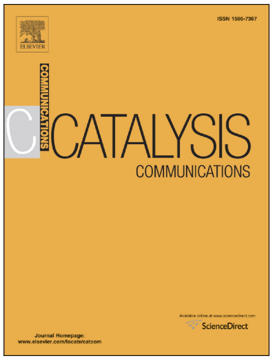

Magnetic core-shell nanoparticle-supported Sc (III): A novel and robust Lewis acid nanocatalyst for the selective oxidation of sulfides to sulfoxides by H2O2 under solvent-free conditions

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Magnetic core-shell nanoparticle-supported Sc (III): A novel and robust Lewis acid nanocatalyst for the selective oxidation of sulfides to sulfoxides by H_2O_2 under solvent-free conditions

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Abstract

For the first time scandium triflate was supported on modified Fe_3O_4 magnetic nanoparticles [MNPs-$PhSO_3$-$Sc(OTf)_2$] and characterized using scanning electron microscopy (SEM), inductively coupled plasma analysis (ICP), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), energy dispersive X-ray spectroscopy (EDX) and vibrating sample magnetometer (VSM) techniques. The MNPs-$PhSO_3$-$Sc(OTf)_2$ was applied as a magnetically recyclable heterogeneous Lewis acid nanocatalyst for the selective oxidation of a variety of sulfides to sulfoxides using hydrogen peroxide as a green oxidant resulting in 90-98% yields under solvent-free conditions at room temperature. It could also be recovered and reused for at least 15 reaction cycles without considerable loss of activity.

Keywords: Magnetic nanoparticles, Scandium triflate, Hydrogen peroxide, Sulfides, Sulfoxides.

1. Introduction

Lewis acid catalysts have been of great interest due to their unique activities and selectivities in the synthesis of organic compounds under mild reaction conditions [1,2]. In this manner, scandium triflate has been introduced as a promising mild, powerful and selective Lewis acid for a variety of functional group transformations [2]. Furthermore, $Sc(OTf)_3$, in contrast to most traditional Lewis acids which are disintegrated into their metal hydroxide in water or protic solvents, and accordingly lose their catalytic activities, does not decompose or deactivate under aqueous workup conditions, so its recovery is often possible. Nonetheless, the most popular recycling methods for the recovery of $Sc(OTf)_3$ are time-consuming and include the successive extraction of organic reaction mixture using deionized water [3,4]. In order to facilitate catalyst reuse and to preserve its catalytic activity, scandium has been immobilized on many different types of supports such as silica [5-7], clays [8], polymer [9,10], zeolite [11] and metal-organic frameworks (MOFs) [12]. Although these protocols represent considerable advances, they still need the classical methods such as extraction, filtration or centrifugation to separate the supported scandium (III) from the reaction solution.

Recently, the traditional supported matrices were replaced by magnetic nanomaterials that have easy preparation and functionalization, large surface area ratio, facile recovery and recyclability *via* magnetic force, as well as low toxicity and price [13,14]. To the best of our knowledge, there are no examples of MNPs-based scandium (III) nanocatalyst. In continuation of our studies on the preparation and application of magnetically recyclable nanocatalysts [15-18], herein, we wish to present the design, synthesis and catalytic properties of a novel Sc(III)-supported onto magnetic nanoparticles and use this catalyst as a novel, eco-friendly and recyclable catalyst in the selective oxidation of sulfides to sulfoxides using hydrogen peroxide as a green oxidant at room temperature under solvent-free conditions (Scheme 1). The significant novelties of the presence work are: (i) this is the first report of a magnetic nanoparticle-supported scandium triflate for use as a robust heterogeneous Lewis acid catalyst, and (ii) it is the first time that Sc(III) catalyst has been used for the chemical oxidation of sulfides to sulfoxides using H_2O_2.

< Scheme 1>

2. Experimental

The magnetic nanoparticle-supported scandium (III) was prepared through a multi-step functionalization procedure, details of which can be found in the provided Electronic Support Information (ESI).

