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PII: S0022-328X(20)30168-6

DOI: <https://doi.org/10.1016/j.jorganchem.2020.121266>

Reference: JOM 121266

To appear in: *Journal of Organometallic Chemistry*

Received Date: 22 February 2020

Revised Date: 20 March 2020

Accepted Date: 28 March 2020

Please cite this article as: F.M. Moghaddam, A. Jarahiyan, M. Eslami, A. Pourjavadi, A novel magnetic polyacrylonitrile-based palladium Core-Shell complex: A highly efficient catalyst for Synthesis of Diaryl ethers, *Journal of Organometallic Chemistry* (2020), doi: <https://doi.org/10.1016/j.jorganchem.2020.121266>.

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A Novel Magnetic Polyacrylonitrile-based Palladium Core–Shell Complex: A Highly Efficient Catalyst for Synthesis of Diaryl Ethers

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Abstract

The present article describes the synthesis of a new magnetic polyacrylonitrile-based Pd catalyst involving polyacrylonitrile modified via 2-aminopyridine as an efficient support to immobilize Pd nanoparticles. The simple reusability, easy separation and high stability of this Pd complex make it an excellent candidate to generate a C-O bond via Ph-X activation which is a really important subject in achieving biologically active compounds. It is worth to note access to good and high yields as well as broad substrate scope have resulted from superior reactivity of this catalyst complex. Furthermore, the structure of the magnetic polyacrylonitrile-based heterogeneous catalyst was characterized by fourier transmission infrared (FT-IR) spectroscopy, field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM), X-ray diffraction (XRD). Also, its thermal properties were studied by thermogravimetric analysis (TGA).

Keywords: Polyacrylonitrile; Magnetic Complex; Unsymmetrical diphenyl ether; Palladium nanoparticle; C–Cl bond Activation;

1. Introduction

Nowadays, catalytic strategies for the synthesis of organic compounds are in focus. Among different types of catalysts, heterogeneous catalysts play a crucial role in many organic reactions due to their recyclability, insolubility in solvents and long-term stability [1, 2]. In this category, designing appropriate supports and development of their synthesis to stabilize various metals have attracted chemists' interest because solid supports' properties can directly influence the catalytic behavior [3, 4]. For this aim, there have been many efforts to utilize polymers as efficient supports like polystyrene, polyaniline, polyacrylonitrile [5,6], cellulose [7], chitosan [8], starch [9] and so on. Their uniform structures, high reusability, chemical stability, high porosity, and high surface area make them suitable candidates for immobilization of various transition metals, metal oxides, and different nanostructured materials [3].

Considering the following advantages, polyacrylonitrile (PAN) is the most attractive polymer in organic synthesis as a immobilization support [10-12]. Having unique properties of low cost, light density, simple production, high thermal

stability, as well as high catalytic efficiency feature large in applying it as a proper starting compound to prepare heterogeneous catalysts [13, 14]. Furthermore, PAN has abundant modifiable nitrile functional groups that can be simply transformed into carboxyl, amino-carbonyl and other functional groups which subsequently can be modified to attain ligands [15-17]. In these regards, PAN has recently become a source of interest; Tao et al. prepared various copper(II)-Schiff bases-functionalized polyacrylonitrile fiber catalysts and their catalytic activities have been explored in one-pot multicomponent copper-catalyzed azide-alkyne cycloaddition reaction and aldehyde, alkyne, amine coupling reaction [18]. In addition to this result, in 2019, Ma et al. designed a series of new prolinamide functionalized polyacrylonitrile fiber catalysts to investigate Knoevenagel condensation and one-pot Knoevenagel-Michael multi-component tandem reactions in a green solvent and efficiency of these catalysts have been proved [19]. In other words, this group paid attention to produce novel sulfonic acid-functionalized polyacrylonitrile fibers as a solid support to synthesize quinoline derivatives, quinazolinone, and 4-hydroxycoumarin with high yields and broad substrate scope in ethanol or water [20]. Besides their advantages, there are still some limitations like low activity, complicated separation,

and reusability of the catalyst which should be improved.

On the other hand, during the previous years, there has been growing interest in C–C, C–O, and C–N bond formation. Among them, diaryl ether structures with C–O bond are one of the most important intermediates for pharmaceuticals, biochemical, agrochemicals and other biologically active scaffolds such as Fenoprofe, Sorafenib, XK469, Tafenoquine, AMG900 that make them interesting synthesis molecules [21–24]. Although versatile copper catalyst's systems have been designed for their synthesis under different conditions, they are often complicated by the formation of byproducts and also high reaction temperatures (125–220 °C), high boiling polar solvents, and the stoichiometric amounts of copper reagents are their drawbacks [25–27].

