

## Research article

# Elucidating the alkene hydrogenation reaction based on cotton textile reduced graphene oxide under the influence of external electric field: Illustration of new noble method

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## ABSTRACT

The hydrogenation reaction of alkene is one of the most used industrial chemical process for various materials of daily life and energy consumption. This is a heterogeneous reaction and traditionally carried out by metallic catalysis. However, these conventional catalytic hydrogenations of alkene suffer from various setbacks such as catalyst poisoning, less recyclability and are environmentally unfriendly. Therefore, in recent years, researchers have been trying to develop the alternatives to metal catalysis hydrogenation of alkene. Heterogeneous catalysis under the external electric field is considered the future of green catalysis. In this paper, we report a comprehensive investigation dealing with the theoretical basis for simulating the phenomenon of heterogeneous catalysis, on a molecular level, under an external electric field. The illustration of the prospect as well as the effects of the mostly used catalytic systems, reduced graphene oxide, under the influence of external electric fields is provided. Moreover, a noble method of alkene hydrogenation reaction based on cotton textile reduced graphene oxide (CT-RGO) under the influence of an external electric field is introduced. The corresponding theoretical investigation was carried out within the framework of the density functional theory (DFT) method using first-principles calculations. The study has been carried out by elucidating DFT calculations for three different proposed catalytic systems, namely without electricity, with electricity and with an external electric field of 2 milli-Atomic unit. The obtained results indicate that adsorption energy of H<sub>2</sub> on the CT-RGO surface is significantly higher when the electric field is applied along the bond axis, suggesting thereby that hydrogenation of alkene can be induced with CT-RGO catalyst support under external electric fields. The obtained results shed light on the effect of the external electricity field on the graphene-hydrogen complex, the activation energy of graphene radicals to achieve the transition states as well as the adsorption of the hydrogen atoms over the graphene surface. Altogether, the theoretical results presented herein suggested that the proposed catalytic system holds promise for facilitating the alkene hydrogenation under external electric fields.

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## 1. Introduction

The effects of the external electric field on heterogeneous catalysis is a central topic of research interests for a while now. Since electric fields are readily exploitable, the oriented electric field can promote chemical reactions occurring on the surface of electrodes [1]. In the context of hydrogenation, Peeters et al. [2] reported the hydrogenation of graphene by applying EEF, where the role of EEF can replace the metallic catalyst in driving the hydrogenation process. The application of EEF enhances the dissociative adsorption of hydrogen molecules [3]. The effects of external electric fields on electrochemical reactions can be rationalized by the interactions of ion charge on the electrodes of the reactor vessel [4]. In this consideration, the ion charge pairs affect the local properties and change the bond strength, ionicity bond dissociation energy and other properties of the reactant molecules and favors towards products. Therefore, the reactant molecules generate non-uniform fields and these fields weaken the covalent adsorbates over longer distances and increase the polar adsorbates, which have direct chemical impact on the double layers [5]. However, it can be considered that specific ions can functionalize the surface over long-range electrostatic changes. These electrostatic changes along with their effects in the major reaction intermediates can control the kinetics of the reactions.

In recent studies, the evaluation of the interfacial electric fields at the junction of a dielectric and conductor was carried out by applying a technique known as vibrational sum frequency generation [6–8]. Bhowmik et al. [9] used the Onsager model for the accounts of system asymmetry and rationalized their argument that metals are significantly responsible for the molecular polarization of tethered molecules in the reaction. Moreover, another study also argued that the ionic concentration in the electrolytes could potentially modulate the interfacial electric fields [10]. Therefore, in the presence of a positive potential, thermodynamic drive for the continuous electrochemical reactions can be increased by the EEF and hence solidifying the claim of effective roles of electric fields in these electrochemical reaction systems. It is interesting to notice that reduction of graphene oxide (GO) is an easy way to obtain uniform and thin conductive coatings on a wide range of substrates, such as textiles [11]. GO can be applied by several techniques, including spray coating [12], solvent casting [13] and dip coating [14]. Then, reduced graphene oxide (rGO) can be obtained by thermal annealing [15] or chemical treatments with proper reducing agents such as ascorbic acid [16] or hydrazine [17]. Chemical treatments have the advantage of preserving the carbon plane structure more efficiently than the thermal annealing processes, which induce the desorption of oxygen-containing functional groups from the GO planes.

