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Saeedeh Pakvojoud, Mehdi Hatefi Ardakani, Samira Saeednia & Esmaeil Heydari-Bafrooei

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Efficient, selective and mild oxidation of sulfides and oxidative coupling of thiols catalyzed by Pd(II)-isatin Schiff base complex immobilized into three-dimensional mesoporous silica KIT-6

Saeedeh Pakvojoud, Mehdi Hatefi Ardakani ^(b), Samira Saeednia and Esmaeil Heydari-Bafrooei

Faculty of Science, Department of Chemistry, Vali-e-Asr University of Rafsanjan, Rafsanjan, Iran

ABSTRACT

In this study, a palladium(II)-isatin Schiff base complex immobilized into three-dimensional (3D) mesoporous silica KIT-6 (Pdisatin Schiff base@KIT-6) was synthesized and characterized by various techniques including inductively coupled plasma (ICP) and Fourier transform infrared (FT-IR) spectroscopies, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive Xray spectroscopy (EDX), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET) technique and thermal gravimetric analysis (TGA). This new heterogeneous catalyst was successfully employed for the selective oxidation of sulfides to sulfoxides with tert-butyl hydroperoxide (tert-BuOOH) and oxidative coupling of thiols into corresponding disulfides using 30% H₂O₂ at room temperature. The products were obtained in good to excellent yields and no over-oxidation of sulfoxides and disulfides was observed. This catalytic system could also be applied for the chemo-selective oxidation of sulfides and thiols in the presence of other functional groups. The studied catalyst can be recovered easily by a simple filtration and reused five times in both oxidation reactions without a remarkable decrease in catalytic activity.

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CONTACT Mehdi Hatefi Ardakani 🖾 m_hatefi_chem@yahoo.com 💽 Faculty of Science, Department of Chemistry, Vali-e-Asr University of Rafsanjan, Rafsanjan 77188-97111, Iran

2 😔 S. PAKVOJOUD ET AL.



1. Introduction

The environmentally friendly catalytic oxidation of sulfides to sulfoxides with high performance has been the subject of numerous studies over the last two decades [1-4]. Sulfoxides have been applied in the synthesis of chemically useful materials such as drugs, flavors, germicides, and biologically active molecules like catabolism regulators [5]. On the other hand, the oxidation of organic sulfides such as dibenzothiophene (DBT) as an impurity in crude oil, is a major challenge in the petroleum industry and its removal is a necessary action in the petrochemical processes. Recently, Doustkhah and co-workers have prepared a green and recyclable catalyst by supporting copper(II) ions onto the internal pore surface of the thiourea-bridged periodic mesoporous organo-aluminosilica material. This catalyst (Cu@Al/Si-PMO-TU) was successfully applied for deep oxidation of dibenzothiophene to dibenzothiophen dioxide with hydrogen peroxide under aqueous conditions at room temperature [6]. Likewise, the conversion of thiols to the corresponding disulfides is a main transformation in both chemical and biological processes [7,8]. Disulfides are used in the sulfonylation of anions such as enolates, preparation of the sulfinyl and sulfenyl compounds as well as the vulcanizing agents for rubber and elastomers [9,10]. In addition, the thiol group can be protected as a disulfide, because disulfides are relatively more stable than the corresponding free thiols in the oxidation, alkylation and acylation reactions [11].

Despite that the homogeneous catalysts show high catalytic activity and selectivity, some fundamental drawbacks including the difficulty in the catalyst recovery and separation of the products, and the catalyst deactivation by the formation of dimeric peroxo- and μ -oxo species hamper their industrial applications [12–14]. The immobilization of homogeneous catalysts on various solid supports is a reliable way to resolve these problems [15,16].

Recently, Kleitz *et al.* [17] synthesized a novel three-dimensional mesoporous silica with *Ia3d* symmetry named KIT-6 (Korean Advanced Institute of Science and Technology number 6). It shows superior textural parameters including high specific surface area, considerable pore volume, and significant chemical and thermal stability for recyclability

[18]. Moreover, the three-dimensional mesoporous structures provide excellent catalyst dispersion and faster diffusion of reactants and products [19].

