

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

Nabih Lolak,[†] Esra Kuyuldar,[‡] Hakan Burhan,[‡] Haydar Goksu,[§] Süleyman Akocak,^{*,†} and Fatih Sen^{*,‡,§}

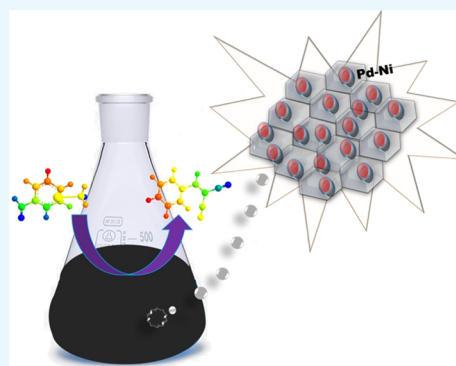
[†]Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Adiyaman University, 02040 Adiyaman, Turkey

[‡]Sen Research Group, Department of Biochemistry, Faculty of Arts and Science, Dumlupınar University, Evliya Çelebi Campus, 43100 Kütahya, Turkey

[§]Kaynasli Vocational College, Duzce University, 81900 Düzce, Turkey

Supporting Information

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.^{1–5} 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.^{6–10} A perusal of the literature reveals many examples of heterogeneous catalysts for the Knoevenagel condensation reaction, such as metal–organic framework (MOF)–NH₂,^{11,12} MOF–Pd,¹³ PMOV1,¹⁴ Zn@ZIF-67,¹⁵ ZIF-8,¹⁶ chitosan,¹⁷ Cd(II)-based coordination polymers,¹⁸ Ni(II)-based coordination polymers,¹⁹ PdAlO(OH),²⁰ mesoporous titanasilicate,²¹ basic MCM-41 silica,²² and acid–base bifunctional mesoporous MCM-41 silica.²³ 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.^{24–29} 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.^{11–17,19–23} Following the development of a new heterogeneous catalyst to increase the reaction rate,^{7,30–33} 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.

Received: February 21, 2019

Accepted: April 2, 2019

Published: April 16, 2019

2. RESULTS AND DISCUSSION

2.1. Characterization of Uniformly Dispersed GO-Supported PdNi Nanoparticles. Preliminary character-

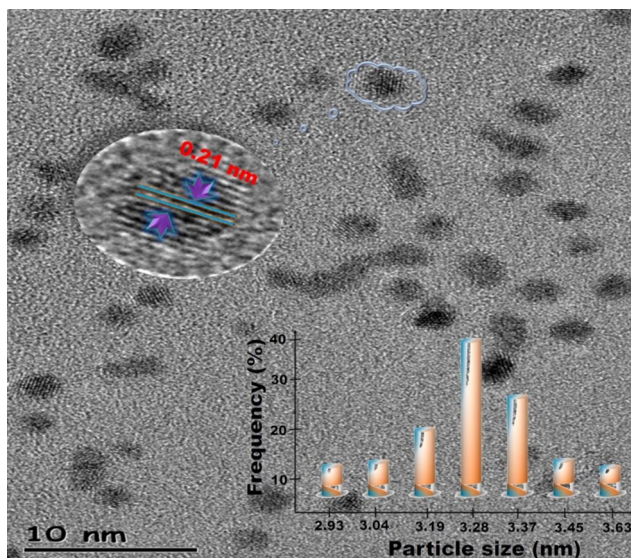


Figure 1. TEM image, HR-TEM image, and the particle size histogram of GO-supported PdNi nanoparticles.

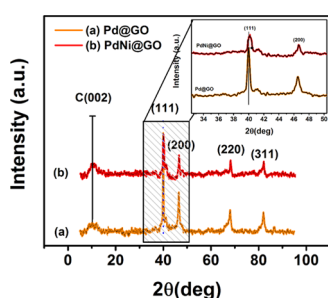


Figure 2. XRD patterns of GO-supported PdNi NPs and Pd@GO NPs.

ization 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 K_2PdCl_4 and $NiCl_2$ using an ultrasonic double-reduction method. In the next step, a solution was obtained, which was refluxed for 2 h,

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



entry	solvent	catalyst (mg)	time (min)	yield (%)
1	CH_2Cl_2	2	100	trace
2	CH_3CN	2	100	10
3	MeOH	2	100	35
4	EtOH	2	100	65
5	IPA	2	100	25
6	H_2O	2	100	55
7	$H_2O/EtOH$ (1:2)	2	25	85
8	$H_2O/EtOH$ (1:1)	2	8	95
9	$H_2O/EtOH$ (1:1)	5	10	92
10	$H_2O/EtOH$ (1:1)		100	trace

^aReaction 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.

followed by reduction of the resulting brownish black Ni^{2+} and Pd^{2+} 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 ($Pd_{54}Ni_{46}$).

