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### Polymer-Graphene Hybrid Stabilized Ruthenium Nanocatalysts for the Dimethylamine -Borane Dehydrogenation at Ambient Conditions

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### Abstract

In this work, we reported a new catalyst consistent of graphene oxide (GO) – poly(N-vinyl-2-pyrrolidone) (PVP) hybrid supported ruthenium nanoparticles and called as Ru@GO-PVP. The GO-coupled PVP nanosheets were prepared with a new and straightforward pathway. The prepared Ru@GO-PVP nanocatalysts were characterized using some advanced analytic measurements such as XPS (X-ray photoelectron spectroscopy), XRD (X-ray diffraction), TEM/HRTEM (Transmission electron microscopy/high resolution transmission electron microscopy), Raman and ICP (Inductively coupled plasma). The mean particle size of the catalyst was found to be 2.09 nm, and this catalyst having small particle size showed one of the highest catalytic activities with a very high TOF value of 896.54  $h^{-1}$  in dehydrogenation of DMAB at room temperature. Therefore, the proposed hybrid and supported catalyst offer a new pathway to enhance the catalytic dehydrogenation of DMAB greatly, and this study presents a universal and powerful technique for such applications.

**Keywords:** Dehydrogenation; DMAB; GO-coupled PVP Nanosheets; Polymer-Graphene Hybrid; Nanocatalyst.

### **1.** Introduction

Hydrogen gas is generally considered as clean, renewable, environmental energy source and used in electricity generation. But, a big problem for a hydrogen economy is unable to store hydrogen. Among the available hydrogen sources, ammonia borane derivations have increasing attention because of their high hydrogen content, availability, stability, ease of use and non-flammability [1-2]. However, they cannot be used as a hydrogen source without a suitable catalyst. A presence of a suitable catalyst in a dehydrogenation reaction of ammonia borane derivatives at ambient conditions can easily produce hydrogen. So far, for this purpose, several types of catalysts have been used in hydrogen generation from ammonia borane derivations. Generally, nanocatalysts have been used for the hydrogen generation from ammonia borane derivations due to their high catalytic activity and small particle size [3-20]. The usage of dimethylamine borane (DMAB, (CH<sub>3</sub>)<sub>2</sub>NHBH<sub>3</sub>)) which is one of the ammonia borane derivatives has received significant attention because of its advantages such as stability, non - toxicity and environmentally-friendly. So far, the studies conducted for the hydrogen generation from dimethylamine borane have revealed that DMAB is a one of the best hydrogen sources compared to the other ammonia borane derivations as shown in Scheme 1 [21-30]. For dehydrogenation of DMAB, [N<sup>5</sup>C<sub>5</sub>H<sub>3</sub>- $1,3(SiMe_3)_2)_2Ti]_2$  has shown one of the best catalytic activity [31] in the hydrogen generation from DMAB as a homogenous catalyst. In prepared catalysts, mostly Ru based nanomaterials have great catalytic activity compared to the others as shown in Table 1. For this purpose, in this study, we have prepared a new Ru based nanocatalyst having some significant advantages such as high reusability, recovery and catalytic activity. Further, the scientist has also used many supporting agent such as carbon and polymer derivatives. [7, 14, 30]

$$2Me_2NHBH_3 \xrightarrow{Catalyst} (MeH_2.BH_2)_2 + 2H_2$$

Scheme 1. The catalytic dehydrocoupling of DMAB.

Hitherto, several studies have arisen dealing with graphene oxide as a support material due to its high electrical conductivity, stability and specific surface area for the preparing catalyst [6-7]. Metal nanocatalyst composed of graphene oxide as supporting materials have shown high catalytic activity, stability and synergistic effect for hydrogen generation and hydrogen applications [10, 26, 27]. However, there are some critical issues with graphite oxide as a

