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Pt Nanoparticles Loaded on Reduced Graphene Oxide as an Effective Catalyst for the Direct Oxidation of 5-Hydroxymethylfufural (HMF) to Produce 2,5-Furandicarboxylic Acid (FDCA) under Mild Conditions

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Abstract:

Reduced graphene oxide (RGO) is one of the most promising catalyst supports since its faintly acidic sites together with large amount of functional groups on its surface. In this report, we prove that, for the first time, Pt loaded RGO (Pt/RGO) is an efficient, robust and durable catalyst oxidizing 5-hydroxymethylfufural (HMF) directly to 2,5-furandicarboxylic acid (FDCA) under mild conditions. The selectivity of FDCA reaches up to 84% along with 100% HMF conversion in the presence of excess base. We deduce that the total reaction on Pt/RGO catalyst includes several consecutive steps, in which 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) acts as an intermediate. The finding in this report is a significant advance not only for RGO-based catalysts development, but also for FDCA scalable production, because the total reaction is performed smoothly without using previously reported harsh reaction conditions.

Keywords: HMF, FDCA, reduced graphene oxide, mild conditions, Pt nanoparticles

Introduction

Nowadays, 5-hydroxymethylfurfural (HMF), a biomass-derived intermediate, is readily available from a variety of renewable biomass resources such as fructose, glucose,[1] polysaccharides,[2] and cellulose.[3] 2,5-furandicarboxylic acid (FDCA) has been considered as a potential biorenewable monomer to replace terephthalic acid in the production of polyethylene terephthalate (PET).[4] Moreover, FDCA has also been identified as one of several important building blocks for the production of biomass-derived value-added chemicals.[5] Generally, the oxidation of HMF to FDCA can be catalyzed by various stoichiometric oxidants, such as $KMnO_4$,[6] or homogeneous metal salts (Co, Mn), those are currently used for terephthalic acid production under high pressure (70 bar air).[7] Different reaction systems using Pt-, Pd- or Ru-based heterogeneous catalysts have been reported for the selective oxidation of HMF to FDCA,[8,9] but these methods require high pressure or high temperature, and have lower catalyst stability and selectivity.

Recently, several reports have been presented using supported Pt catalysts for aqueous HMF oxidation to improve FDCA yields.[10-17] Using the supported Pt as catalysts, as reported by Davis et al.,[13] the addition of homogeneous base (1-20 eqiv. NaOH) and high oxygen pressure (3-20 bar) are required. Strasser et al. shows that the feedstock of HMF degrades rapidly at 353K in alkaline water.[15] In addition, Gupta et al. also reports a base-free oxidation in water over gold catalysts supported on hydrotalcites, yielding FDCA with almost 100% yield at 368K.[14] Although the Pt- and Au-based catalysts seem to be promising, the catalyst design and reaction conditions, especially reaction temperature and pressure must be further optimized.

Carbon material, such as activated carbon, had been reported as catalyst support in HMF oxidation reaction.[10,11,13,15-17] However, to our knowledge, graphene oxide, a novel carbon material, has not been reported as catalyst or support material in this reaction until now. Compared with other carbon materials, graphene oxide has attracted tremendous attentions in recent years due to its relatively stable physical properties and unique two-dimensional planar structure.[18] In addition, graphene oxide is slightly acidic since large amount of functional groups on its surface.[19,20] These functional groups on the surface of graphene oxide can be also utilized as anchoring sites fixing metallic nanoparticles, increasing the dispersion of the supported nanocatalysts and tuning their catalytic performance. Moreover, the graphene sheet has spillover effect under H_2 or O_2 reaction atmospheres especially when noble metal exists as supported catalyst.[21] These special performances may be beneficial for the oxidation of HMF when the Pt loaded reduced graphene oxide (Pt/RGO) is used as catalyst.

In this work, the Pt loaded graphene oxide (Pt/RGO) catalyst was prepared by ethylene glycol reduction method[22] and used in the HMF oxidation reaction to produce FDCA. Other metallic nanoparticles, like Pd, Ru, Rh and Pt, loaded on the reduced graphene oxide were also prepared and their catalytic performances were compared together. As the best catalyst for FDCA production, the Pt/RGO catalyst was investigated in detail. The possible reaction route on the Pt/RGO for HMF oxidation to form FDCA is presented in Figure 1.