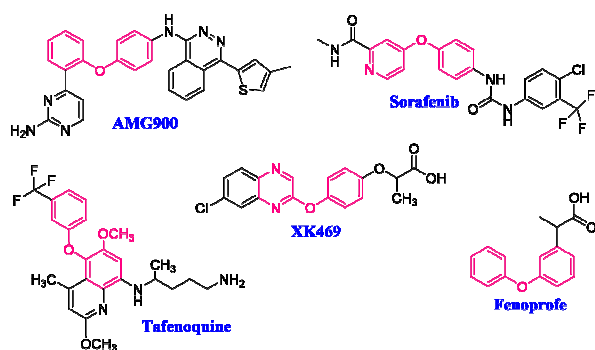
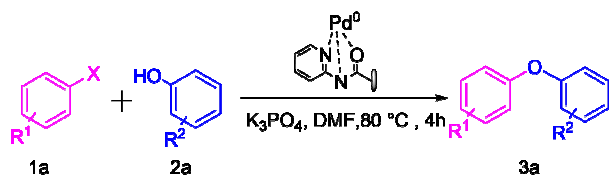


Figure 1. Some biological active compounds containing diaryl ether scaffolds.

Encouraged by this, we have made a new magnetic polyacrylonitrile-based catalyst to embed Pd⁰ with high metal loading, reusability, and stability. To deal with separation problems and metal residue in products, a magnetic catalyst has been prepared. After characterization, our research effort was devoted to developing C–O bond formation as one of the Ullmann-type condensations from the reaction of aryl halides and different phenols under mild reaction conditions and satisfactory results were obtained (Scheme 1).



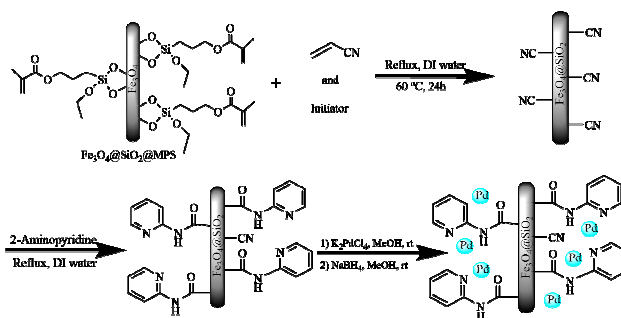
Scheme 1. Pd⁰-catalyzed C–O coupling between aryl halide (1a) and phenols (2a).

2. Results and Discussion

Synthesis and characterization of catalyst

A reusable Pd-based complex was designed for Ullmann type reaction due to the fundamental importance of C–O bond construction in organic synthesis [28–30]. To make a proper support for

immobilization of Pd nanoparticles, first of all, acrylonitrile was polymerized on the modified magnetite nanoparticles' surface (PAN) and then simply functionalized by 2-aminopyridine (AP) because of its modifiable nitrile functional groups. Finally, Pd nanoparticles were held onto the magnetic PAN/AP by applying K₂PdCl₄ as a palladium source (Scheme 2). The prepared catalyst was investigated by fourier transmission infrared (FT-IR) spectroscopy, transmission electron microscopy (TEM), field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD). Also, its thermal properties were studied by thermogravimetric analysis (TGA).



Scheme 2. Synthesis of Pd⁰@magnetic PAN/AP catalyst.

The FT-IR spectra of samples are given in Fig. 1. As shown in Figure 1, Fe–O and Si–O stretching vibration illustrated peaks at 585 and 1093 cm⁻¹. The bands at 1408 and 1714 cm⁻¹ are related to C=C and C=O stretching bonds of 3-(trimethoxysilyl)propylmethacrylate (MPS), respectively [31]. For PAN, the absorption band at 2378 cm⁻¹ is assigned to nitrile stretching vibrations which disappeared after substitution with 2-aminopyridine. The new bands at 1664, 1165, 630, 2886 and 2959 cm⁻¹ are CN of amino stretching vibration peak (N–sp²), N–sp³ C bond, bending vibration of C–H in pyridine heterocyclic ring and CH₂ of the 2-aminopyridine, respectively [32, 33].

