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FULL PAPER

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Graphene Oxide Supported Oxovanadium (IV) Complex for Catalytic Peroxidative Epoxidation of Styrene: An Eye-Catching Impact of Solvent

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Graphene oxide (GO) supported transition metal complexes are apprised as sturdy and everlasting heterogeneous catalysts. GO surface was functionalized with 3-triethoxysilylpropylamine (TSPA) and this amino functionalized GO (A-*f*-GO) nanocomposite with vanadyl Schiff base complex (VO-*f*-GO) was prepared and to give credence of its potentiality, it was chosen for the selective epoxidation of styrene using environmentally benign 30% H_2O_2 to styrene oxide (SO). To evade the detrimental exposure of "*inborn*" water, a selective high boiling and potent hygroscopic solvent, ethylene glycol was chosen to make this transformation productively successful. With the assistance of theoretical studies, we have probed the effect of H_2O_2 on to structural properties, binding mechanism and electronic properties of the catalyst and substrate. Adsorption energy (E_{ad}), energy band gap (E_g) and HOMO-LUMO were also calculated. Based on DFT calculations, resonance Raman and UV/Vis studies, we confirmed the formation of metal-peroxo species and propose the plausible catalytic pathway. The influence of the diverse experimental parameters, like substrate to oxidant mole ratio, catalyst concentration, type of solvents, solvent amount, time, temperature and oxidant were tested. A clear relationship was found between different reaction parameters like solvent amount, oxidant, catalyst concentration and temperature etc. and product distribution. This heterogeneous catalyst yielded styrene oxide as nearly the sole product (selectivity = 98.7%) with a conversion value of 99.2% in the oxidation of styrene with hydrogen peroxide in ethylene glycol.

KEYWORDS
density functional theory, GO supported heterogeneous catalyst, peroxidative epoxidation of styrene, solvent effect

1 | INTRODUCTION

Catalytic oxidation of hydrocarbons is "nitty-gritty" for the industrial production of chemicals. Amongst them, catalytic epoxidation of olefins is even of the utmost prominence, particularly in the pharmaceuticals and fine chemical industries. Epoxides, the oxidized product of olefins are considered to be the most adaptable raw material in scores of organic synthesis[1] due to partly positive carbon and a Lewis-basic oxygen atom in a three-

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Enhancing the potency of surface hydroxyl groups of graphene oxide for selective oxidation of benzyl alcohol

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ABSTRACT

A chemo-selective oxidation of benzyl alcohol (BzA) to benzaldehyde (BzH) was built up using transition metal immobilized amino functionalized graphene oxide [ML-*f*-GO (M = VO^{4+}, Co^{2+}, Cu^{2+})] as heterogeneous catalysts. Surface hydroxyl groups on GO are engaged fundamentally in the fabrication of ML-*f*-GO, was confirmed by density functional theory (DFT), Fourier-Transform Infrared (FTIR), electronic spectra and X-ray photoelectron spectroscopy (XPS) results, besides these X-ray diffraction (XRD), thermogravimetric analysis (TGA), Brauner-Emmett-Teller (BET) results, Raman, scanning electron microscope (SEM) and transmission electron microscopy (TEM) were employed to corroborate the successful fabrication. DFT study was executed in an attempt to elucidate the replacement of hydroxyl groups by amino groups. The propensity of binding energy was $-COOH > C-O-C > -NH_2 > -OH$ which very well corroborate the belief developed from different characterization techniques that the amino groups of substituted amino functionalized moiety replace only surface hydroxyl groups of GO. Energy gap, global hardness and softness were also calculated. Catalytic aptitude of the as-prepared catalysts was weigh-up against oxidation of BzA using 30% H_2O_2 as a greener oxidant. The impact of distinct parameters influencing catalytic activity has also been studied. Under the optimized conditions, CuL-*f*-GO exclusively promoted this transformation with excellent activity to yield 99.5% BzH.

