

The British University in Egypt

BUE Scholar

Chemical Engineering

Engineering

Spring 4-9-2019

Hydrothermal synthesis of graphene supported Pd/Fe₃O₄ nanoparticles as efficient magnetic catalysts for Suzuki Cross – Coupling

Hany A. Elazab Dr

The British University in Egypt, hany.elazab@bue.edu.eg

Follow this and additional works at: https://buescholar.bue.edu.eg/chem_eng

 Part of the [Chemical Engineering Commons](#)

Recommended Citation

Elazab, Hany A. Dr, "Hydrothermal synthesis of graphene supported Pd/Fe₃O₄ nanoparticles as efficient magnetic catalysts for Suzuki Cross – Coupling" (2019). *Chemical Engineering*. 8.
https://buescholar.bue.edu.eg/chem_eng/8

This Article is brought to you for free and open access by the Engineering at BUE Scholar. It has been accepted for inclusion in Chemical Engineering by an authorized administrator of BUE Scholar. For more information, please contact bue.scholar@gmail.com.

Hydrothermal synthesis of graphene supported Pd/Fe₃O₄ nanoparticles as efficient magnetic catalysts for Suzuki Cross – Coupling

Hany A. Elazab^{1,*}, Mamdouh A. Gadalla^{1,4}, Mohamed A. Sadek¹, Tamer T. El-Idreesy^{2,3,*}

¹Department of Chemical Engineering, Faculty of Engineering, The British University in Egypt, El-Shorouk City, Cairo, Egypt.

²Department of Chemistry, Faculty of Science, Cairo University, Giza 12613, Egypt.

³Department of Chemistry, School of Sciences and Engineering, The American University in Cairo, New Cairo 11835, Egypt.

⁴Department of Chemical Engineering, Faculty of Engineering, Port Said University, Egypt

*corresponding author e-mail address: elazabha@vcu.edu

ABSTRACT

This research reports a reproducible, reliable, and efficient method for preparing palladium nanoparticles dispersed on a composite of Fe₃O₄ and graphene as an active catalyst with high efficiency for being used in Suzuki cross – coupling reactions. Graphene supported Pd/Fe₃O₄ nanoparticles (Pd/Fe₃O₄/G) exhibit a remarkable catalytic performance towards Suzuki coupling reactions. Moreover, the prepared catalyst recyclability was up to nine times without losing its high catalytic activity. The catalyst was prepared using hydrothermal synthesis; the prepared catalyst is magnetic in order to facilitate catalyst separation out of the reaction medium after reaction completion simply through using a strong magnet. This approach offers unique advantages including recyclability, mild reaction conditions, and reproducibility. Furthermore, the magnetic properties of the prepared catalyst made a huge enhancement to the ability to purify the reaction products from catalyst and other side products. The high catalytic performance and recyclability of the prepared catalyst are due to the strong interaction between the catalyst and the support. Moreover, the reduced GO nanosheets have defect sites acting as nucleation centers to anchor the Pd and Fe₃O₄ nanoparticles and hence minimize the harmful effect of potential agglomeration and subsequently the anticipated decrease in the catalyst catalytic activity as a direct impact for this unfavorable agglomeration.

Keywords: Graphene, Cross-Coupling, Magnetite (Fe₃O₄), Hydrothermal synthesis, Catalyst recycling.

1. INTRODUCTION

The application of palladium as a transition metal in combination with metal nanoparticles have been attracted so many research efforts to design a new advanced catalytic systems with amazing unique hybrid properties of single metal atoms and bulk metal [1-4]. The main issues in the catalysis field that are associated with environment, economy, catalytic activity, recyclability, reproducibility and scale-up technical problems have been extensively studied during the past few decades [5, 6]. Those previously mentioned drawbacks in the catalysis field were under scientific investigation and huge efforts have been made in the field of research and development to overcome those issues [7-14]. The improvement of those issues took place through several routes including not only introduction of bottom-up approaches, applying strict control of particle size and overall particle size distribution in order to achieve new chemical and physical properties, improvements made in the synthesis protocols and methodologies, but also using different carbon-based supports like graphene and carbon nanotubes [15-25]. The materials at the nanoscale show distinctive properties and remarkable synergistic effects as a result of a combination of several nanostructured materials [23-28]. They simply could be used as heterogeneous catalysts with notably recognized enhancement from the perspective of shape, size, reaction active sites, the structure of the surface, catalytic activity and selectivity [29-31].

