Selective oxidation of benzyl alcohol by reduced graphene oxide supported platinum nanoparticles

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Abstract. The Pt / rGO nanocatalyst was synthesized by the immobilization method by deposition of platinum nanoparticles on reduced graphene oxide (rGO) as a support material. The support (rGO) was prepared from the reduction of graphene oxide (GO) by the reducing agent sodium borohydride (NaBH₄), while (GO) was prepared from the graphite oxidation using the modified Hummer method. Morphological, chemical and structural characteristics of synthesized samples were investigated by Scanning Electron Microscope (SEM), transmission Scanning Microscope (TEM), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), and X-ray and Raman Spectroscopy. The performance of the Pt/rGO catalysts were evaluated in the benzyl alcohol oxidation to produce benzaldehyde using an environmentally friendly oxidizing agent, hydrogen peroxide, under moderate conditions. The variables that were studied on oxidation of benzyl alcohol were temperature, catalyst mass and H₂O₂ concentration. The best results were achieved when the catalyst amount was 10 mg, 50% hydrogen peroxide concentration and 80 °C reaction temperature. The conditions under which the reaction was carried out are moderate reaction conditions, and the oxidizing agent (H₂O₂) is an environmentally friendly oxidizing agent.

Keywords: Pt/rGO, benzyl alcohol, benzaldehyde, selective oxidation, hydrogen peroxide

1. Introduction
Graphene, a single -atom -thick sheet of carbon atoms with a two-dimensional hexagonal lattice structure (2d) material, has attracted extensive interest since the discovery of the material in 2004[1], which has become a revolutionary material due to its excellent electrical, chemical, mechanical, optical and thermal
properties[2-5]. All these features made graphene related materials are promising materials that can be used in many applications such as biosensors[6], gas sensors[7], transistors[8], energy production [9], energy conversion[10] and electronics[11], adsorbents [12] and photocatalysis[13]. However, graphene is conventionally considered as chemically inert and thermodynamically stable due to its saturated C-C bonds [14]. The lattice defects, vacancies, impurities, dopants and chemical modifications are widely considered as main objective to enhance the catalytic activity, catalytic selectivity, recovery and reusability of graphene based catalysts [15, 16]. The development of new heterogeneous catalysts on various supports is necessary to search of more efficient ways to provide a promising solution taking into account environmental considerations and fabrication of an efficient catalyst [17, 18]. Recently, growing interest has emerge in graphene supported metal catalysts (Au,Ag,Pd,Pt,Co,Rh) which have been mainly applied in the liquid phase hydrogenation reactions in various applications reactions and exhibit enhanced catalytic activity[19-23].

Graphene supported Pt nanocomposites showed to be very good catalysts for the synthesis of fine chemicals, especially in selective hydrogenation and oxidation reactions [24]. Selective oxidation processes are used to activate raw materials (alkanes, alcohols) and transform them into useful products, which are of industrial interest, but they are often characterized by low conversions and the formation of unwanted by-products [25]. It has been found that graphene-supported platinum catalysts exhibit excellent catalytic performances in terms of selectivity for the electro-oxidation of formic acid [26], asymmetric hydrogenation α-ketoesters [27], selective hydrogenation of cinnamaldehyde [28] and oxidation of formic acid [29].

Selective catalytic oxidation of aromatic and aliphatic alcohols to corresponding aldehydes or ketones is one of the most essential organic transformations in both scientific and industrial applications [30]. Industrially, oxidation of alcohols is very important due to their use as starting materials for a variety of ketones, aldehydes, acids, etc. required to produce many of synthetic substances like plastics, detergents, paints, cosmetics, food additives and drug intermediates [31]. Indeed, catalytic reaction of inexpensive and widely available chemicals to produce high value added chemicals remains a significant task in many important current industrial and fine chemical processes [32].

The objectives of current work is to investigate the sol-immobilization technique for synthesis reduced graphene oxide based platinum catalyst (Pt / rGO) and investigate the catalytic oxidation of benzyl alcohol. Effects of catalyst dosage, temperature and H2O2 concentration on the catalyst selectivity has been studied. Also the research included characterization study of Pt / rGO by various techniques, such as Fourier-transform infrared (FT-IR), Raman, Field - Emission Scanning Electron Microscopy (FE-SEM), X-ray diffraction powder (XRD), and Transmission electron microscopy (TEM).

