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Improved Catalytic Effect and Metal Nanoparticle Stability using Graphene Oxide Surface Coating and Reduced Graphene Oxide for Hydrogen Generation from Ammonia-Borane Dehydrogenation

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The development of high catalytic effective catalysts for hydrogen generation through dehydrogenation (hydrolysis) of aqueous NH$_3$BH$_3$ (AB) solution is discussed in this work. Bimetallic NiPt, CoPt and monometallic Ni, Co, Pt Nano particles (NPs) supported on mixed graphene oxide (GO) and reduced graphene oxide rGO (carbon materials) were produced and studied for hydrogen generation from AB hydrolytic dehydrogenation. Here, we develop a fine, spherical shaped bimetallic and monometallic Ni, Co, Pt NPs on mixed GO and rGO for incredible reactant productivity for aqueous AB hydrolysis. The Co$_{0.8}$Pt$_{0.2}$/GO and rGO, Ni$_{0.8}$Pt$_{0.2}$/GO and rGO catalysts reach high catalytic performance and high turnover frequency (TOF) of 230.76 and 214.28 (H$_2$) mol. (cat. metal) mol$^{-1}$.min$^{-1}$at 25 °C. This the greatest efficiency ever shown for transitional metal-doped GO and rGO catalysts. The catalysts additionally show superior catalytic stability by maintaining up to 98% activity after 7 runs at 25 °C. The development of well-organized and inexpensive Co$_{0.8}$Pt$_{0.2}$/GO and rGO, Ni$_{0.8}$Pt$_{0.2}$/GO and rGO catalysts improve the possibility of using aqueous AB as chemical hydrogen storage. This permits the discovery of additional hydrogen fell-cell applications. The simple facile production of other GO and rGOs assist in transition metal NPs.

Keywords

Graphene Oxide, Reduced Graphene Oxide, transition-metal NPs (M-Ni, Co and Pt), ammonia borane, catalysts, hydrogen generation, dehydrogenation.
Highlights

- The as-synthesized GO and rGO supported transition metal NPs exhibited excellent catalytic performance for aqueous AB hydrolysis (dehydrogenation).
- Ni$_{0.8}$Pt$_{0.2}$/GO and Co$_{0.8}$Pt$_{0.2}$/GO and rGO NPs provide a TOF of 214.28 and 230.76 (H$_2$) mol. (cat-metal) mol$^{-1}$ min$^{-1}$ for AB hydrolysis at 25 $^\circ$C.
- Ni$_{0.8}$Pt$_{0.2}$/GO and rGO, Co$_{0.8}$Pt$_{0.2}$/GO and rGO NPs activation energy is 23.94 kJ mol$^{-1}$ and 23.60 kJ mol$^{-1}$ for AB hydrolysis.
- Ni$_{0.8}$Pt$_{0.2}$/GO and rGO, Co$_{0.8}$Pt$_{0.2}$/GO and rGO NPs slope values is 1.99 for AB hydrolysis (first order reaction).
1. Introduction

Fossile fuel green degeneration and fast reduction have delivered a consummate economical energy technique for producing hydrogen gas. Hydrogen gas is a wonderful energy carrier that addresses the difficulties in energy conservation issues and future energy alternatives. After several years of development, the H\textsubscript{2} load one of the interesting barriers to hydrogen generation techniques. Characteristic H\textsubscript{2} storage in chemicals mixtures, such as formic acid (HCOOH), hydrous hydrazine (N\textsubscript{2}H\textsubscript{4}•H\textsubscript{2}O), methanol (CH\textsubscript{3}OH), and ammonia borane (NH\textsubscript{3}BH\textsubscript{3}) have hydrogen limits of 4.4, 8.0, 18.8 and 19.6 wt\%, individually. AB is a remarkable H\textsubscript{2} storage catalyst due to its high hydrogen content (19.6 wt\%), high durability in liquid arrangements at room temperature (25 °C), and nontoxicity\textsuperscript{1,2}. It can also generate hydrogen quickly at room temperature (at 25 °C) in a safe system by consuming catalysts. This is truly reasonable for hydrogen generation from AB solution\textsuperscript{3}. The effective catalysts are normally built up from suitable metals, (such as, Pt Pd, Au and Ru)\textsuperscript{4}, which profoundly constrain economical applications. Research into a non-respectable metal-based catalyst for AB hydrolysis to generate hydrogen is really important.