Recently, new strategies had been adopted for the synthesis of magnetic nanoparticles. The synthetic approaches can simply include several techniques like co-precipitation, thermal decomposition, micro-emulsion, microwave-assisted synthesis, and hydrothermal synthesis [15, 16, 19-21]. The development efforts also include using of high surface area support like graphene which is currently considered due to its huge surface area, remarkable thermal, chemical, and mechanical stability [7-14]. The main advantage of using graphene as an ideal support is that the structural defects in its lattice can be used simply to anchor metallic nanoparticles to the surface of the graphene producing new surface functionalities of a tunable metal-support interaction.[32-39] Recently, it was found that the super-paramagnetic behavior of magnetite nanoparticles enabled them from being ideal candidate for potential applications in physical, biological, chemical, biomedical, and environmental engineering fields as well as such industrially important reactions including Suzuki-Miyaura, Heck, Sonogashira cross-coupling reactions, hydrogenation, and hydroformylation [24, 32, 35, 38, 39-48]. In this scientific research, our efforts were mainly focused on the design of a facile hydrothermal synthesis approach to prepare Pd-Fe₃O₄/G nanocomposite with an excellent catalytic activity and recyclability for up to nine times towards Suzuki cross coupling reactions. The main advantage of using magnetite as magnetic nanoparticles (MNPs) is that they offer the platform of a facile

route to separate the catalyst after reaction completion through

using a strong magnet as an external magnetic field.

2. MATERIALS AND METHODS

Chemicals were used as received without any modification or further steps of purification. Palladium acetyl acetonate, and ferric acetyl acetonate, DMSO, aryl bromide, bromobenzene, and potassium carbonate were purchased from Alfa Aesar. Graphite powder with high purity was obtained from Sigma Aldrich.

2.1 Catalyst Synthesis

2.1.1 Synthesis of Graphene Oxide (GO). Hummers - Offeman method was used in order to prepare graphene oxide (GO). The oxidation of graphite powder of high-purity took place with a mixture of H₂SO₄ and KMnO₄. Graphite powder (4.5 g) and sodium nitrate (2.5 g) were mixed and the prepared mixture was kept in a conical flask equipped with ice bath.

Continuous stirring was maintained and a concentrated solution of H₂SO₄ (115 ml) was added slowly. Then, potassium permanganate (15 g) was also added within 2.5 h. Then, deionized water (230 ml) was added and the mixture was maintained at a constant temperature of 80 °C and stirring was continued for 20 min. Then, deionized water (600 mL) along with (10%) H₂O₂ (30 mL) were also added. The entire solution was stirred for another 5 min. Finally, the yellow-brownish cake was then washed for several times using 1M HCl (30 mL) followed by hot deionized water (3 L) and the resulting GO solid was dried under vacuum at 60 °C overnight [40-43].

2.1.2 Hydrothermal synthesis of Graphene supported Pd/Fe₃O₄. In the typical synthetic procedure, 126 mg of ferric acetyl acetonate were dissolved in 30 ml benzyl ether; then the entire mixture was added to a conical flask equipped with a magnetic stirrer. Then, 28 mg palladium acetyl acetonate was added to the previously mentioned solution under stirring conditions. Then, 3.5 ml GO/DMSO were added to the mixture. Hence, a mixture of oleylamine and oleic acid (25 ml each) used as ligating solvents in order to stabilize the nanocrystals through applying passivation to the surfaces was added during stirring for 2 h till a homogeneous solution is formed. The mixture was maintained in an oil bath and

stirring hot plate was used for performing continuous stirring at 110 °C. Stirring continues until obtaining a clear solution. Finally, the entire prepared mixture was used as the starting solution for the hydrothermal synthesis of Pd-Fe₃O₄/G. The stainless steel autoclave with the starting solution was completely sealed and maintained at 130 °C for 5 h in an electric oven. After the hydrothermal treatment, the autoclave was cooled down to room temperature. The obtained nanoparticles were washed with deionized water and the solution was added to centrifuge tubes and centrifugation took place at a rate of 11000 r.p.m for 30 min. and then the solution was washed several times with ethanol and then decanted. The prepared Pd/Fe₃O₄ supported on Graphene was then dried overnight under vacuum at 60 °C.

2.2 Catalyst Characterization.

An electron microscope (JEOL JEM-1230) was used to obtain TEM images. X-ray photoelectron spectroscopy (XPS) was used to perform the surface analysis. The X-ray diffraction patterns were measured using an analytical X-ray diffraction unit.

2.3 General procedure of Suzuki cross-coupling reactions using graphene supported Pd/ Fe₃O₄ catalyst.

4 mL H₂O: EtOH (1:1) was used to dissolve (0.24 mmol, 1 eq.), then aryl bromide was added. Aryl boronic acid (0.3 mmol, 1.2 eq.) and potassium carbonate (1.53 mmol, 3 eq.) were also added and hence, 3.5 g graphene supported palladium/iron oxide catalyst (Pd-Fe₃O₄/G was also added and the reaction mixture was then heated using CEM Discover microwave (250 W, 2.45 MHz) at 80 °C for 10 min. The reaction conversion was measured using GC-MS. The catalyst recycling procedure is implemented immediately after the reaction completion where the used solvent was decanted and the catalyst was removed via applying an external magnetic field like a strong magnet. Catalyst was washed with ethanol several times to remove any residues from the surface of the catalyst. Then, the catalyst is ready for the next run.