2. Experimental

2.1 Chemicals

Graphite powder flakes (60 mesh, 98.5 %) was supplied by LOBA Chemical, India. Benzyl alcohol (99%) was procured from Merck USA, Chloroplatinic acid hexahydrate, polyvinyl alcohol (PVA, 80% hydrolysed, MW ~ 9000-1000 g mol⁻¹) and sodium borohydride (>98.0%) were supplied from Sigma-Aldrich Chemical Pvt. Limited.
Hydrogen peroxide (30%, 50%), potassium permanganate (99%), sulfuric acid (96%), hydrochloric acid (37%), and sodium nitrate (99%) were provided by Scharlau. All chemicals were used without further purification. The water used to prepare all aqueous solutions was purified via Milli-Q system.

2.2. Instruments

To analyze the crystallite sizes and lattice structures, X-ray diffraction (XRD) patterns of as synthesized samples were obtained by Bruker D6 Advance diffraction with Cu Kα radiation source (λ = 1.541 Å). The diffraction data were recorded for 2θ angles between 5 and 80° at a step size of 0.017°. Raman spectra were recorded from 500 to 3000 cm⁻¹ on a Renishaw Invia Raman Microprobe using a 514 nm argon ion laser. Fourier-transformed infrared spectra (FTIR) of synthesized samples were analyzed by the KBr pellet method with a Bruker Vector 22. The JEOL JSM-630LV scanning electron microscopy was employed to show the samples surface morphology and particle size distribution. Moreover, the nanostructure of the representative catalyst was assessed by transmission electron microscopy (TEM; FEI Tecnai G2 f30 SUPER-twin). For the analysis of the oxidation products, a gas chromatograph flame ionization detector (Equipped with a capillary column, DN-Wax column) was used.

2.3. Preparation of chemically reduced graphene oxide

Reduced graphene oxide (RGO) was prepared from the reduced of graphene oxide, which in turn was prepared by oxidizing graphite via modified Hummer's method, by mixing 5 g of graphite powder with 2.5 g of NaNO₃ in a beaker (1L) inside an ice bath at a temperature (0-5 °C) then add 120 ml of H₂SO₄ to the continuously stirring beaker for 3 h, then gradually add 15 g of KMnO₄ as the addition takes 20 min. Stirring continues for 5 minutes after remove the snow bath, and raises the temperature of the mixture to 35 °C with constant stirring for 12 hours, then 500mL of distilled water is added very gradually to the mixture so that the addition takes no less than 20 minutes and then raises the temperature to 98 °C and 90 minutes, then add 30 ml of H₂O₂ (30%) with stirring. The color change of the solution is what proves the success of the oxidation process, as the color change of the solution from dark black to golden yellow, means the conversion of all graphite to caravan oxide. The precipitate is separated and washed with a dilute solution of hydrochloric acid (30%) several times to get rid of impurities, after that the solution is washed with distilled water well for the purpose of getting rid of the acidity of the solution and obtaining a neutral solution. The precipitate leave it in an oven under the vacuum pressure at a temperature of 60 °C until the drying is complete [33, 34].

A standard method for the chemical conversion of graphene oxide into reduced graphene oxide includes the dispersion of graphite oxide (100 mg) in water (50 mL) for 1 hour by sonication treatment. The suspension under continuous stirring was thoroughly combined with NaBH₄, to obtain reduced nanosheets of rGO from transforming GO into solution was stirred at 100 °C for 1 hour. The precipitate was separated from the solution and then washed with distilled water first and then with ethanol, then the precipitate is dried in the oven at 60 °C [35].

