Contents lists available at ScienceDirect





Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

Binding of phenolic model compounds with noble metal doped graphene sheets



Anand Mohan Verma, Kushagra Agrawal, Nanda Kishore*

Department of Chemical Engineering, Indian Institute of Technology Guwahati, Assam 781039, India

ARTICLE INFO

ABSTRACT

Keywords: Graphene Doping Palladium Platinum Phenols Lignin Bio-oil Density functional theory Presence of large number of oxygenates in raw bio-oil restrict its application as transportation fuel. Therefore, there is a strong necessity of finding a viable catalyst for upgrading raw bio-oil to transportation fuel level. In this study, palladium- and platinum- doped graphene sheets are examined theoretically for possible interactions of oxygenates such as guaiacol, phenol, anisole, vanillin, and salicylaldehyde on to metal doped graphene catalyst surfaces to understand preliminary adsorption mechanisms. For this purpose, B3PW91 functional of density functional theory (DFT) has been utilized. Adsorption kinetics, for instance, adsorption free energy, adsorption enthalpy, and equilibrium rate constant at a fixed pressure of 1 atm but over a wide range of temperature (400-800 K) are reported. Briefly results indicate that binding of both metals at vacant site of graphene sheet is found to be high energy releasing process and excellently agree with their contemporary literature results. The interaction of hydroxyl group of salicylaldehyde with Pd-doped graphene (PdGr) surface is most favourable configuration, whereas, Pt-doped graphene (PtGr) surface exhibited superior adsorption stability through phenyl ring. Binding of guaiacol, phenol, and anisole are energetically most favourable by phenyl ring interaction over each surface. Vanillin interacts strongly by oxygen atom of formyl group over PtGr surface. Further the values of adsorption kinetic parameters are very high for all model species; however, temperature increment deteriorates them. Finally, for each adsorption configuration of all model species over both catalyst surfaces, ln(Keg) vs. 1/T relation is proposed.

1. Introduction

Pyrolytic bio-oil derived from lignocellulosic biomass is generally comprised of various organic fractions such as acids, esters, sugars, phenols, aromatics, hydrocarbons, etc. The 'phenolic' fraction of raw bio-oil is a complex mixture of numerous phenolic components such as phenol, guaiacol, catechol, syringol, and many other such compounds [1]. These compounds contribute excessive amount of oxygen content in raw bio-oil which is a root cause of its low pH, low heating value, high viscosity, and high density. Hence, its application in transportation vehicle is not endorsed, therefore, unprocessed bio-oils are generally channelled through various upgrading techniques; and catalytic hydrodeoxygenation (HDO) is one of the best of all available upgrading processes. In the recent past, a significant amount of research has been dedicated to synthesize a viable catalyst for bio-oil upgrading but till date, no optimum catalytic system has been synthesized which is inexpensive, easily available, highly active and product selective. It has been recently reviewed that noble metal catalysts are better option for upgrading bio-oil compared to conventional hydrotreating catalysts,

* Corresponding author. E-mail addresses: nkishore@iitg.ernet.in, mail2nkishore@gmail.com (N. Kishore).

https://doi.org/10.1016/j.comptc.2018.05.001

Received 3 March 2018; Received in revised form 1 May 2018; Accepted 1 May 2018 Available online 02 May 2018

2210-271X/ © 2018 Elsevier B.V. All rights reserved.

i.e., sulfided NiMo or CoMo [2]. Further, catalyst supports, for instance, Al₂O₃, SiO₂, TiO₂, MgO, C, etc. could play a vivacious role in being product selective along with metal catalysts [2]. Unlike acidic and basic catalyst supports, carbon supports show better stability in both acidic and basic environments and, thus, they have received a considerable amount of attention as catalyst support in bio-oil upgrading [2,3]. Furthermore, numerous types of carbon supports are tested, e.g., activated carbon, carbon black and carbon nanostructures; however, amongst all, carbon nanostructures such as graphene sheets, carbon nanotubes and carbon nanofibers are momentously sought after recently as catalyst support because of their impressively high surface area, tensile strength, thermal stability, recyclability, etc. [4,5]. Recently, a comprehensive review is presented by Lam and Luong [6] on superiority of carbon as catalyst support in conversion of biomass to fuel and other valuable products.

Carbon nanostructures, especially, graphene sheets have become widely popular because of their outstanding mechanical and chemical properties, e.g., pristine graphene at room temperature has a very high electron mobility of $\sim 10000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, theoretical specific surface

area of 2630 m² g⁻¹, 2.3% white light absorbance with negligible reflectance, thermal conductivity of 3000–5000 W m⁻¹ K⁻¹, and a Young's modulus of 1 TPa [7–11]. Graphene is a two-dimensional sheet with strong sp²-hybridised carbon atoms in hexagonal monolayer [8]. Further, due to sp² bindings between carbon atoms, it is chemically inert and shows weak interaction with the reaction center which consequences the possibility of graphene as catalyst support for hetero metal atoms [3,12]. Therefore, this combination of noble metal catalyst on graphene support would considerably influence the selectivity and yield of desired products in bio-oil upgrading process. For graphene as catalyst, chemical inertness paves its way; however, recent studies indicate that doping of heteroatom especially transition metal (TM) atom at the defect site of graphene could substantially increase its electronic structure and chemical reactivity [3,13,14]. Thus, transition metal doped graphene sheets have a great potential in catalysis.

