Chemical Engineering   Engineering

Fall 1-6-2019

Investigation of Microwave-Assisted Synthesis of Palladium Nanoparticles Supported on Fe3O4 as Efficient Recyclable Magnetic Catalysts for Suzuki-Miyaura 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

INVESTIGATION OF MICROWAVE-ASSISTED SYNTHESIS OF PALLADIUM NANOPARTICLES SUPPORTED ON FE₃O₄ AS EFFICIENT RECYCLABLE MAGNETIC CATALYSTS FOR SUZUKI-MIYAURA CROSS-COUPLING

Hany A. Elazab (iD)*

Chemical Engineering Department, The British University in Egypt, Cairo, Egypt

In this research, a facile and reproducible approach was implemented for the synthesis of palladium nanoparticles supported on Fe₃O₄ with remarkable activity as an ideal catalyst for Suzuki-Miyaura cross-coupling. Magnetite supported Pd nanoparticles reveal high activity in Suzuki-Miyaura coupling reactions since they could be recycled up to seven times with the same high catalytic activity. This adopted method of catalyst synthesis has many advantages, including reproducibility and the reliability of the adopted synthetic method. The produced catalyst has unique magnetic properties to facilitate catalyst recovery from the reaction mixture by using a strong magnet as an external magnetic field. The synthetic approach adopted in this research is based on the microwave-assisted irradiation (MWI). The distinctive advantage of adopting this approach rather than conventional heating is the simplicity of adding reactants at mild reaction conditions. Moreover, this method offers a high rate of recyclability as the catalyst itself has a high recyclability rate up to seven times under mild reaction conditions, in addition to reproducibility with an excellent turnover number (8500) and a turnover frequency of 95 000 h⁻¹. The magnetic properties of the prepared catalyst increase the possibility to separate and purify the products from the catalyst and other byproducts, leading to an increase in the economic value of the catalyst. The prepared catalyst was characterized by various spectroscopic techniques including x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), vibrating sample magnetometer (VSM), and transmission electron microscopy (TEM).

Keywords: Suzuki-Miyaura coupling reactions, magnetic nanoparticles, microwave irradiation, catalysis, recycling

INTRODUCTION

Recently, nanomaterials, including metal oxides at the nanoscale, have widely attracted the efforts of various research groups in order to explore the possibility of solving critical issues in many scientific fields, including catalysis.[1–4] Metal oxides at the nanoscale were reported as potential ideal supports for transition metal nanoparticles such as Pd, Ag, Pt, Au, and Cu. Those metal oxide-based catalysts were used in many fields including cross-coupling reactions, such as Heck, Sonogashira, and Suzuki-Miyaura cross-coupling.[5–7] Cross-coupling reactions are of vital importance due to their crucial role in organic and pharmaceutical synthesis.[6,8–13] The large-scale applicability and the outstanding physical and chemical properties of the nanomaterials have had a significant impact on recent efforts in the research and development of modern technologies.[6,8–12,14,15]

It is well established that there are certain limitations to using homogeneous metal catalysts in cross-coupling reactions including metal leaching, recyclability, product contamination, and recovery. One of the main advantages of using metal oxides at the nanoscale is that they provide the unique option to be used as ideal supports where transition metals could be deposited on high surface areas, such as palladium deposition on the surface of iron, cobalt, and nickel oxides.[16–18] Therefore, one goal that is currently of interest regarding catalysis is to design quasi-homogeneous catalytic systems that avoid the drawbacks of using homogeneous catalysis, including economic and environmental issues.[19,20] Therefore, heterogeneous catalysis currently plays a critical role in solving the previously mentioned issues that are associate with using homogeneous catalysts.[5,6,9–11,16–18,21] Therefore, magnetite nanoparticle supported catalytic systems could provide a new pathway to achieve synergistic and enhanced properties that could result in unique catalytic systems with uniform and precisely engineered active sites exactly like those of homogeneous catalytic systems but with exceptional specifications.[22,23]

The use of magnetic nanoparticles as a versatile solid support not only provides a simple technique of catalyst separation from the reaction medium by using an external magnetic field like a strong permanent magnet but also to eliminate other separation-related processes such as filtration and centrifugation, reducing energy consumption and catalyst loss during recovery procedures.[1–4,24] The efforts of research groups are currently focused on how to design unique catalytic systems using ligand-free heterogeneous palladium catalysis.

