

Synthesis of Schiff Base-functionalized Fullerene Anchored Palladium Complex as a Recyclable Nanocatalyst in the Heck Reaction and Oxidation of Alcohols

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ABSTRACT: *The use of nanocarbon support materials such as fullerene (C₆₀) helps the dispersion of catalysts and creates a new method to develop nanomaterials as a result of its garbled structure Pd-supported on Schiff base modified fullerene (C₆₀LPd²⁺ and C₆₀LPd⁰) were fabricated. The obtained catalysts were characterized by FT-IR, XRD, TEM, TGA, and ICP. To investigate the catalytic properties, this catalyst was used in aerobic oxidation of alcohols and Heck coupling as model reactions. The results showed that the efficiency of catalysts has about 75% to 92% and 90% to 98% in these two reactions, respectively. The catalyst can be rapidly readily regained and reused at least 5 consecutive cycles without notable leaching and loss of its catalytic actuality.*

KEYWORDS *Polyamine-functionalized C₆₀; Nanocatalyst; Oxidation of alcohol.*

INTRODUCTION

Fullerenes are molecules composed exclusively of carbon that were discovered at Rice University in 1985. Many of the practicable applications of Fullerenes are straight related to their extraordinary properties. The suitable physical, chemical, and optical characteristics of fullerenes have made them vital components for the future of nanoelectromechanical systems and industrial research currently [1]. The great special surface space and the large delocalized π -electron system of fullerene have made it possible to form strong hydrophobic and π -stacking interactions with organic molecules, hence it might be a favorable candidate for a catalyst or catalyst support.

One of the main and general applications of fullerene in the industry is the use of fullerenes as a support medium for heterogeneous catalysis [2]. There are few studies about the application of fullerene as catalysts or catalyst supports [3]. To provide the heterogeneous catalyst, several various carbon materials have been applied to disperse and stabilize nanoparticles of metal [4]. The catalytic properties of these solids are based on the interaction between the carbon support and metal particles. The solid-state chemistry of fullerene-based materials has attracted a lot of attention due to the unique electronic and structural properties of these compounds [5]. Today, transition

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metals are reported as useful heterogeneous catalyst agents in the synthesis of organic compounds [6-11].

There are a great number of reports and reviews that reveal the extensive application of Palladium-based catalysts. However, the recovery and recycling of these catalysts are frequently problematic. Thus, the construction of a heterogeneous palladium catalyst using immobilization of metal on solid support facilitates recovery of catalyst from the reaction mixture and aids to effective recycling of the catalyst. For this reason, immobilization of Pd catalysts on inorganic solid supports [12], organic polymers [13], CNT [14], graphene, and its derivatives have been investigated [15]. Palladium stabilized on different solid substrates that increases their efficiency due to increased contact, are used in several important reactions such as the hydrogenation of carbon-carbon bonds [16], C-heteroatom bond formation [17], including the asymmetric reaction [18], the synthesis and functionalization of heterocycles [19], C-C coupling and alcohols oxidation reactions [20]. Among palladium-catalyzed reactions, the Suzuki–Miyaura coupling, the Heck reaction, and the Sonogashira reaction have been extensively investigated in recent decades [21]. In this study, first, the fullerene was modified with Schiff base ligand (L) and then Pd was immobilized on Schiff base complexes ($C_{60}LPd^{2+}$ and $C_{60}LPd^0$). Moreover, the activity of these Schiff base functionalized Fullerene (C_{60}) anchored palladium complex was studied as a recyclable nanocatalyst for Heck coupling and oxidation of alcohols as model reactions. The results displayed that the catalyst can be easily regenerated and reused at least 5 successive cycles without considerable leaching and loss of its catalytic activity.

EXPERIMENTAL SECTION

Materials and equipment's

Fullerene was ordered from Sigma- Aldrich Company (C_{60} , assay 99 %). In addition, other chemical materials such as sodium naphthalene, thionyl chloride, ethylenediamine, salicylaldehyde, hydrazine hydrate, aliphatic and aromatic alcohols, styrene and derivatives, aryl bromides and aryl iodides, metal salts, organic and inorganic acids, bases, and solvents were purchased from Aldrich, Merck and Fluka no need for further purification. Synthesized compounds were characterized using the Infrared spectra by Shimadzu 8400, 1H - and ^{13}C - NMR spectra by Jeol 90 MHz, elemental analysis for C, H, and

N by Perkin-Elmer 2400 series analyzer, the X-Ray powder Diffractometer (XRD) Philips PW-1840, ThermoGravimetric Analysis (TGA) Mettler Toledo SDTA 85-e at 30-800 °C with 10 °C /Min, Transmission Electron Microscopy (TEM) images by EM10C (Zeiss), quantitative measurements of metal elements with SHIMADZU AA-6100 Absorption Spectrometer (AAS).

