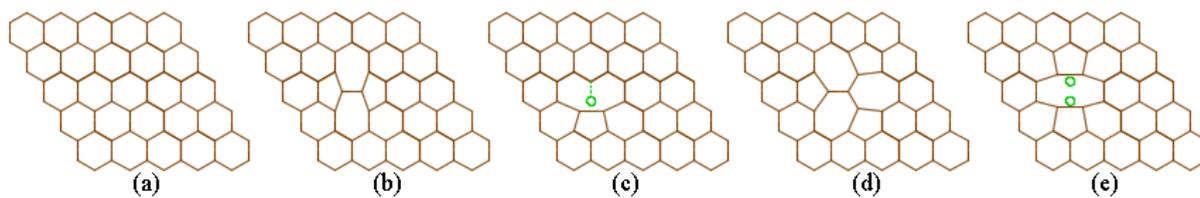[3] charge transfer from the surface to the (dissociated) phenol

Figure 1. Graphene surfaces: (a) pristine graphene, (b) graphene with Stone-Wales defect, (c) asymmetric monovacancy graphene, (d) 555777 divacancy graphene, and (e) 585 divacancy graphene. Green circle is the vacancy and green dashed line is dangling bond.
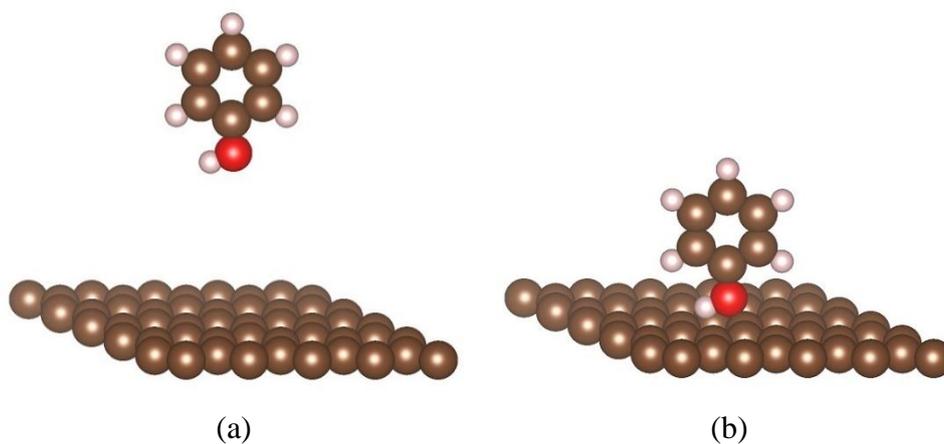
(a)   (b)

Figure 2. Phenol on graphene surfaces, typical initial configuration of (a) reactants, (b) products. Brown, red and white are C, O and H.
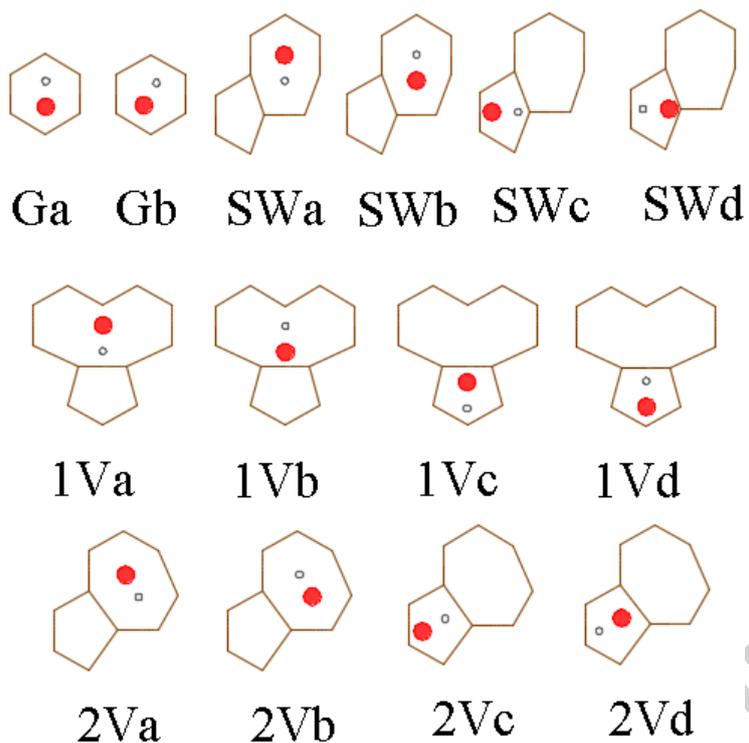
Figure 3. Phenol penetrates the hollow site of graphene surfaces. G, SW, 1V and 2V are pristine graphene (2 cases), Stone-Wales (4 cases), monovacancy (4 cases) and divacancy (4 cases). Large red and small white spheres denote O and H; respectively.
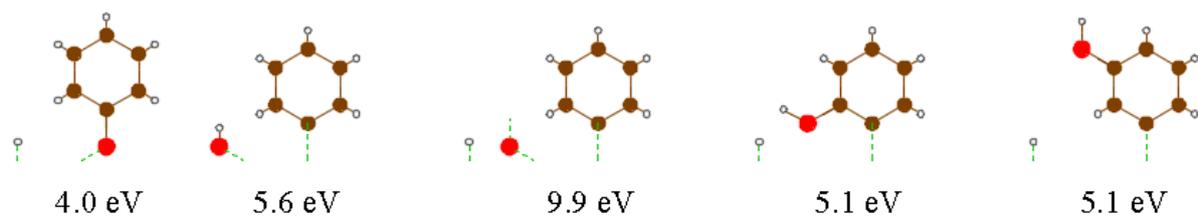
| 4.0 eV | 5.6 eV | 9.9 eV | 5.1 eV | 5.1 eV |

