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Introduction

Hydrogen is a gas which has been considered as a clean and environmentally benign energy carrier for electricity generation. However, the storage of hydrogen is the main obstacle for the hydrogen economy. Among the tested hydrogen sources, NaBH₄ (SBH) looks like one of the most suitable energy carriers due to a high hydrogen content (10.8%), high stability, availability, easy handling and lack of flammability. From recent studies, ammonia boranes (ABs) can also be thought of as one of the most convenient hydrogen energy sources due to a high hydrogen content (19.6%), and high solubility and stability in water at room temperature.^{1,2} Hydrogen generation through the reaction of ABs at room temperature is very simple when a convenient catalyst is present. For the dehydrogenation of ABs, different types of catalysts have been employed until now. Due to a smaller size and better catalytic performances, nanocatalysts are preferred for the hydrogen evolution reaction.³⁻²⁰ Recently, dimethylamine-borane, DMAB, one of the derivatives of ABs, has attracted much attention as it has various advantages such as being nontoxic, a crystalline solid at room temperature, stable in air and water, and environmentally friendly. Of particular interest, recent studies have already

Monodispersed palladium–cobalt alloy nanoparticles assembled on poly(*N*-vinylpyrrolidone) (PVP) as a highly effective catalyst for dimethylamine borane (DMAB) dehydrocoupling[†]

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Herein we report the fabrication of monodispersed poly(*N*-vinyl-2-pyrrolidone) supported palladium– cobalt nanomaterials (3.45 \pm 0.36 nm) and their outstanding efficiency as catalysts in dimethylamineborane dehydrogenation. By the use of an ultrasonic double reduction method, palladium and cobalt cations were co-reduced in PVP solution and then the prepared nanocatalysts were characterized by UV-Vis, XRD, XPS and HR-TEM-EDX analyses. The nanocatalysts could be easily reused, and at extremely low concentrations and temperature they showed record catalytic activity, giving the best catalytic performance yet with a very high turnover frequency (330.94 h⁻¹) and a low E_a value of 50.78 \pm 2 kJ mol⁻¹ for DMAB dehydrocoupling.

> shown that DMAB is really a model substrate since the products are relatively easy to understand compared to those of the other ABs (Scheme 1).

> Furthermore, various homogeneous and heterogeneous catalysts have been tested for the dehydrocoupling of DMAB such as Ru, Rh, Pd, and Ir complexes,²¹ Ru(H)(PMe₃)(PNP) and trans-Ru(H)₂(PMe₃)(PNP^H),²² $[Rh(1,5-cod)(\mu-Cl)]_2$,²³⁻²⁵ $[Cp_2Ti]^{26,27}$ $[RuH_2(\eta^2-H_2)_2(PCy_3)_2]$ and $[RuH_2(\eta^2:\eta^2-H_2B-$ NMe₂)₂(PCy₃)₂],²⁸ RhCl₃, colloidal Rh/[Oct4N]Cl and Rh/Al₂O₃,²³ Rh(0),²⁹ hexanoate-stabilized laurate-stabilized Rh(0).30 aminopropyltriethoxysilane-stabilized Ru(0),31 Re complexes,32 Rh4-6 clusters,³³ RhCl(PHCy₂)₃,³⁴ Ru/ZIF-8, [Ru(p-Cym)(bipy)Cl] Cl,³⁵ Pd(0)/MOF,³⁶ Pt(0)/amylamine,³⁷ Pt(0)/TBA,³⁸ Pt(0)/ TPA@AC,39 and Pt(0)@CNT.40 Although record activity has been achieved using a homogeneous $[\eta^5(C_5H_3-1,3(SiMe_3)_2)_2Ti]_2$ catalyst,41 the current research has focused on the development of new metal nanoparticle catalysts because of their significant advantages in product isolation, catalyst recovery and reusability. We report, for the first time, the preparation and characterization of highly efficient and monodispersed palladiumcobalt nanomaterials stabilized by poly(N-vinyl-2-pyrrolidone) for DMAB dehydrogenation. A few papers have recently reported different PdCo bimetallic alloys that enhance the Pd electrocatalytic activity and stability for chemical reactions.42-46

 $2Me_2NHBH_3 \xrightarrow{\text{catalyst}} (Me_2N.BH_2)_2 + 2H_2$

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Scheme 1 The catalytic dehydrocoupling of dimethylamine-borane ((CH_3)_2NHBH_3, DMAB).

