

IRON PORPHYRIN IMMOBILIZED ON CELLULOSE EXTRACTED FROM *SESBANIA SESBAN* PLANT: A NOVEL ECO-FRIENDLY AND COST-EFFECTIVE CATALYST FOR GREEN OXIDATION OF ORGANIC COMPOUNDS

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Received January 25, 2017

Natural cellulose was extracted from *Sesbania sesban* plant by acid hydrolysis. A novel bio-microhybrid catalyst was prepared by coordinative anchoring of iron (III) meso-tetraphenylporphyrin complex Fe(TPP)Cl on the natural polymer, cellulose (PSAC). This biomimetic hybrid was characterized by thermogravimetric analysis (TGA), FT-IR, inductively coupled plasma atomic emission spectroscopy (ICP-AES) and scanning electron microscopy (SEM). TGA analysis of PSACs showed their high thermostability. The amount of porphyrin loading on the cellulose was determined by ICP-AES. Each gram of heterogeneous catalyst contained 117 μmol Fe(TPP)Cl complex. SEM images of PSACs showed the fibril morphology of this composite material, with fibril sizes of 6-15 μm . This biopolymer material was used as a renewable and recoverable heterogeneous catalyst in the oxidation of sulfides to related sulfones, and of alcohols to related aldehydes or ketones. This system was performed in water as a green solvent by using meta-chloroperoxy benzoic acid (m-CPBA) as an oxidant. The effects of different factors, such as various oxidants, temperature, amount of catalyst, amount of oxidant and reaction time, on the yield of the reactions were considered. The oxidation of alcohols and sulfides occurred with high conversion rate and selectivity under the catalytic activity of this separable catalyst. The practical reusability of this catalyst was confirmed by its recycling.

Keywords: porphyrins, *Sesbania sesban*, cellulose, oxidation, water

INTRODUCTION

Cellulose is an excellent starting polymer for developing more sustainable materials from renewable resources and also a potential feedstock to produce fuel and value-added chemicals.¹ In practice, cellulose can be converted into useful chemicals, such as mannitol, furfural and fuels.²⁻⁴ Extensive research has been devoted to utilizing agricultural by-products as sources of cellulose because of the concerns about both the future price and availability of fossil fuels.⁵

In recent years, oxidation reactions have attracted great academic interest since their products are widely used in the production of epoxy resins, paints, surfactants and intermediates in many organic syntheses. Porphyrins are capable of selectively catalyzing the oxidation of a wide range of substrates.⁶⁻⁸ Homogeneous porphyrins have proved to be of somewhat limited

use because of the difficulties in separating the products and their contamination by the residual catalyst.⁹⁻¹⁰ Therefore, many attempts have been made to heterogenize porphyrins within different supports, such as silicates, zeolites¹¹⁻¹² and molecular sieves.¹³⁻¹⁴ In this regard, the degradable nature of cellulose makes it an attractive alternative for these uses.¹⁵⁻¹⁶

The development of novel, non-toxic, low cost, ecofriendly and recyclable catalytic systems in water are highly desirable in organic synthesis for environmental and economic reasons. Performing organic reactions in aqueous media has attracted much attention because water is abundant, safe, environmentally friendly and economical, compared to organic solvents. Moreover, in many cases, due to the hydrophobic effect, using water as a solvent not only

accelerates the reaction rate, but also enhances the reaction selectivity.¹⁷⁻¹⁹

In line with our research program on the development of new heterogeneous and homogenous catalysts for oxidation of pyrenes and some other organic compounds,²⁰⁻²² Fe(TPP)Cl was immobilized on natural cellulose and used as a new heterogeneous catalyst in oxidation. The cellulose biopolymer was extracted from *Sesbania sesban* plant, which has both economic and biological value.²³ To the best of our knowledge, this is the first time that porphyrin loaded on natural cellulose was designed as a heterogeneous catalyst in the oxidation reactions. In fact, this is one of most cost effective and eco-friendly catalyst systems in oxidation reactions.