In this manuscript, we report on a reliable synthetic approach to synthesize iron oxide supported palladium nanoparticles as highly active catalysts for Suzuki-Miyaura cross-coupling. The adopted synthetic approach is a microwave-assisted synthesis irradiation method as a simple, reliable, versatile, and rapid technique.[6,16,18,21] This method allows the synthesis of the nanoparticles with controlled shape and size. The unique advantage of using microwave dielectric heating is that it enables the addition of the reactants at 25 °C without the need for high-temperature injection.

Experimental

Palladium (II) acetyl acetonate Pd(C₅H₇O₂)₂, iron (III) acetylacetonate Fe(C₅H₇O₂)₃, aryl bromide, bromobenzene, and

potassium carbonate were purchased from Acros. Oleic acid and oleylamine were purchased from Sigma Aldrich, and all chemicals were used without any further purification.

Synthesis of Iron Oxide Supported Palladium Nanoparticles

In the experimental synthetic approach for preparing Pd/Fe_3O_4, different ratios (5, 10, 20, 30 wt%) of palladium supported on iron oxide were prepared according to the procedure that will be discussed later. The following weights, 600.8, 569.1, 505.9, and 442.6 mg of ferric acetyl acetonate $Fe(C_5H_7O_2)_3$, were added to 14.3, 28.6, 57.2, and 85.8 mg of palladium (II) acetyl acetonate, respectively. Then, the solid mixture was dissolved in a mixture of olylamine and oleic acid (20 mL each) used as ligating solvents, which were used to stabilize the nanocrystals by passivating the surfaces. This mixture of olylamine and oleic acid was added while stirring for 1 h to obtain a homogeneous solution. The mixture was then maintained in an oil bath with continuous stirring at a temperature of 110 °C until a dark brown mixture homogeneous in colour was obtained. Finally, the entire prepared mixture was heated by microwave irradiation for 50 s, and the final black precipitate was washed using hot deionized water, followed by ethanol, and finally dried in oven at 80 °C.

Catalyst Characterization

An Agilent 6890 gas chromatograph was used to perform GC-MS analysis. The magnetic properties of the catalyst were measured via vibrating sample magnetometer (VSM). Cross-coupling reactions were performed using a CEM Discover microwave at 250 W. The x-ray photoelectron spectroscopy (XPS) analysis was performed while the x-ray diffraction unit was used to measure x-ray diffraction patterns, and TEM images were captured using a JEOL JEM-1230 electron microscope.

General Procedure for Suzuki-Miyaura Cross-Coupling Reactions

Aryl bromide (0.51 mmol, 1 eq.) was dissolved in a mixture of 4 mL H_2O: EtOH (1:1). Also, aryl boronic acid (0.62 mmol, 1.2 eq.) and potassium carbonate (1.52 mmol, 3 eq.) were added to the previously mentioned mixture. 3.5 mg (2.55 μmol, 0.5 mol%) of palladium supported on magnetite nanoparticles (Pd/Fe_3O_4) was finally added, and then the tube was carefully sealed. The mixture was then heated under microwave irradiation MWI (250 W, 2.45 MHz). After the reaction was completed, the catalyst was easily removed from the mixture by applying an external magnetic field using a strong magnet and washed 3–5 times with 10 mL ethanol and dried until constant weight, in order to be used in the next run. Therefore, an extraction process for the mixture was done using 50 mL of dichloromethane three consecutive times. Hence, the resulting organic layers were dried over anhydrous magnesium sulphate and then filtered. The solid product was extracted from the filtrate by removing the solvent, and then the solid product was purified using flash chromatography over a mixture of hexane and ethyl acetate as eluent. This general procedure has been adopted in several reported research studies.[5,13,17,25–27]

Catalyst Recycling Procedure

In the adopted experimental protocol for catalyst recycling, the same procedure that was mentioned in the General Procedure for Suzuki-Miyaura Cross-Coupling Reactions section, was implemented. Then, the reaction progress was monitored using GC-MS. After completing the reaction, the mixture was then diluted using ethanol and then magnetically decanted while the prepared catalyst was separated by applying a strong magnetic field using a powerful magnet. The catalyst was then washed with ethanol 3–5 times in order for it to be ready to be used in the next run. This recycling protocol was repeated for each run.