Amination of fullerene

In order to produce fullerenes with amine functional groups, at first, Hexa (carboxyl) fullerene was synthesized following a well-known procedure [22-24]. 400 mg (0.556 mmol) of fullerene was added to 250 mL of 1, 2-dimethoxyethane (DME) which has already been dried and degassed. The mixture was stirred for 6 hours. 1.74 g (11.5 mmol) of sodium naphthalene in 50 mL DME was added and stirred until the color of this mixture was changed from dark to brown. Purified CO_2 gas was inserted into the reaction vessel continuously, accompanied by strong stirring. After 3 days, the brown suspension was obtained. This suspension was separated by centrifugation. The precipitate was dissolved in DMF and the unreacted materials, such as fullerene, were separated by centrifugation.

The obtained solution was added dropwise to 4 M HCl with vigorous stirring until a brown precipitate was gained. The solid product was separated from the solution by centrifugation and washed with a limited value of deionized water to remove residual HCl. The product was a brown solid with the formula $C_{60}-(COOH)_6$ with a yield of 56%. The modified fullerene material, unlike fullerene pure, is soluble in water and other polar organic solvents, such as DMF, DMSO, and THF. This product was analyzed quantitatively and qualitatively to the characterization of the carboxylic acid functional groups. The FT-IR spectroscopy investigated the product qualitatively and then the number of COOH groups on the surface of the treated fullerenes was quantitatively determined by the titration method. In a typical experiment, 25 mL of NaOH (0.04 N) standard solution was poured into a flask. Then the modified fullerenes were added to this solution. The mixture was stirred for 20 h and then titrated with HCl (0.04 N) standard solution to determine the excess amount of NaOH in the solution and also the concentration of the carboxylates on the fullerenes. The prepared material was then analyzed by elemental analysis and showed

a significant C, H and N content. Anal. Calc, for C₆₀-(COOH)₆: C, 79.53; H, 1.21; N, 0.0. Found: C, 79.1; H, 1.19; N, 0.0%; IR (KBr, cm⁻¹) ν_{O-H} 3400–3150, ν_{C=O} 1710–1700, ν_{C-H} 2900–2700. ¹H NMR (DMSO-d₆, ppm) δ 11.09 s (COOH), 1.85 s (C₆₀-H).

¹³C NMR (DMSO-d₆, ppm) δ 169.37 (COOH), 143.28 (C₆₀-C), 57.13, 74.62, 138.19, 139.13, 139.08, 139.23, 140.31, 140.47, 142.26, 142.56, 142.75, 142.90, 143.14, 143.20, 143.45, 144.98, 145.16, 145.47, 145.94, 146.19, 146.35, 146.47, 146.51, 146.73, 146.88, 146.99, 147.58, 155.92, 157.56.

In the next step. The dried carboxylated fullerene under vacuum (500 mg, 0.482 mmol) was suspended in a solution of thionyl chloride (SOCl₂, 5 mL) and dimethylformamide (DMF) (20 mL). The suspension was stirred at 65 °C for 24 h, and then filtrated. The separated solid was washed with anhydrous tetrahydrofuran (THF) and dried in a vacuum (517 mg, yield 92%). The acylated fullerene was analyzed by elemental analysis and showed a significant C, H, and N content. Anal. Calc, for C₆₀-COCl: C, 69.08; H, 0.0; N, 0.0. Found: C, 70.04; H, 0.0; N, 0.0%; IR (KBr, cm⁻¹) ν_{C-Cl} 730–550, ν_{C=O} 1771. ¹H NMR (DMSO-d₆, ppm) 1.97 s(C₆₀-H). ¹³C NMR (DMSO-d₆, ppm) δ 68.10 s (COCl) and other ¹³C NMR peaks of this compound and carboxylated fullerene were almost similar. The acylated fullerene (500 mg, 0.429 mmol) was dispersed in (10 mL) chloroform (CH₃Cl), then was added to the solution of ethylenediamine (EDA, 200 mg) and CH₃Cl (5 mL) at a rate of 5.0 mL h⁻¹. The suspension was stirred at 65 °C for 20 h. The mixture was filtered and the gained solid was washed with anhydrous THF several times, and dried in a vacuum oven for 2 hr (319.7 mg, Yield 56%). This fullerene derivative is used as a compound containing primary amine in Schiff base reaction. Anal. Calc. for C₆₀-(CONHCH₂CH₂NH₂)₇: C, 73.13; H, 3.71; N, 14.74; Found: C, 74.18; H, 3.80; N, 14.45; IR (KBr, cm⁻¹) ν_{N-H} 3350–3180, ν_{C-H} 3000–2700, ν_{C=O} 1695. ¹H NMR (DMSO-d₆, ppm) δ 2.09 s(C₆₀-H), 2.15 (NH₂), 8.09 (NH, sec-amide), 3.48, 2.97 (CH₂-CH₂). ¹³C NMR (DMSO-d₆, ppm) δ 40.11 and 42.92s (methylene), 166.9 (amide), 58–160 (C-C and C=C in C₆₀).

