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Optimization of the catalytic performance of Pd/Fe$_3$O$_4$ nanoparticles prepared via microwave-assisted synthesis for pharmaceutical and catalysis applications

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ABSTRACT

Microwave assisted synthesis technique was used to prepare palladium supported on iron oxide nanoparticles. The advantage of using microwave irradiation as a synthetic tool is due to its unique features as a one step, simple, versatile, and rapid process. The reactants are added simply at room temperature without using high-temperature injection. Hydrazine hydrate was added by the following ratios (0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1, 1.6, and 3) ml to the different prepared samples at room temperature in order to investigate its effect on the catalytic performance of the prepared catalysts. The prepared catalyst could be used as an ideal candidate not only for Pharmaceutical industry through cross-coupling reactions but also for low temperature oxidation catalysis of carbon monoxide and pharmaceutical applications as well. The experimental results showed that Pd/Fe$_3$O$_4$ catalyst has a remarkable catalytic activity for carbon monoxide oxidation catalysis due to the strong interaction between palladium and iron oxide nanoparticles. This may be due to the small particle size (7-14 nm) and concentration ratio of the Pd nanoparticles dispersed on the surface of magnetite (Fe$_3$O$_4$). Those nanoparticles were 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: *Microwave-assisted Synthesis, Pd nanoparticles, Magnetite nanoparticles, CO catalytic oxidation catalysis.*

1. INTRODUCTION

Magnetic nanoparticles have vital importance as an attractive class of nanostructured materials according to its unique properties.[1-4] Nanostructured materials are of vital importance not only in industrial catalysis, but also in other research disciplines including advanced technological and medical applications, green chemistry, biology, and material science.[5-17]

Metal oxides play an important role as an ideal support in the field of heterogeneous catalysis in several applications not only including the production of chemicals, hydrocarbons, pharmaceuticals but also including removal of harmful volatile organic compounds and gases in order to minimize the environmental pollution.[9-15,18,19] Metal oxides are capable of providing an easy approach to disperse the particles at the nanoscale on its surface and hence, make it possible to avoid the potential agglomeration and sintering that could happen during the reactions.[5-15] Moreover, metal oxides play an important role via influencing the mechanism of the catalytic oxidation through the metal-metal oxide interface where electron transfer processes can take place.[9,20-23]

The oxidation catalysis of carbon monoxide has significant importance in pollution control due to its severe side effects and other serious symptoms that could lead to death even if under exposure to small amounts (ppm) as it is odorless and invisible gas.[24-27] Fe$_3$O$_4$ nanoparticles are used asideal catalyst supports due to its good chemical stability, low toxicity, and magnetic properties.[9,10,13,15,18] The magnetic catalysts are considered among ideal catalysts that could achieve easy adoption of green chemical synthetic routes due to its easy recovery via applying a strong external magnetic field. [15]Transition metals including Pd, Pt and Rd nanoparticles are considered as the main active catalysts that transform carbon monoxide into carbon dioxide. The type of support, metal precursor, preparation and pre-treatment conditions, and catalytic reaction conditions are essential factors that directly affect the performance of a heterogeneous catalyst for CO oxidation through its impact on activity, selectivity and stability.[28-33]

The catalyst support nature is a decisive factor that could lead to the tendency of carbon monoxide molecules to be adsorbed on the catalyst surface. Hence, this will have a direct impact on the turnover that basically depends on the presence of surface sites that are open for O_2 adsorption and dissociation. Fe$_3$O$_4$ nanoparticles act as ideal catalyst support for CO oxidation due to the presence of the Fe^{2+} ion in Fe$_3$O$_4$ that provides some reducible oxide characters. [34]

In this scientific research, we have made an enhancement to our previous research findings by using different ratios of hydrazine hydrate (0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1, 1.6, and 3) ml in order to investigate its effect on the catalytic performance of the prepared catalysts.