Specifically, rGO coating is very appropriate for cotton textiles, since the residual oxygen-containing functional groups are able to interact via hydrogen bonding with the hydroxyl functional groups of cellulose, ensuring excellent adhesion to the fabric [18]. Also, rGO based coating is properly suitable for piezoresistive applications, being sensitive to mechanical or electrical stresses [19]. However, the intrinsic feature of an EEF for applying in the chemical reactions greatly suffered from two main issues [6]. The first issue being the adjustment of the orientation of the applied electric field along the reaction axis and the second issue involves precise assessment of the field strength for the reaction to proceed forward. Moreover, even though, in the gas phase, the effects of electrostatic interactions could be significantly large enough, but in the solvent phase, these effects tend to diminish as the polarity of the solution increases [20,21]. Even though EEF catalysis possesses high potential and promises for controlling the reactivity and selectivity of the conventional reactions, this process suffers from various technical and theoretical limitations [22]. This is a relatively new field of research and the majority of the work and development of the field are mostly restricted to theoretical investigation due to the orientation and strength issue of the external electric field for specific chemical reactions. The earliest work of controlling reactivity and selectivity of carbon-carbon bond formatting reactions was not until 2016 [23]. The authors used STM-BJ techniques to study the reaction. Though the proposed surface model system was not adequate for larger and practical scale, the study opened the doors to possibility and opportunities to experimentally observe the electrostatic phenomena of various reactions.

The effects of oriented EEF on the reactivity and selectivity raise a series of scientifically interesting and coherent questions. Moreover, Shaik's group also indicated that an oriented electric field can effectively control the chemical reactivity and selectivity [6]. The oriented electric field applied along the reaction axis can efficiently reduce the activation energy of the reactants by a significant amount and thus reducing the reaction barrier and stabilizes the transition states. Aragonés et al. [24] demonstrated these predictions in their STM based experimental study. Moreover, discriminations among the chiral centers can also be achieved by stabilizing the dipole moments of the reactants under the oriented EEF [15]. However, beside the aforementioned reactions, implications of EEF in other organic reactions still remain unexplored. One of such important reaction is the hydrogenation reaction of alkene. Despite industrially and widely adopted conventional metal catalysis of alkene hydrogenation, this approach does not have various environmental and technical hazards in the reaction medium [25]. Therefore, this paper will first discuss the theoretical basis of EEF catalysis. Then, a brief discussion is presented on the reduced graphene oxide (RGO) based catalytic systems that can be structurally and experimentally for alkene hydrogenation under the external electric field. Finally, we introduce a noble method of alkene hydrogenation reaction based on cotton textile reduced graphene oxide (CT-RGO) [26–29] under the influence of an external electric field. The initial DFT calculations of three different systems—without electricity, with electricity and EEF of 2 mAu (milli-Atomic unit). The DFT calculations indicate that adsorption energy of  $H_2$  on the CT-RGO surface is significantly higher when electric field is applied along the bond axis. Therefore, hydrogenation of alkene can be induced with CT-RGO catalyst support under external electric field.

## 2. Theoretical basis of reaction under EEF

Oriented external electric fields, if applied along the bond axis of the molecule, induce various changes in the electronic features of the molecule as well as changes in the bond lengths, bond dissociation energy, ionicity and frequency of the molecule [30]. These changes due to the orientated external electric fields can be explained with the perspective of either molecular orbital theory or

valence bond theory. However, valence bond theory is more suitable due to its conceptual advantages and coherent implications for explaining the features of various EEF reactions. Therefore, this study discusses the theoretical basis of reaction induced by EEF from both molecular orbital (MO) and valence band (VB) theory perspectives, with an extension on VB in the later explanations.

The effects of oriented EEF on the homo-nuclear bonds can be explained based on MO theory. For instance, in case of H—H, the simplest homo-nuclear bond in a molecule, oriented EEF causes orbitals of hydrogen atoms to go through convolution (orbital mixture) if the symmetry of the applied electric field is equivalent to the symmetry of the product of the mixing orbitals [31]. It is important to note that, in absence of an applied electric field, mixing the molecular orbitals generates forbidden symmetry. Therefore, the product of the  $\sigma$  and  $\sigma^*$  molecular orbitals in the H—H molecule will likely mix and hybridize by acquiring electron clouds on either side (right or left) atoms [19]. Let us first focus on a homo-nuclear bond, for example, H—H, and start from the MO perspective. This hybridization is possible due to the equivalent symmetry generated by molecular orbitals and external electric field applied along the bond axis of the molecule. The dipole moment of the molecule is also generated from this hybridization of the molecular orbitals that stabilize the applied electric field energetically [32]. The inversion of the dipole moment can be achieved by flipping the external electric field along the bond axis.