Empowered transition metal NPs have been represented to show amazing catalytic effects\textsuperscript{5,6}. Therefore, a reasonable relationship between catalytic performance and metal support relations is essential. Quantitatively recognizing the nature of metal–support interfaces in the absence of detailed information on hydrolysis reaction and catalytic active sites remains of interest. The established hydrolysis reaction methods below homogeneous catalysis cannot be straightforwardly connected to heterogeneous catalysis in the presence of the phase interface and complex active sites in heterogeneous catalysis\textsuperscript{7}. 
Hydrogen generation by means of thermal decomposition, aqueous AB solution hydrolysis within the sight of an acceptable catalyst produces three moles of hydrogen gas per mole of AB solution at 25 °C (eq 1). This makes it a compelling catalyst for hydrogen generation from AB.

\[
\text{NH}_3\text{BH}_3(\text{aq}) + 2\text{H}_2\text{O} (l) \rightarrow \text{NH}_4^+ (\text{aq}) + \text{BO}_2^- (\text{aq}) + 3\text{H}_2 (g) \ldots \ldots (1)
\]

For the most part, Pt, Ru, Pd based catalysts beat non-noble metals, such as Ni, Cr, Co, RuPd@GO, Ag/Pd, Fe, Ag-Ni based nanoparticles, Au-Pd, mesoporous carbon nitride supported Pd and Pd-Ni NPs, PdNi-CeO$_2$, NiPt NPs with supported CeO$_2$ (efficient hydrogen generation from alkaline solution of hydrazine), N-doped graphene supported Co-CeO$_x$ and transition metal nanoparticles with GO in hydrogen generation from the above conditions. Through the advancement of bimetallic catalysts, for example, Co-Pd, and core-shell species, such as Au@Co improved catalytic effect indifference and monometallic catalysts, the general utilization of these noble metals is restricted by costly charges and the extraordinary amount required. To clarify this issue, the search for abundant metal catalysts and durable catalytic activities that can be utilized at 25 °C, is very urgent and essential.

One superficial and active approach is to modulate the active metal NPs into their proper contribution. A single-atom two-dimensional material, exhibitions interesting properties, such as a specific surface area, high catalytic effect, fine & spherical shaped particles, conserved charge transfer, and is subsequently an ideal substrate for the advancement and affixing of metal NPs, such as, graphene, GO, carbon Nano tubes. In spite of the fact of the staggering expense of graphene, graphene-supported metal NPs have included noteworthy support because of their potential applications in a few specializations, such as catalysis, devices, energy conversion and so on. As of late, metal oxides, such as TiO$_2$, SnO$_2$, Fe$_3$O$_4$, SiO$_2$, CeO$_2$, and so forth have been commonly utilized as catalyst promoters to build reactant stability and metal Nano catalyst activity. Among
the examined metal oxides, rare-earth metal oxide CeO$_2$ is of obvious consideration because of its rich oxygen opportunity defects, high oxygen storage capacity, and cost-effectiveness.$^{40-45}$ In this situation, the reasonable attendance of an M/CeO$_2$/graphene triple convergence, with the CeO$_2$ mixture, a metal, and graphene may potentially produce a catalyst with curiously improved catalytic activity for the dehydrogenation of aqueous AB as well as dispensability in the catalytic process.

Here, we report on green and facile preparation and the synthesis of well-dispersed Co$_{0.8}$Pt$_{0.2}$/GO and rGO, Ni$_{0.8}$Pt$_{0.2}$/GO rGO catalysts utilized for catalytic hydrogen generation from AB hydrolytic dehydrogenation at 25 °C. Incredibly, the prepared honorable noble-metal Co$_{0.8}$Pt$_{0.2}$/GO and rGO, Ni$_{0.8}$Pt$_{0.2}$/GO and rGO catalysts demonstrate higher catalytic performance, 100% hydrogen selectivity and strong durability for hydrogen generation from AB, with 3 equivalents per mmole AB generated within 0.6 and 0.5 min. The CoPt/GO and rGO, NiPt/GO and rGO catalysts demonstrate they have the most important role in improving the metal NP catalytic effect. Because of the synergistic effect among CoPt and NiPt NPs supported on GO and rGO and the strong metal-support interface between the metals and supporter, the acquired Co$_{0.8}$Pt$_{0.2}$/GO and rGO, Ni$_{0.8}$Pt$_{0.2}$/GO and rGO catalysts showed greater catalytic effect for hydrogen generation from an aqueous AB solution, with TOFs of 230.76 and 214.28 min$^{-1}$ at 25 °C, respectively.

2. Experimental section

2.1 Chemical lists

Graphite, sodium nitrate (NaNO$_3$) Fischer synthetic chemicals, sulfuric acid (H$_2$SO$_4$) Sigma Aldrich), Potassium permanganate (KMnO$_4$), Hydrogen peroxide (H$_2$O$_2$), Cobalt (II) nitrate
hexahydrate (Co(NO$_3$)$_2$.6H$_2$O), Nickel(II) nitrate hexahydrate (Ni(NO$_3$)$_2$.6H$_2$O), Chloroplatinic corrosive hexahydrate (H$_2$PtCl$_6$) and Ammonia borane (NH$_3$BH$_3$).