RESULTS AND DISCUSSION

The catalyst was screened for the Suzuki-Miyaura cross coupling reaction, as shown in Scheme 1. The effect of temperature on the catalytic activity was studied for the cross-coupling reaction using a microwave with a 250 W power output under a constant reaction time of 10 min and several tested temperatures (80, 100, 120, and 150 °C) using the iron oxide supported palladium nanoparticles as a catalyst (1 mol%), as shown in Table 1. It was found that only 10 wt% Pd supported on the iron oxide catalyst shows 100 % conversion within 10 min at 120 °C, while the conversion was less than 50 % when testing Pd nanoparticles or magnetite nanoparticles independently, and this may be due to the lack of any kind of support.

The results show the critical effect of temperature on yield of the reaction. It was found that increasing temperature will lead to the higher conversion of reactants into products and the maximum conversion was achieved at 120 °C. This behaviour was found to be dominant for Pd/Fe_3O_4 catalysts that were tested, as shown in Table 1.

It is worth noting that increasing the palladium loading from 5 to 10 wt% increased the catalytic activity. However, this enhancement in the catalytic activity slightly decreased when increasing the palladium loading to 20 wt% at a temperature of 120 °C and higher. This may be due to the agglomeration that happens to the palladium nanoparticle on the surface of magnetite, especially at higher temperatures; however, it is also worth noting that the catalytic activity in this case is still higher than the catalytic activity in the case of using palladium or magnetite alone since the catalytic activity dropped to less than 50 %. This may be due to the lack of using any supports. The substrates diversity study is shown in Tables 2 and 3.
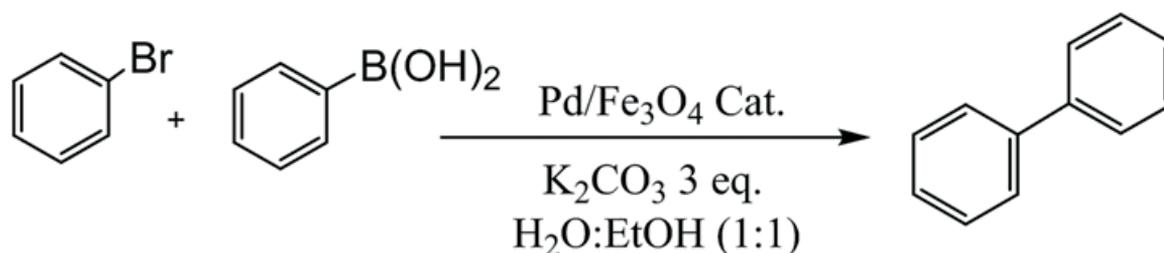
Scheme 1. Pd/Fe_3O_4 catalyst screening for Suzuki-Miyaura cross coupling reactions.

Table 1. The effect of using different ratios of 1 mol% Pd/Fe$_3$O$_4$ within 10 min on the conversion percentage

Catalysts[*]	Temp (°C)	Yield %
5 wt% Pd/Fe$_3$O$_4$	80	41
	100	44
	120	72
	150	84
10 wt% Pd/Fe$_3$O$_4$	80	52
	100	74
	120	100
	150	98
20 wt% Pd/Fe$_3$O$_4$	80	55
	100	78
	120	96
	150	89
Pd Nanoparticles	120	<50
Magnetite Nanoparticles	120	<50

[*]Pd content was found to be exactly 4.5, 8.7, and 18.2 wt% corresponding to the as-prepared 5, 10, and 20, respectively, using ICP-OES.

Figure 1a reveals the TEM images of palladium nanoparticles that were well dispersed with an average size of 8 nm supported on magnetite nanoparticles with an average size of 18 nm, as shown in the histogram in Figure 2.