Experimental Section

Hummer's method was used to prepare Graphite Oxide (GO).[23] 10.0 g graphite powder and 5.0g $NaNO_3$ were mixed in a flask, and cooled in ice bath. 230 ml of concentrated H_2SO_4 solution was added into the above mixture. After stirring for 10 min, $KMnO_4$ was gradually added, and the mixture was kept stirring in an ice bath for another 15 min. The mixture was then kept at 308K and stirred for 50 min until a thick paste was obtained. 460 ml of water was added into the above mixture, and the reaction temperature was gradually increased to 371K. The mixture was kept at 371K and stirred for another 30min. Finally, 1000 ml of deionized water and 3.0 ml of 30% H_2O_2 were slowly added to the mixture and stirred for 5 min. The obtained yellow dispersion was washed by deionized water for several times to remove residual salt, and the solid (GO) was then dried under vacuum for 3 days.

H_2PtCl_6 (aq.) (Pt wt% =4.578%, 0.56 ml) and graphite oxide (1.0 g) were dispersed in 120ml of ethylene glycol (EG) (aq, EG v% = 83.3%) with the assistance of ultrasonic. After being treated ultrasonically for 2 h, the mixture was put into an oil bath and kept at 408K for 15 h. The catalyst was obtained through a redox reaction, and the solid product was then collected by filtration and washed with deionized water and ethanol in sequence, before drying. The final metal loading amount was 5.0 wt%, and the obtained catalyst was defined as Pt/RGO. Other metals loaded RGO catalysts Pd/RGO, Rh/RGO and Ru/RGO were also prepared by same method using $Pd(NO_3)_2$, $Rh(NO_3)_3$, $Ru(NO_3)_3$ as metal sources. Furthermore, pure RGO, as a reference catalyst, was also prepared by this method, but without any metals addition. In order to prove the combined function of active metal Pt and support RGO, another general catalyst support, active carbon (AC), had also been selected to prepare a reference catalyst Pt/AC.

The Pt/RGO catalyst morphologies were characterized with high-resolution transmission election microscope (TEM, JEOL JEM-2100 UHR) operated at 200 kV. The catalyst crystal structure was confirmed by X-ray Diffraction (XRD) with a Rigaku D/max-2250 V diffractometer employing Cu Kα radiation (λ = 1.54 A; scanning rate: 0.02°/s). X-ray photoelectron spectroscopy (XPS) was conducted using ESCALAB 250Xi spectrometer equipped with a pre-reduction chamber. The position of the C1s peak (284.5 eV) was used to correct the XPS binding energies for all catalysts to erase possible charging effect.

HMF oxidation reaction was carried out in a three-neck-flask attached with a glass reflux condenser under oxygen flow (see Figure 2). In each experiment, the reactor was filled with 1.0 mmol of HMF and 5.0 mmol of NaOH in 10 ml of water. 0.1 g M/RGO (M=Pd, Rh, Ru or Pt) was added into the reactor and oxygen was introduced at a flow rate of 50 ml/min with stirring under atmosphere pressure. After reaction, the catalyst was filtered off before the high performance liquid chromatography (HPLC) measurement (Animex HPX-87H column from Bio-Rad Laboratories Co. Ltd, 0.5 ml/min flow rate, 10 nM H_2SO_4 solvent, 323K). The products were analyzed using a refractive index (RI) detector.

Result and discussion

The crystal structure of the best catalyst Pt/RGO was confirmed by XRD. We used XRD to confirm whether the crystal structure of the spent Pt/RGO was identical to that before reaction. In Figure 3, the strong diffraction peak for two samples can be assigned to RGO. The diffraction peaks at $2\theta = 39.6°$, $42.6°$ and $67.5°$ can be ascribed to the characteristic peak of Pt (111), (200), and (220) crystalline planes of Pt respectively, which possesses fcc structure. The diffraction peak of Pt (111) was used to estimate the Pt particle size by Scherrer equation. The calculated average particle size of Pt on RGO sheet is 3.28 nm before the reaction, and 3.60 nm after the reaction, indicating the selected reaction conditions has no obvious effect on Pt nanoparticles size.

