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DOI: 10.1002/adsc.201100149

Efficient and Highly Selective Aqueous Oxidation of Sulfides to Sulfoxides at Room Temperature Catalysed by Supported Iron Oxide Nanoparticles on SBA-15

Fatemeh Rajabi,^{a,*} Sareh Naserian,^a Ana Primo,^b and Rafael Luque^{c,*}

Received: March 3, 2011; Revised: April 15, 2011; Published online: July 22, 2011

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adcs.201100149.

Abstract: The present manuscript describes a simple, efficient and environmentally friendly room temperature aqueous catalytic approach to the selective preparation of sulfoxides from sulfides utilising lowloaded supported iron oxide nanoparticles and aqueous hydrogen peroxide as oxidant. Materials could be easily recovered from the reaction mixture and reused ten times without any loss in activity and no

Introduction

Supported metal catalysts have received a great deal of attention in recent years^[1,2] and indeed have been proved highly successful and versatile in several commercial scale processes.^[3] Mesoporous silica type materials, including SBA-15 and MCM-41, have been some of the most common supports which emerged as tuneable, high surface and stable alternative materials to be decorated with a wide range of nanoparticles from metals (e.g., Au, Pd, Pt) to metal oxides (e.g., CuO, Fe₂O₃).^[1,4-6] These materials have largely found applications in heterogeneous catalysis ranging from redox (hydrogenations and oxidations) processes^[1,4-7] to C–C and C–heteroatom couplings^[1,7a,8] and acid-catalysed processes.^[9]

The selective transformation of sulfides to sulfoxides generates high-added value compounds as starting materials and intermediates (which can subsequently transformed into valuable pharmaceuticals, agrochemicals and related compounds), granting access to industrially and biologically important synthetic organic compounds including chiral auxiliametal leaching was observed during the reaction. This is thus the first selective aqueous oxidation of sulfides using an iron-based heterogeneous system.

Keywords: aqueous chemistry; heterogeneous catalysis; room temperature reactions; SBA-15; sulfide oxidation; supported iron oxide nanoparticles

ries^[10,11] as well as intermediates playing key roles in the activation of enzymes.^[12,13]

Several catalytic systems have been reported to be active in the oxidation of sulfides. These range from metal-containing^[14–20] and metal-free protocols^[21–23] to biocatalysts^[15] using various oxidants including H_2O_2 and O_2 .

Nevertheless, despite considerable progress in the field of sulfide oxidation, the selective synthesis of sulfoxides is still a major challenge as most protocols involve overoxidation of sulfoxides to sulfones. Some others have also inherent drawbacks including the need of a catalysts excess (typically homogeneous metal complexes^[16,18,24]) and/or reagents, the use of toxic solvents as well as lack of good activities and/or selectivities (good yields are only obtained after long reaction times and harsh reaction conditions).^[22,25,26] Furthermore, heterogeneous systems reported for this process either involve complex systems^[27,28] or are unable to efficiently work under aqueous conditions.^[17,23,29–31]

The development of a simple and efficient heterogeneous catalytic methodology that can efficiently

^a Department of Science, Payame Noor University, PO Box: 19395-4697 Tehran, Iran Fax: (+98)-281-334-4081; phone: (+98)-281-333-6366; e-mail: f_rajabi@pnu.ac.ir

^b Instituto de Tecnologia Quimica UPV-CSIC- Universidad Politecnica de Valencia, Av. de los Naranjos s/n, 46022 Valencia, Spain

^c Departamento de Química Orgánica, Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie (C-3), Ctra Nnal Iva, KM 396, 14014 Cordoba, Spain Fax: (+34)-95-721-2066; e-mail: q62alsor@uco.es

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promote a mild aqueous oxidation of sulfides to sulfoxides (either at room temperature or under microwave irradiation with short reaction times and low temperatures) with a green oxidant (e.g., hydrogen peroxide or molecular oxygen) without any contamination by sulfones will be a major achievement in oxidation chemistry. Another important point to be considered is the use of transition metals and particularly the widely available, cheap and non-toxic iron-based heterogeneous catalysts, which have not been reported to date in the oxidation of sulfides.