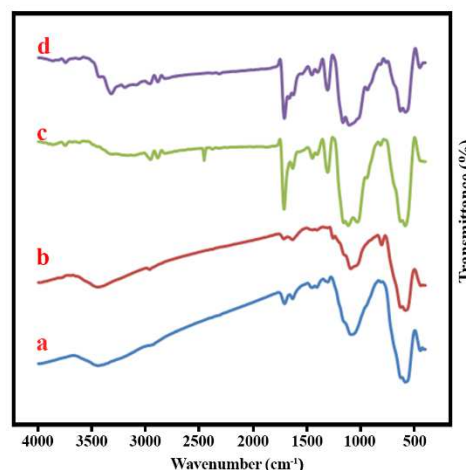


Figure 2. FT-IR spectra of (a) Fe₃O₄@SiO₂, (b) Fe₃O₄@SiO₂@MPS, (c) The magnetic PAN, (d) The magnetic PAN/AP support.

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The XRD pattern was investigated with a copper target ($\lambda = 1.54 \text{ \AA}$) for 2θ in the range of $0-80^\circ$ (Figure 3). This pattern exhibits the crystalline nature of Fe₃O₄ didn't change after completion of catalyst's synthesis and this result is confirmed based on comparing $2\theta = 30, 36, 43, 54, 57, 63$ with related JCPDS Card (No.98-011-1284).

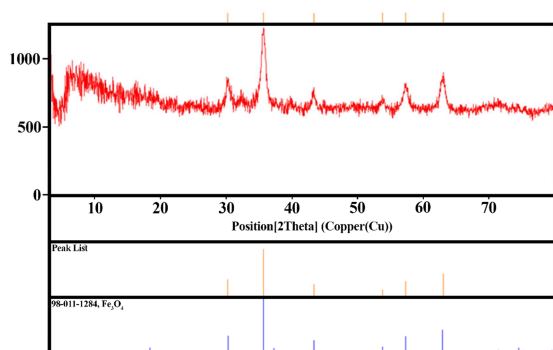


Figure 3. XRD patterns of the magnetic PAN/AP support.

FE-SEM and TEM analysis were performed to investigate morphological properties. The related FE-SEM image of the fresh catalyst showed a smooth surface of the catalyst (Figure 4a) and it didn't significantly change after 8 runs (Figure 4b). Elemental mapping and EDX of prepared catalysts are shown in Figures 5a and b, EDX analysis confirmed the presence of different components of the catalyst and according to the elemental mapping images, Pd nanoparticles were distributed homogeneously onto the prepared support. The TEM image depicts nanoparticles that have mean diameter of 34 nm and core-shell structure can be seen after modifying of magnetite's surface with organic layers in both the fresh and recovered catalyst as well as there is no significant change in the particle size of the recovered catalyst (Figure 6a and b).

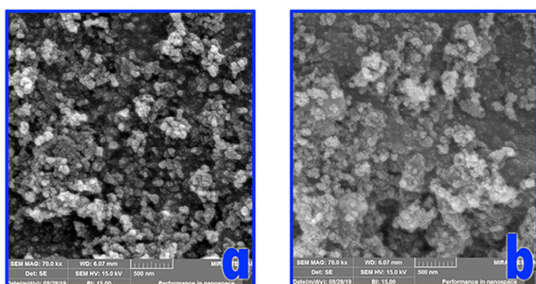


Figure 4. FE-SEM micrographs of Pd⁰@magnetic PAN/AP catalyst (a) The fresh catalyst and (b) The recovered catalyst after 8 runs.

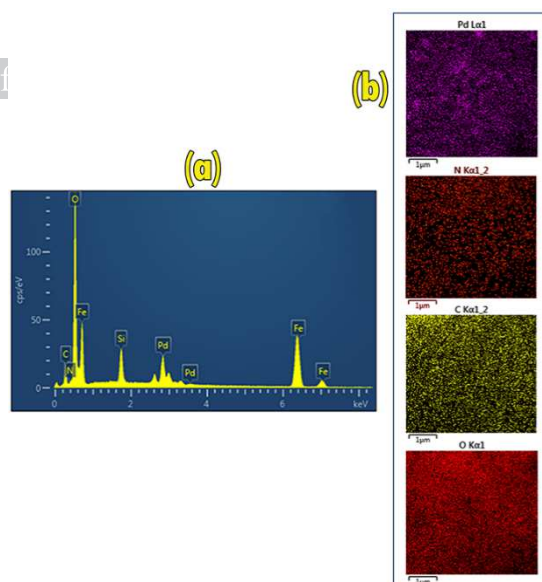


Figure 5. (a) Elemental mapping and (b) EDX of Pd⁰@magnetic PAN/AP catalyst.