### 2.2 Graphene oxide (GO) preparation

In the characteristic synthesis method, pure graphite powder is first oxidized in a modified hummer's procedure to procure graphene oxide (GO). In this strategy, 2 g of graphite powder and one gram of sodium nitrate (NaNO$_3$), are mixed in sulfuric acid solution (H$_2$SO$_4$) 40 ml, Sigma Aldrich) under continuous magnetic stirring for three hours at room temperature. Eight grams of potassium permanganate (KMnO$_4$) was then included slowly into the solution and the solution was constantly stirred until its shading turned dull dark. Deionized (DI) water (100mL) was delicately added to the solution, and the solution was protected at 70 °C for 30 mins. Finally, 250 ml of DI water was added to take out the overabundance of KMnO$_4$. Next, 0.675 ml of hydrogen peroxide (H$_2$O$_2$) was added slowly and continuously stirred for 15 minutes. Next, 1:3 proportions of hydrochloric acid and H$_2$O was included and centrifuged utilizing Table Top Centrifuge 7000 rpm for 5 minutes. At that point, the supernatant was washed with DI water a few times. The washed GO supernatant was dried utilizing a stove at 70 °C for 24 hours to obtain "graphene oxide powder."

### 2.3 Metal-doped GO and rGO NPs preparation

CoNi@GO and rGO, CoPt@GO and rGO, NiPt@GO and rGO, Pt@GO, Co@GO, Ni@GO, 0.2 g of GO and 0.0049 M urea were disengaged in 20 mL of DI water and sonicated to obtain the very much scattered GO solution. A general 5 mL of an aqueous solution containing Co(NO$_3$)$_2$.6H$_2$O (0.1M) and Ni(NO$_3$)$_2$.6H$_2$O and H$_2$PtCl$_6$ (0.012M) was moved into the above solution and sonicated
for five minutes. Subsequently, the solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave. The autoclave was fixed and heated to 180 °C and proceeded for 5 h in an oven. Accordingly, the hydrothermal reaction, the acquired ancestor was gathered through centrifugation and washed with DI water five times. The final product M@GO and rGO (M-Co, Ni and Pt) was acquired after it was dried under an oxygen environment at 70 °C for 24 hours. The item M@GO and rGO was also toughened with calcination at 500 °C for 1 h. The final composition of catalysts was determined by ICP-AES (STable 1). This scheme led to the synthesis of Co$_{0.4}$Ni$_{0.6}$/GO, Co$_{0.6}$Ni$_{0.4}$/GO, Co$_{0.8}$Pt$_{0.2}$/GO and Ni$_{0.8}$Pt$_{0.2}$/GO catalysts.

2.4 Characterization

Powder X-ray diffraction (XRD) pattern were obtained utilizing a Bruker D8 PHASER X-ray diffractometer with GO monochromatized Cu Kα radiation ($\lambda = 1.5406$ Å) at a scanning rate of 5° min$^{-1}$. The microstructure and particle sizes of the catalysts were seen utilizing a transmission electron microscope (TEM). Field emission scanning electron microscopy (FESEM, JEOL JSM 7600F) arranged through energy dispersive X-ray detector (EDX) was utilized for natural investigation and FT-IR spectroscopy were used for identifying the cell hydrogen and oxygen molecule cell arrangements.

2.5 AB hydrogenation

The reaction devices utilized for producing hydrogen generation from aqueous AB solution hydrolysis. Typically, the recess solution (10 mL) having the catalyst was utilized in a two-necked round bottom flask. A hydrogen gas burette stuffed with water was associated with one neck of the
reaction flask (the other neck was shut with a stopper) to amount the mL of hydrogen gas. The reaction flask temperature control remained steady at 25 °C using a flowing water bath under ambient atmosphere. The catalytic reaction was activated once 2 mmol of AB (0.0686 g) solution was added into the reaction flask using a syringe. The mL of the H₂ generation was seen by recording the water displacement in the gas burette technique, as shown in Fig. S1. The reaction was estimated complete when H₂ generation was seen.

The above method was also utilized for characterizing the catalytic effect of further catalysts for H₂ generation from aqueous AB solution hydrolysis. The nM/AB molar ratio for each one of the reactions was kept consistent at 0.04M. Improved catalytic reaction over the Ni₀.₈Pt₀.₂/GO and rGO (optimum catalysts), Co₀.₈Pt₀.₂/GO and rGO NPs were performed at various temperatures (278 K, 283 K, 288 K, 293 K, 298 K, and 303 K) to survey the actuation energy (Eₐ) for the aqueous AB hydrolysis reaction. An equivalent procedure was additionally helpful to the catalytic reaction done the catalysis (100 mg) Nano particles with various base added substances (NaOH, KOH, NaH₂PO₄, NH₄OH, NaCl). However, the predictable added substances were included previously in the gathering of aqueous AB solutions into the reaction bottle.