Schiff base ligands have many advantages, namely relative tolerance, ease of synthesis and facile coordination to the metal centers [20]. Schiff base transition metal complexes have been the subjects of interest to researchers due to their easy synthesis, chemical and thermal stability, as well as their excellent catalytic performance in numerous organic transformations [21]. In addition, Schiff base ligands are widely used due to their biochemical and biological properties. The biological activity of Schiff base was increased when coordinated with metal ions [22]. Some of these Schiff base metal complexes behave as a metallodrug with remarkable antimicrobial properties against bacterial and fungal species, as well as anticancer activity toward cancer cells [23–25].

Isatin (1H-indole-2,3-dione) is a natural heterocyclic compound comprised of an indole ring and two keto groups at 2nd and 3rd positions of the ring. It is a unique class of heterocycles acting as a biological agent [26]. Isatin is the most reported agent for the preparation of Schiff base ligands owing to its reaction with the primary amines [27]. Isatin Schiff base ligands coordinate with a wide variety of transition metal ions. The resulting stable metal complexes display notable clinical, pharmacological and biological properties [28].

Pd-based catalysts have been used in a wide range of organic transformations. Most of the catalysts used in Suzuki–Miyaura and Heck cross-coupling reactions are based on palladium complexes [29]. Also, the immobilized palladium catalysts on various supports such as magnetic nanoparticles, multi-walled carbon nanotubes, resin, two-dimensional mesoporous silica (*e.g.* MCM-41 and SBA-15), periodic mesoporous organosilicas (PMOs), and metal–organic frameworks (MOFs) have been reported [30–39]. Recently, tremendous researches have been reported towards efficient H₂ generation from decomposition of formic acid (HCOOH) as a non-toxic and renewable hydrogen source in the presence of encapsulated ultra-small palladium nanoparticles [40,41]. Considering fossil fuels, hydrogen (H₂) is a super clean energy source with excellent energy density and perfect energy conversion efficiency.

In this research, we successfully synthesized the Pd-isatin Schiff base complex immobilized into three-dimensional mesoporous silica KIT-6 (Pd-isatin Schiff base@KIT-6) for the first time (Scheme 1). The prepared heterogeneous catalyst was applied for selective oxidation of sulfides to sulfoxides and also oxidative coupling of thiols to disulfides at room temperature. Moreover, the reusability of this new heterogeneous catalyst was investigated in both of the oxidation reactions.

2. Results and Discussion

2.1. Preparation and characterization of the catalyst

At first, the mesoporous silica KIT-6 was reacted with 3-aminopropyltriethoxysilane (3-APTES) to produce aminopropyl-modified KIT-6 (KIT-6-pr-NH₂). Then, the condensation reaction between the amine group of KIT-6-pr-NH₂ and the keto group at the 3rd position of isatin resulted in imine-modified KIT-6 (isatin Schiff base@KIT-6). Finally, the Pd-isatin Schiff base@KIT-6 catalyst was obtained through the reaction of palladium (II) acetate with isatin Schiff base@KIT-6 in methanol at room temperature (Scheme 1).





Scheme 1. Preparation route of Pd-isatin Schiff base@KIT-6 catalyst.

The prepared palladium catalyst was characterized by inductively coupled plasma (ICP), Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET) technique and thermal gravimetric analysis (TGA).