Preparation of C₆₀-Schiff base complex

First, the salicylaldehyde (196 mg, 5 mmol) was dissolved in 25 mL of methanol. Then the aminated fullerene (300 mg, 0.225 mmol) in methanol (10 mL) was added drop

by drop to this solution. The solution was placed under a nitrogen atmosphere for 30 min to eliminate oxygen.

The resulting mixture was refluxed for 12 h. The mixture was then cooled and filtered under reduced pressure. The black solid was washed with diethyl ether and dried in the air. For the preparation of C₆₀-Schiff base-Pd²⁺ and C₆₀-Schiff base-Pd⁰, 40 mg of C₆₀-Schiff base was dispersed in 50 mL water. The mixture was sonicated (200 W, 40 kHz) for 10 min. Then 3.1 mg PdCl₂ (0.018 mmol) was added. After sonication for 5 min, the mixture was stirred overnight and then was filtered. The obtained solid was washed with water and acetone, respectively. The obtained C₆₀-Schiff base-Pd²⁺ was dried in a vacuum at room temperature. The reduction of C₆₀-Schiff base-Pd²⁺ by hydrazine hydrate was performed as follows: 20 mg of C₆₀-Schiff base-Pd²⁺ was dispersed in 50 mL of water. Then 90 μL of hydrazine hydrate (80%) was added. The pH of the mixture was increased to 10 by 25% ammonium hydroxide, then the reaction was stirred at 95 °C for 2 h. The final product C₆₀-Schiff base-Pd⁰ was washed with water and dried in a vacuum at 50 °C. Scheme 1, depicted the synthetic procedure of C₆₀-Schiff base-Pd²⁺ and C₆₀-Schiff base-Pd⁰. The concentration of palladium in C₆₀-Schiff base-Pd²⁺ and C₆₀-Schiff base-Pd²⁺ were 2.75 and 2.45 wt%, respectively, which were determined by ICP-AES.