However, from the VB theory perspective, a bond is represented by the superposition of the corresponding wave functions [33]. In this regard, any bond can be considered as a superposition of three valence bond structures: two ionic VB structures ( $\varphi_{i1}$  and  $\varphi_{i2}$ ) and one covalent VB structure ( $\varphi_{cov}$ ) [34]. In the case of mononuclear bonds, such as H—H, the bond wave function of the ground state is generated from the mixture of two ionic structures with the equal covalent structure [35]. Before the mixing, the ionic structures degenerate in absence of an external electric field. When oriented EEF is applied along the bond axis (conventionally z axis) of the molecule, one of the ionic VB structures (say,  $\varphi_{i1}$ ) preferentially mixes with the covalent VB structure ( $\varphi_{cov}$ ) due to the fact that  $\varphi_{i1}$  becomes disproportionately stabilized due to the external field. This mixture of one ionic VB structure and one covalent VB structure produces bond ionicity oriented in the same direction as the orientation of the charges in this ionic structure. Similar to the MO perspective, in VB perspective, inverting the oriented EEF will flip the induced dipole moment since relative stabilization of the ionic structures also gets inverted by flipping the external electric field. Therefore, it is evident that as the strength of the external electric field applied along the axis is increased, the ionic VB structure  $\varphi_{i1}$  will become increasingly more stabilized and tends to approach the energy of the covalent VB structure. The stabilization of a specific ionic VB structure ( $\varphi_{i1}$ ) in a given external electric field strength is related to the dipole moment of the ion-pair. This relationship is expressed by the following equation:

$$\Delta E = \vec{F} \cdot \frac{\vec{\mu}}{4.8} \quad (1)$$

In the above equation,  $\Delta E$  represents stabilization energy (in eV),  $\vec{F}$  is the electric field (in V/Å or in a.u.) and  $\vec{\mu}$  is the dipole moment (in Debye), respectively. The dipole moment in its turn is proportional to the distance between the poles,

$$\vec{\mu} = 4.8Q \cdot \vec{R} \quad (2)$$

In Equation (2),  $Q$  refers to the charge of the poles (usually in e units) and the distance (in Å) between them.

The generalization of Equation (1) and Equation (2) is:

$$\Delta E = Q \times (\vec{F} \cdot \vec{R}) \quad (3)$$

Therefore, maximizing the interaction of the dipole within the given field, will change the geometric preference of the specific ionic structure. In presence of the external electric field, the interaction with the ion-pair's dipole moment will drive apart the oppositely charged ions to the farthest distances, whereas, the absence of the external electric field generates a minimum short range energy from the intrinsic-electrostatic interaction of the ion-pair [36]. Therefore, the bond elongation is observed in the presence of an external electric field when the field strength is increased along the bond axis. Moreover, bond heterolysis among the ionic VB structures was also observed at some critical field strength [33]. This is due to the fact that, at some critical field strength, the ionic structure is likely to lose its minimum intrinsic electrostatic energy and overcome the covalent structure.

However, unlike the homo-nuclear bond, in case of hetero-nuclear bond, one of the ionic VB structures remains readily dominant in the absence of the external electric field. The direction of the applied oriented EEF essentially stabilizes the dominant VB structure [37]. For instance, if the direction of applied EEF is towards the reaction axis which increases the stability of the dominant VB structure and increases the polarization and bond ionicity of the molecule towards the direction of  $\varphi_{i1}$ . The oppositely directed applied EEF will have the opposite effects on ionicity and polarization which destabilizes the dominant VB structure. In case of increase in the bond ionicity, at a significantly lower electric field, the bond dissociation is much faster, especially in the presence of atoms or groups which are highly polarizable. In case of decrease in bond ionicity, the opposite phenomenon is observed. Though, in presence of strong electric fields the ionic structures will inevitably cross each other and lead to the reversal in bond ionicity [38]. This action is facilitated by the increasing energy in one of the ionic VB structure (say,  $\varphi_{i1}$ ) compared to the other ionic structure as the field strength is increased. This phenomenon was not observed in the absence of an external electric field.