2.6 Durability test

For the durability test, after the catalytic hydrolysis of aqueous AB solution was finished, the catalyst was kept in the reaction flask, and a further aliquot of aqueous AB solution (2 mmol (0.0686 g)) was consequently added into the resection flask. Such catalyst recovery tests for aqueous AB solution hydrolysis were carried out for 10 runs at 25 °C.
2.7 Calculation method

The turnover frequency (TOF) values described at this time total TOF values established on the number of metal atoms in the catalyst, as calculated from Equation (S1)

\[
\text{TOF} = \frac{n_{H_2}}{nM \times t} \quad \text{(S1)}
\]

where \(n_{H_2}\) is the number of moles of hydrogen, \(nM\) is the number of moles of metal in the catalyst, and \(t\) is the reaction time (minutes).

3. Results and Discussion

3.1 Structure and morphology

A simple advanced chemical reduction method is utilized for the combination of Ni–Pt/GO, Co–Pt, Ni–Co NPs (Scheme 1). Typically, for the preparation of Ni\(_{0.8}\)Pt\(_{0.2}/\)GO and rGO, Co\(_{0.8}\)Pt\(_{0.2}/\)GO and rGO, Co(NO\(_3\))\(_2\)⋅6H\(_2\)O (0.1M) and Ni(NO\(_3\))\(_2\)⋅6H\(_2\)O and H\(_2\)PtCl\(_6\) (0.012M) are mixed with 5 mL of an aqueous solution containing great dispersed GO (0.2g) and moved into the above solution with sonication for five minutes. The solution was moved to a 50 mL Teflon-lined stainless steel autoclave. The autoclave was fixed and heated to 180 °C and continued for 5 h in an oven. After completion, the Ni\(_{0.8}\)Pt\(_{0.2}/\)GO and rGO, Co\(_{0.8}\)Pt\(_{0.2}/\)GO and rGO NPs item were acquired and utilized as a catalyst for hydrogen generation from AB hydrolysis at 25 °C (for details, see the Experimental Section).
Scheme 1. The Metals@GO and rGO Nano sheets (M-Co, Ni and Pt) synthesis process.

The Ni$_{0.8}$Pt$_{0.2}$/GO and rGO, Co$_{0.8}$Pt$_{0.2}$/GO and rGO NPs morphologies are characterized using scanning electron microscopy (FESEM) and transition electron microscopy (TEM) images as shown in Fig. 1. The process can be seen from Fig. 1b, the NiPt NPs with fine and small sizes of around 1.5 nm (Fig. 1c) are fine and well spread onto the GO and rGO sheets, as shown by the FESEM result (Fig. 1a). In any case, the CoPt/GO and rGO NPs synthesized have a small, spherical shaped particle size of about 1.9 nm (Fig. 1 b' and c'). By observing the TEM images of Ni$_{0.8}$Pt$_{0.2}$/GO and rGO NPs, Co$_{0.8}$Pt$_{0.2}$/GO and rGO NPs, it is clearly shown that CoO doping into NiO NPs can energize the decrease in metal NP sizes. In order to further investigate the metal-doped GO NPs obtained with a (Co +Ni) different molar ratio are entitled as CoNi/GO respectively. The typical FESEM and TEM images of the obtained CoNi/GO catalysts are demonstrated in SFig. 3. The Nano sheet shape of GO is wide-ranging and uniform after the CoNi NPs load via the reduction rate measured system. It can be seen from the FESEM (SFig. 3a), bright-field TEM (SFig. 3b) images
that the CoNi NPs acquired through a rapid reduction process (Co + Ni) are highly distributed into the Co\(_{0.6}\)Ni\(_{0.4}\)/GO and Co\(_{0.4}\)Ni\(_{0.6}\)/GO NPs. The mean particle sizes are around 3.2 nm and 4.2 nm (SFig. 3c and f) with further evidence of the existence of Co, Ni and Pt in the doped samples. EDX was used to observe the elemental composition of the doped samples. After the EDX spectroscopy investigation, the results expose that the samples are composed of C, O, Co, Ni, and Pt elements perceived in all catalysts and the total compositional atomic percentages of C, O, Co, Ni and Pt were estimated. Tables summarized (inside the EDX spectrum) the elements on the Nano structures, respectively (SFig. 4) and the occurrence of Ni, Co, C, and O was recognized by elemental mapping (SFig. 5 and 6). It can be obviously seen that the distribution of Ni, Co, C and O elements is very consistent from FESEM images.

