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Eco-friendly hydrogenation of aromatic aldehyde compounds by tandem dehydrogenation of dimethylamine-borane in the presence of reduced graphene oxide furnished platinum nanocatalyst
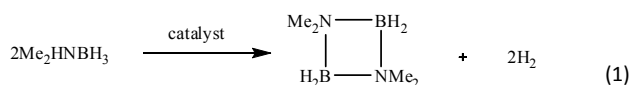
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Addressed herein, highly monodisperse platinum nanoparticles supported with reduced graphene oxide in the presence of tripentylamine (TPA) (Pt(0)/TPA@rGO NPs) are stable, isolable, bottleable, long-lived, highly efficient and exceptional reusable heterogeneous catalyst for eco-friendly hydrogenation of various aromatic aldehyde compounds with unprecedented catalytic performance. Pt(0)/TPA@rGO NPs have been used for the first time for these types of synthesis reactions and these NPs were characterized by transmission electron microscopy (TEM), the high resolution electron micrograph (HRTEM), X-ray diffraction (XRD), Atomic Force Microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Herein, current catalyst have been used for tandem dehydrogenation of dimethylamine-borane (DMAB) and hydrogenation of aromatic aldehyde compounds in aqueous methanol at room temperature in reaction times ranging from 1.0 to 25 min with yields reaching up to 95%. The presented catalytic methodology is highly efficient for as well as being exceptional reusability performance. This process can be assessed as an eco-friendly method with both reusable reduced GO-supported platinum nanocatalyst and hydrogen source (DMAB).

Introduction

Reduction with simple and cheap methods of aldehyde compounds to alcohols is very important for organic intermediates, drugs, polymers and antioxidants. Recently, chemists have focused on eco-friendly methods for alcohol production.[1-3] For this reason, they have generated alcohols with novel reusable and recyclable heterogenous catalysts in water like green solvent.[4a,5,6] In literature, the reduction of carbonyl compounds is mainly achieved by using hydrides,[7,8] molecular hydrogen[9,10] and transfer hydrogenation.[11-13] Todays, among the hydrogenation process, transfer hydrogenation is more convenient and reliable method because hydrogen production can be easily controlled in reaction medium.[14,15] More recently, NaBH$_4$,[16] LiAlH$_4$,[17] MgH$_2$,[18] and NH$_3$BH$_3$[4] have been extensively used as hydrogen sources. Alternatively,

dimethylamine-borane (DMAB) can be a hydrogen surrogate, even it is not frequently used in literature.[19] It is also non-toxic, non-flammable, easily accessible, highly stable, cheap and water-soluble as well as having high volume/mass hydrogen density (3.5 wt.%). Two moles of hydrogen gas per one mole DMAB can easily be generated via its dehydrogenation in the presence of catalyst and water at room temperature (Equation 1).[19,20]

$$2Me_2HNBH_3 \xrightarrow{\text{catalyst}} \begin{array}{c} Me_2N\text{——}BH_2 \\ | \qquad | \\ H_2B\text{——}NMe_2 \end{array} + 2H_2 \qquad (1)$$

In the transfer hydrogenation reactions, the various catalyst systems are used for effective reduction.[13,19,21,22] Because active transition metal content catalysts play an important role in hydrogenation reactions. The larger the surface area of the catalyst depending on the type of metal is carried out more effectively reduction reactions. One way to increase surface area is to reduce the particle size.[23-25]

Herein we describe a new method for the transfer hydrogenation of various aromatic aldehyde compounds with Pt(0)/TPA@rGO NPs introduced by our group for the first time. The eco-friendly hydrogen source DMAB contributed to reduction reaction in a mild condition and in a very small amount of solvent

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(1.5 ml of water/methanol). The processes were achieved in the presence of Pt(0)/TPA@rGO NPs in eco-friendly solvent system with one of the highest yield and shortest time.

