

The catalytic performance of metal-free defected carbon catalyst towards acetylene hydrochlorination revealed from first principle calculations

Sajjad Ali^{‡,†,*}, Muhammad Baber Azam Khan[±], Said Alam Khan[€] and Noora[§]

[‡] Department of Physics, Southern University of Science and Technology, 518055 Shenzhen, China

[†] Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, Liaoning, China

[±] Government Post Graduate College Jehanzeb College, Swat, Pakistan

[€] Department of Physics, University of Malakand, 18800 Lower Dir, Pakistan

[§] Abdul Wali Khan University, 23200, Mardan, Pakistan

KEYWORDS: Metal-free catalyst, defected carbon, acetylene hydrochlorination, density functional theory

ABSTRACT: The defected carbon materials as a metal-free catalyst shown superior stability and catalytic performance in the acetylene hydrochlorination reaction. Through DFT calculation, for the first time several different defected configurations comprising mono, di-vacancies, and Stone Wales defect on single-walled carbon nanotubes (SWCNTs) have been used as a direct catalyst for acetylene hydrochlorination reaction. These defective sites on SWCNTs are the most active site for acetylene hydrochlorination reaction compared to pristine SWCNT. The different configuration of defects have different electronic structure, which specify that mono-vacancy defect, have more states adjacent to the Fermi level. The reactant acetylene (C_2H_2) adsorbed strongly than hydrogen chloride (HCl) and expected to be the initial step of the reaction Acetylene adsorbed strongly at mono-vacancy defected SWCNT compared to other investigated defects. The reaction pathways analysis revealed that mono- and di-vacancy defected SWCNT has a minimum energy barriers and shows extraordinary performance towards acetylene hydrochlorination. This work suggests the potential of metal-free defected carbon to catalyze acetylene hydrochlorination and provide a solid base for future developments in acetylene hydrochlorination.

1. INTRODUCTION

Vinyl chloride is polymerized to obtain polyvinyl chloride (PVC) which is important chemicals to manufacture engineering plastics¹⁻⁵. Moreover, acetylene hydrochlorination is the most important chemical process for obtained vinyl chloride. The industrial catalyst used worldwide for acetylene hydrochlorination is supported mercury. However, mercury is a toxic material to human health and environment¹⁻³. Recently the use of mercury in the PVC industry has been banned in the Minamata accord signed in Japan⁶⁻⁸. Therefore, the exploration of less expansive and most active catalysts to replace mercury is an important task.

The nanostructured carbon (NC) for example carbon nanotube, graphene, and nanodiamond are reported to be active metal-free catalysts in several catalytic reactions such as oxidative dehydrogenation⁹⁻¹⁴, oxygen reduction reaction¹⁵⁻¹⁸, and CO_2 electroreduction reaction etc¹⁹⁻²². Moreover, with doping or creating defects, we can further tune the properties of these carbon materials²³⁻²⁸. Vacancies in carbon materials are the most active sites for reactant molecules adsorption²⁵. SWCNTs and graphene have different types of defects like vacancies, dangling bonding, and Stone-Wales (SW) defects²⁹⁻

³². Recent research verified that these defects improve the physical and chemical properties of carbon materials²⁸. The existence of mono and di-vacancy in SWCNT has been verified experimentally by Krashennnikov *et al*³³. and Jin *et al*³⁴. Similarly, the Stone-Wales (SW) defect (5-7-7-5 configuration) is also observed in carbon materials^{29,35,36}. The SW defects are deliberately constructing into carbon materials to obtained positive functionality³⁷.

In this research by applying first principles, DFT calculations we for the first time use defected SWCNT catalyst that illustrated exceptional catalytic performance for acetylene hydrochlorination reaction. We have studied three kinds of defects in SWCNTs, i.e., a SW defect (i.e., a 5-7-7-5 defect formed by bond-rotation), a mono-vacancy (i.e., missing a single C-atom), and di-vacancy (i.e., missing two C-atoms). The interactions between reactants molecules i.e., acetylene (C_2H_2), hydrogen chloride (HCl) and the defected SWCNT are examined. Furthermore, the reaction mechanism is explored for acetylene hydrochlorination and the mono- and di-vacancy sites are determined to be the most active site from the calculated energy barrier among other defects. Our current research sheds the light on the potential catalytic ability of metal-free defected

carbon systems towards acetylene hydrochlorination reaction in the PVC industry.