3. RESULTS

3.1 Suzuki cross – coupling reaction using Graphene supported Pd/Fe₃O₄.

Table 1 gives an overview of the impact of using graphene supported Pd/ Fe₃O₄ as an ideal catalyst for the reaction between bromobenzene and phenyl boronic acid could achieve complete conversion of 100%. The reactants could easily be converted to biphenyl within a short reaction time of 10 min at a temperature of 120 °C, while less catalytic activity was recorded within 10 min, at 80, 100 and 150 °C.

Figure 1-a shows the obtained TEM images of graphene supported Pd/Fe₃O₄ catalyst before the reaction and after the recycling process. TEM images reveal the nice dispersion of palladium and iron oxide nanoparticles of size (12 - 16 nm) and (40 - 60 nm) on the grapheme support respectively, while there

was a severe agglomeration after the catalyst ninth recycling step. The TEM images are supporting the experimental findings of a remarkable catalytic performance in case of graphene supported Pd/Fe₃O₄ catalyst when compared with the same catalyst after the ninth recycling step. This is mainly because of the agglomeration as shown in **Figure 1-b**. It is interesting to notice the remarkable role of graphene as an ideal support in nanoparticles formation with a smaller particle size that has a good dispersion on the graphene surface.

The Suzuki cross-coupling reaction was investigated as shown in (**Scheme 1**). The effect of temperature on the catalytic activity was carried out at a fixed reaction time (10 min) but for several temperatures (80, 100, 120, 150 °C) using the synthesized Pd- Fe₃O₄/GO catalysts (1 mol %). The experimental data refers to

the great influence of temperature variation on the yield as it was found that increasing the temperature leads to a higher conversion to as in **Table 1**.

Table 1 The impact of using Graphene supported Pd/Fe₃O₄ on the conversion percentage.

Catalysts	Mol %	Temperature (°C)	Time (min.)	Conversion %
Pd-Fe ₃ O ₄ /G	1	80 °C	10	Conversion < 80
Pd-Fe ₃ O ₄ /G	1	100 °C	10	92
Pd-Fe ₃ O ₄ /G	1	120 °C	10	100
Pd-Fe ₃ O ₄ /G	1	150 °C	10	Conversion < 80

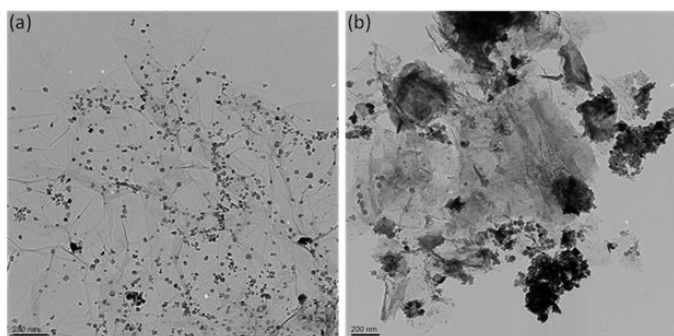
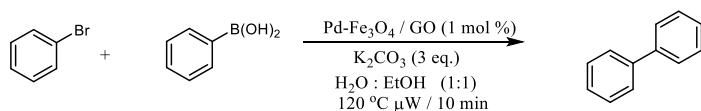


Figure 1. Graphene supported Pd/Fe₃O₄ catalyst TEM images (a) before reaction (b) after ninth run.



Scheme 1. Suzuki cross coupling reactions using Graphene supported Pd/Fe₃O₄ catalyst.

Table 2. Suzuki cross coupling using Pd/Fe₃O₄ and Pd- Fe₃O₄/GO catalyst.

Entry	Aryl halide	Boronic acid	Product	Conversion ^a (%)	Conversion ^b (%)
1				80 %	100 %
2				75 %	95 %
3				68 %	90 %
4				74 %	96 %
5				72 %	88 %

^a Aryl halide (0.32 mmol, 1 eq.), aryl boronic acid (0.382 mmol, 1.2 eq.), potassium carbonate (0.96 mmol, 3 eq.), and Pd- Fe₃O₄/G (1 mol%) in 4 mL (H₂O:EtOH) (1:1) were heated at 120 °C (MWI) for 10 min.

** Conversions were determined by GC-MS.

^a Conversion was calculated using (1 mol%) Pd/Fe₃O₄ catalyst.

^b Conversion was calculated using (1 mol%) Pd- Fe₃O₄/G catalyst.

It is remarkable that repeating the cross-coupling reaction using optimized conditions (10 min and 120 °C) but with replacing Pd-Fe₃O₄/G catalyst with Pd/Fe₃O₄ nanoparticles lead to lower conversion to the desired product. Those experimental data confirm obviously the positive effect of graphene as an ideal support that could efficiently minimize the agglomeration of Pd nanoparticles and hence increase the catalyst activity. The use of different substrates was explored in Table 2 & 3.

