**Composites of Palladium–Nickel Alloy Nanoparticles and Graphene Oxide for the Knoevenagel Condensation of Aldehydes with Malononitrile**

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**ABSTRACT:** Herein, we have described uniformly dispersed palladium–nickel nanoparticles furnished on graphene oxide (GO-supported PdNi nanoparticles) as a powerful heterogeneous nanocatalyst for the promotion of Knoevenagel reaction between malononitrile and aromatic aldehydes under mild reaction conditions. The successful characterization of PdNi nanoparticles on the GO surface was shown by X-ray diffraction, X-ray photoelectron spectroscopy, high-resolution transmission electron microscopy (HR-TEM), and TEM. GO-supported PdNi nanoparticles, which are used as highly efficient, stable, and durable catalysts, were used for the first time for the Knoevenagel condensation reaction. The data obtained here showed that the GO-supported PdNi nanocatalyst had a unique catalytic activity and demonstrated that it could be reused five times without a significant decrease in the catalytic performance. The use of this nanocatalyst results in a very short reaction time under mild reaction conditions, high recyclability, excellent catalytic activity, and a straightforward work-up procedure for Knoevenagel condensation of malononitrile and aromatic aldehydes.

1. **INTRODUCTION**

Knoevenagel condensation of benzylidenemalonitrile (BMN) derivatives of aryl aldehydes is a diverse group of valuable organic intermediates that are adaptable to many synthetic reaction transformations, and biologically valuable molecules such as carbohydrates, heterocycles, and different types of enzyme inhibitors are used. The Knoevenagel condensation of aldehydes with activated carbon-containing compounds is an essential and powerful tool in the synthesis of fine chemicals as well as some heterocyclic compounds that have biological significance. A perusal of the literature reveals many examples of heterogeneous catalysts for the Knoevenagel condensation reaction, such as metal–organic framework (MOF)–NH, MOF–Pd, PMOVI, Zn@ZIF-67, ZIF-8, chitosan, Cd(II)-based coordination polymers, Ni(II)-based coordination polymers, PdAlO(OH), mesoporous titanosilicate, basic MCM-41 silica, and acid–base bifunctional mesoporous MCM-41 silica. However, many of these catalysts generally suffer from disadvantages such as low reaction yields, tedious work-up procedures, harsh reaction conditions, toxic and expensive solvents or chemicals, prolonged reaction times, and low reusability. Therefore, further efforts are needed toward the development of more efficient and reusable heterogeneous nanocatalysts to achieve mild and green reaction conditions. In recent studies, researchers have focused on these properties to synthesize BMN derivatives to benefit from the important catalytic properties of heterogeneous nanocatalysts such as reusability, easy removal from the reaction medium, and recyclability.

Following the development of a new heterogeneous catalyst to increase the reaction rate, in the current work, we report a clean and environmentally friendly synthetic method to obtain benzylidenemalonitrile derivatives of aryl aldehydes by using the efficient nanocatalyst graphene oxide (GO)-supported PdNi nanoparticles. For the catalyst in which palladium, nickel, and graphene oxide with different coordination constraints are present, changes in the reaction rate are expected due to the synergistic effect of the two metals. For this reason, the current heterogeneous GO-supported PdNi nanocomposites have been used for the first time, to the best of our knowledge, as a nanocatalyst for the two-component Knoevenagel condensation of malononitrile and aromatic aldehydes under mild conditions to produce compounds in high yields. All reactions were carried out by using the water/ethanol (v/v, 1:1) solvent system at room temperature.

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2. RESULTS AND DISCUSSION

2.1. Characterization of Uniformly Dispersed GO-Supported PdNi Nanoparticles. Preliminary characterization of GO-supported PdNi NPs was performed using transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and high-resolution (HR)-TEM methods. Monodisperse GO-supported PdNi NPs were produced in the presence of K2PdCl4 and NiCl2 using an ultrasonic double-reduction method. In the next step, a solution was obtained, which was refluxed for 2 h, followed by reduction of the resulting brownish black Ni2+ and Pd2+ ions, Ni(0) and Pd(0), from their bimetallic nanoparticles. Composition analyses results, microstructural properties, and morphology of PdNi@GO nanoparticles using TEM were obtained as observed in Figure 1. In this figure, it was observed that the average maximum particle size was around 3.28 ± 0.35 nm. The HR-TEM image of the catalyst components was obtained, in which they were found to be spherical as shown in Figure 1. Also, monodisperse and stable Pd−Ni@GO nanoparticles were obtained from HR-TEM for visualization of atomic lattice fringes. These fringes are found to be 0.21 nm, which is a bit smaller than the nominal Pd (111) range of 0.22 nm.34,35 This case indicates that the prepared materials are alloys. Besides, the inductively coupled plasma indicates that the Pd/Ni ratio is nearly 1:1 (Pd54Ni46).