Scheme 1 shows that aldehyde compounds were converted into primary alcohols in a short time, with high yields and in the presence of Pt(0)/TPA@rGO NPs and DMAB.
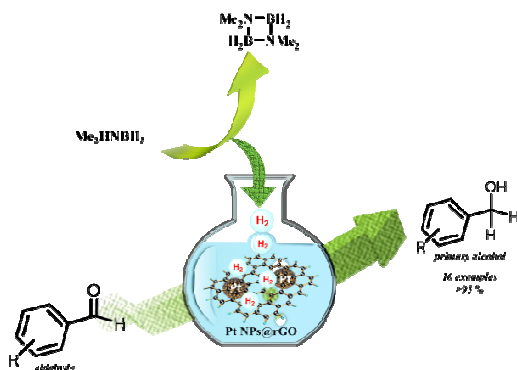
Scheme 1 Synthesis of primary alcohol derivatives in the presence of Pt(0)/TPA@rGO NPs

Results and discussion

Highly monodisperse Pt(0)/TPA@rGO NPs nanoparticles have been quickly and repeatedly generated by sonochemical double solvent reduction method of $PtCl_4$ in an anhydrous THF solution of TPA ligand in the presence of rGO at room temperature. Without stabilizing ligand like TPA and supporting material like rGO, rapid agglomeration and precipitation of the initially formed platinum(0) nanoparticles out of THF solution was observed. In contrast, highly monodisperse Pt(0)/TPA@rGO NPs were very stable towards agglomeration for months when both TPA ligand and rGO have been used in the solution. This observation confirms that both TPA and rGO are very strong supporting and stabilizing agent for the nanoparticles, respectively. The highly monodisperse Pt(0)/TPA @rGO NPs can be obtained simply as solid by vaporizing solvent under vacuum after washing it with dry ethanol for clearing away excess ligand.

The highly monodisperse Pt(0)/TPA@rGO NPs have been characterized by the use of ICP-OES, XRD, TEM, HRTEM, AFM and XPS techniques. XRD data showed that highly monodisperse Pt(0)/TPA@rGO NPs displays distinct diffraction patterns as shown in Fig. 1. The peak at around 24.8^o is attributed to the graphite (002) plane of rGO. Further, the diffraction peaks at 2θ = 39.90, 46.29, 67.70, 81.40 and 85.92^o are due to Pt (111), (200), (220), (311) and (320) planes of the face-centered cubic (fcc) crystal lattice of platinum, respectively. (JCPDS-ICDD, Card No. 04-802). This indicates that Pt /TPA@rGO NPs is in the face-centered cubic (fcc) crystalline structure. The Pt (220) diffraction peak of prepared catalyst is used for counting the lattice parameter (αPt) values and average crystallite sizes of the metal particles in the catalyst. The lattice parameter value of highly monodisperse Pt(0)/TPA@rGO NPs

was obtained as 3.912 Å using the following equation that is in good agreement with 3.923 Å for pure Pt.[26]

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

Moreover, the average crystallite platinum particle size of monodisperse Pt(0)/TPA@rGO NPs have been calculated as about 3.57 ± 0.47 nm using the following equation;[27]

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

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).
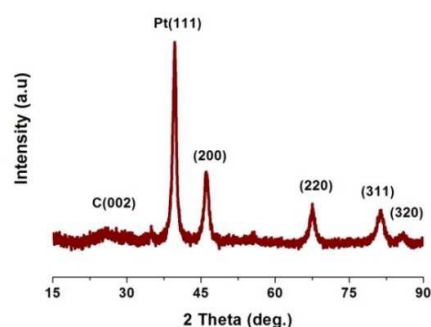
Fig. 1 XRD pattern of highly monodisperse Pt(0)/TPA@rGO NPs

The particle size distribution of the Pt(0)/TPA@rGO NPs have been analysed by TEM as shown in Fig. 2 and it was found to be 3.58±0.41 nm. The high resolution electron micrograph (HRTEM) of the catalyst is also illustrated in Fig.2, which exhibits the morphology of the prepared catalyst as well. From HRTEM data, it was observed that most of the particles were in as spherical shape, and no agglomerations were observed in synthesized catalyst. Furthermore, HRTEM image for monodisperse Pt(0)/TPA@rGO NPs NPs have also been used to see the atomic lattice fringes in Fig. 2. As a result of these fringes, Pt (111) plane were observed with spacing of 0.228 nm on the prepared catalyst, which is very close to nominal Pt (111) spacing of 0.227 nm, respectively.[28]