Table 3. Diversity study using Pd/ Fe₃O₄ and Pd- Fe₃O₄/G catalyst.

Entry	Aryl halide	Boronic acid	Product	Conversion ^a (%)	Conversion ^b (%)
1				70 %	94 %
2				67 %	95 %
3				81 %	92 %
4				60 %	88 %
5				68 %	92 %
6				82 %	87 %

* Aryl halide (0.32 mmol), aryl boronic acid (0.382 mmol, 1.2 eq.), K₂CO₃ (0.96 mmol, 3 eq.), and Pd-Fe₃O₄/G (1 mol %) in 4 mL (H₂O:EtOH) (1:1) were heated at 120 °C (MWI) for 10 min.

** Conversions were determined by GC-MS

^a Conversion was calculated using (1 mol%) Pd/Fe₃O₄ catalyst.

^b Conversion was calculated using (1 mol%) Pd- Fe₃O₄/G catalyst.

Figure 2 displays the X-ray diffraction pattern of palladium, magnetite and palladium/magnetite supported on Graphene. The previously mentioned catalyst was prepared using hydrothermal synthesis. The XRD pattern shows fcc typical pattern with a sharp diffraction peak at 2θ = 40° in case of palladium. The XRD patterns also confirm the presence of spinal Fe₃O₄ (magnetite) as shown in Figure 2.

Characterization of graphene supported Pd-Fe₃O₄ samples prepared by hydrothermal method was also investigated using several techniques including XPS, XRD, and TEM characterization techniques.

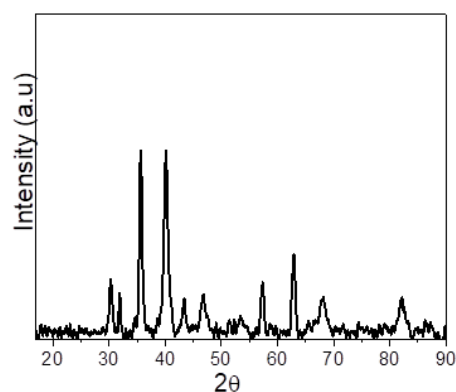


Figure 2. X-ray Diffraction Pattern of Pd/ Fe₃O₄ supported on Graphene.

The XPS technique was used to investigate the surface analysis of the prepared catalyst as shown in Figure 3. The catalyst has a binding energy of Fe 2P^{3/2} at 710.5 eV, and also another binding energy of Fe 2P^{1/2} at 723.7 eV which are characteristic to the presence of Fe₃O₄. The presence of Pd as Pd⁰ was confirmed as the binding energies of Pd 3d^{5/2} at 334.8 eV, and Pd 3d^{3/2} were recognized.

Hydrothermal synthesis of graphene supported Pd/Fe₃O₄ nanoparticles as an efficient magnetic catalysts for Suzuki Cross – Coupling

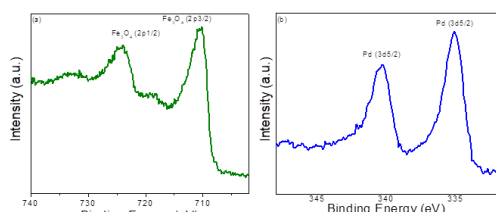


Figure 3. (a) XPS (Fe2p) and (b) XPS (Pd3d) of Pd/ Fe₃O₄ supported on Graphene.

The recycling protocol was explained as shown in Figure 4. It is remarkable that using magnetite could significantly enhance the process of catalyst separation from the reaction mixture as it can be easily separated using a strong magnet.

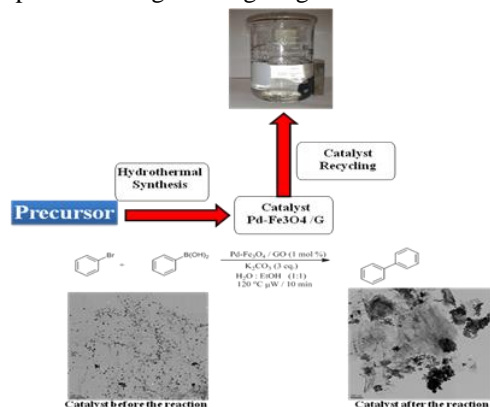


Figure 4. Separating the Pd-Fe₃O₄/G catalyst from reaction mixture.

Table 4. Recycling experimental data for Pd-Fe₃O₄/G catalyst using a concentration of 0.5, 1 mol %.^a

Run	Conversion (%) ^b (0.5 mol %)	Conversion (%) ^b (1 mol %)
1	100	100
2	98	100
3	96	100
4	94	100
5	80	98
6	62	96
7	60	92
8	55	88
9	53	82

^a Aryl halide (50 mg), boronic acid (47 mg), potassium carbonate (133 mg.), and Pd-Fe₃O₄/G (0.5 mol%) or (1 mol%) in 4 mL (H₂O:EtOH) (1:1) were heated at 120 °C (MWI) for 10 min.