Herein, the use of Pd–Co@PVP nanocatalysts in the dehydrogenation reaction of DMAB and their outstanding performance is explained. The production of the nanocatalyst was performed using a special method in which both of the metals were coreduced by an ultrasonic double reduction method, preferred for its stability for nanoparticle dispersion, and analytical techniques such as UV-Vis, XRD, TEM and XPS were carried out for the characterization. Nanocatalysts containing noble metals like Pd are known to be expensive, however, their exceptional performances as catalysts give them a special position in compact hydrogen production systems employing DMAB as a hydrogen containing compound eliminating worries regarding the high catalyst charge.

Experimental methods

Pd-Co nanomaterials stabilized by PVP production

In the preparation of Pd–Co@PVP (poly(*N*-vinyl-2-pyrrolidone)) NPs, an ultrasonic double reduction method^{47,48} was used and PVP was utilized for stabilization and reduction. Firstly, PVP (2.5 mmol), CoCl₂ (0.25 mmol) and K₂PdCl₄ (0.25 mmol) were stirred together under ultrasonic conditions. Later, refluxing of the resulting mixture was performed at 90 °C for 2 h. At room temperature, the color of the palladium–cobalt nanomaterials stabilized by PVP is brownish black and they have good stability. Analytical investigations of the prepared Pd–Co@PVP NPs, their catalytic and reusability performances for DMAB dehydrogenation and investigation of the E_a of Pd–Co@PVP NPs have been examined in detail in the ESI.†

Results and discussion

Production and analytical investigation of the Pd–Co nanomaterials stabilized by PVP

The monodispersed Pd-Co@PVP NPs have been characterized with the use of UV-VIS, XRD, TEM, HRTEM and XPS techniques. The fabrication of the Pd-Co@PVP NPs was carried out by an ultrasonic double reduction method in which in the presence of poly(N-vinyl-2-pyrrolidone), CoCl2 and K2PdCl4 were reduced together under ultrasonic conditions. The function of PVP is stabilizing and reducing the compound. After this, the resulting mixture was refluxed for 2 h, and a brownish black colored solution was observed, which implied that the Pd²⁺ and Co²⁺ ions were reduced to Pd(0) and Co(0) to form bimetallic nanoparticles. In order to see this change, UV-VIS data were used. The UV-VIS results (Fig. S1[†]) demonstrate the conversion of the Pd and Co salts by poly(N-vinyl-2-pyrrolidone) to Pd-Co nanomaterials. Because of the d-d transitions of the Pd²⁺ and Co²⁺ ions, absorption lines vanish at the end of the reflux, showing that all these cations have been reduced.

Furthermore, the size, morphology and composition of the Pd–Co@PVP NPs were investigated by TEM-EDX analyses as shown in Fig. 1 and the average particle size was found to be 3.45 ± 0.36 nm. The high resolution electron micrograph (HRTEM) of the catalyst is also illustrated in Fig. 1, which shows the morphology of the prepared catalyst as well. From HRTEM data, it was observed that most of the particles were a spherical



Fig. 1 $\,$ HR-TEM, particle size histogram (a) and EDX (b) of Pd-Co@PVP (1 : 1 ratio) NPs.

shape, and no agglomerations were observed in the synthesized catalyst. Furthermore, the HRTEM image for the monodispersed Pd–Co@PVP NPs has also been used to see atomic lattice fringes in Fig. 1. As a result of these fringes, a Pd (111) plane was observed with spacing of 0.22 nm on the prepared catalyst, which is exactly the same as a nominal Pd (111) spacing of 0.22 nm.^{49,50} Besides, an EDX spectrum of the Pd–Co@PVP NPs confirmed the alloy structure and 1 : 1 ratio of Pd : Co. The 1 : 1 ratio of Pd : Co was also confirmed by ICP analysis (Pd₅₃Co₄₇).