1. Introduction

Developing dynamic, choosy and energy proficient heterogeneous catalytic processes are extremely indispensable to an inexhaustible future because heterogeneous catalysis is at the central part of the chemicals and pharmaceutical industries. The fabrication and execution of selective heterogeneous catalytic processes could have a marvelous encouraging impact on the globe as it may perform the catalytic reaction at a lower temperature, pressure and/or in less time thus wealth can be saved in up-scale reactions. Contrast to this, catalyst deactivation is the subject of considerable seriousness [1], which is the major impediment to research, design and advancing stable catalysts. That's why it is necessary to be acquainted with the reason and remedy for catalytic deactivation. Research on the catalyst deactivation has been spreading gradually across-the-board, since last three decades [2–15]. Deactivation broadly classifieds into three type viz. chemical, mechanical and thermal which includes metal poisoning, foiling, thermal degradation, leaching, solid-solid interactions and mainly support [16–18]. However, it can be lessened by vigilant control of process conditions and by a cautious choice of support materials.

According to archaic aphorism “prevention is better than cure”, we have to be more careful in choosing the support. In this days and age of rising, heaps of supports are available but most of them are inept due to deactivation [17,18]. With the determination to overcome this ineptness, the pursuit of the heterogeneous acid catalyst has resulted in the consideration of carbon-based nanomaterials (CNMs) [19,20]. Interestingly, this era was lessened with graphite as the eye-catching scientific significance of graphene as a catalyst and catalytic support in heterogeneous catalysis has grown very impressively over the past several years [21]. Characteristically, graphene has a two-dimensional crystal structure, sp^2 bonded carbon atoms densely packed in a hexagonal honeycomb-shaped lattice and plenty of functional groups on its basal plane and edges. During the recent time, chemically modified graphene (CMG) as graphene oxide (GO) based research has gained a stupendous strength owing to their latent outstanding quality especially in the field of catalysis [22,23]. Unique properties like high surface area [24] of ~2630 m^2/g, promising high thermal stability, elevated tensile strength [25], promotes mass transfer and superior resistivity towards

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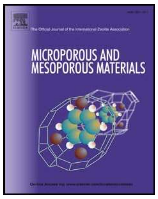

Zeolite-Y entrapped metallo-pyrazolone complexes as heterogeneous catalysts: Synthesis, catalytic aptitude and computational investigation

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ABSTRACT

Transition metal [M = VO(IV) and/or Co(II)] complexes with Schiff base ligand (Z)-3-methyl-1-phenyl-4-(2,2,2-trifluoro-1-(2-hydroxyphenyl)imino)ethyl)-1H-pyrazol-5-ol (H_2L) have been entrapped in the super cages of zeolite-Y by Flexible Ligand Method. These nanohybrid materials have been characterized by preferential physico-chemical techniques such as ICP-OES, elemental analyses, (FT-IR, ^1H and ^{13}C-NMR and electronic) spectral studies, BET, scanning electron micrographs (SEMs), AAS, X-ray diffraction patterns (XRD) and thermogravimetric analysis. The density functional theory calculations are performed to find optimized structures together with the bond angles, bond lengths, dihedral angles and electronic properties of ligand and neat complexes. The catalytic competence of zeolite-Y entrapped metallo-pyrazole complexes was examined by the oxidation of olefins viz. limonene, cyclohexene, styrene, and α-pinene using H_2O_2 as an oxidant. So as to ensure the shielding effect of the nanohybrid over the active center on the catalytic properties, the performance of the entrapped complexes (heterogeneous system) was weighing up against the neat complexes (homogeneous system). The effect of experimental variables (such as solvents, mole ratio of substrate and oxidant, the amount of catalyst and reaction time) with their probable justification on the conversion of limonene was discussed. Under the optimized reaction conditions, $[VO(L)\cdot H_2O]$-Y was found to be potential candidate, achieving 87.44%, 90.01%, 82.01%, and 85.44% conversions of limonene, cyclohexene, styrene, and α-pinene oxidation reactions, respectively.