4. CONCLUSIONS

An efficient method was adopted to generate a highly active nanoparticle based catalyst supported on graphene as an ideal support. The Pd-Fe₃O₄/G catalyst was synthesized via using hydrothermal synthesis technique. Furthermore, the recovery and the recycling process of the catalyst could be implemented up to seven times with high catalytic activity near 100% thus providing high economic viability. It can be easily concluded from

5. REFERENCES

- [1] Chen S.T., Synthesis of Pd/Fe₃O₄ Hybrid Nanocatalysts with Controllable Interface and Enhanced Catalytic Activities for CO Oxidation, *Journal of Physical Chemistry C*, 116, 23, 12969-12976, 2012, <http://dx.doi.org/10.1021/jp3036204>
- [2] Radwan N.R.E., El-Shall M.S., Hassan H.M.A., Synthesis and characterization of nanoparticle Co₃O₄, CuO and NiO catalysts prepared by physical and chemical methods to minimize air pollution, *Applied*

^b Conversions were examined using GC-MS.

Table 4 confirms that the catalyst has an ideal performance that is reflected in its high catalytic activity. The catalyst was recycled up to four times with almost 100 % conversion in case of using 0.5 mol %; while it was recycled up to seven times with conversion near 100 % when the catalyst mole percentage was doubled to be 1 mol % as shown in figure 4. The structural defects in graphene play a crucial role in improving interaction with anchored metal nanoparticles [32, 35, 39].

TEM images can be used as a proof of catalyst deactivation that took place due to the agglomeration of palladium and magnetite nanoparticles on the graphene surface as shown previously in Figure 1-b.

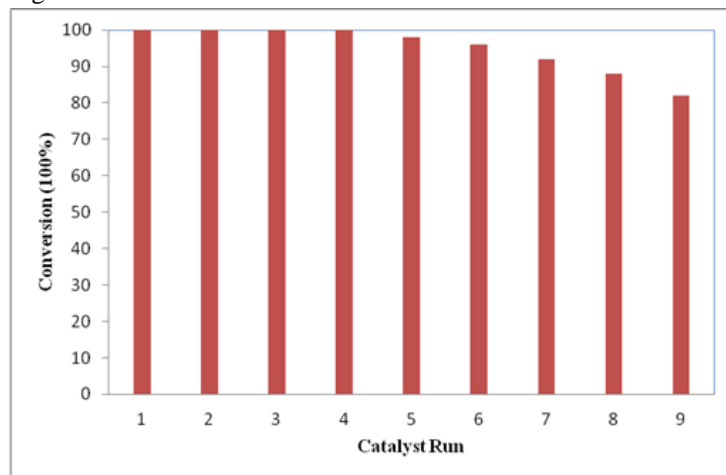


Figure 5. Recycling experiments of Pd - Fe₃O₄ / G catalyst for Suzuki cross coupling reaction.

The leaching process of palladium from prepared catalyst was investigated by repeating the reaction in the presence of 0.5 mol% catalyst at 150 °C for 10 min under heating using microwave assisted synthesis technique. Hence, the resulting mixture was filtered and then the palladium content was measured in the filtrate and it was found to be 145 ppm based on the ICP-MS analysis.

characterization that palladium nanoparticles and magnetite nanoparticles are uniformly dispersed onto the surface of graphene nanosheets.

This easy and efficient recycling process of the catalyst is simply due to the magnetic properties of magnetite, thus lead to achieving high yields over different substrates for Suzuki cross coupling reactions.

Catalysis A: General, 331, 0, 8-18, 2007, <https://doi.org/10.1016/j.apcata.2007.07.005>.

[3] Wang H.L., Ni(OH)₂ Nanoplates Grown on Graphene as Advanced Electrochemical Pseudocapacitor Materials, *Journal of the American Chemical Society*, 132, 21, 7472-7477, 2010, <https://doi.org/10.1021/ja102267j>.

[4] Wang W.W., Zhu Y.J., Ruan M.L., Microwave-assisted synthesis and magnetic property of magnetite and hematite nanoparticles, *Journal of*