2.4. Catalysts Preparation

In this study platinum nanoparticles were loaded on reduced graphene oxide by sol immobilization method. An aqueous solution of the desired concentration of H₂PtCl₆·6H₂O (Pt: 6 mg/mL) was prepared. Polyvinylalcohol
(PVA) (1 wt% solution) was added (PVA/Pd (by wt) = 0.25). Then, freshly prepared aqueous solution of NaBH4 (0.1 M, NaBH4/Pd (mol/mol) = 5) was added to form a dark-brown sol. After 5 minutes, the suspension was acidified at pH 2 consuming sulfuric acid, and the support reduced graphene oxide nanosheets (1 g) was added under vigorous stirring. The amount of material required for the support was estimated to have a total final metal loading of 1wt%. After 1 hour, the slurry was filtered and washed copiously with distilled water (2-3 L) to remove impurities, such as Na+ and Cl−) and dried at 80 °C overnight under static air to obtain the Pt/rGO nanocomposite.

2.5. Effect of catalyst on conversion and selectivity efficiencies
The catalytic efficacy of the Pt/rGO catalyst through benzyl alcohol oxidation has been evaluated. 10 mL of benzyl alcohol was mixed with the required amount of Pt/rGO, then, H2O2 was added as an oxidant agent without use of any solvent and the mixture was heated to required temperature in oil bath. The reaction was carried out in a double necked bottom round flask (50 mL). The curved flask at the bottom was attached to a reflux condenser and agitated by magnetic stirrer for 4 hours. After the reaction was completed the mixture was cooled down to 25 °C and the catalyst was got by centrifuging the reaction mixture at 6000 rpm, then, the sample (0.5 mL) was diluted with 0.5 mL of standard substance solution (mesitylene) as an internal standard and kept in a cool place for the purpose of displaying it with a gas chromatography (GC) flame ionization detector (Equipped with a capillary column, DN-Wax column). It measured the benzaldehyde product according to the standard procedure. In GC straight 0.5 μL injection of the reaction mixture has been used. The benzaldehyde concentrations were measured using the internal calibration curve. The calibration factor (CF) was determined as detailed. The concentrations of benzyl alcohol were used to achieve a calibration plot for benzyl alcohol and the calibration element was considered as:

\[
CF = \frac{\text{Mole}(\text{benzyl alcohol})}{\text{Mole}(\text{mesitylene})} \times \frac{\text{Area}(\text{mesitylene})}{\text{Area}(\text{benzyl alcohol})}
\]

\[
\text{Mole of Compound} = \text{Mole}(\text{mesitylene}) \times \frac{\text{Area}(\text{benzyl alcohol})}{\text{Area}(\text{mesitylene})}
\]

The conversion of the reactants were calculated by equation (3), and the selectivity of the resulting materials was determined by equation (4).

\[
\text{Conversion} (%) = \frac{\text{Moles of benzyl alcohol reacted}}{\text{Total Moles of benzyl alcohol}} \times 100
\]

\[
\text{Selectivity} (%) = \frac{\text{Moles of product formed}}{\text{Moles of benzyl alcohol reacted}} \times 100
\]

3. Results and discussion
3.1. Characterization of synthesized materials

3.1.1. Fourier Transform Infrared Spectra
FT-IR spectroscopy can supply insights into the extent of addition of oxygen groups to graphite (G) for formation graphene oxide (GO) and removal it to production of reduced graphene oxide (rGO) during the oxidation and reduction process. Figure 1, shows spectrum for G, GO, rGO and Pt/rGO. The graphite spectrum showed the presence of a broad peak at 3422 cm−1 consequent to the stretched vibrations (O−H) due to the H2O molecules which
the graphite absorbs, and the absorption band that appeared at 3010 cm\(^{-1}\) are attributable to the C-H groups within of the graphite structure, as well as the presence of peak at 1624 cm\(^{-1}\) consequent to the vibration stretch of the C=C groups present in the graphite [36]. After the oxidation of graphite (G) with the oxidizing agents to obtain graphene oxide (GO), many peaks appear in the spectrum of GO, including a absorption band at 3424 cm\(^{-1}\) and 2924 cm\(^{-1}\) which were attributed to the vibrations of O-H and C-H, respectively, while the peaks at 1745 cm\(^{-1}\)and which is due to the vibration of the group (C=O). While the peak indicates at 1624 cm\(^{-1}\) to stretch vibration (C=C) which is not oxidized within the carbon structure. In addition, the peak at 1060 cm\(^{-1}\) was related to vibration of epoxy group (C-O-C) [36, 37]. The presence of oxygen-rich functional groups is evidence of the oxidation of graphite to graphene oxide. The presence of oxygen-rich functional groups is evidence of the oxidation of graphite to graphene oxide. Through the infrared spectrum of reduced caravan oxide, it is clear that all oxygen groups have reduced their peaks, which confirms the removal of these groups by the reduction process by sodium borohydride (NaBH\(_4\)) [38]. With respect to the FT-IR spectrum for the Pt/rGO catalyst, the oxygen groups represented by the carbonyl and epoxy groups, the strength of their peaks is lower than in the FT-IR spectrum of graphene oxide, indicating the role of the reducing agent in the reduction process. However, the catalyst spectrum still contains small peaks for these aggregates.

