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Journal Name

ARTICLE

Reduced Graphene Oxide Supported Nickel-Palladium Alloy Nanoparticles as a Superior Catalyst for the Hydrogenation of Alkenes and Alkynes under Ambient Conditions

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Addressed herein is the superior catalytic performance of reduced graphene oxide supported Ni₃₀Pd₇₀ alloy nanoparticles (rGO-Ni₃₀Pd₇₀) for the direct hydrogenation of alkenes and alkynes to alkanes, which surpasses the commercial Pd/C catalyst both in activity and stability. A variety of cyclic or aromatic alkenes and alkynes (total 17 examples) were rapidly reduced to the corresponding alkanes with high yields (>99%) via the presented direct hydrogenation protocol under ambient conditions. Compared to the commercially available Pd/C (10 wt%) catalyst, the rGO-Ni₃₀Pd₇₀ catalyst provided higher yields in shorter reaction times under the optimized conditions. Moreover, the rGO-Ni₃₀Pd₇₀ catalysts were more stable and durable than the commercial Pd/C catalysts by preserving its initial activity after five consecutive runs in the hydrogenation reactions.

Introduction

Hydrogenation of unsaturated hydrocarbons such as alkenes and alkynes is a versatile tool in synthetic organic chemistry for the synthesis of various organic compounds that are important building blocks used in the total synthesis and industrial products.¹⁻³ In the classical hydrogenation reactions that have been known since the 19th century and widely used in various industries,⁴ unsaturated organic compounds react with molecular hydrogen in the presence of a transition metal catalyst to yield the corresponding alkanes under high pressure and temperature using a special hydrogenation equipment. The commercially available Pd/C is still a popular choice as catalyst for the direct hydrogenation reactions although many other Pd-based or other metal catalyst systems have been developed.^{5,6} However, Pd/C is an expensive catalyst and there are other drawbacks for its use in the hydrogenation reactions such as having very limited reusability and being flammable upon the exposure to air after the hydrogenation reactions. Therefore, a more economical, safer and reusable Pd-based catalysts system that has a potential to be commercialized is still required for the direct hydrogenation reactions.

In recent years, the use of Pd nanoparticles (NPs) has attracted great attention in the organic synthesis because of

their high surface to volume ratio and more active/selective surface atoms compared to those of bulk Pd catalysts.⁷⁻¹¹ However, Pd is a noble metal and their use as catalysts is not practical in industrial applications because of its high price and limited source. In recent years, both to reduce the amount of Pd present in the catalyst system¹² and to further enhance Pd catalyst activity, Pd is alloyed with a first-row transition metal.^{13,14} These bimetallic Pd alloy NPs showed much enhanced catalytic performance than their monometallic counterparts owing to the synergistic effects resulted from two metal interactions.¹⁵⁻¹⁷ In our recent studies, we have successfully demonstrated that monodisperse NiPd,¹⁸ CoPd¹⁹ and CuPd²⁰ alloy NPs supported on reduced graphene oxide (rGO) were highly active catalysts in various organic reactions compared to their monometallic counterparts. Those studies demonstrated that the alloying of a first row transition metal with Pd has a great effect on its activity and selectivity in organic synthesis besides the preparation of more economical Pd catalysts. Moreover, the unique role of rGO on the high activity of the MPd alloy NPs that either stems from the well-dispersion NPs over the rGO nanosheets or the presence of a 2D graphitic plane near each rGO-MPd catalysts helps to pull organic reactants in close range contact with the NPs has been demonstrated by our recent studies as well.^{21,22}

On the other hand, alkenes and alkynes are widely found in petroleum, synthetic and natural products that led the researchers to develop more efficient methods for their reduction.²³ Catalytic reduction of a double bond or a triple bond can be accomplished under either homogeneous^{24,25} or heterogeneous²⁶ catalytic conditions. In this regard, we recently reported an efficient method for homogeneous reduction of C=C bonds and C≡C bonds with diimide that is generated in situ from hydrazine hydrate by oxidation with oxygen.²⁷ In our