2. COMPUTATIONAL METHODS

Density functional theory (DFT) in the form of the Vienna ab initio simulation package (VASP)³⁸⁻⁴⁰ has been used for all calculations. The Revised Perdew Burke Ernzerhof (RPBE) functional has been employed to define the exchange-correlation energy⁴¹. A $1 \times 1 \times 3$ k-points and 400 eV energy cutoff have been used for the optimized structures. To describe Van der Waals's corrections to the DFT calculations, we included the DFT-D3 correction method of Grimme⁴².

The adsorption energy (E_{ads}) was calculated using the following equation 1:

$$E_{\text{ads}} = E_{\text{ad-state}} - (E_{\text{reactants}} + E_{\text{SWCNT}}) \quad (1)$$

In equation 1, $E_{\text{ad-state}}$, E_{reactant} , and E_{SWCNT} are the total energies of the SWCNT with reactant adsorption, the isolated C_2H_2 or HCl, and the clean SWCNT respectively.

A $16 \times 16 \times 12 \text{ \AA}^3$ hexagonal supercell of SWCNTs was used for x, y, and z-direction. SWCNTs are periodic z-direction whereas the distance between neighboring cells is 12.5 \AA . For the edge calculation, we used a finite tube of both armchair and zigzag SWCNTs saturated with hydrogen atoms at the edges. The force convergence criterion was set to 0.05 eV/\AA in an optimized structure. The climbing image nudged elastic band (CI-NEB) method⁴³ was used to find a minimum energy path along the reaction pathways. The scheme of Bader was used for charge analysis^{44,45}.

3. RESULTS AND DISCUSSION

In the current research, we explore the role of metal-free defected SWCNT for acetylene hydrochlorination reaction. We comprehensively studied the effect of mono-, di-vacancy and Stone wales defects in SWCNTs, which shows excellent performance as a metal-free direct catalyst for acetylene hydrochlorination reaction as shown in Figure 1.

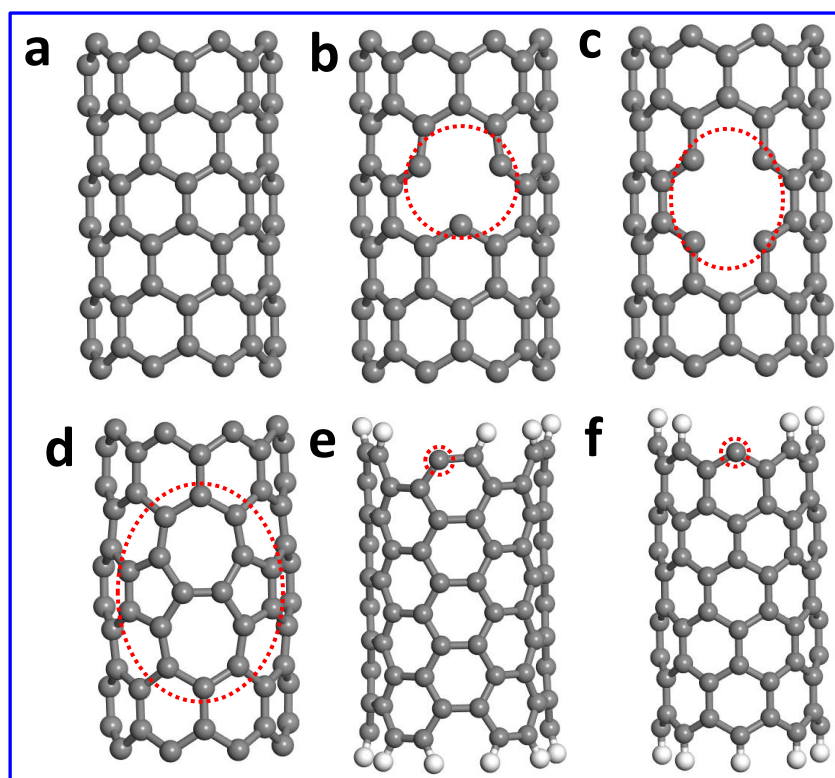


Figure 1. The optimized configuration of (a) pristine, (b) mono-vacancy, (c) di-vacancy, (d) Stone Wales defect, (e) armchair edge and (f) zigzag edge in SWCNTs respectively. The red circle represents the defective sites in SWCNTs.

Armchair and zigzag SWCNT saturated with hydrogen at the open ends are also considered for edge calculation. We have remove one hydrogen to create a defect the edge of these SWCNTs.