Figure 1 represents the FT-IR spectra of KIT-6, KIT-6-pr-NH₂, isatin Schiff base@KIT-6 and the Pd-isatin Schiff base@KIT-6 catalyst. For the mesoporous silica KIT-6 (Figure 1(a)), the bands detected at 1085, 806 and 467 cm^{-1} can be related to Si-O-Si asymmetrical stretching vibrations, symmetrical stretching vibrations and bending



Figure 1. FT-IR spectrum of (**a**) KIT-6, (**b**) KIT-6-pr-NH₂, (**c**) isatin Schiff base@KIT-6, and (**d**) Pd-isatin Schiff base@KIT-6.

vibrations, respectively [19]. These bands are observed in the FT-IR spectra of KIT-6-pr-NH₂, isatin Schiff base@KIT-6 and Pd-isatin Schiff base@KIT-6 (Figure 1(b-d), as well. Moreover, KIT-6 shows an IR broad band around 3435 cm⁻¹ correspondings to the hydroxyl stretching vibrations of Si-OH groups (Figure 1(a)). On the functionalization of KIT-6 with 3-aminopropyltriethoxysilane (3-APTES), the intensity of O-H stretching bands diminishes due to the interaction between the surface Si-OH groups and 3-APTES (Figure 1(b)). Furthermore, a new continuing band emerged in the region of $3000-3290 \text{ cm}^{-1}$ due to the stretching vibration of the $-\text{NH}_2$ groups and also the appearance of the stretching vibration modes of aliphatic CH₂ groups around 2935 cm⁻¹ confirm the aminopropylation of KIT-6 [44]. For isatin Schiff base@KIT-6 (Figure 1(c)), the two new IR bands at 1629 and 1736 cm^{-1} assinged to C = N and C = O stretching vibrations, respectively, prove the successful formation of imine (C = N) group by the reaction of isatin with KIT-6-pr-NH₂. In the FT-IR spectrum of catalyst (Figure 1(d)), the C = N and C = O stretching vibrations bands are observed at lower wavenumbers (1621 and 1728 cm⁻¹, respectively); this evidences the successful coordination of C = N and C = O groups of isatin Schiff base@KIT-6 to the metal ions [28].

The low angle XRD patterns of KIT-6 and Pd-isatin Schiff base@KIT-6 are exhibited in Figure 2. The diffractogram of the pure KIT-6 sample (Figure 2(a)) reveals an intense peak at $2\theta = 1.3^{\circ}$ corresponding to (2 1 1) plane and one weak peak at $2\theta = 2.1^{\circ}$ belonging to (2 2 0) plane indicating the cubic *Ia3d* symmetry [45]. In the case of the synthesized catalyst (Figure 2(b)), the intensity of (2 1 1) peak decreased and (2 2 0) one disappeared probably



Figure 2. XRD patterns of (a) KIT-6 and (b) Pd-isatin Schiff base@KIT-6.

due to the filling of KIT-6 pores by organic groups or metal ions. These observations demonstrate the immobilization of Pd-Schiff base complex inside the mesoporous KIT-6.

The SEM micrographs of KIT-6 and Pd-isatin Schiff base@KIT-6 are shown in Figure 3. As seen, KIT-6 consists of spherical sponge-like particles (Figure 3(a)) due to the aggregation of the fine threads of KIT-6 [46]. The similar surface morphology of Pd-isatin Schiff base@KIT-6 (Figure 3(a)) indicates the structurally unchanged KIT-6 after modification and the anchorage of the palladium Schiff base complex inside the channels of KIT-6. In addition, the comparison of the EDX spectrum of the pure KIT-6 with that of the Pd-isatin Schiff base@KIT-6 catalyst (Figure 4) confirms the existence of palladium species in the catalyst.

Figure 5 shows the TEM images of KIT-6 and Pd-isatin Schiff base@KIT-6. The both samples show the well-ordered arrangement of parallel pore channels which confirms that the mesoporous structure of KIT-6 retains intact after anchoring of the Pd-isatin Schiff base into the KIT-6 channels.

The N₂ adsorption-desorption isotherms of KIT-6 and Pd-isatin Schiff base@KIT-6 are presented in Figure 6. Their textural parameters are also given in Table 1. According to the IUPAC classification, both of the samples display type IV isotherms with a H1 hysteresis loop; this evidences the uniformity of the synthesized KIT-6 and the supported catalyst [47]. Moreover, the decrease observed in the values of textural parameters of the catalyst with respect to the mesoporous KIT-6 (Table 1) confirms the immobilization of the Pdisatin Schiff base complex inside the KIT-6 channels.