EXPERIMENTAL

Materials

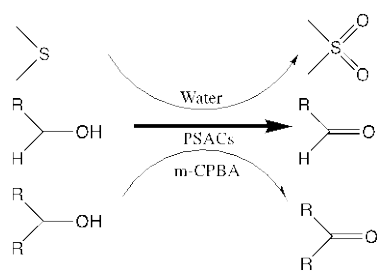
(3-Aminopropyl) triethoxysilane and ethanol were purchased from EXIR GmbH (Wien, Austria). A NICOLET iS10 FT-IR spectrophotometer (USA) was used to obtain the FT-IR spectra. A Shimadzu

thermogravimetric analyzer (TG-50, Japan) was used for thermogravimetric analysis (TGA). For investigating the products morphology, a Hitachi Model s4160 scanning electron microscope (SEM) (Japan) was used at an accelerating voltage of 15 kV. The free-base porphyrin: H₂(TPP) was prepared and purified by methods reported previously. The content of Fe in the catalyst was determined by an OPTIMA 7300DV ICP analyzer. The iron complex was obtained as reported in the literature.²⁴

Extraction of cellulose from *Sesbania sesban*

First, at a pH value of 3.8-4.0 and 75 °C, sodium chlorite (adjusted with acetic acid) was added to *Sesbania sesban* wood. After 2 h, the reaction was filtrated and the residue was washed with deionized water and ethanol for several times, and dried in an oven at 50 °C.²⁵⁻²⁶

Then, 10% KOH was added to these dried holo-cellulose residues at room temperature for 10 hours. After filtration, the residues were washed with ethanol and water for several times. Finally, the samples were dried in an oven at 50 °C for 16-20 h. Microcrystalline cellulose obtained from *Sesbania sesban* wood (MCC) is a white crystalline powder.



Scheme 1: Oxidation of organic compound catalyzed by PSAC using m-CPBA in water

Silanation of activated cellulose (SACs)

An amount of 3 g of dry activated cellulose (AC) powder was mixed with 40 mL of ethanol to produce a homogenously mixed solution, which was then subjected to sonication for half an hour. Then, 0.3

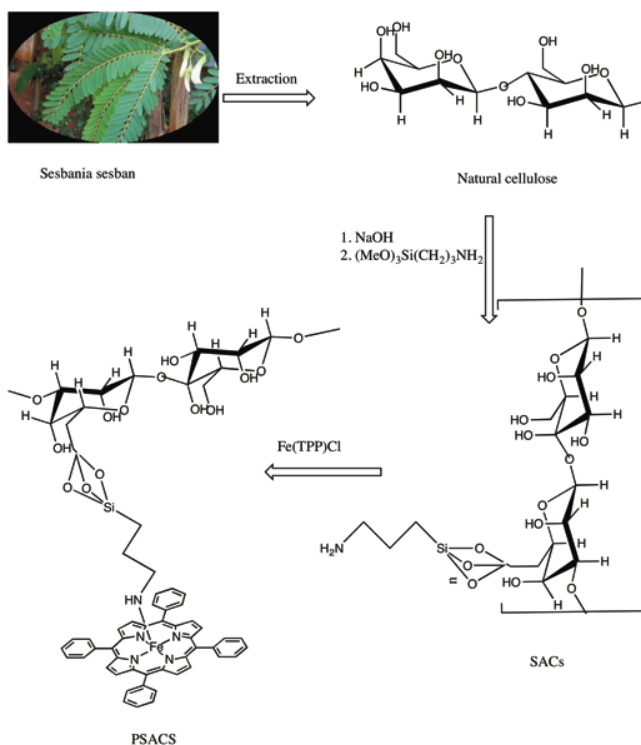


Figure 1: Synthesis of PSACs

mmol of (3-aminopropyl) triethoxysilane (APS) was added under mechanical stirring for 24 h at room temperature. The SACs were washed by ethanol to eliminate excess reactants, then centrifuged at 7000 rpm for 20 min and dried under vacuum.