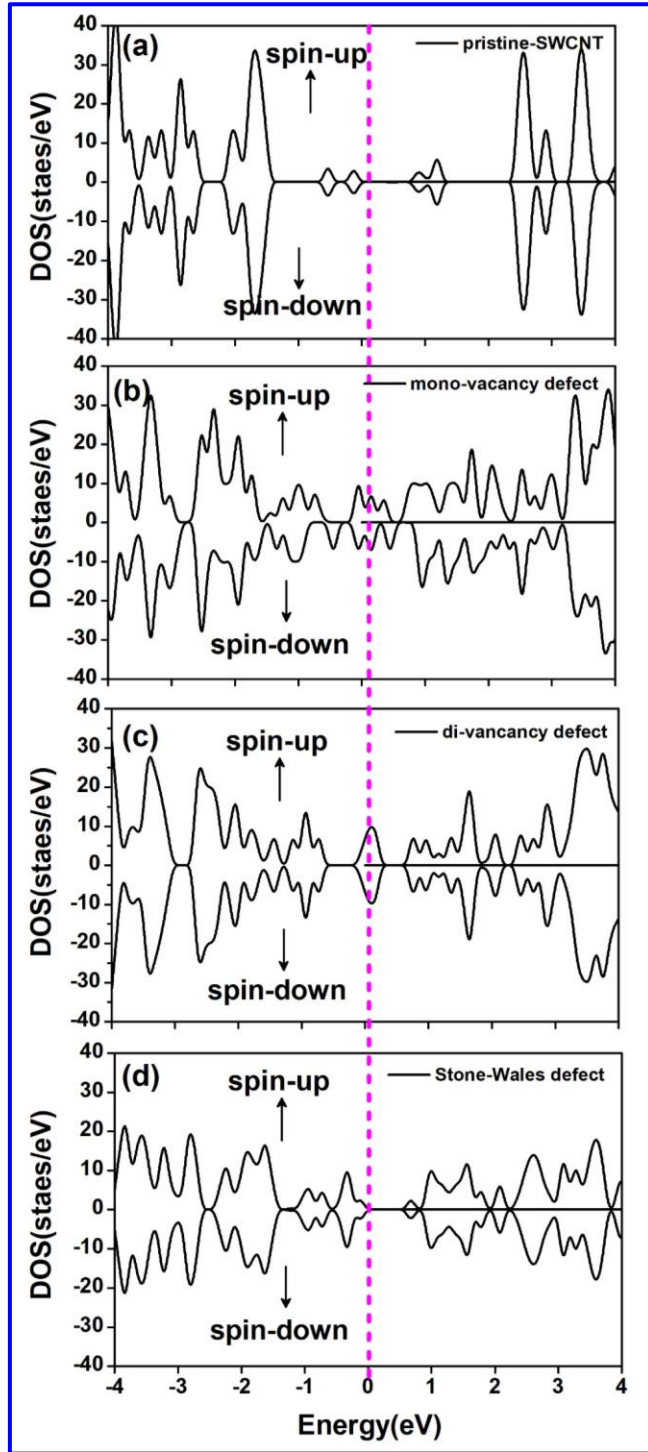


Figure 2. The total density of states (TDOS) of (a) pristine SWCNTs, (b) mono-vacancy defect, (c) di-vacancy defect, and

(d) Stone Wales defect in SWCNTs respectively. The Spin-up (↑) and spin-down (↓) states indicate positive and negative values, respectively. The Fermi level (E_F) is set to zero.

Firstly, due to its unique geometry, it is expected that electronic structures with different defects should have different characteristics. Therefore we have calculated and plotted TDOS of pristine, mono-vacancy defect, di-vacancy defect and Stone Wales defect in SWCNTs as shown in Figure 2. It is revealed from Figure 2 that mono and di-vacancy defects in SWCNT have more states adjacent to Fermi level compared to pristine and Stone Wales defect. Particularly, pristine and Stone Wales defected SWCNTs have insignificant contributing states around the Fermi level. The electronic structure has direct influence on the reactivity of different defects. As it is clear from Figure S1 that the LUMO and HOMO orbitals of C_2H_2 are mainly situated on the two carbons. Consequently, the C_2H_2 adsorption mostly takes place through the interactions between two carbon atoms with the active center.

The comparison among defective sites in SWCNT and the pristine site for reactants (C_2H_2 and HCl) adsorption and energy barrier results excellent reactivity of defective site. First, the adsorption energy of the reactants (C_2H_2 and HCl) are calculated.