2. MATERIALS AND METHODS

2.1. Chemicals. All purchased chemicals were used without any other purification. Palladium nitrate, Fe (NO$_3$)$_3$.9H$_2$O, and hydrazine hydrate (80%, Hydrazine 51%) were purchased from Sigma Aldrich. For experimental synthesis described here, a

microwave oven (2.45 GHz) operating at 600 – 1000 W was used in experimental procedure.
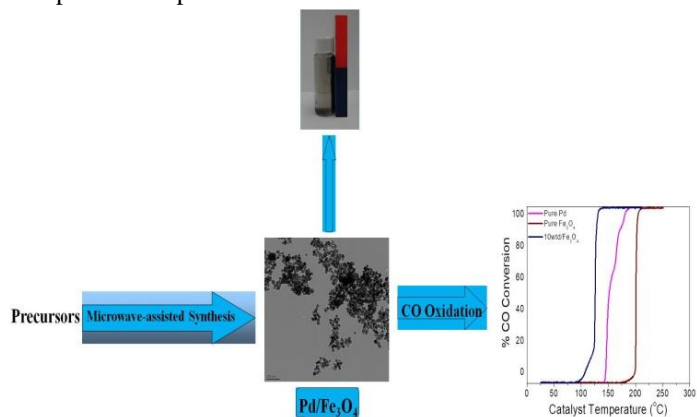

Figure 1. Graphical Abstract of Synthesis of Pd nanoparticles Supported on iron oxide

2.2. Microwave-assisted Synthesis of Pd/Fe₃O₄.

In the experimental procedure of Pd/Fe₃O₄ synthesis, different samples of a fixed ratio have been prepared with the ratio 20 wt % palladium nitrate supported on 80 wt % iron nitrate. Typically, 868 mg of Fe (NO₃)₃.9H₂O were added to 20 ml Deionized water in 200 ml beaker and the solution was sonicated for 2 hr. Then, 582 μl of palladium nitrate was added to the solution while stirring process continues for 1 hr. Then, hydrazine hydrate was added by the following ratios (0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1, 1.6, and 3) ml to the differently prepared samples at room temperature in order to investigate its effect on the catalytic performance of the prepared catalysts.

3. RESULTS

From analysis of data obtained using flow reactor under ambient pressure; it was found that increasing the added ratio of hydrazine hydrate to the mixture of palladium nitrate and iron nitrate enhanced the catalytic performance of the catalyst as shown in figure 5. So, the complete conversion was accomplished at lower temperatures until our best temperature at which complete conversion happened was 135 ˚C as shown in table 1 in the case of 0.4 ml hydrazine hydrate catalyst. While higher temperatures were noticed when using palladium nitrate and iron nitrate alone and also for higher weight ratios of palladium. This may be due to a kind of agglomeration as there is no support used in these two cases which are in agreement with literature.

Table 1. Temperatures at which CO conversion reaches 50% (T_{50}) and 100% (T_{100}) for Pd, Fe₃O₄, and the supported catalysts Pd/Fe₃O₄ using 0.4 ml Hydrazine Hydrate (H.H).

Wt % Pd/Fe₃O₄	$T_{50\%}$ (℃)	$T_{100\%}$ (℃)
5	194	204
10	180	185
20	125	135
30	130	138
40	142	150
50	162	172
Pd nanoparticles	165	182
Fe₃O₄ nanoparticles	218	225

The color of the mixture turned to reddish brown and then, it was heated by microwave for (120) s and the black product was finally obtained. The product was then 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. The product was washed several times using hot deionized water and then ethanol and finally dried in oven at 80˚C overnight under vacuum.

2.3. General procedure of Suzuki cross-coupling reactions using 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, 5 g palladium/iron oxide catalyst (Pd-Fe₃O₄) was also added and the reaction mixture was then heated using 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 then washed with ethanol several times to remove any residues from the surface of the catalyst. Then, the catalyst is ready for the next run.

2.4. Characterization of Catalyst.

TEM images were captured via using a Joel JEM-1230 electron microscope. The small angle X-ray diffraction patterns were measured using an X'Pert Philips Diffractometer. The X-ray photoelectron spectroscopy (XPS) spectra were measured on a Thermo Fisher Scientific ESCALAB 250. The prepared catalyst catalytic activity for CO catalytic oxidation was measured using a programmable tube furnace.
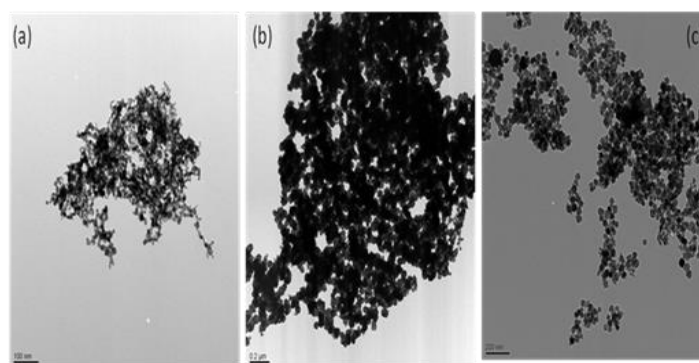

Figure 2. TEM of nanoparticles of: (a) Pd, (b) Fe₃O₄, (c) Pd/Fe₃O₄.