The morphologies of the Pt/RGO catalyst were also characterized by TEM. As shown by Figure 4(a,b), highly dispersed Pt nanoparticles with a uniform size of 3.28 nm loaded on RGO surface were obtained by heating H_2PtCl_6 and GO in the ethylene glycol aqueous solution. In Figure 4(c,d), the Pt nanoparticle size of Pt/RGO increased slightly to 3.60 nm after reaction for 24h. These TEM images confirmed that the highly dispersed Pt nanoparticles with uniform size had been successfully synthesized and well located on the RGO sheets through ethylene glycol reduction method.

X-ray photoelectron spectra (XPS) using ESCALAB 250Xi spectrometer equipped with a pre-reduction chamber was used to investigate the surface composition of Pt/RGO catalyst. As shown in Figure 5(a), Pt 4f spectra of Pt/RGO exhibited the expected doublets of Pt 4f 7/2 and Pt 4f 5/2, with Pt^0, Pt^{2+} and Pt^{4+} states. It is interesting to note that a respectable percentage of Pt remained still in its metallic state (Pt^0) in Pt/RGO after being used for even 3 times, which can be found in Figure 5(b). In addition, two different types of Pt cations could be assigned, suggesting that the oxygen linkages existed between Pt nanoparticles and RGO surface, and the oxide layers formed on the Pt nanoparticles surface.

Besides C-C sp^2 (284.2eV) and C-C sp^3 (285.7eV), C-O (286.4eV) and C=O (288.9eV) are also observed by XPS, proving that a lot of functional groups formed on Pt/RGO catalyst surface.

Using wavelength dispersive X-ray flourescence spectrometer, it is clarified that oxygen content decreased slightly after reaction, 53.2wt% to 52.1wt% for GO while 20.8wt% to 19.8wt% for 5% Pt/RGO, due to the co-existing NaOH base. This changing trend is in accordance to the reported findings [24-26], where high-concentration NaOH solution treatment lowered the oxygen content in GO.

Different kinds of metallic nanoparticle such as Pd, Rh, Ru, Pt loaded on RGO were also prepared and evaluated. All the catalysts were prepared by the same EG reduction method. As listed in Table 1, Pd/RGO and Pt/RGO catalysts demonstrated almost 100% conversion of HMF. Pt/RGO and Pd/RGO yielded FDCA, whereas Ru/RGO and Rh/RGO gave HMFCA as main product, along with some decomposition by-products such as levulinic acid and 2,5-bishydroxymethylfuran (BHMF). Pt/RGO catalyst resulted in the highest yield of FDCA about 41%. The order of FDCA yield is as follows: Pt/RGO>Pd/RGO. In addition, Pt supported on activated carbon (Pt/AC), as a reference catalyst, was prepared and tested under the same reaction condition. Pt/AC provided a poor HMF conversion together with lower FDCA selectivity than Pt/RGO.

The BET surface area of Pt/AC was 950 m^2g^{-1} and that of Pt/RGO was 327 m^2g^{-1}. Although the surface area of Pt/RGO catalyst was lower, its higher activity indicated that its Pt dispersion and its tuned Pt reduction degree, along with the electronic state provided by the special two-dimensional planar structure from RGO, determined highly efficient redox reaction happening on its surface. It is referred that very fine Pt particles on the activated carbon with large surface area are readily oxidized but difficult to be reduced, lowering the redox reaction efficiency.

As shown in Table 2, Pt/RGO and Pd/RGO catalysts were compared in a shorter time experiment, 30min. Both conversion and FDCA selectivity of Pt/RGO were higher than those of Pd/RGO.

Time course of product formation for HMF oxidation over Pt/RGO was shown in Figure 6. According to the reaction process, about 71% of HMF was converted in first 2 h, and it was completely converted in another 5 h. 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) was obtained as a critical intermediate at the initial step of the reaction without any by-products. This tendency was in good agreement with previous study using Pt/C under different reaction conditions.[15] In the initial step of reaction, HMF was selectively converted into HMFCA, suggesting that CHO group reacted faster than CH_2OH group. The yield of FDCA increased with time by oxidizing both aldehyde and alcohol groups, and 84% yield of FDCA was obtained at reaction time of 24 h. To date, 5-formyl-2-furancarboxylic acid (FFCA), another oxidation product, has been observed by Gupta el et.[14] However, in our experiments, we could not find FFCA in product. We deduce that it was rapidly converted into FDCA through a possible reaction route as in Figure 7.