Table 1: List of adsorption energy (eV) and charge $|Q|$ on C_2H_2 and HCl.

| Defect in SWCNTs | C_2H_2 -adsorption | $ Q $ on C_2H_2 | HCl-adsorption | $ Q $ on HCl |
|------------------|----------------------|-------------------|----------------|--------------|
| pristine | -1.1 | -0.02 | -0.15 | +0.01 |
| mono-vacancy | -2.65 | +0.2 | -0.83 | +0.32 |
| di-vacancy | -1.63 | +0.09 | -0.3 | +0.02 |
| Stone Wales | -1.27 | +0.13 | -0.22 | +0.014 |
| armchair edge | -1.97 | +0.02 | -0.17 | +0.009 |
| Zigzag edge | -2.44 | +0.03 | -0.11 | +0.003 |

Our DFT calculation specified that defective sites in SWCNTs have stronger adsorption energy compared to pristine

SWCNT. The adsorption energy of C_2H_2 and HCl is listed in Table 1. C_2H_2 and HCl adsorbed readily on defective sites however, C_2H_2 adsorption energy is stronger than HCl as it is clear from Table 1. The corresponding structures of C_2H_2 and HCl adsorbed on SWCNTs are shown in Figure 3. From Table

1 it is clear that defective sites in SWCNTs are stable adsorption sites for C_2H_2 adsorption compared to pristine SWCNT.

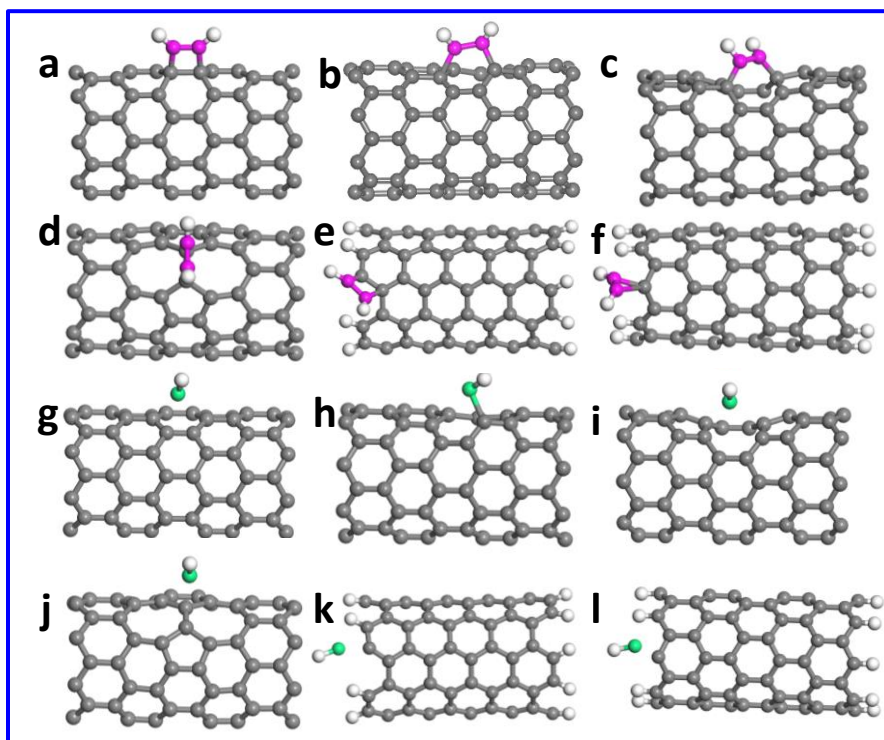


Figure 3. Optimized structure of (a-f) C_2H_2 adsorption and (g-l) HCl adsorption on pristine, mono-, di-vacancy, Stone Wales defect armchair edge and zigzag edge defected SWCNTs respectively. The grey, white, green and magenta color represents carbon atoms in SWCNT, hydrogen atoms, chlorine atoms and carbon atoms in acetylene molecule respectively.

We also considered other adsorption sites for C_2H_2 and HCl on these defective SWCNTs. However, defective sites are more stable for reactant adsorption. According to the Bader charge analysis, the charge is transferred from C_2H_2 to defective SWCNT whereas in pristine SWCNT the charge is transferred from the support to C_2H_2 . Therefore, C_2H_2 is a “Janus” molecule, which can accept and donate an electron and is consistent with previous literature study^{46,47}. Furthermore, it is very important to elaborate carefully the reaction pathway on pristine and defective SWCNTs as shown in Figure 4. Acetylene hydrochlorination is taking place in five steps along the reaction path. These steps are C_2H_2 adsorption (shown “A” in Figure 4), HCl interaction with C_2H_2 (B), the activation of HCl (C), the

product vinyl chloride formation and desorption (D, E, and F). As it is clear from Table 1 that C_2H_2 adsorbed strongly compared to HCl on pristine and defective SWCNTs therefore the first step of reaction pathways is C_2H_2 adsorption. This step is exothermic and is a barrier-less process, as it is clear from Figure 4. On the next step along with this reaction process HCl, attacks on adsorbed C_2H_2 , which is also an exothermic process. The bond distance between carbons in C_2H_2 with H, Cl, in states B indicated in Figure 4 is listed in Table S1. In the next step, vinyl chloride is formed by passing through the first transition states (C, TS1). As it is clear from Figure 4 that defective, SWCNTs have the lowest energy barrier on this step.

