



# Phosphate functionalized graphene oxide with enhanced catalytic activity for Biginelli type reaction under microwave condition



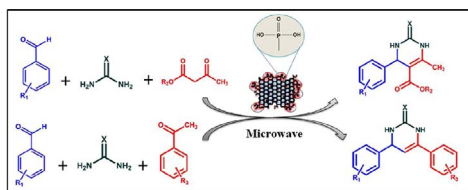
L. Satish K. Achary<sup>a</sup>, Aniket Kumar<sup>a</sup>, Lipeeeka Rout<sup>a</sup>, Swaroop V.S. Kunapuli<sup>a</sup>, Rajendra S. Dhaka<sup>b</sup>, Priyabrat Dash<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, National Institute of Technology, Rourkela, Orissa 769008, India

<sup>b</sup> Department of Physics, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India

## GRAPHICAL ABSTRACT

Highly active phosphate functionalised graphene oxide (PGO) nanocomposite has been designed via simple Arbuzov reaction and used as an efficient catalyst for Biginelli reaction in microwave condition.



## ARTICLE INFO

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## ABSTRACT

Phosphate functionalized graphene oxide (PGO), prepared by covalently bonding triethylphosphite on to the surface of graphene oxide (GO) via Arbuzov reaction has been demonstrated as an efficient catalyst for three component Biginelli condensation reaction with excellent yield (96%) under microwave condition. The PGO nanocatalyst was thoroughly characterized by Fourier transform infrared spectra (FTIR), FT-Raman spectroscopy, Powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Field-emission Scanning electron microscopy (FE-SEM), Energy dispersive X-ray spectroscopy (EDS), N<sub>2</sub> adsorption/desorption study, Ammonia temperature-programmed desorption analysis (NH<sub>3</sub>-TPD) and Thermogravimetric analysis (TGA). The presence of acidic groups on PGO which play an important role in the catalytic transformation were measured by NH<sub>3</sub>-TPD analysis. Based on the catalytic results, a feasible catalytic mechanism has been proposed. Besides high catalytic activity, this nanocatalyst showed good recyclability, suggesting its potential applications for the synthesis of other important organic molecules.

## 1. Introduction

Synthesis of a nitrogen-based heterocycles moiety, a key structure in many natural and therapeutic products via one-pot multicomponent reactions has become a remarkable area of research interest. Among different nitrogen-based heterocyclic compounds, pyrimidines and their derivatives have found to be important for pharmaceutical applications. Pyrimidines are an important class of nitrogen-based heterocyclic

compound which have become the important backbone in the world of synthetic organic chemistry [1]. These compounds naturally occur in substances such as vitamins (thiamine and riboflavin), folic acid, nucleic acids components (uracil, cytosine, and thiamine), purines, pterins and alkaloids obtained from tea and coffee [2]. Pyrimidines contain a special class of derivative known as pyrimidones which are having efficient biological activities like antibacterial activity, antifungal activity, antiviral activity, antitumor activity and antimalarial activity

\* Corresponding author.

E-mail address: [dashp@nitrrkl.ac.in](mailto:dashp@nitrrkl.ac.in) (P. Dash).

[3]. Mainly, 3,4-dihydropyrimidin-2(1H)-ones (DHPMs) and 4,6-diairlypyrimidones (DAPM) are the class of pyrimidones which have attracted a great deal of research attention over the years.

DHPMs are synthesized by one-pot condensation of urea, aldehydes, and 1,3-dicarbonyl compounds via a very popular reaction reported by Biginelli in 1891 [4]. Later Biginelli-type reactions methodology were used to synthesize 4,6-diairlypyrimidinones (DAPMs) by Wang et al. in the presence of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and Trimethylsilyl Chloride (TMSCl) as catalysts [5]. A number of metal oxide-based nanocatalysts have been reported for the synthesis of pyrimidones via Biginelli reactions such as alumina supported Mo catalysts [6], nano ZnO base catalyst [7],  $\text{TiO}_2$  nanoparticles [8], Mg-Al- $\text{CO}_3$  and Ca-Al- $\text{CO}_3$  hydrotalcite [9],  $\text{Bi}_2\text{O}_3/\text{ZrO}_2$  nanocomposite [10],  $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-Fe}_3\text{O}_4$  [11], imidazole functionalized  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  [12], alumina supported  $\text{MoO}_3$  [13] and  $\text{Fe}_3\text{O}_4$ @mesoporous SBA-15 [14]. However all these catalysts suffer from some major drawbacks such as lack of residual energy, high reaction temperature, prolonged reaction time, strong lewis acidity of the catalyst, stoichiometric amounts of catalysts, high price, low availability, and leaching of metals. All these drawbacks inspire the scientific community to find an alternative catalyst for the synthesis of pyrimidones. With ever increasing demand of green chemistry in organic synthesis, finding greener method along with novel catalyst would be the need of hour for these molecules syntheses.

