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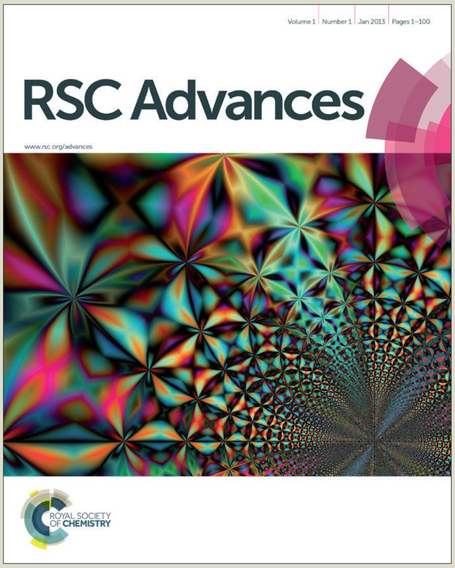

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DOI: 10.1039/C6RA19832E

Journal Name

COMMUNICATION

Oxidative dehydrogenation of thiols to disulfides at room temperature using silica supported iron oxide as an efficient solid catalyst

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Selective transformation of thiols to disulfides by means of oxidative dehydrogention has been described using silica supported iron oxide under base and solvent free reaction condition at room temperature in open atmosphere. The easiness of catalyst preparation, green reaction condition, easy separation technique of the formed products and catalyst from the reaction mixture, recyclability of the catalyst are the most attractive facets of our synthetic procedure which being ecofriendly will find immense applications in academic and industrial sections.

Introduction

Molecular alteration is a prime dynamic force for chemical research and present approaches focus emergent awareness of the environmental impact of chemical production. The development of clean synthetic methodologies can put forward new doorway to gentle and cost-effective processes. Central aspects of research toward more sustainable processes for chemical synthesis involve replacements of heavy and toxic metal catalysts, organic solvents as reaction media, development of strategy to achieve higher atom economy, escaping from strong basic reaction conditions, and energy saving procedures.[1] Oxidative dehydrogenations catalyzed by various metal oxides including iron oxides are well known in literature and attract considerable attention over the years in the arena of industrial and academic research[2] because naturally occurring iron oxides are ubiquitously found in the environment and are considered to be non-toxic to the environment in general. Iron oxides also find extensive usage as magnetic storage, medication, chemical industries and in water refining. Supported or modified iron oxides catalyzed reactions are one of the attracting alternatives for green chemical synthesis[3] because of the facilities associated with heterogeneous catalyst system and environmental concern of non toxic iron oxide.[4] Iron and iron oxides are abundant in nature and iron is one of the most versatile transition metals which act as important red-ox centre in biological systems and in many chemical transformations.[5] On the other hand, disulfides are key intermediates in a broad range of organic syntheses. Organic compounds containing disulfides play crucial roles in chemistry and biology[6] e.g. disulfide bond formation is important in peptides[7] and bioactive molecules.[8] Moreover, thiols can be conveniently protected as disulfides and can be regenerated by cleavage of the S–S bond.[9] Due to the low bond energy of the sulfur–sulfur bond in disulfides, thiols can be easily over-oxidized giving thiosulfinates, thiosulfonates, and sulfonic acids and hence revisions are fixed on their selective oxidation to disulfides without over oxidation which has been exhaustively investigated over the years.[10]

Among the several methods of preparing disulfides,[11] most straightforward methodology involves oxidative coupling of thiols to disulfides.[12] In recent times, cleaner protocols have been described by A. Talla et al[12a] under photocatalytic condition using acetonitrile or ethanol as solvent and equivalent amount of TMEDA; and under solvent-free conditions by Montazerozohori et al.[12f] Instead of significant efforts being made so far, most of these protocols are suffering from use of expensive and/ lethal reagents, organic or inorganic bases, longer reaction time, strong oxidizing agents or flow of molecular oxygen.[11,12] Among some approaches involving iron/iron oxide as heterogeneous catalysts for oxidative coupling of thiols to disulfides,[12d (cross ref 45)] H. Garcia et al. described Fe-BTC as catalyst for the selective preparation of disulfides in acetonitrile solvent at 70° C with the help external oxygen flow. Although, their method did work effectively in several cases; moderate yields (60–70%) were obtained with aliphatic thiols and with longer reaction time. More recent approach using SBA-15 supported iron

