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# Synthesis and Characterization of Nearly Monodisperse Pt Nanoparticles for C<sub>1</sub> to C<sub>3</sub> Alcohol Oxidation and Dehydrogenation of Dimethylamine-borane (DMAB)

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Highly efficient nearly monodisperse Pt NPs catalyze C1 to C3 alcohol oxidation with very high electrochemical activities and provides one of the highest catalytic activities (TOF =  $21.50 \text{ h}^{-1}$ ) in the dehydrogenation of DMAB at room temperature. The exceptional stability towards agglomeration, leaching and CO poisoning for the prepared catalyst allow these particles to be recycled and reused in the catalysis of both DMAB dehydrogenation and C1 to C3 alcohol oxidation. After four subsequent reaction and recovery cycles, catalyst retained  $\geq 80\%$  activity towards the complete dehydrogenation of DMAB. The prepared catalyst structures were determined by the X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), atomic force microscopy (AFM) and transmission electron microscopy (TEM) respectively.

**Keywords:** Direct Alcohol Fuel Cells (DAFCs), Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM), Platinum NPs, X-ray Photoelectron Spectroscopy.

# **1. INTRODUCTION**

Even fossil fuels are still primary energy consumption in the world; sustainable renewable energy sources are becoming more popular due to the environmental problems and more energy demands.<sup>1-5</sup> Nowadays, direct type fuel cell has attracted interest for an electrical power source of the next generation, especially for the compact system. Fuel cells convert chemical energy directly into electrical energy with high efficiency and low emission of pollutants and can be used for stationary energy generation as well as for vehicles and portable devices.<sup>6-10</sup> Direct methanol fuel cells (DMFCs) have been the subject of great interest in recent years due to their potential application in electric vehicles and portable power sources.<sup>11-14</sup> The electrocatalytic oxidation of methanol has been thoroughly investigated, since methanol is an essential and considerable reagent for direct methanol fuel cells (DMFC).15-17 Alternatively, ethanol is another important fuel due to its non-toxic property and it can easily be produced in large quantity by the fermentation of sugar-containing raw materials, agricultural products and biomass.<sup>18, 19</sup> In addition, the high theoretical mass energy density (about 8.00 kWh kg<sup>-1</sup>) provides the fuel cells with a potential candidate for this type of fuel.<sup>20,21</sup> 2-propanol might also be a convenient fuel, not only the high energy content and availability, but also fewer oxidation products, faster oxidation kinetics, and lower tendency for cross over.22,23 Although these alcohols show promise as alternative fuels, their slow reaction kinetics in acidic environments emphasize the need for a catalyst.<sup>24</sup> Recently, Pt nanocatalyst has been mostly used to activate these alcohols. These nanoparticles can also be used as catalyst for the dehydrogenation of amine borane derivatives which have considerable attention in hydrogen storage. For this purpose, nearly monodisperse Pt NPs have been synthesized and were also well characterized by using some surface characterization techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Transmission electron microscopy (TEM), Atomic force microscopy (AFM) and reported their catalytic activities for both alcohol oxidation and the dehydrogenation of ammine borane adducts.

## 2. EXPERIMENTAL DETAILS

#### 2.1. Materials

PtCl<sub>4</sub> (99%) was purchased from Alfa; tetrahydrofuran (THF, 99.5%), methanol ( $\geq$ 99.5), ethanol (99.9%),

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2-propanol (%99.8) and  $\text{HClO}_4$  (60%) were obtained from Merck; lithium triethylborohydride (superhydride, 1.0 M) and *N*,*N*-dioctyl-1-octanamine were obtained from Aldrich and activated carbon was purchased from Cabot Europe Ltd.

Transmission electron microscopy (TEM) images were obtained on a JEOL 200 kV TEM instrument. Samples catalyst onto 400-mesh copper grids,  $\sim 0.5$  mg/ml CCl<sub>4</sub> may be prepared by placing a drop of the solution and analysis prior to solvent was allowed to evaporate.