Immobilization of Fe(TPP)Cl on cellulose (PSACs)

An amount of 3.15 g of dry SAC powder was mixed with 30 mL of ethanol to produce a homogeneously mixed solution, which was then subjected to sonication for 30 min. 0.5 g Fe(TPP)Cl was added under mechanical stirring and the mixture was heated to 80 °C for 7 h. The free porphyrins were removed through Soxhlet extraction with ethanol (Fig. 1).

Recycling procedure

After completion of the thioanisole oxidation, the product was isolated by ethyl acetate (6 mL). The solid catalyst was separated and washed with ethyl acetate (3 mL), dried and reused for similar reactions.

RESULTS AND DISCUSSION

Characterization of PSACs

At first, the cellulose was activated by NaOH (4 molL⁻¹) and then, an appropriate concentration of 3-aminopropyl trimethoxy silane was added to obtain the SAC samples. The white SACs were reacted with Fe(TPP)Cl to obtain the PSACs.

The size, structure and morphology of PSACs were evaluated using scanning electron microscopy (SEM). SEM images (Fig. 2) showed uniform and fibril-like morphology of the cellulose samples, with an average diameter from

6-15 μm.

The FT-IR spectra of PSACs are shown in Figure 3. The anchoring of aminopropyl groups on cellulose was confirmed by stretching vibrations appearing at about 2800-3000 and 3446 cm⁻¹.²⁷⁻²⁸ Other bands derived from deformation and stretching vibrations of the porphyrin complex covalently anchored to this natural support, along with amino functionality. The amount of porphyrin complex immobilized on the cellulose is very low. As a result, the spectra do not exhibit any significant band relating to the complex. The stretching vibration band of the phenyl rings in the meso-positions appears at 1633 cm⁻¹. The signal at 1453 cm⁻¹ could be assigned to the deformation vibration of the pyrrole fragments of the porphyrin molecule.²⁹⁻³¹

TGA and DTA of PSACs were used to determine their thermal stability and the content of organic functional groups on the surface of natural celluloses (Fig. 4). A small amount of weight loss around 100 °C was attributed to the evaporation of adsorbed water. Another mass loss appeared at around 200 °C, while the organic parts decomposed completely at 800 °C.