2.1 General procedure for the oxidation of sulfides to sulfoxides

The sulfide (1 mmol) was added to a mixture of 30% H_2O_2 (3.6 mmol) and MNPs-$PhSO_3$-Sc(OTf)$_2$) (25 mg), and the mixture was then stirred at room temperature for the time specified. The progress of reaction was monitored by TLC (EtOAc/*n*-hexane, 3/10). After completion of the reaction, the catalyst was separated from the reaction mixture by an external magnet and the mixture was decanted. The product was extracted with Et_2O (2 × 5 mL) and the combined organic phases were washed with brine (10 mL) and dried over anhydrous Na_2SO_4. The evaporation of solvent under reduced pressure gave the pure products in 90–98% yields. All the products were known and characterized by comparison of their ^{1}H NMR spectra and physical properties (melting point) with those of authentic samples [19-22].

3. Results and discussion

3.1. Preparation and characterization of MNPs-$PhSO_3$-Sc(OTf)$_2$

Scandium triflate successfully was immobilized on MNPs by using the surface modification strategy as descripted in Scheme 1.

< Scheme 1>

To illustrate the successful synthesis of the MNPs-PhSO$_3$-Sc(OTf)$_2$, we characterized its chemical composition using different techniques. One indication of bond formation between the nanoparticles and the catalyst can be inferred from TGA. The TGA curve of the MNPs-PhSO$_3$-Sc(OTf)$_2$ shows the mass loss of the organic materials as they decompose upon heating (Fig. 1). The weight loss at temperatures below 120˚C is due to the removal of physically adsorbed solvent and surface hydroxyl groups [23,24]. Organic groups have been reported to desorb at temperatures above 130˚C. The curve shows a weight loss ~ 21% from 130 to 700˚C, resulting from the decomposition of organic spacer grafting to the MNPs surface.

<Fig. 1 >

The FT-IR spectra for the MNPs, MNPs-SiO$_2$, and MNPs-PhSO$_3$-Sc(OTf)$_2$ samples are shown in Fig. 2. As can be seen from the FT-IR spectrum of MNPs, the strong band at 583 cm^{-1} corresponds to Fe–O vibrations of the magnetite core, and the stretching vibration at 3421 cm^{-1} is attributed to the O–H bonds, which are attached to the surface iron atoms. The bond formation between MNPs and TMOS is confirmed by the Fe–O–Si absorption band that appears at 631 cm^{-1}. The band at 1099 cm^{-1} represents Si–O bonds, and IR bands at 3381 and 1626 cm^{-1} correspond to the stretching and bending vibrations of Si–OH, respectively. In the FT-IR spectrum of the MNPs-PhSO$_3$-Sc(OTf)$_2$ (Fig. 2), the IR bands at ~ 693 and 1101 cm^{-1} are attributed to the asymmetric bending absorption mode of CF$_3$ groups and the asymmetric C-F stretching absorption of the CF$_3$ group, respectively. In addition, the sulfate stretching vibration absorption IR band at 1409 cm^{-1} could also be found in the MNPs-PhSO$_3$-Sc(OTf)$_2$ sample.

<Fig. 2 >

Superparamagnetic particles are beneficial for magnetic separation. The magnetic property of the MNPs-PhSO$_3$-Sc(OTf)$_2$ has been compared with bare MNPs using the vibrating sample magnetometer (VSM) technique (Fig. 3). VSM measurements for MNPs (74.3 emu g^{-1}) [25] is higher than MNPs-PhSO$_3$-Sc(OTf)$_2$ (27.71 emu g^{-1}). Decrease in magnetic property of MNPs-PhSO$_3$-Sc(OTf)$_2$ can originate from the grafting of organic layers and scandium triflate on Fe_3O_4 nanoparticles.

<Fig. 3>

The SEM image of the MNPs-PhSO$_3$-Sc(OTf)$_2$ confirmed that the catalyst was made up of uniform nanometer-sized particles of less than 22 nm (Fig. S1). EDX microanalysis was performed to provide qualitative determination of the elemental composition. The EDX spectrum of MNPs-PhSO$_3$-Sc(OTf)$_2$ confirmed the presence of Fe, Si, O, S, C and Sc (Fig. S2). The loading of the scandium function in MNPs-PhSO$_3$-Sc(OTf)$_2$ can be calculated from Inductively Coupled Plasma (ICP) analysis, which confirmed a loading of ~ 0.6 %.