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Electronic Supplementary Information (ESI) available: [UV, IR, TGA, SEM analysis of support and catalyst, and scanned copy of 1H and 13C NMR spectra of selected disulfides]. See DOI: 10.1039/x0xx00000x

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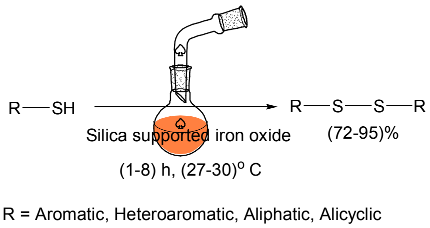
oxide nanoparticles for disulfide synthesis involves use of H_2O_2 in acetonitrile solvent at room temperature.[12g] But the scope of this procedure is limited to fluoro thiophenol as the reaction needs 0°C temperature; inertness of aliphatic thiols to undergo self coupling or coupling with aromatic thiols to produce unsymmetrical disulfides. Thus a very careful survey of literature reports encourages us to invent general and straightforward procedure for the synthesis of disulfides from thiols without over oxidation following the principles of green chemistry. Herein, we report an efficient method for synthesizing disulfides from thiols using silica supported iron oxide catalyst at room temperature without the need of any solvent, external oxygen flow or the presence of highly oxidizing agents and bases (Scheme 1).

Scheme 1 Silica supported iron oxide catalyzed disulfide synthesis from thiols.



Results and discussions

In continuation of searching for better synthetic methodology using silica or silica supported iron catalysts;[13] we have prepared silica supported iron oxide within a very short time which then employed to establish a general procedure for conversion of thiols selectively and efficiently to corresponding disulfides for which 99% atom efficiency and a high TON/TOF ($8000/1143h^{-1}$; Table 1, entry 7) is achieved easily.

We have prepared a series of catalysts by varying the addition of an accurately weighed amount of ferric chloride to 1 g of silica (MERK, Silica Gel G for tlc) in a 100 mL round bottomed flask and then 6 mL acetone is added to the flask. The acetone is then evaporated under continuous stirring of the mixture at 35° C. After complete evaporation of acetone, the flask (containing yellow solid mass) is heated at 250° C for three hour in an oil bath under continuous magnetic stirring in open atmosphere. The yellow solid mass turns to deep amber colour. The solid catalyst Silica supported iron oxide thus prepared is then employed for selective transformation of thiols to disulfides. The series of catalysts with decreasing iron content is designated as Catalyst A (Prepared by mixing 1 mmol $FeCl_3$ with 1g silica gel G); Catalyst B (Prepared by mixing 0.5 mmol $FeCl_3$ with 1g silica); Catalyst C (Prepared by mixing 0.25 mmol $FeCl_3$ with 1g silica); Catalyst D (Prepared by mixing 0.1 mmol $FeCl_3$ with 1g silica).

The silica supported iron oxide prepared by the thermal decomposition of ferric chloride is then characterized by solid state UV and FT-IR spectroscopy and TGA analysis and SEM analysis.

DRS-UV analysis in the range of 200-800 nm shows distinct difference between the silica gel G and catalyst B. Catalyst B shows three absorbance peaks viz. a sharp peak around 250 nm; another peak around 350 nm, and a broad peak in between 500-600 nm (Fig 1.b) whereas, silica gel G does not show any characteristic peaks in this region (Fig. 1.a).

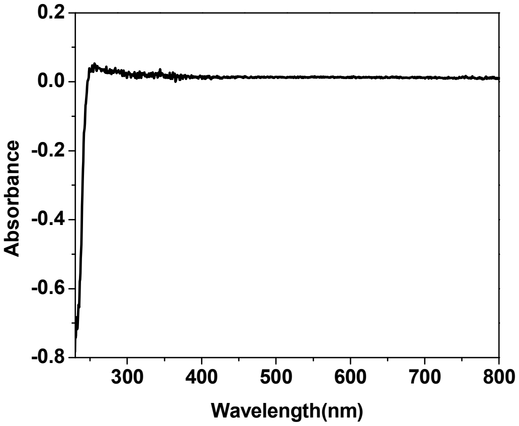


Figure 1.a; DRS-UV analysis of silica gel G.