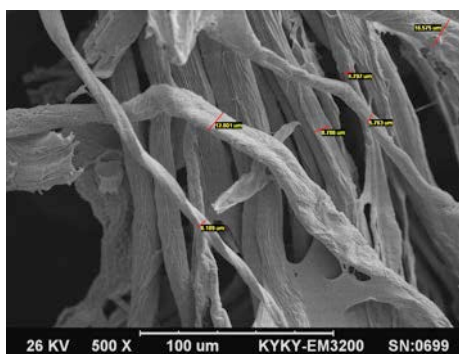


Figure 2: SEM image of PSAC

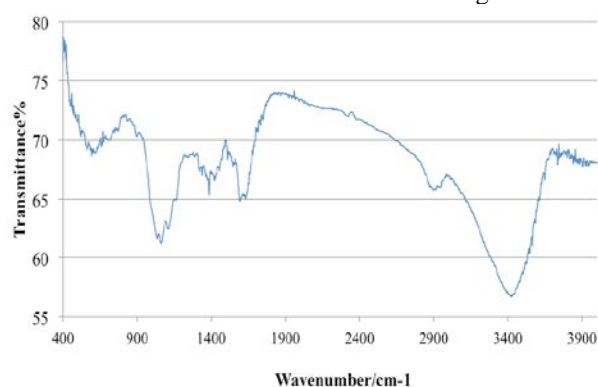


Figure 3: FT-IR spectra of synthesized PSACs

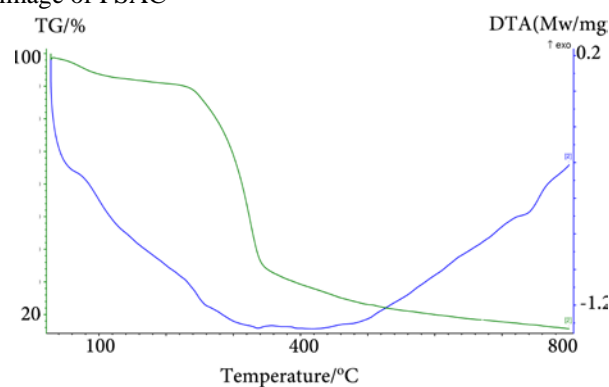


Figure 4: Thermogravimetric analysis of PSACs

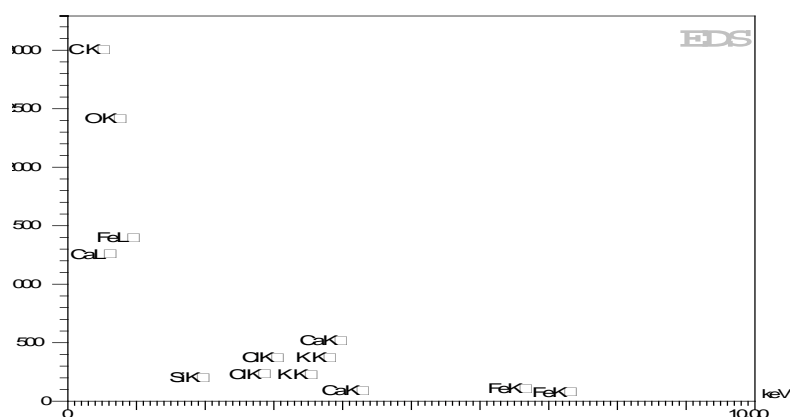


Figure 5: EDAX spectra of PSACs

Table 1
Effects of temperature on the oxidation of thioanisole catalyzed by PSACs

Entry	Temperature, °C	Conversion, %	Sulfone selectivity, %
1	25	100	100
2	15	100	70
3	10	35	18

Reaction conditions: air atmosphere, aqueous medium, duration of 60 min, molar ratio of 200:600:1 for sulfide/m-CPBA/catalyst

Table 2
Effects of m-CPBA amount on the oxidation of thioanisole catalyzed by PSACs

Entry	m-CPBA, mmol	Conversion, %	Sulfone selectivity, %
1	0.5	40	100
2	1	48	100
3	2	79	100
4	3	89	100
5	6	100	100

Reaction conditions: air atmosphere, aqueous medium, duration of 60 min, molar ratio of 200:x:1 for sulfide/m-CPBA/catalyst

According to the TGA profile of PSACs, the amount of organic components immobilized on cellulose was estimated to be of 0.12 mmol g⁻¹. ICP analysis revealed that the contents of linked Fe was of 8.81 wt%. Therefore, each gram of heterogeneous catalyst contained 117 μmol Fe(TPP)Cl complex. We also conducted the EDAX analysis to confirm the formation of the catalyst (PSACs) (Fig. 5). In the spectra, Si, Fe and Cl peaks were observed. These observations confirm that chemical modification of the cellulose was achieved.

Aqueous oxidation of sulfides to sulfoxides

Preliminary experiments were focused on

oxidation of thioanisole (0.1 mmol) with m-CPBA (0.15 mmol) in neat water under air. The mixture of the related sulfoxide (35%) and sulfone (5%) was obtained after 10 min at room temperature. Fe(TPP)Cl was used as catalyst (0.5 mol%) and 50% sulfone was obtained. Then, this iron complex was immobilized on SACs and its catalytic potential in aqueous oxidation of sulfides was evaluated. When 0.5 mol% of PSACs was added to the reaction mixture, the conversion rate enhanced significantly and sulfone (100%) was obtained after 60 min at 25 °C. The effects of various temperatures on the conversion of the product were investigated. By decreasing the temperature, the selectivity of sulfone and the

conversion of sulfide were decreased (Table 1).

The effects of different solvents were considered on the oxidation of thioanisole catalyzed by PSACs. The examination of different solvents, such as dichloromethane (17%), chloroform (20%), toluene (21%), ethylacetate (1%), hexane (5%), ethanol (67%) and water (100%), has revealed that water as a green solvent promoted the yield of the sulfone product. We believe that the pronounced effect of protic solvents, such as CH₃OH and H₂O, on the catalytic activities of PSACs is due to hydrogen bonding.