Despite such great advantages, only a little research work in bio-oil upgrading area utilizing graphene sheet as catalyst support or metal doped graphene sheet as catalyst exist in literature. For instance, Wu et al. [15] performed hydrogenation of levulinic acid to produce Yvalerolactone (GVL) over graphene supported ruthenium nanoparticles. They observed high catalytic activity and reported 96% of GVL yield at low temperature of only 30 °C. In addition, they also concluded that electron rich Ru nanoparticles are due to π-electron structure of graphene which enhances activity of hydrogenation of C=O bonds in levulinic acid. Similarly, Shi et al. [16] carried out conversion reactions of aromatic bio-oil compounds over Ru nanoparticles encapsulated within nitrogen doped graphene (Ru-G) sheets. In addition, they also compared their results with other supports such as activated carbon, SiO₂, Al₂O₃, Fe₃O₄, and MgO; and showed that hydrogenation of all aromatic compounds with very high percentages of selectivity and conversion over Ru-G sheets compared to all other supports. Wang et al. [17] analysed difference between performances of reduced graphene oxide (rGO) and benzenesulphonic acid functionalized reduced graphene oxide (rGO-S) supported Ru nanoparticles for hydrogenation of levulinic acid to produce GVL. They observed higher yield of GVL over Ru/rGO-S compared to Ru/rGO because of bifunctionality of catalytic system.

On the other hand, theoretical works applying graphene supported catalytic HDO of raw bio-oil are only a few. The application of graphene as catalyst support for Ru nanoparticles is carried out by Rubeš et al. [18] for HDO of phenol numerically. The $C_{aromatic}$ —OH bond scission over bare Ru nanoparticles were reported unstable; however, graphene supported Ru nanoparticles stabilized C—O bond scission which, in turn, reduced energy requirement. Another theoretical work is due to Fellah [19] who carried out decarbonylation reaction of furfural to produce furan over Pt-doped graphene sheet. They reported overall activation energy as 19.6 kcal/mol with conclusion of furan formation elementary reaction step as rate controlling reaction step. On the other hand, authors have not found any theoretical study pertaining to surface characteristics of metal doped graphene sheets in adsorptions of bio-oil model compounds.

Furthermore, binding of substrate to catalyst surface is a key step in order to understand structural favourability because it helms reaction progress due to its interaction with surface. For instance, noble metal catalysts with neutral support, e.g. carbon allotrope, exhibit excellent hydrogenation activity for aromatic oxygenated compounds because phenyl ring binds strongly to the surface compared to other functional groups, whereas, noble metals with acidic supports exhibit strong deoxygenation capability due to its strong functional interaction and very low ring instability [2]. Consequently, it is mandatory to understand binding configurations of substrates on to catalyst surface. Therefore, in this work, the adsorption characteristics of a few phenolic bio-oil model compounds such as phenol, anisole, guaiacol, salicylaldehyde (2-HB), and vanillin (see Fig. 1 for molecular structures) over Pd- and Pt-doped graphene sheets are considered under density functional theory (DFT) framework. In this process, various adsorption



Fig. 1. Molecular structures of considered phenolic species.

configurations of model compounds are considered and reported their kinetics over Pd and Pt metal doped graphene sheets over a wide range of temperature, i.e., 400–800 K at an interval temperature of 100 K.

2. Computational details

Pristine graphene sheet is developed employing 14 benzene rings which included 42 carbon atoms. Dangling carbon atoms at the edges are terminated using 16 hydrogen atoms (Fig. 2a). Further, a single vacancy is created in the graphene sheet by removing a carbon atom (Fig. 2b) so that to allow deposition of Pd or Pt metal atom. The existence of defect site in graphene sheet could allow deposition of transition metal atoms and recently, various literature observations have avowed this phenomena [13,14,20]. Deposition of heteroatom over graphene vacancy is a very vital amendment because it modifies electronic and magnetic properties of graphene that may be helpful in synthesizing a novel and advanced catalyst [12,13,20]. Nevertheless, upon deposition of Pd or Pt atom over monovacant site of graphene, metal atom binds with neighbouring carbon atoms of graphene with release of high energy (see Fig. 2c and Fig. 2d for Pd and Pt doping, respectively). The spin state analyses of metal doped graphene are performed through single point energy calculations at various spin multiplicities (SM = 2S + 1, where S is total spin of the system); and relative energies at various spin multiplicities are presented in Table 1. Further, metal atom doped graphene is applied for adsorption of phenolic species, i.e., phenol, anisole, guaiacol, 2-HB, and vanillin with fixed spatial movement of graphene surface. The adsorption energies of metal atoms over monovacant graphene and phenolic components over metal doped graphene are evaluated using following equations:

$$E_{ads}(Pd \text{ or } Pt) = E_{Pd} \text{ or } Pt \text{ doped graphene} - (E_{Pd} \text{ or } Pt + E_{monovacant graphene})$$
(1)

 $E_{ads}(Phenolic Components) = E_{adsorbate+metal doped graphene}$

$$-(E_{adsorbate} + E_{metal \ doped \ graphene})$$
(2)

Further, chemical hardness (η), chemical potential (μ) and electronegativity (χ) of metal doped graphene sheets are evaluated using following equations, respectively:

$$\eta \cong (I - A)/2 \tag{3}$$

Download English Version:

https://daneshyari.com/en/article/7838813

Download Persian Version:

https://daneshyari.com/article/7838813

Daneshyari.com