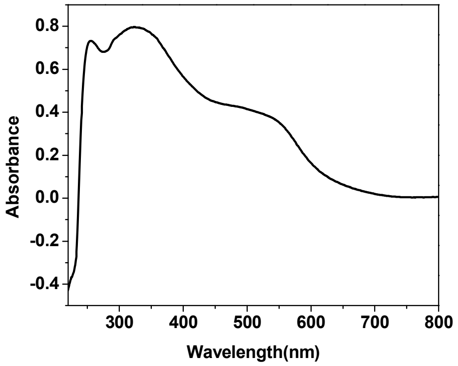


Figure 1.b; DRS-UV analysis of Catalyst B.

The FT-IR study of silica Gel G (Fig. 2.a) and catalyst B (Fig. 2.b) does not show much distinctive difference in between and both spectra contain O-H stretching at 3400 cm^{-1}, and at 582 cm^{-1} for Si-O stretching.

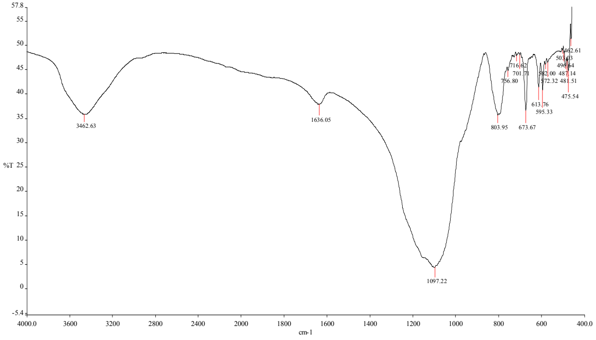


Figure 2.a; FT-IR analysis of silica gel G.

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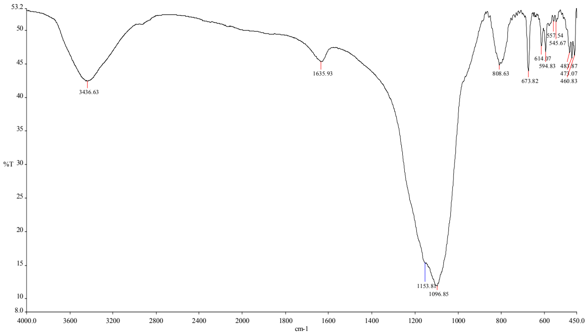

Figure 2.b; FT-IR analysis of Catalyst B.

The thermal stability of the catalyst B in comparison to the support silica gel G is examined by the TG/DTA analysis (Fig. 3). The study is carried out in the range of (25-500)^{o} C with 10^{o} C/ min. heating rate. The initial steady decrease of the line graph of TG/DTA spectrum of silica Gel G (Fig. 3.a) and catalyst B (Fig. 3.b) may be due to the loss of water present in the silica matrix and the absence of any sharp changes in the range of (200-250) ^{o}C for catalyst B (Fig. 3.b) signifies the continuity of the same phase present in the catalyst system B.

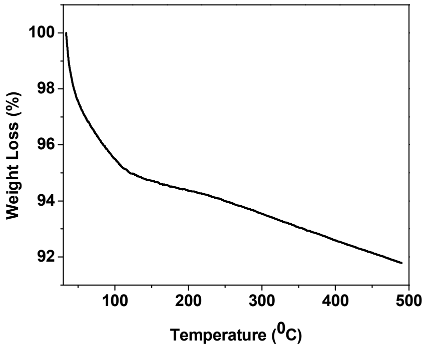

Figure 3.a; TG/DTA analysis of silica gel G.

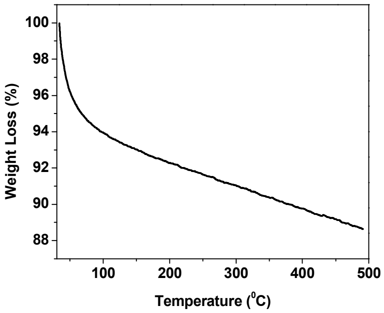

Figure 3.b; TG/DTA analysis of Catalyst B.

SEM analysis of catalyst B is performed and the pictures are given in Fig. 4. (Plots are included in the Electronic Supplementary Information).