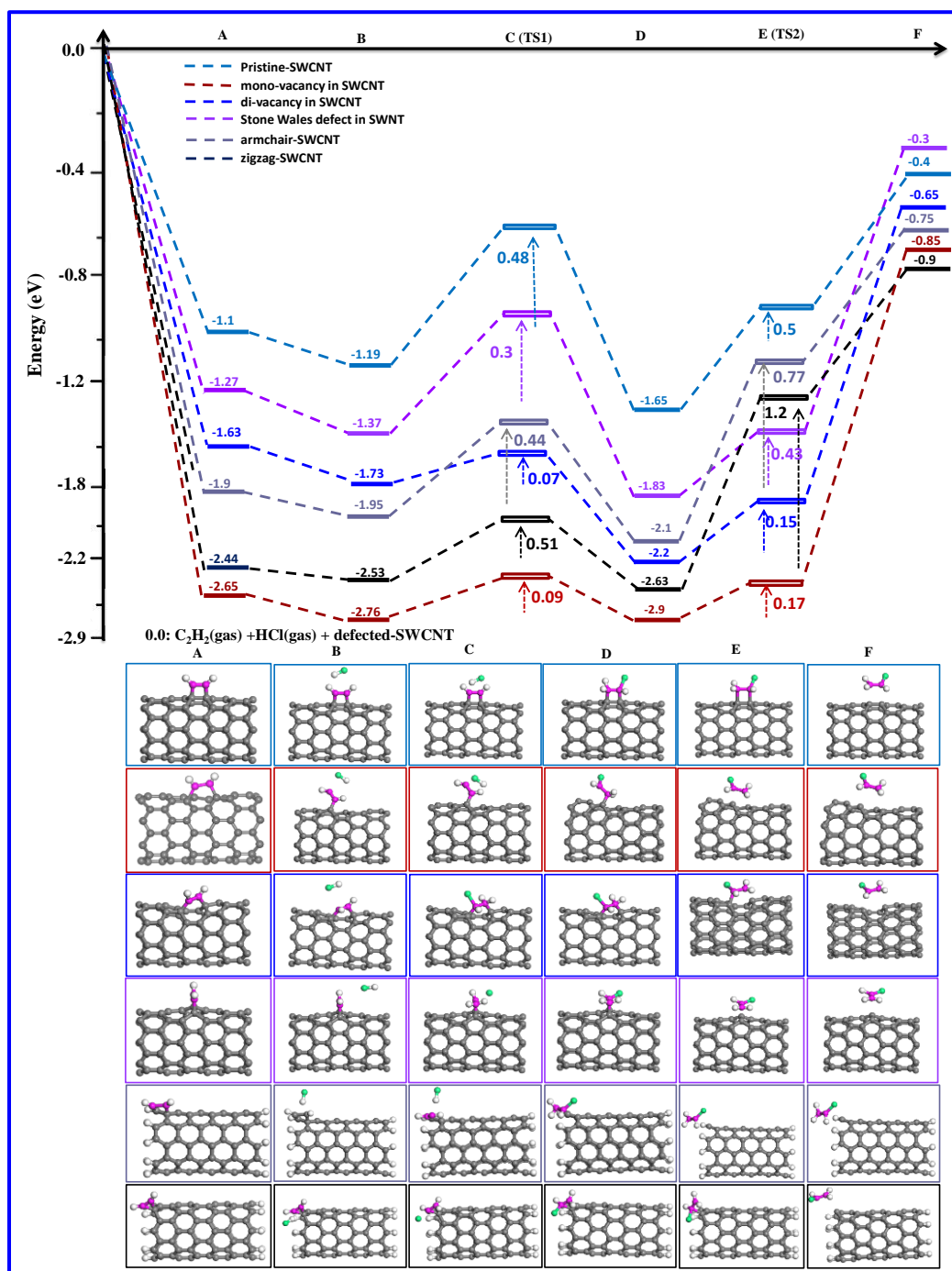


Figure 4. The reaction pathway of acetylene hydrochlorination. TS1 and TS2 signify the transition states. The zero points for energy represents the reactants (HCl and C₂H₂) in the gas phase and defected SWCNT. The adsorption energy and the barrier are measured in eV. The structures A, B, C, D and F on these reaction pathways are also included.

The final step of reaction path is product desorption from the support which also needs to surmount an energy barrier (E, TS2) The bond distance between carbon in C₂H₂ with H, Cl, in

C (TS1) and E (TS2) and energy barrier indicated in Figure 4 is listed in Table S2 and Table S3.