In our continuing recent endeavours devoted to the preparation of environmentally friendly and reusable catalysts (e.g., supported nanoparticles in porous materials) in view of their applications in heterogeneous catalysis, we report here the use of highly efficient and active Fe(III) oxide nanoparticles supported on SBA-15 in the chemoselective oxidation of sulfides to sulfoxides at room temperature using H_2O_2 as a green oxidant. This catalyst has been proved to be highly versatile, active and reusable under the investigated reaction conditions.

Results and Discussion

The search for an effective simple and efficient catalytic system suitable for the synthesis of sulfoxides from sulfides prompted us to design alternative heterogeneous catalysts based on iron-supported nanoparticles on silica-type materials. These catalysts were previously reported to have excellent activities in a range of oxidations including alcohols and alkenes^[32] as well as acid-catalysed processes (e.g., alkylations).^[9] Therefore, a similar system was devised and synthesised for the selective aqueous oxidation of sulfides to sulfoxides.

The material, characterised by a series of techniques including XRD, SEM, TEM and XPS, was found to be mostly composed of supported Fe₂O₃ nanoparticles (hematite phase) on the SBA-15 material, which exhibited a well ordered hexagonal structure typical of SBA-15 materials (Figure 1).^[33] Metal oxide nanoparticle sizes were *ca.* 5–7 nm, with an excellent homogeneous dispersion of the Fe oxide NP on the support (Figure 2). Fe content was around 0.5– 0.7 wt%, similar to that reported for related materials from our group.^[9,32] Fe species were mostly hematite (Fe₂O₃) as concluded from wide angle XRD (not shown) and XPS peaks at B.E. 712 and 724.1 eV, typical of iron(III) oxide.^[34,35]

A preliminary screening of the Fe/SBA-15 material in the model oxidation reaction of methyl phenyl sulfide (Scheme 1, R^1 =Ph; R^2 =Me) under different conditions and solvents has been included in Table 1. Reactions were initially performed at room temperature (r.t.) using 30% aqueous H₂O₂ as green oxidant.



Figure 1. XRD pattern of Fe/SBA-15 material.



Figure 2. TEM micrograph of Fe/SBA-15 (*top*). Image of the material at a higher magnification (*bottom*) in which several iron oxide NPs of *ca*. 6–7 nm can be clearly observed.



Scheme 1. Selective aqueous oxidation of sulfides to sulfoxides at room temperature.

Table 1. Screening of solvents and reaction conditions in the oxidation of methylphenyl sulfide.^[a]

Entry	Solvent	Cat. (mol%)	<i>t</i> [h]	Yield [%]
blank	H ₂ O		10	< 10
SBA-15	H_2O		10	99
1	EtOH	_	2.5	99
2	MeOH	10	2	45
3	toluene	10	5	30
4	<i>n</i> -hexane	10	5	58
5	CH_2Cl_2	10	5	99
6	H_2O	10	2	99
7	H_2O	10	2	99
8	H_2O	10	2	99
9	H_2O	5	2	< 10

^[a] Reaction conditions: 1 mmol methylphenyl sulfide, 0.5 mmol aqueous H_2O_2 (30% v/v), 1 mL solvent, Fe/ SBA-15 as catalyst, room temperature.

Blank runs (in the absence of catalyst) gave no yields of products even after 10 h reaction times (Table 1, entry 1). In comparison, quantitative yields to methyl phenyl sulfoxide could be obtained in different solvents (EtOH, MeOH and H_2O) after 2–2.5 h reaction times.

The efficiency of the supported catalyst was primarily found to be affected by the nature of the solvent and the quantity of the catalyst used in the reaction. Polar solvents (alcohols, water) were found to be particularly suitable for the oxidation reaction as compared to organic solvents, which is probably related to the better mixing with the aqueous hydrogen peroxide utilised as oxidant in the process (organic solvents will, in contrast, lead to a clear biphasic system). The possibility to use water as reaction medium is a remarkable advantage of the proposed methodology which greatly increases its green credentials. Aqueous phase reactions were indeed proved to provide the best yields in the reaction, despite the very low solubility of organic sulfides in water.