![FT-IR spectra](image)

**FIGURE 1** FT-IR spectra of (a) G, (b) GO, (c) rGO, and (d) Pt/rGO.

### 3.1.2. X-ray diffraction patterns

X-ray diffraction study has confirmed structural features of G, GO, rGO and Pt/rGO. When comparing the spectra with each other, as shown in Figure 2, it is clearly shown that the typical G (002) peak appeared at \(2\theta = 26.7^\circ\). The feature of this peak is that it is very sharp compared to the peaks of GO and rGO, as the distance between its layers is 0.33nm [39]. However, after the oxidation of graphite, the distance between the layers of graphene oxide expands to 0.79 nm, which has a prominent peak (001) that appears at \(2\theta = 11.6^\circ\) [40]. The XRD spectra of reduced graphene oxide clearly shows that the broad peak, d-spacing 0.349 nm, shifts to higher angle after reduction by sodium
borohydride, appears at $2\theta = 23.9^\circ$, is due to the diffraction of the (002) plane rGO suggesting that GO was reduced by NaBH$_4$ and this led to an arranged of the crystal structure [41,42], In general, it can obviously be seen the patterns of the Pt catalysts have crystalline structure with peaks appearing at 39.5°, 46.8° and 67.6° can be indexed to the (111), (200) and (220) planes of the face center cubic (fcc) structure of Pt (JCPDS 04-0802). The diffraction peaks at $2\theta=23.7^\circ$, is assigned to the reflections of the reduced graphene oxide support. Based on Shearer's equation, it was found that the size of platinum nanoparticles is 6.63 nm.

![XRD patterns of (a) G, (b) GO, (c) rGO, and (d) Pt/rGO.](image)

FIGURE 2  XRD patterns of (a) G, (b) GO, (c) rGO, and (d) Pt/rGO.

3.1.3. Raman spectra

Raman spectra is a valuable analytical method for the analysis of graphene compounds [43] by tracking the displacement of the D and G bands when placed under chemical influences. Figure 3, shows the Raman spectra for graphite (G), graphene oxide (GO), reduced graphene oxide (rGO) and Pt/rGO, through which it is clear that the positions of the G and D bands in the graphite are located at 1582 cm$^{-1}$ and 1350 cm$^{-1}$ respectively, these bands are displaced from their positions by after the oxidation of graphite approximately 10 cm$^{-1}$ to the graphene oxide, due to
the decrease in the sp² domain, to appear in new locations is 1600 cm⁻¹ for the G band and to 1364 cm⁻¹ for the D band. G and D bands back to their first positions again after the reduction of GO to rGO and pt/rGO to appear at 1582 cm⁻¹ and 1352 cm⁻¹, respectively in rGO and 1582 cm⁻¹ and 1357 cm⁻¹, respectively in Pt/rGO. The displacement of the G and D bands from their positions in the graphite and their appearance in a new location, then their return to their first locations is what proves the success of the oxidation of graphite and the reduction of the graphene oxide. Moreover, the ratio between the intensity of the D and G bands (D/G) in the Raman spectrum is an important factor in characterization carbon compounds, as it is an indication of the extent of the breakdown of the carbon structure [44]. The results shown in Figure 3 show that the D/G ratio of graphite is 0.77, for graphene oxide 0.97, 1.09 for reduced graphene oxide and 1.12 for catalyst (Pt/rGO).