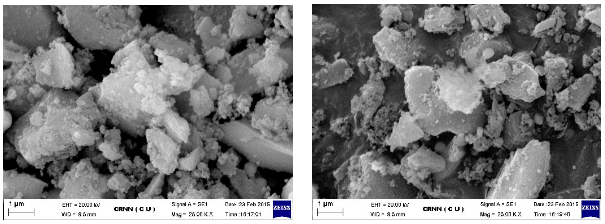

Figure 4. SEM analysis of Catalyst B

Table 1. A comparative study of oxidative dehydrogenation of thiophenol (2 mmol) to diphenyl disulfide under different conditions at room temperature.

Entry	Catalyst	Amount of catalyst	Time	Conv. (%)[a]
1	Nil	Nil	24h	5
2	silica	250 mg	24 h	7
3	Cat. A	250 mg	40 min.	100
4	Cat. B	500 mg	50 min.	100
5	Cat. B	250 mg	1 h	100
6	Cat. C	250 mg	2h 30 min.	100
7	Cat. D	250 mg	7 h	100
8	Cat. A$^{\#}$	250 mg	50 min.	100
9	Cat. B$^{\#}$	250 mg	1h 20 min.	100[b]
10	Cat. C$^{\#}$	250 mg	2h 40 min.	100
11	Cat. D$^{\#}$	250 mg	9 h	100
12	Fe_2O_3	20 mg	30 h	85

a; % conversions were checked by HPLC using MeOH as solvent. b; Reaction carried out by using commercially available Fe_2O_3; Cat. A$^{\#}$ (1 mmol Fe_2O_3 mixed with 1g silica); Cat. B$^{\#}$ (0.5 mmol Fe_2O_3 mixed with 1g silica); Cat. C$^{\#}$ (0.25 mmol Fe_2O_3 mixed with 1g silica); Cat. D$^{\#}$ (0.1 mmol Fe_2O_3 mixed with 1g silica).

We have started our study of synthesizing disulfides from thiols taking thiophenol as the model substrate to optimize the reaction condition. The results are summarized in table 1. We have observed the formation of disulfide only in trace amount under neat condition without any catalyst or support, or in presence of support without catalyst (Table 1, entry 1 and 2 respectively). The reaction proceeds to full conversion to disulfide with 250 mg of catalyst A within very short reaction time without any requirement of base or solvent (Table 1, entry 3). The time needed for complete conversion increases with decreased catalyst loading as expected (Table 1, entries 3-7). The fact that silica supported iron oxide catalyst (prepared by thermal pyrolysis of $FeCl_3$) shows comparable activity[14] with commercially available iron oxide (mixed by mechanical grinding in a mortar pestle with silica (MERK, Silica Gel G for tlc)) (Table 1, entries 8-11) emphasizes that Fe_2O_3 moiety is

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active catalytic phase in our catalyst system. The importance of silica as support[13] in this study is revealed by the fact that 85% conversion of thiophenol to corresponding disulfide requires as long as 30h when we employ commercially available iron oxide to the reaction under neat condition (Table 1, entry 12), while, our system took only 1h for complete conversion (Table 1, entry 5). This result may be due to the coating of iron oxide particle by the formed diphenyl disulfide thereby inhibiting the chances of showing any further catalytic activity under neat catalytic condition. But the situation is different for Silica supported iron oxide system where the formed diphenyl disulfide gets distributed over a large surface area provided by the mesoporous support and the catalytically active centres remain free for further reaction. These amazing observations excel importance of silica as an indispensable support for this reaction. With the optimization data in our hand, we have chosen the reaction with 250 mg of the supported catalyst B (0.5 mmol $FeCl_3$ supported on 1g silica) to convert 2 mmol of the thiophenol to corresponding disulfide as the model one. Table 2 is clearly showing the efficiency and cleanliness of our procedure in comparison to some recent developments of methodology for preparing disulfides from thiols by photocatalytic method without metal catalyst (Table 2, entry 1); solid state method (Table 2, entry 2) and iron catalyzed systems (Table 2, entries 3-7).

Table 2; Comparative table of the present catalyst system with the other reported catalysts.