3.2. Catalytic application of MNPs-PhSO$_3$-Sc(OTf)$_2$ in the oxidation of sulfides to sulfoxides

The catalytic activity of MNPs-PhSO$_3$-Sc(OTf)$_2$ was investigated in the selective oxidation of sulfides to sulfoxides using 30% H_2O_2 as a green oxidant. To optimize the reaction conditions, we evaluated the influence of different amounts of catalyst and hydrogen peroxide on the oxidation of methyl phenyl sulfide as a model compound under solvent-free conditions at room temperature. As shown in Table 1, the optimum amount of H_2O_2 (3.6 mmol) in the presence of MNPs-PhSO$_3$-Sc(OTf)$_2$ (25 mg) is ideal for complete conversion of methyl phenyl sulfide to methyl phenyl sulfoxide (Table 1, entry 5).

<Table 1>

The generality of this approach has been demonstrated by a facile oxidation of a wide variety of aryl, benzylic, linear, cyclic and heterocyclic sulfides, as shown in Table 2. The reactions went on well to afford products in excellent yields ranging from 90-98% in short times. The TON and TOF values of the process confirm the catalytic efficiency of the method (Table 2). Meanwhile, to show the chemoselectivity of this method, the sulfide containing oxidation-prone functional group such as OH was subjected to the sulfoxidation reaction that this functional group remained intact during the conversion of sulfide to sulfoxide (Table 2, entry 15).

<Table 2>

The leaching of the catalyst was also checked in the oxidation of dibenzyl sulfide to dibenzyl sulfoxide using hydrogen peroxide. The magnetic nanocatalyst was removed by an external magnet from the reaction mixture after 30 min, and the mixture was allowed to react further for 60 min. The GC yield of the product after 30 min was 70%, whereas there was no significant increase in the yield of the product after 60 min. This study clearly demonstrated that there was no significant amount of leaching.

For practical purposes, the ability to easily recover and recycle the catalyst is highly desirable. To investigate this issue, the recovery and reuse of MNPs-$PhSO_3$-$Sc(OTf)_2$ was examined for the oxidation of methyl phenyl sulfide to give methyl phenyl sulfoxide. We found that this catalyst rapidly recovered and demonstrated remarkably excellent recyclability. In particular, after the first run, the catalyst was separated by an external magnet, washed thoroughly with ether and dried under vacuum, and reused as such for subsequent experiments under the above mentioned reaction conditions (general procedure). The catalyst was reusable for up to 15 cycles without any significant loss of activity (Fig. S3). The SEM image of the reused MNPs-$PhSO_3$-$Sc(OTf)_2$ catalyst (Fig. S4) also indicated that nanoparticles size has been increased to 43 nm because of nanoparticles aggregation during the reaction and the recycling stages. EDX analysis (Fig. S5) of the MNPs-$PhSO_3$-$Sc(OTf)_2$ catalyst after 15 runs was used to confirm the presence of Fe, O, S, C, Si and Sc elements in the reused magnetic nanocatalyst. The ICP analysis of the reused magnetic nanocatalyst was performed to evaluate the remaining quantity of the loaded scandium, illustrating ~ 0.54% for scandium value. This implies that the scandium quantity in the magnetic nanocatalyst after recycling is comparable with the fresh magnetic nanocatalyst and the catalyst can be recovered and reused without any significant leaching of scandium.

Based on previously reported mechanisms for the catalytic application of scandium triflate as Lewis acid in organic synthesis [3,7], it is proposed that scandium (III) polarizes the O-O bond in H_2O_2 to produce the reactive oxygen transfer agent followed by the oxygen transfer to the sulfide as shown in Scheme 2.