1. Introduction

Now-a-days the oxidation of olefins has pulled up a great meaning as its oxygen functionalized derivatives are fateful intermediates used in various fields like fragrant, pharmaceutical, plasticizer, coating material etc. [1–4]. Due to significance of selective and partial oxidations, catalytic oxidation of olefins has achieved enormous attention because it is the most enviable pathway for the synthesis of highly selective and vital industrial products such as epoxides, carbonyl compounds, diols and products obtained by cleavage of C-C bond.

Merely in attendance of this, there is an eagle-eye to discover a catalyst which can adequately carry out such oxidation reactions with generous yield and stability besides first-rate conversion with desired selectivity. For this rationale, great efforts are being put to build up solid support based catalytic systems and different approaches were being applied such as grafting on polymers [5], immobilization in polysiloxanes [6], sulfonic acid-functionalized mesoporous SBA-15 [7], silica-based mesoporous organic–inorganic hybrid materials like MOFs [8,9] and zeolites [10–13].

In today's era, zeolite-Y has acquired attention to great extent as solid support [14–16] due to properties like high surface area, large pore volume and well-defined arrays of channels as well as cavities made it suitable support for entrapment of transition metal complexes. Madadi and Rahimi [17] reported zeolite-Y entrapped Fe(III), Mn(III) and/or Co(III) complexes with 5,10,15,20-tetra(4-methoxyphenyl)porphyrin as heterogeneous catalysts for the epoxidation of monoterpenes. The catalytic results showed that Fe(III) complexes were more efficient ((R)-(+)-limonene conversion: 81%) than Mn(III) and Co(III) complexes. Xia et al. [18] have studied numerous heterogeneous Mn^{2+}-zeolite catalysts for instance, Mn-beta, Mn-Y, Mn-ZSM-5 and/or Mn-A for the epoxidation of alkenes with 30% H_2O_2 in sodium hydrocarbonate solution. Amongst all, Mn-Y has demonstrated high conversions of 98.5–99.9 mol%. Low active oxygen content is another critical concern for the sustainability of the reactions, for this reason, numerous oxidants have been employed such as oxygen, hydrogen peroxide, *tert*-butyl hydroperoxide (TBHP) and iodosobenzene diacetate ($PhI(OAc)_2$) [17]. Owing to ecologically aware oxidant, H_2O_2 is more desirable, as the active oxygen content is around 50% with producing no- or only

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Ionic liquid infiltrated within metal loaded zeolites for Baeyer–Villiger oxidation reaction under solvent-free condition

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Abstract We demonstrate the infiltration of ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate) skeleton within robust Co metal loaded mesoporous zeolites viz. Co/ZSM-5 and/or Co/HY to prepare the ([BMIM]BF_4@Co/ZSM-5) and/or ([BMIM]BF_4@Co/HY) host–guest systems and characterized by various physico–chemical techniques. The catalytic activity of these catalysts was investigated in the liquid phase Baeyer–Villiger (BV) oxidation of cyclohexanone under solvent-free condition. Amongst them, [BMIM]BF_4@Co/HY was found to be potential candidate by showing excellent performance with 54.88% conversion of cyclohexanone and 86.36% ε-caprolactone selectivity with elevated TOF and TON values of 4312.43 h^{-1} and 25874.58, respectively. In addition to this, the host–guest system could be successfully recycled six times without significant loss of activity.

Keywords Heterogeneous catalyst · Zeolitic support · Ionic liquid · BV oxidation of cyclohexanone