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 11.34° . The strong signals of the prepared materials are mostly from Pd metals as shown in Figure 2. The observed peaks at around $2\theta = 42.1$, 47.5 , 68.7 , and 83.3° , which relate to (111), (200), (220), and (311) indicate the face-centered cubic structure of the

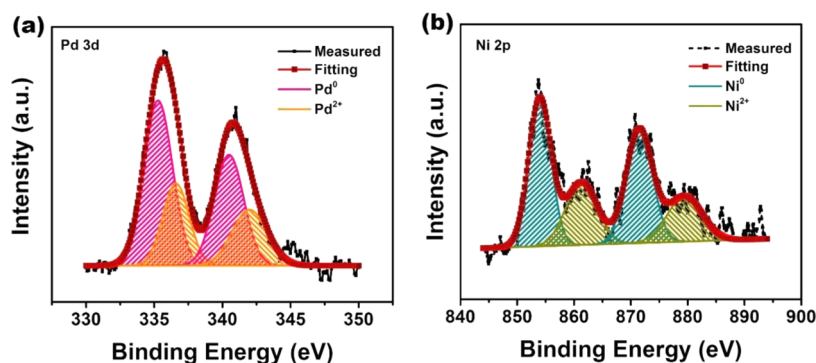
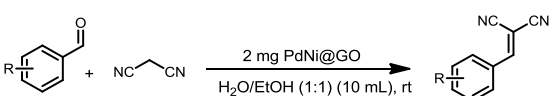




























Figure 3. XPS spectra of palladium 3d (a) and nickel 2p (b) of Pd–Ni@GO nanoparticles.

Table 2. Knoevenagel Condensation of the Monodisperse GO-Supported PdNi Nanocatalyst with Aromatic Aldehydes and Malononitrile



Entry	Substrate	Product	Yield (%)	Time (min)	Entry	Substrate	Product	Yield (%)	Time (min)
1			95	8	8			95	7
2			98	6	9			90	8
3			98	5	10			92	8
4			94	5	11			95	8
5			95	10	12			96	6
6			92	8	13			92	7
7			90	10					

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 ± 0.38 nm;^{34–39} further, using the following equation, lattice parameter values of GO-supported PdNi nanoparticles were calculated as 3.88 \AA , which is close to the pure Pd value of 3.89 \AA .^{40–42}

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

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 (± 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

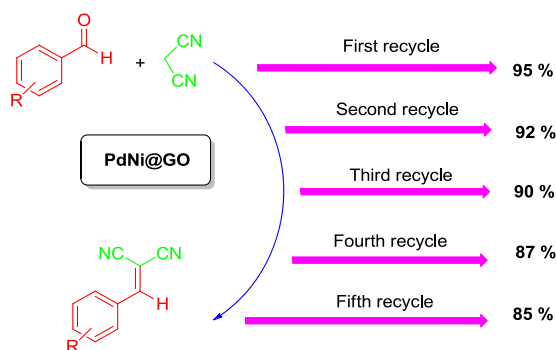


Figure 4. Reusability of the uniformly dispersed nanocatalyst GO-supported PdNi.

2+ oxidation states of Pd and Ni. The shift of the binding energy of nickel to the $2p_{3/2}$ peak indicates the alloying of nickel with palladium at a low energy.^{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 benzylidenemalonitrile (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 benzylidenemalonitriles 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 advantages 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 method⁴⁶ and its characterization was presented in our previous works.⁴⁷ GO-supported PdNi nanoparticles were