supporting material: (1) Irreversibly restacking of GO sheets resulting from their strong interactions causes most catalyst nanoparticles to be embedded between GO layers and unavailable to reactants [32]. (2) Due to the high surface energy and poor interaction on the GO surface, the dissolution and sintering of the nanoparticles reduce nanocatalyst activity in fuel cells [33]. (3) Due to the carbon corrosion of the graphene oxide, the structural integrity of the nanocatalyst is dissipated so that the nanoparticles are dispersed [34-36] and thus reduce the usage of nanocatalyst. To solve the mentioned above problems, various strategies have been tested such as making spaces between the graphene oxide layers, surface applications of GO for preventing carbon corrosion and spontaneously stabilize nanoparticles on the GO [37, 38]. It is extremely difficult to develop a nanocatalyst based graphene oxide that can address all the above problems. In this study, we report preparation of Ru @GO-PVP (poly(N-vinyl-2-pyrrolidone)) nanocatalyst and a one-step preparation method prevention interaction between graphene oxide sheets. The mentioned method gives a new aspect for solving the main problems. To accomplish this at the beginning, the nanoparticles facilitate the mass transfer that allowing more contact with the active site in the catalyst, that allows the catalyst to be used in an efficient manner [39, 40]. In the second stage PVP particles having stable manner are stacked between the GO layers that give a stable structure to GO, hence the corrosion of GO is prevented [39, 40]. At the last stage, compared to GO, PVP is more compatible with inorganic materials and a conductive material. At the same time, PVP, which contains more nitrogen atoms, provides a controllable structure with metal nanoparticles, and that enhance anchor effects [14]. The PVP coupled GO nanoparticles prepared according to the described methods both have acquired a more stable structure and can be used effectively. So, prepared PVP-GO systems can be used actively in hydrogen applications. For this reason, in this work, the preparation of PVP-GO decorated Ru nanoparticles (Ru@GO-PVP), its outstanding catalytic activity in the dehydrogenation of DMAB and its characterization were investigated. In the study, the preparation of the catalyst was carried out by the ultrasonic reduction method (given later); hence the stability of the Ru@GO-PVP catalyst was ensured. The characterization of Ru@GO-PVP catalyst was investigated using advanced analytical techniques such as TEM, HRTEM, ICP, XPS, and Raman.

### **Experimental methods**

#### The preparation of Ru@GO-PVP Nanocatalysts

The preparation route for Ru@GO–PVP nanocatalysts is explained as below. The synthes of graphene oxide from graphite powder was performed according to Hummer's method as shown in Supporting Information. For this purpose, a required amount of GO obtained from powder graphite powder was mixed in pure water using ultrasonic method for 2 h, then the same amount of water and PVP were transferred into the GO mixture, at last, the resulting slurry was stirred for another 2 h. At the end of this time, a solution containing 148 mg DMAB and 2 ml 0.01 M RuCl<sub>3</sub> was added into the above mixture under the same condition. The resulting solution was stirred in reflux at 90 °C temperature for 2 h. The obtained solid Ru@GO–PVP nanocatalysts was centrifugated, washed with distilled water and ethanol. The catalyst was dried in a vacuum oven at 25 °C. Ruthenium nanocatalysts decorated with graphene oxides or poly(N-vinyl-2-pyrrolidone) were also prepared according to the procedure given above, the prepared catalyst system was indicated as Ru@GO and Ru@PVP nanocatalysts, respectively.

#### **Results and discussion**

### The analytical techniques and characterization of Ru@GO-PVP Nanocatalysts

Analytical investigations of catalytic performances of the prepared Ru@GO-PVP nanocatalysts and reusability of Ru@GO-PVP nanocatalysts have examined after fully characterization of prepared nanomaterials. For this purpose, firstly, the Ru@GO-PVP nanocatalysts have been characterized using TEM, HRTEM, ICP, XPS, and Raman techniques. The chemical composition and particle size of Ru@GO-PVP nanocatalysts were also investigated using TEM analysis, given in Fig. 1a. HR-TEM (high-resolution transmission electron microscopy) analysis was conducted to reveal the composition and morphology of Ru@GO-PVP nanocatalysts in more detail; the results are given in Fig. 1b. According to the data of HR-TEM, whole particles of the prepared catalyst have a spherical shape, and any agglomeration wasn't observed in the preparation of the catalyst. And again, thanks to HR-TEM analysis, the atomic lattice fringes on the catalyst have been revealed in Fig. 1b. Further, the mean particle size of Ru@GO-PVP nanocatalysts was found to be  $2.09 \pm 0.23$  nm as shown in Figure 1c. The calculated fringes for Ru (111) were found to be 0.21 nm which is the same as nominal Ru (111) space of 0.21nm [9, 27]. The EELS line profile also indicates the existence of the Ruthenium in prepared nanomaterials as shown in Figure 1d.