Our DFT calculation clearly has shown that the product vinyl chloride is easily desorbed from the mono and di vacancy defected SWCNTs compared to other defective sites in SWCNTs. A comparison of the energy barriers for acetylene hydrochlorination in the rate-limiting step obtained with different catalysts is listed in Table S4 where metal-free defected SWCNTs has minimum energy barrier.

Hence defective sites in SWCNTs show good catalytic performance compared to pristine SWCNTs regarding adsorption energies and reaction barriers. Whereas, among all defective SWCNT, mono- and di-vacancy in SWCNT shows excellent performance towards acetylene hydrochlorination reaction.

4. CONCLUSIONS

In this work, several different defected configurations comprising mono-, di-vacancies, and stone wales defect on single-walled carbon nanotubes (SWCNTs) have been used as a direct catalyst for acetylene hydrochlorination reaction. The defective sites in SWCNTs are the most active site for acetylene hydrochlorination reaction compared to pristine SWCNT. The reactant acetylene (C_2H_2) adsorbed strongly than hydrogen chloride (HCl) and expected to be the initial step of the reaction. Acetylene adsorbed strongly at mono-vacancy defected SWCNT compared to other investigated defects. The reaction pathways analysis revealed that mono- and di-vacancy defected SWCNTs have a minimum energy barriers and shows remarkable performance towards acetylene hydrochlorination. This work suggests the potential of metal-free defected carbon to catalyze acetylene hydrochlorination and provide a solid base for future developments in acetylene hydrochlorination.

ASSOCIATED CONTENT

AUTHOR INFORMATION

Corresponding Author

* Sajjad Ali.: e-mail, sajjad@alum.imr.ac.cn;

sajjad@sustec.edu.cn

ACKNOWLEDGMENT

This work is supported by southern University of Science and Technology.

REFERENCES

- (1) Zhu, M.; Wang, Q.; Chen, K.; Wang, Y.; Huang, C.; Dai, H.; Yu, F.; Kang, L.; Dai, B. Development of a Heterogeneous Non-Mercury Catalyst for Acetylene Hydrochlorination. *ACS Catalysis* **2015**, *5*, 5306-5316.
- (2) Oliver-Meseguer, J.; Doménech-Carbó, A.; Boronat, M.; Leyva-Pérez, A.; Corma, A. Partial Reduction and Selective Transfer of Hydrogen Chloride on Catalytic Gold Nanoparticles. *Angewandte Chemie International Edition* **2017**, *56*, 6435-6439.
- (3) Johnston, P.; Carthey, N.; Hutchings, G. J. Discovery, Development, and Commercialization of Gold Catalysts for Acetylene Hydrochlorination. *Journal of the American Chemical Society* **2015**, *137*, 14548-14557.
- (4) Liu, X.; Conte, M.; Elias, D.; Lu, L.; Morgan, D. J.; Freakley, S. J.; Johnston, P.; Kiely, C. J.; Hutchings, G. J. Investigation of the active species in the carbon-supported gold catalyst for acetylene hydrochlorination. *Catalysis Science & Technology* **2016**, *6*, 5144-5153.
- (5) Xu, H.; Meng, S.; Luo, G. Ionic liquids-coordinated Au catalysts for acetylene hydrochlorination: DFT approach towards reaction mechanism and adsorption energy. *Catalysis Science & Technology* **2018**, *8*, 1176-1182.
- (6) Li, X.; Pan, X.; Yu, L.; Ren, P.; Wu, X.; Sun, L.; Jiao, F.; Bao, X. Silicon carbide-derived carbon nanocomposite as a substitute for mercury in the catalytic hydrochlorination of acetylene. *Nature Communications* **2014**, *5*, 3688.
- (7) Chao, S.; Zou, F.; Wan, F.; Dong, X.; Wang, Y.; Wang, Y.; Guan, Q.; Wang, G.; Li, W. Nitrogen-doped Carbon Derived from ZIF-8 as a High-performance Metal-free

Catalyst for Acetylene Hydrochlorination. *Scientific Reports* **2017**, 7, 39789.

(8) Malta, G.; Kondrat, S. A.; Freakley, S. J.; Davies, C. J.; Lu, L.; Dawson, S.; Thetford, A.; Gibson, E. K.; Morgan, D. J.; Jones, W.; Wells, P. P.; Johnston, P.; Catlow, C. R. A.; Kiely, C. J.; Hutchings, G. J. Identification of single-site gold catalysis in acetylene hydrochlorination. *Science* **2017**, 355, 1399.