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)	H ₂ O	reflux	14	86	3
GO (1.5 mg/mL)	solvent free	rt	240	97	43
mpg-C ₃ N ₄ -Bu (50 mg)	CH ₃ CN	70	120	67	44
ZnO (100 mg)	solvent free	rt	80	92	45
Fe ₃ O ₄ -cystamine hydrochloride (0.05 g)	H ₂ O/EtOH (1:1)	50	20	93	2
MOF-Pd	DMSO- <i>d</i> ₆	rt	5	42	13
PMOVI	solvent free	70	45	86	14
GO supported PdNi	H ₂ O/EtOH (1:1)	rt	8	95	this work

obtained by the ultrasonic double-reduction method^{36,37,48} stabilized by graphene oxide. Initially, an ultrasonic agitation was performed, and then 2.5 mmol GO, 0.25 mmol NiCl₂, and 0.25 mmol K₂PdCl₄ 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 rewashed 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 ¹H NMR and ¹³C NMR analysis (see Supporting Information for the spectra).

■ ASSOCIATED CONTENT

📄 Supporting Information

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

¹H NMR spectra of BMN derivatives; 2-benzylidenemalononitrile (2) (Figure S1); 2-(4-chlorobenzylidene)malononitrile (4) (Figure S2); 2-(3,4-dichlorobenzylidene)malononitrile (10) (Figure S3) (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: akocaksuleyman@gmail.com.

*E-mail: fatihsen1980@gmail.com.

ORCID

Fatih Sen: 0000-0001-6843-9026

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank DPU BAP for funding (2014-05).

■ REFERENCES

(1) Elinson, M. N.; Feducovich, S. K.; Stepanov, N. O.; Vereshchagin, A. N.; Nikishin, G. I. A New Strategy of The Chemical Route to The Cyclopropane Structure: Direct Transformation of Benzylidenemalononitriles and Malononitrile into 1,1,2,2-Tetracyanocyclopropanes. *Tetrahedron* **2008**, *64*, 708–713.

(2) Maleki, R.; Kolvari, E.; Salehi, M.; Koukabi, N. Fe₃O₄–cysteamine Hydrochloride Magnetic Nanoparticles: New, Efficient and Recoverable Nanocatalyst for Knoevenagel Condensation Reaction. *Appl. Organomet. Chem.* **2017**, *31*, e3795–e3803.

(3) Shirini, F.; Daneshvar, N. Introduction of Taurine (2-Aminoethanesulfonic Acid) as A Green Bio-Organic Catalyst for The Promotion of Organic Reactions under Green Conditions. *RSC Adv.* **2016**, *6*, 110190–110205.

(4) Hu, Q.; Shi, X.-L.; Chen, Y.; Han, X.; Duan, P.; Zhang, W. Revisiting The Knoevenagel Condensations: A Universal and Flexible Bis-Ammoniated Fiber Catalyst for The Mild Synthesis of α,β -Unsaturated Compounds. *J. Ind. Eng. Chem.* **2017**, *54*, 75–81.

(5) Xu, H.; Pan, L.; Fang, X.; Liu, B.; Zhang, W.; Lu, M.; Xu, Y.; Ding, T.; Chang, H. Knoevenagel Condensation Catalyzed by Novel Nmm-Based Ionic Liquids in Water. *Tetrahedron Lett.* **2017**, *58*, 2360–2365.

(6) Almáši, M.; Zeleňák, V.; Opanasenko, M. V.; Čejka, J. Efficient and Reusable Pb(II) Metal–Organic Framework for Knoevenagel Condensation. *Catal. Lett.* **2018**, *148*, 2263–2273.

(7) Gilanizadeh, M.; Zeynizadeh, B. Binary Copper and Iron Oxides Immobilized on Silica-Layered Magnetite as A New Reusable Heterogeneous Nanostructure Catalyst for the Knoevenagel Condensation in Water. *Res. Chem. Intermed.* **2018**, *44*, 6053–6070.

(8) Turpaev, K.; Ermolenko, M.; Cresteil, T.; Drapier, J. C. Benzylidenemalononitrile Compounds as Activators of Cell Resistance to Oxidative Stress and Modulators of Multiple Signaling Pathways. A Structure-Activity Relationship Study. *Biochem. Pharmacol.* **2011**, *82*, 535–547.

(9) Gazit, A.; Yaish, P.; Gilon, C.; Levitzki, A.; Tyrphostins, I. Synthesis and Biological Activity of Protein Tyrosine Kinase Inhibitors. *J. Med. Chem.* **1989**, *32*, 2344–2352.