Overoxidation is often observed in the oxidation of sulfides. Interestingly, no overoxidation to the corresponding sulfone was observed under the investigated conditions. This is believed to be due to the mild conditions utilised in our proposed methodology (room temoperature, 2-5 h).

Optimised conditions for the model reaction (1 mol% catalyst, 2 h reaction, aqueous medium,

room temperature) afforded a quantitative isolated yield of methylphenyl sulfoxide.

The heterogeneous nature of the proposed methodology was subsequently investigated. With this purpose, the catalyst was filtered off after different times (typically half way through the reaction) and the filtrate and reused catalyst were separately allowed to react further.

The results included in Table 2 clearly point to heterogeneous catalysis taking place in the protocol as the filtration liquor reacted significantly more slowly (at a similar rate to the reaction performed in the absence of the catalyst) as compared to the reused material at different times (Table 2, entries 1 and 2). AAS analysis of the final reaction mixture (upon completion after the end of the first cycle) confirmed that almost no iron could be detected in the solution phase (<2 ppm Fe).

For practical applications of heterogeneous systems, the lifetime of the catalyst and its recovery and extension of reusability are very important factors. We therefore devised a set of experiments to recover and reutilise the Fe/SBA-15 catalyst in the model oxidation process. All reactions were carried out under similar conditions.

To our delight, the supported catalyst was highly reusable under the investigated reaction conditions, preserving almost unaltered its initial catalytic activity after ten uses (Table 3). No significant quantity of Fe (<3 ppm) was found in solution as determined by ICP, in good agreement with AAS results of the filtrate previously obtained in this work.

Table 2. Leaching studies of the Fe/SBA-15 catalyst in the oxidation of methylphenyl sulfide.^[a]

Entry	Reaction	Time [min]	Yield [%]
1	Fe/SBA-15 (normal reaction)	30	40
	Fe/SBA-15 (recovered after 30 min,	30	35
	further reacted with added fresh sub- strates)	60	65
	Filtrate (upon filtration after 30 min reaction, further reacted with added fresh substrates)	30+30	42
2	Fe/SBA-15 (normal reaction)	90	78
	Fe/SBA-15 (recovered catalyst after	30	32
	90 min, further reacted with added	90	70
	fresh substrates)	120	>98
	Filtrate (upon filtration after 90 min reaction, further reacted with added fresh substrates	90+90	79

^[a] The catalyst was typically filtered off from the reacting mixture at different times (Fe/SBA-15, normal reaction) and then the filtrate and the recovered catalyst were separately left to react after the addition of fresh substrates.

Table 3. Reuses of Fe/SBA-15 in the selective oxidation of methylphenyl sulfide.^[a]

Run no.	1	2	3	4	5	6	7	8
Yield [%]	99	99	98	99	99	99	97	95
Time [min]	120	120	120	120	120	150	150	180

^[a] *Reaction conditions:* 2.5 mmol sulfide, 0.5 mmol H₂O₂, 1 mol% catalyst, 1 mL water, room temperature.

Having proved the activity and stability of the supported iron oxide nanoparticles in the model reaction, the scope of the protocol was subsequently extended to a range of the sulfides as shown in Table 4. Excellent conversions and selectivities to sulfoxides were

Table 4. Selective oxidation of a range of sulfides using Fe/ SBA-15.^[a]

Entry	Substrate	Time [min]	Yield [%]
1	S_	120	99
2	S	150	99
3	S S	220	98
4	S	150	99
5	CI	210	98
6	S	150	99
7	MeO	130	99
8	SS	210	97
9	CI S	240	95
10	CI S	240	98
11	S S	210	99
12	MeO	210	97

generally obtained for Fe/SBA-15 after 2–4 h reaction at room temperature, with the exception of moderate to good yields (*ca.* 58–75%) observed for the particular case of aliphatic sulfides (Table 4, entries 13–15).