In the XRD spectrum of Figure 2, the crystal structure and the average crystallite size of the palladium−nickel nanoparticles supported on the graphene oxide is shown. A slight breakdown peak shift was observed in the prepared nanomaterials, as compared with pure Pd, showing the GO-supported PdNi NP alloy formation as seen in Figure 2. The peak for graphene oxide was observed at around 2θ = 11.34°. The strong signals of the prepared materials are mostly from Pd metals as shown in Figure 2. The observed peaks at around 2θ = 42.1, 47.5, 68.7, and 83.3°, which relate to (111), (200), (220), and (311) indicate the face-centered cubic structure of the prepared PdNi alloy.

Table 1. Optimization of Reaction Parameters for the Knoevenagel Condensation of Benzaldehyde with Malononitrile

| entry | solvent | catalyst (mg) | time (min) | yield (%) |
|-------|---------|---------------|------------|-----------|
| 1     | CH2Cl2  | 2             | 100        | trace     |
| 2     | CH3CN   | 2             | 100        | 10        |
| 3     | MeOH    | 2             | 100        | 35        |
| 4     | EtOH    | 2             | 100        | 65        |
| 5     | IPA     | 2             | 100        | 25        |
| 6     | H2O     | 2             | 100        | 55        |
| 7     | H2O/EtOH (1:2) | 2  | 25 | 85        |
| 8     | H2O/EtOH (1:1) | 2  | 8  | 95        |
| 9     | H2O/EtOH (1:1) | 5  | 10 | 92        |
| 10    | H2O/EtOH (1:1) | 100 | trace |           |

Reaction conditions: benzaldehyde (1 mmol), malononitrile (1.1 mmol), and 10 mL of solvent or solvent mixture and the catalyst GO-supported PdNi at room temperature.

Figure 1. TEM image, HR-TEM image, and the particle size histogram of GO-supported PdNi nanoparticles.

Figure 2. XRD patterns of GO-supported PdNi NPs and Pd@GO NPs.

Figure 3. XPS spectra of palladium 3d (a) and nickel 2p (b) of Pd−Ni@GO nanoparticles.
prepared materials. Besides, the calculation of the mean crystalline particle size of monodisperse GO-supported PdNi nanoparticles was performed using the Scherrer equation. As a result of this calculation, the crystalline particle size was found to be around $3.42 \pm 0.38$ nm; $^{34-39}$ further, using the following equation, lattice parameter values of GO-supported PdNi nanoparticles were calculated as 3.88 Å, which is close to the pure Pd value of 3.89 Å. $^{40-42}$ 

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

The oxidation state of nickel and palladium metals in monodisperse GO-supported PdNi nanoparticles was determined using X-ray photoelectron spectroscopy (XPS). Using the Gaussian–Lorentzian method, the Ni 2p and Pd 3d regions of the spectrum were analyzed. As a reference, the C 1s peak was used at 286.4 eV and the correct binding energy was determined ($\pm 0.3$ eV) in all XPS spectra of the prepared materials. $^{39,40}$

For the prepared materials, experimental binding energies of Pd 3d and Ni 2p were found (Figure 3), and it is shown that palladium and nickel are mostly in the zero oxidation states. There are also some oxidized and unreduced species like the