(10) Şen, B.; Akdere, E. H.; Şavk, A.; Gültekin, E.; Paralı, Ö.; Göksoy, H.; Şen, F. A Novel Thiocarbamide Functionalized Graphene Oxide Supported Bimetallic Monodisperse Rh–Pt Nanoparticles (RhPt/TC@GO NPs) for Knoevenagel Condensation of Aryl Aldehydes Together with Malononitrile. *Appl. Catal., B* **2018**, *225*, 148–153.

(11) Taher, A.; Lee, D.-J. J.; Lee, B.-K. K.; Lee, I.-M. M. Amine-Functionalized Metal–Organic Frameworks: An Efficient and Recyclable Heterogeneous Catalyst for the Knoevenagel Condensation Reaction. *Synlett* **2016**, *27*, 1433–1437.

(12) Martínez, F.; Orcajo, G.; Briones, D.; Leo, P.; Calleja, G. Catalytic Advantages of NH₂-Modified MIL-53(Al) Materials for Knoevenagel Condensation Reaction. *Microporous Mesoporous Mater.* **2017**, *246*, 43–50.

(13) Ezugwu, C. I.; Mousavi, B.; Asraf, M. A.; Luo, Z.; Verpoort, F. Post-Synthetic Modified MOF for Sonogashira Cross-Coupling and Knoevenagel Condensation Reactions. *J. Catal.* **2016**, *344*, 445–454.

(14) Viswanadham, B.; Jhansi, P.; Chary, K. V. R. R.; Friedrich, H. B.; Singh, S. Efficient Solvent Free Knoevenagel Condensation over Vanadium Containing Heteropolyacid Catalysts. *Catal. Lett.* **2016**, *146*, 364–372.

(15) Zanon, A.; Chaemchuen, S.; Verpoort, F. Zn@ZIF-67 as Catalysts for the Knoevenagel Condensation of Aldehyde Derivatives with Malononitrile. *Catal. Lett.* **2017**, *147*, 2410–2420.

(16) Tran, U. P. N.; Le, K. K. A.; Phan, N. T. S. Expanding Applications of Metal–Organic Frameworks: Zeolite Imidazolate Framework Zif-8 as An Efficient Heterogeneous Catalyst for The Knoevenagel Reaction. *ACS Catal.* **2011**, *1*, 120–127.

(17) Sakthivel, B.; Dhakshinamoorthy, A. Chitosan as A Reusable Solid Base Catalyst for Knoevenagel Condensation Reaction. *J. Colloid Interface Sci.* **2017**, *485*, 75–80.

(18) Karmakar, A.; Paul, A.; Mahmudov, K. T.; Guedes Da Silva, M. F. C.; Pombeiro, A. J. L. PH Dependent Synthesis of Zn(II) and Cd(II) Coordination Polymers with Dicarboxyl-Functionalized Arylhydrazone of Barbituric Acid: Photoluminescence Properties and Catalysts for Knoevenagel Condensation. *New J. Chem.* **2016**, *40*, 1535–1546.

(19) Agarwal, R. A.; Mukherjee, S. Two-Dimensional Flexible Ni(II)-Based Porous Coordination Polymer Showing Single-Crystal

to Single-Crystal Transformation, Selective Gas Adsorption and Catalytic Properties. *Polyhedron* **2016**, *105*, 228–237.

(20) Göksu, H.; Gü, E.; Göksu, H.; Gültekin, E. Pd Nanoparticles Incarcerated in Aluminium Oxy-Hydroxide: An Efficient and Recyclable Heterogeneous Catalyst for Selective Knoevenagel Condensation. *ChemistrySelect* **2017**, *2*, 458–463.

(21) Karmakar, B.; Chowdhury, B.; Banerji, J. Mesoporous Titanosilicate Ti-TUD-1 Catalyzed Knoevenagel Reaction: An Efficient Green Synthesis of Trisubstituted Electrophilic Olefins. *Catal. Commun.* **2010**, *11*, 601–605.

(22) Parida, K. M.; Rath, D. Amine Functionalized MCM-41: An Active and Reusable Catalyst for Knoevenagel Condensation Reaction. *J. Mol. Catal. A: Chem.* **2009**, *310*, 93–100.