Moreover, heterolytic bond dissociation is induced by oriented EEFs strong enough to push one of the ionic structures below the covalent structure [39]. Though, in presence of moderate electric field, the bond strength of the hetero-nuclear molecules can still be strongly affected. This is mostly reflected in the measurement of bond dissociation energy of the reactant heterolytic molecules under the electric field which has the magnitude lower than the bond dissociation threshold [40]. Moreover, the effects of field strength on the bond dissociation energy of the reactant molecules could potentially control the reactivity factors and hence, could revolutionize the field of modern synthetic chemistry [41]. Furthermore, oriented electric fields affect the  $\pi$ -bonds and  $\sigma$ -bonds very

differently [24]. This anomaly among the  $\pi$ -bonds and  $\sigma$ -bonds is due to the fact that  $\sigma$ -bonds confine the  $\pi$ -ionic structures over short distances. As a consequence, the  $\pi$ -ionic structures, which can lie up to 8 eV above the ground state in typical unsaturated hydrocarbons, cannot be lowered sufficiently to impact the properties of such a bond.

### 3. Possible RGO based catalytic system

Catalysts play a significant role in the modern chemical industry. Conventional catalysts suffer from various bottlenecks such as environmental and ecological hazards, catalysts poisoning, high production cost, less recyclability and so on. The main functional principle of catalysts is to reduce the activation energy during the ongoing chemical reaction without being consumed by the reactants or the products [42]. Recent advances in catalysis reported successful and effective use of various hybrid, cluster and composite materials in many chemical reactions as catalyst promoters [43,44]. GO and RGO materials have become a hot topic due to their simple structure and various important properties including electrical, chemical and electrochemical properties [45–47]. A wide variety of studies regarding the catalytic effects of GO and RGO, have been conducted by numerous researchers. In the following discussion, the synthesis and structural characteristics of RGO are discussed and then finally, the effects of orientated EEF on the RGO catalytic activity is presented.

#### 3.1. Synthesis processes of GO and RGO

Principally, graphene oxide (GO) can be transformed to reduced graphene oxide (RGO) by procedures similar to the reductive exfoliation [48]. The main advantage in this process is that graphene-like properties can be preserved after RGO production. Therefore, RGO is generally used as an effective mediator between graphene and graphene oxide. The synthesis and production of RGO is relatively easy and can be achieved by a variety of processes such as photo-assisted thermal methods, electrochemical and microwave assisted approaches [49]. Some of the modern techniques in RGO synthesis include solar mediated reduction, radiation-induced reduction, multi-step hybrid reduction and serigraph-guided reduction. Though a variety of RGO synthesis processes is possible, however, it should be noted that various reduction processes produce RGO with different quality that could exhibit altered properties and other characteristics alterations based on the degree of RGO reduction process [50]. For instance, one of the common reduction processes of GO is the chemical reduction which can be performed in room temperature or in normal heating conditions [51]. Mostly, the chemical reduction process is performed using chemical reagents such as hydrazine and its derivatives hydrazine hydrate and dimethylhydrazine. During the chemical reduction of GO to RGO, the addition of these chemical solvents induces the hydrophobicity to a GO aqueous dispersion [52]. Moreover, other chemical reagents such as hydriodic acid, ascorbic acid and sodium borohydride as well as dehydration process including combination of concentrated sulfuric acid and sodium borohydride are also being used for better reduction of GO to RGO [53].

Though, when electrochemical methods are applied for the reduction process, the chemical reagents can be absolutely avoided. During the electrochemical reduction of GO to RGO, the exchange of electrons in the GO-electrode inside the electrochemical cell in the presence of an aqueous buffer solution, facilitates the reduction process of GO sheet [54,55]. However, thermal reduction is also another well adopted technique for the reduction of GO sheets to RGO. Thermal reduction is associated with the rapid annealing at high temperatures and generates CO or CO<sub>2</sub> gas by removing the oxygen functional group through the exfoliation of graphite/graphene oxide [56]. The thermal reduction process is extremely temperature sensitive and the properties of generated RGO largely depend on the temperature level of the reduction process [57]. For example, obtaining high quality RGO with good conductive properties requires reduction temperatures to be as high as 1100 °C.

Moreover, the application of microwave- and photo-assisted methods has also been performed in thermal reduction of GO due to the advantage of these methods in uniform heating process of the materials [58,59]. Among the various synthesis processes of RGO, Hummer's method, a special chemical reduction process of GO by reducing agent, is the most commonly used procedure. This method involves reduction of GO by hydrazine hydrate. For a detailed procedure of Hammer's method please refer to [60]. The main advantage of this method is that it is very cost effective and a large amount of GO can be easily prepared by this method. However, this method shows higher structural defects than thermal and photo-assisted synthesis of RGO.