In order to study the stability of Pt/RGO catalyst, it was reused for 3 times, without obvious deactivation as in Figure 8. The catalyst was simply reused again after washing with water at room temperature followed by vacuum drying. HMF was completely converted for all cases, and the FDCA yield was generally stable but accompanied by slight decrease.

Conclusions

In summary, Pt/RGO catalyst was prepared by ethylene glycol reduction method. The Pt/RGO catalyst exhibited high activity and selectivity for the oxidation of 5-hydroxymethylfufural (HMF) to produce 2,5-furandicarboxylic acid (FDCA) in water solution at room temperature. 84% yield of FDCA was achieved by using this Pt/RGO as catalyst. HMFCA was observed as an only intermediate during reaction process. The Pt/RGO catalyst could be reused at least for three times without obvious deactivation.

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Figure captions

Figure 1. 2,5-Furandicarboxylic acid (FDCA) synthesis from oxidation of 5-hydroxymethylfurfural (HMF) catalyzed by Pt/RGO.

Figure 2. Reaction apparatus of HMF oxidation.

Figure 3. XRD patterns of Pt/RGO (before and after reaction).

Figure 4. TEM images of Pt/RGO before reaction (a), (b) and after reaction (c), (d). The (e) and (f) give the Pt particles size distribution of two samples.

Figure 5. XPS spectra of Pt/RGO before(a) and after reaction(b).

Figure 6. Time course of product distribution for HMF oxidation over Pt/RGO catalyst in water using atmospheric pressure of oxygen at 298 K. Reaction conditions: HMF (1 mmol), H_2O (10 ml), 5 wt% Pt/RGO (0.1 g), NaOH (5 mmol), under O_2 flow (50 ml min^{-1}), 298 K. HMF conversion (●), HMFCA yield (■), and FDCA yield (▼).

Figure 7. A proposed reaction route.

Figure 8. Recycling of Pt/RGO catalyst. *Reaction conditions*: HMF (1 mmol), H_2O (10 ml), 5 wt% Pt/RGO (0.1 g), NaOH (5 mmol), under O_2 flow (50 ml min^{-1}), 298 K, 24h.

Table 1. HMF oxidation in water using M/RGO as catalyst under mild conditions.

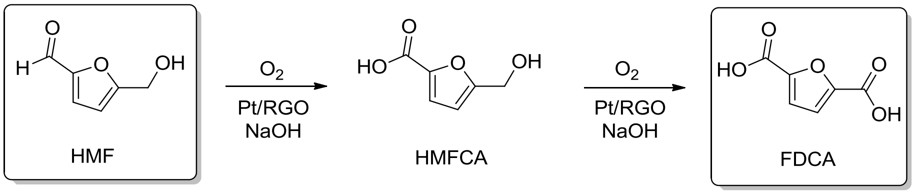
Entry	Catalyst	HMF Conv. (%)	FDCA Selec. (%)	Yield (%) HMFCA	FDCA	By products
1	GO	17.2	0	15.3	0	2.0
2	RGO	79.8	0	50.7	0	29.1
3	5% Pd/RGO	100	30.5	69.5	30.5	0
4	5% Ru/RGO	47.2	0	28.5	0	18.7
5	5% Rh/RGO	35.4	0	24.2	0	11.1
6	5% Pt/RGO	100	40.6	59.4	40.6	0
7	5% Pt/AC	62.6	38.2	38.7	23.9	0

Reaction conditions: HMF (1 mmol), H_2O (10 ml), catalyst (0.1 g), NaOH (5 mmol), under O_2 flow (50 ml min^{-1}), 298 K, 6h. The metals loading amount for every metals supported catalyst was 5 wt%.

Table 2. Product distribution of HMF oxidation in short reaction time.