- Nanoparticle Research*, 9, 3, 419-426, 2007, <https://doi.org/10.1007/s11051-005-9051-8>.
- [5] Elazab H., Microwave-assisted synthesis of Pd nanoparticles supported on FeO, CoO, and Ni(OH) nanoplates and catalysis application for CO oxidation, *Journal of Nanoparticle Research*, 16, 7, 1-11, 2014.
- [6] Mankarious R.A., et al., Bulletproof vests/shields prepared from composite material based on strong polyamide fibers and epoxy resin, *Journal of Engineering and Applied Sciences*, 12, 10, 2697-2701, 2017.
- [7] Mohsen W., Sadek M.A., Elazab H.A., Green synthesis of copper oxide nanoparticles in aqueous medium as a potential efficient catalyst for catalysis applications, *International Journal of Applied Engineering Research*, 12, 24, 14927-14930, 2017, <https://doi.org/10.4066/2591-8036.e105>.
- [8] Mostafa A.R., Omar H.A.-S., Hany A.E., Preparation of Hydrogel Based on Acryl Amide and Investigation of Different Factors Affecting Rate and Amount of Absorbed Water, *Agricultural Sciences*, 8, 2, 11, 2017, <https://doi.org/10.4236/as.2017.82011>.
- [9] Radwan M.A., et al., Mechanical characteristics for different composite materials based on commercial epoxy resins and different fillers, *Journal of Engineering and Applied Sciences*, 12, 5, 1179-1185, 2017.
- [10] Andrade A.L., Catalytic Effect of Magnetic Nanoparticles Over the H(2)O(2) Decomposition Reaction, *Journal of Nanoscience and Nanotechnology*, 9, 6, 3695-3699, 2009, <https://doi.org/10.1166/jnn.2009.NS53>.
- [11] Kustov A.L., CO methanation over supported bimetallic Ni-Fe catalysts: From computational studies towards catalyst optimization, *Applied Catalysis a-General*, 320, 98-104, 2007, <https://doi.org/10.1016/j.apcata.2006.12.017>.
- [12] Lohitharn N., Goodwin J.G., Impact of Cr, Mn and Zr addition on Fe Fischer-Tropsch synthesis catalysis: Investigation at the active site level using SSITKA, *Journal of Catalysis*, 257, 1, 142-151, 2008, <https://doi.org/10.1016/j.jcat.2008.04.015>.
- [13] Moreau F., Bond G.C., CO oxidation activity of gold catalysts supported on various oxides and their improvement by inclusion of an iron component, *Catalysis Today*, 114, 4, 362-368, 2006, <https://doi.org/10.1016/j.cattod.2006.02.074>.
- [14] Sarkari M., Fischer-Tropsch synthesis: Development of kinetic expression for a sol-gel Fe-Ni/Al₂O₃ catalyst, *Fuel Processing Technology*, 97, 130-139, 2012.
- [15] Elazab H., The Effect of Graphene on Catalytic Performance of Palladium Nanoparticles Decorated with FeO, CoO, and Ni (OH): Potential Efficient Catalysts Used for Suzuki Cross-Coupling, *Catalysis Letters*, 147, 6, 1510-1522, 2017, <https://doi.org/10.1007/s10562-017-1990-z>.
- [16] Elazab H.A., The continuous synthesis of Pd supported on Fe₃O₄ nanoparticles: A highly effective and magnetic catalyst for CO oxidation, *Green Processing and Synthesis*, 6, 4, 413-424, Year, <https://doi.org/10.1515/gps-2016-0168>.
- [17] Elazab H.A., Sadek M.A., El-Idreesy T.T., Microwave-assisted synthesis of palladium nanoparticles supported on copper oxide in aqueous medium as an efficient catalyst for Suzuki cross-coupling reaction, *Adsorption Science & Technology*, 2018, <https://doi.org/10.1177/0263617418771777>.
- [18] Elazab H.A., Highly efficient and magnetically recyclable graphene-supported Pd/Fe₃O₄ nanoparticle catalysts for Suzuki and Heck cross-coupling reactions, *Applied Catalysis A: General*, 491, 58-69, 2015, <https://doi.org/10.1016/j.apcata.2014.11.033>.
- [19] Hirvi J.T., et al., CO oxidation on PdO surfaces, *Journal of Chemical Physics*, 133, 8, 2010, <https://doi.org/10.1063/1.3464481>.
- [20] Iglesias-Juez A., Nanoparticulate Pd Supported Catalysts: Size-Dependent Formation of Pd(I)/Pd(0) and Their Role in CO Elimination, *Journal of the American Chemical Society*, 133, 12, 4484-4489, 2011, <https://doi.org/10.1021/ja110320y>.
- [21] Ivanova A.S., Metal-support interactions in Pt/Al₂O₃ and Pd/Al₂O₃ catalysts for CO oxidation, *Applied Catalysis B-Environmental*, 97, 1-2, 57-71, 2010, <https://doi.org/10.1016/j.apcatb.2010.03.024>.
- [22] Kim H.Y., Henkelman G., CO Oxidation at the Interface between Doped CeO₂ and Supported Au Nanoclusters, *Journal of Physical Chemistry Letters*, 3, 16, 2194-2199, 2012, <https://doi.org/10.1021/jz300631f>.