Activities in the systems were particularly reduced when electron-withdrawing groups (EWG) were directly bonded to the sulfur atom (Table 4, entries 9 and 10). The oxidation of other aryl methyl sulfides also proceeded with high yields (Table 4, entries 5 and 6). However, bulky sulfides including benzyl tolyl sulfide were more slowly oxidized (Table 4, entry 11) and needed longer reaction times (360 min and above) to reach quantitative conversion to the sulfoxide product under the optimised reaction conditions. Sulfoxides were selectively obtained in all cases (> 99%) in the most selective and mild protocol to date reported for the oxidation of sulfides. Furthermore, the efficiency of H_2O_2 was found to be remarkably high for the reported oxidation in most cases, reaching values >90% for the majority of the investigated substrates (e.g., >95% for methyl phenyl sulfide). Only for the more challenging compounds (e.g., linear sulfides and thiophene), was the H₂O₂ efficiency reduced (50-70%).

TOF values for the different reactions and substrates were in the 70 (for methyl phenyl sulfide as substrate) to 8 h⁻¹ range (for thiophene as substrate) Most substrates had TOF values ranging from 70 to $35 h^{-1}$ (Table 4, entries 1 to 12). As comparison, some of the most relevant systems reported to date have been included in Table 5. These results clearly point out the efficiency of the proposed methodology (Table 5, last entry) in both activity, selectivity and recyclability of the Fe/SBA-15 catalyst as compared to literature reports involving several homogeneous and heterogeneous systems under various conditions (Table 5, entries 1–10).^[16–18,23,24,27–31]

Conclusions

A supported iron oxide nanoparticles SBA-15 catalyst was found to be an efficient and easily recoverable catalyst in the aqueous selective oxidation of sulfides to sulfoxides using hydrogen peroxide. The protocol featuring an easy work-up, simplicity and mild reaction conditions as well as high selectivity toward sulfoxides is highly advantageous compared to alternative reported methodologies. We envisage the extension of this highly efficient system to related aqueous phase transformations including oxidations of biomass-derived platform molecules (e.g., sugars and polyols) to high-added value chemicals, studies in this direction are currently underway in our laboratories.

 [[]a] Reaction conditions: 1 mmol sulfide, 1 mol% catalyst, 0.5 mmol H₂O₂, 1 mL water, room temperature.

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Ref.	Sulfide	Catalyst	H ₂ O ₂ (equiv.)	Solvent	Temp. [°C]	Time	Yield [%]		Uses
		Homogeneous catalysts	non-reusa	ıble			sulfoxide	sulfone	
[16]	S_	Na ₂ WO ₄ , C ₆ H ₅ PO ₃ H ₂ , and PTC	1.1	_	0	9 h	93	7	_
[18]	S_	VO(acac) ₂ /ligand	1.1	CH ₂ Cl ₂	r.t.	24 h	98	-	_
[24]	S_	Mn-salen complexes	1	1% DMF in water	r.t.	5 h	56	_	_
		Heterogeneous catalysts	in organi	ic solvents					
[30]	S_	Si-V10-2 gel	1	МеОН	r.t.	20 min	94	99	4 reaction cycles with- out loss in activity
[17]	S_	silica-based tungstate interphase	3	CH ₂ Cl ₂ :MeOH	r.t.	90 min	82	-	8 reaction cycles with- out loss in activity
[23]	S_	2 NaBO ₃ ·4 H ₂ O, 2 Na ₂ CO ₃ ·3 H ₂ O ₂ , silica, sulfuric acid, KBr, wet SiO ₂ (50% w/w)	-	CH ₂ Cl ₂	r.t.	120 min	57	-	_
[29]	S_	HAuCl ₄ ·4H ₂ O	30% H ₂ O ₂	CH ₃ OH	r.t.	60 min	97	3	6 reaction cycles with- out loss in activity
[31]	S_	МСМ-Мо	1.5	CH ₃ CN	40	60 min	>99	none (when adding only 1 equiv of oxidant)	4 reaction cycles with- out loss in activity
		Heterogeneous catalysts	in aqueo	us solvents					5 reaction
[27]	S_	VO(acac) ₂ -resin	1.1	H ₂ O	r.t.	15 min	>99	-	cycles with- out activity loss
[28]	S_	tungstate-exchanged Mg-Al-LDH catalyst	1	H ₂ O	r.t.	30 min	88	12	6 reaction cycles with- out activity loss
This work	S_	Fe/SBA-15	0.5	H ₂ O	r.t.l	120 min	>99	-	10 reaction cycles with- out activity loss