**Figure 1.** (a) The TEM (b) HR-TEM image (c) the mean particle size (d) the EELS line profile scanned on the arrow shown in HRTEM for ruthenium elements of Ru@ GO-PVP nanocatalysts.

The electronic structure for ruthenium on the catalyst, its surface distribution on Ru@GO-PVP nanocatalysts were investigated by XPS analysis. Fig 2a shows XPS data of Ru 3p region on Ru@GO-PVP nanocatalysts. As shown in this figure, two apparent peaks are seen for Ru (3p) at 483.5 eV and 487.4 eV which can be ascribed to metallic ruthenium and ruthenium oxy and/or hydroxyl species, respectively [41]. These results revealed that ruthenium atoms present on the catalysts are in mostly metallic state.



Figure 2. (a) Ru (3p) XPS spectra (b) The Raman spectra of Ru@GO-PVP nanocatalysts.

In addition to the analytical techniques given above, Raman spectroscopy was also conducted for understanding the ordered and disordered carbon in the catalyst, data in Raman spectroscopy for GO, GO-PVP and Ru@GO-PVP are given in Fig. 2b. Two distinct peaks in the range 1348, and 1599 cm<sup>-1</sup> can be associated with D band and G-band of the carbon atom for GO, GO-PVP, and Ru@ GO-PVP, respectively. The degrees of defect for GO-PVP could be determined by using the intensity ratio of D/G (ID/IG) for GO, GO-PVP, and Ru@GO-PVP, and ID/IG were found to be 0.92, 1.03 and 1.05 for GO, GO-PVP, and Ru@GO-PVP, respectively. This data proves the formation of Ru@GO-PVP.

### The catalytic performance of monodisperse Ru@GO-PVP nanocatalysts

After fully characterization of prepared nanomaterials, the catalytic experiments related to the dehydrogenation of DMAB were performed with the help of Ru@GO-PVP nanocatalysts and the results showed that Ru@GO-PVP nanoparticles have very high catalytic activity and efficiency. In those experiments, the hydrogen generation began linearly and continued until

the end of the catalytic reaction of dehydrogenation of DMAB. After the dehydrogenation reaction of DMAB, the complete conversion of DMAB (CH<sub>3</sub>)<sub>2</sub>NHBH<sub>3</sub> ( $\delta$ = ~-12.7 ppm) to  $[(CH_3)_2NBH_2]_2$  ( $\delta = -5$  ppm) were shown with the help of NMR. The results of experiments conducted for dehydrogenation of DMAB with Ru@GO-PVP nanocatalysts at different temperatures in the range of 20- 35 °C are given in Fig. 3a. Furthermore, Fig. 3b (Arrhenius plot) and Fig. 3c (Eyring plot) were used to determine the activation energy ( $E_a$  as 11.45  $\pm$  2 kJ/mol), activation enthalpy ( $\Delta H^{\#}$  = 8.96 kJ mol<sup>-1</sup>) and activation entropy ( $\Delta S^{\#}$  = -194.02 J mol-1 K<sup>-1</sup>) for dehydrogenation of DMAB catalyzed Ru@GO-PVP nanocatalysts. It can be stated that the high negative value of entropy indicate that a associative mechanism in the conversion process of DMAB with Ru@GO-PVP nanocatalysts. The recycle performance for dehydrogenation of DMAB catalyzed by Ru@GO-PVP nanoparticles were performed after the fifth run of catalytic reaction by adding the same amount of DMAB. The intial catalytic performance of Ru@GO-PVP nanocatalysts was found to be 78 % even after the 5<sup>th</sup> run (Fig. S1) for dehydrogenation of DMAB. The decrease in the catalytic activity occurring in the catalyst may be related to the decreasing active sites of catalyst due to the covering of the active zones of catalysts with the resulting products at the end of the 5<sup>th</sup> cycle. Besides, ICP analysis revealed that there were no leaching problems, which means that the catalyst maintained its initial content.



**Figure 3.** (a) % conversion/Time (b) In k/(1/T) (c) In (k/t)/(1/T) plots for dehydrogenation of DMAB catalyzed by Ru@PVP-GO nanocatalysts at various temperatures.