- [23] Chattopadhyay K., Dey R., Ranu B.C., Shape-dependent catalytic activity of copper oxide-supported Pd(0) nanoparticles for Suzuki and cyanation reactions, *Tetrahedron Letters: International Organ for the Rapid Publication of Preliminary Communications in Organic Chemistry*, 50, 26, 3164-3167, 2009, <https://doi.org/10.1016/j.tetlet.2009.01.027>.
- [24] Hoseini S.J., Modification of palladium-copper thin film by reduced graphene oxide or platinum as catalyst for Suzuki-Miyaura reactions, *Applied Organometallic Chemistry*, 31, 5, 2017, <https://doi.org/10.1002/aoc.3607>.
- [25] Hosseini-Sarvari M., Razmi Z., Palladium Supported on Zinc Oxide Nanoparticles as Efficient Heterogeneous Catalyst for Suzuki Miyaura and Hiyama Reactions under Normal Laboratory Conditions, *Helvetica Chimica Acta*, 98, 6, 805-818, 2015, <https://doi.org/10.1002/hlca.201400331>.
- [26] Nasrollahzadeh M., Ehsani A., Jaleh B., Preparation of carbon supported CuPd nanoparticles as novel heterogeneous catalysts for the reduction of nitroarenes and the phosphine-free Suzuki Miyaura coupling reaction, *New Journal of Chemistry*, 39, 2, 1148-1153, 2015, <https://doi.org/10.1039/C4NJ01788A>.
- [27] Nasrollahzadeh M., Palladium nanoparticles supported on copper oxide as an efficient and recyclable catalyst for carbon(sp²) carbon(sp²) cross-coupling reaction, *Materials Research Bulletin*, 68, 150-154, 2013, <https://doi.org/10.1016/j.materresbull.2015.03.051>.
- [28] Mandali P.K., Chand D.K., Palladium nanoparticles catalyzed Suzuki cross-coupling reactions in ambient conditions, *Catalysis Communications*, 31, 16-20, 2016, <https://doi.org/10.1016/j.catcom.2012.10.020>.
- [29] Wang Y., CuO Nanorods-Decorated Reduced Graphene Oxide Nanocatalysts for Catalytic Oxidation of CO, *Catalysts*, 6, 12, 214, 2016, <https://doi.org/10.3390/catal6120214>.
- [30] Igarashi H., Uchida H., Watanabe M., Mordenite-supported noble metal catalysts for selective oxidation of carbon monoxide in a reformed gas, *Chemistry Letters*, 11, 1262-1263, 2000, <https://doi.org/10.1246/cl.2000.1262>.
- [31] Liu W.H., Fleming S., Lairson B.M., Reduced intergranular magnetic coupling in Pd/Co multilayers, *Journal of Applied Physics*, 79, 7, 3651-3655, 1996, <https://doi.org/10.1063/1.361193>.
- [32] Luo J.Y., Mesoporous Co(3)O(4)-CeO(2) and Pd/Co(3)O(4)-CeO(2) catalysts: Synthesis, characterization and mechanistic study of their catalytic properties for low-temperature CO oxidation, *Journal of Catalysis*, 254, 2, 310-324, 2008, <http://dx.doi.org/10.1016/j.jcat.2008.01.007>.
- [33] Pavlova S.N., The influence of support on the low-temperature activity of Pd in the reaction of CO oxidation on Kinetics and mechanism of the reaction. *Journal of Catalysis*, 161, 2, 517-523, 1996, <https://doi.org/10.1006/jcat.1996.0213>.
- [34] Diyarbakir S.M., Can H., Metin Ā.n., Reduced Graphene Oxide-Supported CuPd Alloy Nanoparticles as Efficient Catalysts for the Sonogashira Cross-Coupling Reactions, *ACS Applied Materials & Interfaces*, 7, 5, 3199-3206, 2015, <https://doi.org/10.1021/am507764u>.
- [35] Feng Y.-S., et al., ChemInform Abstract: PdCu Nanoparticles Supported on Graphene: An Efficient and Recyclable Catalyst for Reduction of Nitroarenes, *ChemInform*, 46, 4, 2015.
- [36] Feng Y.-S., et al., PdCu nanoparticles supported on graphene: an efficient and recyclable catalyst for reduction of nitroarenes, *Tetrahedron*, 70, 36, 6100-6105, 2014, <https://doi.org/10.1016/j.tet.2014.04.034>.
- [37] Liu Y., et al., Ultrasensitive electrochemical immunosensor for SCCA detection based on ternary Pt/PdCu nanocube anchored on three-dimensional graphene framework for signal amplification, *Biosensors & Bioelectronics*, 79, 71-78, 2016, <https://doi.org/10.1016/j.bios.2015.12.013>.
- [38] Shafaei Douk A., Saravani H., Noroozifar M., Novel fabrication of PdCu nanostructures decorated on graphene as excellent electrocatalyst toward ethanol oxidation, *International Journal of Hydrogen Energy*, 42, 22, 15149-15159, 2017, <https://doi.org/10.1016/j.ijhydene.2017.04.280>.
- [39] Hany A. Elazab, Investigation of Microwave-assisted Synthesis of Palladium Nanoparticles Supported on Fe₃O₄ as an Efficient Recyclable Magnetic Catalysts for Suzuki Cross – Coupling, *The Canadian Journal*