1 Introduction

Baeyer–Villiger (BV) oxidation provides an important method for converting ketones into esters or lactones, an effective route to formulate pharmaceuticals products and fine chemicals, has been fascinating much attention since reported in 1899 [1–3]. This reaction was subsequently extended to the oxidation of aldehydes to the corresponding esters of formic acid or their hydrolysis products with other oxidants such as organic peracids, peroxides and hydrogen peroxide. Now-a-days, BV oxidation reaction has been accomplished as a prominent reaction in synthetic organic chemistry due to number of intrinsic advantages: its excellent functional group tolerance, widely usable oxidants, highly predictable regioselectivity and stereoselectivity. The versatility and major synthetic interest of this reaction is witnessed by a large range of applications spanning such diverse areas as the synthesis of natural products (e.g., antibiotics, steroids), pheromones for agrochemistry, monomers for polymerization, etc. ε-caprolactone, the main product of the BV oxidation of cyclohexanone is one of the most essential organic intermediates for synthesizing polymers and coating materials. This oxidation route involves some traditional organic peroxyacids as oxidants, akin to m-chloro perbenzoic acids, peroxybenzoic acids and trifluoroperacetic acids which are expensive, hazardous besides dangerous in transit and storage and also produces massive amounts of the corresponding carboxylic acid as wastes, includes halogenated solvent during reaction, using a buffer (sodium phosphate etc.) to fend off transesterification. From the atom economy and environmentally friendly viewpoint, it was pertinent to replace peroxyacids with hydrogen peroxide, which contains large amount (40% by weight) of active oxygen, relatively stable, easy to handle, commercially available and relatively cheap reagent and only H_2O is formed as by-product. However, H_2O_2 is the weakest oxidant comparing a wide range of available peroxides and peroxyacids and therefore catalyst is needed to increase its nucleophilicity. For this intent, a number of homogeneous and heterogeneous

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Baeyer-Villiger oxidation of cyclopentanone over zeolite Y entrapped transition metal-Schiff base complexes

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Transition metal [M = VO (IV) and/or Cu (II)] complexes with Schiff base ligand, (Z)-2-((2-hydroxybenzylideneamino)phenol (H_2L) have been entrapped in the super cages of zeolite-Y by Flexible Ligand Method. Synthesized materials have been characterized by preferential physico-chemical techniques such as inductively coupled plasma optical emission spectroscopy (ICP-OES), elemental analyses (CHN), fourier transmission infrared spectroscopy (FTIR), electronic and UV-reflectance spectra, Brunauer–Emmett–Teller (BET) surface area measurements, scanning electron micrographs (SEMs), X-ray diffraction patterns (XRD) and thermogravimetric analysis (TGA). The catalytic competence of zeolite-Y entrapped transition metal complexes was examined in Baeyer-Villiger (BV) oxidation of cyclopentanone using 30% H_2O_2 as an oxidant beside neat complexes to check the aptitude of heterogeneous catalysis over the homogeneous system. The effect of experimental variables such as mole ratio of substrate to an oxidant, amount of catalyst, reaction time, varying oxidants and solvents on the conversion of cyclopentanone was also tested. Under the optimized reaction conditions, one of the zeolite-Y entrapped transition metal complex viz. [VO(L)H_2O]-Y [where L = (Z)-2-((2-hydroxybenzylideneamino)phenol] was found to be a potential contender by providing 80.22% conversion of cyclopentanone (TON: 10479.42), and the selectivity towards δ-valerolactone was 83.56%.

KEYWORDS
Baeyer-Villiger oxidation of cyclopentanone, flexible ligand method, heterogeneous catalysts, zeolite-Y entrapped transition metal complexes

1 | INTRODUCTION

For chemical transformation in both academia and industry, catalyst technology is nowadays used as a powerful tool because it plays a vital role in chemical reactions, allowing faster conversion of a wide variety of starting material to high-value products at lower cost with minimum generation of by-product. In this day and age, the meadow of heterogeneous catalysts has pulled up as eco-sustainable catalytic systems transforming various organic substrates into valuable intermediates for environmentally benign industrial processes due to its high stability, activity and effortless separation from reaction mixtures. On the other hand, homogeneous systems are often regarded as imprecise with many restrictions, including the decomposition and deactivation due to the formation of dimeric μ-oxo- and peroxo- bridged species, and separation problem as well.[1] With added benefits of flexibility in immobilization of various chemical moieties and/or nanomaterials into the reaction channels, molecular sieves have been expanded into an imposing group of inorganic-crossbreed materials (active heterogeneous catalysts) with huge number of industrial applications, mainly in the field of catalysis. It comprises zeolites, mesoporous materials, and metal–organic frameworks. Predominantly, zeolites