Figure 2- shows TEM image of the Pd nanoparticles prepared by the chemical reduction of Pd (NO₃)₂ using hydrazine hydrate (HH) under microwave assisted synthesis approach. However, the nanoparticles were of small size range 7-14 nm, but they reveal a significant degree of aggregation due to the absence of a capping agent or support.[9]

Figures 2-bdisplay TEM image of the Fe₃O₄ nanoparticles. In the case of Fe₃O₄, most of the nanoparticles have irregular shapes with diameters between 27-32 nm. Figures 2-c display the TEM images of palladium nanoparticles supported on the Fe₃O₄ nanoparticles where most of the Pd particles appear to be deposited on the support magnetite nanoplates.

Table 2. Effect of Hydrazine Hydrate ration on CO conversion for supported catalysts 20 wt % Pd/Fe₃O₄.

No.	H.H (ml)	$T_{100\%}$ (℃)
1	0.1	246
2	0.2	233
3	0.3	203
4	0.4	135
5	0.6	130
6	0.8	122
7	1	148
8	1.6	165
9	3	195

Table 2 shows the analysis of data obtained using Type F21100 Tube Furnace under ambient pressure; it was found that increasing the added ratio of hydrazine hydrate to the mixture of palladium nitrate and iron nitrate enhanced the catalytic performance and activity of the catalyst. So, the complete conversion was accomplished at lower temperatures until our best temperature at which complete conversion happened was 135 ˚C as shown in table 1 in case of 0.4 ml hydrazine hydrate catalyst. Increasing hydrazine hydrate could also enhance the complete conversion as it took place at 130, 122 ˚C for using 0.6 and 0.8 ml hydrazine hydrate respectively.

While higher temperatures were noticed when using palladium nitrate and iron nitrate alone and also for higher ratios of hydrazine hydrate. This may be due to a kind of agglomeration as there is no support used in these two cases which are in agreement with literature.

Figure 3 shows the XRD diffraction patterns of Pd, Fe₃O₄, and 20 wt% Pd/Fe₃O₄ nanoparticles [9]. The typical fcc pattern of Pd crystalline particles was confirmed (JCPDS-46-1043). The characteristic peaks of Fe₃O₄ nanoparticles were confirmed for the spinal Fe₃O₄ phase (ICCD-00-003-0863) in addition to the presence of a small percentage of the α-Fe₂O₃ phase confirmed by the 2θ peaks at 33.3 and 49.6 (JCPDS-33-0664), while for 20 wt% Pd/Fe₃O₄ nanoparticles, characteristic peaks of Pd and Fe₃O₄ were confirmed without any indication of the presence of the α-Fe₂O₃ phase. These results are in good agreement with other reported data [34-37].
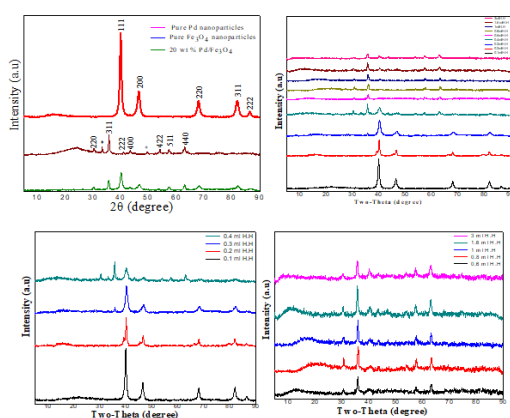

Figure 3. (a) XRD patterns of Pd, Fe₃O₄, and 20 wt% Pd/Fe₃O₄ prepared using 0.4 ml hydrazine hydrate. (b, c, d) XRD patterns of 20 wt% Pd/Fe₃O₄ prepared using different hydrazine hydrate ratios. (* is due to Fe₂O₃).

The characterization of the surface composition of the supported nanocatalysts, was carried out via using XPS measurements as shown in Figures 4 (a) and 4 (b). The presence of Fe(III) was confirmed through peaks at 724.2 eV and 710.5 eV corresponding to the binding energies of the $2p^{1/2}$ and $2p^{3/2}$ electrons, respectively [35-37].