In recent times, carbon-based materials are one of the best options for the synthesis of various organic compounds as they have excellent properties such as large specific surface area, high porous structure, low mass density, and strong interactions between carbon and hydrogen atoms. Among various carbon-based materials, graphene oxide is a promising candidate for a wide variety of catalytic applications [15]. Graphene oxide is a flat two-dimensional (2D) monolayer of  $\text{sp}^2$  and  $\text{sp}^3$  hybridized carbon atoms packed into a honeycomb lattice. Due to its unique properties like high carrier mobility, good catalytic activity, thermal stability [16] and good mechanical property [17], it has received increasing attention since its discovery. Graphene oxide is the graphene-derived sheet having similar properties to that of graphene produced by oxidation of graphite through modified Hummers' method [18]. GO sheets are heavily oxygenated bearing carbonyl, carboxylic group at the edges and epoxide and hydroxyl group located on the basal plane due to which these sheets are strongly hydrophilic [19]. These hydroxyl, carboxylic groups on graphene oxide surface can be further functionalized with inorganic and organic functional groups via covalent or non covalent interactions [20]. This type of interaction with functional group generate a novel bifunctional hybrid material which would display high catalytic activities for the one-pot multi component condensation reaction. Recently, acidic group functionalized graphene oxides has attracted special research efforts as it enhances the bifunctional behaviour of GO surface. This is attributed to the high density and homogeneous distributions of the acid functional groups and unique 2D structure of the GO supports [21]. Different acidic groups such as hyaluronic acid [20], 3-carboxyphenylboronic acid [22], phosphate [23] and sulfonate functional group [24] have been used to modify the graphene oxide surface. Similar to sulfonated GO, phosphonated GO

would be an ideal way in order to design highly efficient solid acid catalyst. This is because, phosphoric acid have high charge carrier concentration, thermal stability, and oxidation resistance [25]. More importantly, it is advantageous due to its possible proton conduction in the dry state by forming dynamic hydrogen bond networks. So far, the functionalization of other carbonaceous materials like Carbon nanotubes (CNTs) with phosphoric acid has been widely studied in catalysis [26]. However, phosphonated GO have not yet been explored for catalytic applications. Hence, there was an urgent need to explore the use of phosphonated GO in catalytic applications as solid acid catalyst. We envisioned that utilizing the unique features of phosphoric acid as functional group and GO as support, highly efficient solid acid catalyst can be designed.

In the synthetic organic chemistry, the current demand is to minimize the energy consumption and use of a toxic solvent. The use of microwave method is found to be one of the most efficient and green technique to address this problem [27]. As compared to traditional method, microwave assisted reactions have gained importance due to its simplicity of operation, improvement of the rate of reaction, high product yield, and much reduction of time and formation of the pure product. The specific combination of solid catalyst with microwave radiation synergistically shows various beneficial characteristics as they can serve as an internal heat source medium for reactions and most solid catalysts absorb microwave irradiation [28]. It has been found that microwave heating is the most uniform, direct and selective heating that can be provided to any heterogeneous catalytic reaction as it occurs on the surface of catalyst which decreases the reaction time remarkably. Given the unique benefits associated with both phosphated GO and microwave method, a combination of these two would be highly beneficial for organic synthesis, particularly heterocyclic molecules syntheses.

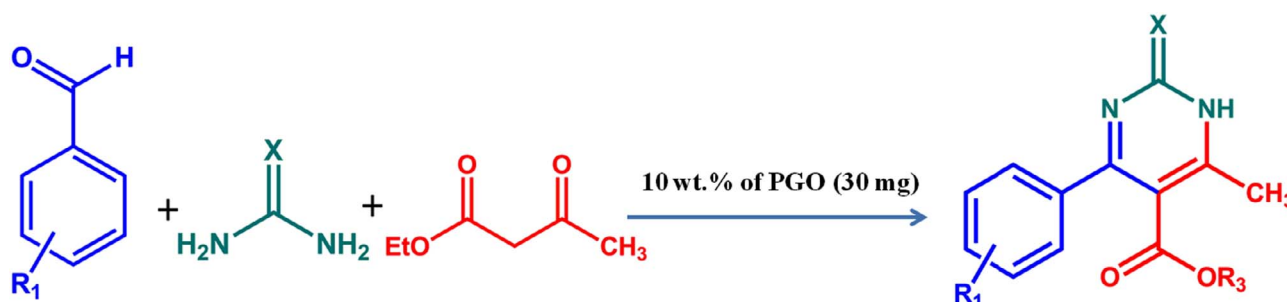
Herein, we report the microwave assisted synthesis of DHPM and DAPM molecules using phosphate functionalized GO (PGO) as an efficient heterogeneous catalyst. The Pyrimidones synthesis was obtained via ternary condensation of urea, aldehydes, and 1, 3-dicarbonyl in the presence of PGO nanocatalyst (Scheme 1) and the same protocol was applied to other pyrimidone derivatives syntheses. With our designed catalyst all the reactions proceeded in a shorter reaction time as compared to traditional reported catalysts. Moreover, our catalyst shows an excellent stability after five reaction cycles with minimal loss in activity in solvent free system.

## 2. Experiment

### 2.1. Catalyst preparation

#### 2.1.1. Starting materials

Graphite powder,  $\text{CDCl}_3$ , LiBr and triethylphosphite were purchased from Sigma-Aldrich.  $\text{H}_2\text{O}_2$  (30%), ethanol,  $\text{NaNO}_3$ ,  $\text{KMnO}_4$ , HCl,  $\text{H}_2\text{SO}_4$  (98%) and silica gel (100–200 mesh) were purchased from Hi-Media. All the chemicals were used without any further purification. 18 M $\Omega$  cm Milli-Q water was used throughout the synthesis.



Scheme 1. A model reaction for the synthesis of 3,4-dihydropyrimidin-2(1H)-one.

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