TEM images could surprisingly provide an accurate explanation of the deviation in the catalytic performance of the Pd/Fe$_3$O$_4$ catalyst before the reaction (Figure 1a), compared to the same catalyst after the seventh run (Figure 1b). This deviation is probably due to the agglomeration of the particles that took place after the reaction and its harmful effect on the catalytic activity.
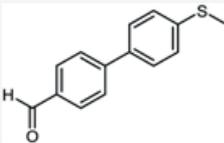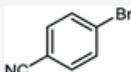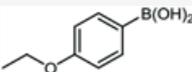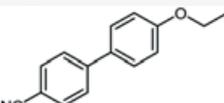
Figure 3 shows the XRD patterns where the characteristic peak of palladium was found at $2\theta = 40\,°$, while XRD patterns for magnetite (Fe$_3$O$_4$) was found at a sharp diffraction peak at $2\theta = 35\,°$. The characterization of Pd/Fe$_3$O$_4$ samples was investigated using XPS and VSM. The palladium content in the Pd/Fe$_3$O$_4$ catalyst was confirmed by using inductively coupled plasma optical emission spectroscopy (ICP-OES).

In Figure 4, using the XPS technique for the prepared samples confirmed that the presence of Fe was in the form of Fe$_3$O$_4$ with characteristic binding energy at 710.5 eV ascribed to Fe 2P$^{3/2}$ and also the characteristic binding energy at 723.7 eV ascribed to Fe 2P$^{1/2}$. Similarly, the binding energy at 334.8 eV was ascribed to Pd 3d$^{5/2}$ and at 340.1 eV was as to Pd 3d$^{3/2}$. This can be used as evidence of the presence of Pd as Pd^0. The binding energy at 341.38 and 336.23 eV are ascribed to Pd 3d$^{3/2}$ and Pd 3d$^{5/2}$, respectively, and this confirms that Pd was present as PdO (Pd^{2+}). This is in agreement with other reported data showing the role of the addition of Fe on the activity of the Pd-containing catalysts.[1,2,24,29–35]

Figure 5 shows the procedure of catalyst recycling, and it is worth noting that it is easy to implement the catalyst separation process by using a strong magnet and applying an external magnetic field. TEM images of Pd/Fe$_3$O$_4$ before and after the reaction can be used as an indication of the deactivation process of the catalyst as a result of the agglomeration and accumulation process of Pd nanoparticles that took place on the surface of Fe$_3$O$_4$ as shown.

The magnetic behaviour of the prepared catalyst was confirmed by the properties measured using the vibrating sample

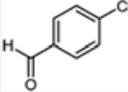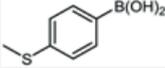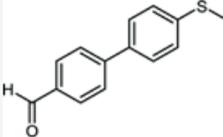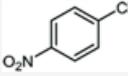**Table 2**. Diversity study for various substrates using the Pd/Fe$_3$O$_4$ catalyst[*]

Entry	Aryl halide	Boronic acid	Product	Yield[a] (%)	Yield[b] (%)
1				100	100
2				95	98
3				96	98
4				94	96
5				92	98
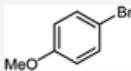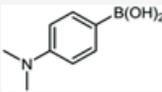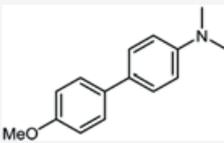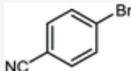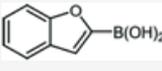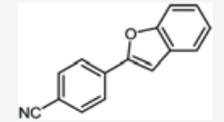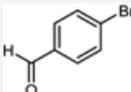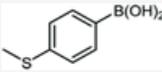
[*]Aryl halide (0.32 mmol, 1 eq.), aryl boronic acid (0.382 mmol, 1.2 eq.), potassium carbonate (0.96 mmol, 3 eq.), and 10 wt% Pd supported on Fe$_3$O$_4$ in 4 mL (H$_2$O:EtOH) (1:1) were heated at 120 °C (MWI) for 10 min.[28]
[a]Yield was calculated using 0.5 mol% Pd/Fe$_3$O$_4$ catalyst.
[b]Yield was calculated using 1 mol% Pd/Fe$_3$O$_4$ catalyst.