Thermo Scientific spectrometer was used for X-ray photoelectron spectroscopy (XPS) analysis and K $\alpha$  lines of Mg (1253.6 eV, 10 mA) was utilized as a X-ray source. XPS peak has been fitted by using Gaussian function. For this purpose, the Pt 4*f* region of the spectrum was analyzed and the fitting of XPS peak was performed by Gaussian-Lorentzian method. The relative intensity of the species was estimated by calculating the integration of each peak, after smoothing, subtraction of the Shirleyshaped background. In the XPS spectrum, accurate binding energies ( $\pm 0.3 \text{ eV}$ ) were determined by referencing to the C 1s peak at 284.6 eV.

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

AFM measurements were performed with the sample at ambient temperature using Park Systems AFM XE-100E operated in the intermittent contact ("tapping") mode to see the surface topographies of the prepared catalyst. For this measurements, firstly, we prepare a sample for AFM by first diluting the product solutions by 300-fold or more with DI water and place 2.5  $\mu$ L of the final solution directly onto the freshly cleaved mica disk (supporting material) and a solvent was dried in a vacuum at room temperature for at least 12 h.

Cyclic voltammetry measurements have been performed by a microcomputer-controlled potentiostat/galvanostat, (Gamry Reference 3000), at room temperature. At least ten cyclic voltammogram measurements were recorded for the prepared catalyst.

The amount of platinum in prepared catalyst was determined by Leeman Lab ICP.

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

#### 2.2. Methods

### 2.2.1. The Preparation of Pt NPs

Pt NPs were formed by superhydride reduction method in an ultrasonic sonicator. Shortly,  $PtCl_4$  0.25 mmol (8.1 mg of anhydrous tetrahydrofuran) and 0.25 mmol of *N*,*N*-dioctyl-1-octanamine was dissolved and reduced with 0.25 mmol superhydride in an ultrasonic conditions. A brown-black solid has proved the formation of platinum

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nanoparticles. Then, the solid was dried under vacuum at room temperature.

## 2.2.2. Catalytic Activity of Pt NPs in the Dehydrogenation of DMAB

The dehydrogenation of DMAB reaction was typically occurred in a three-necked reaction flask connected to a dry nitrogen tank. Catalytic activites of Pt NPs were determined by measuring the amount of hydrogen generated by dehydrogenation of DMAB. Typically, 31.0 mg DMAB (1.0 mmol) was dissolved in 4.0 ml THF solution in a reaction flask and then 1.0 ml THF solution of Pt NPs was transferred into the reaction flask thermostated in  $25.0 \pm 0.1$  °C. Thereafter, about 0.5 mL aliquots of the reaction solution in the reactor is removed with a glass Pasteur pipette and 1.0 g of CDCl<sub>3</sub> was added in a quartz NMR tubes.

## 2.2.3. Reusability Performance of Pt NPs in the Dehydrogenation of DMAB

After the first run of the dehydrogenation of 1 mmol DMAB with Pt NPs, three-necked reaction flask detached from the line and the connected to a vacuum line. After evaporation of volatiles, the solid residue was weighed and re-used in the dehydrogenation of 1 mmol DMAB reaction under the same conditions.  $(25.0\pm0.1 \text{ °C})$ . This procedure was followed up to four catalytic runs.

## 2.2.4. Mercury (Hg(0)) Poisoning of Pt NPs in the Dehydrogenation of DMAB

Experimental Hg (300 eq.) containing 5.0 mL THF solution containing Pt NPs were added into a reaction flask and the mixture was stirred for 4 hours. Then, this solution was used in the dehydrogenation of 1.0 mmol DMAB under the same conditions given above.

# 3. RESULTS AND DISCUSSION

## 3.1. Characterization of Pt NPs

Pt NPs were readily and reproducibly obtained by superhydride reduction of  $PtCl_4$  in an anhydrous THF solution of *N*,*N*-dioctyl-1-octanamine ligand at room temperature.



Figure 1. XRD of catalyst Pt NPs.

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Figure 2. Pt 4f electron spectra of Pt NPs.

Absence of capping ligand caused to both agglomeration of the initially formed Pt NPs and precipitation out of the THF solution. In contrast, the presence of ligand provided stable Pt NPs for a long time. Afterwards, Pt NPs were cleaned up dry ethanol to remove excess ligand and was obtained as solid by evaporation of solvent under vacuum atmosphere.