(9) Sun, X.; Han, P.; Li, B.; Mao, S.; Liu, T.; Ali, S.; Lian, Z.; Su, D. Oxidative dehydrogenation reaction of short alkanes on nanostructured carbon catalysts: a computational account. *Chemical Communications* **2018**, 54, 864-875.

(10) Li, B.; Su, D. S. Theoretical Studies on Ethylene Selectivity in the Oxidative Dehydrogenation Reaction on Undoped and Doped Nanostructured Carbon Catalysts. *Chemistry-an Asian Journal* **2013**, 8, 2605-2608.

(11) Pelech, I.; Soares, O.; Pereira, M. F. R.; Figueiredo, J. L. Oxidative dehydrogenation of isobutane on carbon xerogel catalysts. *Catalysis Today* **2015**, 249, 176-183.

(12) Mao, S. J.; Li, B.; Su, D. S. The first principles studies on the reaction pathway of the oxidative dehydrogenation of ethane on the undoped and doped carbon catalyst. *Journal of Materials Chemistry A* **2014**, 2, 5287-5294.

(13) Qi, W.; Su, D. S. Metal-Free Carbon Catalysts for Oxidative Dehydrogenation Reactions. *Acs Catalysis* **2014**, 4, 3212-3218.

(14) Sun, X. Y.; Ding, Y. X.; Zhang, B. S.; Huang, R.; Su, D. S. New insights into the oxidative dehydrogenation of propane on borate-modified nanodiamond. *Chemical Communications* **2015**, 51, 9145-9148.

(15) Song, J.; Liu, T.; Ali, S.; Li, B.; Su, D. The synergy effect and reaction pathway in the oxygen reduction reaction on the sulfur and nitrogen dual doped graphene catalyst. *Chemical Physics Letters* **2017**, 677, 65-69.

(16) Gong, K. P.; Du, F.; Xia, Z. H.; Durstock, M.; Dai, L. M. Nitrogen-Doped Carbon Nanotube Arrays with High Electrocatalytic Activity for Oxygen Reduction. *Science* **2009**, 323, 760-764.

(17) Ricca, C.; Labat, F.; Zavala, C.; Russo, N.; Adamo, C.; Merino, G.; Sicilia, E. B,N-Codoped graphene as catalyst for the oxygen reduction reaction: Insights from periodic and cluster DFT calculations. *Journal of Computational Chemistry* **2018**, 39, 637-647.

(18) Wang, T.; Chen, Z. X.; Chen, Y. G.; Yang, L. J.; Yang, X. D.; Ye, J. Y.; Xia, H. P.; Zhou, Z. Y.; Sun, S. G. Identifying the Active Site of N-Doped Graphene for Oxygen Reduction by Selective Chemical Modification. *Acs Energy Letters* **2018**, 3, 986-991.

(19) Liu, T. F.; Ali, S.; Lian, Z.; Li, B.; Su, D. S. CO₂ electroreduction reaction on heteroatom-doped carbon cathode materials. *Journal of Materials Chemistry A* **2017**, 5, 21596-21603.

(20) Hursan, D.; Janaky, C. Electrochemical Reduction of Carbon Dioxide on Nitrogen-Doped Carbons: Insights from Isotopic Labeling Studies. *Acs Energy Letters* **2018**, 3, 722-723.

(21) Chai, G. L.; Guo, Z. X. Highly effective sites and selectivity of nitrogen-doped graphene/CNT catalysts for CO₂ electrochemical reduction. *Chemical Science* **2016**, 7, 1268-1275.

(22) Kumar, B.; Asadi, M.; Pisasale, D.; Sinha-Ray, S.; Rosen, B. A.; Haasch, R.; Abiade, J.; Yarin, A. L.; Salehi-Khojin, A. Renewable and metal-free carbon nanofibre catalysts for carbon dioxide reduction. *Nature Communications* **2013**, 4.

(23) Ali, S.; Fu Liu, T.; Lian, Z.; Li, B.; Sheng Su, D. The effect of defects on the catalytic activity of single Au atom supported carbon nanotubes and reaction mechanism for CO oxidation. *Physical Chemistry Chemical Physics* **2017**, 19, 22344-22354.

(24) Ali, S.; Liu, T.; Lian, Z.; Li, B.; Su, D. S. The tunable effect of nitrogen and boron dopants on a single walled carbon nanotube support on the catalytic properties of a single gold atom catalyst: a first principles study of CO oxidation. *Journal of Materials Chemistry A* **2017**, 5, 16653-16662.