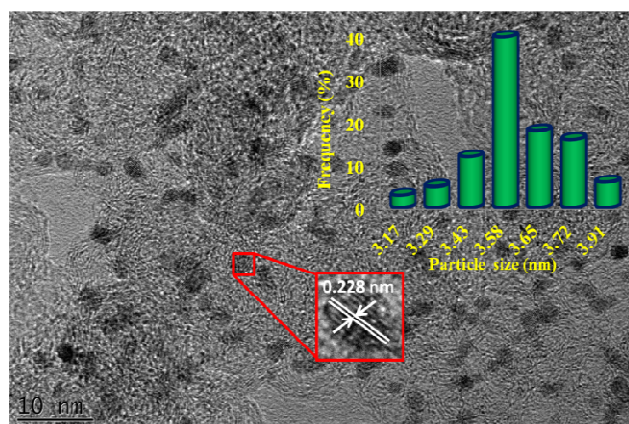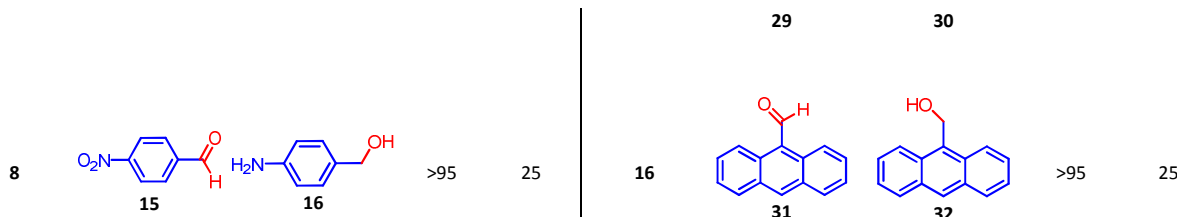**Fig. 2** High resolution transition electron micrograph and particle size histogram of Pt(0)/TPA@rGO NPs

height diameters of Pt(0)/TPA@rGO NPs were found as 3.71 ± 0.49 that is in good agreement with XRD and TEM data.

The surface compositions and chemical oxidation states of Pt in the highly monodisperse Pt(0)/TPA@rGO NPs have been investigated by using X-ray photoelectron spectroscopy (XPS). For this purpose, Pt 4f region of the spectrum was evaluated by Gaussian-Lorentzian method and the estimation of the relative intensity of the species have been performed by counting the integral of each peak, after smoothing, subtraction of the Shirley-shaped background. In the XPS spectrum, accurate binding energies (±0.3 eV) have been determined by referencing to the C 1s peak at 284.6 eV. The Pt 4f photoelectron spectrum has been comprised of two pairs of doublet as shown in Figure 3 for the highly monodisperse Pt(0)/TPA@rGO NPs. The most intense doublet at about 71.1 and 74.4 eV is a signature of metallic platinum [29a,b,c] and the other doublet at around 74.3 and 77.6 eV is most likely due

Atomic force microscopy (AFM) has also been used to see the particle height distributions as shown in Fig. S1 and the average

Table 1 Pt(0)/TPA@rGO NPs catalysed tandem reduction of various aldehyde compounds

Entry	Substrate	Product	Yield (%)	Time (min.)	Entry	Substrate	Product	Yield (%)	Time (min.)
1	1	2	>95	15	9	17	18	>95	5
2	3	4	>95	25	10	19	20	>95	3
3	5	6	>95	3	11	21	22	>95	1
4	7	8	>95	2	12	23	24	>95	1
5	9	10	>95	3	13	25	26	>95	3
6	11	12	>95	2	14	27	28	>95	5
7	13	14	>95	20	15			>95	15

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8 [structure] **15   16** >95   25 | **16** [structure] **31   32** >95   25