The preliminary characterization of Pt NPs were performed by ICP-OES, XRD, TEM, HRTEM, AFM and XPS. XRD data indicates that Pt NPs exhibit diffraction patterns as illustrated in Figure 1. The diffraction peaks at  $2\theta = 39.85$ , 46.27, 67.68, 81.56 and 85.98 are mainly due to Pt (111), (200), (220), (311), and (320) respectively, planes of the face-centered cubic (fcc) crystal lattice of platinum. (JCPDS-ICDD, Card No. 04-802) The Pt (220) diffraction peak of the prepared catalyst was used to calculate the lattice parameter ( $\alpha$ Pt) values and average crystallite dimensions of the metal particles. The lattice parameter was found to be 3.930 Å using the equation in literature<sup>25</sup> which is in good agreement with 3.923 Å for pure Pt. The average crystallite size of the platinum particles was calculated approximately  $3.93 \pm 0.42$  nm using the following equation.<sup>26</sup>

$$d(\text{Å}) = \frac{k\lambda}{\beta\cos\theta}$$

where

k = a coefficient (0.9)

 $\lambda$  = the wavelength of X-ray used (1.54056 Å)

 $\beta$  = the full width half-maximum of respective diffraction peak (rad)

 $\theta$  = the angle at the position of peak maximum (rad).

X-ray photoelectron spectroscopy (XPS) was used to determine the surface composition and the oxidation state of Pt. The doublet consists of two double Pt 4*f* photoelectron spectrums for the prepared catalyst as shown in Figure 2. The ratio of the  $4f_{7/2}/4f_{5/2}$  signals for Pt NPs was found to be 4/3, which agree with the literature.<sup>25-27</sup> The line at 71.0–74.1 eV is undoubtedly due to Pt(0), while the higher binding energy component, 74.3–77.6 eV, is most probably due to the presence of Pt(IV) species such as PtO<sub>2</sub> or Pt(OH)<sub>4</sub>. This result indicate that Pt is mostly in zero oxidation state (%70.6) in our catalyst.

Atomic force microscopy (AFM) was used to see the height and lateral diameter distribution. AFM results showed that the height value of Pt NPs is  $\sim$ 3.76 nm that exhibit similar value with the XRD and TEM results as shown in Figure 3. It should be noted, however, that AFM lateral diameter of the prepared catalyst is found as  $\sim$ 54.3 and much larger than the size of those obtained by the XRD and TEM results due to likely tip contamination and/or the tip convolution.<sup>27–29</sup>

In The high resolution electron micrograph (HRTEM) and particle size histogram of the prepared catalyst are shown in Figure 4 which is representative of the morphology of the prepared catalyst as well. Uniform distribution of the catalyst particles with a relatively narrow range on activated carbon support was observed. HRTEM results also indicated that most of the particles are in a spherical shape, and no agglomerations are observed in our catalyst. Figure 4 also displays the representative atomic lattice fringes obtained by high resolution transmission electron microscopy for Pt NPs. As a result of these fringes, Pt (1 1 1) plane was observed with spacing of 0.225 nm on the prepared catalyst, respectively, which is very close to nominal Pt (1 1 1) spacing of 0.227 nm, respectively.<sup>30</sup>



Figure 3. AFM images of Pt NPs (a). Histogram of height of particles obtained from AFM data (b). Histogram of lateral diameter of particles obtained from AFM data (c).

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Figure 4. High resolution transition electron micrograph and particle size histogram of Pt NPs.

# **3.2. Electrochemical Measurements**

The prepared catalyst has a much defined typical oxygen and hydrogen adsorption/desorption regions which reflects the electrochemical surface area (ECSA) of the Pt NPs catalyst. In general, ECSA of the catalyst is one of the most important parameters to determine the catalytic properties of electrocatalyst for alcohol electro-oxidation since this reaction is surface-sensitive and could be determined from the integrated charge in the hydrogen adsorption region of the cyclic voltammogram using the following formula;<sup>31, 32</sup>

$$ECSA = \frac{Q \text{ (mC)} 5.101.217.13 \text{ On: Su}}{Pt \text{ loading on electrode } \times 0.21 \text{ mC/cm}^2 \text{ erican}}$$

where Q is the amount of charge exchanged during the electro adsorption of hydrogen atoms on Pt and 0.21 mC/cm<sup>2</sup> represents the charge required to oxidize a monolayer of H<sub>2</sub> on platinum. The Chemical Surface Areas (CSA) of the catalyst were calculated using the following equation, assuming homogenously distributed and spherical particles,<sup>33</sup>

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

where *d* is the mean Pt crystalline size in Å (from the XRD results) and  $\rho$  is the density of Pt metal (21.4 g/cm<sup>2</sup>).<sup>34</sup> Comparing these two areas (ECSA and CSA), it is possible to estimate the Pt utilization efficiency (%) using

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

 Table I.
 The comparisons of particle size, ECSA, CSA and % Pt utility for the Pt NPs with commercial Pt catalysts.