< Scheme 2>

4. Conclusions

The first magnetic core-shell nanoparticles-based scandium (III) nanocatalyst was successfully synthesized by immobilizing scandium triflate into sodium benzenesulfonate-functionalized magnetic nanoparticles. The present catalyst shows excellent activity in the oxidation of sulfides to sulfoxide using H_2O_2. The system also couples the advantages of homogeneous Sc(III) based systems (high activity and reproducibility) and heterogeneous (easy separation and excellent reusability of up to 15 runs), which make it as a promising material for practical and large-scale applications. The other merits of the protocol are the use of a commercially available, eco-friendly, cheap and chemically stable oxidant, the mild reaction conditions, operational simplicity, practicability, short reaction times and high yields of products.

Acknowledgment

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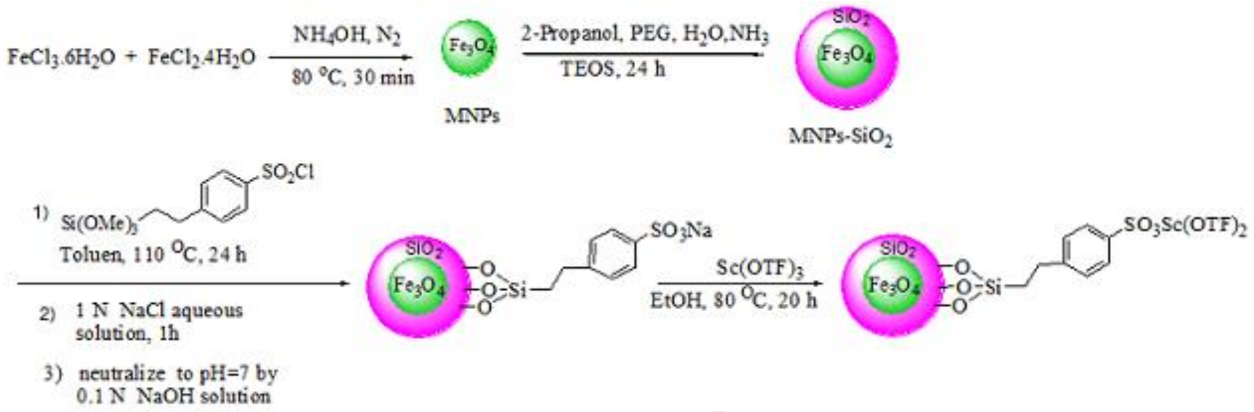
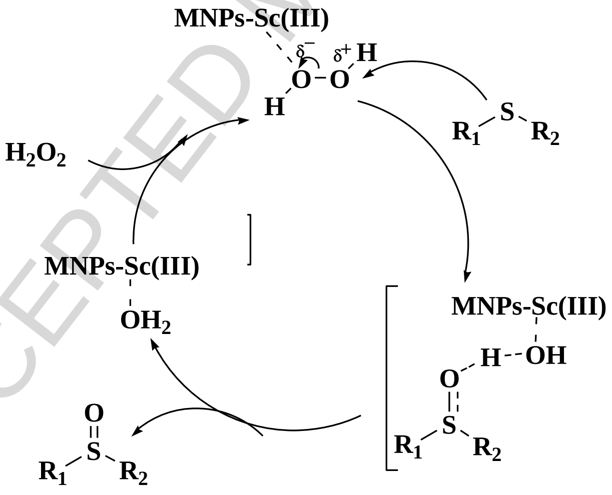
Schemes



Scheme 1. The process for the preparation of MNPs-PhSO$_3$-Sc(OTf)$_2$.



Scheme 2. A possible mechanism for the oxidation of sulfides to sulfoxides using H$_2$O$_2$ catalyzed by MNPs-PhSO$_3$-Sc(OTf)$_2$.