| Entry | Substrate | Product | Yield (%) | Time (min) | Entry | Substrate | Product | Yield (%) | Time (min) |
|-------|-----------|---------|-----------|------------|-------|-----------|---------|-----------|------------|
| 1     | ![Image 1](image1.png) | ![Image 2](image2.png) | 95        | 8          | 8     | ![Image 3](image3.png) | ![Image 4](image4.png) | 95        | 7          |
| 2     | ![Image 5](image5.png) | ![Image 6](image6.png) | 98        | 6          | 9     | ![Image 7](image7.png) | ![Image 8](image8.png) | 90        | 8          |
| 3     | ![Image 9](image9.png) | ![Image 10](image10.png) | 98        | 5          | 10    | ![Image 11](image11.png) | ![Image 12](image12.png) | 92        | 8          |
| 4     | ![Image 13](image13.png) | ![Image 14](image14.png) | 94        | 5          | 11    | ![Image 15](image15.png) | ![Image 16](image16.png) | 95        | 8          |
| 5     | ![Image 17](image17.png) | ![Image 18](image18.png) | 95        | 10         | 12    | ![Image 19](image19.png) | ![Image 20](image20.png) | 96        | 6          |
| 6     | ![Image 21](image21.png) | ![Image 22](image22.png) | 92        | 8          | 13    | ![Image 23](image23.png) | ![Image 24](image24.png) | 92        | 7          |
| 7     | ![Image 25](image25.png) | ![Image 26](image26.png) | 90        | 10         |       |                     |                     |           |            |

Table 2. Knoevenagel Condensation of the Monodisperse GO-Supported PdNi Nanocatalyst with Aromatic Aldehydes and Malononitrile
2+ oxidation states of Pd and Ni. The shift of the binding energy of nickel to the 2p3/2 peak indicates the alloying of nickel with palladium at a low energy.\textsuperscript{39,40}

After full characterization of GO-supported PdNi NPs, their catalytic performance was evaluated for the synthesis by the Knoevenagel condensation reaction of malononitrile and aromatic aldehydes. In this study, our goal was to synthesize the compounds with a minimum amount of nanocatalyst and solvent in a very short reaction time at room temperature. Hence, to find the optimized reaction conditions, various reaction parameters such as solvent systems, the amount of nanocatalyst, and the reaction time were examined. Benzaldehyde and malononitrile were chosen as model reactants. Various solvents and solvent systems were used, such as acetonitrile, methanol, ethanol, water, dichloromethane, isopropanol, and different ethanol and water combinations. From the model reaction, ethanol and water in a 1:1 (v/v) combination gave the best results with the shortest reaction time and the highest yield among them. The reaction was also carried out with different amounts of monodisperse GO-supported PdNi NPs as the nanocatalyst at room temperature and it was found that 2 mg of GO-supported PdNi NPs was enough for the maximum catalytic performance. It can be concluded that 2 mg of GO-supported PdNi NPs is the amount of catalyst needed to conduct this Knoevenagel condensation reaction with ethanol/water (1:1) as a solvent system at room temperature (Table 1).

The optimized reaction conditions were further extended to utilize monodisperse GO-supported PdNi nanoparticles in the two-component Knoevenagel condensation of various aromatic aldehydes with malononitrile to produce benzylidenemalononitrile (BMN) derivatives. The results of the obtained products are summarized in Table 2. All reactions were successfully carried out using malononitrile (1.1 mmol), aromatic aldehyde (1 mmol), and the nanocatalyst GO-supported PdNi (2 mg) in a water/EtOH (1:1) mixture as the solvent at room temperature. The corresponding BMN derivatives were obtained in high yields within 5–10 min.

The reusability and recoverability of the monodisperse GO-supported PdNi nanocatalysts were also examined to test their stability as shown using the model reaction under standardized reaction conditions. This recycling study shows that the prepared heterogeneous nanocatalyst GO-supported PdNi can be reused over five successive runs without any significant decrease of catalytic performance (Figure 4). There is only a slight decrease in the catalytic performance of the catalysts due to the leaching of the prepared catalyst. Lastly, as illustrated in Table 3, on a comparison, it was observed that the prepared nanocatalyst system of GO-supported PdNi had one of the best catalytic performances for the model reaction as compared with that of other catalyst systems in the literature.

3. CONCLUSIONS

As a conclusion, an efficient, clean, environmentally friendly, and simple synthetic method was reported for the two-component Knoevenagel condensation reaction of aromatic aldehydes and malononitrile. For the first time, the highly monodisperse GO-supported PdNi nanocatalyst was successfully applied to these types of reactions. The prepared nanomaterials were fully characterized using many techniques and it was found that the prepared nanomaterials were homogeneously dispersed on the surface of GO. The corresponding benzylidenemalononitriles were obtained in excellent yields within 5–10 min by using the monodisperse GO-supported PdNi nanocatalyst under mild reaction conditions (water/ethanol, 1:1) at room temperature. Also, the model reaction carried out with the help of the prepared GO-supported PdNi nanoparticles has some superior advantageous such as a safe, simple work-up procedure, very short reaction times, great yields, and ambient reaction conditions. On the other hand, the prepared nanocatalyst could be recovered and reused several times in the subsequent runs without any significant loss of activity. After all, the prepared monodisperse nanomaterials can also be used for many other types of reactions as a catalyst.