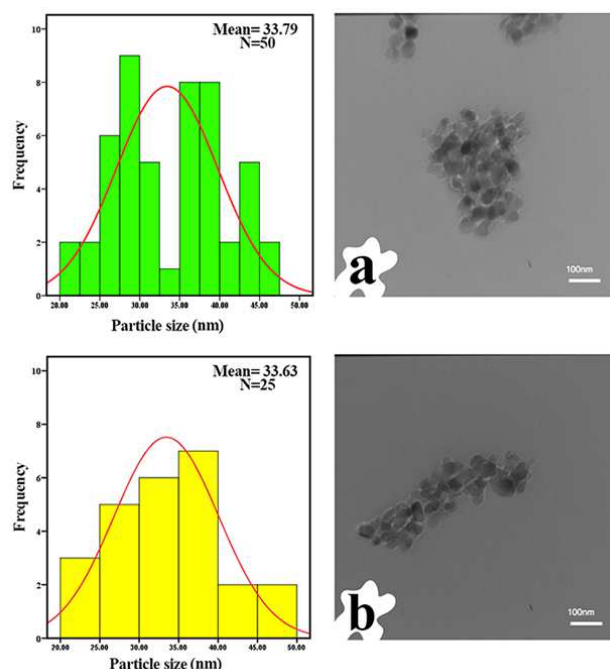


Figure 6. TEM micrographs of Pd⁰@magnetic PAN/AP catalyst (a) The fresh catalyst and (b) The recovered catalyst after 8 runs.

TGA analysis was used to measure thermal weight loss of the catalyst under an argon atmosphere to measure the amount of organic phase which immobilized on the Fe₃O₄. This weight loss around 100°C is attributable to the elimination of adsorbed water and others are related to the burning of polymer chains and organic groups. As seen in Figure 7, the catalyst shows good thermal stability and about 20 % of ligand immobilized on the magnetic PAN/AP support.

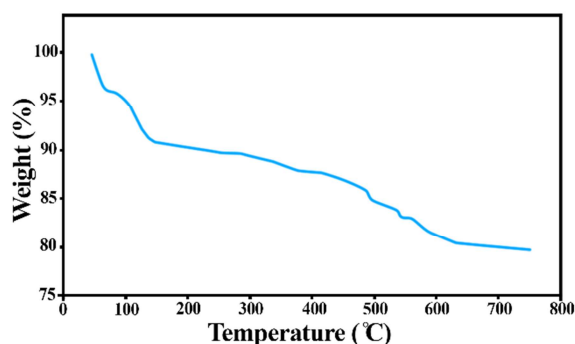


Figure 7. TGA thermogram of the magnetic PAN/AP support.

According to the CHN analysis of the magnetic PAN/AP support, the contents of various components in the support were examined and the results were summarized as follows: %C= 22.15, %H= 3.09, and %N= 5.95 in comparison with its previous step: %C= 11.43, %H= 2.60, and %N= 4.10. This result is momentous evidence to confirm that PAN and 2-aminopyridine were loaded onto the magnetic core as confirmed by TGA analysis. Besides, the Pd⁰ content was investigated by ICP - OES and the loading of palladium revealed that the high loading of metal on the surface of the support (0.69 mmol. g⁻¹).