3.1.4. Field Emission-Scanning Electron Microscopy images

Scanning electron microscope is one of the most important and widely tools used in characterization of nanostructures. The signals that derive from SEM technique reveal information about surface morphology and chemical composition of the synthesized materials [45]. FESEM micrographs of graphite, graphene oxide, reduced graphene oxide and catalyst (Pt/rGO) were shown in figure 4. The G consists of several layers that are stacked on top of each other, with a flat and smooth surface [46, 47]. FE-SEM image of GO nanosheets after oxidation shows a wavy frizzy look because the layers are separated and the edges of the sheets are foggy. That can be caused by attachment of residual water molecules, carboxyl and hydroxyl groups to sheets. The rGO nanosheets have a thin, wrinkled texture and stacked with sharp edges, meaning that the reduction process is complete [48]. The FE-SEM image of the Pt/rGO catalyst is shown in Figure 4, platinum nanoparticles scattered over the rGO surface.
3.1.5. Transmission Electron Microscopy of catalyst

This technique was used to study and know the nature of the spread of metal nanoparticles on the support. Figure 5. Illustrates the TEM image of Pt/rGO catalyst, where it is clear that Pt nanoparticles are in the form of nanoclusters uniformly distributed on graphene plates [49] and the average size of Pt nanoparticles is 6-13 nm. These results are consistent with previous results calculated using the Scherer equation in XRD technology.

3.2. Catalytic behavior of catalyst

The Pt / rGO catalyst's performance was tested by benzyl alcohol oxidation to benzaldehyde. The best conditions for the catalyst mass, temperature of the reaction, and concentration of the oxidant (H₂O₂) were measured.

3.2.1. Effect of temperature
In order to determine the ideal temperature for the oxidation reaction of benzyl alcohol, the reaction was carried out at two different temperatures (60, 80 °C), with a fixed amount of catalyst (5 mg) and the concentration of the oxidizing agent (H₂O₂) was 30%. The results shown in Figure 6, show that the conversion ratio and selectivity of benzaldehyde has increased with increasing temperature, but with the passage of time of reaction the selectivity of benzaldehyde decreases, and the reason for this is that with continued oxidation and high temperature, benzaldehyde is oxidized to benzoic acid [50,51].

![Figure 6](image1.png)

**FIGURE 6.** Effect of temperature on selectivity and conversion of reaction at 60 °C and 80 °C.

3.2.2. Effect of catalyst mass

The effect of the catalyst amount Pt / rGO was studied on the oxidation process of benzyl alcohol, after the temperature was fixed at 80 °C as the optimum temperature and the concentration of H₂O₂ was 30%, the catalyst mass under study was 5, 10 mg. It was found that there is a noticeable increase in the conversion ratio and the selectivity of benzaldehyde as shown in Figure 7, when increasing the amount of the catalyst from 5 to 10 mg, because the increase in the amount of the catalyst leads to a rapid dissociation of hydrogen peroxide, which in turn affects the oxidation process [51]. Through the above figure, it is clear that with the continuation of the reaction path, the increase in the conversion rate is accompanied by a decrease in the selectivity of benzaldehyde, due to the oxidation of aldehydes to carboxylic acids.

![Figure 7](image2.png)

**FIGURE 7.** Effect of catalyst mass on selectivity and conversion of reaction at 5 mg and 10 mg.

3.2.3. Effect of different concentration of H₂O₂
Figure 8 shows the effect of the oxidizing force (H$_2$O$_2$) on the ratio of the conversion of the reactants to the products and selectivity of benzaldehyde when using two different concentrations of hydrogen peroxide, 30% and 50%, with a choice of optimal conditions for the reaction of 10 mg of catalyst amount and 80 °C reaction temperature. The results indicated that there is a noticeable increase in the ratio of reaction conversion and selectivity of benzaldehyde, especially in the conversion rates when using a concentration of 50% of the oxidizing factor, and this is due to the increase in the self-dissociation of hydrogen peroxide at high concentrations, in addition to the effect of both the catalyst amount and the high temperature. This increase in the rate of reaction conversion is offset by a decrease in selectivity when continuing the reaction to the specified time (240 min), because the above conditions encourage the oxidation of benzaldehyde to benzoic acid.