Reaction Conditions: *0.25 mmol substrate, 4 eqv. DMAB, 4 mg* Pt(0)/TPA@rGO NPs*, 1.5 mL of water/methanol (v/v= 1/2), room temperature.*

to a very small fraction of oxidized Pt^{4+} species possibly due to unreduced Pt precursor or PtOx species produced during the catalyst exposure to the atmosphere. Furthermore, the ratio of Pt(0) to Pt(IV) forthe prepared catalyst has been calculated as 6.24 from the relative peak area of the Pt 4f spectrum.
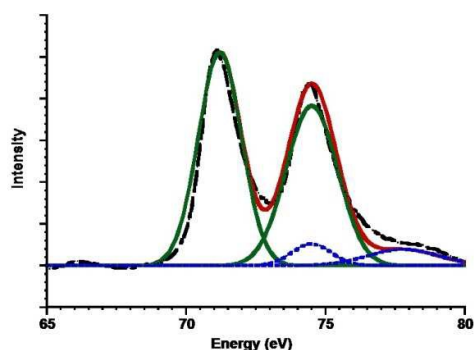

Fig. 3 Pt 4f electron spectra of monodisperse Pt(0)/TPA@rGO NPs

It is worth mentioning that Pt NPs are often used as a catalyst in alcohol oxidation, dehydrogenation, super-capacitors, hydrogen storage, batteries and sensor[30-33] but its use as a catalyst for eco-friendly hydrogenation of aromatic aldehyde compounds by tandem dehydrogenation of dimethylamine-borane has not been reported before.

Table 1 summarizes the results obtained from Pt(0)/TPA@rGO NPs catalyzed tandem reactions. All series of aldehyde compounds were succesfully reduced to the respective primary alcohols with the excellent yields in 1.0-25 min at room temperature. Both electron donating groups such as methyl, hydroxy and methoxysubstituents and electron withdrawing groups such as nitro and halogen subsitutents attached to the aromatic aldehyde ring gave corresponding benzylalcohols with one of the highest yields in a shortest time. Conversion of electronically rich aromatic aldehydes into alcohols would be expected in a very short time (Table 1, entries 8,12). Surprisingly, for example, reduction process of electronically rich polysubstituted compounds such as 3,4,5-trimethoxybenzaldehyde (30) persisted quite long time respect to monosubsituted compounds such as 4-methoxybenzaldehyde (19) probably due to the surfactant structure of catalyst (Table 1, entries 10,15). Benzaldehyde (1) was reduced into benzyl alcohol (2) at a 95% yield in 15 min (Table 1, entry 1). 4-(dimethylamino)benzaldehyde (3) was reduced into 4-(dimethylamino) benzyl alcohol (4) at a 95% yield in 25 min (Table 1, entry 2). 4-chloro-, 4-bromo- and 4-iodo benzaldehydes (5, 7, 9) were all reduced with one of the highest reaction efficiency, producing the related benzyl alcohols (6, 8, 10) in quantitative yield (Table 1, entries 3-5). 3,4-dichlorobenzaldehyde (11) were reduced into (3,4-dichlorophenyl)methanol (12) in 2 min (Table 1, entry 6). For *meta*- and *para*-nitro benzaldehydes (13, 15), both nitro and aldehyde groups were quantitatively reduced to related amines and

Catalyst	Reaction Conditions	Time	Yield (%)	Ref.
$RuCl_2(mtppms)_2$[a]	Substrate (1 mmol), catalyst (5.0×10^{-6} mol), HCOONa (6 mmol), water (4 mL), 2-propanol (3.5 mL), 30 ^{o}C	1 h	82	34
Ru/AlO(OH)	Substrate (2 mmol), catalyst (100 mg), H_2O (30 mmol), DMF (5 mL), 100 ^{o}C, N_2 atmosphere	2 h	>99	35
$Pd/Ca_{12}Al_{14}O_{33}$	Substrate (0.25 mL), catalyst (0.025 g), H_2 (8 bar), diethyl ether (10 mL), 120 ^{o}C	5 h	91	36
G-NiPd	Substrate (1 mmol), catalyst (4 mg), NH_3BH_3 (3 mmol), H_2O/MeOH (10 mL), RT	10 min	99	4a
$Fe(BF_4)_2.6H_2O/PP_3$	Substrate (0.5 mmol), catalyst (0.4 mol%), HCOOH (1.1 mmol), THF (1 mL), 60 ^{o}C	2 h	96	37