Figure 4. Products of phenol dissociation with its dissociation energies with respect to phenol in the gas phase. Brown, red and white are C, O and H. Green dashed line is dangling bond.
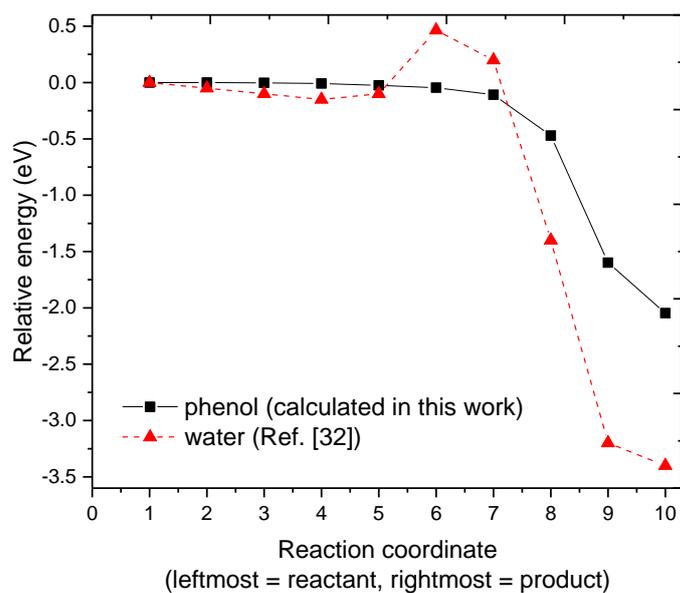
Figure 5. Reaction paths for phenol (1Va case, calculated in this work) and water (Figure 8 in Ref. [32]) dissociated onto asymmetric monovacancy graphene. The ordinate is relative to energy of the reactant.
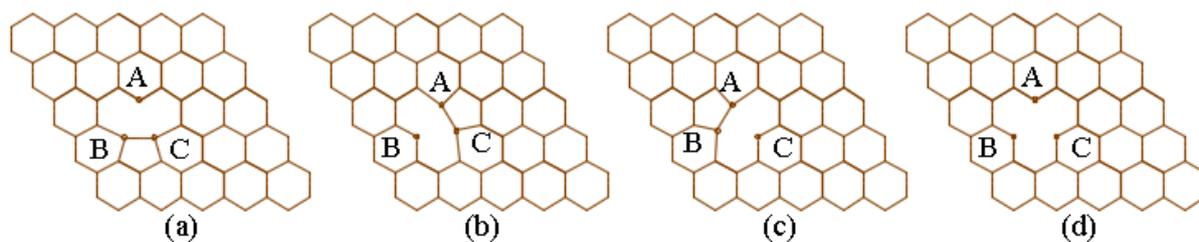
Figure 6. (a), (b) and (c) are equivalent configurations of monovacancy graphene. (d) is the average image of (a), (b) and (c) as seen in the aberration-corrected transmission electron microscopy (AC-TEM) characterizations.