The amount of m-CPBA as oxidant could have a direct effect on the reaction yields. The best conversion was achieved using 0.3 mmol of oxidant (Table 2). To evaluate the oxidizing potential of various oxidants, methyl phenyl sulfide was subjected to the oxidation protocol using O₂, H₂O₂, t-butyl hydroperoxide (tBuOOH), NaIO₄ and UHP. Under the catalytic influence of PSACs, only trace amounts of the desired products were observed using these oxidants (Fig. 6). When the reaction was carried out using m-CPBA, 100% of sulfone was observed under the same conditions.

It seems that good dispersity of PSACs in aqueous solution is the most important factor of efficiency. Two experimental procedures were performed to confirm the effect of dispersity on the product yield during 60 min at room temperature. In the first experiment, which involved magnetic stirring, a yield of 83% of methyl phenyl sulfone was obtained. In the second experiment, the catalyst was sonicated for 10 min and then the oxidant was added and stirred magnetically, which led to 95% yield of the related sulfone product. In fact, the movement of PSACs in water is enhanced by ultrasonic irradiation.

The presence of additives (10 times *vs.* catalyst), such as imidazole (8%), pyridine (12%), sodium dodecyl sulfate at SDS condition (28%), and also performing the reaction in inert atmosphere (Ar, 68 and 77% for 20 and 40 min) did not improve the yield of the sulfone product.

Then, different standard buffered solutions were used to analyze the effect of water pH on the yield of thioanisole oxidation (Fig. 7). The maximum conversion and selectivity were attained at around neutral pH, which is advantageous for industrial application. Therefore, this clean process would be more cost-effective than other oxidation systems requiring

acidic or basic media.

Finally, different sulfides were subjected to reaction in the presence of PSACs and the results are listed in Table 3. All the substrates could be smoothly converted to sulfone with high/excellent yields and excellent selectivities under mild conditions. A unique feature of the present oxidation system is its excellent selectivity of sulfone products as sole products. The promising results obtained in the oxidation of sulfones encouraged us to evaluate the chemoselectivity of this clean catalytic system. Sulfides having a benzylic C-H bond (entry 6) and carbon-carbon double bond (entries 4 and 8) were cleanly transformed into the corresponding sulfones, with an excellent yield and without formation of any epoxide, alcohol or carbonyl by-products. To confirm the effect of cellulose morphology on the yield and selectivity of sulfides, Fe(TPP)Cl was immobilized on microcrystalline celluloses purchased from Aldrich (PCs) by the same procedure as that for PSACs, and the results were compared. The yield and selectivity of several sulfone products from PSACs were much better than those obtained by PCs (see Table 3). Besides its fibril morphology, the main features of PSAC that promote its use as catalyst consist in its large specific surface area, large aspect ratio and availability of the activated sites.

In order to show the merit of the present method for oxidation of thioanisole, we have compared our results obtained using PSAC with some of those reported in the literature for the synthesis of methyl phenyl sulfone (Table 4). These results indicate clearly the superior activity of PSAC to that of other catalysts, especially for the synthesis of methyl phenyl sulfone from thioanisole. Most of the reported methods have low conversion or selectivity.³²⁻³⁷

The oxidation of alcohols was investigated under the same conditions, benzyl alcohols were converted to benzaldehyde (40%), and 100% of benzaldehyde was obtained at 80 °C during 2 hours. Fortunately, wide ranges of primary and secondary alcohols were oxidized to related aldehydes and ketons under the optimized conditions (Table 5). Primary and secondary alcohols having various substitutions, containing electron-donating or electron-withdrawing groups, have high to excellent yields.