- (25) Andzelm, J.; Govind, N.; Maiti, A. Nanotube-based gas sensors – Role of structural defects. *Chemical Physics Letters* **2006**, *421*, 58-62.
- (26) Ali, S.; Liu, T.; Lian, Z.; Sheng Su, D.; Li, B. The stability and reactivity of transition metal atoms supported mono and di vacancies defected carbon based materials revealed from first principles study. *Applied Surface Science* **2019**, *473*, 777-784.
- (27) Qiu, Y.; Ali, S.; Lan, G.; Tong, H.; Fan, J.; Liu, H.; Li, B.; Han, W.; Tang, H.; Liu, H.; Li, Y. Defect-rich activated carbons as active and stable metal-free catalyst for acetylene hydrochlorination. *Carbon* **2019**, *146*, 406-412.
- (28) Ciraci, S.; Dag, S.; Yildirim, T.; Gülseren, O.; Senger, R. T. Functionalized carbon nanotubes and device applications. *Journal of Physics: Condensed Matter* **2004**, *16*, R901-R960.
- (29) Stone, A. J.; Wales, D. J. Theoretical studies of icosahedral C₆₀ and some related species. *Chemical Physics Letters* **1986**, *128*, 501-503.
- (30) Charlier, J. C.; Ebbesen, T. W.; Lambin, P. Structural and electronic properties of pentagon-heptagon pair defects in carbon nanotubes. *Physical Review B* **1996**, *53*, 11108-11113.
- (31) Krasheninnikov, A. V.; Lehtinen, P. O.; Foster, A. S.; Nieminen, R. M. Bending the rules: Contrasting vacancy energetics and migration in graphite and carbon nanotubes. *Chemical Physics Letters* **2006**, *418*, 132-136.
- (32) Ersan, F.; Üzengi Aktürk, O.; Aktürk, E.; Ciraci, S. Metal–Insulator Transition and Heterostructure Formation by Glycines Self-Assembled on Defect-Patterned Graphene. *The Journal of Physical Chemistry C* **2018**, *122*, 14598-14605.
- (33) Krasheninnikov, A. V.; Lehtinen, P. O.; Foster, A. S.; Pyykko, P.; Nieminen, R. M. Embedding Transition-Metal Atoms in Graphene: Structure, Bonding, and Magnetism. *Physical Review Letters* **2009**, *102*.
- (34) Jin, C.; Suenaga, K.; Iijima, S. Plumbing carbon nanotubes. *Nat Nano* **2008**, *3*, 17-21.
- (35) Dienes, G. Mechanism for Self-Diffusion in Graphite. *Journal of Applied Physics* **1952**, *23*, 1194-1200.
- (36) Lu, X.; Chen, Z.; Schleyer, P. v. R. Are Stone–Wales Defect Sites Always More Reactive Than Perfect Sites in the Sidewalls of Single-Wall Carbon Nanotubes? *Journal of the American Chemical Society* **2005**, *127*, 20-21.
- (37) Talukdar, K.; Mitra, A. K.: *The Role of Stone-Wales Defects in the Mechanical Behavior of a Zigzag SWNT*, 2009.
- (38) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science* **1996**, *6*, 15-50.
- (39) Kresse, G.; Furthmüller, J. Efficient iterative schemes for total-energy calculations using a plane-wave basis set. *Physical Review B* **1996**, *54*, 11169-11186.
- (40) Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. *Physical Review B* **1993**, *47*, 558-561.
- (41) Hammer, B.; Hansen, L. B.; Nørskov, J. K. Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. *Physical Review B* **1999**, *59*, 7413-7421.
- (42) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *The Journal of Chemical Physics* **2010**, *132*, 154104.
- (43) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *The Journal of Chemical Physics* **2000**, *113*, 9901-9904.
- (44) Bader, R. Atoms in Molecules: A Quantum Theory *Oxford University Press* **1990**.
- (45) Henkelman, G.; Arnaldsson, A.; Jónsson, H. A fast and robust algorithm for Bader decomposition of charge density. *Computational Materials Science* **2006**, *36*, 354-360.
- (46) Ali, S.; Qiu, Y.; Lian, Z.; Olanrele, S.; Lan, G.; Li, Y.; Su, D. S.; Li, B. Screening of active center and reactivity descriptor in acetylene hydrochlorination on metal-free doped carbon catalysts from first principle calculations. *Applied Surface Science* **2019**, *478*, 574-580.

(47) Ali, S.; Olanrele, S.; Liu, T.; Lian, Z.; Si, C.; Yang, M.; Li, B. Single Au Anion Can Catalyze Acetylene Hydrochlorination: Tunable Catalytic Performance from Rational Doping. *The Journal of Physical Chemistry C* **2019**, *123*, 29203-29208.