(top view)   (top view)   (top view)

(oblique view)   (oblique view)   (oblique view)

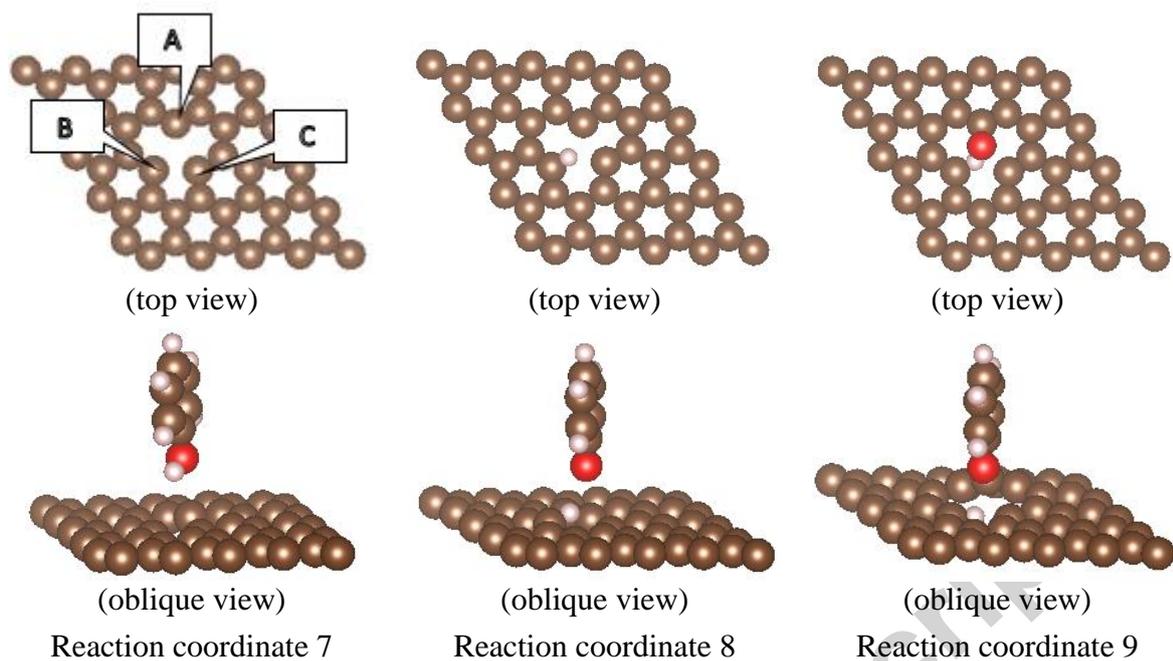Reaction coordinate 7   Reaction coordinate 8   Reaction coordinate 9
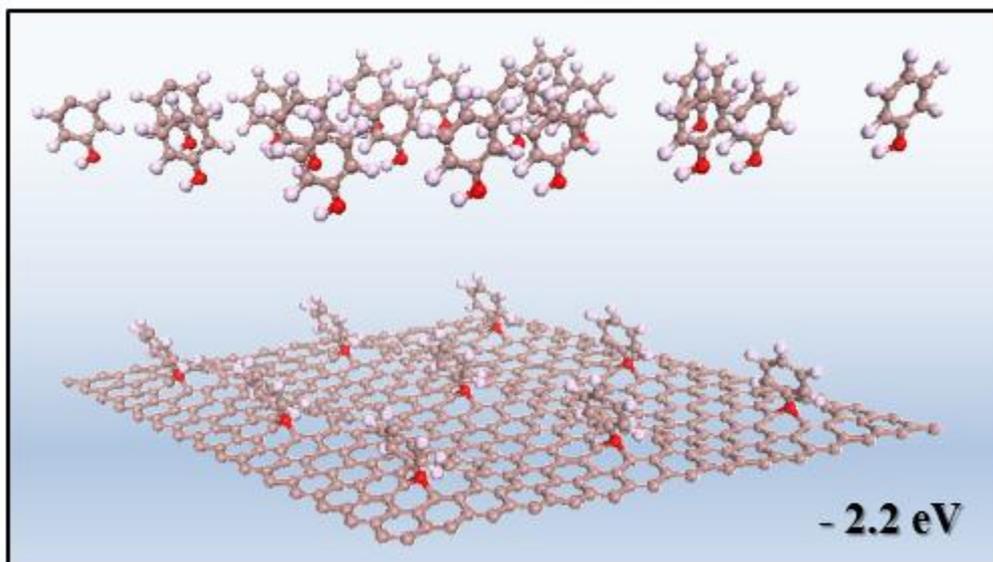
Figure 7. Phenol dissociation mechanism onto asymmetric monovacancy graphene (1Va). Brown, red and white are C, O and H. For the top view, phenol's atoms that are not connected to the surface are not shown for clarity.

- 2.2 eV

Highlights

- This contribution inspects phenol dissociation on both pristine and defective grapheme.

- Graphene with asymmetric monovacancy dissociates phenol into phenoxy and an H atom.
- Fission of the phenol O-H bond on this defective grapheme appears barrierless with reaction exothermicity as high as 2.2 eV.