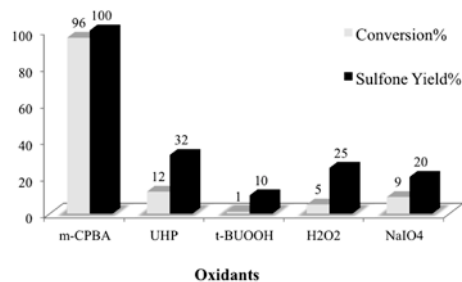


Figure 6: Effect of different oxidants on the oxidation of thioanisole catalyzed by PSACs, using m-CPBA

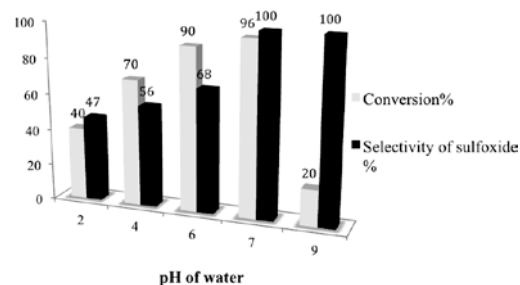


Figure 7: Effect of water pH on the oxidation of thioanisole catalyzed by PSACs, using m-CPBA

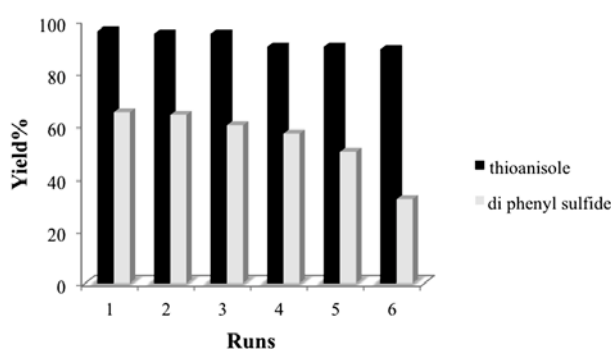


Figure 8: Recycling the catalytic system for oxidation of thioanisole and diphenyl sulfide in water

Recovery of catalyst

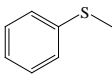

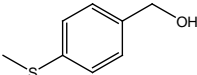
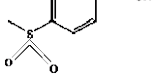
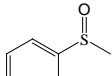

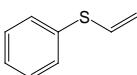
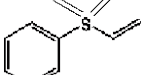
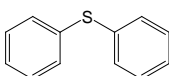
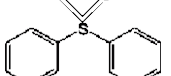
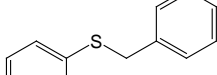
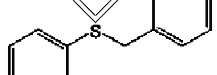
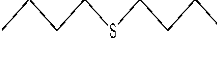
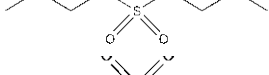
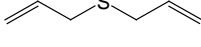
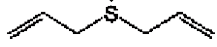
The heterogeneous property of PSACs facilitates efficient recovery of the catalyst from the reaction mixture during the workup procedure. After completing the thioanisole oxidation using m-CPBA, EtOAc was added to the reaction mixture. The catalyst was separated through centrifugation from the reaction mixture, washed with EtOAc as a safe solvent and reused for a consecutive run under the same reaction conditions. The average isolated yields of the product for oxidation of methyl phenyl sulfide and diphenyl sulfide for six consecutive runs were of 98 and 88%, which clearly demonstrates the practical reusability of this catalyst (Fig. 8). Therefore, the developed methodology is cost-effective and environmentally benign due to using water as reaction medium, reusing the catalyst, easy isolation of hydrophobic organic products and no need to use surfactants, nitrogen donors, toxic reagents or organic solvents. The use of a semi scale-up procedure (5.00 mmol) for oxidation of thioanisole in the presence of PSACs led to isolation of the methyl phenyl sulfone with an 87% yield. Furthermore, standard leaching

experiments in the oxidation reaction of thioanisole (using the hot filtration method and ICP-AES) demonstrated negligible iron loss in the filtrate and the recovered heterogeneous catalyst was found to contain 8.6 wt% of Fe after the 5th run according to ICP analysis. This result indicates that the complex was anchored to the cellulose support very well.