XRD was used to define the crystal structure and average crystallite size of the Pd–Co@PVP NPs. The crystal structures of Pd–Co@PVP NPs are determined to be face centered cubic structures, as shown in Fig. 2. As can be seen from this figure, the diffraction peaks for the catalyst containing palladium and cobalt were slightly shifted to higher 2θ values compared to those of pure Pd, which indicates the formation of the Pd–Co@PVP NP alloy. Furthermore, the peak at around 24.8° is attributed to PVP. The XRD pattern of the pure Co sample prepared by reduction of Co²⁺ with PVP exhibited a single broad peak around $2\theta = 44.3^{\circ}$ indicative of the amorphous structure of the Co species (JCPDS no. 15-0806). Due to the relatively strong signal for the Pd species, no significant diffraction peaks characteristic of the Co species were detected from the XRD



Fig. 2 XRD of Pd@PVP, Co@PVP and Pd–Co@PVP NPs.

pattern for the Pd–Co samples, which is likely to be related to their amorphous structure. In addition to the presence of the weak Co (111) diffraction peak in the curve of the Pd–Co@PVP NPs, peaks at $2\theta = 40.3^{\circ}$, 46.7° , 68.3° and 82.2° correspond to Pd (111), (200), (220) and (311) crystal planes, respectively. Moreover, the average crystallite particle size of the monodispersed Pd–Co@PVP NPs have been calculated to be about 3.71 ± 0.43 nm using the following equation:^{49,51,52}

$$d\left(\mathring{A}\right) = \frac{k\lambda}{\beta\cos\theta}$$

where k = a coefficient (0.9); $\lambda =$ the wavelength of X-ray used (1.54056 Å); $\beta =$ the full width half-maximum of the respective diffraction peak (rad); $\theta =$ the angle at the position of the peak maximum (rad).

The Pd (220) diffraction peak of the prepared catalyst is used for calculating the lattice parameter (α Pd) values. The lattice parameter value of the highly monodispersed Pd–Co@PVP NPs was obtained as 3.88 Å using the following equation and is in good agreement with the 3.89 Å value for pure Pd.^{49–51}

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

The surface compositions and chemical oxidation states of Pd and Co in the monodispersed Pd–Co@PVP NPs have been investigated using X-ray photoelectron spectroscopy (XPS). For this purpose, the Pd 3d and Co 2p regions of the spectrum were evaluated by the Gaussian–Lorentzian method and the estimation of the relative intensity of the species have been performed by calculating the integral of each peak, after smoothing, and subtracting the Shirley-shaped background. In the XPS spectrum, accurate binding energies ($\pm 0.3 \text{ eV}$) have been determined by referencing to the C 1s peak at 284.6 eV.⁵¹

XPS spectra (Fig. 3a) show that the surface Pd and Co are found to be metallic, not oxides, by comparing experimental binding energies (Pd-3d_{5/2}: 335.2 eV, Co-2p_{3/2}: 778.1 eV) to those in the literature (Pd-3d_{5/2}: 334.4 eV, Co-2p_{3/2}: 781.5 eV). As for



Fig. 3 Co 2p (a) and Pd 3d (b) XPS spectra of Pd-Co@PVP NPs.

the binding energy of Co, the shift of the 2p_{3/2} peak to lower energy indicates the alloying of Co with Pd.49-51 These results indicate that Co and Pd are present as elements in the Pd-Co@PVP NPs rather than oxygen-containing compounds due to the PVP wrapping of Pd(0) and Co(0) metals during the catalyst fabrication. The $Pd(\pi)$ and $Co(\pi)$ peaks in Fig. 3 may be caused by the surface oxidation and/or chemisorption of environmental oxygen during the preparation process. Since the sensitivity factor of Pd-3d is 2-3 times higher than that of Co-2p the peak area of Pd is larger than that of Co. Furthermore, by carrying out some comparative studies in which the catalytic performances during the dehydrogenation of DMAB of several types of compositions of the metals (Pd and Co nanoparticles, physically mixed with a ratio of 1:1, and Pd-Co bimetallic nanomaterials (1:1) were investigated, the production of the alloy character of Pd-Co@PVP was proven. The turnover frequencies (TOFs) of 42, 18, 64 and 330.94 h^{-1} for Pd@PVP nanoparticles, Co@PVP nanoparticles, physical mixture of Pd@PVP-Co@PVP nanoparticles, and PdCo@PVP bimetallic nanoparticles, respectively, were obtained. The comparatively larger catalytic value of the Pd-Co@PVP nanoparticles to a simple mixture of Pd and Co nanometals determined that the fabricated catalyst didn't contain a Pd and Co nanograin

mixture, rather it consisted of a Pd–Co alloy in Pd–Co@PVP bimetallic nanomaterials.