Figure 7 shows the TGA patterns of KIT-6 and synthesized Pd-isatin Schiff base@KIT-6 catalyst. The TGA curve of KIT-6 sample (Figure 7(a)) exhibits an initial weight loss $(\sim 1.5\%)$ below about 100°C corresponding to the desorption of physically adsorbed water



Figure 3. SEM images of (a) KIT-6 and (b) Pd-isatin Schiff base@KIT-6.

molecules inside the KIT-6 channels [48]. As seen, increasing the temperature, resulted in no change in weight loss was of KIT-6. Whilst, the Pd-isatin Schiff base@KIT-6 catalyst experienced three weight losses in the range of 25–800°C (Figure 7(b)). The first weight loss ($\sim 2\%$) being below ~ 100 °C is due to the removal of adsorbed water. The second



Figure 4. EDX spectra of (a) pure KIT-6 and (b) Pd-isatin Schiff base@KIT-6.

 Table 1. Textural properties of KIT-6 and Pd-isatin Schiff base@KIT-6 catalyst.

Pore vol. (cm ³ g ^{-1})	Pore diam. by BJH method (nm)	S_{BET} (m ² g ⁻¹)	Sample
0.639	5.42	555	KIT-6
0.323	4.76	236	Pd-isatin Schiff base@KIT-6

one in the 280–550°C temperature range ($\sim 6\%$) is related to the decomposition of aminopropyl groups. Furthermore, the last weight loss ($\sim 8\%$) observed at 550–800°C is likely due to the thermal decomposition of the isatin Schiff base complex.

2.2. Catalytic performance

2.2.1. Oxidation of sulfides with tert-BuOOH catalyzed by Pd-isatin Schiff base@KIT-6

After preparation and characterization of the Pd-isatin Schiff base@KIT-6 catalyst, its catalytic activity was explored in the oxidation of sulfides at room temperature. To achieve the optimized reaction conditions, a number of solvents including methanol, ethanol, acetonitrile, water, acetone, and chloroform, as well as solvent-free conditions were utilized in the



Figure 5. TEM images of (a) KIT-6 and (b) Pd-isatin Schiff base@KIT-6.

oxidation of dibenzyl sulfide as a model substrate. Among the studied solvents, ethanol as the reaction medium gave the best sulfoxide yield (Table 2, Entries 1–7). Subsequently, the model reaction was done in the presence of different amounts of the catalyst and the superior sulfoxide yield was obtained with 20 mg of it (Table 2, Entries 2, 9–12). It is notable that the oxidation of dibenzyl sulfide cannot complete without Pd-isatin Schiff base@KIT-6 catalyst even after 24 h (Table 2, Entries 8 and 9). Additionally, the ability of different oxidants such as 30% H₂O₂, urea hydrogen peroxide (UHP), *tert*-butyl hydroperoxide (*tert*-BuOOH, 70% aqueous solution) and NaIO₄ for the oxidation of dibenzyl sulfide was examined in the presence of Pd-isatin Schiff base@KIT-6. Based on the obtained results, *tert*-BuOOH as a green oxidant provides the best sulfoxide yield (Table 2, Entries 2, 13–16).



Figure 6. N₂ adsorption-desorption isotherms of (a) KIT-6 and (b) Pd-isatin Schiff base@KIT-6.



Figure 7. TGA curves of (a) KIT-6 and (b) Pd-isatin Schiff base@KIT-6.