Entry	Aryl halide	Boronic acid	Product	Yield[a] (%)	Yield[b] (%)
1				82	94
2				87	95
3				81	92
4				70	88
5				68	92
6				82	87
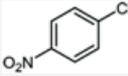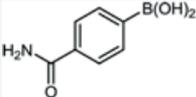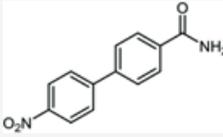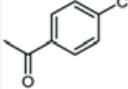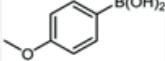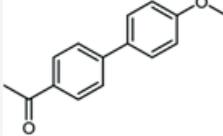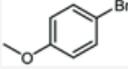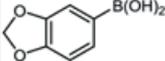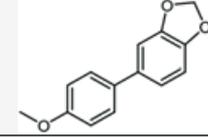
[*]Aryl halide (0.32 mmol), aryl boronic acid (0.382 mmol, 1.2 eq.), potassium carbonate (0.96 mmol, 3 eq.), and 10 wt% Pd supported on Fe$_3$O$_4$ in 4 mL (H$_2$O: EtOH) (1:1) were heated at 120 $^\circ$C (MWI) for 10 min.[28]
[a]Yield was calculated using 0.5 mol% Pd/Fe$_3$O$_4$ catalyst.
[b]Yield was calculated using 1 mol% Pd/Fe$_3$O$_4$ catalyst.

Figure 1. TEM images of Pd supported on Fe$_3$O$_4$ catalyst: (a) before the reaction; and (b) after the seventh run.

Figure 2. The histogram of magnetite nanoparticles.
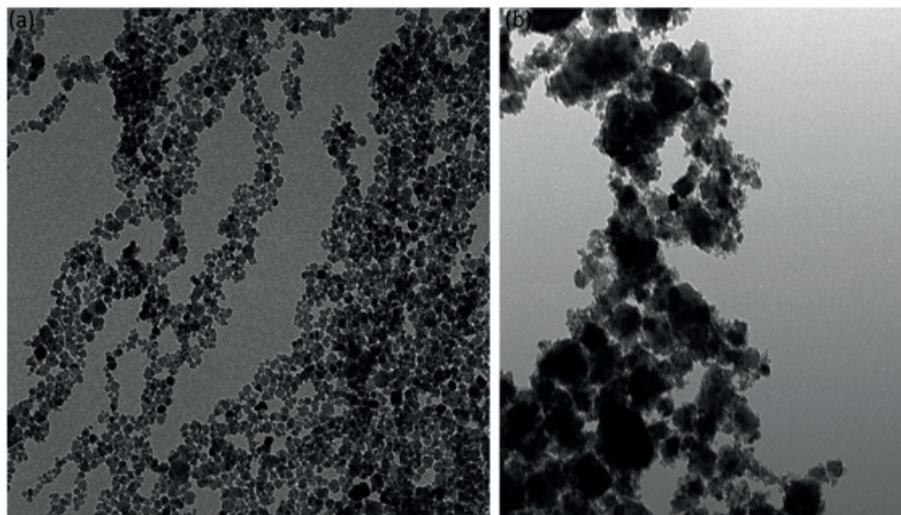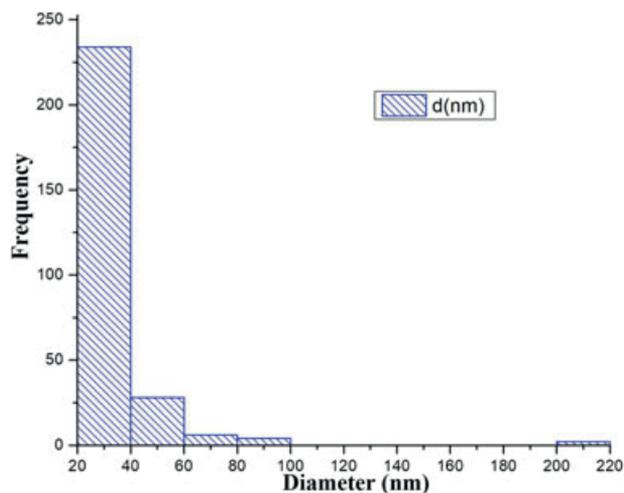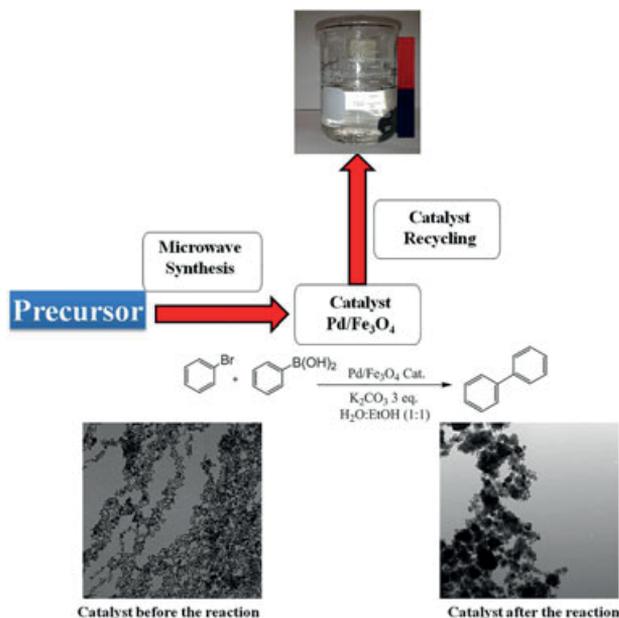