The performance examination of Pd–Co nanomaterials stabilized by PVP

The experiments revealed that the as-fabricated Pd-Co@PVP NP catalysts had high efficiency for the catalytic dehydrogenation of DMAB. The graph of $nDMAB/nH_2$ versus time (s) (Fig. 4) shows DMAB dehydrogenation in the existence of nanocatalysts with various amounts (0.1, 0.2, 0.3, 0.4 and 0.5 mM) at 25.0 \pm 0.1 °C. Sudden hydrogen evolution begins linearly without any initiation time (induction period) and goes on until the catalytic dehydrogenation reaction of DMAB finishes. NMR data proves the complete conversion of $(CH_3)_2$ NHBH₃ ($\delta = \sim 12.7$ ppm) to $[(CH_3)_2NBH_2]_2$ ($\delta = \sim 5$ ppm) which shows the dehydrocoupling reaction of DMAB (at 1.0 equiv. H₂ generation) even at room temperature. At different temperatures (20, 25, 30 and 35 °C), the results obtained from the catalytic dehydrogenation of DMAB with Pd-Co@PVP NPs are shown in Fig. 5. This figure was used to calculate the rate constants of the fabricated hydrogen during the dehydrogenation of DMAB at the five various temperatures. The rate constants were also employed to find the $E_{\rm a}$ to be 50.78 \pm 2 kJ mol⁻¹ from the Arrhenius graph (Fig. 6a) and also the activation enthalpy ($\Delta H^{\#} = 47.01 \text{ kJ mol}^{-1}$) and activation entropy ($\Delta S^{\#} = -139.95 \text{ J mol}^{-1} \text{ K}^{-1}$) from the Eyring plot (Fig. 6b) for dehydrogenation.

Moreover, it is understood that there is an associative mechanism in the transition state for the catalytic dehydrocoupling of DMAB between the higher negative value of the activation entropy and the small value of the activation enthalpy.

In summary, it is valuable to note that in a very short time hydrogen gas (1.0 mol H₂/mol DMAB) is entirely emitted, analogous to a highest approximate TOF number of 330.94 h⁻¹ at 25.0 \pm 0.1 °C, in the catalytic dehydrogenation of DMAB with Pd–Co@PVP nanoparticles. To the best of our knowledge,



Fig. 4 Plot of nDMAB/nH₂ versus time (s) for the DMAB dehydrocoupling in the presence of Pd–Co@PVP NPs in different catalyst concentrations at 25.0 \pm 0.1 °C.



Fig. 5 Plot of % conversion *versus* time for the Pd–Co@PVP NP (7.5% mol) catalysed dehydrocoupling of DMAB in THF at various temperatures.

record catalytic activity has been obtained using the Pd– Co@PVP NPs (330.94 h⁻¹) for DMAB dehydrocoupling. This TOF data is almost 5.52 times larger than the literature data of $60 h^{-1}$ for Rh(0) NPs which was the best ever catalyst until now.⁵³ In order to compare the TOF data of different catalysts for the dehydrogenation reaction of DMAB, Table 1 was prepared. As shown from this table, it is obvious that the initial TOF value of the Pd–Co@PVP NPs (330.94 h⁻¹) is higher than all other heterogeneous and homogeneous catalysts listed in Table



Fig. 6 (a) Arrhenius and (b) Eyring plots for the Pd–Co@PVP NP catalysed dehydrocoupling of DMAB at various temperatures.

Paper

 Table 1
 The data of turnover frequencies of the different investigations for DMAB dehydrogenation