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† Electronic Supplementary Information (ESI) available: GC-MS spectra of all starting and products compounds and TEM image of Pd/C

another study, we have reported the monodisperse NiPd alloy nanoparticles (NPs) assembled on reduced graphene oxide (rGO) as catalysts for the transfer hydrogenation of aromatic nitro or nitriles to primary amines by using ammonia borane ($\text{NH}_3\text{-BH}_3$) as a hydrogen reservoir in aqueous methanol solutions at room temperature.²² Although the Ar-NO₂ or Ar-CN compounds were successfully reduced by the rGO-Ni₃₀Pd₇₀ catalysed transfer hydrogenation reactions, the protocol did not work over the reduction of alkenes and alkynes. This was most probably due to the hydridic character of the catalytic transfer hydrogenation protocol.²⁸ Therefore; we then decide to test the rGO-Ni₃₀Pd₇₀ catalyst for the direct hydrogenation of alkenes and alkynes to alkanes. Herein, we report the superior performance of the rGO-Ni₃₀Pd₇₀ catalyst overshadowing the commercial Pd/C catalyst for the direct hydrogenation of alkenes and alkynes under 1 atm H₂ gas in methanol at room temperature.

Experimental

Materials

Palladium(II) acetylacetonate ($\text{Pd}(\text{acac})_2$, 99%), Nickel(II) acetate tetrahydrate ($\text{Ni}(\text{ac})_2\cdot 4\text{H}_2\text{O}$, 98%), , oleylamine (OAm, >70%), borane-tert-butylamine (BTB, 97%), 1-octadecene (tech. grade, 90%), hexanes (99%), ethanol (99%), all the chemicals used for the graphene synthesis except natural graphite flakes and all alkenes and alkynes used in the hydrogenation reactions were purchased from Sigma-Aldrich and used as received. Natural graphite flakes (325 mesh) were purchased from Alfa-Aesar. Pd/C catalyst (10 wt. % Pd) was purchased from ACROS Organics.

Instrumentation

Transmission electron microscope (TEM) images were obtained by using FEI Tecnai G2 Spirit BioTwin High-Contrast microscope operating at 120 kV. The X-ray diffraction pattern (XRD) was recorded on a Rigaku Miniflex diffractometer with $\text{CuK}\alpha$ (30 kV, 15 mA, $\lambda = 1.54051 \text{ \AA}$). The metal content of the NiPd alloy NPs and G-Ni₃₀Pd₇₀ catalysts was determined by using Leiman series inductively coupled plasma-mass spectroscopy (ICP-MS) after each sample was completely dissolved in aqua-regia (HNO_3/HCl : 1/3 v/v ratio). The monitoring of the hydrogenation reactions was followed by an Agilent GC-MS instrument equipped with electron impact (EI) technique using helium as carrying gas.

Synthesis of monodisperse Ni₃₀Pd₇₀ alloy nanoparticles

The monodisperse Ni₃₀Pd₇₀ alloy NPs were synthesized by using our well-established protocol published elsewhere.²²

Synthesis of reduced graphene oxide (rGO) and supporting Ni₃₀Pd₇₀ alloy nanoparticles on rGO

The reduced graphene oxide used in this study was prepared by using well-established two-step chemical route and the Ni₃₀Pd₇₀ NPs were supported on rGO via liquid-phase self-assembly method which are published elsewhere.¹⁹⁻²²

General procedure for the direct hydrogenation of alkenes and alkynes

All catalytic hydrogenation reactions either on alkene or alkyne substrates were performed in a 50 mL round bottom flask under 1 atm hydrogen gas at room temperature. In the typical catalytic hydrogenation experiment, 1 mmol of substrate and 2 mg of catalysts (G-Ni₃₀Pd₇₀ or Pd/C) were mixed in 5 mL of methanol in the flask, and following purged with H₂ gas for three times and then proceeded under 1 atm of H₂ gas at room temperature. The progression of hydrogenation reactions was followed by the GC-MS at certain time intervals.

Reusability of rGO-Ni₃₀Pd₇₀ catalysts in the hydrogenation reactions

The reusability of rGO-Ni₃₀Pd₇₀ catalysts was investigated by performing the hydrogenation on styrene. For a typical reusability experiment, the hydrogenation reaction on styrene was initiated by using the recovered rGO-Ni₃₀Pd₇₀ catalysts and analyzing the conversion for each run. After each catalytic run, the solvent was evaporated and the residue was dissolved in 5 mL ethanol. The mixture was centrifuged in 9000 rpm by 10 min and the catalyst was recovered. After the top phase was decanted, the recovered catalysts were washed with ethanol and dried under vacuum. The catalyst isolated was reused for the next run under the same reaction conditions described as in the section entitled "General procedure for the direct hydrogenation of alkenes and alkynes".