Figure 3. X-ray diffraction pattern of Pd/Fe₃O₄ nanoparticles.

Figure 5. Separating the Pd-Fe₃O₄ catalyst from reaction mixture.

magnetometer (VSM) analysis. Figure 6 shows the magnetic properties of the prepared palladium supported on magnetite and its hysteresis loop. This figure shows that the hysteresis loop is obtained for Pd/Fe₃O₄ by applying a field ranging from −30–30 kOe. This hysteresis loop shows the super-paramagnetic behaviour of the catalyst.

Table 4 gives an overview of the remarkable catalytic activity of the prepared catalyst. It was experimentally found that the catalyst could be recycled up to five times in the case of using 0.5 mol%, while the catalyst could be recycled up to seven times by increasing the mole percentage to 1 mol%, as also shown in Figure 7.

To investigate the palladium leaching from the prepared catalyst, the reaction was carried out in the presence of a 0.2 mol% catalyst at 120 °C for 5 min under microwave heating. Upon the completion of the reaction, the palladium content was found to be 185 ppm using ICP-MS analysis. Moreover, there was no further catalytic activity observed in the filtrate solution after heating the fresh reaction mixture under the same conditions. This
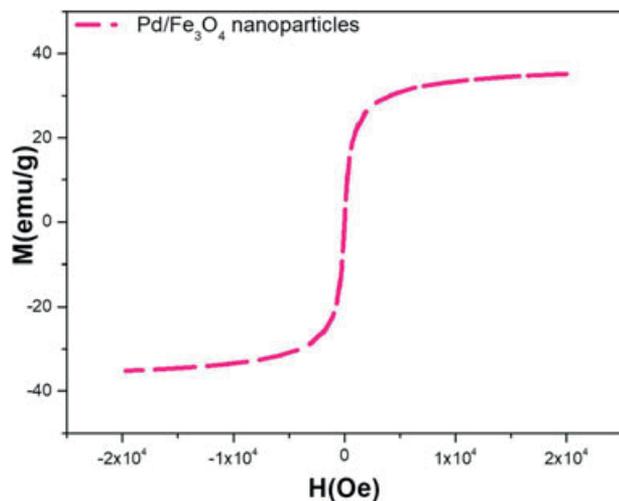

Figure 4. (a) XPS (Fe 2p); and (b) XPS (Pd 3d) of Pd/Fe₃O₄ nanoparticles.

Figure 6. The magnetic behaviour of Pd/Fe₃O₄ nanoparticles.

Table 4. Pd/Fe₃O₄ catalyst recyclability study using a concentration of 0.5, 1 mol%*

Run	Yield (%)ᵃ (0.5 mol%)	Yield (%)ᵇ (1 mol%)
1	100	100
2	96	100
3	95	98
4	94	96
5	92	95
6	86	94
7	75	92

*Aryl halide (0.32 mmol), aryl boronic acid (0.382 mmol, 1.2 eq.), potassium carbonate (0.96 mmol, 3 eq.), and 10 wt% Pd supported on Fe₃O₄ in 4 mL (H₂O:EtOH) (1:1) were heated at 120 °C (MWI) for 10 min.[18,28]

ᵃYield was calculated using 0.5 mol% Pd/Fe₃O₄ catalyst.
ᵇYield was calculated using 1 mol% Pd/Fe₃O₄ catalyst.