Catalyst	HMF Conv. (%)	FDCA Selec. (%)	Yield (%) HMFCA	FDCA	Byproducts
5% Pt/RGO	19.2	23.2	14.7	4.5	0
5% Pd/RGO	13.8	15.4	11.6	2.1	0

Reaction conditions: HMF (1 mmol), H_2O (10 ml), catalyst (0.1 g), NaOH (5 mmol), under O_2 flow (50 ml min^{-1}), 298 K, 30min. The metals loading amount for every metals supported catalyst was 5 wt%.



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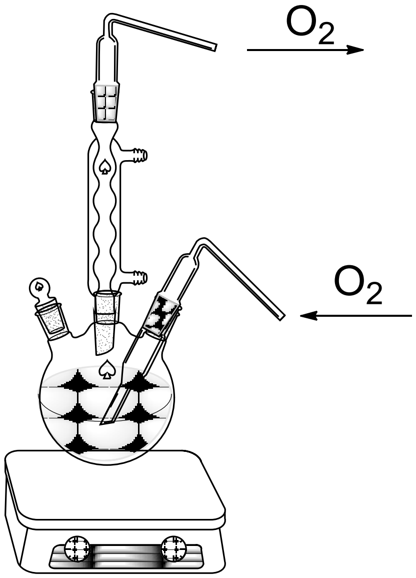

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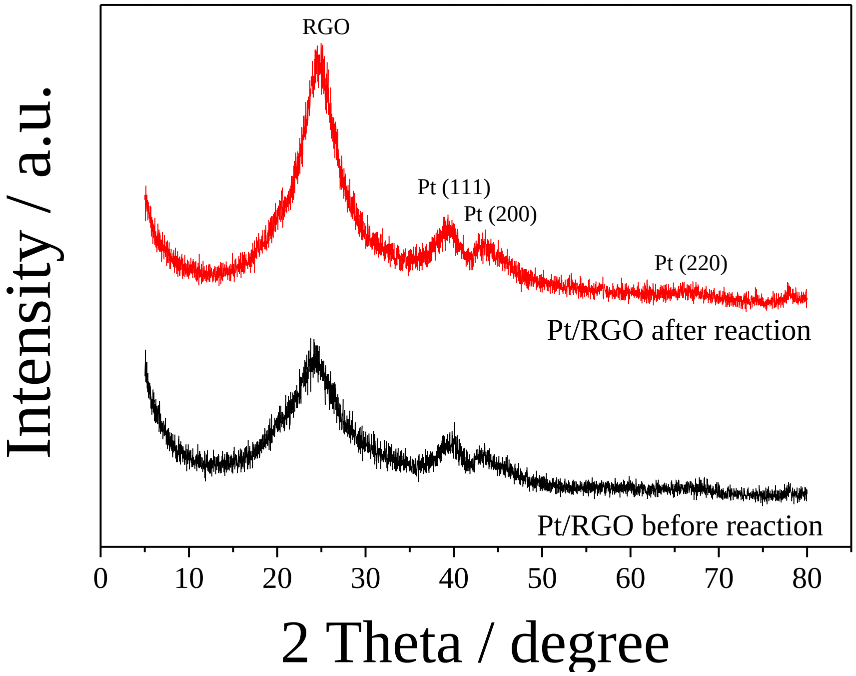