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PAPER

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Highly efficient FeNP-embedded hybrid bifunctional reduced graphene oxide for Knoevenagel condensation with active methylene compounds†

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We have synthesized atypical highly active bifunctional FeNPs implanted on amino-modified reduced graphene oxide (FeNPs/Am@rGO) [where FeNPs = Fe nanoparticles; Am = Primary aromatic amine derivatives such as *p*-phenylenediamine (PPD) and/or aniline (AN)] as nanocatalysts *via* the acid–base dual-activation mechanism by introducing primary aromatic amines on the basal and/or edge sites of rGO that offer base characteristics and FeNPs anchored onto the surface of rGO that supply the Lewis acidic nature. These nanocatalysts were well corroborated through assorted physicochemical techniques. Impressively, FeNPs/Am@rGO significantly promoted a one-pot Knoevenagel condensation reaction with different aromatic aldehydes and active methylene compounds, thus bestowing excellent activity to give synthetically valuable multifunctional benzylidene derivatives. The impact of different parameters influencing the catalytic activity has also been monitored. Under the optimized conditions, FeNPs/PPD@rGO exclusively promoted the aforementioned reaction, leading to 100% benzaldehyde conversion with 100% yield of the product along with TON and TOF (h^{-1}) values of 350.8 and 100.2, respectively. Besides, it could be effortlessly recycled by centrifugation after each run and reused afterwards without significant loss in its catalytic activity in a six cycle test.

1. Introduction

The formation of carbon–carbon bond *via* Knoevenagel condensation reaction of aldehyde/ketone with compounds containing activated methylene groups is being paid great attention to by the researchers because of its deployment in the synthesis of fine chemicals,[1] therapeutic drugs,[2] natural products,[3] and functional polymers.[4] Typically, this base catalyzed organic reaction is of great importance in the chemical process industry, which plays a vital role in achieving higher aldehyde conversion.[5] In the last few decades, the Knoevenagel condensation reaction has conventionally been performed by soluble base catalysts such as aliphatic amines, urea, thiourea, and piperidine or their corresponding ammonium salts and/or amino acids. Despite having distinct advantages, the aforesaid system suffers from several snags such as difficult separation, longer reaction time, un-satisfactory yields, reusability, high costs, harsh reaction conditions, as well as the use of stoichiometric amounts of catalyst.[6]

Now-a-days, frontier scientific and technological research fields have highlighted the use of solid supported base modified catalysts, which can be adequately applied for condensation reactions, giving better yield and stability besides first-rate conversion with the desired selectivity. Different types of heterogeneous base modified catalytic systems have flourished such as amino-functionalized mesoporous silica,[7] diamine-functionalized mesopolymers,[8] amine functionalized K10 montmorillonite,[9] super paramagnetic mesoporous Mg–Fe bi-metallic oxides,[10] mesoporous titanosilicate,[11] basic MCM-41 silica,[12] acid–base bifunctional mesoporous MCM-41 silica,[13] nanocrystalline ceria–zirconia,[14] zeolites exchanged with alkylammonium cations,[15] Cu(II)-based metal–organic framework,[16] chitosan hydrogel,[17] acrylic resin immobilized lipase,[18] organic–inorganic hybrid silica materials containing imidazolium and dihydro imidazolium salts,[19] IRMOF-3,[20] and ZIF-8.[21] In contrast, these basic solid catalysts have endured a number of downsides such as high temperature, longer reaction time, poor selectivity, and tedious work-up procedures.