4. MATERIAL AND METHODS

4.1. Preparation of GO-Supported PdNi Nanocomposites. Graphene oxide was synthesized using the hummers method\textsuperscript{45} and its characterization was presented in our previous works.\textsuperscript{47} GO-supported PdNi nanoparticles were synthesized by the impregnation of a solution of palladium chloride and nickel chloride into graphene oxide and then reduction of the metal precursors with NaBH₄. The obtained nanocomposites were characterized using various techniques such as X-ray diffraction, energy-dispersive X-ray spectroscopy, and transmission electron microscopy.

Table 3. Comparison of the GO-Supported PdNi Nanocatalyst with Recently Published Works for the Knoevenagel Condensation of Benzaldehyde and Malononitrile

| Catalyst | Solvent | Temp. (°C) | Time (min) | Yield (%) | Ref. |
|----------|---------|------------|------------|-----------|------|
| Taurine (25 mg) | H₂O | reflux | 14 | 86 | 3 |
| GO (1.5 mg/mL) | solvent free | rt | 120 | 67 | 44 |
| mpg-C₃N₄·Bu (50 mg) | CH₂CN | 70 | 240 | 97 | 43 |
| ZnO (100 mg) | solvent free | rt | 80 | 92 | 45 |
| Fe₃O₄·cystamine hydrochloride (0.05 g) | H₂O/CH₃CN (1:1) | 50 | 20 | 93 | 2 |
| MOF-Pd | DMSO-d₆ | rt | 6 | 42 | 13 |
| PMOV1 | solvent free | rt | 45 | 86 | 14 |
| GO supported PdNi | H₂O/CH₃OH (1:1) | rt | 8 | 95 | this work |
obtained by the ultrasonic double-reduction method\textsuperscript{36,37,48} stabilized by graphene oxide. Initially, an ultrasonic agitation was performed, and then 2.5 mmol GO, 0.25 mmol NiCl\textsubscript{2} and 0.25 mmol K\textsubscript{2}PdCl\textsubscript{4} were added. In the subsequent process, reflux was performed for the mixture obtained at 90 °C for 2 h. After this process, the mixture that has been taken to room temperature is allowed to cool down here. Palladium–nickel nanomaterials stabilized by graphene oxide are seen in a brownish black color. In the experiment, the homogeneity of the catalyst and the stability at the same location gave outstanding results.

4.2. Two-Component General Synthetic Procedure of Malononitrile and Aromatic Aldehydes Using Knoevenagel Condensation. First, 2 mg of nanocatalyst (GO-supported PdNi nanoparticles), 1 mmol aldehyde derivative, and 1.1 mmol malononitrile were added to 10 mL of water/ethanol (v/v, 1:1) in a vessel, and the mixture was sealed after mixing. The reaction mixture was continuously stirred at room temperature. The reaction was continued for 5–10 min, depending on the substitution of aldehydes. After the completion of the reaction (thin layer chromatography monitoring), the catalyst was centrifuged at 7500 rpm. Then, the nanocatalyst was recycled, washed several times with ethanol and water, and reused after drying. In the next process, the catalyst was reashed in ethanol and water to be used again and then dried. The resulting solution was evaporated under vacuum and products were purified by column chromatography for use (EtOAc/hexane 1:5). The obtained final pure products were characterized by \textsuperscript{1}H NMR and \textsuperscript{13}C NMR analysis (see Supporting Information for the spectra).

■ ASSOCIATED CONTENT

\begin{itemize}
\item Supporting Information
\end{itemize}

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00485.

\textsuperscript{1}H NMR spectra of BMN derivatives; 2-benzylidene-(E)-(1H)-1-naphthylidene-malononitrile (2) (Figure S1); 2-(4-chlorobenzylidene)malononitrile (3) (Figure S2); 2-(3,4-dichlorobenzylidene)malononitrile (10) (Figure S3) (PDF)

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Notes

The authors declare no competing financial interest.

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