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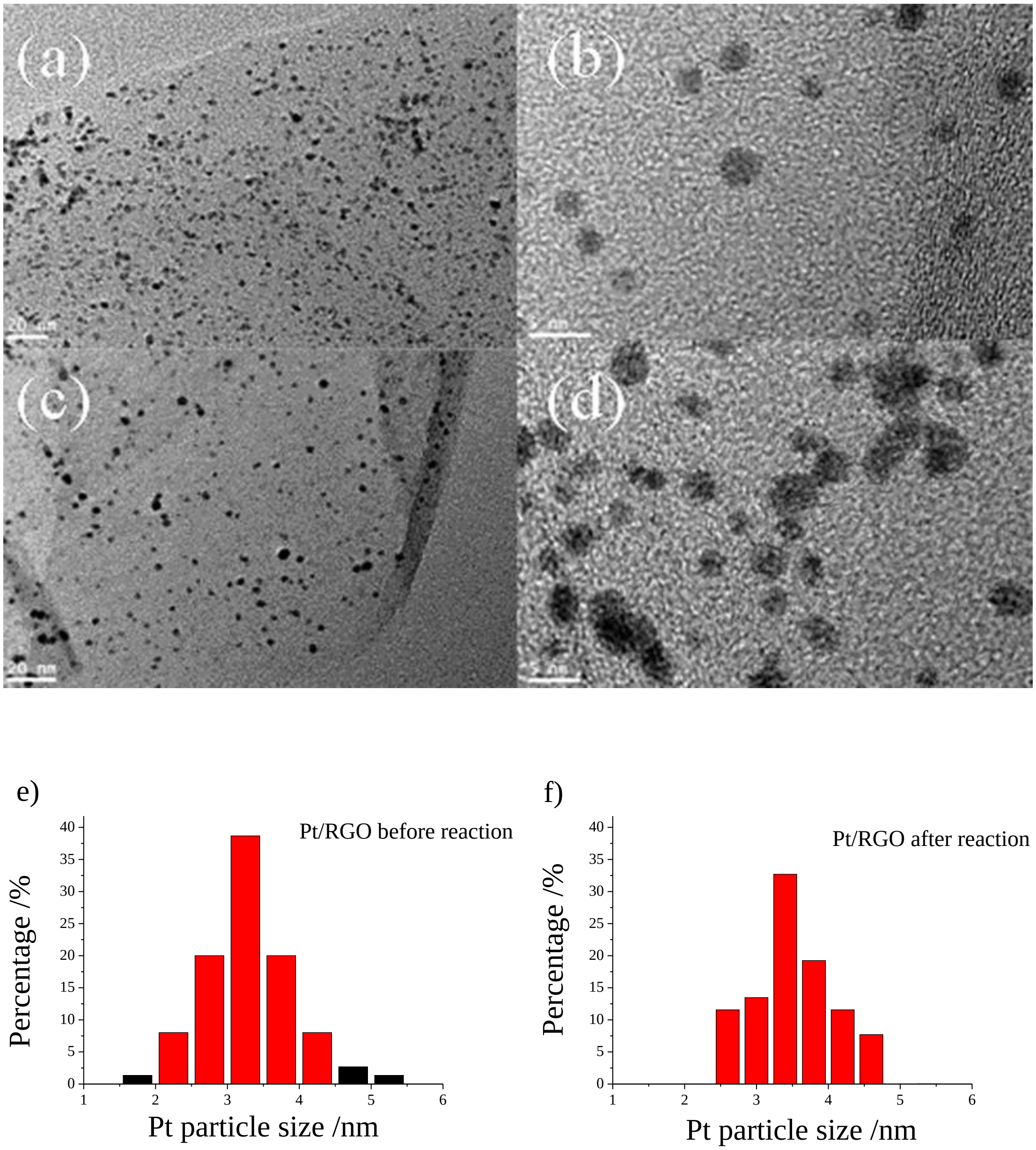

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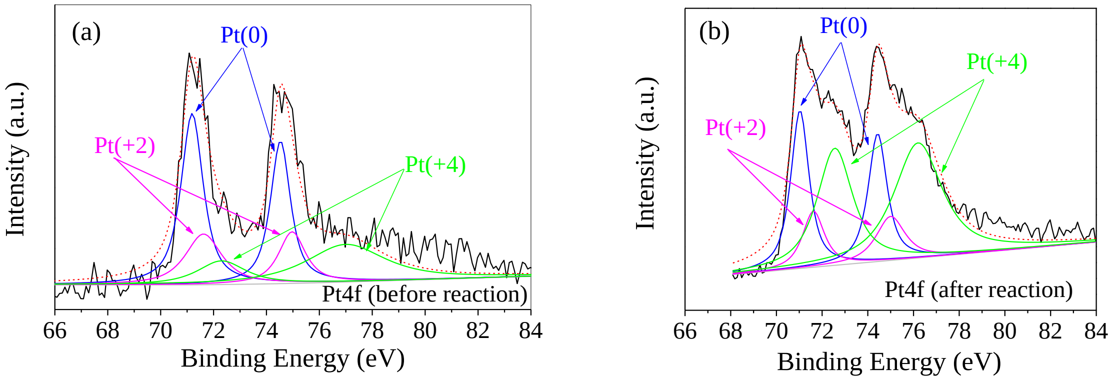