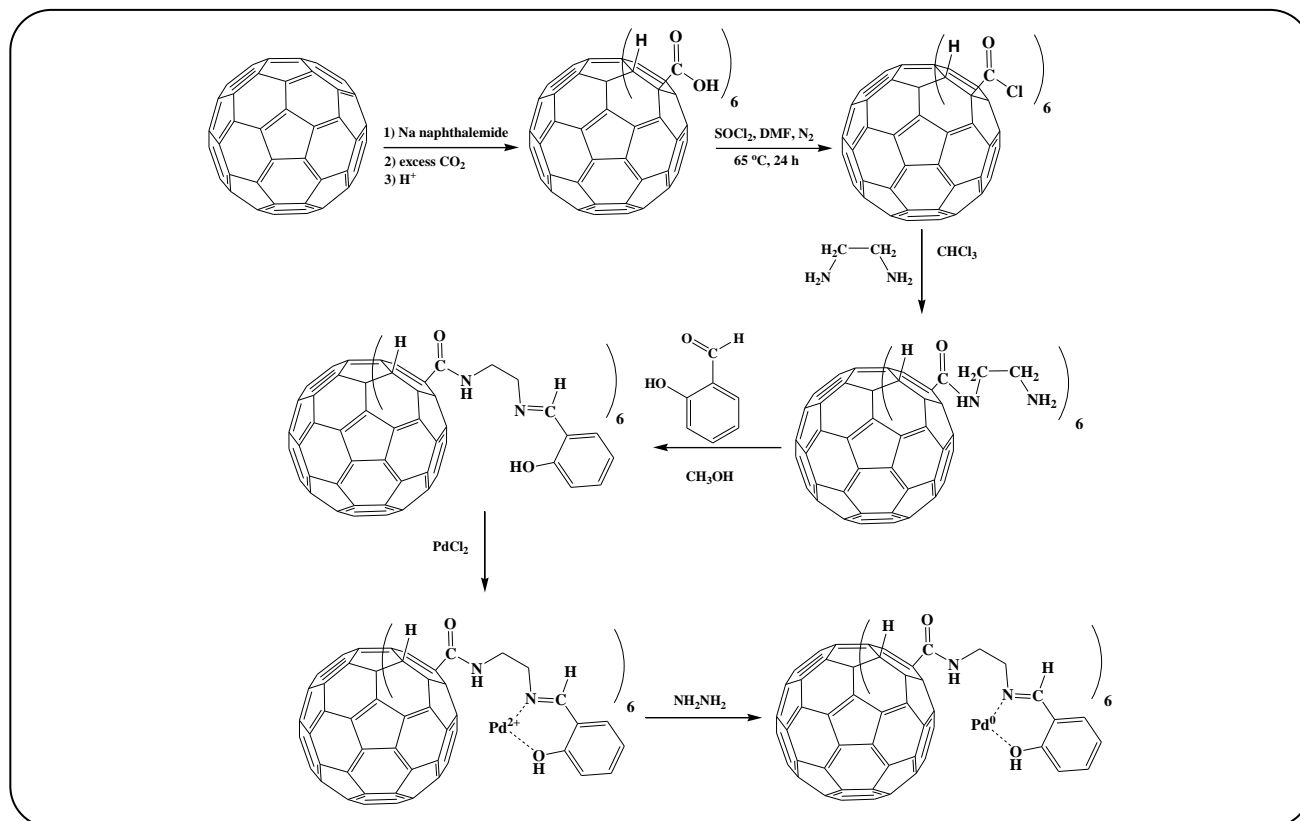
Catalytic testing

Aerobic oxidation of alcohols

The typical procedure for aerobic oxidation of alcohol is as follows: Alcohol (1 mmol), K₂CO₃ (1 mmol), and supported palladium catalyst C₆₀-Schiff base-Pd²⁺ (1 mol%) was added to 5 mL of toluene. The reaction mixture was stirred at 80 °C under 1 atm of O₂ (O₂ bubbling rate, 20 mL/min). After the reaction is complete, the catalyst was removed from the solution by filtration and washed with toluene. By using the solvent reduction under reduced pressure, the corresponding carbonyl compounds were obtained.

Heck coupling reaction

In a conical flask (50 mL), a mixture of bromobenzene (1mmol), styrene (1.5 mmol), trimethylamine (2 mmol), DMF (3 mL), and C₆₀-Schiff base-Pd⁰ (1 mol%) was added and stirred at 110 °C for 5 h (The reaction was monitored by TLC). After completion of the reaction, the reaction mixture was cooled to room temperature. In the next step,



Scheme 1: Schematic diagram synthesis of $C_{60}LPd^{2+}$ and $C_{60}LPd^0$.

the catalyst was removed by centrifuge. The recovered catalyst was washed with ethanol and ethyl acetate. The combined organic layer was dried over anhydrous sodium sulfate and its volume was reduced by a rotary evaporator. Purification of the obtained crude product was performed using column chromatography.

RESULTS AND DISCUSSION

Owing to interests and also as a part of our ongoing research program on the application of catalysts for the development of useful new synthetic methodologies [25], herein, we report a novel way to functionalized fullerene with a Schiff base to immobilized palladium nanoparticles and its applications in the oxidation of alcohols and also heck coupling as model reactions. Based on the results, it was realized that the new catalyst while being easily separable and reusable, but has the reactivity characteristic of a homogeneous catalyst.

The catalyst was prepared via grafting ethylenediamine onto chemically modified acylated fullerene C_{60} , followed by the reaction of polyamine-fullerene with salicylaldehyde and palladium chloride and then the

reduction with hydrazine. FT-IR results indicated that functionalization has been successfully and palladium immobilized on the carrier via coordinate bond in this catalyst.

The FT-IR spectra of the C_{60} , C_{60} -COOH, C_{60} -COCl, C_{60} -CO-EDA, C_{60} -CO-Schiff base, C_{60} -CO-Schiff base/Pd(II) ($C_{60}LPd(II)$) are shown in Fig. 1. The FT-IR spectra of C_{60} -COOH (curve b) show a band at 1701 cm^{-1} due to C=O stretching vibration of the carboxylic acid group, which showed the carboxylic derivative of C_{60} was prepared successfully. The presence of peak near 1760 cm^{-1} stretching in curve c approved the converting of the carboxylic acid groups (C_{60} -COOH) into the acyl chloride intermediate (C_{60} -COCl). After modification C_{60} -COCl with ethylenediamine (EDA), several new peaks were revealed in the spectrum.

The new peaks can be assigned as follows: the peak at 1651 cm^{-1} is due to C=O stretching vibration that confirmed successfully amidation (curve d). The peak at 1563 cm^{-1} is caused by C-N stretching vibration and N-H bending vibration [26]. The IR spectral data in the curve e for the C_{60} -Schiff base derivative showed characteristic

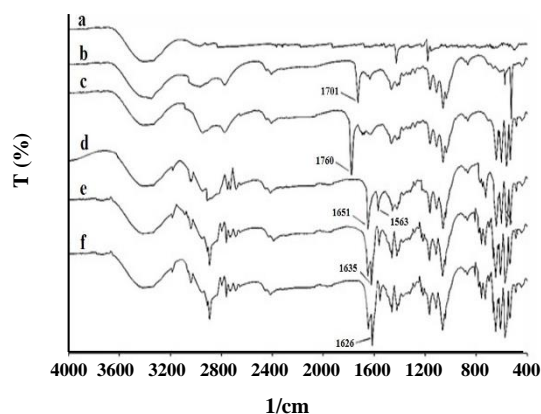


Fig. 1: FTIR spectra of (a) C_{60} , (b) C_{60} -COOH, (c) C_{60} -COCl, (d) C_{60} -CO-EDA, (e) C_{60} -CO-Schiff base, (f) C_{60} -CO-Schiff base/Pd(II) (C_{60} LPd(II)).