10

Entry	Solvent	Catalyst (mg)	Oxidant	Isolated yield (%)	
1	CH₃OH	20	tert-BuOOH	75	
2	EtOH	20	tert-BuOOH	90	
3	CH₃CN	20	tert-BuOOH	67	
4	H ₂ O	20	tert-BuOOH	45	
5	CH ₃ COCH ₃	20	tert-BuOOH	52	
6	CHCl ₃	20	tert-BuOOH	35	
7	Solvent-free	20	tert-BuOOH	8	
8 ^b	EtOH	20	tert-BuOOH	0	
9 ^c	EtOH	0	tert-BuOOH	0	
10	EtOH	5	tert-BuOOH	20	
11	EtOH	10	tert-BuOOH	55	
12	EtOH	15	tert-BuOOH	70	
13	EtOH	20	30% H ₂ O ₂	75	
14	EtOH	20	$Urea/H_2O_2$ (UHP)	43	
15	EtOH	20	NalO ₄	25	
16	EtOH	20	No oxidant	5	

Table 2. Optimization of the reaction parameters in the oxidation of dibenzyl sulfide catalyzed by Pd-isatin Schiff base@KIT-6 at room temperature (25°C)^a.

^aReaction conditions: dibenzyl sulfide (1 mmol), solvent (2 mL), oxidant (3 mmol), catalyst, reaction time (1 h). ^bisatin Schiff base@KIT-6 was used instead of Pd-isatin Schiff base@KIT-6.

^{b,c}Reaction time (24 h).



Scheme 2. Oxidation of sulfides with tert-BuOOH catalyzed by Pd-isatin Schiff base@KIT-6.

Under the obtained optimal reaction conditions, different sulfides were oxidized in the presence of the Pd-isatin Schiff base@KIT-6 catalyst (Scheme 2). The results are given in Table 3 show that in this catalytic system, different sulfides were selectively oxidized to their corresponding sulfoxides with the good to excellent yields. The sterically hindered sulfides such as diphenyl sulfide can also be successfully oxidized in this system (Table 3, Entry 5). Furthermore, the sulfoxidation of the linear chain of diethyl sulfide achieved with a good yield (Table 3, Entry 9). The present oxidizing system could be applied to the chemoselective oxidation of sulfides containing other functional groups. In the case of 2-hydroxyl ethyl phenyl sulfide, the hydroxyl group oxidation did not occur under the mentioned conditions (Table 3, Entry 8). Similarly, the C = C bonds in allyl methyl sulfide and diallyl sulfide remained intact during the sulfide oxidation (Table 3, Entries 10 and 11).

2.2.2. Oxidative coupling of thiols to disulfides with 30% H₂O₂ catalyzed by Pd-isatin Schiff base@KIT-6

As the second part of our project, we studied the catalytic activity of Pd-isatin Schiff base@KIT-6 in the oxidative coupling of thiols into the corresponding disulfides. In this manner, 4-methyl thiophenol was chosen as the model substrate and the reaction conditions including the kind of solvent (Table 4, Entries 1–7), the amount of catalyst (Table 4, Entries 4, 9–13) and the kind of oxidant (Table 4, Entries 4, 14–17) were optimized in this reaction.

12 😓 S. PAKVOJOUD ET AL.

Entry	Sulfide	Product	Time (h)	Yield (%) ^b
1	s C		1	90
2	S CH3	S CH3	1	90
3	s s		1	87
4	CH ₃	СН3	1	90
5	s contraction of the second se		1	85
6	H ₃ C	H ₃ C U	1	92
7	CH ₃	CH ₃	1	88
	S OH	В ОН		
8 ^c		о Ш	2	85
9 ^c	<u></u>		2	85
10 ^c	ss		2	83
11 ^c	\$ <u></u>		2	82

Table 3. Oxidat	ion of sulfides to sulfoxides	with tert-BuOOH cat	talyzed by Pd-isatin S	chiff base@KIT-6 at
room temperatu	ure (25°C) ^a .			

^aReaction conditions: sulfide (1 mmol), *tert*-BuOOH (3 mmol), catalyst (20 mg), EtOH (2 mL). ^bIsolated yields.

^cYields determined by GC.