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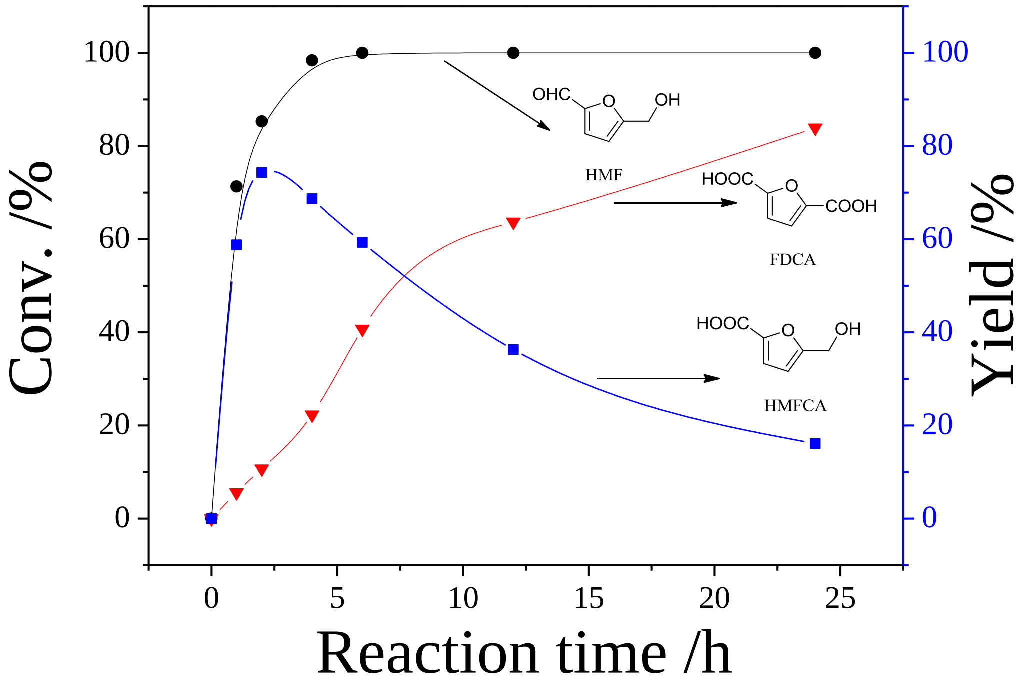

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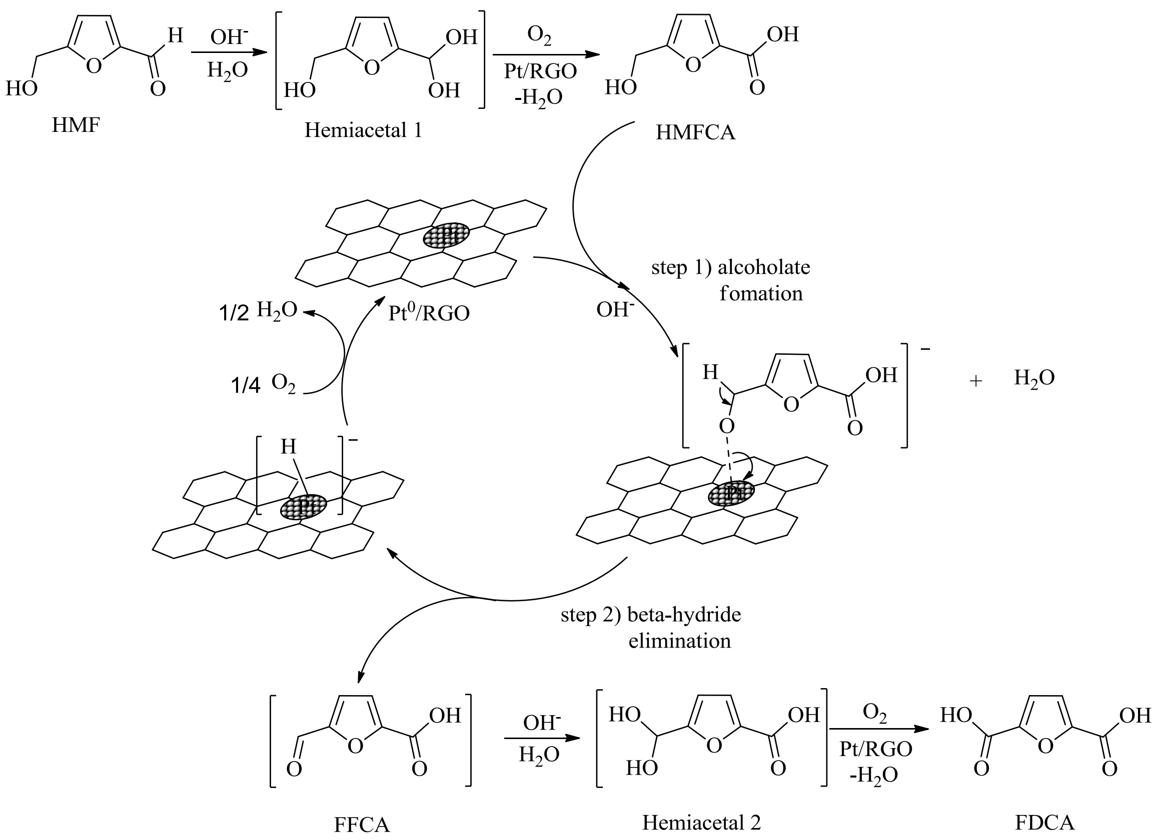