#### 3.2. Structure and characteristics of GO and RGO (chemically reduced)

The structural information and specific properties of GO and RGO materials play significant roles in the implementations of RGO catalysis. Unlike graphene, which has a uniform and defined structure consisted of discrete graphene sheets based on only sp<sup>2</sup> hybridization in honeycomb crystal structure, GO and RGO contain both sp<sup>2</sup> and sp<sup>3</sup> hybridization among the carbon atoms in a hexagonal ring-based carbon networks where oxygen functional groups produced by Hummer's method are attached [61]. However, due to the amorphous characteristics, the structure of RGO is not quite clear yet. Therefore, researchers have proposed several structural modelings. The mostly used structure of GO and RGO materials was observed by Klinowski and Lerf [62]. The proposed structural model is a nonstoichiometric structure in which the carbon plane is decorated with hydroxyl and epoxy(1,2-ether) functional groups, and the edges are decorated with carbonyl groups.

In general, sp<sup>2</sup> hybridized areas are associated with the oxidized regions in the structure of GO, whereas the sp<sup>3</sup> hybridization is associated with the covalently bonded oxygen functional groups such hydroxyl and carboxyl groups [63]. In fact, the sp<sup>2</sup> regions of the honeycomb lattice structure of RGO surface are considered to be the un-oxidized regions while both sides of the graphene plane are sp<sup>3</sup> hybridized and uniformly adored with randomly distributed carbon clusters [64]. The use of nuclear magnetic resonance

spectroscopy (NMR) related analysis revealed more detailed structural information of graphene oxide and reduced graphene oxide materials [65]. The detailed and in depth structure of GO and RGO materials have been studied by various techniques. One recent study applied high resolution annular dark field (ADF) under the experimental observation with scanning transmission electron microscopy (STEM) in order to investigate the distribution of oxygen atoms over the GO monolayer sheets [66]. The findings of the study indicated that roughness and distortion of the surface is the primary factors for the amorphous characteristics of the RGO sheets. Other studies used more advanced techniques such as atomic force microscopy (AFM) to evaluate the thickness of the mono-layer GO/RGO and the number layers in the sheets.

Moreover, in the structure of GO, the intact and defective regions were observed by an atomic level imaging technique known as scanning tunneling microscopy (STM). The findings of STM studies indicated that the amorphous and disordered structure of the GO is due to the oxygen functional groups, which were obtained by the chemical oxidation of graphene sheets [67]. Therefore, both non-oxidized intact regions and randomly distributed defective regions are present within the RGO structure. The degree of functionalization of the RGO sample can be estimated by computing the ratio between the intact and defective regions. The atomic structure of GO/RGO were also studied by using aberration-corrected high-resolution transmission electron microscopy (HRTEM). The observed various shapes of disordered regions, such as clustered heptagons and pentagons, and distortion within the plane as well as strain in the surrounding lattice structure of GO sheets [68]. The HRTEM observation of the GO atomic structure also exhibited the presence of holes, disordered regions and graphitic regions within the atomic scale of GO structure. Holes in the GO sheets can be formed by the release of carbon mono-oxide and carbon-dioxide gas during the chemical oxidation process graphene sheets, while formation of honeycomb like graphitic structures could be the results of incomplete oxidation [60]. However, the disordered regions of chemically produced GO and RGO are mostly due to the presence of various functional groups such as hydroxyl, carboxyl and epoxy groups in the GO sheets.

### 3.3. Electric properties GO and RGO

From the atomic structure of GO, it is evident that GO is an electronically hybridized material due to the presence of both  $sp^2$  and  $sp^3$  regions in the structure [68]. Therefore, GO can be electrically conductive due to the  $\pi$ -electrons from the  $sp^2$  hybridized carbon atoms, while also can be insulator due to the carrier transport gap (large energy gap) of the  $\sigma$ -bonded carbon atoms due to the  $sp^3$  hybridization [69,70]. The ratio between the  $sp^2$  and  $sp^3$  sites (regions) can be changed by the reduction process of the GO sheets. Therefore, chemical reduced GO (RGO) provides a great opportunity for controlling the energy gap in the GO structure and hence, electrical conductivity of GO sheets can be retained by chemical or thermal reduction techniques [49]. Reduction by hydrazine is the mostly used chemical reduction process of reducing aqueous graphene oxide suspensions. In this process a paper like sheet of RGO is produced after filtration with moderate conductivity at  $200 \text{ S m}^{-1}$  [71]. This electric conductivity of hydrazine reduced graphene oxide (RGO) can be boosted by the addition of KOH the graphene oxide dispersion. In this process, the  $K^+$  ions of from KOH functionalize the carboxylate anions at the edge of GO structure. The activation of the edge carboxylate anions increases the electric conductivity of the GO sheets significantly. The electrical conductivity of KOH modified RGO material was observed at approximately  $690 \text{ S m}^{-1}$  [72]. However, controlling the pH of the GO dispersion can also dramatically increase the electric conductivity of GO material [70].