As seen in Table 4, the best yield of the desired disulfide was obtained with acetonitrile as the solvent, and in the presence of 25 mg of the catalyst using 30% H₂O₂ as the oxidant. Afterward, a series of thiols were subjected to the oxidative transformation under the optimal reaction conditions (Scheme 3). As seen from Table 5, different aromatic thiols were successfully converted to their corresponding disulfides with excellent yields. Furthermore, in this oxidizing system, 2-mercaptoethanol was chemo-selectively oxidized to

Entry	Solvent	Catalyst (mg)	Oxidant	lsolated yield (%) ^b
1	Solvent-free	25	30% H ₂ O ₂	10
2	CH₃OH	25	30% H ₂ O ₂	45
3	EtOH	25	30% H ₂ O ₂	75
4	CH ₃ CN	25	30% H ₂ O ₂	95
5	H ₂ O	25	$30\% H_2 O_2$	63
6	CH ₃ COCH ₃	25	$30\% H_2 O_2$	57
7	CHCl ₃	25	30% H ₂ O ₂	35
8 ^b	CH ₃ CN	25	30% H ₂ O ₂	0
9 ^c	CH ₃ CN	0	30% H ₂ O ₂	0
10	CH ₃ CN	5	30% H ₂ O ₂	20
11	CH ₃ CN	10	30% H ₂ O ₂	45
12	CH ₃ CN	15	30% H ₂ O ₂	65
13	CH ₃ CN	20	$30\% H_2 O_2$	82
14	CH ₃ CN	25	tert-BuOOH	75
15	CH ₃ CN	25	Urea/H ₂ O ₂ (UHP)	30
16	CH ₃ CN	25	NaIO ₄	37
17	CH ₃ CN	25	No oxidant	Trace

Table 4. Optimization of the reaction conditions in the oxidative coupling of 4-methyl thiophenol catalyzed by Pd-isatin Schiff base@KIT-6 at room temperature (25°C)^a.

^aReaction conditions: 4-methyl thiophenol (1 mmol), solvent (2 mL), oxidant (5 mmol), catalyst, reaction time (0.5 h). ^bisatin Schiff base@KIT-6 was used instead of Pd-isatin Schiff base@KIT-6.

^{b,c}Reaction time (24 h).

Scheme 3. Oxidative coupling of thiols with 30% H₂O₂ catalyzed by Pd-isatin Schiff base@KIT-6.

the corresponding disulfide (Table 5, Entry 8). In this substrate, alcohol oxidation was not observed.

The efficiency of Pd-isatin Schiff base@KIT-6 catalyst in the oxidation of methyl phenyl sulfide was also compared with the some reported catalysts. As shown in Table 6, the present catalytic system shows higher catalytic activity in terms of reaction time and yield of product in comparison with other reported catalytic protocols.

2.2.3. Catalyst reusability

The reusability of the Pd-isatin Schiff base@KIT-6 catalyst was checked in the oxidation of dibenzyl sulfide and also the oxidative coupling of 4-methyl thiophenol under the optimized reaction conditions. After each catalytic cycle, the catalyst was separated by a simple filtration, washed by absolute methanol and dried in an oven of 90°C for 4 h. Then, the recovered catalyst was placed into a fresh reaction mixture. The results are shown in Figure 8 reveal that it is possible to reuse the catalyst several times in both of the catalytic oxidation reactions without significant loss of its initial activity.

The structure of the recycled catalyst was studied by FT-IR spectroscopy. FT-IR spectrum of the recovered catalyst after 5th run was similar to that of fresh catalyst and showed expected Si-O-Si (464, 805 and 1085 cm⁻¹), C = N (1623 cm⁻¹), C = O (1728 cm⁻¹) and aliphatic CH₂ (2932 cm⁻¹) vibration bands (Figure 9). This observation revealed that the structure of Pd-isatin Schiff base@KIT-6 remained intact after five recoveries.

S. PAKVOJOUD ET AL.



Table 5. Oxidative coupling of thiols into disulfides using 30% H₂O₂ catalyzed by Pd-isatin Schiff base@KIT-6 at room temperature (25°C)^a.

Table 6. Comparison of catalytic activity of Pd-isatin Schiff base@KIT-6 with some other catalysts reported for the oxidation of methyl phenyl sulfide and 4-methyl thiophenol.