Similarly, the characteristic binding energies of 334.8 eV and 340.1 eV confirm the presence of Pd^0 and Pd^{2+} (due to the presence of PdO)[6, 9, 10, 13, 15, 18, 35-37].
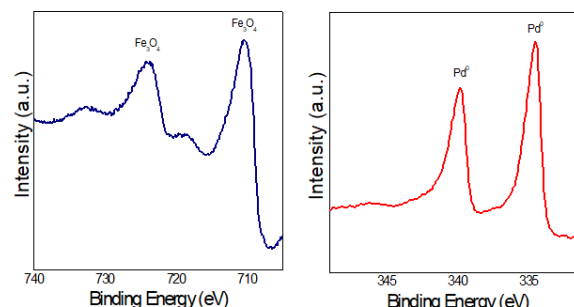

Figure 4. XPS binding energy of (a) Fe 2p region (b) Pd 3d region for Pd/Fe₃O₄.
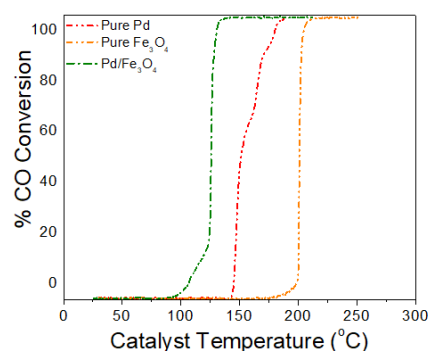

Figure 5. CO catalytic oxidation by 20 wt % Pd/Fe₃O₄ with pure Pd and Fe₃O₄ nanoparticles.

Figure 5 compares the catalytic activity of oxidation of carbon monoxide over pure Fe₃O₄, pure Pd nanoparticles, and 20 wt% Pd/Fe₃O₄. The catalytic activities of pure Pd and pure support nanoparticles were measured as a standard in order to compare with the supported catalysts.

It was found that both the pure Fe₃O₄ and pure Pd nanoparticles reveal poor activities with 100% conversion temperatures of 225 ᵒC and 182 ᵒC, respectively as discussed before in table 1. This is mostly due to the aggregation of the Pd and magnetite nanoparticles due to the absence of using any kind of supports. However, catalysts containing 20 wt % Pd show excellent catalytic behavior with 100% conversion temperatures of 125 ᵒC compared to the pure Pd and pure magnetite nanoparticle catalyst indicating the well-established significant role of the support in dispersing the catalyst nanoparticles and decreasing their tendency for aggregation and sintering. Therefore, it appears that the 20 wt% Pd/Fe₃O₄ catalyst provides reasonable optimization between the adsorption of the CO and O₂ molecules on the Pd-Fe₃O₄ interfaces to allow efficient oxidation of CO which is in good agreement with other reported data for similar catalytic systems[38-46].

4. CONCLUSIONS

In conclusion, a facile one-step approach has been adopted for the synthesis of Pd nanoparticle catalysts supported on Fe_3O_4 nanoparticles via microwave assisted synthesis. Moreover, the recovery and the recycling process of the catalyst could be implemented up to five times with high catalytic activity near 100% thus providing high economic viability. It can be easily concluded from characterization that palladium nanoparticles are uniformly dispersed onto the surface of magnetite 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 which is one of the main reactions used in pharmaceutical applications.

The important advantage of this method over other methods besides the fast synthetic route is the reproducibility of the final product in order to avoid other issues raised by other techniques.

Furthermore, the current research results reveal that the Pd/Fe_3O_4 catalyst has particularly high activity for CO oxidation as a result of the strong interaction between the Pd nanoparticles and the Fe_3O_4 nanoparticles. It was found that the prepared catalyst containing 20 wt % Pd reveal excellent catalytic performance with 100% conversion temperatures of 125 ^{o}C compared to the pure Pd and pure magnetite nanoparticle catalyst indicating the well-established significant role of the support in dispersing the catalyst nanoparticles and decreasing their tendency for aggregation and sintering. Optimizations of the particle size, chemical composition, and shape of those catalysts could help to design more efficient nanocatalysts with higher catalytic activity. We are currently exploring other effects of microwave heating duration; different supports including carbon based structures as well as the effect of particle size, and shape of the supported metal nanoparticle catalysts.

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6. ACKNOWLEDGEMENTS