### 3.4. Effects of EEF on RGO-based catalytic reaction

RGO is one the most used, computationally explored and simplest active catalysts used in various processes. The highest occupied molecular orbital (HOMO)—lowest unoccupied molecular orbital (LUMO) gap is reasonably high [63]. Therefore, the presence of active catalysts (such as RGO) in the reaction medium, changes the bond angle of the unsaturated organic compounds before entering the transition states [73]. Since HOMO is a  $d\pi$ -type donor orbital and the LUMO is an  $\sigma$ -type acceptor orbital, the change in bond angle reduced the energy difference between the HOMO–LUMO gap. In this process, the LUMO orbital pattern generates an electron-deficient region at the surface of the RGO catalysts in the presence of an external electric field [10]. Therefore, the RGO surface is surrounded by the negative potential from the  $d\pi$  electron cloud. The unique structure of RGO initiates the process of bonding and back-bonding necessary for the activation of the bonds in the reactant molecules. Furthermore, based on the analysis of valence-bond state correlation diagrams (VBSCD), the effects of oriented EEF on the RGO catalysts are primarily dependent on the extent of mixing of charge transfer states into the total ground state wave function of the transition state [74]. This mixing also generates the dipole moment along the reaction axis. This mixing is maximized when the applied field and the transition state geometry are in perfect alignment with the reaction axis (in accordance with the Equation (3)).

## 4. Proposed method of alkene hydrogenation under EEF

From the discussion in Section 2 and Section 3, it is implicated that a RGO based catalyst system can be produced that could be useful in some important chemical reactions such as hydrogenation of primary alkenes. Hydrogenation of alkenes is one of the most industrially used reactions. However, the current reaction process requires metal-based (such as Ni, Pd, and Pt) catalysis. The use of heavy metals is not only environmentally and ecologically unfavorable but also increases the cost of production, less recyclability and catalyst poisoning. Therefore, there is a need for green and better catalyst design for this kind of reaction. In the following, a CT-RGO (cotton textile reduced graphene oxide) based catalyst system is proposed for alkene hydrogenation. Later on, the possible catalytic activity for the proposed system is also discussed based on the initial DFT calculation.



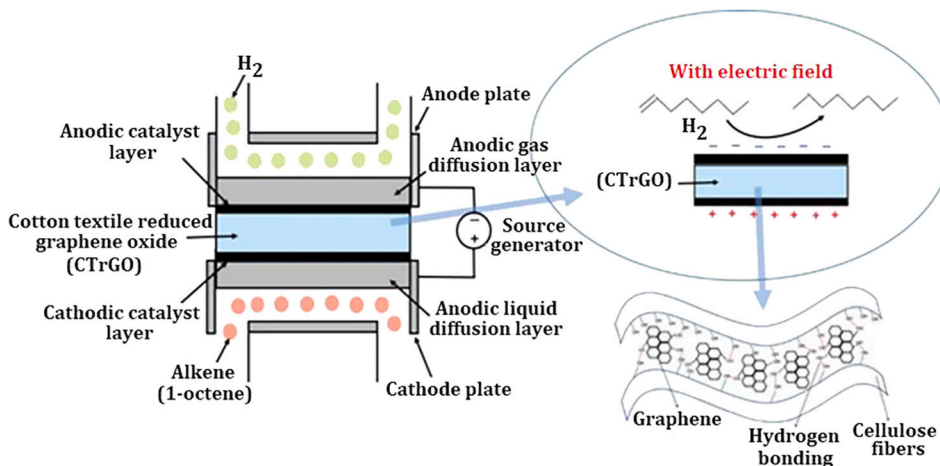


Fig. 1. Schematic diagram of the fabricated reaction vessel.