**Fig. 4** (a) Graph of  $nH_2/nDMAB$  versus time for the dehydrogenation of DMAB with different amount of Ru@GO-PVP nanocatalysts at room temperature. (b) Graph of  $nH_2/nDMAB$  versus time for the dehydrogenation of DMAB with different amount of substrate concentrations at room temperature.

Besides, the results of a set of experiments with different nanocatalyst concentration in the range of 2.25-9.00 mM at room temperature are given in Figure 4a. As shown in the inset plot of this figure, the logarithmic function of  $H_2$  production rate is nearly first (0.8066) order with respect to the catalyst concentration. Further, as shown in the inset plot of Figure 4b, the logarithmic function of hydrogen production rate is also nearly first (0.9059) order depending upon the substrate concentration (75, 100, 125, 150 mM). It can be stated that, the rate law for this reaction can be written by;

$$-\frac{d\left[(CH_3)^2HNBH_3\right]}{dt} = +\frac{d\left[((CH_3)^2NBH^2)^2\right]}{dt} = +\frac{[H^2]}{dt} = [cat]^{0.8066} \cdot [DMAB]^{0.9059}$$

The hydrogen evaluation (1.0 mol H<sub>2</sub>/mol DMAB) from the dehydrogenation reaction of DMAB catalyzed by Ru@GO-PVP nanoparticles was completed with TOF value of 896.54 h<sup>-1</sup> at room temperature. This current study showed that Ru@GO-PVP nanocatalyst has showed very good catalytic activity (896.54 h<sup>-1</sup>) for catalytic dehydrogenation of DMAB. Table 1 shows a comparison of different catalyst TOF values for catalytic dehydrogenation of DMAB. Compared to the TOF values of the catalysts given in this table, it is clear that the obtained

value (896.54 h<sup>-1</sup>) for the Ru@GO-PVP catalyst is really high compared to the others. Thus, the obtained Ru@GO-PVP catalyst stabilized with GO-PVP is the catalyst showing very good stability and activity for the catalytic dehydrogenation of DMAB. Additionally, the catalytic activities of Ru@PVP, Ru@GO, and Ru@GO-PVP nanoparticles were tested, compared for dehydrogenation of DMAB, and their results are also given in Table 1. It is easy to see that the catalytic activity of Ru@GO-PVP nanocatalyst is very high compared to other prepared catalysts in this study. This is mainly due to the large surface area provided by GO-PVP and the synergistic effect of GO-PVP with the monodisperse distribution of Ru metal. The method used to prepare the obtained catalyst is very effective, easy, controllable, understandable, and this method can be used to prepare very high catalytic activity materials for fuel cells. The materials used in the preparation of catalysts have porous structures that enable a large surface area and homogeneous distribution of metal nanoparticles for dehydrogenation of DMAB.

	Catalysts	Conversion	TOF (h	Reference		
		(%)	<sup>1</sup> )			
1	Ru@GO-PVP	100	896.54	This study		
2	Ru@GO	100	361.66	This study		
3	Ru@PVP	100	403.67	This study		
4	RhCl <sub>3</sub>	90	7.9	8		
5	Pd/C	95	2.8	8		
6	trans-RuMe <sub>2</sub> (PMe <sub>3</sub> ) <sub>4</sub>	100	12.4	8		
7	Cp <sub>2</sub> Ti	100	12.3	10		
8	$[Ir(1,5-cod)m-Cl]_2$	95	0.7	8		
9	$[Rh(1,5-cod)(dmpe)]PF_6$	95	1.7	8		
10	$[Rh(1,5-cod)m-Cl]_2$	100	12.5	8		
11	$[Rh(1,5-cod)_2]Otf$	95	12.0	8		
12	[RuH(PMe <sub>3</sub> )(NC2H4PPr <sub>2</sub> ) <sub>2</sub> ]	100	1.5	9		
13	IrCl <sub>3</sub>	25	0.3	8		
14	[Cr(CO) <sub>5</sub> (thf)]	97	13.4	11		
15	$Rh(0)/[Noct_4]Cl$	90	8.2	8		
16	[RhCl(PHCy <sub>2</sub> ) <sub>3</sub> ]	100	2.6	12		
17	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	100	4.3	8		
18	(Idipp)CuCl	100	0.3	15		
19	Ni(skeletal)	100	3.2	13		