Entry	Catalyst/oxidant	Catalyst/oxidant Amount	Additive	Solvent	RSH	Temp.	Time	Yield%	Reference
1	Eosin Y	1 mol%	TMEDA (1 equiv. occasional adding)24 W CFL, air	Ethanol	Aromatic, heteroarmatic, aliphatic	Not mentioned	16 h	93-99	Ref[12a]
2	Moist sodium periodate	1mmol	--	--	Aromatic, heteroarmatic, benzyl, aliphatic	Rt	(1.5-5) min.	70-96	Ref[12f]
3	Fe(BTC)/External oxygen flow	100 mg	--	Acetonitrile (4 mL)	Aromatic, heteroarmatic, benzyl, aliphatic	70° C	(1-20) h	55-91	Ref[cross ref no.45 of Ref. 11(a)]
4	Fe-NPS@SBA-15/H_2O_2	1 mol%	--	Acetonitrile (3 mL)	Aromatic, heteroarmatic, benzyl	25° C	(15-360) min.	70-99	Ref[12g]
5	Fe(TPP)Cl/UHP	0.02 mol/1mmol	--	Methanol (10 mL)	Aromatic, heteroarmatic, benzyl	0° C	(10 -90) min.	60-91	Ref[12e]
6	Nano Fe_2O_3	80 mg	Ionic liquid	Methanol	Aromatic, aliphatic	60° C	(10-75) min.	45-99	Ref[12i]
7	Cobalt–iron magnetic composites	0.1 wt%	--	DMF	Aromatic	(25-50)° C	(0.5-3) h	100	Ref[12h]
8	Silica supported iron oxide	250 mg (0.1 mol%)	--	--	Aromatic, heteroarmatic, benzyl, aliphatic	(27-30)° C	(1-8) h	(72-95)	*Our procedure*

We explore the scopes and limitations of our reaction protocol by employing different thiols and the observations are summarized in table 3. Ortho- and para- substituted aromatic thiophenols including heteroaromatic thiol (pyridyl) result in very good yield of the corresponding disulfides exclusively (82-95 %) within a very short reaction time (1-5) h (Table 3, entries 1-5; except in the case of 2-napthalene thiophenol Table 3, entry 4 and 2-pyridyl thiol). The methoxy substituted thiophenols (both ortho and para) require comparatively longer reaction time (8 h) to produce very good yield of disulfides (Table 3, entry 6, 7). Halogenated thiols also produce very good yield within a reasonable time period (Table 3, entries 8, 9). Alicyclic thiol viz. cyclohexylthiol, and other aliphatic straight chain thiols namely pentane and heptane thiol also produce excellent yield of the corresponding disulfides (Table 3, entries 11-13). We have isolated disulfide of thioglycolic acid in very good yield and in this case product has been separated after esterification of carboxylic group with ethanol in one pot reaction procedure. Here, worth mentioning is that Garcia et al. reported only good yields of the disulfides in case of heteroaromatic thiols, moderate yield with benzyl thiol and low yield with thioacetic acid.

Depending on the fact that iron oxide can be involved in redox reaction in heterogeneous condition or on solid surface[14,15] we propose the plausible mechanism for oxidative dehydrogenation as depicted in scheme 2. In the first step the acidic hydrogen of –SH gets attached to one of the doubly bonded oxygen of iron oxide through the lone pair of electron thereby weakening the strength of the –S—H bond [**E**]. The electron deficiency thereby formed on the iron centre can be partially meet up by the electron donating capability of sulphur of thiophenol group [**F**] which causes further weakening of –S—H bond. In the next step S atom of another thiol attacks the S atom of the catalytically bonded thiol [**G**] which ultimately forms the desired disulfide bond through [**H**]. Blue colour signifies developing bond and red one is for breaking bond.

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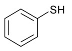
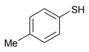
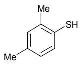
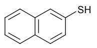
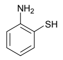
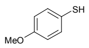
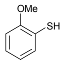
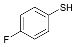
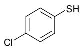
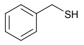
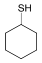
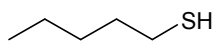
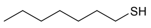
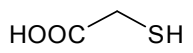
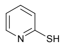
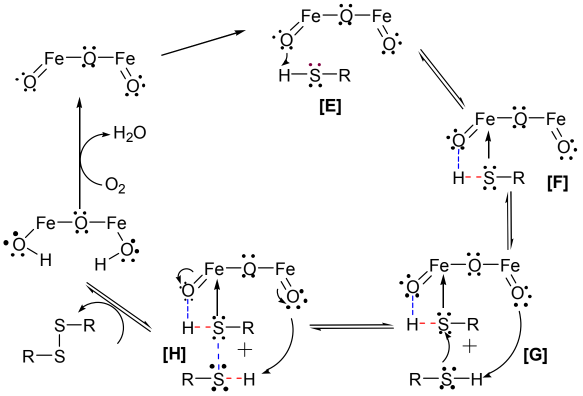
Table 3 Selective conversion of thiols to disulfides using silica supported iron oxide, Catalyst B.