In investigating the feasibility of NPs collection, we observed and associated the monometallic Pt/GO and Co/GO catalyst microstructure in the as-prepared, respectively. The TEM images of monometallic Pt/GO and Co/GO show that separate Pt/GO and Co/GO NPs are homogeneously dispersed on GO with an average particle size of around 4.3 nm and 30.2 nm (SFig. 7) were observed. The Pt and Co NPs particle size in this study is smaller. Histograms of the NPs were achieved by including at least 50 particles. The Pt and Co NPs size of the Pt/GO catalyst is about 4.3 nm, whereas the Co size of the Co/GO catalyst is distributed 30.2 nm. The mean size of the Pt/GO of the catalyst is smaller than that of the Co/GO NPs.
**Fig. 1** FE-SEM and TEM images of the as-synthesized Ni_{0.8}Pt_{0.2}/GO and rGO NPs (Fig. 1a) and Co_{0.8}Pt_{0.2}/GO and rGO NPs (Fig. 1a’). TEM images (Fig. 1b) of Ni_{0.8}Pt_{0.2}/GO and rGO NPs and Fig. 1b’ Co_{0.8}Pt_{0.2}/GO and rGO. The inset in (c) and (c’) are the average particle size distribution of the Ni_{0.8}Pt_{0.2}/GO and rGO, Co_{0.8}Pt_{0.2}/GO and rGO, respectively.
**Fig. 2** Shows typical XRD patterns of the as-prepared GO Nano sheet (a), CoNi/GO and rGO, (b), CoOPt/GO and rGO (c), NiPt/GO and rGO NPs.

Fig. 2 demonstrates characteristic powder-XRD patterns of the as-arranged of GO and rGO and metal mixtures. All peaks could be recorded with face-centered cubic (fcc) structures. The first graphene oxide (GO) sample demonstrated a strong diffraction peak centered at $2\theta=13.01$, corresponding to an interlayer spacing of about 0.76 nm, compared to the (001) reflection of graphene oxide, so broader than that of pristine graphite. After surface doping, the metals doped (Ni, Co, and Pt) GO revealed negligible C (001) peaks contrasted with GO. For the metal-doped materials after small heat behavior, the GO peak widened and rGO ($2\theta=26.39$) (022) peak plane of rGO with interlayer spacing of 0.34 nm, representing the reduction in graphene oxide to rGO. The GO peak broadens upon high temperature exposure. Furthermore, as observed from the XRD pattern in Fig.
2, the diffraction peaks at $\theta=39.64^\circ$, 46.36$^\circ$ and 67.55$^\circ$ could be indexed to the characteristic (111), (200) and (220) cubic crystalline structured Pt, respectively. The NiO and CoO (96-900-8619) peaks are very solid for Co support to that NiO, CoO is improved detached on the GO, and rGO support with smaller and fine particles demonstrating their high crystallinity. These observed results clearly exhibit the advancement of Ni, Co, and Pt/GO NPs. What's more, a wide peak at 31.16$^\circ$, 36.64$^\circ$ and 59.14$^\circ$ was likewise seen in the three metal oxides, representing to the formation of rGO and GO enlivened with metal NPs. Compared with the monometallic catalysts, the bimetallic catalysts were determined to undergo considerably more structural alteration and therefore created a greater number of active sites for the catalytic reactions.

Raman spectroscopy was used to further distinguish the reduction of GO, with two prominent peaks at 1338.26 and 1594 cm$^{-1}$ conforming to the D and G bands of C atomic crystals, respectively. The NiPt/GO and rGO, CoPt/GO and rGO catalysts redshifted to 1339.06, 1346.48 and 1598.74, 1596.86 cm$^{-1}$ conforming to the D and G bands after 1h reduction at 500 $^\circ$C as shown in Fig. 3. The D-peak represents the defects in the lattice of C atom, while the G-peak in-plane stretching vibration of sp$^2$ hybridization of C atom. Furthermore, the D/G intensity ratio was significantly broadening after reduction, from 0.83 for GO to 0.84 and 0.84 for NiPt/GO and rGO, CoPt/GO and rGO after 1 h reduction, representing that the large amounts of graphite carbon were presented in the sample, respectively. The redshift of the G band and an increase in the D/G intensity ratio both indicate the renovation of sp$^2$ carbon provinces.
Fig. 3 Raman spectra for GO, NiPt/GO and rGO and CoPt/GO and rGO.