**Table 1.** The comparison of TOF values for dehydrocoupling of DMAB.

20	$[Cp*Rh(m-Cl)Cl]_2$	100	0.9	16
21	$[Cr(CO)_5(\eta^1-BH3NMe_3)]$	97	19.9	11
22	Ru(cod)(cot)	40	1.6	8
23	RuCl <sub>3</sub> .3H2O	77	2.7	8
24	$[(C_5H_3-1,3(SiMe_3)_2)_2Ti]_2$	100	420.0	31
25	$[Ru(1,5\text{-cod})Cl_2]n$	70	2.5	8
26	HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub>	5	0.1	8
27	trans-PdCl <sub>2</sub> (P(o-tolyl) <sub>3</sub> ) <sub>2</sub>	20	0.2	8
28	Pt(0)/BA	100	24.88	17
29	Pt(0)/TBA	100	31.24	17
30	Pt(0)/AA	100	15.0	22
31	Pt(0)/TPA@AC	100	34.14	19
32	PdCo@PVP	100	330	14
33	RuPtNi@GO	100	727	42
34	RuCo@f-MWCNT	100	775.28	43
35	PdNi@PEDOT	100	451.28	44
36	Pt@PANI-rGO	100	42.94	45
37	PdNi@GO	100	271.90	46
38	Pd@GO	100	38.02	47
39	Pt NPs@CBH	100	70.28	48

### Conclusions

In this study, we have shown the preparation GO, PVP and GO-PVP nanocatalysts decorated ruthenium nanomaterials using an efficient, controllable, understandable process in dehydrogenation reaction of DMAB. With this method, a uniform distribution of the ruthenium metal nanoparticles on the GO-PVP materials having stable structure was achieved using a reduction of ruthenium with one step stage. The characterization of Ru@GO-PVP nanocatalyst was performed by advanced analytic techniques such as XPS, XRD, TEM-HRTEM, ICP, and Raman spectroscopy. The mean particle size of monodisperse Ru@GO–PVP nanocatalyst was found to be 2.09±0.23 nm. The obtained TOF value for Ru@GO–PVP in the catalytic reaction of DMAB was compared to the previous studies (Table 1) and the catalytic reactions and the analytical techniques revealed that Ru@GO-PVP nanocatalyst has a very high catalytic activity with a unique TOF value of 896.54 h<sup>-1</sup> at room temperature. The investigation of kinetic studies was performed to find activation parameters such as activation

energy ( $E_a$  as 11.45 ± 2 kJ/mol), activation enthalpy ( $\Delta H^{\#}$ = 8.96 kJ mol<sup>-1</sup>) and activation entropy ( $\Delta S^{\#}$ = -194.02 J mol<sup>-1</sup> K<sup>-1</sup>) for dehydrogenation of DMAB catalyzed by Ru@GO-PVP nanocatalysts. As a result of an investigation of the kinetic studies, we have reached that the very high negative value of entropy indicate that an associative mechanism in the conversion process of DMAB with the help of Ru@GO-PVP nanocatalysts. The reusability experiments revealed that Ru@GO-PVP nanocatalysts have a heterogeneous and isolable structure in dehydrogenation reaction even after 5<sup>th</sup> runs, it remained the initial catalytic activity of 79 % with complete conversion DMAB at 25 °C. Besides, H<sub>2</sub> production rate showed that it is first (0.8066) order with respect to both the catalyst and substrate concentration. Analytic techniques used in the study showed that GO-PVP has a large surface area and a great enhanced monodisperse distribution of Ru nanometals with a synergistic effect for the dehydrogenation of DMAB. In summary, the method used in the study offers a new, effective and easy way to prepare nanomaterials for fuel cells and extensive applications in other catalytic reactions with high activities.

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### Highlights

- The synthesis and characterization of Ru NPs @GO-PVP for hydrogen evolution reaction
- Ru NPs decorated on Graphene Oxide- Polyvinylpyrrolidone as highly efficient and stable catalysts
- Monodisperse Ru@GO-PVP provides one of the record catalytic performances
- Ru@GO-PVP catalysed dehydrocoupling of DMAB depending upon catalyst and substrate concentration.