Figures

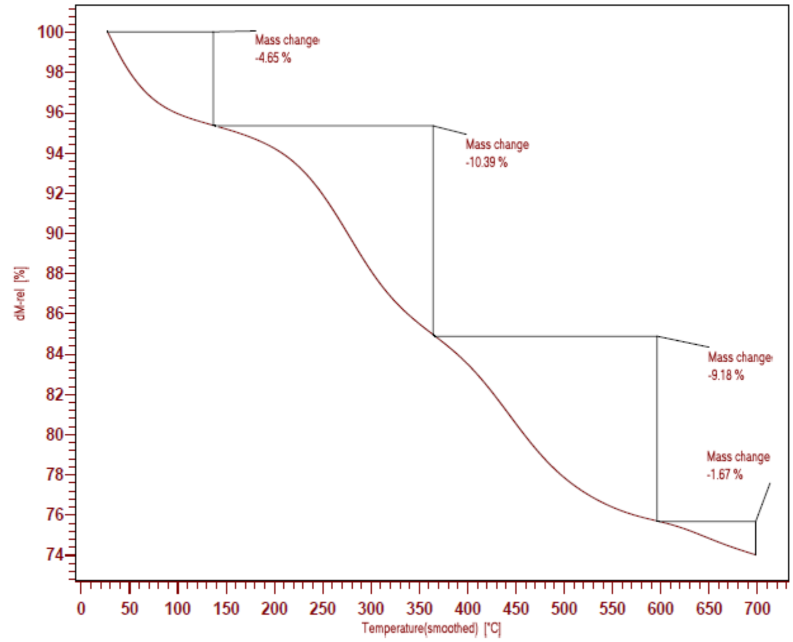


Fig. 1. TGA curve of MNPs-PhSO$_3$-Sc(OTf)$_2$.

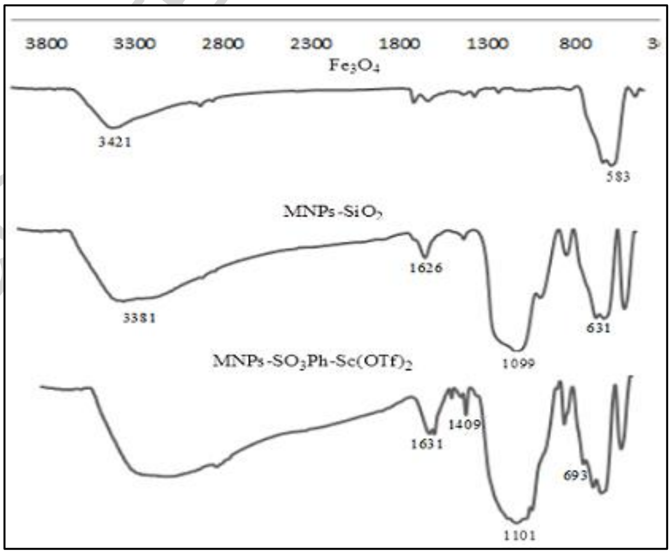


Fig. 2. FT-IR spectra of MNPs, MNPs-SiO$_2$ and MNPs-PhSO$_3$-Sc(OTf)$_2$

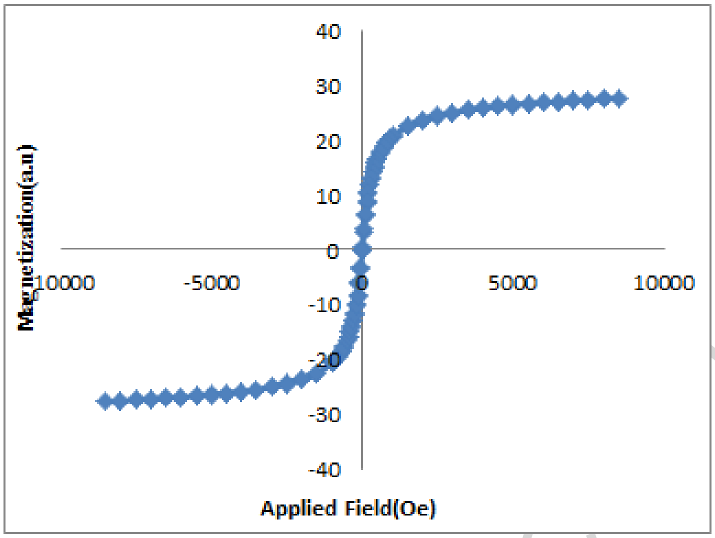


Fig. 3. Magnetization curve for MNPs-PhSO$_3$-Sc(OTf)$_2$ recorded at room temperature.