3. Catalytic activity

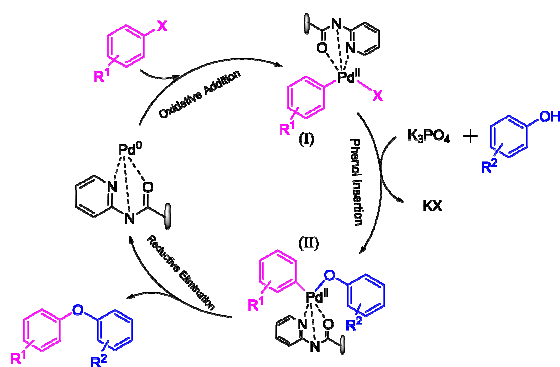
In the past few years, the continuous efforts toward the construction of the C-O bond have produced different procedures for the synthesis of various copper and palladium catalysts [34-37]. So, the new Pd⁰@magnetic PAN/AP was studied as an efficient catalyst to improve the reaction condition of the O-arylation of phenols with aryl halides. The model reaction involves the reaction of the phenol, bromobenzene, and K₃PO₄ by varying the catalyst precursor, temperature, solvent and reaction time as seen in Table 1. According to this table, no reaction took place without a transition metal catalyst even under harsh conditions and in the presence of strong inorganic bases (entry 17-19). The combination of Pd catalyst (5 mol%), K₃PO₄ (2 mmol) in DMF at 80°C for 2h was optimal, affording product 3a in 90% isolated yield (entry 12). Both DMF and NMP have been optimal solvents as aprotic polar ones but since DMF is a more common solvent for organic reactions, it has been chosen as a solvent (entry 1, 2). Among various bases, K₃PO₄ and Cs₂CO₃ with strong basic properties were found to be optimal but Cs₂CO₃ is a moisture-sensitive and more expensive base; on the other hand, K₃PO₄ is a cost-effective base which a variety of polar solvent such as NMP can be used with it [38]. In addition, other bases such as KOH, NaOH, K₂CO₃, and NaHCO₃ decreased the product yield. For instance, K₂CO₃ can be applied to deprotonated phenols but it acts moderately. And also, NaHCO₃ with weak basic properties can be decreased

the reaction rate and subsequently products' yield (entry 7-11). Moreover, applying 2 mmol of K₃PO₄ instead of 1 mmol increased the product yield. The reaction efficiency was increased when 80°C was applied rather than room temperature. To access the optimal amount of catalyst, different amounts of Pd⁰@magnetic PAN/AP were performed (entry 1, 12-16). As mentioned in Table 1, using 5 mol% of catalyst was sufficient to provide excellent yield and increasing the amount of catalyst has no remarkable effect on the product's yield, finally, only a trace amount of the favorite product was created by use of catalyst without a transition metal (entry 17-19).

Our optimal approach is to use phenol (1 mmol), aryl halide (1mmol), Pd⁰@magnetic PAN/AP catalyst (5 mol%) and K₃PO₄ (2 mmol) in DMF at 80°C for 2h. These conditions were applied to obtain different diaryl ether derivatives and the results have been summarized in Table 2. The substitution variation on starting substrates was investigated like several electron-donating and -withdrawing groups on aryl halide (1a-h), phenol (2a-e), 1-naphthol (2f) and 2-naphthol (2g) to study electronic effects. First, the scope of phenols was investigated, with electron-donating groups on phenol substrates such as methoxy and methyl, diaryl ethers are formed in fair to good yield (entry 4 and 5) and on the contrary, electron-withdrawing groups on it like a nitro group show lower yield (entry 24) because such groups can reduce the nucleophilicity of phenols. The reaction between 1-naphthol and electron-withdrawing aryl halides required a longer reaction time to attain high yields (entry 33). In aryl halides scope, different groups were examined (1a-h) and the best results were obtained when aryl iodides and bromides substrates were used rather than unactivated aryl chlorides. It is worth to note aryl chlorides are less active halides which in this case they have generated the expected products. Also, the electron-rich and weak electron-poor groups on aryl halides have provided a similar yield of the desired product and strong electron-withdrawing groups indicate high yield despite using aryl chloride (entry 6) but a steric hindrance in 1-chloro-2-nitro benzene can reduce product yield (entry 7 and 20).

Based on the literature review, a catalytic cycle is demonstrated in Scheme 3. It is suggested that the reaction begins with an oxidative - addition step of obtained Pd (0) catalyst to generate aryl-Pd (II) intermediate I. Subsequently, insertion of phenol or 1-naphthol, 2-naphthol produces intermediate II. After reductive elimination of intermediate II, the expected product is made and active Pd (0) catalyst is returned to the next reaction cycle.

To study the recyclability of the catalyst, a series of the model reaction was performed and the prepared Pd catalyst was isolated after each reaction, washed with methanol (3×10 mL), dried at 60 °C for 12 h, and prepared for the next reaction to prove the reusability of the catalyst (Figure 8). Interestingly, based on ICP result, no remarkable metal leaching was observed in the eighth run. Besides, the recovered catalyst reused several times without significantly change in the products' yield.



Scheme 3. Proposed Mechanism.