Table 1, represents the best results obtained from the oxidation of benzyl alcohol with the use of a Pt / rGO catalyst prepared by the Immobilization method and in moderate conditions represented by 10 mg mass of the catalyst, 80 °C reaction temperature and 50% hydrogen peroxide concentration. These results are consistent with previous studies that used hydrogen peroxide as an environmentally friendly oxidizing agent in the oxidation of benzyl alcohol, as shown in a table 2 [52,53].

| Catalyst  | Time (min) | Conversion (%) | Selectivity (%) |
|-----------|------------|----------------|-----------------|
|           | 30         | 3.3            | 3.8 89.6 6.6    |
| Pt/rGO    | 120        | 10.7           | 3.1 87.4 9.6    |
|           | 240        | 16.2           | 1.8 85.5 12.7   |

These results confirm that Pt/rGO nanocomposite was were successfully fabricated via immobilization method, with promising catalytic activity when, compared to other catalyst synthesized via immobilization method or other one. E.g. 1 % Au-Pd/C$_{Si}$ [52] and Au-Pd/C$_{Si}$ [53] which conversed 15.1% and 15.2%
respectively. Table 1 shows a comparison with other catalyst fabricated for selective oxidation of benzoyl alcohol is assistance of H$_2$O$_2$.

**TABLE 2: Previous studies have used hydrogen peroxide to oxidize benzyl alcohol.**

| No. | Catalysts         | Conv. % | Select. % | Condition                                | ref |
|-----|-------------------|---------|-----------|------------------------------------------|-----|
| 1   | 1% Pt/rGO         | 3.3     | 89.6      | V = 10 mL, Wt = 0.01 g, t = 4 h, T = 353 K, rpm = 600 | This work |
| 2   | 1% Au/C$_{st}$    | 5.5     | 88.8      | V = 10 mL, Wt = 0.15-0.3 g, t = 4 h, T = 353 K, rpm = 200-300 | 52  |
| 3   | 1% Au-Pd/C$_{st}$ | 15.2    | 89.4      | V = 10 mL, Wt = 0.15-0.3 g, t = 4 h, T = 353 K, rpm = 200-300 | 53  |
| 4   | 1% Pd/rGO         | 3.3     | 89.6      | V = 10 mL, Wt = 0.01 g, t = 4 h, T = 353 K, rpm = 600 | 54  |

* Active carbon.

### 3.3. Mechanism of benzyl alcohol

Benzyl alcohol (1) is often used as a typical reaction for alcohol oxidation. This is due to the high efficiency and its ability to form a number of different compounds, as shown in scheme (1). Some of these compounds are major and desirable products, such as benzaldehyde (2) and benzoic acid (3), but benzyl benzoate (4), benzene (5) and toluene (6) are byproducts formed depending on the reaction conditions and the type of catalyst used. Benzaldehyde and benzoic acid are formed by the oxidation of the benzyl alcohol, while the by-products of benzene, toluene and benzyl benzoate formed as a result of a series of side reactions, which are hydrogenolysis, decarbonylation and esterification respectively [55-58].
4. Conclusions
In this study, platinum nanoparticles were successfully deposited on reduced graphene oxide by immobilization method using sodium borohydride as a reducing agent and poly vinyl alcohol as a stabilizer agent. Reduced graphene oxide was obtained as supporting material to improve the catalytic properties of Pt. The XRD diffraction indicate the presence of Pt and reduced graphene oxide in the synthesized samples. Moreover, the SEM and TEM results confirmed that the Pt nanoparticles strongly deposited on the surface of rGO nanosheets. Additionally, the present work shows that the selective oxidation of benzyl alcohol to benzaldehyde can be achieved with a Pt/rGO (10 mg weight, 80 °C and 50% concentration of H₂O₂), this significantly enhanced activity attributed to the strong interaction between platinum nanoparticles and the rGO material as well as a significantly enhanced dehydrogenation capability.

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