At present, potent and sophisticated heterogeneous catalysts with tunable multifunctionalities are in high demand in the area of green and sustainable science and technology. The combination of both acidic and basic sites employed in designing and advancing heterogeneous catalysts with bifunctional assets is

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Harnessing the N-dopant ratio in carbon quantum dots for enhancing the power conversion efficiency of solar cells†

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Nowadays, green materials are being prepared to a greater extent to conserve the environment. Due to their outstanding properties, carbon quantum dots (CQDs) are becoming the alternatives of the conventional semiconductor-based quantum dots and organic dyes. We reported the one-step synthesis of CQDs and nitrogen-doped carbon quantum dots (NCQDs) by the solvothermal treatment of green and renewable non-centrifugal cane sugar. The successful syntheses of CQDs and NCQDs were substantiated by various physicochemical techniques such as Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The photoluminescence quantum yields of CQDs and NCQDs were observed to be 5.2% and 9.8%, respectively. Due to their commendable photostability, these NCQDs with different loadings of nitrogen were applied as green sensitizers in TiO_2-based solar cells. These NCQDs achieved the highest power conversion efficiency of 1.20% under 0.1 sun illumination (AM 1.5). We believe that this competitiveness of the fabrication of CQDs from the cheapest and green source is the most promising and useful for light harvesting.

Introduction

In the last more than two decades, inorganic semiconductor quantum dots (ISQDs) have received much attention due to their unique and versatile characteristics such as a tunable band gap, high absorption coefficient, better fluorescence properties, and control of photophysical and electronic properties.[1–6] These salient features of ISQDs have paved the way for a wide range of applications such as photovoltaic devices,[7–9] photocatalysts,[10] sensors,[11,12] bioimaging elements[13] and medicine.[14] Among all these applications, to satisfy the global energy requirement, the use of ISQDs in photovoltaic devices as one of the prominent light harvesting materials is emerging. As a third generation solar cell, a quantum dot solar cell (QDSC) has evolved as an alternative of a dye-sensitized solar cell,[15] where the dyes have been replaced by ISQDs. Due to the tunable band gap and high absorption coefficient of the quantum dots, QDSCs have been well developed and have exhibited the best power conversion efficiency (PCE) of 12.75% along with good stability.[7,15] However, the main disadvantage of the ISQD-based solar cell devices is their toxicity due to the presence of heavy metal elements and they produce harmful effects on the environment.[16] Moreover, the synthesis of ISQDs with a controlled size and shape requires complicated processes.[17] Apart from this, the corrosion of ISQDs in the presence of the conventional I^-/I_3^- electrolyte affects the stability and causes decrement in PCE of the solar cell devices.[18] Hence, considerable research efforts must be driven towards the development of alternatives of ISQDs that possess low toxicity and are less harmful to the environment with good optical and electrical properties, which will facilitate the development of eco-friendlier systems for photovoltaic devices.

In recent times, carbonaceous nanomaterials, particularly carbon quantum dots (CQDs), a new class of carbon materials, have become the centre of attraction. This quasi-spherical-shaped zero-dimensional[19] material consists of an sp^2/sp^3 carbon core with diverse functional groups on the surface having a size of around 10 nm. Since the first report by Xu *et al.*[20] on CQDs, due to their prominent properties such as low toxicity, abundance, biocompatibility, easy, convenient and inexpensive