3.2 Catalytic hydrolysis of aqueous AB

To evaluate the catalyst catalytic effect, the hydrolysis of AB catalyzed by M/GO and rGO (M-Co, Ni, Pt) was examined. The hydrogen generation curves are shown in Fig. 4. Ni$_{0.8}$Pt$_{0.2}$/GO and rGO, Co$_{0.8}$Pt$_{0.2}$/GO and rGO NPs completed the hydrolysis reaction within 0.5 and 0.6 min at 25 °C and exhibited a higher catalytic effect than monometallic Ni/GO, Co/Pt, and pure materials. To determine the optimal ratio of Pt/Co for Co$_{0.8}$Pt$_{0.2}$/GO and rGO NPs a series of composite catalysts with a constant Pt content were prepared. Their catalytic activities show a volcano shaped change with increasing Pt/Co ratios, as shown in Fig. 4, and reach a peak value at a Pt/Co ratio. Further increasing the Co content ([Co]) leads to a sharp decrease in activity. Without bimetallic doped GO and rGO showed improvement over the organized progressive Nano structure, while the nearness of GO and rGO enhanced the dispersion of metal NPs. This energy is perceived due to the reduced
amount of Ni, Co and Pt NPs load, which was the fundamental giver to the catalytic hydrolysis of AB. The presence of Ni$_{0.8}$Pt$_{0.2}$/GO and rGO, Co$_{0.8}$Pt$_{0.2}$/GO and rGO NPs assisted to produce the well-scattered and ultrafine metal NPs and increasing the load amount of metals NPs. The activity maintained as the amount of Pt metal reaching over 0.3 wt% and 0.5 wt %, but decreased when the added amount of Pt metal reaching 5 wt%, this may be attributed to the preventing of thick Pt shell for the diffusion of AB molecules to hydrolyze on the surface of nanoparticles. The optimal catalytic can be realized on a catalytic surface with median binding energies of the reactive intermediates. If the reactant binds to the catalyst surface too weakly, then it cannot be activated. Though, if it binds to the surface too strongly, it will occupy all available surface sites and poison the catalyst. Thus, it is believed that there is an optimal ratio between Pt and Co ratio to show the highest catalytic activity for the hydrolysis of AB complex. Monometallic Ni/GO, Co/GO and Pt/GO NPs showed a little less catalytic effect for AB hydrolysis associated with a hierarchical Nano structure. These effects demonstrate that the arranged hierarchical Nano structure required the increase in B-H bond catalytic performance. Other catalysts, including the Ni/GO did not display promising catalytic effects. Subsequently, the Ni$_{0.8}$Pt$_{0.2}$/GO and rGO, Co$_{0.8}$Pt$_{0.2}$/GO and rGO NPs performed as the main catalytic species for AB hydrolysis. Considering H$_2$ selectivity and the amount of Ni, Co and Pt NPs load was chosen as the best catalysts. The optimized Ni$_{0.8}$Pt$_{0.2}$/GO and rGO, Co$_{0.8}$Pt$_{0.2}$/GO and rGO NPs completed the highest TOF value of 230.76 and 214.28 min$^{-1}$ in AB hydrolysis as shown in Fig. 5 and STable 2.
**Fig. 4** Hydrogen productivity vs. reaction time for hydrogen release from an aqueous AB solution (100 mM, 10 mL) catalyzed by M/GO and rGO (M-Co, Ni, Pt) at 298 K ($n_{Ni}/n_{AB} = 0.04$).
Various supports changed structures, carrying about different catalytic performance. At that point the absorbent inorganic catalysts Al₂O₃ and SiO₂ were utilized as supports to synthesize Ni and Co NPs catalysts using a similar method as that for NiPt/GO and rGO. The TEM images showed that the Ni and Co NPs in NiPt/Al₂O₃, CoNi/Al₂O₃, and NiPt/SiO₂ likewise had a small size (Fig. S8). However, they were greater than those of NiPt/GO and rGO. The synergist catalysts in NiPt/Al₂O₃, CoNi/Al₂O₃, and NiPt/SiO₂ had lower reactant exercises than NiPt/GO and rGO (Fig. 6), but their catalytic performance was still high were among the announced honorable noble-metal free catalysts (STable 3). These distinctive catalyst exhibitions may be created by the various materials, among which the high specific surface area of metal NPs and the solid adsorption of NH₃BH₃ into its pores led to the quick reactant dehydrogenation of AB. In addition, these consequences including various
types of supports additionally assigned the assumption of improved synergist effect over amorphous metal NPs.
**Fig. 6** Plots of time versus hydrogen generation volume from NH$_3$BH$_3$ aqueous solution over (a) NiPt/Al$_2$O$_3$, NiPt/SiO$_2$ and (c) CoNi/Al$_2$O$_3$ and the corresponding TOF values using different catalysts.

In addition, detailed examination of the kinetic reaction for the aqueous AB hydrolysis reaction was produced by changing the number of catalysts, a similar amount of AB at room temperature (25 °C). Fig. 7a shows the influence of the amount of catalyst on catalytic reaction hydrogen generation, where the amount of AB multifaceted was kept at 2 mmol at 25 °C and the catalytic amounts were set at 20, 40, 60, 80 and 100 mg. We can see that the catalysts can effectively start the AB complex hydrolysis. The hydrogen generation efficiency was improved with an expanded measure of the catalyst in the measured range. Fig. 7b demonstrates the plot of hydrogen generation mole versus catalyst amount on a logarithmic scale. The slope of 1.99 shows that the catalytic hydrolysis reaction of aqueous AB is first-order concerning the catalyst amount and the observation is in good agreement.
3.3 Kinetic study

Fig. 8 demonstrates the plots of time versus mole of hydrogen generation at various temperatures. For a known temperature, hydrogen is created directly through a stoichiometric volume of six moles. Close to the temperature rise from 25 °C to 60 °C, hydrogen is grown rapidly, proposing quicker reaction kinetics. The reaction rate constant (k) is determined by the condition (eq 2) below,

\[ \frac{-d[NH_3BH_3]}{3dt} = \frac{d[H_2]}{dt} = k \]  

\[ \text{(2)} \]
The activation energy is accordingly assumed from the Arrhenius equation (eq 3) between ln k and 1/T as follows.

\[
\ln k = \frac{-E_a}{R \cdot \frac{1}{T}} + \ln A \quad \ldots \ldots \ldots \ldots \ldots \ldots (3)
\]

where \( E_a \) is the activation energy, \( R \) is the gas constant, \( T \) is the absolute temperature in kelvins, and \( A \) is the pre-exponential factor.
Fig. 8 (a, c) Plots of time versus hydrogen evolution catalyzed by Ni$_{0.8}$Pt$_{0.2}$/GO and rGO, Co$_{0.8}$Pt$_{0.2}$/GO and rGO NPs at various temperatures; (b, d) Corresponding Arrhenius plot (ln $k$ versus $1/T$).

