



Journal of Nanoscience and Nanotechnology Vol. 16, 5951–5958, 2016 www.aspbs.com/jnn

Monodisperse Pt Nanoparticles Assembled on Reduced Graphene Oxide: Highly Efficient and Reusable Catalyst for Methanol Oxidation and Dehydrocoupling of Dimethylamine-Borane (DMAB)

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Herein, monodisperse platinum (0) nanocatalyst assembled on reduced graphene oxide (Pt(0)@RGO) was easily and reproducibly prepared by the double solvent reduction method at room temperature. Pt(0)@RGO was characterized by X-ray diffraction (XRD), X-ray photoelectron microscopy (XPS) and transmission electron microscopy (TEM) measurements that verify the formation of monodisperse Pt (0) nanoparticles on RGO. The catalytic and electrocatalytic performances of Pt(0)@RGO in terms of activity, isolability and reusability were investigated for both methanol oxidation and the dehydrocoupling of dimethylamine-borane (DMAB) in which Pt(0)@RGO was found to be highly active and reusable heterogeneous catalyst even at room temperature. The prepared nanoparticles can also electrocatalyze methanol oxidation with very high electrochemical activities (5.64 A/cm² at 0.58 V for methanol,). The activation energy (Ea), activation enthalpy ($\Delta H^{\#}$), and activation entropy ($\Delta S^{\#}$) for DMAB dehydrogenation were calculated to be 59.33 kJ mol⁻¹ 56.79 kJ mol⁻¹ and -151.68 J mol⁻¹K⁻¹, respectively. The exceptional stability of new Pt(0)@RGO nanoparticles towards agglomeration, leaching and CO poisoning allow these particles to be recycled and reused in the catalysis of DMAB dehydrogenation and methanol oxidation. After four subsequent reaction and recovery cycles, Pt(0)@RGO retained >75% activity towards the complete dehydrogenation of DMAB.

Keywords: Dehydrogenation, Direct Methanol Fuel Cells (DMFCs), Nanocatalyst, Electrochemical Activities.

1. INTRODUCTION

The development of powerful and clean energy sources currently represents an important issue. With the increasing concern for environmental protection and the depleting of fossil fuel, there is a pressing need to find cleaner and greener energy sources.^{1–5} Over the last two decades, there has been a significant increase in research and development in fuel cell due to its ability to convert chemical energy of fuel into electricity without causing much pollution. Direct alcohol fuel cells could be pivotal in the future because of the high energy content of low molecular weight alcohols, easy handling, storage, and transportation, and their potential application in powering vehicles.⁶

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Compared to the pure hydrogen, the use of low-molecular weight alcohols as energy sources has several advantages, including the ease with which these materials can be easily handled, stored and transported.^{7–9}

The general equation for alcohol oxidation reactions may be written as:

$$C_n H_{2n}$$
 + 1OH + (2*n* − 1)H₂O
 \rightarrow (*n*)CO₂ + (6*n*)H⁺ + (6*n*)e⁻ (1)

The direct methanol fuel cell (DMFC), powered by electrooxidation of methanol has been studied extensively. DMFC is one of the most common direct alcohol fuel cells. Moreover, among the various fuel cell technologies, the direct methanol fuel cell (DMFC), which utilizes methanol as its fuel, is a promising candidate for its high-efficiency,

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near-zero pollution, ease in refueling and application as a portable power source such as cellular phones and notebook computers, etc.¹⁰⁻¹³ However, there are several limitations associated with the application of direct methanol fuel cells, including the high price of the finished devices, low levels of electrocatalytic activity and poor durability.14-17 To date, the majority of the direct methanol fuel cells used as electrocatalysts have contained platinum (Pt) and platinum allovs because of the excellent electrocatalytic activities of these materials. Those materials can also be used other types of reactions like the dehydrogenation of ammine boranes. Recent studies have shown that amine-boranes also need to be considered as hydrogen storage materials among the various kinds of solid hydrogen storage materials because of the following advantageous properties:

- (i) having high hydrogen content,
- (ii) having high stability,
- (iii) being environmentally benign.