Results and discussion

Monodisperse Ni₃₀Pd₇₀ alloy NPs were synthesized by using our well-established protocol reported earlier.²² According to a typical synthesis procedure, coreduction of palladium(II) acetylacetonate (0.2 mmol) and nickel(II) acetate tetrahydrate (0.2 mmol) in oleylamine solution was achieved with borane-tert-butylamine at 100 °C to yield monodisperse Ni₃₀Pd₇₀ alloy NPs. The colloidal Ni₃₀Pd₇₀ NPs were deposited on rGO via liquid phase self-assembly method to use them as catalysts for the direct hydrogenation reactions. As we reported full characterization of Ni₃₀Pd₇₀ alloy NPs and rGO-Ni₃₀Pd₇₀ catalyst, we herein only report a limited characterization data which are recorded by transmission electron microscope (TEM) and inductively-couple plasma mass spectrometer (ICP-MS). **Figure 1** shows representative TEM images of colloidal Ni₃₀Pd₇₀ NPs and rGO-Ni₃₀Pd₇₀ catalysts revealing the uniform particle distribution of the alloy NPs over entire TEM grid with an average particle size of 3.5 nm (**Figure 1A**) and preservation of their size and morphology on rGO support (**Figure 1B**). To show the crystal structure of the rGO-Ni₃₀Pd₇₀ catalysts, the XRD pattern was presented in SI (Figure S3). Besides the composition Ni₃₀Pd₇₀ alloy NPs, the metal content of rGO-Ni₃₀Pd₇₀ was also determined to be 14 wt% (Ni+Pd) by ICP-MS analyses. According to the ICP-MS results, the Pd content of rGO-Ni₃₀Pd₇₀ catalysts was calculated to be 9.8 wt%, which makes the rGO-Ni₃₀Pd₇₀ catalyst suitable to compare its catalytic performance with the commercial 10 wt% Pd/C catalyst in the same reaction. The rGO-Ni₃₀Pd₇₀ catalyst was used without any further purification in

the direct hydrogenation reactions of alkenes and alkynes under 1 atm hydrogen gas pressure in methanol at room temperature. In the initial study, the direct hydrogenation of styrene (**1**) was selected as a test reaction to determine the optimum reaction conditions for the rGO-Ni₃₀Pd₇₀ catalyzed direct hydrogenation reactions. In the course of optimization experiments, the effect of several reaction parameters were studied including solvent, temperature, catalyst loading and reaction time. It is found that 1 mmol styrene was quantitatively converted to ethylbenzene (**2**) within 10 min when the reaction proceeded by using 2 mg of G-Ni₃₀Pd₇₀ catalysts in 5 mL of methanol under 1 atm H₂ gas at room temperature. Under the optimized reaction conditions, we then examine the performance of commercial Pd/C catalyst in the direct hydrogenation of styrene. The Pd/C catalyst was also efficient in catalyzing the hydrogenation reaction, but the quantitative conversion of styrene to ethylbenzene was completed in 50 min. This simple test clearly reveals that rGO-Ni₃₀Pd₇₀ catalyst is much more active than the commercial Pd/C catalyst in the direct hydrogenation reaction.