(23) Shang, F.; Sun, J.; Wu, S.; Yang, Y.; Kan, Q.; Guan, J. Direct Synthesis of Acid-Base Bifunctional Mesoporous MCM-41 Silica and Its Catalytic Reactivity in Deacetalization-Knoevenagel Reactions. *Microporous Mesoporous Mater.* **2010**, *134*, 44–50.

(24) Li, C.; Sato, T.; Yamauchi, Y. Electrochemical Synthesis of One-Dimensional Mesoporous Pt Nanorods Using the Assembly of Surfactant Micelles in Confined Space. *Angew. Chem., Int. Ed.* **2013**, *52*, 8050–8053.

(25) Jiang, B.; Li, C.; Malgras, V.; Imura, M.; Tominaka, S.; Yamauchi, Y. Mesoporous Pt Nanospheres with Designed Pore Surface as Highly Active Electrocatalyst. *Chem. Sci.* **2016**, *7*, 1575–1581.

(26) Li, C.; Iqbal, M.; Lin, J.; Luo, X.; Jiang, B.; Malgras, V.; Wu, K. C.-W.; Kim, J.; Yamauchi, Y. Electrochemical Deposition: An Advanced Approach for Templated Synthesis of Nanoporous Metal Architectures. *Acc. Chem. Res.* **2018**, *51*, 1764–1773.

(27) Li, C.; Tan, H.; Lin, J.; Luo, X.; Wang, S.; You, J.; Kang, Y.-M.; Bando, Y.; Yamauchi, Y.; Kim, J. Emerging Pt-Based Electrocatalysts with Highly Open Nanoarchitectures for Boosting Oxygen Reduction Reaction. *Nano Today* **2018**, *21*, 91–105.

(28) Yamauchi, Y.; Takai, A.; Nagaura, T.; Inoue, S.; Kuroda, K. Pt Fibers with Stacked Donut-Like Mesospace by Assembling Pt Nanoparticles: Guided Deposition in Physically Confined Self-Assembly of Surfactants. *J. Am. Chem. Soc.* **2008**, *130*, 5426–5427.

(29) Fujita, N.; Castle, T.; Terasaki, O.; Yamauchi, Y.; et al. Shape- and Size-Controlled Synthesis in Hard Templates: Platinum Nanoparticles. *J. Am. Chem. Soc.* **2011**, *133*, 14526–14529.

(30) Akocak, S.; Şen, B.; Lolak, N.; Şavk, A.; Koca, M.; Kuzu, S.; Şen, F. One-Pot Three-Component Synthesis of 2-Amino-4H-Chromene Derivatives by Using Monodisperse Pd Nanomaterials Anchored Graphene Oxide as Highly Efficient and Recyclable Catalyst. *Nano-Struct. Nano-Objects* **2017**, *11*, 25–31.

(31) Şen, B.; Lolak, N.; Paralı, Ö.; Koca, M.; Şavk, A.; Akocak, S.; Şen, F. Bimetallic PdRu/Graphene Oxide Based Catalysts for One-Pot Three-Component Synthesis of 2-Amino-4H-Chromene Derivatives. *Nano-Struct. Nano-Objects* **2017**, *12*, 33–40.

(32) Pamuk, H.; Aday, B.; Şen, F.; Kaya, M. Pt NPs@GO as A Highly Efficient and Reusable Catalyst for One-Pot Synthesis of Acridinedione Derivatives. *RSC Adv.* **2015**, *5*, 49295–49300.

(33) Esirden, İ.; Erken, E.; Kaya, M.; Sen, F. Monodisperse Pt NPs@rGO as Highly Efficient and Reusable Heterogeneous Catalysts for The Synthesis of 5-Substituted 1H-Tetrazole Derivatives. *Catal. Sci. Technol.* **2015**, *5*, 4452–4457.

(34) Bozkurt, S.; Tosun, B.; Sen, B.; Akocak, S.; Savk, A.; Ebeoğlul, M. F.; Sen, F. A Hydrogen Peroxide Sensor Based on TNM Functionalized Reduced Graphene Oxide Grafted with Highly Monodisperse Pd Nanoparticles. *Anal. Chim. Acta* **2017**, *989*, 88–94.

(35) Şen, B.; Aygün, A.; Şavk, A.; Akocak, S.; Şen, F. Bimetallic Palladium–iridium Alloy Nanoparticles as Highly Efficient and Stable Catalyst for The Hydrogen Evolution Reaction. *Int. J. Hydrogen Energy* **2018**, *43*, 20183–20191.