To demonstrate the temperature effect on aqueous AB hydrolytic dehydrogenation, the Ni$_{0.8}$Pt$_{0.2}$/GO and rGO, Co$_{0.8}$Pt$_{0.2}$/GO and rGO kinetics of catalytic hydrogen generation was studied at different temperatures (25 °C~60 °C). Fig. 8 (a, c) shows the hydrolytic dehydrogenation amount of AB catalyzed by Ni$_{0.8}$Pt$_{0.2}$/GO and rGO, Co$_{0.8}$Pt$_{0.2}$/GO and rGO NPs. The reaction was increased
to a 25 °C–60 °C temperature range. The rate of the reaction is obviously improved by increasing the temperature. As indicated by the Arrhenius plot in Fig. 8 (b, d), the achieved recognizable activation energy ($E_a$) of AB hydrolysis catalyzed by Ni$_{0.8}$Pt$_{0.2}$/GO and rGO, Co$_{0.8}$Pt$_{0.2}$/GO and rGO NPs is 23.94 kJ/mol, 23.60 kJ/mol, which is lower than those of as recently reported noble metal catalysts.$^{31,31}$ As shown in SFig. 9, the hydrogen generation rate increases with increasing temperature. The catalytic reactions for hydrogen generation from aqueous AB solution were completed in 0.6, 0.5, 0.4, 0.3, 0.2 min (Ni$_{0.8}$Pt$_{0.2}$/GO and rGO) and 0.62, 0.55, 0.42, 0.33, 0.21 min (Co$_{0.8}$Pt$_{0.2}$/GO and rGO) and 25, 30, 40, 50, 60 °C, respectively; agreeing with the TOF values of 214.0, 250.0, 333.3, 500.0 and 750.0 min$^{-1}$ (Ni$_{0.8}$Pt$_{0.2}$/GO and rGO) and 176.4, 230.7, 300.0, 428.5, 681.8 min$^{-1}$ (Co$_{0.8}$Pt$_{0.2}$/GO and rGO) (SFig. 9).
Fig. 9 Reusability of Ni$_{0.8}$Pt$_{0.2}$/GO and rGO, Co$_{0.8}$Pt$_{0.2}$/GO and rGO Nano catalyst for AB hydrolysis for successive 10 cycles at 25 °C.

Seeing the significance of catalytic stability in practical application, the recyclability and stability of the Ni$_{0.8}$Pt$_{0.2}$/GO and rGO, Co$_{0.8}$Pt$_{0.2}$/GO and rGO NPs were studied at 25 °C by adding the same amount of AB solution. When the first cycle was completed, as shown in Fig. 9, the hydrogen generation volume was unaltered after 10 cycles. The initial activity was continued, showing its great recyclability. However, the hydrogen generation amount displayed a slight decrease. After the stability test, the Ni$_{0.8}$Pt$_{0.2}$/GO and rGO, Co$_{0.8}$Pt$_{0.2}$/GO and rGO NPs were then characterized by TEM. The TEM image of the burned through Ni$_{0.8}$Pt$_{0.2}$/GO and rGO, Co$_{0.8}$Pt$_{0.2}$/GO and rGO NPs catalyst clearly showed that no perilous tuning was recognized for the morphology of the reused catalysts. The CoPt and NiPt NPs in the GO support were still well-scattered without the presence of clusters. The effective catalytic performance and stability can be similarly disseminated with smaller sized CoPt and NiPt NPs produced. Additionally, the pyrolysis-inferred GO layer could likewise help to assistance the CoPt and NiPt NPs.
In further analysis, as shown in SFig. 10, the Ni$_{0.8}$Pt$_{0.2}$/GO and rGO, Co$_{0.8}$Pt$_{0.2}$/GO and rGO morphology is well preserved. Although some mixture is detected, which might be the reason for the slight decrease in activity during the durability test; TEM images of the recovered catalyst show no significant variation in the particles (SFig. 10c,10d). Moreover, there is a small change in the particle size and agglomeration is observed, signifying that the Ni$_{0.8}$Pt$_{0.2}$/GO and rGO, Co$_{0.8}$Pt$_{0.2}$/GO and rGO NPs structure remains unchanged after usage. The Ni$_{0.8}$Pt$_{0.2}$/GO and rGO, Co$_{0.8}$Pt$_{0.2}$/GO and rGO catalyst demonstrates very high catalytic stability and durability to AB hydrolytic dehydrogenation. In addition, SFig. 11 shows the X-ray diffraction (XRD) pattern of the reused catalyst for Ni$_{0.8}$Pt$_{0.2}$/GO and rGO NPs. Obviously, in addition to the GO (2θ=13.26º) diffraction peak, only one broad diffraction peak at around 2θ=43.0º representing the disappearance of rGO was observed. This indicates that the Ni$_{0.8}$Pt$_{0.2}$/GO and rGO NPs have a low crystalline structure as shown in SFig. 11.
Fig. 10 (a). Hydrogen production as a function of time from AB aqueous solution over the as-prepared catalysts at different temperatures, (b) according to the TOF values for AB hydrolysis at different temperatures 5~15 °C (metal/AB =0.04).