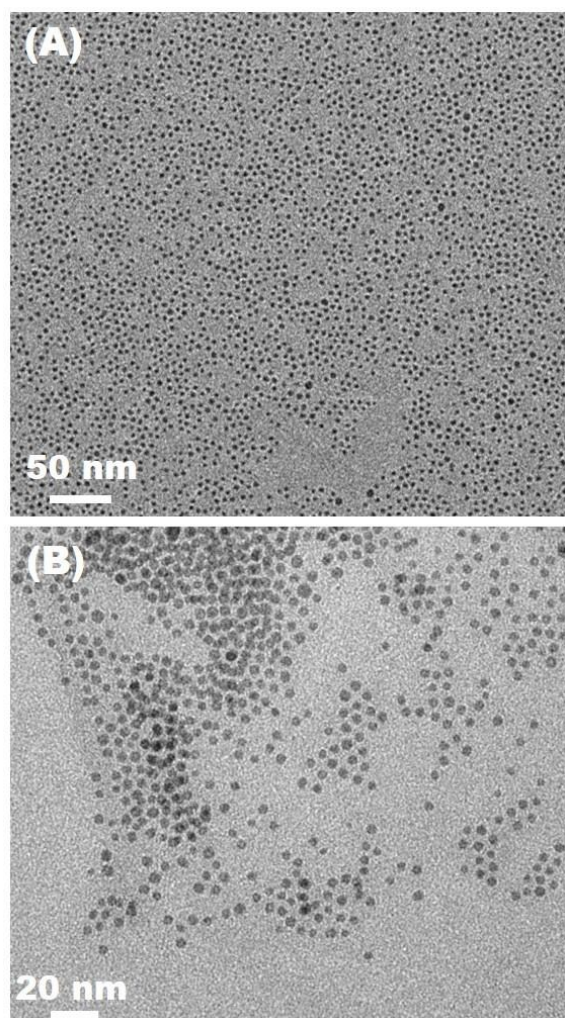










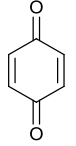
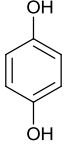
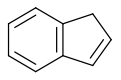
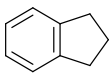
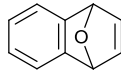
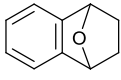
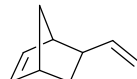
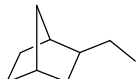
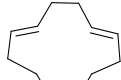
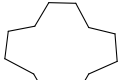


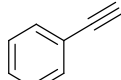
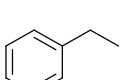
Figure 1. Representative TEM images (A) of colloidal Ni₃₀Pd₇₀ alloy NPs and (B) rGO-Ni₃₀Pd₇₀ catalysts.

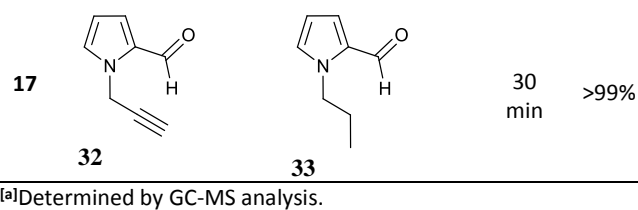
The optimized reaction conditions in hand, we then investigated the scope of the rGO-Ni₃₀Pd₇₀ catalyzed hydrogenation reaction over various alkenes and alkynes and the results were depicted in **Table 1**. The product analysis was studied by GC-MS after certain time intervals. The reduction of alkenes **1**, **3**, **5**, and **7** to corresponding alkanes **2**, **4**, **6**, and **8** were completed in 10-20 min (**Table 1, entries 1-4**). The reduction of 1,3-cyclooctadiene (**9**) and 1,5-cyclooctadiene (**11**) were completed in 2 h and 7 h with yields of >99%, respectively (**Table 1, entries 5 and 6**). The conjugated diene unit in **9** was reduced faster than the isolated diene unit in **11**. Furthermore, the reduction of cycloheptatriene (**13**) to cycloheptane (**14**) was completed in 4 h (**Table 1, entry 7**). *p*-benzoquinone (**15**) and 5-vinyl-2-norbornene (**21**) were reduced in yields of >99% within 100 and 50 min, respectively (**Table 1, entries 8 and 11**). Both, bicyclic compound 1*H*-indene (**17**) and tricyclic 1,4-dihydro-1,4-epoxynaphthalene (**19**) were converted to corresponding alkanes in 12 min in yields of >99% (**Table 1, entries 9 and 10**). We assume that the strained double bonds incorporated in a ring are reduced much rapidly. (1*Z*,5*E*,9*E*)-cyclododeca-1,5,9-triene (**23**) was reduced to cyclododecane (**24**) in 8 h in high yield (>99%) (**Table 1, entry 12**). Finally, the hydrogenation of α -pinene (**25**) to 2,6,6-trimethylbicyclo-[3.1.1]heptane (**26**) was completed in 48 h in a yield of 84% (**Table 1, entry 13**). The decreased reactivity of **25** was attributed to the steric hindrance around double bond caused by bridge methyl groups. Furthermore, we examined the scope of the reaction by submitting a range of alkynes (conjugated and nonconjugated) to reduction under the same reaction conditions. Phenylacetylene (**27**) was reduced to ethylbenzene (**2**) in 18 min (**Table 1, entry 14**). However, diphenylacetylene (**28**) was less reactive than the phenylacetylene, which is reduced to 1,2-diphenylethane in 20 min. Strong electron withdrawing groups in **30** did not have much effect on the reduction kinetics. Pyrrole derivative having a nonconjugated alkyne functionality (**32**) was also smoothly reduced to *N*-propyl pyrrole derivative (**33**) within 30 min almost in quantitative yield.