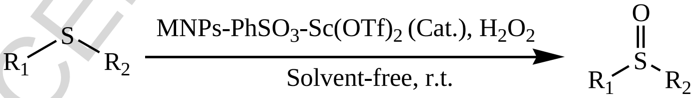
Tables

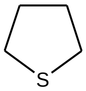
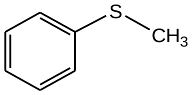
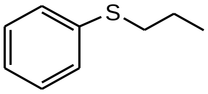
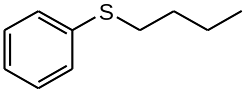
Table 1. The oxidation of methyl phenyl sulfide to methyl phenyl sulfoxide under different conditions.

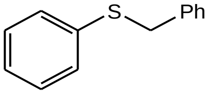
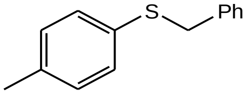
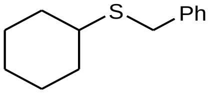
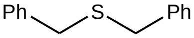
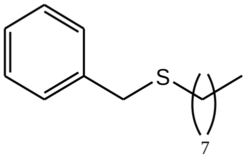
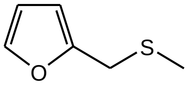
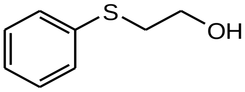
Entry	Catalyst (mg)	H_2O_2 (mmol)	Time (min)	Solvent	Yield (%)[a]
1	Catalyst-free	3.6	24h	-	40
2	Fe_3O_4 MNPs (15)	3.6	2h	-	40
3	MNPs-$PhSO_3Na$ (15)	3.6	75	-	75
4	MNPs-$PhSO_3$-Sc$(OTf)_2$ (15)	3.6	8		70
5	**MNPs-$PhSO_3$-Sc$(OTf)_2$ (25)**	**3.6**	**8**	**-**	**98**[b]
6	MNPs-$PhSO_3$-Sc$(OTf)_2$ (35)	3.6	8	-	98
7	MNPs-$PhSO_3$-Sc$(OTf)_2$ (25)	2.4	8	-	80
8	MNPs-$PhSO_3$-Sc$(OTf)_2$ (25)	4.8	8	-	98
9	MNPs-$PhSO_3$-Sc$(OTf)_2$ (25)	3.6	8	CH_3CN	50
10	MNPs-$PhSO_3$-Sc$(OTf)_2$ (25)	3.6	8	EtOH	45

[a]Conversion of sulfide to sulfoxide was determined by GC. [b]The bold represents the most effective conditions.

Table 2. MNPs-$PhSO_3$-Sc$(OTf)_2$ (25 mg) catalyzed selective oxidation of sulfides (1 mmol) to sulfoxides using 30% H_2O_2 (3.6 mmol).



Entry	sulfide	Time (min)	Yield (%)[a]	TON	TOF(h^{-1})
1		3	>98	294	5886
2		8	>95	285	2143
3		9	>95	285	1900
4		12	>95	285	1425

5		30	90	270	540
6		120	91	273	137
7		5	>95	285	3434
8		60	94	282	282
9		65	92	276	255
10	$CH_3(CH_2)_7\ S\ (CH_2)_2CH_3$	15	92	276	1104
11	$CH_3(CH_2)_7\ S\ (CH_2)_5CH_3$	15	93	279	1116
12	$CH_3(CH_2)_3\ S\ (CH_2)_2CH_3$	12	>95	285	1425
13	$CH_3S\ CH_3$	5	>95	285	3434
14		10	95	285	1707
15		5	>95	285	3434

[a] Isolated yield.

Highlights

- The first MNPs-$PhSO_3$-$Sc(OTf)_2$ was easily synthesized and characterized.
- MNPs-$PhSO_3$-$Sc(OTf)_2$ catalyzed highly efficient chemoselective oxidation of sulfides.
- The catalyst allows for greener method while keeping high yields and low times.
- The catalyst was reused up to 15 times without significant loss of activity.