The aqueous AB solution catalytic effect was approved and prepared at various temperatures in the 5~15 °C range starting with Ni$_{0.8}$Pt$_{0.2}$/GO and rGO and 100 mM AB in 10mL of H$_2$O. As shown in Fig. 10a, the hydrogen generation rate steadily increased with increasing temperatures and the TOF value reaches the maximum with 15 °C, respectively. Along these lines, the Ni$_{0.8}$Pt$_{0.2}$/GO and rGO catalyst was chosen in all further study experiments.

Based on the above presumptions and the consequences of the following investigations, a mechanism to explain the GO-AB cross-type Nano structure arrangement is advanced. It appears in Fig. 11 that GO Nano sheets have their basal planes brightened with hydroxyl groups. These groups empower the proto analysis of the B−H bond in a portion of the AB molecules, which were presented in the middle of the isolated GO sheets. This causes the development of cationic AB connected to the contrarily charged oxygen through an electrostatic influence (Fig. 11b). While other presented AB atoms are not protonated and circulated inside the interlayer space, and the GO sheets are
inclined to restack to make a sandwiched GO-AB-GO structure as the dissolvable material was evacuated. AB and its cationic initiator moved toward becoming encapsulated inside the GO interlayer.

**Fig. 11** (a) Schematic representation of the GO-AB Nano structure arrangement. (b) The point by point representation of the communication between AB cation and contrarily charged oxygen from GO.

For the current metal catalyzed reaction, the initiation procedure happens on the metal catalyst surface, as proposed by the zero order kinetics reaction. A trustworthy mechanism is shown in Fig. 12. It proposes that there is an interface between the AB molecules and the metal particle surface to create an initiated complex species in the rate-deciding phase, to which attack by a water molecule readily results in the deliberate separation of the B–N bond and hydrolysis of the following BH$_3$ middle to form the borate ion together with H$_2$ generation (equation-1). According to the literature,
without water, dehydrocoupling between the AB molecule occurs, which produces new B–N bonds, in all likelihood by means of a thoroughly connected in-between, on the metals surface.\textsuperscript{46-50}

![Diagram](Image)

**Fig. 12** The suggested mechanism for AB catalytic dehydrogenation.

4. Conclusion

In summary, we developed graphene oxide supported transition metals NiCo, NiPt and CoPt NPs catalysts essentially prepared using hydrothermal reactions at 180 °C and proceeded for 5 h in an oven under an ambient atmosphere. The enhanced bimetallic Ni\textsubscript{0.8}Pt\textsubscript{0.2}/GO and rGO, Co\textsubscript{0.8}Pt\textsubscript{0.2}/GO and rGO catalysts show incredible catalytic effect towards H\textsubscript{2} generation from aqueous AB solution hydrolysis in association with their bimetallic supplements at 25 °C with a TOF value of 214.28 min\textsuperscript{-1}, 230.76 min\textsuperscript{-1}, which is the most elevated reaction between all of the GO and rGO supported transition-metal catalysts ever revealed for this reaction. The Ni-Pt and Co-Pt oxide maintenance, which can adsorb and break BH\textsubscript{4}⁻ B-H bonds and weaken H\textsubscript{2}O H-O bonds via the hydrogen generation electron transmission effect. Amazing Co\textsubscript{0.4}Ni\textsubscript{0.6}/GO, Co\textsubscript{0.5}Pt\textsubscript{0.1}/GO, and Co\textsubscript{0.6}Ni\textsubscript{0.4}/GO catalysts likewise show great catalytic effect for hydrogen generation from aqueous AB solution at
25 °C. The catalysts also demonstrate the greatest recycling properties, with reserved catalytic activity presence around 98% after the seventh reaction cycle. This outstanding GO and rGO supported transition metal heterogeneous catalyst effect demonstrates a promising methodology towards the improvement of AB as a believable chemical hydrogen storage material for application in fuel cells. In addition, this technique can be effectively extended to the preparation of other graphene oxide supported transitional-metal modified methods for several other applications.

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