	Particle	ECSA	Roughness	CSA	Pt utility
	size (nm)	(m²/g)	factor (Rf)	(m²/g)	(%)
Pt NPs	3.73	59.40	121.2	71.34	83.26
Pt (ETEK)	2.70	50.60	103.3	103.0	49.10

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Figure 5. Anodic part of the cyclic voltammogram of Pt NPs in 0.1 M  $HCIO_4 + 0.5$  M methanol, ethanol and 2-propanol at room temperature. Scan rate is 50 mV/s.

Moreover, roughness factor, Rf (m<sup>2</sup> g<sup>-1</sup> Pt cm<sup>-2</sup>) can be used to describe the enhancement of the real ECSA in comparison with the geometric area,  $A_{\rho}$  (cm<sup>2</sup>)<sup>35</sup>

$$Rf = \frac{\text{ECSA}}{A_g}$$

CSA, ECSA, Rf and % Pt utility for the prepared catalyst were summarized in Table I. It can be seen that Pt NPs has higher active surface area, Rf, and % Pt utility compared to the commercial Pt (ETEK) catalyst which could be attributed to the higher catalytic activity.

When methanol, ethanol and 2-propanol were added to the 0.1 M  $\text{HClO}_4$  electrolyte solution the classical alcohol oxidation response was observed for the prepared catalyst. Figure 5 indicates the anodic parts of the cyclic voltammogram for the prepared catalyst against oxidation of methanol, ethanol and 2-propanol, respectively. Considering the electrochemical oxidation results, it is possible



**Figure 6.** % conversion versus time graph for the catalytic dehydrogenation of DMAB in THF at room temperature starting with 7.5% mol of Pt NPs and  $PtCl_4$ .



Figure 7. % conversion versus time plot for Pt NPs (7.5% mol) catalyzed dehydrogenation of DMAB in THF at various temperatures.

to conclude that Pt NPs has very high catalytic activity ( $\sim$ 0.65 A/mg Pt at 0.72 V for methanol,  $\sim$ 0.30 A/mg Pt at 0.66 V for ethanol and 0.76 A/mg Pt at 0.56 V for 2-propanol) towards C1 to C3 alcohol oxidation reactions. Moreover, the activity of this catalyst is about 8.64, 12.0 and 10.1 times higher than commercially available E-TEK Pt ones for methanol, ethanol and 2-propanol oxidation reactions, respectively<sup>36,37</sup> due to the higher ECSA, roughness factor and Pt(0) to Pt(IV) ratio of the prepared catalyst. Furthermore, it is clear that the current densities of 2-propanol oxidation at corresponding potentials are higher than that of methanol and ethanol oxidation on our catalyst due to the lower reaction rate of the intermediate formation for 2-propanol than that of other alcohols. This can be explained by a direct reaction path from 2-propanol to acetone, which does not go through an intermediate. Therefore, the performance of our catalyst for 2-propanol oxidation is higher than that of other alcohols in this study. Besides, the similar trend was observed for the onset potentials of C1 to C3 alcohols oxidations. Namely, the overall oxidation rate of 2-propanol was higher than the other alcohols.