Fe-complex	Substrate (1 mmol), catalyst (3 mol%), Na$_2$CO$_3$ (3 mmol), DMSO/H$_2$O (1:1), paraformaldehyde (10 mmol), 120 ^{o}C	24 h	77	38
[ReOBr$_2$(hmpbta)(PPh$_3$)][b]	Substrate (1 mmol), catalyst (5 mol%), PhSiH$_3$ (2 mmol), TBAF (1 mmol), reflux	15 min	88	39
Pt(0)/TPA@rGO NPs	**Substrate (0.25 mmol), catalyst (4 mg), DMAB (4 mmol), H$_2$O/MeOH (1:2, 1.5 mL), RT**	**15 min**	**>95**	**This study**

Table 2 Previous published works about hydrogenation of benzaldehyde

[a]Sodium 3-diphenylphosphinobenzenesulfonate [b]2-(2-hydroxy-5-methylphenyl)benzotriazole

alcohols (14, 16) after 20 and 25 min of reaction, respectively (Table 1, entries 7,8). The methyl, methoxy and hydroxy groups in the para position were observed to facilitate the reduction of aldehydes to primary alcohols (Table 1, entries 9, 10, 12). Pt(0)/TPA@rGO NPs were also active for tandem hydrolysis of DMAB and hydrogenation of 3-hydroxybenzaldehyde (21), 2,5-dihydroxybenzaldehyde (25), 2,5-dimethoxybenzaldehyde (27) and 3,4,5-trimethoxybenzaldehyde (29a,b,c) compounds. They were all converted to respective alcohol derivatives (22, 26, 28, 31, 22) with the 95% yields in 1.0-15 min (Table 1, entries 11, 13, 14, 15). Anthracene-9-carbaldehyde (32) was reduced into anthracen-9-ylmethanol (33) with good yields as well in 25 min (Table 1, entry 16).

Fig. 4 Comparison of Pt(0)/TPA@rGO NPs with previously published works about hydrogenation of benzaldehyde

A novel process for reduction of aromatic aldehydes was compared to recent published works as seen in Figure 4. Our system has more advantages such as one of the lowest temperature, shortest time, and use of minimum amount of solvent and catalyst (Table 2).

Table 3 Reusability performance of Pt(0)/TPA@rGO NPs

Entry	Substrate	Product	Yield (%) 1st run	Yield (%) 5th run
1			>95	94
2			>95	93

Reaction Conditions: 0.25 mmol substrate, 4 eqv. DMAB, 4 mg monodisperse Pt(0)/TPA@rGO NPs, *1.5 mL of water/methanol (v/v= 1/2), room temperature*

In order to see the reusability performance of the Pt(0)/TPA@rGO NPs, the current catalyst was recovered from the reaction media by simple centrifugation, washed with ethanol, dried in the

atmospheric conditions and re-used for five times primary alcohol formations. It can be obviously observed that there is no loss in yield of products and in an activity of catalyst (Table 3). The ICP-OES analyses performed on the catalytic reaction solutions showed that the metal content in the solution was determined as about 0.4 ppm. The value of the platinum leaching into the reaction solution after reuse can be tolerated.
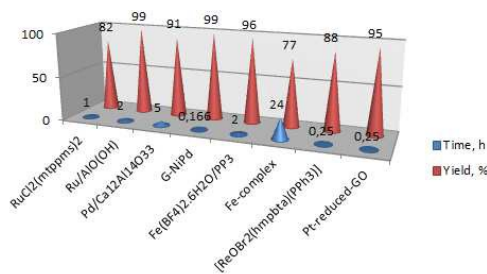
Conclusions