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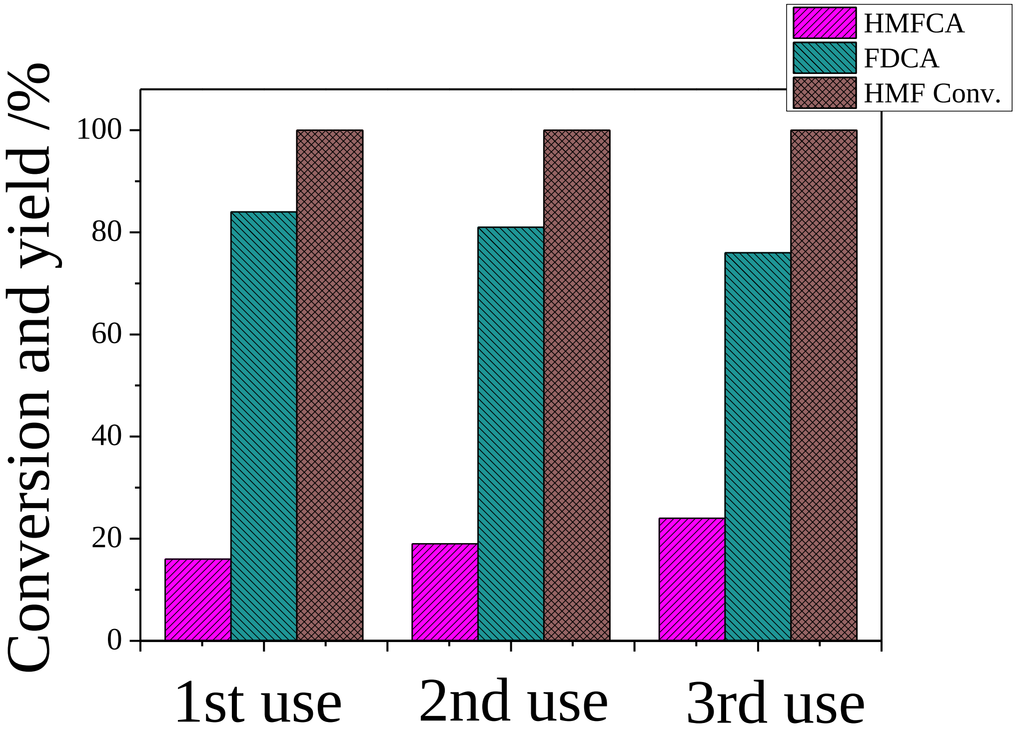

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Pt loaded on reduced graphene oxide (Pt/RGO) can be used as an efficient and durable catalyst for the direct oxidation of 5-hydroxymethylfufural (HMF) to 2,5-furandicarboxylic acid (FDCA) with a high yield of 84% at room temperature.