Entry	Thiol	Time	Yield (%)[a]
1		1 h	95
2		3 h	92
3		2.5 h	93
4		8 h	72
5		3 h	92
6		8 h	82
7		8 h	83
8		3 h	86
9		5 h	87
10		2 h	86
11		3 h	85
12		5 h	88
13		7 h	85
14		8 h	83[b]
15		8 h	82

a; % yield represents yield after column chromatographic purification however, solid disulfides could be obtained by simple filtration followed by evaporation of the filtrate. b; Disulfide was isolated by esterification of the acid by ethanol after completion of the reaction in one pot procedure.

In this reaction sequence iron oxide gets partially reduced to (--FeOH) which gets converted to iron oxide again by aerial oxygen.



Scheme 2. Probable mechanism for aerobic oxidation of thiols to disulfides using silica supported iron oxide.

The advantage of silica supported iron oxide in this reaction is examined by its recovery and reuse after the first run (Table 4) taking thiophenol as the reactant. After completion of the reaction, the solid mixture is centrifuged repeatedly with dicholoromethane (2mL x 3). The dicholoromethane extract is examined under AAS which shows bare existence of leached iron. The solid is then dried in a hot air oven at 100^o C for 2 h and then the next batch of reaction is performed with the recovered silica-supported iron oxide and found to be equally active in catalyzing the process. Table 3 shows the results of six consecutive recycle runs. The DRS-UV analysis and FT-IR spectra of catalyst B after six recycle run does not show difference in spectral pattern (Fig. 5a and 5b respectively) and SEM analysis performed on the reused catalyst B (Fig. 5c) shows that catalyst looses granularity in comparison to the fresh catalyst (Fig. 4). The catalyst is air stable and can be used after six months of preparation. The reaction is scaled up to 10 mmol of thiophenol with 250 mg of catalyst B which took 38 h for 100% conversion to diphenyl disulfide.

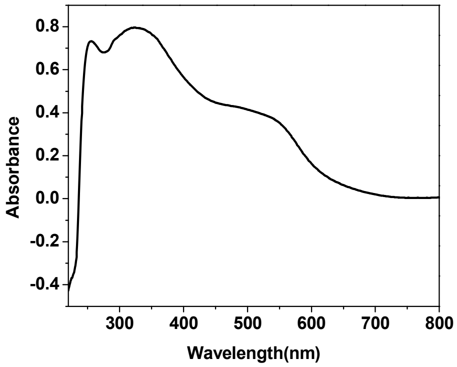


Figure 5a. DRS-UV analysis of Catalyst B after six run.

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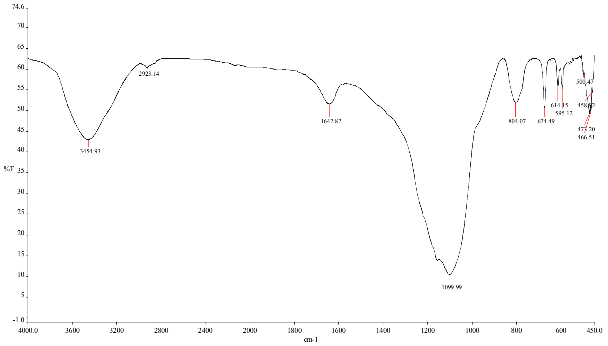

Figure 5.b; FT-IR analysis of Catalyst B after six recycle run.

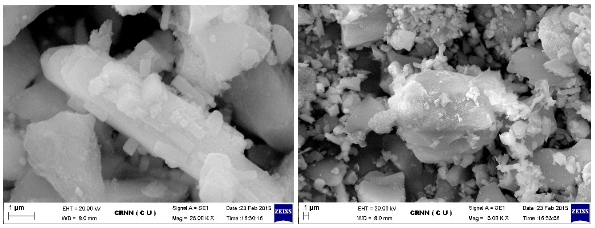

Figure 5c. SEM analysis of Catalyst B after sixth cycle.