In conclusion, we have described an easy, effective and practical synthetic method for the reduction of aldehyde compounds in the presence of highly stable, exceptional reusable, isolable, bottleable, long-lived and highly efficient monodisperse Pt(0)/TPA@rGO NPs as the catalyst. The reaction was carried out in an eco-friendly solvent mixture in which water is the main component. Corresponding alcohols were exclusively obtained by the reaction of Pt(0)/TPA@rGO NPs as reusable catalyst with dimethylamine-borane (DMAB) as hydrogen source in a one of the shortest time with excellent yields at room temperature. This nano sized heterogeneous catalyst showed excellent catalytic activity for both dehydrogenation of DMAB and transfer of hydrogen gas to alcohols in mild condition most likely due to high monodispersity, low crystalline particle size, high chemical surface area and high % Pt (0) contents of the prepared Pt(0)/TPA@rGO NPs. This reusable catalyst offers advantages like practical, eco-friendly, simple work-up and one of the highest yield. Furthermore, the given methodology is efficient and environmentally benign. This method, which enabled the alcohol derivatives to be prepared in excellent yields and shortest reaction times, would be a rather attractive synthetic method in near future.

Experimental

The preparation of monodisperse Pt(0)/TPA@rGO NPs

Highly monodisperse Pt(0)/TPA@rGO NPs have been prepared by using sonochemical double solvent reduction method. Summarizing this method, superhydride and ethanol were used to reduce the mixture of 0.25 mmol of PtCl$_4$ lysed in small amount of dehydrated tetrahydrofuran and 0.25 mmol of tripentylamine (TPA) ligand in an ultrasonic conditions. The observation of a brown-black color in the solution indicates the formation of Pt NPs.28a-e Lastly, in the room temperature, the solid Pt(0)/TPA NPs was dried under vacuum. rGO was obtained by the hydrazine reduction of GO which was synthesized from graphite powder using modified Hummer's method [Supplementary section]. The prepared platinum nanoparticles were mixed in a 1:1 ratio with rGO by using tip sonicator.

General procedure for the catalytic reduction of aromatic aldehydes via DMAB hydrolysis

Pt /TPA@rGO NPs (4 mg) were added to a solution of an aldehyde compound (0.25 mmol) in 1.5 ml water/methanol (v/v = 1:2). The mixture was stirred for 5 min at room temperature. Next, DMAB (4 mmol) was added to the reaction mixture and the vessel was closed. Reaction was then continued under vigorous stirring at room temperature. The progress of the catalytic reaction was monitored by thin layered chromatography (TLC). The most of the reaction completed over the time period of 1.0-25 min. After completion of the reaction, the catalysts were removed by centrifugation at 4500 rpm and washed three times with water and methanol. Then, the catalyst was allowed to dry for the further uses. The solvent was removed under reduced pressure. Finally, the crude residue was directly purified by column chromatography on silica gel (50.0 g) eluting with hexane/ethylacetate (70:30). After removal solvent, corresponding alcohol was obtained with high yield (95%). The yields of the reduced compounds were determined by ^{1}H NMR with CD$_3$OD or CDCl$_3$ as the solvent depending on the product separated.

Syntheses[4,40-46]

Benzyl alcohol (2). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.42-7.29 (m, 5H), 4.72 (s, 2H), 2.1 (bs, 1H).

(4-(dimethylamino)phenyl)methanol (4). ^{1}H NMR (400 MHz, CD$_3$OD): δ 7.18 (d, J = 8.8 Hz, 2H), 6.72 (d, J = 8.8 Hz, 2H), 4.85 (bs, 1H), 4.47 (s, 2H), 2.87 (s, 6H).

(4-chlorophenyl)methanol (6). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.31 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 4.62 (s, 2H), 2.11 (bs, 1H).

(4-bromophenyl)methanol (8). ^{1}H NMR (400 MHz, CD$_3$OD): δ 7.37 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 4.68 (s, 2H).

(4-iodophenyl)methanol (10). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.65 (d, 2H, J = 8.2Hz), 7.06 (d, 2H, J = 8.0Hz), 4.58 (s, 2H), 2.04 (bs, 1H).