Table 5. Comparison of literature reports on the selective oxidation of methyl phenyl sulfide under various conditions.

Experimental Section

Preparation of SBA-15-NH₂

Aminopropyl-functionalised SBA-15 materials (denoted as SBA-NH₂) were synthesised according to the procedure described by Wang et al.^[36] Pluronic 123 (4 g) was dissolved in 125 g of 2.0M HCl solution at room temperature. After TEOS had been added, the resultant solution was equilibrated at 40 °C for pre-hydrolysis, and then APTES was

slowly added into the solution. The molar composition of the mixture was 0.9 TEOS:0.1 APTES:6.1 HCI:0.017 P123:165 H₂O. The resulting mixture was stirred at 40 °C for 20 h and then aged at 90 °C under static condition for 24 h. The solid product was recovered by filtration and dried at room temperature overnight. The template was removed from the material by refluxing in excess ethanol for 24 h. Finally, the material was filtered, washed several times with water and ethanol, and dried at 50 °C.

Preparation of Supported Iron Oxide Nanoparticles on SBA-15 Supports

A solution of salicylaldehyde (2 mmol, 0.244 g) in an excess of absolute MeOH was added to the aminopropyl-functionalised SBA-15 materials (2.35 g, NH₂ loading 0.85 mmol g⁻¹). The solution became yellow due to imine formation. After 6 h, Fe(NO)₃·9H₂O, (1 mmol), was added to the solution, and the mixture was gently heated for 24 h, when a dark red colour was observed due to the formation of the metal oxide nanoparticles on the SBA-15. The final product was washed with MeOH and water until the washings were colourless. Further drying of the solid product was carried out in an oven at 80 °C for 8 h.

Typical Procedure for Selective Oxidation of Sulfides to Sulfoxides

In a typical oxidation reaction, 30% aqueous H_2O_2 (0.5 mmol) was added to a solution of the corresponding thioether (1 mmol) and Fe/SBA-15 (0.01 mmol) in water. The mixture was stirred at room temperature for the various reaction times as indicated in Table 4. The reaction was followed by TLC. The catalyst was separated by filtration, washed with ethyl acetate and heated at 70°C prior to its reuse in the next reaction. The combined filtrate and ethyl acetate washings were then washed with water and the organic layer separated and dried over magnesium sulfate. The product was obtained after removal of the solvent. The conversion was determined by ¹H NMR (400 MHz) spectroscopic analysis and compounds were characterised by ¹H and ¹³C NMR (see Supporting Information). In most cases, the products could be isolated in their pure forms by simple filtration and evaporation of the solvent (products from en-tries 14 and 15).^[37,38] Further purification required column chromatography in some cases. The identity and purity of all new compounds was additionally verified by elemental analysis. H_2O_2 efficiency (%) was calculated as products (mol) per consumed H_2O_2 (mol) × 100.

Reuse Experiments

Upon completion of the first reaction to afford a quantitative yield of the corresponding sulfoxide (99% yield), the catalyst was recovered by filtration, washed and finally dried at 70 °C. A new reaction was then performed with fresh solvent and reactants under identical conditions.

Acknowledgements

FR is grateful to Payame Noor University and Iran National Science Foundation (INSF) for support of this work. RL gratefully acknowledges support from Ministerio de Ciencia e Innovacion, Gobierno de España through a Ramon y Cajal contract (ref. RYC-2009-04199) and funding from Consejeria de Ciencia e Innovacion, Junta de Andalucia (project P10-FQM-6711).

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