Entry	(Pre) catalysts	Conv. (%)	TOF	Ref.
1	Pd-Co@PVP NPs	100	330	This study
2	RhCl ₃	90	7.9	23
3	Pd/C	95	2.8	23
4	trans-RuMe ₂ (PMe ₃) ₄	100	12.4	23
5	Cp ₂ Ti	100	12.3	26
6	[Ir(1,5-cod)m-Cl] ₂	95	0.7	23
7	[Rh(1,5-cod)(dmpe)]PF ₆	95	1.7	23
8	$[Rh(1,5-cod)m-Cl]_2$	100	12.5	23
9	$[Rh(1,5-cod)_2]Otf$	95	12.0	23
10	$[RuH(PMe_3)(NC_2H_4PPr_2)_2]$	100	1.5	22
11	IrCl ₃	25	0.3	23
12	$[Cr(CO)_5(thf)]$	97	13.4	54
13	Rh(0)/[Noct ₄]Cl	90	8.2	23
14	[RhCl(PHCy ₂) ₃]	100	2.6	34
15	RhCl(PPh ₃) ₃	100	4.3	23
16	(Idipp)CuCl	100	0.3	55
17	Ni(skeletal)	100	3.2	56
18	$[Cp*Rh(m-Cl)Cl]_2$	100	0.9	21
19	$[Cr(CO)_5(\eta^1-BH_3NMe_3)]$	97	19.9	54
20	Ru(cod)(cot)	40	1.6	31
21	$RuCl_3 \cdot 3H_2O$	77	2.7	31
22	[(C ₅ H ₃ -1,3(SiMe ₃) ₂) ₂ Ti] ₂	100	420.0	41
23	$[\operatorname{Ru}(1,5\operatorname{-cod})\operatorname{Cl}_2]_n$	70	2.5	31
24	$HRh(CO)(PPh_3)_3$	5	0.1	23
25	<i>trans</i> -PdCl ₂ (P(o -tolyl) ₃) ₂	20	0.2	23
26	Pt(0)/BA	100	24.88	38
27	Pt(0)/TBA	100	31.24	38
28	Rh(0) NPs	100	60.0	53
29	Pt(0)/AA	100	15.0	37
30	Pt(0)/TPA@AC	100	34.14	39
31	Pt(0)@CNT	100	57.32	40

1, except for the prior homogeneous catalyst⁴¹ ($420 h^{-1}$) which is not isolable or reusable. As a conclusion, Pd–Co@PVP NPs are the best catalytic examples of an isolable and reusable nanocatalyst utilized in this substantial catalytic reaction most probably due to the adequate stability of PVP, and the cooperative and synergistic impact of Pd and Co in our catalyst system that results in the decreased particle magnitude of the catalyst and of course much greater catalytic performance.

In addition, the cycle property of the PVP-promoted Pd-Co nanomaterials was examined by subsequent introduction of DMAB after the initial run of the catalysis reaction in the dehydrogenation reaction of DMAB. The PVP-promoted Pd-Co nanocatalyst maintains 80% of its beginning performance during the reaction of DMAB, after the 5th experiment. The decrease in the catalytic activity of the Pd-Co@PVP NPs in the dehydrocoupling of DMAB is most probably due to the passivation of the nanoparticles' surface by the increase of the amount of product, which decreases the accessibility of the active sites and increases the aggregation of the nanoparticles as shown in the TEM image of the catalyst taken after the fifth cycle of the catalytic experiment (Fig. S4,† scale line shows 10 nm). This is because even after the fifth cycle, the catalyst retains its initial content as found by the ICP (17.42% metal based) study.

Conclusions

In conclusion, several significant points related to the fabrication, analytical examination and utilization of PVP-stabilized palladium–cobalt nanomaterials as efficient catalysts for the catalytic dehydrogenation of DMAB are listed as follows:

• By an ultrasonic double reduction method, Pd-Co@PVP nanopieces can be fabricated following a facile route, in which palladium and cobalt salts are co-reduced together by the help of PVP under ultrasonic conditions. The ultrasonication method was employed to increase the Pd-Co NP dispersion on PVP. The data show that the route is very effective for the uniform distribution of Pd-Co NPs on PVP and for the agglomeration problem of Pd-Co NPs.

• Pd-Co@PVP nanopieces have an extraordinary catalytic performance in the dehydrogenation of DMAB, with the best ever catalytic effectiveness.

 \bullet A record TOF (330.94 $h^{-1})$ is achieved for the dehydrocoupling of DMAB.

• A 50.78 \pm 2 kJ mol^{-1} $E_{\rm a}$ was obtained for the catalytic reaction of DMAB in the presence of the Pd–Co@PVP nanocatalysts.

• Pd–Co@PVP nanograins can be considered as promising alternative catalysts possessing the greatest performance for simple implementation to provide hydrogen gas from the catalytic reaction of DMAB for fuel cells.

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