(3,4-dichlorophenyl)methanol (12). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.39-7.44 (m, 2H), 7.16 (dd, J = 8.3, 2.0 Hz, 1H), 4.63 (s, 2H), 2.22 (bs, 1H).

(3-aminophenyl)methanol (14). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.14 (m, 1H), 6.72 (m, 2H), 6.61 (m, 1H), 4.60 (s, 2H), 3.65 (bs, 2H), 1.60 (bs, 1H).

(4-aminophenyl)methanol (16). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.18 (d, J = 8.5 Hz, 2H), 7.09 (d, J = 8.5 Hz, 2H), 4.51 (s, 2H), 3.10 (bs, 3H).

p-tolylmethanol (18). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.24 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 4.60 (s, 2H), 2.35 (s, 3H), 2.15 (bs, 1H).

(4-methoxyphenyl)methanol (20). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.25 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 4.56 (s, 2H), 3.78 (s, 3H), 2.20 (bs, 1H).

3-(hydroxymethyl)phenol (22). ^{1}H NMR (400 MHz, CD$_3$OD) δ 7.12 (m, 1H), 6.80 (m, 2H), 6.68 (m, 1H), 4.87 (bs, 2H), 4.52 (s, 2H).

4-(hydroxymethyl)phenol (24). ^{1}H NMR (400 MHz, CD$_3$OD): δ 7.16 (d, J = 8.0 Hz, 2H), 6.72 (d, J = 8.0 Hz, 2H), 4.45 (s, 2H).

2-(hydroxymethyl)benzene-1,4-diol (26). ^{1}H NMR (400 MHz, CD$_3$OD): δ 6.49 (s, 1H), 6.45 (d, J = 2.9 Hz, 1H), 6.32 (d, J = 2.9 Hz, 1H), 6.32 (d, 1H, J = 2.8 Hz), 4.58 (s, 2H).

(2,5-dimethoxyphenyl)methanol (28). ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.87 (m, 1H), 6.78 (m, 2H), 4.63 (s, 2H), 3.80 (s, 3H), 3.75 (s, 3H).

(3,4,5-trimethoxyphenyl)methanol (30). ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.49 (s, 2H), 4.51 (s, 2H), 3.75 (s, 9H), 2.93 (bs, 1H).

Anthracen-9-ylmethanol (32). ^{1}H NMR (400 MHz, CD$_3$OD): δ 8.46-8.38 (m, 3H), 7.99-8.01 (m, 2H), 7.42-7.54 (m, 4H), 5.56 (s, 2H).

## Acknowledgements

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Table of contents entry

Eco-friendly hydrogenation of aromatic aldehyde compounds by tandem dehydrogenation of dimethylamine-borane in the presence of reduced graphene oxide furnished platinum nanocatalyst

Haydar Goksu [a‡], Yunus Yıldız[b‡], Betül Çelik[b], Melike Yazici[c], Benan Kilbas*[c], and Fatih Sen*[b]
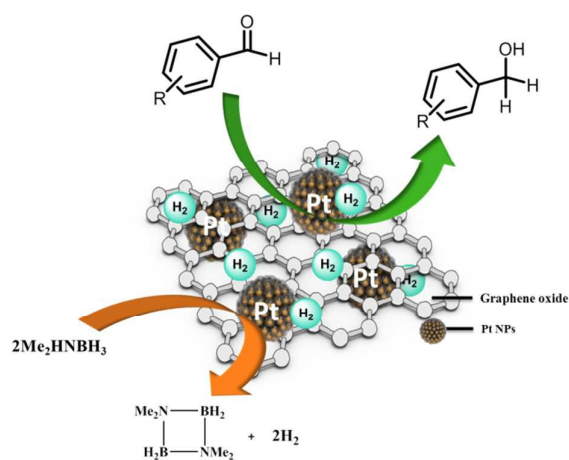
Easy, effective, eco-friendly and practical synthetic method has been developed for the reduction of aldehyde compounds in the presence of highly efficient monodisperse Pt(0)/TPA@rGO NPs as the catalyst.