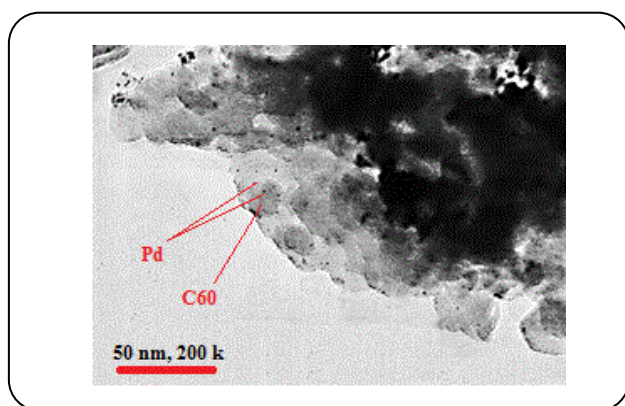


Fig. 2: TEM images of C_{60} -Schiff base/Pd(0).

imine (C=N) stretching vibration in the range of 1635 cm^{-1} . Upon complexation of the C_{60} -Schiff bases with PdCl_2 , a subtle shift in the imine stretching vibrations was observed from 1635 cm^{-1} to 1626 cm^{-1} (compared curve f with e)[27, 28].

These peaks at curves f and e displayed the successful attachment of organic ligand and subsequent coordination of Pd^{2+} ions within the material. TEM image showed that the supported palladium is in the form of proximate spherical particles smaller than 5 nm diameter and well dispersed on the surface of the carrier (Fig. 2) [29, 30]. The metal loading was defined using ICP-AES. The results indicated Pd loading of 0.24 mmol/g (2.5%). Therefore for the palladium catalysts, the metal has occupied almost 20% of the ligand.

Fig. 3 shows the XRD pattern obtained for (a) C_{60} , (b) C_{60} -COOH, (c) C_{60} -COCl, (d) C_{60} -CO-EDA, (e) C_{60} -Schiff base-Pd (II), and (f) C_{60} -Schiff base-Pd (0). In the XRD pattern of pure

fullerene C_{60} (curve "a") diffraction peaks is observed at $2\theta = 10.8, 17.6,$ and 20.7 . This pattern confirms a face-centered-cubic structure for Solid C_{60} at room temperature [31, 32].

The peaks of fullerene are observed in the XRD patterns of C_{60} Pd(II) Schiff base complex (curve "e") and C_{60} -Pd(0) Schiff base complex (curve "f") which approved the attendance of C_{60} in catalysts and indicated that C_{60} has maintained its crystallinity and morphology during the functionalized method. Four major peaks in XRD pattern of Pd (0) complex appearing in a 2θ of $39.9, 47.4, 68.7,$ and 82.0 can be attributed to the diffraction from the four reflection indexes of (100), (200), (220), and (311), respectively (card 05-0681 in the JCPDS file). The peak at $2\theta = 20.7^\circ$ is chosen to calculate the average diameter using the Scherrer equation which is 27.5, 62.2, and 62.4 nm for C_{60} -COOH, C_{60} -Schiff base-Pd(II), and C_{60} -Schiff base-Pd(0), respectively.

Fig. 4 shows the TGA curves C_{60} (curve "a"), C_{60} -Ligand-Pd (II) (curve "b") and C_{60} -Ligand-Pd (0) (curve "c"). The first mass loss in the thermal analysis of C_{60} occurs in the temperature range $100\text{--}650^\circ\text{C}$. The second mass loss is observed in region $660\text{--}780^\circ\text{C}$. The results display that removal solvents such as water begin at 100°C and decomposition carbon cage and amorphous carbon begin at 650°C [33]. In the TGA Curve C_{60} -Ligand-Pd (II) (curve "b") there are several mass losses for C_{60} -Pd (II) Schiff base complex. The first mass loss observes at a temperature range of $100\text{--}310^\circ\text{C}$ that can be assigned the removal of the trapped solvent in the complex. The second weight-loss detects at the temperature range of $310\text{--}450^\circ\text{C}$ that is attributed to the loss of ligand in the complex. The third weight loss appears in region $600\text{--}800^\circ\text{C}$ which can be assigned to the decomposition of C_{60} . This part of the thermogravimetry determines the extents of supported Ligand on fullerene which is calculated 20% (w/w). The TGA Curve C_{60} -Pd (0) Schiff base complex (Curve "c") is similar to curve "b". The residue mass percent for curves "a", "b", and "c" until 800°C is equal to 0, 1.4, and 1.5, respectively. The residue mass of C_{60} is zero because all fullerene carbons, at a temperature of 800°C , burned and converted to carbon dioxide. The residue mass for the complexes is 2.8% and 2.5% which indicated that the metal palladium is supported on the fullerene.