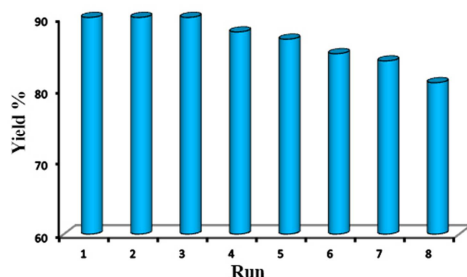


Figure 8. The recyclability of catalyst.

To compare the efficiency and activity of the synthesized catalyst, several methods have been collected in Table 3. The use of complex and bulky ligands and expensive bases like Cs_2CO_3 , long reaction time, low yield and low scope of reaction are some of the limitations of previous works. As can be understood from these results, we have tried to find a new catalytic system that can develop reaction time, product yield, as well as catalyst loading and reusability.

4. Conclusion

To sum up, an effective procedure for the construction of a magnetic polyacrylonitrile-based Pd catalyst has been described to synthesis C-O bond formation. The importance of the diaryl ether derivative scaffolds in pharmacologically active compounds encouraged us to design a new catalyst analog for the synthesis of such substrates to improve reaction conditions. In the following, the scope of various aryl halide and phenol was studied which have demonstrated high yield even in less reactive starting materials.

5. Experimental Section

5.1. Synthesis of Pd^0 @magnetic PAN/AP catalyst

The synthesis procedure includes several steps: (1) immobilization of (3-Mercaptopropyl)trimethoxysilane (MPS) on Fe_3O_4 @ SiO_2 ; (2) polymerization of acrylonitrile on Fe_3O_4 @ SiO_2 @MPS microspheres; (3) immobilization of 2-aminopyridine (AP) on it; and (4) preparation of Pd^0 @Magnetic PAN/AP. In the following, the synthesis details will be described:

5.1.1. Immobilization of MPS on Fe_3O_4 @ SiO_2

The magnetic nanoparticles were synthesized by the co-precipitation method. First, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (10 mmol, 2 g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (20 mmol, 5.4 g) were dissolved in 50 ml of deionized water in a three-necked flask. Subsequently, ammonium hydroxide (28% v/v) was added slowly into the mixture, with the solution pH held in 10. The reaction was performed under an argon atmosphere and mechanical stirrer at room temperature for 30 min. The resulting magnetite nanoparticles were collected by a magnet and washed with deionized water (30 ml) and methanol (3×30 ml), and then dried in a vacuum oven at 60°C for 12h. In the following step, 1.0 g of obtained Fe_3O_4 was dispersed in dry ethanol (20 ml) and 2 ml of ammonium hydroxide (28% v/v) by ultrasonication for 30 min. Then, 10 mmol of tetraethylorthosilicate (TEOS) was added dropwise to the flask and the mixture was stirred at 60°C for 24 h. In the end, the Fe_3O_4 @ SiO_2 nanoparticles were separated using an external magnet, washed with deionized water and methanol three times, and finally dried in a vacuum oven at 60°C for 24 h. After dispersing 1.0 g of Fe_3O_4 @ SiO_2 by ultrasonic waves in 20 mL dry ethanol, 2 mL of NH_3 was added to the flask. Then, 3-(trimethoxysilyl)propylmethacrylate (MPS) (10 mmol, 3 mL) was added dropwise during 10 min to the previous mixture and it was stirred at 60°C for 48 h. The Fe_3O_4 @ SiO_2 @MPS nanoparticle was isolated from the supernatant by use of a magnet, washed them thoroughly with methanol and dried in a vacuum oven at 60°C for 12 h.

5.1.2. Polymerization of acrylonitrile on Fe_3O_4 @ SiO_2 @MPS Microspheres

Polyacrylonitrile-coated Fe_3O_4 @ SiO_2 @MPS was synthesized as follows. 0.50 g of Fe_3O_4 @ SiO_2 @MPS in 30 mL deionized water, 3 mL of acrylonitrile and 10 mg of AIBN were mixed in a single-necked flask, completely degassed under N_2 atmosphere and refluxed for 24h. The resulting magnetite nanoparticles were separated by an external magnet and washed with deionized water and methanol (3×30 ml), and then dried in a vacuum oven at 60°C for 12h to give the Magnetic PAN.