Entry	Substrate	Catalyst	Conditions	Time(min)	Yield (%)	Ref.
1	Methyl phenyl sulfide	SiO ₂ -W ₂ -Py	CH ₃ OH/CH ₂ Cl ₂ / H ₂ O ₂ , r.t.	150	90	[49]
2	Methyl phenyl sulfide	Fe ₃ O ₄ @SiO ₂ @VO(salen)	CH ₃ OH/CH ₂ Cl ₂ /UHP, r.t.	360	83	[50]
3	Methyl phenyl sulfide	Fe ₃ O ₄ @SiO ₂ APTES(Fe(acac) ₂)	EtOH/H ₂ O ₂ , r.t.	120	85	[51]
4	Methyl phenyl sulfide	Fe ₃ O ₄ /salen of Cu(II)	EtOH/H ₂ O ₂ , 60°C	180	83	[52]
5	Methyl phenyl sulfide	SBA-15/lm/WO ₄ ²⁻	CH ₃ COCH ₃ /H ₂ O ₂ , r.t.	360	97	[53]
6	Methyl phenyl sulfide	Pd-isatin Schiff base@KIT-6	EtOH/TBHP, r.t.	60	90	This work
7	4-methyl thiophenol	Silica sulfuric acid	AI(NO ₃) ₃ .9H ₂ O/CH ₂ Cl ₂ , r.t	100	98	[54]
8	4-methyl thiophenol	$(C_2H_5)_3NH^+[CrO_3F]^-$	CH_2CI_2 , r.t	115	84	[55]
9	4-methyl thiophenol	Fe ₃ O ₄ @SiO ₂ -NH ₂ @Mn(III)	CH ₂ Cl ₂ /CH ₃ OH, UHP, r.t.	120	83	[56]
10	4-methyl thiophenol	Ni-SMTU@boehmite	$EtOH/H_2O_2$, r.t.	80	94	[57]
11	4-methyl thiophenol	Pd-isatin Schiff base@KIT-6	CH ₃ CN/H ₂ O ₂ , r.t.	30	95	This work

3. Conclusions

In summary, we have synthesized a palladium-isatin Schiff base complex immobilized into the three-dimensional mesoporous silica KIT-6. This new heterogeneous catalyst was successfully applied for the selective oxidation of sulfides to sulfoxides with tert-butyl hydroperoxide (tert-BuOOH) and the oxidative coupling of thiols to disulfides using 30% H₂O₂ at room temperature. Moreover, the catalyst was highly reusable and recycled several times in both of the oxidation reactions without any noticeable loss of its initial activity.

14

^aReaction conditions: thiol (1 mmol), CH₃CN (2 mL), 30% H₂O₂ (5 mmol), catalyst (25 mg). ^{b,c}Yield determined by GC.



Figure 8. Reusability of the Pd-isatin Schiff base@KIT-6 catalyst in the oxidation of dibenzyl sulfide and oxidative coupling of 4-methyl thiophenol.



Figure 9. FT-IR spectrum of the recovered Pd-isatin Schiff base@KIT-6.

4. Experimental

4.1. Materials and methods

All the materials used were commercial reagents acquired from Merck or Fluka chemical companies. Triblock copolymer pluronic P123 (EO₂₀PO₇₀EO₂₀; M = 5800) was obtained from Aldrich. The Fourier transform infrared spectra of the synthesized samples were recorded as KBr disks on a Thermo SCIENTIFIC NICOLET iS10 FT-IR spectrophotometer. An ICP-SpectroCiros CCD instrument was used for the inductively coupled plasma spectroscopy to determine the metal content of the catalyst. A Panalytical X['] pert Pro

16 😓 S. PAKVOJOUD ET AL.

diffractometer with Cu-K α radiation was employed to obtain the X-ray powder diffraction (XRD) patterns of the powder samples at room temperature. A Zeiss Sigma VP-500 FE-SEM instrument was used to take scanning electron micrographs and EDX spectra. TEM images were recorded using a Zeiss-EM10C transmission electron microscope. The N₂ adsorption–desorption isotherms (BET) were recorded at 77 K on a BELSORP Mini instrument. Thermal gravimetric analysis (TGA) was performed with a Rheometric SCIENTIFIC STA 1500 instrument. The thin-layer chromatography (TLC) on silica-gel polygram SILG/UV 254 plates was carried out to check the reactions progress. A Philips GC-PU 4600 instrument equipped with a flame ionization detector (FID) was employed for the gas chromatography analyses.