The ammonia-borane can release hydrogen gas either upon heating to temperatures above 70 °C or on the hydrolysis under mild conditions. Therefore in this study; monodisperse platinum (0) nanocatalyst assembled on reduced graphene oxide (Pt(0)@RGO) were easily and reproducibly prepared by double solvent reduction method at room temperature. The prepared platinum nanoparticles have been investigated by a variety of techniques: X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) (surface characterization); cyclic voltammetry (CV) and chronoamperometry (CA) (electrochemical) for alcohol oxidation and the dehydrogenation of DMAB.

2. EXPERIMENTAL DETAILS

2.1. Reagents and Instrumentation

PtCl4 (99% Alfa Aesar), tetrahydrofuran (THF) (99.5%, Merck), methanol (\geq 99.5%), and HClO4 (60%) were purchased from Merck, lithium triethylborohydride (1.0 M dissolved in THF), DMAB and Propan-1-amine (PA) were obtained by Sigma Aldrich). De-ionized water was filtered by Millipore water purification system (18 M Ω) analytical grade. All glassware and Teflon-coated magnetic stir bars were cleaned with aqua regia, followed by washing with distilled water before drying.

Transmission electron microscopy (TEM) images were obtained on a JEOL 200 kV TEM instrument. Sample preparation for TEM analysis involves placement of a drop of 0.5 mg/mL ethanol solution of the prepared catalyst with a RGO support on a carbon covered 400-mesh copper grid, the solvent is then allowed to evaporate. Excess solution was removed with an adsorbent paper and the sample was dried under vacuum at room temperature before analysis. More than 300 particles were calculated to get the integrated information about the overall distribution of Ptbased catalyst sample. Thermo Scientific spectrometer was used for X-ray Photoelectron Spectroscopy (XPS) measurements and the X-ray source was K α lines of Mg (1253.6 eV, 10 mA). Samples were prepared by depositing the catalyst on Cu double-sided tape (3 M Inc.). C 1s line at 284.6 eV was chosen as a reference point and all XPS peaks were fitted using a Gaussian function and the C 1s line at 284.6 eV was used as the reference line.

A Panalytical Emperian diffractometer with Ultima + theta-theta high resolution goniometer, having an X-ray generator (Cu K α radiation, k = 1.54056 Å) and operating condition of 45 kV and 40 mA, were employed in XRD analysis.

Electrochemical measurements including Cyclic voltammetry (CV) and Chronomperometry (CA) were carried out in a three-electrode electrochemical cell using a microcomputer-controlled potentiostat/galvanostat (Gamry Interface 1000) at room temperature. The reference, counter and working electrodes were the saturated calomel electrode (SCE), glassy carbon, and prepared catalysts, respectively. The working electrode was a 3 mm glassy carbon disk, polished with Al_2O_3 paste and washed in distilled water and a heterogeneous mixture was prepared by our previous studies.¹⁸

¹¹B NMR spectra were taken on a Bruker Avance DPX 400 MHz spectrometer (128.2 MHz for ¹¹B NMR).

2.2. Methods 2.2. 1 2.2.1. The Preparation of Pt(0)@RGO

Pt(0)@RGO has been prepared by double solvent reduction method. As a summary of this method, superhydride and ethanol were used to reduce the mixture of 0.25 mmol of PtCl₄ dissolved in small amount of anhydrous tetrahydrofuran and 0.25 mmol of PA ligand. The observation of a brown-black color in the solution indicates the formation of platinum nanoparticles. Finally, the solid Pt nanoparticles were dried under vacuum at room temperature. The prepared platinum nanoparticles were mixed in a 1:1 ratio with RGO, which is used as a support.