confirms that the catalyst is not reacting by leaching or redeposition but it is obviously in a strictly heterogeneous mode. This general procedure has been adopted in several reported research studies.[5,13,17,25–27]
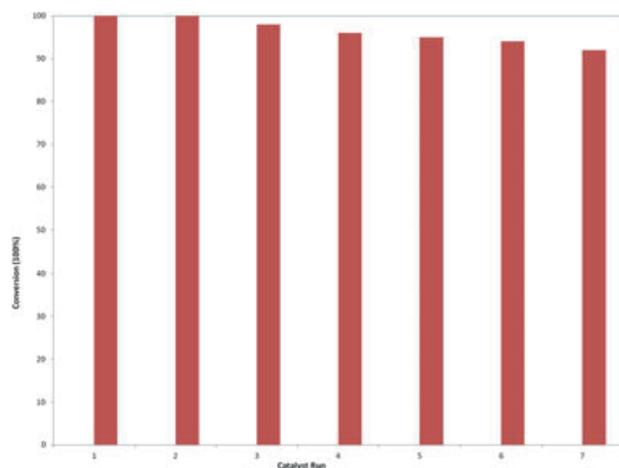

Figure 7. Recycling experiments of the Pd/Fe₃O₄ catalyst.

CONCLUSION

The effect of using magnetic magnetite as an ideal potential support was investigated. A comprehensive comparative study has been completed using and without using magnetite to monitor the effect of the prepared catalyst on catalytic performance. Nanoparticles of Pd supported on magnetite (Fe₃O₄) have been prepared by a facile synthetic approach using a simple microwave-assisted synthesis method that successfully resulted in the preparation of a highly active, magnetic, and recyclable catalyst that has remarkable catalytic activity in the Suzuki cross-coupling reaction and could be easily recycled up to seven times with the same high catalytic performance.

It is important to notice that the catalytic activity of Fe₃O₄ was enhanced by using palladium. However, there are many efforts still devoted to understanding the catalytic reaction mechanism.

In summary, the bimetallic structure of the prepared catalyst offers enormous advantages not only in terms of high reactivity and selectivity but also for use in mild reaction conditions. Moreover, it has an excellent turnover number (8500) and a turnover frequency of 95 000 h⁻¹, which is comparable to other reported data, however, our adopted method has many advantages.[1,24,31,32] The magnetic properties of iron oxide enable the easy isolation and recycling of the catalyst, thus significantly enhancing the capability of reaction products separation, purification, and the potential reuse of the catalyst after the regeneration process.

It is worth recognizing that the defects in magnetite can contribute to the unique catalytic activity of the prepared catalysts.[5,13,17,25–27]

This high catalytic performance and the recyclability of this catalyst are due to a strong catalyst support interaction since the defect sites in the magnetite nanoparticles act as nucleation centres that anchor the Pd nanoparticles and, consequently, minimize the anticipated agglomeration and the potential decrease in the catalyst's catalytic activity as a direct impact of this unfavourable agglomeration.[17,18,28]

REFERENCES

[1] B. Baruwati, V. Polshettiwar, R. S. Varma, *Tetrahedron Lett.* **2009**, *50*, 1215.

[2] P. A. Chernavskii, J. A. Dalmon, N. S. Perov, A. Y. Khodakov, *Oil Gas Sci. Technol.* **2009**, *64*, 25.

[3] J. Dong, Z. H. Xu, S. M. Kuznicki, *Adv. Funct. Mater.* **2009**, *19*, 1268.

[4] M. Epifani, E. Pellicer, J. Arbiol, J. R. Morante, *Chem. Mater.* **2009**, *21*, 862.

[5] H. A. Elazab, S. Moussa, K. W. Brinkley, B. Frank Gupton, M. Samy El-Shall, *Green Process. Synth.* **2017**, *6*, 413.

[6] W. Mohsen, M. A. Sadek, H. A. Elazab, *International Journal of Applied Engineering Research* **2017**, *12*, 14927.

[7] K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem. Int. Edit.* **2005**, *44*, 4442.

[8] B. Ashraf, M. A. Radwan, M. A. Sadek, H. A. Elazab, *International Journal of Engineering and Technology* **2018**, *7*, 1295.

[9] R. A. Mankarious, M. A. Radwan, M. Shazly, H. A. Elazab, *J. Eng. Appl. Sci.* **2017**, *12*, 2697.