4.2. Synthesis of KIT-6

The mesoporous silica KIT-6 was prepared according to the procedure of Ref. [42]. A solution containing 4 g of P123 (as structure-directing agent) and 7.9 g of HCl (35 wt%) in 144 g distilled water was prepared and stirred mechanically for 2 h at 35°C. Subsequently, 4 g of *n*-butanol was added as the co-solvent to the above-mentioned mixture with the continuous agitating at 35°C for 2 h. Afterwards, 8.6 g of tetraethylorthosilicate (TEOS) was added to the resulted clear solution, followed by stirring at 35°C for 24 h and keeping in an oven of 100°C for 24 h. Then the white solid precipitate was filtered and, without washing, dried at 100°C overnight. Finally, the obtained product was calcined at 550°C for 5 h with the heating ramp of 2°C/min in the furnace in the open air.

4.3. Preparation of Pd-isatin Schiff base@KIT-6 catalyst

First, a mixture of 3-aminopropyltriethoxysilane (0.268 g, 1.2 mmol) and KIT-6 (1 g) in dry toluene (25 mL) was agitated and refluxed in N₂ environment for 24 h. The resulted white solid KIT-6-pr-NH₂ was filtered, washed with toluene and then dried at 100°C for 4 h [43]. Subsequently, a solution of isatin (0.147 g, 1 mmol) in absolute methanol (25 mL) was added to a suspension of freshly prepared KIT-6-pr-NH₂ (1 g) in methanol (50 mL). This mixture was actively agitated under reflux for 24 h. The achieved light brown solid isatin Schiff base@KIT-6 was filtered, washed carefully with methanol and dried at 90°C for 4 h. Finally, a mixture of isatin Schiff base@KIT-6 (1 g) and Pd(OAc)₂ (0.224 g, 1 mmol) in absolute methanol (25 mL) was prepared and magnetically stirred at room temperature for 24 h. Afterwards, the obtained light green solid catalyst was filtered and washed with methanol using a Soxhlet apparatus and then dried at 90°C for 6 h. Based on the ICP results, the Pd content in the catalyst was determined about 0.24 mmol per gram of the supported catalyst.

4.4. General procedure for the oxidation of sulfides to sulfoxides with tert-butyl hydroperoxide catalyzed by Pd-isatin Schiff base@KIT-6

The catalyst (20 mg), sulfide (1 mmol) and *tert*-BuOOH (70% aqueous solution, 3 mmol) were mixed in ethanol (2 mL) inside a test tube. Then, the reaction mixture was magnetically stirred at room temperature. The reaction progress was checked by gas chromatography (GC) or thin-layer chromatography (TLC). After completion of the reaction, the solid

catalyst was collected through a simple filtration and the products were extracted with CH_2Cl_2 (3 × 10 mL). Finally, the products were purified by a silica-gel column.

4.5. General procedure for the oxidative coupling of thiols with 30% H₂O₂ catalyzed by Pd-isatin Schiff base@KIT-6

A mixture of the catalyst (25 mg), thiol (1 mmol) and 30% H_2O_2 (5 mmol) as the oxidant in acetonitrile (2 mL) was stirred at room temperature. The TLC technique was used for monitoring the reaction progress. After completion of the reaction, the catalyst was filtered and the product was extracted with CH_2Cl_2 (3 × 10 mL) and refined by a silica-gel column.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

ORCID

Mehdi Hatefi Ardakani D http://orcid.org/0000-0002-2216-6840

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18 😔 S. PAKVOJOUD ET AL.

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20 🔄 S. PAKVOJOUD ET AL.

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