(36) Sen, B.; Kuzu, S.; Demir, E.; Akocak, S.; Sen, F. Polymer-Graphene Hybride Decorated Pt Nanoparticles as Highly Efficient and Reusable Catalyst for the Dehydrogenation of Dimethylamine–borane at Room Temperature. *Int. J. Hydrogen Energy* **2017**, *42*, 23284–23291.

(37) Şen, B.; Kuzu, S.; Demir, E.; Akocak, S.; SüleymanŞen, F. Highly Monodisperse RuCo Nanoparticles Decorated on Functionalized Multiwalled Carbon Nanotube with The Highest Observed Catalytic Activity in The Dehydrogenation of Dimethylamine–borane. *Int. J. Hydrogen Energy* **2017**, *42*, 23292–23298.

(38) Şahin, B.; Aygün, A.; Gündüz, H.; Şahin, K.; Demir, E.; Akocak, S.; Şen, F. Cytotoxic Effects of Platinum Nanoparticles Obtained from Pomegranate Extract by The Green Synthesis Method on The MCF-7 Cell Line. *Colloids Surf., B* **2018**, *163*, 119–124.

(39) Koskun, Y.; Şavk, A.; Şen, B.; Şen, F. Highly Sensitive Glucose Sensor Based on Monodisperse Palladium Nickel/Activated Carbon Nanocomposites. *Anal. Chim. Acta* **2018**, *1010*, 37–43.

(40) Goksu, H.; Yıldız, Y.; Çelik, B.; Yazici, M.; Kilbas, B.; Sen, F. Eco-Friendly Hydrogenation of Aromatic Aldehyde Compounds by Tandem Dehydrogenation of Dimethylamine-Borane in The Presence of A Reduced Graphene Oxide Furnished Platinum Nanocatalyst. *Catal. Sci. Technol.* **2016**, *6*, 2318–2324.

(41) Çelik, B.; Yıldız, Y.; Sert, H.; Erken, E.; Koşkun, Y.; Şen, F. Monodispersed Palladium–cobalt Alloy Nanoparticles Assembled on Poly(N-Vinyl-Pyrrolidone) (PVP) as a Highly Effective Catalyst for Dimethylamine Borane (DMAB) Dehydrocoupling. *RSC Adv.* **2016**, *6*, 24097–24102.

(42) Şen, B.; Kuzu, S.; Demir, E.; Yıldırım, E.; Şen, F. Highly Efficient Catalytic Dehydrogenation of Dimethyl Ammonia Borane via Monodisperse Palladium–Nickel Alloy Nanoparticles Assembled on PEDOT. *Int. J. Hydrogen Energy* **2017**, *42*, 23307–23314.

(43) Islam, S. M.; Roy, A. S.; Dey, R. C.; Paul, S. Graphene Based Material as a Base Catalyst for Solvent Free Aldol Condensation and Knoevenagel Reaction at Room Temperature. *J. Mol. Catal. A: Chem.* **2014**, *394*, 66–73.

(44) Su, F.; Antonietti, M.; Wang, X. Mpg-C3N4 as a Solid Base Catalyst for Knoevenagel Condensations and Transesterification Reactions. *Catal. Sci. Technol.* **2012**, *2*, 1005–1009.

(45) Basude, M.; Sunkara, P.; Puppala, V. S. ZnO Catalyst for Knoevenagel Condensation in Aqueous Medium at Ambient Temperature. *J. Chem. Pharm. Res.* **2013**, *5*, 46–50.

(46) Hummers, W. S.; Offeman, R. E. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* **1958**, *80*, 1339.

(47) Demir, E.; Savk, A.; Sen, B.; Sen, F. A Novel Monodisperse Metal Nanoparticles Anchored Graphene Oxide as Counter Electrode for Dye-Sensitized Solar Cells. *Nano-Struct. Nano-Objects* **2017**, *12*, 41–45.

(48) Yıldız, Y.; Kuzu, S.; Sen, B.; Savk, A.; Akocak, S.; Şen, F. Different Ligand Based Monodispersed Pt Nanoparticles Decorated with RGO As Highly Active and Reusable Catalysts for The Methanol Oxidation. *Int. J. Hydrogen Energy* **2017**, *42*, 13061–13069.