5.1.3. Immobilization of 2-aminopyridine (AP) on functionalized magnetite nanoparticles

The magnetic PANs (0.50 g) in deionized water (25 mL) and 2-aminopyridine (10 mmol) were heated to reflux for 5h. Then, the nanoparticles were separated, washed with deionized water and methanol (3×30 ml), and dried in a vacuum oven at 60°C for 12h to give the Magnetic PAN/AP.

5.1.4. Preparation of Pd@Magnetic PAN/AP

At the final step, 0.25 mmol of K_2PdCl_4 and 0.50 g of magnetic PAN/AP in 10 mL methanol were added to a round bottom flask and stirred at room temperature for 48h. After that, the obtained catalyst charged with $NaBH_4$ (15 mg) to give Pd⁰@magnetic PAN/AP. The catalyst was separated by a magnet, washed with methanol three times (3×20 mL), and dried under reduced pressure.

5.2. Application in Ullmann Cross-coupling Reactions;

The catalytic efficiency of Pd⁰@magnetic PAN/AP was investigated in the Ullmann Cross - coupling reaction. Briefly, 1 mmol of aryl halides, 1 mmol of phenols, 2 mmol of Tripotassium phosphate and catalyst (5 mol%) in solvent (2 ml) were added into a round - bottom flask at 80 °C. The progress of the reactions was monitored by thin-layer chromatography (TLC) (EtOAc/n - Hexane, 1:10) and after their completion; the catalyst was isolated by an external magnet, washed with methanol and dried under vacuum oven at 60 °C for 12 h for next runs. On the other hand, the mixtures were worked up, purified by plate chromatography and prepared for ¹HNMR and ¹³CNMR analysis.

Acknowledgments

This work was supported by the Research Affairs Division Sharif University of Technology (SUT), Islamic Republic of Iran and we acknowledge its support.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/.....>

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Journal Pre-proof

Captions for Schemes:

Scheme 1. Pd⁰-catalyzed C-O coupling between aryl halide (**1a**) and phenols (**2a**).

Scheme 2. Synthesis of Pd⁰@magnetic PAN/AP catalyst.

Scheme 3. Proposed Mechanism.

Captions for Figures:

Figure 1. Some biological active compounds containing diaryl ether scaffolds.

Figure 2. FT-IR spectra of (a) Fe₃O₄@SiO₂, (b) Fe₃O₄@SiO₂@MPS, (c) The magnetic PAN, (d) The magnetic PAN/AP support.

Figure 3. XRD patterns of the magnetic PAN/AP support.

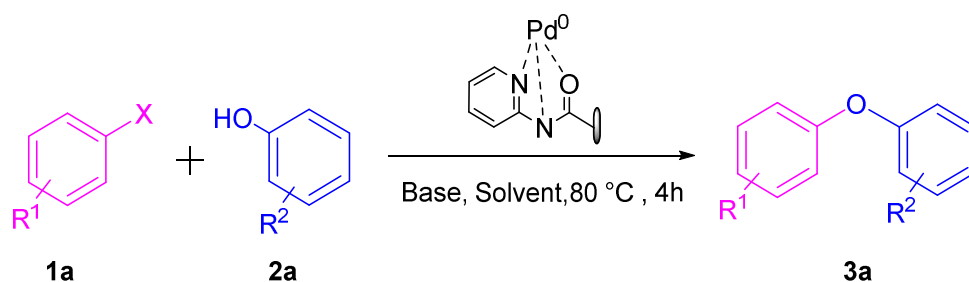
Figure 4. FE-SEM micrographs of Pd⁰@magnetic PAN/AP catalyst (a) The fresh catalyst and (b) The recovered catalyst after 8 runs.

Figure 5. (a) Elemental mapping and (b) EDX of Pd⁰@magnetic PAN/AP catalyst.

Figure 6. TEM micrographs of Pd⁰@magnetic PAN/AP catalyst (a) The fresh catalyst and (b) The recovered catalyst after 8 runs.

Figure 7. TGA thermogram of the magnetic PAN/AP support.

Figure 8. The recyclability of the catalyst.