## 3.3. Catalytic Activity of Pt NPs in the Dehydrogenation of Dimethylamine-borane (DMAB)

Pt NPs were also examined in the dehydrogenation of DMAB at  $25 \pm 0.1$  °C. Hydrogen progression starts immediately with a first initial turnover frequency of 21.50  $h^{-1}$  and continues until 1 equivalent H<sub>2</sub> per mol DMAB released. It is observed only  $\sim 8\%$  conversion after an induction time period (~10 min.) when  $PtCl_4$ is used as pre-catalyst under the same conditions in the dehydrogenation of DMAB (Fig. 6), at the end of the reaction, the Pt particles starts to agglomerate within 10 min. Since weakly coordinating chloride anion without stabilizer does not provide adequate stabilization for Pt(0) nanoparticles.<sup>38</sup> After the dehydrogenation reaction of DMAB (at 1.0 equiv. H<sub>2</sub> generation), NMR shows the complete conversion of  $(CH_3)_2NHBH_3$  ( $\delta =$ ~12.4 ppm) to  $[(CH_3)_2NBH_2]_2$  ( $\delta = \sim 5$  ppm) even at room temperature.<sup>27</sup> Besides, the DMAB dehydrogenation of Pt NPs queried by performing experiments heterogeneous nature of mercury poisoning, and the reaction was found to be completely stopped by addition of 300 Eq. Pt NPs as a heterogeneous catalyst is moving forward Hg (0) per Pt.

## 3.4. Detection of Activation Parameters (Ea, $\Delta H^{\#}$ , and $\Delta S^{\#}$ ) for Pt NPs Catalyzed Dehydrogenation of DMAB

The stoichiometric ratio of produced H<sub>2</sub> to  $(CH_3)_2NHBH_3$ was expressed for the catalytic dehydrogenation of DMAB starting with Pt NPs and the rate constants  $(k_{obs})$  of hydrogen generation were measured from the linear portions of the plots given in Figure 7 at four different temperatures in the range of 20–35 °C. It is found that even at low temperature (20 °C), Pt NPs is able to catalyze the dehydrogenation of DMAB at 1.0 equiv. of H<sub>2</sub> generation. The activation energy (Ea = 48.36 kJ mol<sup>-1</sup>), activation enthalpy  $(\Delta H^{\#} = 45.82 \text{ kJ mol}^{-1})$ , and activation entropy  $(\Delta S^{\#} = -112.99 \text{ J mol}^{-1} \text{ K}^{-1})$  have been calculated by using from the Arrhenius<sup>39</sup> and Eyring<sup>40</sup> plots (Fig. 8). The activation



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

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energy value (48.36 kJ mol<sup>-1</sup>) provided by Pt NPs is not only higher than Rh(0) nanoparticles (34 kJ mol<sup>-1</sup>), but still smaller than the activation energies reported in the literature for the same reaction (Table II). Moreover, there is an associative mechanism in the transition issues for the catalytic dehydrogenation of DMAB between the higher negative value of the activation entropy and the small value of the activation enthalpy.

# **3.5. Reusability Performance of Pt NPs in the Catalytic Dehydrogenation of DMAB**

Pt NPs were also tested for the isolability and recycling in the dehydrogenation of DMAB at room temperature. After the complete dehydrogenation of DMAB, Pt NPs were isolated as black solid by drying in a vacuum and then bottled under N<sub>2</sub> atmosphere. Interestingly, the isolated Pt NPs were still active in the dehydrogenation of DMAB. Even if at the fourth catalytic period, they retain  $\geq 80\%$  of their initial activity (Fig. 9). This indicates that the prepared platinum nanoparticles can be isolable, bottleable, and redispersible for a long time. In other words, they can be repeatedly used as active catalyst in the dehydrogenation of DMAB. The slight decrease in catalytic activity may be attributed to the formation of a precipitate of bulk Pt(0) metal. This becomes visible at the end of the 4th catalytic run, finally yielding a clear, colorless