of *Chemical Engineering*, 96, 12, 250-261, 2018, <https://doi.org/10.1002/cjce.23402>.

[40] Hany A. Elazab, Laser Vaporization and Controlled Condensation (LVCC) of Graphene supported Pd/Fe₃O₄ Nanoparticles as an Efficient Magnetic Catalysts for Suzuki Cross – Coupling., *Biointerface Research in Applied Chemistry*, 8, 3, 3314 – 3318, 2018.

[41] Hany A. Elazab, The catalytic Activity of Copper Oxide Nanoparticles towards Carbon Monoxide Oxidation Catalysis: Microwave – Assisted Synthesis Approach, *Biointerface Research in Applied Chemistry*, 8, 3, 3278 – 3281, 2018.

[42] M. A. Radwan, Omar Al-Sweasy, M. A. Sadek, Hany A. Elazab, Investigating the Agricultural Applications of Acryl Amide based Hydrogel, *International Journal of Engineering and Technology(UAE)*, 7, 4.29, 168-171, 2018.

[43] Fatma Zakaria, M. A. Radwan, M. A. Sadek, Hany A. Elazab, Insulating material based on shredded used tires and inexpensive polymers for different roofs, *International Journal of Engineering and Technology(UAE)*, 7, 4, 1983-1988, 2018.

[44] Reem Nasser, M. A. Radwan, M. A. Sadek, Hany A. Elazab, Preparation of insulating material based on rice straw and inexpensive polymers for different roofs, *International Journal of Engineering and Technology(UAE)*, 7, 4, 1989-1994, 2018.

[45] Mostafa Ghobashy, Mamdouh Gadallah, Tamer T. El-Idreesy, M. A. Sadek, Hany A. Elazab, Kinetic Study of Hydrolysis of Ethyl Acetate using Caustic Soda, *International Journal of Engineering and Technology(UAE)*, 7, 4, 1995-1999, 2018.

[46] Nourhan Sherif Samir, Mostafa A. Radwan, M. A. Sadek, Hany A. Elazab, Preparation and Characterization of Bullet-Proof Vests Based on Polyamide Fibers, *International Journal of Engineering and Technology(UAE)*, 7, 3, 1290-1294, 2018, <http://dx.doi.org/10.14419/ijet.v7i3.13175>.

[47] Basant Ashraf, Mostafa A. Radwan, M. A. Sadek, Hany A. Elazab, Preparation and Characterization of Decorative and Heat Insulating Floor Tiles for Buildings Roofs, *International Journal of Engineering and Technology (UAE)*, 7, 3, 1295-1298, 2018.

[48] Mandali P.K., Chand D.K., Palladium nanoparticles catalyzed Suzuki cross-coupling reactions in ambient conditions, *Catalysis Communications*, 31, 5, 16-20, 2016, <https://doi.org/10.1016/j.catcom.2012.10.020>.

[49] Wang Y., CuO Nanorods-Decorated Reduced Graphene Oxide Nanocatalysts for Catalytic Oxidation of CO, *Catalysts*, 6, 12, 214-223, 2016, <https://doi.org/10.3390/catal6120214>.

[50] Pavlova S.N., The influence of support on the low-temperature activity of Pd in the reaction of CO oxidation on Kinetics and mechanism of the reaction, *Journal of Catalysis*, 161, 2, 517-523, 1996, <https://doi.org/10.1006/jcat.1996.0213>.

[51] Diyarbakir S.M., Can H., Metin Ā.n., Reduced Graphene Oxide-Supported CuPd Alloy Nanoparticles as Efficient Catalysts for the Sonogashira Cross-Coupling Reactions, *Acs Applied Materials & Interfaces*, 7, 5, 3199-3206, 2015, <https://doi.org/10.1021/am507764u>.

[52] Elazab H., Investigation of Microwave-assisted Synthesis of Palladium Nanoparticles Supported on Fe₃O₄ as an Efficient Recyclable Magnetic Catalysts for Suzuki Cross – Coupling, *The Canadian Journal of Chemical Engineering*, 97, 4, 920-928, 2019, <https://doi.org/10.1002/cjce.23402>.

[53] M. A. Radwan, Mohamed Adel Rashad, M. A. Sadek, Hany A. Elazab, Synthesis, Characterization and Selected Application of Chitosan Coated Magnetic Iron Oxide Nanoparticles, *Journal of Chemical Technology and Metallurgy*, 54, 2, 303-310, 2019.

6. ACKNOWLEDGEMENTS

We express our deep gratitude to the British University in Egypt (BUE) for supporting this work through Young Investigator Research Grant (YIRG). We also acknowledge EAF, EPRI, and STCE.



© 2019 by the authors. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).