#### 4.1. Proposed system and materials

The preparation of CT-RGO is divided into three phases. In the first phase, graphene oxide is prepared by Hammer's method via chemical oxidation. In this process, graphite powder is oxidized by concentrated chemical treatment of  $\text{NaNO}_3$ ,  $\text{KMnO}_4$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  according to the method described in. As soon as the GO is obtained, in the second phase, a stable dispersion of GO is prepared from the sonicating mixture of GO and deionized water. The preparation of GO dispersion is basically a two-step process. In the first step, the cotton textile is boiled in deionized water containing anhydrous sodium carbonate. At the end of this step, the pH of the solution should have remained at neutral level ( $\text{pH} = 7$ ). The second step of producing stable GO dispersion involves continuous dipping of a piece of dewaxed cotton textile in the previous GO solution under constant stirring. Then the dewaxed cotton is dried in a woven. This second step is repeated several times to ensure impregnation of enough GO molecules into the cotton textile. Then the non-attached GO molecules are washed away by treating with deionized water and ethanol. In the final phase of CT-RGO preparation, some cotton textile pieces (obtained at the end of second phase) step, is treated with hydrazine to reduce the GO into RGO according to the proper treatment and necessary precautions.

The generated CT-RGO sheets serve as the catalytic platform for the intended hydrogenation of 1-octene. The reaction vessel has four layers: anodic gas and liquid diffusion layers as well as cathodic and anodic diffusion layers (Fig. 1). The CT-RGO is placed between the anode and cathode for EEF induced reactions. This serves as the catalytic platform for the hydrogenation of alkene. Meanwhile, the rGo/cotton fabric shall be sandwiched between anode and cathode plates for electric field-driven reactions. The hydrogen gas is channeled to anode plate and diffused through anodic catalyst layer and anodic gas diffusion layer to reach the cotton textile reduced graphene oxide platform. Meanwhile, alkene (1-octene) is channeled to the cotton textile reduced graphene oxide platform via anodic liquid diffusion layer and cathodic catalyst layer. Therefore, once hydrogen gets absorbed on the surface of the CT-RGO, it reacts with 1-octene and generates n-octane.

#### 4.2. Possible catalytic activity of CT-RGO

The chemisorption of hydrogen atoms over a graphene surface can only be facilitated if a significant lattice reconstruction is observed within the graphene structure. However, the reconstruction of lattice might induce a superficial impurity that might produce a magnetic moment and band gap by inducing changes in magnetic and electronic properties. The geometrical deformation owed to the chemisorption of H/G on the active sites might affect the electron mobility and dissociation or cleavage of the  $\pi$  bonds on the alkene-graphene complex, representing the structural parameters that measure deformation. The distance between the hydrogen atom and the bonded carbon atom, the relative position of the bonded carbon atom to the graphene plane, and the chemisorption bond distance will be evaluated and their respective effects on the reaction progress might put an insight into the understanding of the electronic activity of the intended EEF induced phase boundary catalysis. In the absence of EEF, two processes were chosen for selecting the effectiveness of the catalytic system and optimum process to the reactor vessel. Process one involves passing the hydrogen gas through the membrane (CT-RGO) and then it is placed (or passes the gas) in the alkene directly and according to GC yield was 0.58% octane. The second process involves dipping the CT-RGO membrane in alkene and then passing the hydrogen gas through it. According to the GC, the yield from the second process was 0.22% octane. Therefore, the first process could be more effective for hydrogenation reactions under EEF.

From the above discussion, it is evident that the absorption of alkene and a hydrogen atom on the surface of the RGO sheet might regulate the electron mobility and charge dispersion during the catalytic hydrogenation. Therefore, selectivity of the reactions can be effectively controlled by regulating the orientation of the adsorbates along the catalytic surface under the external electric field. Moreover, the movement of the molecules (both rotational and translational) in the reaction medium is significantly affected by the applied fields. The changes on the adsorbate orientation and molecular movements directly influence the frequency factor of the

**Table 1**  
DFT calculations of the CT-RGO catalytic system.

System	System 1 (without EEF)	System 2 (with Electricity)	System 3 (EEF = 2 mAu)
	Unit (Hartree)		
A = H <sub>2</sub>	-1.179572	-1.178539	-1.17854
B = Graphene	-2399.469354	-2399.469354	-2399.476221
C = Graphene + H	-2400.117837	-2400.117979	-2400.123541
Adsorption E <sub>G-H</sub> = C-(A+B)	0.531089	0.529914	0.53122

reaction and thus change the reaction kinetics. However, manipulating the molecular orbitals effectively changes the stability and reactivity of the adsorbates. Therefore, not only the molecules with dominant dipole moment are affected by the external electric fields but also all the molecules present in the reaction medium. Therefore, it is evidently clear that external electric field effectively controls the selectivity and reactivity of chemical reactions.