CONCLUSION

In summary, the Fe(TPP)Cl complex was immobilized on cellulose as a new recyclable heterogeneous catalyst for selective oxidation of sulfides to sulfones in water using m-CPBA. The catalyst was easily isolated from the reaction mixture through centrifugation and was reused six times without significant degradation in its activity. No need of surfactant, organic co-solvent and co-catalyst, as well as the rapid and convenient isolation of products and catalysts from the reaction mixture, are the outstanding features of this simple and clean catalytic method. The simplification of work-up procedures and the reuse of the catalyst are the practical advantages of this system.

Table 3
Oxidation of various sulfides catalyzed by PSACs and using m-CPBA as oxidant^a

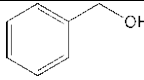
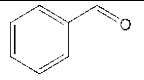
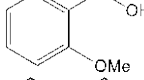
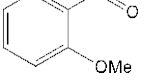
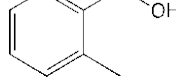
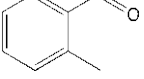
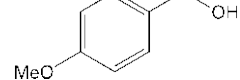
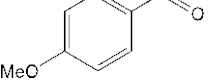
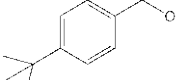
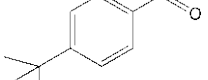
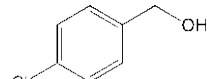
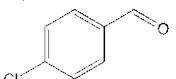
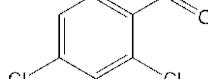
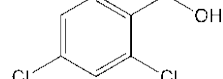
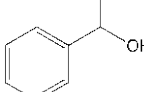
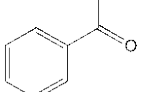
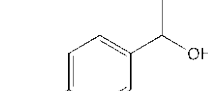
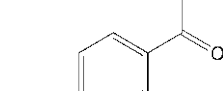
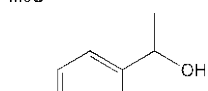
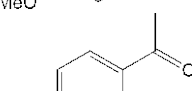
Sulfides	Product	Sulfone isolated yield, % (sulfone selectivity, %) ^c	Sulfone isolated yield, % (sulfone selectivity, %) ^b
		100(100)	96(100)
		100(100)	87(85)
		100(100)	94(95)
		100(100)	93(100)
		90(100)	65(80)
		97(100)	88(97)
		100(100)	100(100)
		100(100)	100(100)

^a Reaction conditions: air atmosphere, room temperature, duration of 60 min, molar ratio of 200:600:1 for sulfide/m-CPBA/catalyst; ^b The catalyst is Fe(TPP)Cl immobilized on cellulose bought from Aldrich; ^c The catalyst is Fe(TPP)Cl immobilized on cellulose extracted from *Sesbania sesban*

Table 4
Oxidation of thioanisole to related sulfone products in the presence of reported reagents or catalysts

Entry	Catalyst	Solvent	Oxidant	Conversion	Selectivity of sulfone, %	Reference
1	PyPS ₄ PMo ₁₀ V ₂	Ethanol	H ₂ O ₂	70	30	32
2	Pd/C	Water	H ₂ O ₂	55	60	33 (13 MPa overall pressure)
3	[Bmim] ₄ Mo ₈ O ₂₆	Acetonitrile	H ₂ O ₂	95	84	34
4	Amberlyst 15	Acetic acid and water	H ₂ O ₂	70	100	35
5	Fe(TCPP)Cl@MWCNT	Water	UHP	100	33	36
6	Fe ₃ O ₄ @Si-APFSB-MoO ₂	Solvent free	H ₂ O ₂	100	5	37
7	PSAC	Water	m-CPBA	100	100	This work

Table 5
Oxidation of alcohols catalyzed by PSACs using *m*-CPBA as oxidant^a

Entry	Alcohol	Product	Yield (%)
1			90
2			85
3			85
4			85
5			90
6			85
7			75
8			95
9			95
10			90

^a Reaction conditions: air atmosphere, 80 °C, molar ratio of 200:600:1 for alcohols/*m*-CPBA/PSACs

ACKNOWLEDGMENTS: The support for this work by the Research Council of Birjand University of Technology Research Council and the University of Jiroft is highly appreciated.

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