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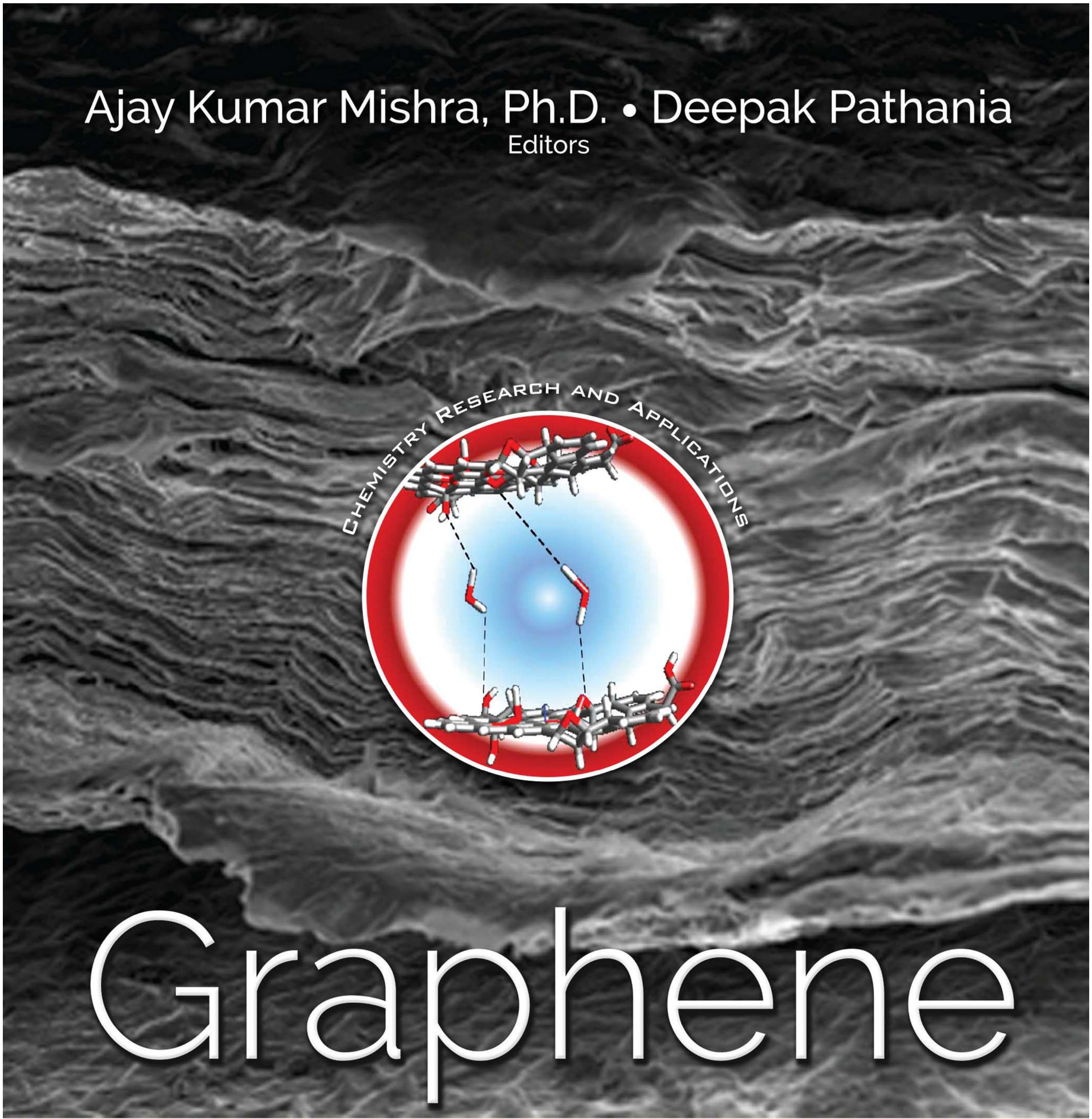

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Editors

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Graphene Oxide

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Chapter 9

AN IMMENSE UPRISING: FUNCTIONALIZATION AND FINE-TUNING OF 2D GRAPHENE DESIGNED FOR HETEROGENEOUS CATALYSIS TO MAKE THINGS GREENER

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ABSTRACT

In contemporary times human beings are noticingly aware of the atmospheric pollution, a matter of serious care, which is augmenting as a result of indiscriminate industrialization. It generates vicious by-products that can cause hazards to human being and the surroundings. Consequently, climes all over the globe have changed over a period, and people envisage myriad problems. Now a days to remedy this central concern, the sole approach is to bring in acquiring advantages of catalysts. At its heart, a catalyst is a modus operandi to save environment and energy as preponderance of manufacturing units which require inputs of energy to proceed. Crucial problems with catalysts are of high price, poor efficacy and recyclability but with innovative technologies like support the catalyst, one can trim down the cost with greater competence. They can be straightforwardly separated from the reaction mixture, resulting in drop down of waste and adverse environmental footprint, enhancement of inherent process safety and recycling of catalyst, and then they can be used continuously at increasing rate.

Many solid supports are available to get hold of first-rate catalytic proficiency. However, deployment of carbonaceous material like graphite is lately garnered out of the

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