The initial DFT calculations of the proposed catalytic system were performed using Gaussian 16 software. The summary of the DFT calculation is presented in Table 1. From the DFT calculation, it is evident that the adsorption energy of both hydrogen and graphene molecules is higher in the presence of an external electric field, while the adsorption energy decreases when no electric field is applied to the system. This finding implies that under that external electricity field, the activation energy of graphene radicals to achieve the transition states as well as the adsorption of the hydrogen atoms over the graphene surface is significantly lower. Moreover, a reduction in the graphene-hydrogen complex is also notable in the presence of external electric fields. Therefore, it can be implied that under the external electric field, the transition state energy of the reactant molecules is lower and hence facilitating the forward reaction. However, this is not the complete DFT calculations, the future DFT calculations involving transition states and products as well as the computations relative to the coordinates of the reaction axis will put more insight into the catalytic activity of the proposed system.

Finally, it is important to note that the growing interest in molecular simulation of alkene hydrogenation reaction based on cotton textile reduced graphene oxide (CT-RGO), should be usefully accompanied by the development of a theoretical tool in the field of DFT calculation [75]. However, a variety of experimental and computational techniques, continue to reveal that most of these models have to be improved [76]. Furthermore, there is also increasing evidences that indicate that alkene hydrogenation reactions based on cotton textile reduced graphene oxide (CT-RGO) could be modeled by quantum chemical methods in conjunction with the solvent reaction field [76].

## 5. Conclusions

Herein we report on the theoretical basis of simulating the phenomenon of heterogeneous catalysis, on a molecular level, under the effect of external fields based on the existing literature. The different theoretical considerations exhibit that the oriented effect of the external field, applied along the reaction axis, could change the chemical and physical properties of the reactants by stabilizing the dipole moment around the bond axis. The observed changes can be optimally controlled to facilitate the reactivity and the selectivity of some specific chemical reactions under the influence of external fields. Interestingly, the analysis of reduced graphene oxide structure and its corresponding characteristics indicates that reduced graphene oxide constitutes a promising potential catalyst or a catalyst promoter since it contains both sp<sup>2</sup> and sp<sup>3</sup> hybridization, which make reduced graphene oxide to work like a semiconductor material. The proposed cotton textile reduced graphene oxide catalytic system reveals interesting features enabling it to be considered as a potential approach in promoting the alkene hydrogenation reaction under oriented effect of external fields. In addition, a theoretical investigation was carried out within the framework of the density functional theory (DFT) method using first-principles calculations in order to validate the experimental approach presented herein dealing with the noble method of alkene hydrogenation reaction based on cotton textile reduced graphene oxide (CT-RGO) under the influence of an external electric field. The study has been illustrated by providing DFT calculations for three catalytic systems, namely without electricity, with electricity and with an external electric field of 2 milli-Atomic units. The results presented in this paper enable for the pursuant conclusions and observations:

- (i) The obtained results reveal that adsorption energy of H<sub>2</sub> on the CT-RGO surface is significantly higher when the electric field is applied along the bond axis.
- (ii) This finding suggests that hydrogenation of alkene can be induced with CT-RGO catalyst support under external electric fields.
- (iii) The theoretical results performed with the present approach shed light on the effect of the external electricity field on the graphene-hydrogen complex, the activation energy of graphene radicals to achieve the transition states as well as the adsorption of the hydrogen atoms over the graphene surface.
- (iv) The theoretical results presented herein suggested that the proposed catalytic system holds promise for facilitating the alkene hydrogenation under external electric fields.

Finally, we should emphasize that the enlargement of theoretical investigation presented herein by exploring complete DFT calculations may illuminate the way for treating the whole reaction system including transition states. Moreover, the characterization of the CT-RGO catalytic system by various experimental methods as well as reaction kinetics and recyclability of the proposed catalyst should be envisaged. The present study represents a fragment of such an approach.

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## CRediT authorship contribution statement

Ghozlan Elbashir Amer, Fazira Abdul Razak, Suhaila Sapari, Siti Aminah Setu: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper. Hadi Nur: Analyzed and interpreted the data; Wrote the paper.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available upon request.

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