Table 1. Optimization condition for Pd⁰@magnetic PAN/AP catalyst on diaryl ether formation^a

Entry	Solvent	Base	Catalyst (mg)	Temperature (°C)	Time (h)	Yield (%) ^b
1	DMF	K ₃ PO ₄	10	80	2	91
2	NMP	K ₃ PO ₄	10	80	2	91
3	CH ₃ CN	K ₃ PO ₄	10	80	2	52
4	DMSO	K ₃ PO ₄	10	80	2	73
5	1,4-Dioxane	K ₃ PO ₄	10	80	2	65
6	Toluene	K ₃ PO ₄	10	80	8	46
7	DMF	KOH	10	80	2	67
8	DMF	NaOH	10	80	2	71
9	DMF	K ₂ CO ₃	10	80	8	48
10	DMF	NaHCO ₃	10	80	8	Trace
11	DMF	Cs ₂ CO ₃	10	80	2	89
12 ^c	DMF	K ₃ PO ₄	5	80	2	90
13	DMF	K ₃ PO ₄	2.5	80	2	70
15	DMF	K ₃ PO ₄	1	80	2	51
16	DMF	K ₃ PO ₄	7.5	80	2	91
17	DMF	K ₃ PO ₄	-	80	24	Trace
18	DMF	K ₃ PO ₄	-	120	24	Trace
19	DMF	Cs ₂ CO ₃	-	120	24	Trace

^aphenol (1 mmol), bromobenzene (1 mmol), base (1 mmol), catalyst, solvent (2 ml) and temperature.

^bIsolated yield.

^cphenol (1 mmol), bromobenzene (1 mmol), base (2 mmol), catalyst, solvent (2 ml).

Table 2. Reaction Scope of C-O bond formation via Pd⁰@Magnetic PAN/AP catalyst.

Entry	1	2	Yield [%] ^[b]
1-3			$\frac{X=I}{X=Br}{X=Cl}$ $\frac{92}{90}{81}$
4			91
5			88
6			83
7			76
8			88
9-11			$\frac{X=I}{X=Br}{X=Cl}$ $\frac{95}{92}{85}$
12			90
13			89
14-16			$\frac{X=I}{X=Br}{X=Cl}$ $\frac{83}{91}{83}$
17			89
18			88
19			85
20			81
21-23			$\frac{X=I}{X=Br}{X=Cl}$ $\frac{90}{87}{83}$
24			81
25-27			$\frac{X=I}{X=Br}{X=Cl}$ $\frac{75}{71}{Trace}$
28-30			$\frac{X=I}{X=Br}{X=Cl}$ $\frac{91}{86}{81}$
31			88
32			91
33			82
34			79
35-37			$\frac{X=I}{X=Br}{X=Cl}$ $\frac{91}{86}{77}$
38			90
39			86

Table 3. Comparison of catalysts activity in C-O coupling reactions of aryl halides with phenols.

Entry	Catalyst(Loading)	Reaction conditions	Time X=I/ Br /Cl	Yield X=I/ Br /Cl	Reference
1	[(Cinnamyl)PdCl] ₂ (0.025 mol%)	Bulky biarylphosphine ligand, Toluene/DME, K ₃ PO ₄ , r.t.	-/16h/-	-/91/-	[39]
2	CuFe ₂ O ₄ (5 mol %)	2,2,6,6-tetramethylheptane- 3,5-dione, NMP, Cs ₂ CO ₃ , 135 °C, Argon atmosphere	24/24/24	91/34/trace	[40]
3	CuI (5mol%)	Picolonic acid, DMSO, K ₃ PO ₄ , 80 °C	21/-/-	85/-/-	[41]
4	UiO-66-NH ₂ -MIm/CuO NPs (5mol%)	DMSO, KOH, 110 °C, N ₂ atmosphere	18/18/24	95/93/30	[42]
5	CuBr	ACHN initiator, DMF, Cs ₂ CO ₃ , 100 °C, Microwave	-/1.5/-	-/55/-	[43]
6	Pd/ZnO nanoparticles (0.05 mol%)	K ₂ CO ₃ , 120 °C	5/15/20	98/80/70	[44]
7	Pd-ZnFe ₂ O ₄ (10 mol%)	DMSO, K ₃ PO ₄ , 110 °C	4/4/3.5	84/88/90	[45]
8	Pd ⁰ @Magnetic PAN/AP	DMF, K ₃ PO ₄ , 80 °C	2/2/4	92/90/81	This work

Highlights

- ❖ Synthesis of Diaryl ethers via a Palladium-Magnetic Polyacrylonitrile Catalyst.
- ❖ Unexpected C–Cl Bond Activation.
- ❖ The simple reusability, easy separation and high stability of catalyst.
- ❖ The good and high yields as well as broad substrate scope have been resulted.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: