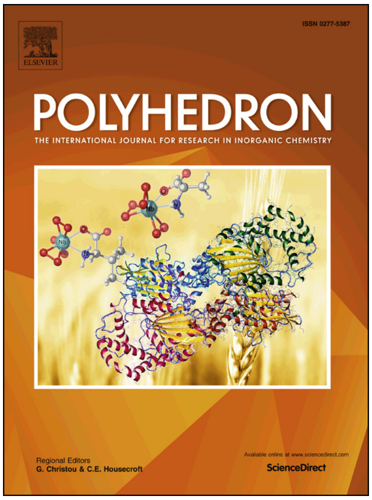


Fe_3O_4- AMPD-Pd: a novel and efficient magnetic nanocatalyst for synthesis of sulfides and oxidation reactions

Taiebeh Tamoradi, Nazanin Moeini, Mohammad Ghadermazi, Arash Ghorbani-Choghamarani

PII: S0277-5387(18)30389-9
DOI: https://doi.org/10.1016/j.poly.2018.07.002
Reference: POLY 13267

To appear in: *Polyhedron*

Received Date: 20 February 2018
Revised Date: 10 June 2018
Accepted Date: 2 July 2018

Please cite this article as: T. Tamoradi, N. Moeini, M. Ghadermazi, A. Ghorbani-Choghamarani, Fe_3O_4- AMPD-Pd: a novel and efficient magnetic nanocatalyst for synthesis of sulfides and oxidation reactions, *Polyhedron* (2018), doi: https://doi.org/10.1016/j.poly.2018.07.002

Fe_3O_4- AMPD-Pd: a novel and efficient magnetic nanocatalyst for synthesis of sulfides and oxidation reactions

Taiebeh Tamoradi [a], Nazanin Moeini [a], Mohammad Ghadermazi,[a,*] Arash Ghorbani-Choghamarani[b,*]

[a] University of Kurdistan, Department of Chemistry, Faculty of Science, Sanandaj, Iran
e-mail: mghadermazi@yahoo.com
[b] Department of Chemistry, Faculty of Science, Ilam University, P.O. Box, 69315516, Ilam, Iran
e-mail: a.ghorbani@mail.ilam.ac.ir

A B S T R A C T

A novel magnetic nanoparticle was synthesized with effective catalytic properties and recyclable ability. This heterogeneous nanocatalyst was identified using Fourier transform infrared, scanning electron microscopies, X-ray diffraction, vibrating sample magnetometer, inductively coupled plasma atomic emission spectroscopy and thermogravimetric analysis methods. The nanocatalyst was used for the synthesis of the one-pot C–S coupling synthesis of sulfide in the presence of KOH, S_8 as the sulfur source in DMSO as the solvent at 100 ˚C. Also, the oxidation of sulfides to sulfoxides and oxidative coupling of thiols to disulfides in the presence of the catalyst was tested. The catalyst has unique properties such as ability of magnetic separation from the reaction, high repeatability, and high thermal and chemical stability.

Keywords: Pd, magnetic nanoparticle, sulfides, sulfoxides, disulfides

---

[*] Address correspondence to University of Kurdistan, Department of Chemistry, Faculty of Science, Sanandaj, Iran.; e-mail: mghadermazi@yahoo.com (M. Ghadermazi). Ilam University, Faculty of Science, Department of Chemistry, Ilam, Iran.; e-mail: a.ghorbani@mail.ilam.ac.ir

1. Introduction

Heterogeneous and homogeneous catalysts are two main types of catalysts. Homogeneous catalysts have higher catalytic activities than heterogeneous catalysts as the catalysts and reactive substances are in the same phase. In contrast, the recovery of most of heterogeneous catalysts is much easier than homogeneous ones [1, 2]. In order to combine the advantages of homogeneous and heterogeneous catalysts, nanoparticles (NPs) have recently emerged as great and useful heterogeneous supports for the immobilization of homogeneous catalysts [3, 4]. However, nanoparticles cannot be separated by conventional methods such as filtration. Their separation from the reaction mixture requires special techniques, such as centrifuge, which is not economically feasible [5]. Therefore, by using efficient magnetic nanoparticles, this problem can be overcome because magnetic nanoparticles can be recovered in the presence of an external magnetic field and subsequently reused, which is more effective than a centrifuge. MNPs can be intermediate between homogeneous [6] and heterogeneous materials [7, 8]. They represent an economical, practical and environmentally benign means for catalyst recovery [9]. Also, magnetic nanoparticles can be functionalized by organic and organometallic catalysts [10]. Easy preparation, large surface area ratio, facile recovery and recyclability by a magnet, and low toxicity and price are the other advantages of magnetic nanoparticles [11]. In recent years, Fe_3O_4 magnetic nanoparticles (MNPs) have been attracted a great attention as a heterogeneous catalyst because of easy synthesis, simple handling, and ease of recovery with an external magnetic field, high surface area, and eco-friendliness [12].

The selective oxidation of sulfides to sulfoxides is useful for the synthesis of chemical and biological medicine. They are useful in the activation of enzymes [13]. Antiulcer, antifungal, antihypertensive, antibacterial and anti-atherosclerotic are other important biological roles of sulfoxides that can be mentioned [14, 15]. Disulfides, as the product of oxidative coupling of thiols, play interesting roles in biological and chemical fields such as DNA cleavage properties, stabilization of peptides in proteins, protecting groups, vulcanizing agents, and oils for rubber [16, 17].

The formation of the carbon-sulfur bond is one of the most important chemical reactions because of its great applications in medicinal chemistry, organic synthesis and in materials sciences [18-20]. Transition-metal-catalyzed cross-coupling reactions of aryl halides with thiols are the most common synthetic methods for the preparation of diaryl sulfides [21]. The main limitations of the C–S coupling reactions consist of the direct use of highly volatile, foul smelling and toxic thiols, which threatens health [22, 23]. Furthermore, there are reports of C-S coupling reactions with several heterogeneous catalysts such as Cu-MPIOS, MCM-41-Adenine-Zr, PdNP–PNF, SBA-15@Adenine-Pd, MCM 41@Serine@Cu(II), etc . But, above-mentioned catalysts have complicated recovery process; therefore magnetic catalysts have been proposed as a primary solution [24-28]. To overcome these disadvantages, recently, various sulfur sources have been employed for converting aryl halides to aryl thioesters by transition metal catalysts such as nickel or palladium nanoparticles [29-31]. S_8 is commonly used for S-arylation among sulfur reagents because it is low cost and odorless [32]. Herein, we report the synthesis and characterization of Fe_3O_4-AMPD-Pd as a heterogeneous nanocatalyst for one-pot odorless carbon-sulfur bond formation in the presence of S_8. Also, we use the nanoparticle as a catalyst for the oxidation of sulfides and oxidative coupling of thiols in the presence of H_2O_2. Moreover, the catalyst separation is done easily by an external magnet and the nanocatalyst can be reused for several times without significant degradation in activity.

2. Experimental

2.1. General remarks

Chemical materials and solvents were purchased from Merck, Sigma-Aldrich and Fluka companies and used without further purification. The FT-IR spectrum of the sample in KBr pellets was recorded using a VERTEX 70 model BRUKER FT-IR spectrophotometer. The X-ray powder diffraction (XRD) data were collected with Co Kα radiation (λ= 1.78897 Å) operating at 40 keV. The particle size and morphology were investigated by FESEM-TESCAN MIRA3. The amount of Pd was measured by inductively coupled plasma-optical emission spectrometry (ICP-OES). The thermogravimetric analysis (TGA) curves were recorded by Shimadzu DTG-60 instrument. ^{1}H NMR spectra were recorded on a Bruker AVANCE300 spectrometer operating at 400 MHz. Melting point was measured with an Electrothermal 9100 apparatus. The supermagnetic properties of the catalyst were measured on a Vibrating Sample Magnetometer (VSM) MDKFD.

2.2. Preparation of Catalyst

First step: Fe_3O_4 nanoparticles were synthesized by coprecipitation method [33]. Second step: for preparation Fe_3O_4-Cl, 1g of synthesized black precipitation and 1.5 mL of 3-chloropropyltrimethoxysilane (CPTMS) were added to 20 mL of toluene under reflux condition for 24 h. The synthesized of Fe_3O_4-Cl was separated by a magnetic separator and washed with hexane and dried at 50 °C. Third step: for the functionalization of Fe_3O_4-Cl with 2-amino-2-methyl-1,3-propanediol (AMPD), 1g of the previous nanocomposition was dispersed in toluene, then 3 mL trimethylamine and 0.21 g AMPD were added to the reaction vessel. The mixture was stirred at 100 °C for 48 h. The nanoparticles were separated from the reaction solution with an external magnet, and washed with deionized water and ethanol several times and dried. In the last step, Fe_3O_4- AMPD nanoparticles was used as a ligand for anchoring to palladium. In this process, 0.5 g of the nanocomposite and 0.25 g $Pd(OAc)_2$ were added to 30 mL pure ethanol and was refluxed for 24 h. The resulting nanoparticles were separated by a magnetic field. Then it was washed using ethanol and dried at room temperature.

2.3. General procedure for the oxidation of sulfides to the sulfoxides

To prepare the sulfoxide from the desired sulfide, 1 mmol of sulfide, 0.3 mL of hydrogen peroxide 33% and 0.005 g of synthesized nanocatalyst were added to the test tube. The mixture was stirred until the sulfoxide was produced. The reaction completion was monitored by thin layer chromatography (TLC). The magnetic nanocatalyst was separated from the reaction by a magnetic field, and then the reaction mixture was washed with EtOAc. After evaporation of the excess solvent, the yields of the synthesized products were measured.

2.4. General procedure for the oxidative coupling of thiols to the disulfides

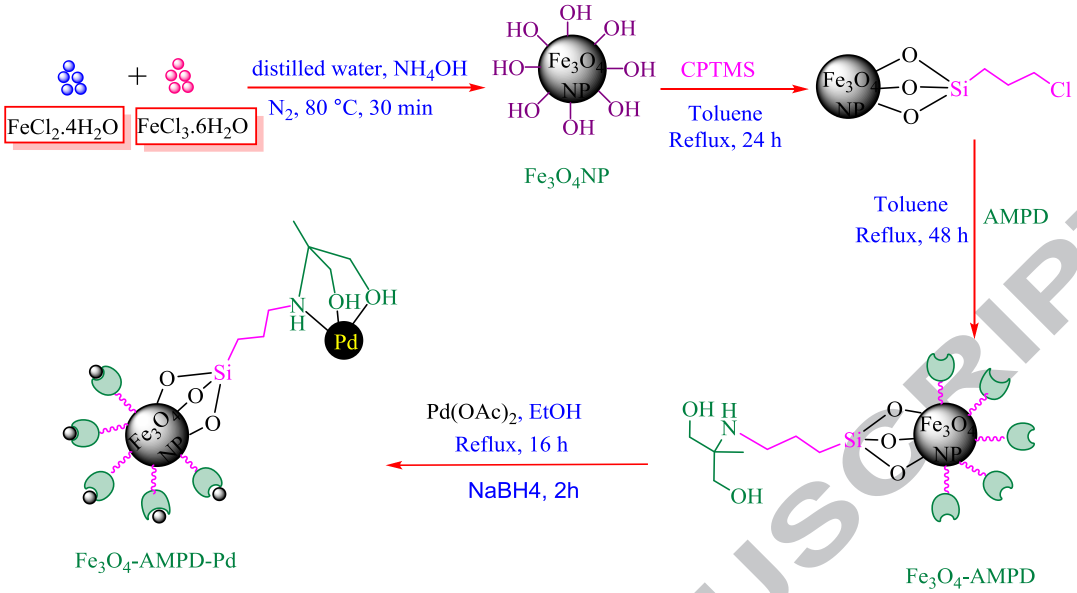
0.005 g Fe_3O_4- AMPD-Pd was added to a mixture including 1 mmol thiol, 0.4 mL H_2O_2 33% and free solvent were stirred at room temperature. The reaction was followed by TLC after completion. The nanocatalyst was isolated by a simple magnet.

2.5. General procedure for the synthesis of sulfides

For synthesis of sulfide, 1 mmol S_8, 1mmol aryl halide, 0.4 g KOH, 0.06 g Fe_3O_4-AMPD-Pd nanocatalyst in 2 mL DMSO solvent at 100 °C were stirred. The reaction was checked by TLC. After ensuring the complete synthesis of sulfide, a few ethyl acetate was added to the mixture, and then washed with H_2O several times. At the last step, the magnetic nanoparticle was separated from the mixture with a magnet. After evaporation of the organic solvent, sulfide yields were calculated.

3. Results and discussion

Scheme 1 shows the preparation of a new magnetic nanoparticle catalyst.



Scheme 1. Preparation of Fe_3O_4- AMPD-Pd nanoparticles.

3.1. Characterizations of the nanocatalyst

The pattern of XRD is shown in Fig. 1. The peaks at 2θ = 29.05°, 35.8°, 43.6°, 54.4°, 57.6° and 63.15° assigned to diffraction (200), (311), (400), (422), (511) and (440), respectively, which make a concordance of the data of the magnetite. The peaks at 2θ = 39.85°, 46.85° and 68.15° are indexed to the presence of palladium on a magnetic substrate [35].

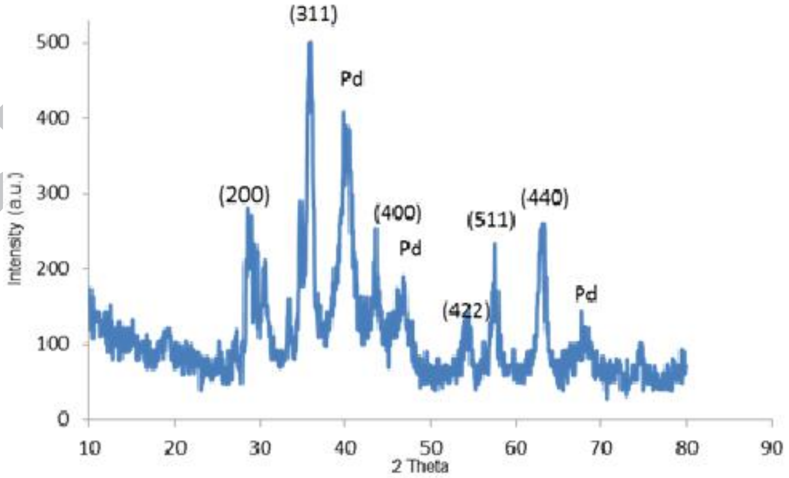


Fig. 1. XRD pattern of Fe_3O_4- AMPD-Pd MNPs

The average particle size and surface morphology of the magnetic nanoparticle were investigated by TEM and are shown in Fig.2. Also, elements of synthesized nanoparticle were identified by EDX spectrum which contained C, N, O, Si, Fe, and Pd. As shown in Fig. 3.

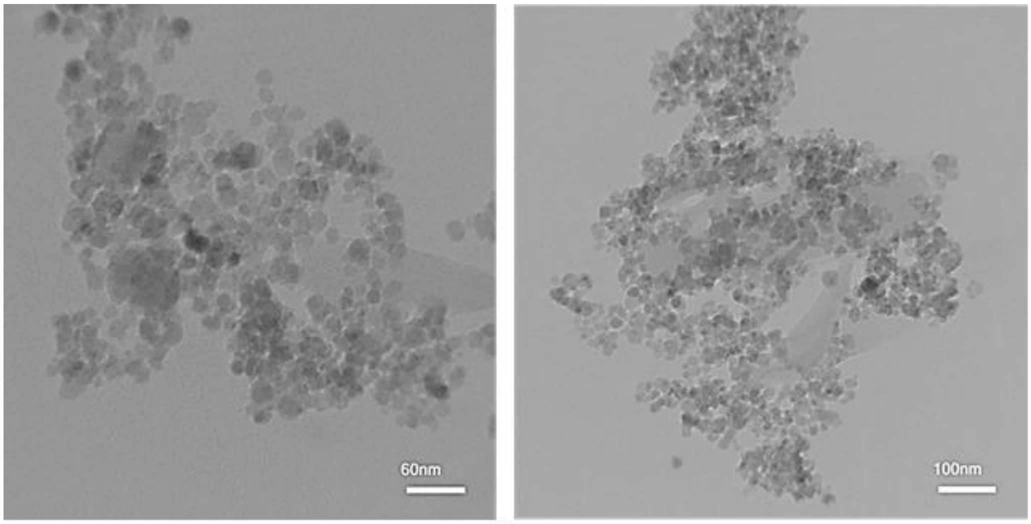


Fig. 2. The TEM images of Fe_3O_4- AMPD-Pd at different magnifications

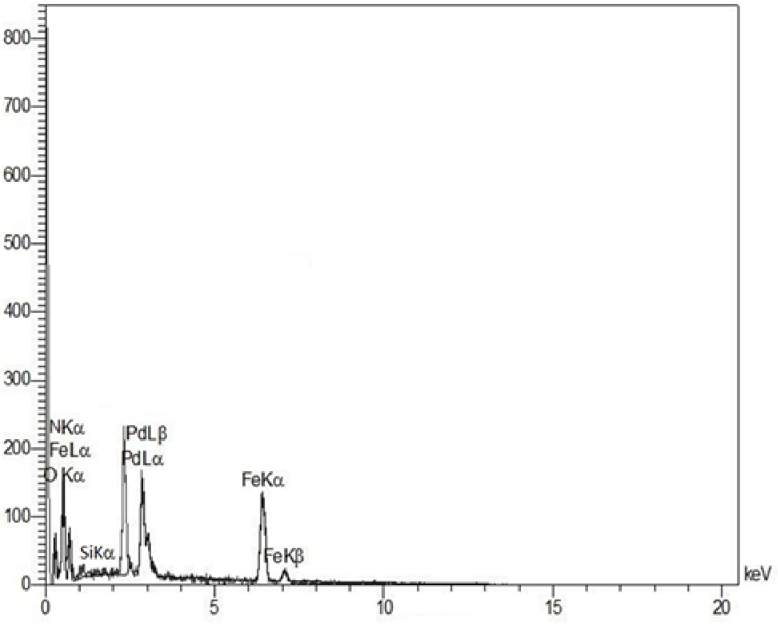


Fig. 3. The EDX image Fe_3O_4- AMPD-Pd

In Fig. 4, the thermogravimetric analysis (TGA) curves of Fe_3O_4 and Fe_3O_4-AMPD-Pd nanocatalyst are shown. Weight loss in the range of 50 to 200 °C relates to the removal of water and solvents on the surface of magnetic nanoparticles [36]. The observed weight loss (26%) between 200 and 550 °C is due to thermal decomposition of the organic part stabilized on the MNPs substrate.

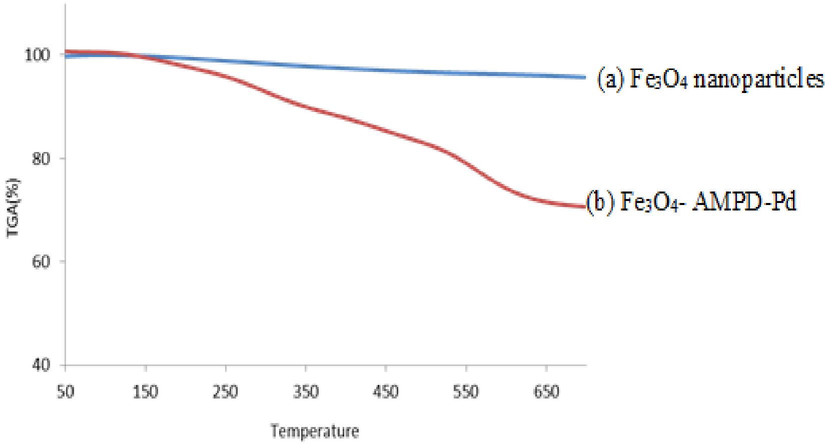


Fig. 4. TGA curves of (a) Fe_3O_4 nanoparticles and (b) Fe_3O_4- AMPD-Pd

FT-IR spectrums of Fe_3O_4 nanoparticles, Fe_3O_4-Cl, Fe_3O_4-AMPD, and Fe_3O_4-AMPD-Pd are shown in Fig. 5. The characteristic peak around 582 is related to Fe-O bonds in Fe_3O_4 nanoparticles [37, 38]. Hydrogen group on the surface of Fe_3O_4 is recorded at 3000-3500 cm^{-1}. The sharp peak at 1000-1100 cm^{-1} is assigned to Si-O stretching vibration. The peak about 1550-1600 cm^{-1} is due to the N-H vibrations.

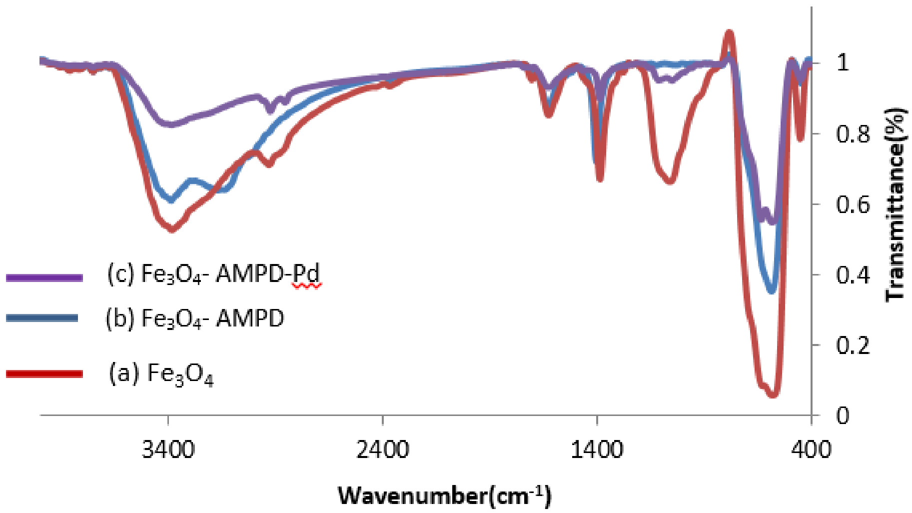


Fig. 5. FT-IR spectra for the (a) Fe_3O_4 nanoparticles, (b) Fe_3O_4- AMPD, (c) Fe_3O_4- AMPD-Pd

The VSM curve of Fe_3O_4-AMPD-Pd shows their value of saturation magnetization to be 40.1 emu g^{-1} (Fig. 6). The saturation magnetization of the Fe_3O_4 nanoparticle is 73 emu g^{-1} which is higher than Ms value of synthesized nanocatalyst. This confirms immobilization of organic layer on the surface of Fe_3O_4 nanoparticles [39, 40]. Based on the ICP analysis, the amount of palladium loaded on Fe_3O_4-AMPD is computed (1.23×10^{-3} mol/g).

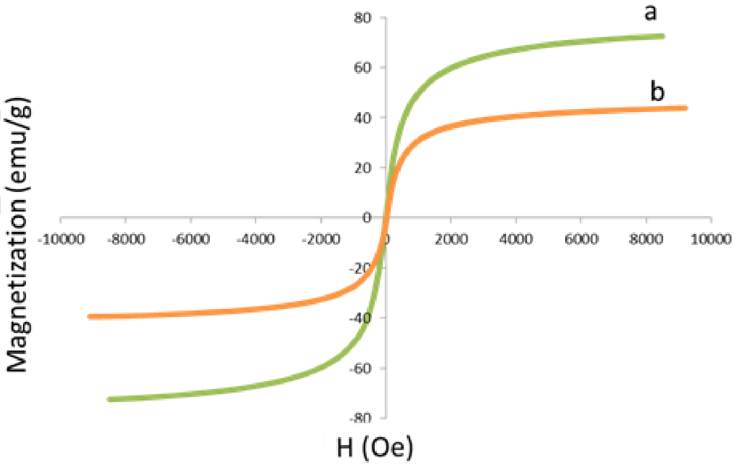
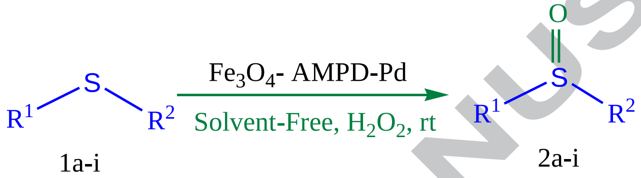


Fig. 6. VSM curve of (a) Fe_3O_4 nanoparticles and (b) Fe_3O_4- AMPD-Pd

3.2. Catalytic activity

Herein, we examined the catalytic activity of Fe_3O_4- AMPD-Pd catalyst in the oxidation of sulfides to sulfoxides using H_2O_2 (30%) as oxidant under neat conditions at room temperature (Scheme 2). As shown in Table 1, the solvent-free condition in the presence of Fe_3O_4- AMPD-Pd (0.005 gr) and H_2O_2 (0.3 mL) at room temperature was found to be ideal reaction conditions for the conversion of methylphenylsulfide to the methylphenylsulfoxide.



Scheme 2. Fe_3O_4- AMPD-Pd catalyzed the oxidation of sulfides to sulfoxides.

Table 1

Optimization of oxidation of sulfides to the corresponding sulfoxides using Fe_3O_4- AMPD-Pd nanoparticles under various conditions.

Entry	Solvent	H_2O_2	Catalyst (mg)	Time (min)	Yield (%)[a]
1	Acetonitrile	0.3	5	85	89
2	Ethanol	0.3	5	55	93
3	Ethyl acetate	0.3	5	70	87
4	Solvent-Free	0.3	5	15	95
5	Solvent-Free	0.3	6	13	96
6	Solvent-Free	0.3	4	22	85
7	Solvent-Free	0.2	5	20	87
8	Solvent-Free	0.4	5	14	96

[a] Isolated yields

As shown in Table 2, various sulfides including aromatic and aliphatic sulfides have been tested using the optimum conditions and the products were obtained in good to excellent yields. In the

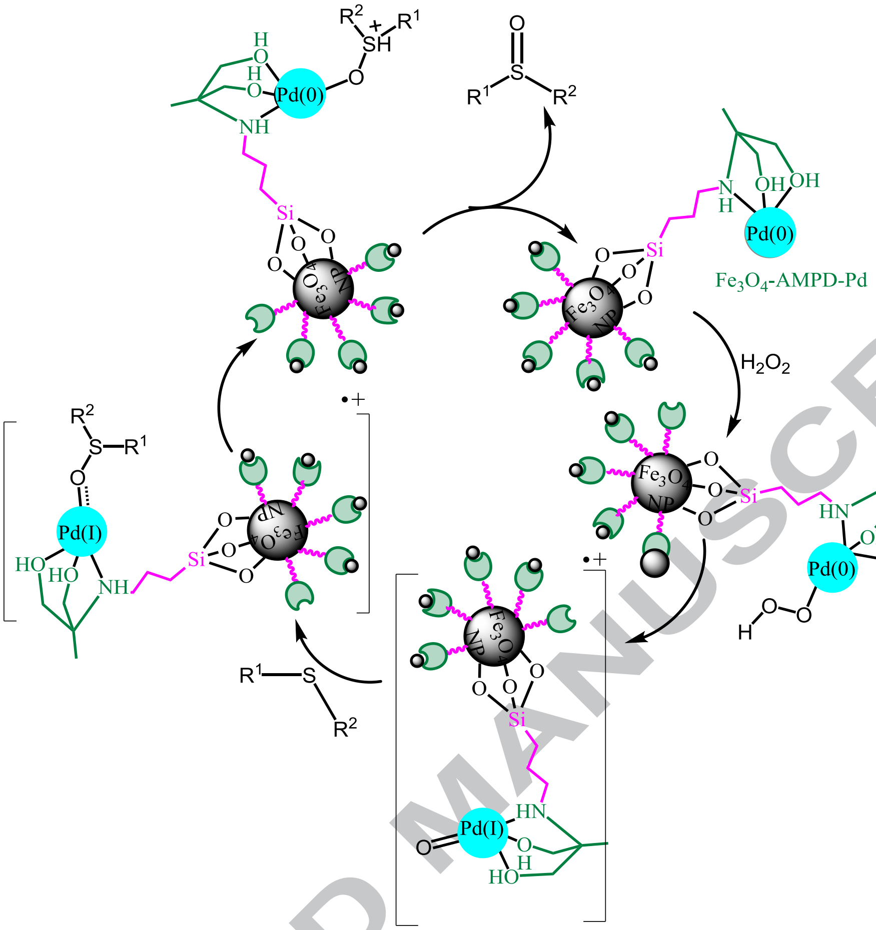
Scheme 3, possible reaction mechanism for the oxidation of sulfides is shown based on the literature results [33, 34].

Table 2

Oxidation of sulfides to the sulfoxides in the presence of Fe_3O_4- AMPD-Pd

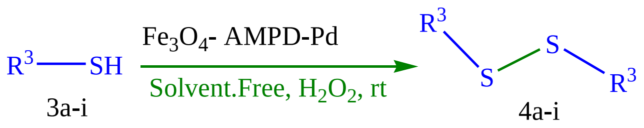
Entry	Substrate	Product	Time (min)	Yield (%)[a]	M.p.(°C)
1	Tetrahydrothiophene	2a	5	89	Oil [41]
2	Dimethylsulfide	2b	35	96	Oil [41]
3	Dodecylmethylsulfide	2c	45	94	68 [41]
4	Methylphenylsulfide	2d	20	95	Oil [40]
5	2-(Phenylthio)ethanol	2e	30	91	Oil [39]
6	Dipropylsulfide	2f	40	95	Oil [41]
7	Diethylsulfide	2g	35	97	Oil [41]
8	Dibenzylsulfide	2h	25	91	123 [41]
9	Benzylphenylsulfide	2i	30	92	115 [41]

[a] Isolated yields



Scheme 3. Fe_3O_4- AMPD-Pd catalyzed the oxidation of sulfides

As the second part of our organic study, we tested the catalytic activity of Fe_3O_4- AMPD-Pd in the synthesis of disulfide compounds using H_2O_2 as the oxidant at room temperature under solvent-free conditions (Scheme 4). In order to choose the reaction conditions, we examined the oxidation of benzyl mercaptan as a model compound in the presence of different amounts of the catalyst in various solvents. It was found that the best results were obtained in the presence of Fe_3O_4- AMPD-Pd (0.005 g) and H_2O_2 (0.4 mL) at room temperature (Table 3).



Scheme 4. Fe_3O_4- AMPD-Pd catalyzed the oxidative coupling of thiols into disulfides.

Table 3

Optimization of oxidative coupling of thiols using MCM-41-Adenine-Zr nanoparticles under various conditions.

Entry	Solvent	H_2O_2	Catalyst (mg)	Time (min)	Yield (%)[a]
1	Acetonitrile	0.4	5	80	85
2	Ethanol	0.4	5	40	91
3	Ethyl acetate	0.4	5	95	78
4	Solvent-Free	0.4	5	35	98
5	Solvent-Free	0.3	5	45	89
6	Solvent-Free	0.5	5	30	98
7	Solvent-Free	0.4	3	45	84
8	Solvent-Free	0.5	7	30	98

[a] Isolated yields

In order to gain further insight into this process and with optimal conditions in hand, oxidation reactions for a wide range of thiols with different functional groups were performed in the presence of Fe_3O_4- AMPD-Pd as catalyst under mild and completely heterogeneous conditions at room temperature (Table 4). After reaction completion, the products were extracted by simple filtration and prepared in the short reaction time and in good to excellent yields. Scheme 5 shows, a plausible mechanism for this process based on the literature results [33, 34].

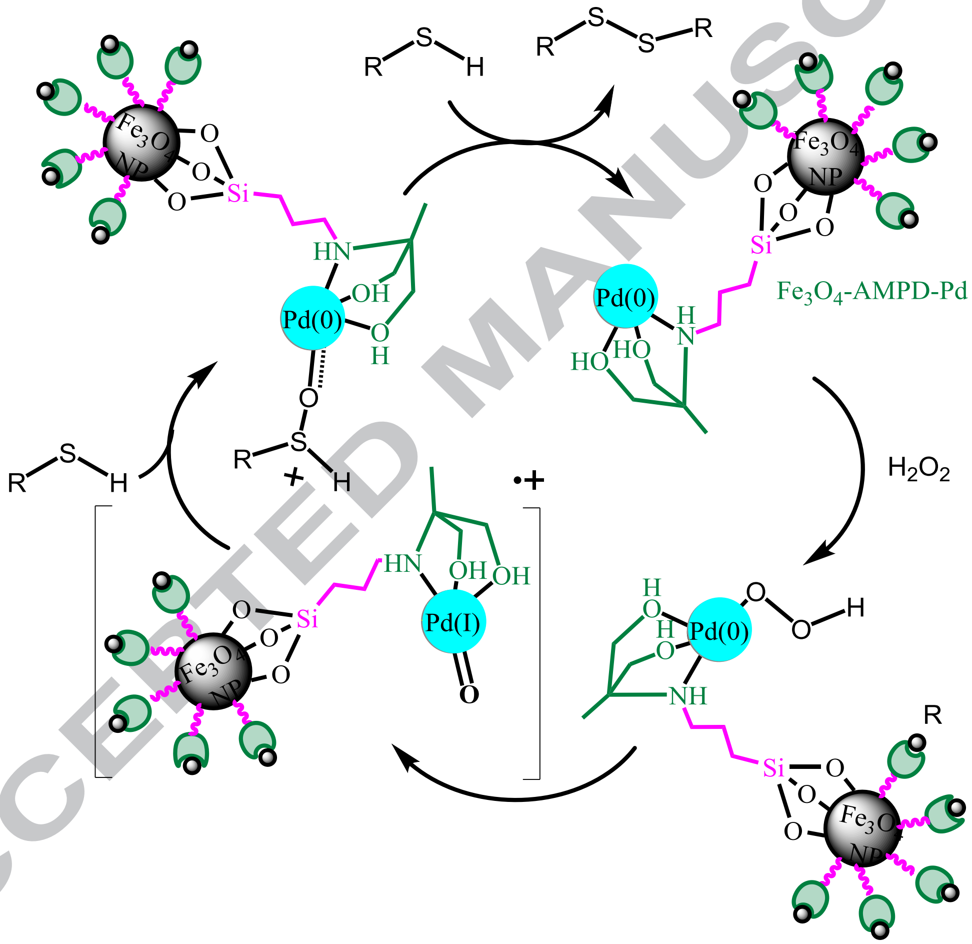
Table 4

Oxidative coupling of thiols into disulfides using H_2O_2 in the presence of Fe_3O_4- AMPD-Pd.

Entry	Substrate	Product	Time (min)	Yield (%)[a]	M.p. (°C)
2	4-Methylbenzenethiol	4b	65	96	40 [41]

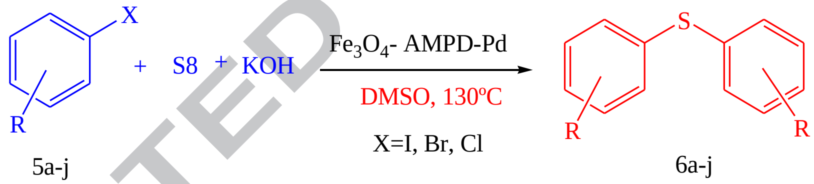
3	benzyl mercaptanas	4c	35	98	56 [41]
4	Naphthalene-2-thiol	4d	30	97	135 [41]
5	2-Mercaptobenzoic acid	4e	40	89	276 [39]
6	Benzo[d]thiazole-2-thiol	4f	15	94	169 [40]
7	2-Mercaptoethanol	4g	30	98	Oil [39]
8	4-Bromothiophenol	4h	55	89	90-92 [40]
9	Benzo[d]oxazole-2-thiol	4i	60	93	95 [39]

[a] Isolated yields



Scheme 5. Fe$_3$O$_4$- AMPD-Pd catalyzed the oxidative coupling of thiols to disulfides.

We finally investigated the synthesis of sulfides derivative in good to excellent yields. It should be mentioned that the sulfur was selected for the direct synthesis of organic sulfides from aryl halides using Fe_3O_4- AMPD-Pd as catalyst (Scheme 6). Then, the reaction parameters such as amount of the catalyst, nature of solvent and temperature were optimized for the synthesis of sulfides. For this purpose, iodobenzene (1 mmol), S_8 (1 mmol) as a sulfur source and KOH were chosen for a model reaction. It was found that in the absence of a catalyst, the reaction does not go well even after prolonged heating. It should be noted that the desired product is not obtained in solvents such as H_2O_2, EtOH, and PEG-400. But, it was found that in polar aprotic solvents such as DMSO and (DMF), the reaction is highly effective. Additionally, the role of the types of the base was evaluated and the desired product is obtained with 0.4 g of KOH. Also the important role of the amount of catalyst was investigated in the synthesis of sulfides. As shown in Table 5, we observed that the best results were obtained in presence Fe_3O_4- AMPD-Pd catalyst (0.06 g), 0.4 g KOH in DMSO (2 mL) at 100 ˚C. The results of this study are summarized in Table 5.



Scheme 6. Fe_3O_4- AMPD-Pd catalyzed the synthesis of sulfides.

Table 5
Optimization of the reaction conditions for the C–S coupling using Fe_3O_4- AMPD-Pd catalyst

Entry	Solvent	Base	Temp. (˚C)	Catalyst (mg)	Time (min)	Yield (%)^a
1	DMF	KOH	100	60	130	58
2	PEG	KOH	100	60	130	N.R
4	EtOH	KOH	100	60	130	N.R
5	H_2O	KOH	100	60	130	N.R
7	DMSO	KOH	130	60	130	81
8	DMSO	KOH	100	60	130	79
9	DMSO	KOH	80	60	130	61

10	DMSO	KOH	100	40	130	49
11	DMSO	KOH	100	80	130	85
12	DMSO	KOH	100	100	130	89
13	DMSO	NaOH	100	60	130	39
14	DMSO	Na_2CO_3	100	60	130	26
15	DMSO	Et_3N	100	60	130	41

[a]Isolated yields

In order to generalize the scope of the reaction, C-S cross-coupling reactions of S_8 and aryl halides catalyzed by Fe_3O_4-AMPD-Pd catalyst, a variety of aromatic halides were employed to the synthesis of sulfides derivatives for the appropriate time in good to excellent yields (Table 6).

Table 6

Synthesis of symmetrical sulfides via reaction of sulfur and aryl halides using DMSO in the presence of Fe_3O_4- AMPD-Pd

Entry	Substrate	Product	Time (min)	Yield (%)[a]	M.p. (°C)
1	2-Methoxyiodobenzene	6a	180	61	Oil [12]
2	Iodobenzene	6b	130	79	Oil [12]
3	4-Bromonitrobenzene	6c	140	52	158-16 [12]
4	Bromobenzene	6d	190	65	Oil [12]
5	Benzylbromide	6e	270	59	44-46[12]
6	4-Iodotoluene	6f	160	50	Oil [42]
7	4-Chloronitrobenzene	6g	150	41	160-162[43]
8	4-Bromotoluene	6h	210	33	Oil[42]
9	Chlorobenzene	6i	310	28	Oil [12]
10	4-Iodonitrobenzene	6j	40	50	157-160[42]

[a] Isolated yields

The comparison of Fe_3O_4-AMPD-Pd nanocatalyst with other catalysts for oxidation of methyl phenyl sulfide to methyl phenyl sulfoxide was done. The results are summarized in Table 7.

Table 7

Comparison of Fe_3O_4- AMPD-Pd for oxidation of methyl phenyl sulfide with previously reported catalysts

Entry	Substrate	Catalyst	Time (min)	Yield (%) [a]	Ref.
1	Ph–SCH_3	Fe_3O_4- AMPD-Pd	20	98	This work
2	Ph–SCH_3	Cu-SPATB/Fe_3O_4	95	98	[44]
3	Ph–SCH_3	Fe_3O_4-adenine-Ni	55	98	[33]

[a] Isolated yields

The reusability of the heterogeneous nanocatalyst was examined in the C-S coupling reaction. After the first use of nanocatalyst for the synthesis of sulfide from aryl halide in optimized condition, the catalyst was separated by a magnet, washed and reused under similar conditions. Also, the recyclability of Fe_3O_4- AMPD-Pd was investigated for the oxidation of sulfide and thiols. The results show 8, 10, and 10 runs for the synthesis of sulfide, oxidation of sulfide and thiol, respectively, without significant loss of their catalytic properties (Fig.7).

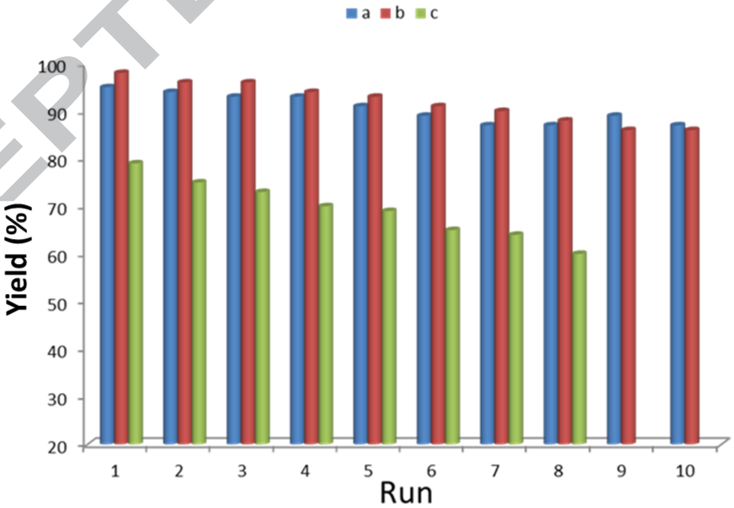


Fig. 7. Reuse of the nanocatalyst in the (a) oxidative coupling of thiols, (b) oxidation of sulfides and (c) synthesis of sulfides

4. Conclusions

An effective and non-toxic catalyst has been prepared by anchored palladium complex onto the surface of Fe_3O_4 nanoparticles via simple procedure and inexpensive materials.Then, the prepared nanostructure was characterized by TGA, ICP-OES, FT-IR, EDX, XRD and SEM techniques.Also, the catalytic activity of this nanostructured was investigated in the synthesis of sulfide and the oxidation reactions. More importantly, excellent yields, easy preparation, short reaction time, cheapness, easy magnetic separation, eco-friendliness, and chemical stability are outstanding benefits of this protocol.

Acknowledgments

Authors thank the research facilities of University of Kurdistan and Erfan Ghadermazi from Tehran University for financial support of this research project.

References

[1] F. Dehghani, A.R. Sardarian, M. Esmaeilpour, J. Organomet. Chem. 743 (2013) 87-96.

[2] V. Polshettiwar, R.S. Varma, Tetrahedron. 66 (2010) 1091-1097.

[3] D. Astruc, F. Lu, J.R. Aranzaes, Angew Chem Int Ed Engl. 44 (2005) 7852-72.

[4] A. Ghorbani-Choghamarani, Z. Darvishnejad, B. Tahmasbi, Inorganica Chim. Acta. 435(2015) 223-231.

[5] F. Shahbazi, K. Amani, Catal. Commun.55 (2014) 57-64.

[6] D.J. Cole-Hamilton, Science. 299 (2003) 1702-1706.

[7] S. Shylesh, V. Schunemann, W.R. Thiel, Angew Chem Int Ed Engl. 49 (2010) 3428-59.

[8] A.H. Lu, E.L. Salabas, F. Schuth, Angew Chem Int Ed Engl. 46 (2007) 1222-44.

[9] T. J. Yoon, W. Lee, Y. S. Oh, J. K. Lee, New J Chem. 27 (2003) 227-229.

[10] C.S. Gill, B.A. Price, C.W. Jones, J. Catal. 251 (2007) 145-152.

[11] R.B.N. Baig, R.S. Varma, Chem Comm. 49 (2013) 752-770.

[12] G. Azadi, Z. Taherinia, A. Naghipour, A. Ghorbani-Choghamarani, J. Sulfur Chem. 38 (2017) 303-313.

[13] I. Fernández, N. Khiar, Chem. Rev. 103 (2003) 3651-3706.

[14] A. Shaabani, A.H. Rezayan, Catal. Commun. 8 (2007) 1112-1116.

[15] M. Nikoorazm, A. Ghorbani-Choghamarani, N. Noori, J Prous Mater. 22 (2015) 877-885.

[16] S.J. Behroozi, W. Kim, K.S. Gates, JOC. 60 (1995) 3964-3966.

[17] A. Ghorbani-Choghamarani, Z. Darvishnejad, M. Norouzi, Appl. Organomet. Chem. 29 (2015) 170-175.

[18] A. Gangjee, Y. Zeng, T. Talreja, J.J. McGuire, R.L. Kisliuk, S.F. Queener, J. Med. Chem. 50 (2007) 3046-3053.

[19] G. Liu, J.R. Huth, E.T. Olejniczak, R. Mendoza, P. DeVries, S. Leitza, E.B. Reilly, G.F. Okasinski, S.W. Fesik, T.W. von Geldern, J. Med. Chem.44 (2001) 1202-1210.

[20] I.P. Beletskaya, V.P. Ananikov, Chem. Rev. 111 (2011) 1596-1636.

[21] A. Van Bierbeek, M. Gingras, Tetrahedron Lett. 39 (1998) 6283-6286.

[22] J. Mondal, P. Borah, A. Modak, Y. Zhao, A. Bhaumik, Org. Process Res. Dev. 18 (2013) 257-265.

[23] S. Jammi, S. Sakthivel, L. Rout, T. Mukherjee, S. Mandal, R. Mitra, P. Saha, T. Punniyamurthy, JOC. 74 (2009) 1971-1976.

[24] P. Bhanja, R. Gomes, L. Satyanarayana, A. Bhaumik, J. Mol. Cat. A: Chem. 415 (2016) 104-112.

[25] T. Tamoradi, A. Ghorbani-Choghamarani, M. Ghadermazi, Appl. Organomet. Chem. 32 (2018) 4340-4352.

[26] A. Ghorbani-Choghamarani, Z. Taherinia, RSC Adv. 6 (2016) 59410-59421.

[27] T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, J Prous Mater. In press doi:10.1007/s10934-018-0623-2.

[28] T. Tamoradi, A. Ghorbani-Choghamarani, M. Ghadermazi, Catal. Lett. 148 (2018) 857–872.

[29] H. Firouzabadi, N. Iranpoor, M. Gholinejad, Adv. Synth. Catal. 352 (2010) 119-124.

[30] M. Soleiman-Beigi, F. Mohammadi, Synlett. 26 (2015) 911-914.

[31] A. Ghorbani-Choghamarani, Z. Taherinia, RSC Adv. 6 (2016) 59410-59421.

[32] K. Amiri, A. Rostami, A. Rostami, New J Chem. 40 (2016) 7522-7528.

[33] T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani. Appl. Organomet. Chem. 32 (2018) 3974-3985.

[34] T. Tamoradi, B. Mehraban-Esfandiari, M. Ghadermazi, A. Ghorbani–Choghamarani, Res Chem Intermed. 2018, 44, 1363-1380.

[35] T. Tamoradi, A. Ghorbani-Choghamarani, M. Ghadermazi, Polyhedron. 145 (2018) 120-130.

[36] T. Tamoradi, A. Ghorbani-Choghamarani, M. Ghadermazi, New J Chem. 42 (2018) 5479-5488.

[37] A. Ghorbani-Choghamarani, M. Norouzi, Appl. Organomet. Chem. 30 (2016) 140-147.

[38] A. Ghorbani-Choghamarani, Z. Darvishnejad, B. Tahmasbi, Inorganica Chim. Acta. 435 (2015) 223-231.

[39] M. Darabi, T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, Transition Met. Chem. 42 (2017) 703-710.

[40] T. Tamoradi, A. Ghorbani-Choghamarani, M. Ghadermazi, New J Chem. 41 (2017) 11714-11721.

[41] T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, S. Molaei, Res Chem Intermed, (2018) in press, 10.1007/s11164-018-3367-3

[42] X. Ku, H. Huang, H. Jiang, H. Liu, J. Comb. Chem. 11 (2009) 338-340.

[43] V. Pilyugin, S. Kuznetsova, Y.E. Sapozhnikov, G. Chikisheva, G. Kiseleva, T. Vorob'eva, E. Klimakova, N. Sapozhnikova, R. Davletov, Z. Galeeva, Russ. J. Gen. Chem. 78 (2008) 446-450.

[44] A. Ghorbani-Choghamarani, B. Tahmasbi, P. Moradi, N. Havasi, Appl. Organomet. Chem. 30 (2016) 619-625.

Graphical abstract

Fe_3O_4- AMPD-Pd: a novel and efficient magnetic nanocatalyst for synthesis of sulfides and oxidation reactions

Taiebeh Tamoradi [a], Nazanin Moeini [a], Mohammad Ghadermazi,[a,*] Arash Ghorbani-Choghamarani[b,*]

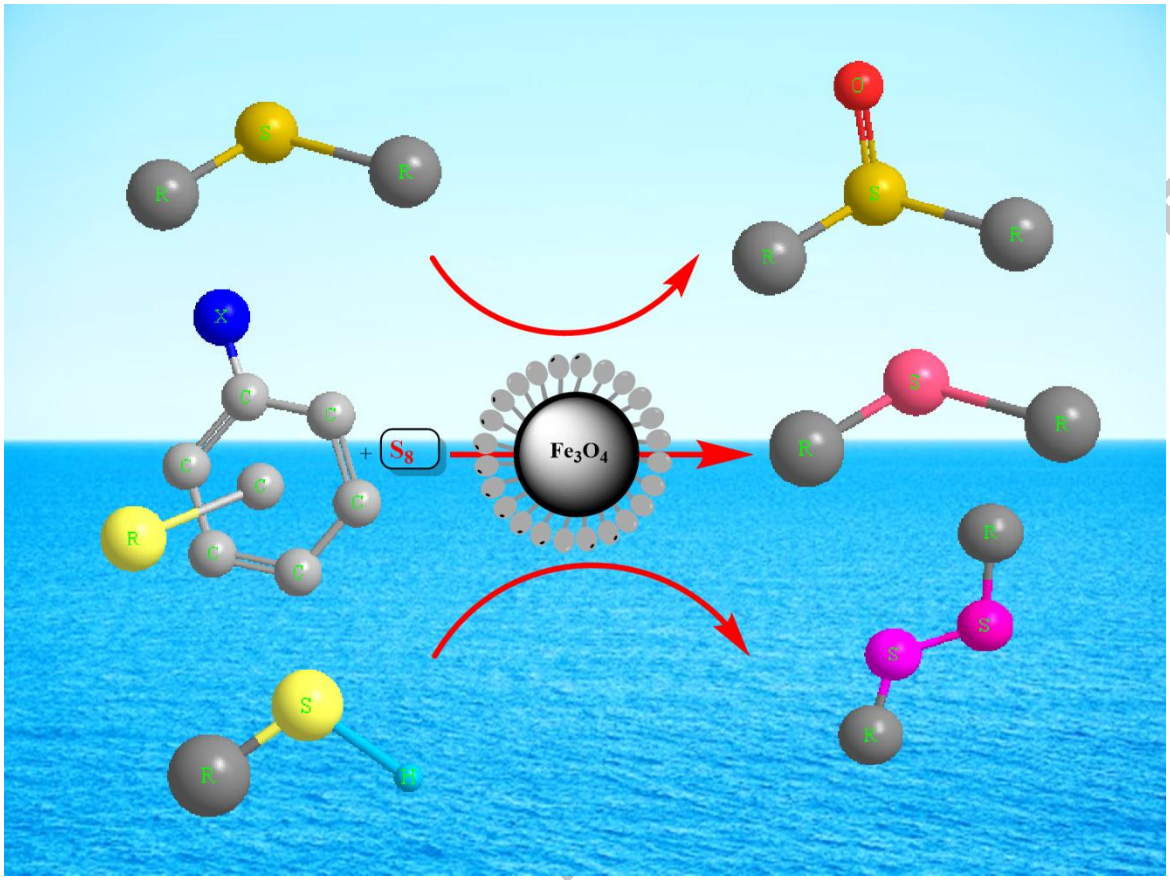
[a] University of Kurdistan, Department of Chemistry, Faculty of Science, Sanandaj, Iran
e-mail: mghadermazi@yahoo.com
[b] Department of Chemistry, Faculty of Science, Ilam University, P.O. Box, 69315516, Ilam, Iran
e-mail: a.ghorbani@ ilam.ac.iR

---

[*] Address correspondence to University of Kurdistan, Department of Chemistry, Faculty of Science, Sanandaj, Iran.; e-mail: mghadermazi@yahoo.com (M. Ghadermazi). Ilam University, Faculty of Science, Department of Chemistry, Ilam, Iran.; e-mail: a.ghorbani@mail.ilam.ac.ir

Graphical Abstract - Synopsis

The present work describes the synthesis of novel magnetic nanoparticle with effective catalytic properties and recyclable ability. This heterogeneous nanocatalyst was identified by FT-IR, SEM, TEM, EDX, ICP-OES, XRD, TGA and VSM. The nanocatalyst was used for synthesis of sulfides and oxidation reactions. The catalyst has unique properties such as Use of green medium, easy separation, excellent reusability of the nanocatalyst.


R
S
R
O
S
R
R
X
C
C
C
C
C
C
C
R
+
S8
Fe3O4
R
S
R
R
S
S
R
R
S
H