In order to evaluate the catalytic performance of C_{60} -Ligand-Pd $^{2+}$, the aerobic oxidation of alcohols to aldehydes or ketones was studied (Scheme 2). Various

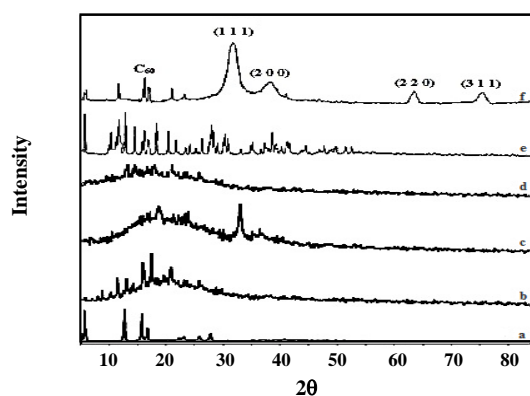


Fig. 3: XRD spectra of (a) C_{60} , (b) C_{60} -COOH, (c) C_{60} -COCl, (d) C_{60} -CO-EDA, (e) C_{60} -Schiff base-Pd(II), (f) C_{60} -Schiff base-Pd(0).

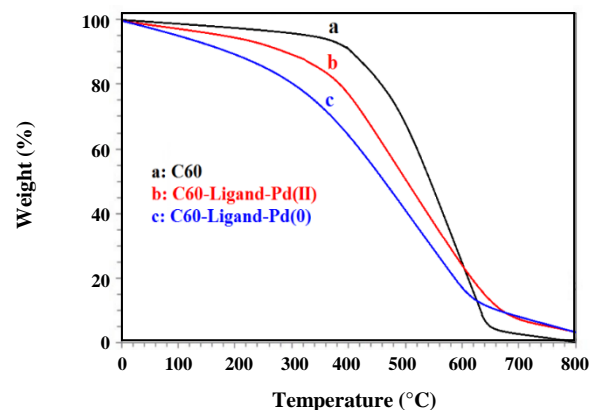
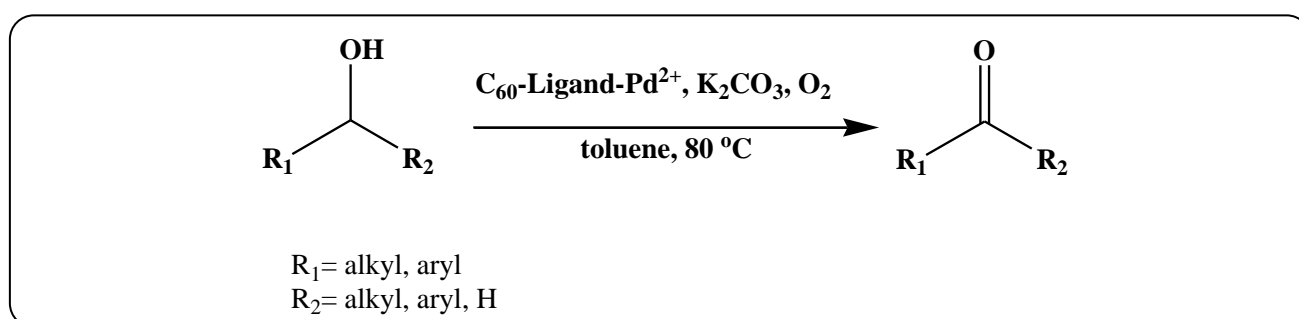


Fig. 4: TGA spectra of (a) C_{60} , (b) C_{60} -Ligand-Pd(II), (c) C_{60} -Ligand-Pd(0).



Scheme 2: Schematic diagram aerobic oxidation of alcohols to aldehydes or ketones.

alcohols were used to investigate the activity of C_{60} -Ligand-Pd²⁺, (loading amount at 1.25%) in aerobic oxidation, as listed in Table 1. In a control experiment, a prepared catalyst was used for the aerobic oxidation of benzyl alcohol. Benzyl alcohol was oxidized to corresponding aldehydes with the conversion of 100% in 2 h when C_{60} -Ligand-Pd²⁺ was used as the catalyst in the presence K_2CO_3 and O_2 at 80 °C (Table 1, entry 1). It should be noted that oxidation did not proceed in the absence of a catalyst. This result clearly indicates that alcohols can be oxidized with high selectivity by palladium nanoparticles deposited on the surface of modified- C_{60} .

Afterward, this catalyst was used in the aerobic oxidation of a wide range of alcohols under the same conditions. Substituted benzyl alcohols containing electron-donating groups such as CH_3 and OCH_3 (Table 1, entries 2, 3) are more easily oxidized compared to those that contain electron-withdrawing groups (Table 1, entry 4). Secondary benzylic alcohols, as well as were transformed to the corresponding ketones with high yields (Table 1, entry 5, 6, 9). For example, cinamyl alcohol,

allylic alcohol, was completely converted to aldehyde within 1.5 h (Table 1, Entry 7). The C=C double bonds stayed entire without an intermolecular