Table 4 Recycling table with thiophenol as the reactant using catalyst B.

Entry	Cycle	Yield %[a]
1	0	95
2	1	92
3	2	94
4	3	94
5	4	92
6	5	92
7	6	91

a; Represents % yield after column chromatographic purification.

Conclusions

In conclusion, atmospheric oxidation of thiols to disulfides can be performed using silica supported iron oxide as the reusable catalyst under very mild reaction condition. The catalyst is effectively applicable for a very wide range of thiols including aromatic, aliphatic, alicyclic, benzylic and heteroaromatic thiol and easy separation of the reaction product from the reaction mixture only by simple filtration makes the procedure economically more viable than demonstrated by Fe(BTC) or SBA 15 supported iron oxide catalyst.[12d,g] The reaction protocol does not require any extra flow of oxygen or highly oxidizing agent such as hydrogen peroxide or sodium periodate; the condition does not require presence strong inorganic bases or organic base like TMEDA. The catalyst precursor $FeCl_3$ is very cheap and the final catalyst is environmentally non hazardous. This protocol being eco-friendly will find immense industrial and academic applications. Finding out more insights of this reaction mechanism are underway in our laboratory. The discovery that disulfide bond can be prepared under solvent free condition on oxide support at room temperature could find a new window to investigate the mechanism of biological evolution process where disulfide bond formation plays a key role in peptide synthesis and determining tertiary and quaternary structure of proteins.

Acknowledgements

Susmita Paul thankfully acknowledges UGC DS Kothari funding agency for financial support (No. F.4-2/2006/(BSR)/CH/13-14/0075); Prof. Anilava Kabiraj, Department of Zoology, University of Kalyani for recording AAS spectra, Mominul Islam and Mita Halder for recording spectroscopic data; SMI acknowledges Department of Science and Technology, New Delhi, Govt. of India, (DST-SERB), University grant Commission, New Delhi, Govt. of India, (UGC), and Department of Science and Technology, Govt. of West Bengal (DST-W.B.) for financial support. We gratefully acknowledge DST and UGC Govt. of India for providing support to the Department of Chemistry, University of Kalyani under FIST, PURSE and SAP programme.

Notes and references

‡ **Experimental**

§ **Representative procedure for the synthesis of di-phenyl-di-sulfide:** Silica supported iron oxide (Catalyst B, 250 mg) was taken in a glass mortar and then 2 mmol of thiophenol was added to the catalyst and mixed by a pestle. After mixing the solid mass was transferred to a 25 mL round bottomed flask fitted with a guard tube and a small magnet was introduced for continuous magnetic stirring for 1 h at room temperature. After the completion of the reaction (checked by tlc); the reaction mixture was washed successively with dichloromethane (2mL x 3) and filtered through Whatmann 42 filter paper. The filtrate was then evaporated to obtain white crystal of di-phenyl di-sulfide. The product was then characterized by 1H, 13C NMR spectral data and melting point was compared with literature report.

Table 2, Entry 1: 1H NMR ($CDCl_3$, *d* ppm^{-1} relative to TMS, 300 MHz): 7.18–7.31 (6H, m); 7.48–7.50 (4H, d, *J* = 7.5 Hz); ^{13}C NMR (CDCl3, *d* ppm^{-1}, 75 MHz): 127.1, 127.4, 129, 136.9. Melting point observed 60^{o} C [(59-62)^{o}C (lit.)]

The representative procedure for the synthesis of diphenyl disulfide is followed for the preparation of other disulfides mentioned in table 3.

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View Article Online
DOI: 10.1039/C6RA19832E

Graphical Abstract

Title: Oxidative dehydrogenation of thiols to disulfides at room temperature using silica supported iron oxide as an efficient solid catalyst

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Selective transformation of thiols to disulfides by means of oxidative dehydrogention has been described using silica supported iron oxide under base and solvent free reaction condition at room temperature in open atmosphere. The easiness of catalyst preparation, green reaction condition, easy separation technique of the formed products and catalyst from the reaction mixture, recyclability of the catalyst are the most attractive facets of our synthetic procedure which being ecofriendly will find immense applications in academic and industrial sections.