Graphene oxide (GO) was synthesized from graphite powder using modified Hummer's method. In brief, 1 g of graphite and 0.5 g of sodium nitrate were mixed together followed by the addition of 23 ml of conc. sulphuric acid under constant stirring. After 1 h, 3 g of KMnO₄ was added gradually to the above solution while keeping the temperature less than 20 °C to prevent overheating and explosion. The mixture was stirred at 35 °C for 12 h and the resulting solution was diluted by adding 500 ml of water under vigorous stirring. To ensure the completion of reaction with KMnO₄, the suspension was further treated with 30% H_2O_2 solution (5 ml).¹⁹ The resulting mixture was washed with HCl and H₂O respectively, followed by filtration and drying, graphene oxide sheets were thus obtained. RGO was obtained by the hydrazine reduction that was performed by adding of hydrazine monohydrate (98%)

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2.2.2. Catalytic Activities, Reusability Performances and Mercury (Hg(0)) Poisoning of Pt(0)@RGO in the Dehydrogenation of DMAB

All reactions and manipulations were performed under dry nitrogen atmosphere using standard Schlenk techniques including a vacuum system unless otherwise specified. The dehydrogenation of DMAB by the help of Pt(0)@RGO was performed in a typical jacketed, three necked reaction flask connected to the water-filled cylinder glass tube. The jacketed reaction flask was kept under vacuum at least for 15 min and filled with nitrogen to remove any trace of oxygen and water present prior to all the catalytic reactions. The catalytic activity of Pt(0)@RGO in the dehydrogenation of DMAB was determined by measuring the rate of hydrogen generation. In a typical set of experiment, 1.0 mmol of DMAB was dissolved in a small amount of THF, and the solution was transferred into the jacketed reaction flask containing a 1.0 mL THF solution of the prepared catalyst thermostated at 25.0 ± 0.1 °C. Hydrogen gas release from the catalytic reaction solution was achieved using a typical water-filled gas burette system and recording the displacement of the water level in the column every minute until no more hydrogen evolution was observed. When no more hydrogen generation was observed, the experiment was stopped, the reactor was disconnected from the water-filled column, and the hydrogen pressure was released. Next, approximately 0.5 mL of the reaction solution in the reactor was withdrawn with a glass Pasteur pipet and added to 1 g of CDCl₃ in a quartz NMR sample tube for NMR analysis.

For the reusability performance experiments, upon the complete dehydrogenation of 1.0 mmol of DMAB using freshly prepared catalyst, the jacketed, three-necked reaction flask was detached from the line and connected to a vacuum line. After evaporation of the volatile solutions, the remaining solid residue containing the catalyst was weighed and used again in the dehydrogenation reaction under the same conditions (in a small amount of THF at 25.0 ± 0.1 °C). This reaction and recovery cycle was repeated four times.

A small amount of elemental Hg (300 equiv.) was added to a THF solution containing the prepared catalyst in a

(200)

2 Theta (deg.)

60

(220) (311)

80

(320)

(111)



20

C(002)

ntensity (a.u.

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Figure 2. High resolution transition electron micrograph and particle size histogram of a Pt(0)@RGO.

jacketed, three-necked reaction flask, and the mixture was stirred for 4 h for mercury (Hg(0)) poisoning studies. This solution was then used in the dehydrogenation of 1.0 mmol DMAB under the same conditions described above.

3. RESULTS AND DISCUSSION

3.1. Characterization of Pt(0)@RGO

The preliminary characterization of Pt(0)@RGO was performed by XRD, TEM, HRTEM and XPS and applications of the catalyst were examined by CV and CA for methanol oxidation reaction and hydrogen generation tests for the dehydrogenation of DMAB.

The analysis of the crystalline structure and the size of Pt(0)@RGO nanocatalysts were performed by using XRD. As can be seen in Figure 1, Pt(0)@RGO exhibit distintict diffraction patterns and they can be assigned to Miller indices (111), (200), (220), (311), and (320), respectively, planes of the face-centered cubic (fcc) crystal lattice of platinum.

The lattice parameters (α Pt) and average crystallite sizes of the metal particles was calculated by using the Pt (220) diffraction peaks of the prepared catalyst. The lattice



Figure 3. Pt 4f electron spectra of Pt(0)@RGO.

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Figure 4. Cyclic voltammogram of Pt(0)@RGO in 0.1 M $HClO_4 + 0.5$ M methanol (CH_3OH). Scan rate is 50 mV/s.

constant values for Pt(0)@RGO were found to be 3.917 Å which is in good agreement with 3.923 Å for pure Pt, using the following equation.²⁰

$$\sin\theta = \frac{\lambda\sqrt{h^2 + k^2 + l^2}}{2a} \text{ (for a cubic structure)}$$

From the full width half maximum of the (220) peaks in XRD, the average crystallite size of Pt(0)@RGO was calculated as 3.60 ± 0.34 nm using Scherrer equation;²¹

$$d(\text{\AA}) = \frac{k\lambda^{12}}{\beta\cos\theta} \text{ Copyright: American Statement of the second sta$$

where k = a coefficient (0.9); λ = the wavelength of X-ray used (1.54056 Å); β = the full width half-maximum of respective diffraction peak (rad) θ = the angle at the position of peak maximum (rad)

In order to reinforce the results of diffraction measurements, TEM was used. The high resolution electron micrograph and particle size histogram of the Pt(0)@RGO are shown in Figure 2. Uniform and monodisperse distribution of catalyst particles with a relatively narrow range was observed. The average particle sizes were found to be 3.53 ± 0.37 nm for Pt(0)@RGO. This result is in good agreement with the results from the XRD imaging. The most of the particles are in spherical shape, and no agglomerations are observed in the prepared catalyst. Figure 2 also displays the representative atomic lattice fringes obtained by high resolution transmission electron microscopy for Pt(0)@RGO. As an example, Pt (1 1 1)

 Table I.
 The comparison of particle size, ECSA, CSA, Rf and % Pt utilization for the prepared catalyst with commercial Pt catalyst.

	Particle	ECSA	Roughness	CSA	Pt utility
	size (nm)	(m²/g)	factor (Rf)	(m²/g)	(%)
Pt(0)@RGO	3.53	46.63	95.2	79.43	58.70
Pt (ETEK)	2.70	50.60	103.2	103.0	49.10



Figure 5. Chronoamperometric curves of Pt(0)@RGO towards methanol oxidation at 0.6 V (vs. SCE) in 0.1 M HClO₄+0.5 M CH₃OH.

and $(2\ 0\ 0)$ planes of Pt(0)@RGO were observed with a spacing of 0.226 and 0.195 nm, respectively, which is very close to the nominal Pt $(1\ 1\ 1)$ and $(2\ 0\ 0)$ spacing of 0.227 and 0.196 nm, respectively.²²

X-ray photoelectron spectroscopy has been used to obtain information about the oxidation state of the Pt(0)@RGO. As most of the atoms in small particle clusters are surface atoms, the oxidation state measured as such would also reflect well the bulk oxidation state. The fittings of all XPS peaks were performed by Gaussian-Lorentzian method and the relative intensities of the species were estimated by calculating the integral of each peak, after smoothing, subtraction of the Shirley-shaped background. As the binding energy (BE) for the line of zero valent platinum at 284.3 eV is very close to the C1s line resulting from adventitious carbonaceous species, the spectrum was used instead for the analysis of Pt oxidation state. It is shown that Pt is mostly in zero oxidation state at about 71.0 and 74.3 eV (71.75%).²³⁻³¹ As shown in Figure 3, the other Pt (74.7 and 78.0 eV) doublet has



Figure 6. % conversion versus time graph for the catalytic dehydrogenation of DMAB in THF at room temperature starting with 7.5% mol of Pt(0)@RGO.



Figure 7. % conversion versus time graph for Pt(0)@RGO (7.5% mol) catalyzed dehydrogenation of DMAB in THF at various temperatures.

emerged in higher binding energies due to exposure to the atmosphere of the type of PtOx.

3.2. Electrochemical Measurements for Methanol Oxidation

Cyclic voltammograms of Pt(0)@RGO in 0.1 M HClO₄ at room temperature were recorded several times over a 3 month period, and no change was observed, indicating the stability of the prepared catalysts. Typical hydrogen and oxygen adsorption and desorption features were observed on the prepared catalyst. The addition of methanol to the electrolyte resulted in a dramatic change in the appearance of the voltammograms due to the alcohol oxidation reaction taking place on the surface of platinum nanoparticles as shown in Figure 4. The electrooxidation of methanol on prepared nanoparticle was characterized by two well-defined current peaks on the forward and reverse scans. In the forward scan, the oxidation peak is corresponding to the oxidation of freshly chemisorbed species which come from methanol adsorption. The reverse scan peak is primarily associated with removal of carbonaceous species which are not completely oxidized in the forward scan. The magnitude of the peak current on the forward scan indicates the electrocatalytic activity of the

electrocatalysts for the oxidation reaction of methanol. The anodic parts of the cyclic voltammogram for the prepared catalyst showed that Pt(0)@RGO has 9.2 times higher catalytic activities than commercially available Pt-ETEK catalyst. Because alcohol electro-oxidation of this heterogeneous catalyst is surface-controlled, the ECSA of the catalyst is an important parameter for determining the catalytic properties of the electro catalyst. The ECSA of the catalyst in m^2g^{-1} could be determined from the integrated charge in the hydrogen adsorption region of the cyclic voltammogram using the following formula.^{32–36}

$$ECSA = \frac{Q (mC)}{Pt \text{ loading on electrode} \times 0.21 mC/cm^2}$$

where Q is the electric charge for hydrogen desorption and 0.21 mC/cm² represents the charge required to oxidize a monolayer of H₂ on platinum. Roughness factor, Rf (m²g⁻¹Pt cm⁻²) describes the enhancement of the real electrochemical surface area (ECSA) in comparison with the geometric area, Ag (cm²), The Chemical Surface Areas (CSA) of the catalysts were calculated using the following equation, assuming homogenously distributed and spherical particles.³⁴

$$CSA = \frac{6 \times 10^3}{\rho \times d}$$

where *d* is the mean Pt crystalline size in Å (from the XRD results) and is the density of Pt metal (21.4 g/cm²). The Pt utilization efficiency can be calculated using the ratio of the ECSA to CSA.^{36–39}

Utilization (%) =
$$\frac{\text{ECSA}}{\text{CSA}} * 100$$

Table I indicates the CSA, ECSA, Rf and % Pt utility for the prepared catalysts. As shown in the table, Pt(0)@RGO has a higher active surface area, Rf and % Pt utility compared to commercial available Pt (ETEK), which may contribute to higher catalytic activity.

CA was used to examine the long-term stability of Pt(0)@RGO in the methanol oxidation. Figure 5 shows the representative CA curves for methanol oxidation on



Figure 8. Arrhenius (a) and Eyring plots (b) for Pt(0)@RGO catalyzed dehydrogenation of DMAB at various temperature.

Pt(0)@RGO at the potential 0.6 V (vs. SCE) for 3,600 s. There is a sharp current drop in the first ten minutes due to poisoning of the Pt surface and then quite a slow decay of the curve is observed.

3.3. Catalytic Activity of Pt(0)@RGO in the Dehydrogenation of Dimethylamine-Borane (DMAB)

Pt(0)@RGO was studied in the dehydrogenation of DMAB by measuring the volume of hydrogen generated during the reaction at 25 ± 0.1 °C and also found to be highly active for this reaction. The hydrogen evolution starts immediately after injection of DMAB into the THF solution of Pt(0)@RGO. The initial turnover frequency (TOF) of 20.83 h^{-1} for Pt(0)@RGO, were obtained from the slope of the linear portion of the plot given Figure 6 and continues until 1 equivalent of H₂ per mol DMAB is released. As shown Figure 6, only \sim 8–9% conversion is observed after an induction period ($\sim 10 \text{ min}$), when PtCl₄ is used as pre-catalyst under the same conditions in the dehydrogenation of DMAB. After induction period, the Pt particles precipitate out of solution due to the weakly coordination of chloride anion of PtCl₄ that is not strong enough to stabilize the Pt (0) nanoparticles for an extended period of time.40 After the dehydrogenation reaction of DMAB (at 1.0 equiv. H₂ generation), NMR shows the complete conversion of $(CH_3)_2$ NHBH₃ ($\delta = \sim 12.3$ ppm) to $[(CH_3)_2NBH_2]_2$ ($\delta = \sim 5.1$ ppm) even at room temperature. In order to test heterogeneity of Pt(0)@RGO in the dehydrogenation of DMAB, a series of poisoning experiments were carried out adding of 300 equiv. of Hg (0) per Pt, entirely stops the reaction, verifying that Pt(0)@RGO contribute to heterogeneous catalysis in the dehydrogenation of DMAB.

Rate constants (kobs) for the dehydrogenation of DMAB were measured from the linear portions of the plots given in Figure 7 at four different temperatures in the range of 20-35 °C, and they were used to calculate the activation energy of 59.33 kJ mol⁻¹ (Ea), activation enthalpy of 56.79 kJ mol⁻¹ ($\Delta H^{\#}$), and activation entropy of $-151.68 \text{ J} \text{ mol}^{-1}\text{K}^{-1}$ ($\Delta \text{S}^{\#}$) from the Arrhenius and Eyring plots for Pt(0)@RGO (Fig. 8). Even though the activation energy values provided by Pt(0)@RGO are higher than those of the one of the best catalysts, Rh(0)nanoparticles (34 kJ mol⁻¹), it is smaller than the activation energies reported in the literature for the same reaction.³⁵ Furthermore, there is an associative mechanism in the transition state for the catalytic dehydrogenation of DMAB between the higher negative value of the activation entropy and the small value of the activation enthalpy.

3.4. Reusability Performance of Pt(0)@RGO in the Catalytic Dehydrogenation of DMAB

The isolability, recovery and reusability of Pt(0)@RGO were also evaluated in the dehydrogenation of DMAB



Figure 9. % conversion versus time graph for Pt(0)@RGO catalyzed dehydrogenation of DMAB in THF at room temperature for 1st and 4th catalytic runs.

at room temperature. Pt(0)@RGO was isolated as black powder by vacuum drying and then bottled under a N₂ atmosphere after the complete dehydrogenation of DMAB. Such covered catalyst was found to be still catalytically active in the dehydrogenation of DMAB. They still retained \geq 75% of its initial activity (Fig. 9) after its fourth run. This indicates that the prepared Pt(0)@RGO are easily recoverable and redispersible while remaining catalytically active. The slight decrease in catalytic activity over multiple runs can be attributed to the formation of a precipitate Diversity of Auckland

Table II. Catalysts tested in the dehydrogenation of DMAB under mild conditions (\leq 25 °C).

Entry	(Pre) Catalysts	Cov. (%)	TOF	Ref.
1	Pt(0)@RGO	100	20.83	This study
2	$[(C_5H_3-1,3(SiMe_3)_2)_2Ti]_2$	100	420.0	[42]
3	RhCl(PPh ₃) ₃	100	4.3	[44]
4	$[Cr(CO)_5(thf)]$	97	13.4	[45]
5	RhCl ₃	90	7.9	[44]
6	Cp ₂ Ti	100	12.3	[46]
7	Ru(cod)(cot)	40	1.6	[33]
8	Ni(skeletal)	100	3.2	[47]
9	$[Rh(1,5-cod)_2]Otf$	95	12.0	[44]
10	$[Ru(1,5-cod)Cl_2]n$	70	2.5	[43]
11	Rh(0)NPs	100	60.0	[33]
12	[Rh(1,5-cod)(dmpe)]PF ₆	95	1.7	[44]
13	trans-PdCl ₂ (P(o-tolyl) ₃) ₂	20	0.2	[44]
14	Pd/C	95	2.8	[44]
15	IrCl ₃	25	0.3	[44]
16	RuCl ₃ .3H ₂ O	77	2.7	[43]
17	$Rh(0)/[Noct_4]Cl$	90	8.2	[44]
18	trans-RuMe ₂ (PMe ₃) ₄	100	12.4	[44]
19	(Idipp)CuCl	100	0.3	[48]
20	$[RuH(PMe_3)(NC_2H_4PPr_2)_2]$	100	1.5	[49]
21	HRh(CO)(PPh ₃) ₃	5	0.1	[44]
22	$[Cr(CO)_5(h1-BH_3NMe_3)]$	97	19.9	[45]
23	$[Ir(1,5-cod)m-Cl]_2$	95	0.7	[44]
24	Ru(0)/APTS	100	55.0	[33]
25	[RhCl(PHCy ₂) ₃]	100	2.6	[50]
26	$[Cp * Rh(m-Cl)Cl]_2$	100	0.9	[44]
27	$[Rh(1,5-cod)m-Cl]_2$	100	12.5	[44]
28	Pt (0)/AA	100	15.0	[34]

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of bulk Pt(0). This becomes visible at the end of the fourth catalytic run, yielding a clear, colorless (i.e., Pt(0) nanoparticle free) solution by increasing the concentration of boron products, which is known to decrease the accessibility of the active sites. The P-XRD pattern of the sample after the fourth catalytic run verifies the agglomeration of Pt(0) nanoparticles.⁴¹

3.5. Catalytic Performance Comparison of Pt(0)@RGO with the Previous Catalyst Systems Tested in the Catalytic Dehydrogenation of DMAB

As shown in Table II, the apparent initial TOF value of $Pt(0)@RGO (20.83 h^{-1})$ is higher than most of the other heterogeneous and homogeneous catalysts reported in the literature. However, it is still lower than the best known heterogeneous $(60 h^{-1})^{35}$ and homogeneous $(420 h^{-1})^{42}$ catalysts. To the best of our knowledge, our prepared catalysts are one of the a few example of an isolable and reusable nanocatalyst used in this important catalytic reaction aside from the Ru(0)/APTS.⁴³

4. CONCLUSIONS

In the current work, highly efficient and monodisperse Pt(0)@RGO has been prepared, characterized and used as heterogeneous catalysts in both methanol oxidation and to: UDMAB dehydrogenation. Some of the major findings of un, this study can be summarized below: Copyright: American S

(a) Pt(0)@RGO was prepared, for the first time, using a simple and reproducible double solvent reduction method. The ICP-OES, XRD, XPS, TEM, AFM, CV and CA characterizations of these nanoparticles indicated the formation of monodisperse Pt(0) nanoparticles.

(b) The data indicate that Pt(0)@RGO has higher electrocatalytic activity than commercially available catalysts due to the high ECSA, percent platinum utility, roughness factor, and Pt(0) to Pt(IV) ratio. Pt(0)@RGO has 9.2 times higher catalytic activities than commercially available Pt-ETEK catalyst.

(c) Pt(0)@RGO was also used heterogenous catalyst for the dehydrogenation of DMAB, a promising material for efficient chemical hydrogen storage. Pt(0)@RGO provides one of the highest catalytic activities (TOF = 20.83 h⁻¹) reported in the literature in the dehydrogenation of DMAB at room temperature. Pt(0)@RGO was also isolable, recoverable and reusable, retaining \geq 75% of the initial activity after four runs.

(d) The dehydrogenation of DMAB using Pt(0)@RGO was carried out at different temperatures (20 to 35 °C) to evaluate the activation parameters (Ea, ΔH^{\neq} , ΔS^{\neq}). We found that Pt(0)@RGO provide one of the lowest activation energies (Ea = 59.33 kJ/mol) reported among the heterogeneous catalysts tested in the same reaction. The activation enthalpy and entropy values suggest an

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associative mechanism for Pt(0)@RGO catalyzed dehydrogenation of DMAB.

Easy preparation, high stability, catalytic versatility, efficient recovery, prolonged stability, reusability and high catalytic performance of Pt(0)@RGO offer a promising candidate to develop highly efficient portable hydrogen generation systems depending on DMAB as a CO-free, economical point of view, H₂ storage and generation system for fuel cell applications.

Acknowledgments: The authors would like to thank to TUBITAK (213 M 448) for the financial support. The authors gratefully acknowledge DPU-ILTEM and Duzce University Central Laboratory (DUBIT). The partial supports by Science Academy are gratefully acknowledged.

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Received: 26 November 2014. Accepted: 26 March 2015.

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