[10] A. R. Mostafa, H. A.-S. Omar, A. E. Hany, *Agricultural Sciences* **2016**, *8*, 11.

[11] M. A. Radwan, M. M. Naeem, M. A. Sadek, H. A. Elazab, *J. Eng. Appl. Sci.* **2017**, *12*, 1179.

[12] N. S. Samir, M. A. Radwan, M. A. Sadek, H. A. Elazab, *International Journal of Engineering and Technology* **2018**, *7*, 1290.

[13] H. A. Elazab, M. A. Sadek, T. T. El-Idreesy, *Adsorpt. Sci. Technol.* **2018**, *36*, 1352.

[14] F. Zakaria, M. A. Radwan, M. A. Sadek, H. A. Elazab, *International Journal of Engineering and Technology* **2018**, *7*, 1983.

[15] R. Nasser, M. A. Radwan, M. A. Sadek, H. A. Elazab, *International Journal of Engineering and Technology* **2018**, *7*, 1989.

[16] M. Ghobashy, M. Gadallah, T. T. El-Idreesy, M. A. Sadek, H. A. Elazab, *International Journal of Engineering and Technology* **2018**, *7*, 1995.

[17] H. Elazab, S. Moussa, A. Siamaki, B. Gupton, M. El-Shall, *Catal. Lett.* **2017**, *147*, 1510.

[18] H. A. Elazab, A. R. Siamaki, S. Moussa, B. F. Gupton, M. S. El-Shall, *Appl. Catal. A-Gen.* **2015**, *491*, 58.

[19] O. A. Fouad, M. S. El-Shall, *Nano* **2012**, *5*, 185.

[20] G. Glaspell, H. M. A. Hassan, A. Elzatahry, V. Abdalsayed, M. S. El-Shall, *Top. Catal.* **2008**, *47*, 22.

[21] H. A. Elazab, M. A. Sadek, T. T. El-Idreesy, *Adsorpt. Sci. Technol.* **2018**, *36*, 1352.

[22] K. Chattopadhyay, R. Dey, B. C. Ranu, *Tetrahedron Lett.* **2009**, *50*, 3164.

[23] M. Nasrollahzadeh, S. M. Sajadi, A. Rostami-Vartooni, A. Azarian, *Mater. Res. Bull.* **2016**, *68*, 150.

[24] R. Arundhathi, D. Damodara, P. R. Likhar, M. L. Kantam, P. Saravanan, T. Magdaleno, S. H. Kwon, *Adv. Synth. Catal.* **2017**, *353*, 1591.

[25] H. A. Elazab, *Biointerface Research in Applied Chemistry* **2018**, *8*, 3314.

[26] H. A. Elazab, *Biointerface Research in Applied Chemistry* **2018**, *8*, 3278.

[27] H. A. Elazab, M. A. Radwan, T. T. El-Idreesy, *Int. J. Nanosci. Ser.* **2018**, *6*, 235.

[28] A. R. Siamaki, A. E. S. Khder, V. Abdelsayed, M. S. El-Shall, B. F. Gupton, *J. Catal.* **2011**, *279*, 1.

[29] E. V. Golubina, E. S. Lateva, V. V. Lunin, N. S. Telegina, A. Y. Stakheev, P. Tundo, *Appl. Catal. A-Gen.* **2006**, *302*, 32.

[30] S. R. Borhade, S. B. Waghmode Beilstein, *J. Org. Chem.* **2007**, *6*, 250.

[31] H. Firouzabadi, N. Iranpoor, M. Gholinejad, J. Hoseini, *Adv. Synth. Catal.* **2012**, *353*, 125.

[32] C. G. Frost, L. Mutton, *Green Chem.* **2016**, *12*, 1687.

[33] A. V. Gaikwad, A. Holuigue, M. B. Thathagar, J. E. ten Elshof, G. Rothenberg, *Chem.-Eur. J.* **2007**, *13*, 6908.

[34] D. Tsvelikhovsky, I. Popov, V. Gutkin, A. Rozin, A. Shvartsman, J. Blum, *Eur. J. Org. Chem.* **2009**, *2009*, 98.

[35] H. Elazab, S. Moussa, B. Gupton, M. El-Shall, *J. Nanopart. Res.* **2014**, *16*, 1.