Table II. Catalysts tested in the dehydrogenation of DMAB under mild

Entry	(Pre) catalysts	Conv. (%)	TOF	Ref
1	Pt NPs	100	21.5	This study
2	$RuCl_3 \cdot 3H_2O$	77	2.7	[41]
3	$[Cr(CO)_5(thf)]$	97	13.4	[40]
4	$[Ru(1,5-cod)Cl_2]n$	70	2.5	[41]
5	Rh(0)NPs	100	60.0	[27]
6	trans-PdCl <sub>2</sub> (P(o-tolyl) <sub>3</sub> ) <sub>2</sub>	20	0.2	[34]
7	$[RhCl(PHCy_2)_3]$	100	2.6	[34]
8	(Idipp)CuCl	100	0.3	[39]
9	Ru(0)/APTS	100	55.0	[27]
10	Pd/C	95	2.8	[34]
11	[Cp*Rh(m-Cl)Cl] <sub>2</sub>	100	0.9	[34]
12	$[Cr(CO)_5(h1-BH_3NMe_3)]$	97	19.9	[40]
13	Ru(cod)(cot)	40	1.6	[27]
14	$HRh(CO)(PPh_3)_3$	5	0.1	[34]
15	$[Rh(1,5-cod)m-Cl]_2$	100	12.5	[34]
16	Cp <sub>2</sub> Ti	100	12.3	[36]
17	$[RuH(PMe_3)(NC_2H_4PPr_2)_2]$	100	1.5	[38]
18	IrCl <sub>3</sub>	25	0.3	[34]
19	$[(C_5H_3-1,3(SiMe_3)_2)_2Ti]_2$	100	420.0	[33]
20	$Rh(0)/[Noct_4]Cl$	90	8.2	[34]
21	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	100	4.3	[34]
22	[Rh(1,5-cod)(dmpe)]PF <sub>6</sub>	95	1.7	[34]
23	$[Ir(1,5-cod)m-Cl]_2$	95	0.7	[34]
24	$[Rh(1,5-cod)_2]Otf$	95	12.0	[34]
25	trans-RuMe <sub>2</sub> (PMe <sub>3</sub> ) <sub>4</sub>	100	12.4	[34]
26	Ni(skeletal)	100	3.2	[42]
27	RhCl <sub>3</sub>	90	7.9	[34]
28	Pt(0)/AA	100	15.0	[41]

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Figure 9. % conversion versus time graph for Pt NPs (7.5% mol) catalyzed dehydrogenation of DMAB in THF at room temperature for 1st and 4th catalytic runs.

(i.e., Pt(0) nanoparticle free) by increasing boron products, which decreases reach of active sites.<sup>27</sup> The apparent initial TOF value of Pt NPs (21.50 h<sup>-1</sup>) is higher than the majority of those of other heterogeneous and homogeneous catalysts as shown in Table II, apart from the prior best heterogeneous<sup>27</sup> (60 h<sup>-1</sup>) and homogeneous<sup>33</sup> (420 h<sup>-1</sup>) catalysts. As far as we know, our catalyst is the one of the few examples of an isolable and reusable nanocatalysts used for DMAB dehydrogenation reaction in literature.<sup>27</sup> Most importantly, the reusability performance of Pt NPs is better than the one of Rh(0) nanocatalyst previously known as the most active catalyst.<sup>27</sup>

## 4. CONCLUSIONS

In the current work, highly efficient and active nearly monodisperse Pt NPs have been prepared, characterized and used as a heterogeneous catalyst for both C1 to C3 alcohol oxidation and DMAB dehydrogenation reaction. Some of the fundamental findings of this study are summarized below:

• Nearly monodisperse Pt NPs have been prepared by using a simple and reproducible superhydride reduction method in an ultrasonic sonicator. The ICP-OES, XRD, XPS, TEM, AFM characterizations of these nanoparticles confirmed the formation of well-dispersed Pt(0) nanoparticles supported on activated carbon.

• Pt NPs provide one of the highest catalytic activities  $(TOF = 21.50 h^{-1})$  found in the literature in the dehydrogenation of DMAB at room temperature. The catalyst developed in this study was also recoverable and reusable, retaining  $\geq 80\%$  of the initial activity after four runs. The used capping ligand provided exceptional stability against clumping and leaching throughout the catalytic dehydrogenation of DMAB.

• The dehydrogenation of DMAB using Pt NPs was carried out at different temperatures to examine the activation parameters (Ea,  $\Delta H^{\neq}$ ,  $\Delta S^{\neq}$ ). We found that Pt NPs provide one of the lowest activation energies (Ea = 48.36 kJ/mol) reported among the heterogeneous catalysts tested in the same reaction. The activation enthalpy ( $\Delta H^{\neq} = 45.82$  kJ/mol) and activation entropy ( $\Delta S^{\neq} = -112.99$  J/mol K) values calculated from the Eyring plots suggest an associative mechanism for the Pt NPs dehydrogenation of DMAB.

With the advantages in the ease of synthesis, relatively high activities, catalytic versatility, efficient recovery, and prolonged stability and reusability, Pt NPs offer a promising approach towards realizing a commercially viable technology using DMAB as a CO-free,  $H_2$  storage and generation system for fuel cell applications.

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