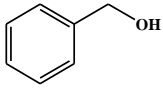
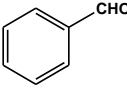
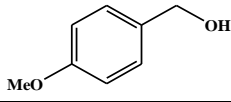
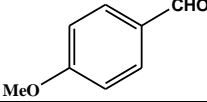
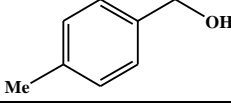
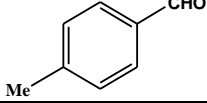
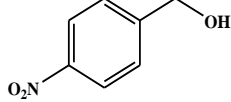
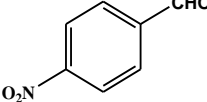
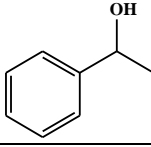
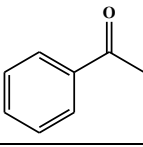
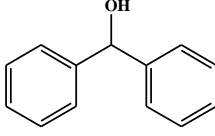
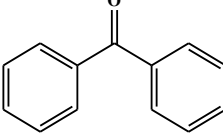
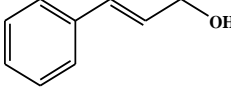
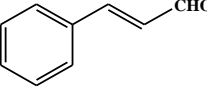
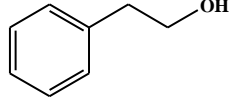
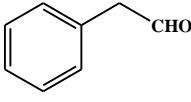
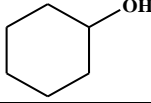
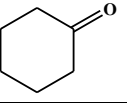
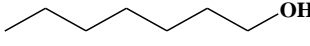
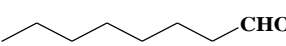
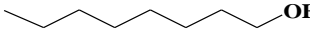
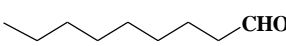
hydrogen transfer over C_{60} Ligand-Pd²⁺ under the investigated conditions. The mentioned catalyst was also used for the oxidation of the linear aliphatic alcohols (primary and secondary) and cyclic aliphatic alcohols and converted them to corresponding aldehydes or ketones in high yields (Table 1, entries 8–11).

In order to evaluate catalytic activity of the prepared hybrid material C_{60} -Schiff base-Pd⁰ as a heterogeneous nanocatalyst, the Heck coupling reaction between bromobenzene and styrene as a model reaction was investigated (Scheme 3).

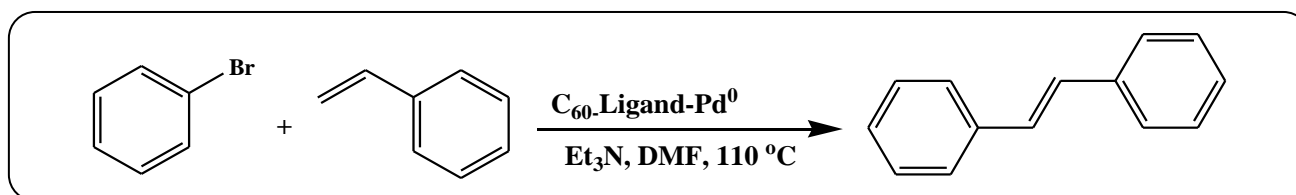
The best result (yield 96%) was obtained with 1 mol% of the catalyst in the presence of Et_3N as a base in DMF.

After optimizing the reaction conditions, a number of aryl bromides and aryl iodides were used in the reaction using 1 mol % of C_{60} -Schiff base-Pd⁰ in the presence of 2 equivalent of Et_3N in DMF at 110 °C, and the results were summarized in Table 2.

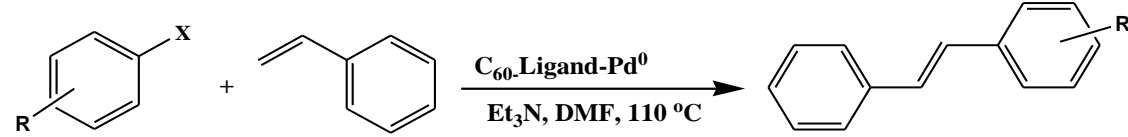
Table 1: Aerobic oxidation of various alcohols catalyzed by C_{60} -Ligand- Pd^{2+} .

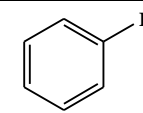
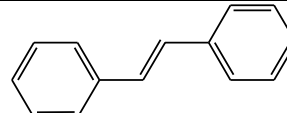
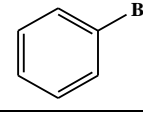
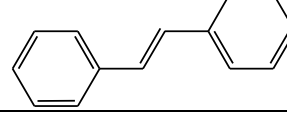
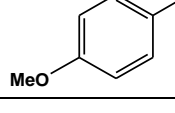
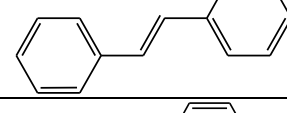
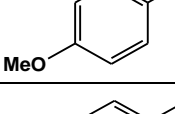
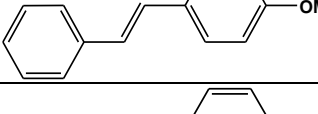
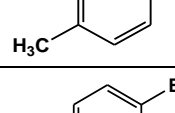
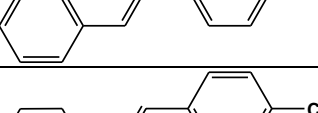
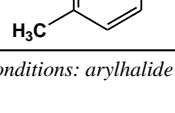
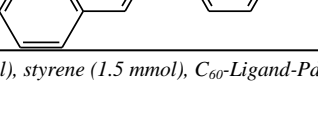
Entry	Substrates	Products	Time (h)	Conversion (%)	Yield (%)
1			1.5	100	92
2			1.0	98	90
3			1.2	98	90
4			5.0	90	82
5			1.5	98	90
6			2.0	95	90
7			1.5	95	87
8			2.0	95	90
9			4.0	80	75
10			1.5	95	90
11			2.0	95	90