Table 1. Scope of rGO-Ni₃₀Pd₇₀ catalyzed direct hydrogenation

Entry	Substrate	Product	Time	Yield (%) ^[a]
1			10 min	>99%
2			12 min	>99%
3			12 min	>99%

$$\begin{array}{ccc} \text{Alkene or Alkyne (1 mmol)} & \xrightarrow[1 \text{ atm H}_2, \text{ methanol (5 mL), rt}]{\text{rGO-Ni}_{30}\text{Pd}_{70} \text{ (2 mg)}} & \text{Alkane} \end{array}$$

4			20 min	>99%
5			2 h	>99%
6			7 h	>99%
7			4 h	>99%
8			100 min	>99%
9			12 min	>99%
10			12 min	>99%
11			50 min	>99%
12			8 h	>99%
13			48 h	84%
14			18 min	>99%
15	$\text{Ph}-\text{C}\equiv\text{C}-\text{Ph}$ 28	$\text{Ph}-(\text{CH}_2)_2-\text{Ph}$ 29	20 min	>99%
16	$\text{R}-\text{C}\equiv\text{C}-\text{R}$ $\text{R} = \text{COOEt}$ 30	$\text{R}-(\text{CH}_2)_2-\text{R}$ $\text{R} = \text{COOEt}$ 31	20 min	>99%



To understand whether the presented protocol can be scaled-up, another experiment was performed by increasing the amount of styrene up to 10 mmol whereas the amount of catalyst was kept constant at 2 mg. The progress of the reaction was monitored by doing product analysis with GC-MS at certain time intervals (10, 30, 50, 60, 70, 80, 90 min) and the results were depicted in **Table 2**. As clearly seen from **Table 2**, only 4% of yield was obtained within initial 10 min, but the complete reduction was achieved after 90 min. These results clearly indicate that there is no major effect of substrate amount (by keeping the catalyst amount at constant) in the catalytic hydrogenation protocol and the presented catalytic protocol has a potential to be used in industry. Moreover, the same scale-up test was also performed by using the commercial Pd/C catalyst (2 mg) and the quantitative conversion of styrene to ethylbenzene completed in 400 min. This is another important evident for the obvious advantageous of rGO-Ni₃₀Pd₇₀ catalyst over the commercial Pd/C one.

Table 2. Hydrogenation of styrene (**1**) (10 mmol) with rGO-Ni₃₀Pd₇₀ catalysts (2 mg).

Time (min)	Yield (%) ^[a]
10	4
30	21
50	37
60	59
70	77
80	95
90	100

^[a]Determined by GC-MS analysis.

Another significant aspect was the study of the reusability of the catalysts (rGO-Ni₃₀Pd₇₀) for industrial applications. Therefore, we tested the reusability of rGO-Ni₃₀Pd₇₀ catalysts in the hydrogenation of styrene (**1**). The results are shown in **Table 3**. As it can be clearly seen from the **Table 3**, the rGO-Ni₃₀Pd₇₀ catalyst preserved its initial activity after five consecutive runs indicating its durability in the direct hydrogenation reactions. We performed same reusability test in the presence of the commercial Pd/C catalyst and it is observed that the Pd/C catalyst loss its 20% of its initial activity after the five consecutive runs indicating that rGO-Ni₃₀Pd₇₀ is more durable catalyst than the Pd/C in the direct hydrogenation reaction.

Table 3. Reusability of the rGO-Ni₃₀Pd₇₀ catalyst in the hydrogenation of styrene

Run	1	2	3	4	5
Yield(%) ^[a]	>99%	>99%	>99%	>99%	>99%

^[a]Determined by GC/MS analysis.

Conclusions

In summary, we have demonstrated a facile catalytic method for the reduction of alkenes and alkynes. The catalytic reduction method presented here has distinct advantages over the existing one such as being rapid, using a recyclable and more economical Pd catalysts and being applicable and scale-up for variety of alkenes or alkynes under very mild conditions. Moreover, it has been demonstrated by many times that rGO-Ni₃₀Pd₇₀ catalyst showed much better performance than the commercial Pd/C one and we believe that rGO-Ni₃₀Pd₇₀ catalyst has a potential to surpass the commercial Pd/C catalyst in organic synthesis.

Acknowledgments

We thank to the Scientific and Technological Research Council of Turkey (TUBITAK, Grant No. TBAG-112T360), the Middle East Technical University, the Atatürk University and the Turkish Academy of Sciences (TUBA) for financial support of this work.

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Graphical Abstract

rGO-Ni₃₀Pd₇₀ catalyst showed a superior catalytic performance surpassing the commercial Pd/C catalyst both in activity and stability for the hydrogenation of alkenes and alkynes to alkanes.