^aReaction conditions: benzyl alcohol (1 mmol), catalyst (Pd 1 mol%), K_2CO_3 (1 mmol), Toluene (5 mL), 80 °C,



Scheme 3: Schematic diagram Heck reaction of aromatic aryl halides and styrene

Table 2 Heck reaction of aromatic aryl halides and styrene catalyzed C_{60} -Ligand- Pd^0


Entry	Aryl Halides	Products ^b	Time (h)	Isolated Yield(%)	Mp(°C)	
					Found	Rep. ^{Ref}
1			2	98	122-124	121-123[34]
2			3	96	122-124	121-123[34]
3			5	96	134-136	135-137[34]
4			7	92	134-136	135-137[34]
5			4	95	118-120	117-119[35]
6			5	90	118-120	117-119[35]

^aReaction conditions: arylhalide (1mmol), styrene (1.5 mmol), C_{60} -Ligand- Pd^0 (40 mg, 1 mol%), Et_3N (2 mmol), DMF (3 mL). ^bisolated yield

Fig. 5 shows the reusability of the C_{60} -Ligand- Pd^{2+} for aerobic oxidation of benzyl alcohol and C_{60} -Schiff base- Pd^0 for heck coupling bromobenzene and styrene, respectively. After the reaction, the catalyst was separated from the reaction mixture by centrifugation and washed with ethanol. Then it was reused as a catalyst in subsequent runs under identical reaction conditions. The results included in Fig 5 indicate that no efficiency loss and palladium leaching was observed in the aerobic oxidation of alcohol and heck coupling bromobenzene and styrene for up to five runs.

Heck Reaction Mechanism

The general mechanism for the Heck reaction has been widely accepted for many years; however, numerous recent and ongoing studies are revealing subtle mechanistic details of this transformation. Recent reviews on this topic provide a thorough discussion of mechanistic investigations of the Heck cyclization. A brief overview of the Heck reaction mechanism is provided here. The basic mechanism for the Heck reaction of aryl halides

involves the initial oxidative addition of a Pd (0) catalyst to afford a σ -arylpalladium(II) complex. Coordination of an alkene and subsequent carbon-carbon bond formation by syn addition provide a σ -alkylpalladium(II) intermediate, which readily undergoes β -hydride elimination to release the alkene Heck product. A base is required for the conversion of the hydridopalladium(II) complex to the active Pd (0) catalyst to complete the catalytic cycle [36].

Aerobic oxidation of alcohols to aldehydes or ketones Reaction Mechanism

There are several crucial steps involved in palladium-catalyzed alcohol oxidation. These can roughly be divided into 6 sections [37].

- (1) generation of an open coordination site for alcohol coordination
- (2) alcohol coordination
- (3) deprotonation of the palladium bound alcohol
- (4) generation of an open coordination site for β -H elimination

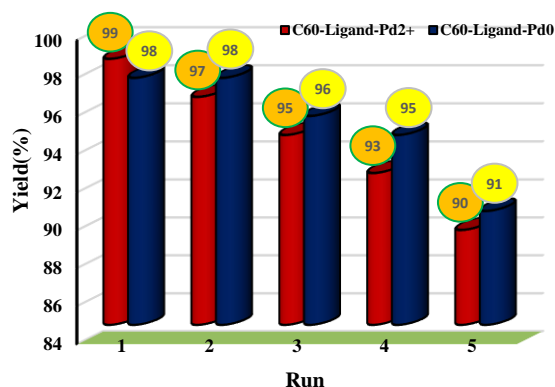


Fig.5: Reusability of the C₆₀-Ligand-Pd²⁺ for aerobic oxidation of benzyl alcohol and C₆₀-Ligand-Pd⁰ for Heck coupling bromobenzene and styrene

(5) β-H elimination to yield the oxidized product and Pd-H or Pd (0)

(6) reoxidation of Pd and ligand exchange to regenerate the active species

CONCLUSIONS

In this paper a new and recyclable palladium catalyst supported on Schiff base- modified fullerene was constructed. The built catalyst was characterized by XRD, FT-IR, TGA, ICP, and TEM. The results indicated that the stability of the catalysts was much improved and C₆₀-Ligand-Pd²⁺ and C₆₀-Schiff base-Pd⁰ were efficient and recyclable catalysts for the aerobic oxidation of alcohols and Heck coupling, respectively. The catalysts can be readily recovered and reused without significant loss of their catalytic activity.

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