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Metal- and halogen-free hydrogensulfate ionic liquid/SBA-15 as catalyst in clean oxidation of aromatic and aliphatic organic sulfides with aqueous hydrogen peroxide

Sadegh Rostamnia*, Behnam Gholipour, Habib Golchin Hosseini

Organic and Nano Group (ONG), Department of Chemistry, University of Maragheh, P.O. Box 55181-83111, Maragheh, Iran

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ABSTRACT

An efficient, and eco-friendly procedure for the oxidation of aromatic and aliphatic sulfides to sulfoxides using H_2O_2 catalyzed by hydrogensulfate ionic liquid/SBA-15 [IL- H_2SO_4 @SBA-15] has been developed. This atom-economical protocol affords the target products in good to high yields. The products can be separated by a simple extraction with organic solvent, and the catalytic system can be recycled and reused without loss of catalytic activity even after fourteen runs.

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1. Introduction

Water-medium organic process could reduce the pollution and cost resulting from organic solvents and simultaneously facilitate the separation of the solid heterogeneous catalyst from the products (Gawande et al., 2013; Alizadeh et al., 2009). Among various multi-phase water-medium reaction, use of immobilized H^+ -acids function as solid catalysts are more challenging because conventional Brønsted acids immobilization such as $HClO_4$, HBF_4 , and H_2SO_4 always have interaction with water rather than the substrates, resulting in serious leaching of the H^+ from the surface of solid supports (Sinou, 1999; Chen and Li, 2006; Serrano-Ruiz et al., 2011; Gordon, 2001; Rostamnia et al., 2012a). Also, based on our recent studies on SBA-15/ OSO_3H and $\gamma-Fe_2O_3$ @ SiO_2 / OSO_3H , in water media

process the acidic functions of $-OSO_3H$ act as homogeneous catalyst by hydrolysis of the acid groups to H_2SO_4 (Rostamnia et al., 2012a).

In recent years, designing synthetic process using supported ionic liquids (ILs) as reusable catalyst and reaction media has received extensive attention (Breitenlechner et al., 2004; Peppel et al., 2011; Dupont et al., 2002; Khazaei et al., 2012; Hu et al., 2014). The design and development of new and novel ILs with air and moisture stability have provided renewed vigor in ionic liquid chemistry. The key issue in supported IL is effective immobilization of ILs onto solid to avoid the loss of ILs. Since some organic reactions normally uses H^+ -acids function as the catalyst, if the H^+ can be effectively immobilized in IL/solid systems, it would then be possible to enable the easy separation and recycling of

* Corresponding author. Tel.: +98 4212278001 108.

E-mail addresses: rostamnia@maragheh.ac.ir, srostamnia@gmail.com (S. Rostamnia).

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H⁺-catalyst in the reaction cycles (Gordon, 2001; Rostamnia et al., 2012a; Breitenlechner et al., 2004; Peppel et al., 2011; Dupont et al., 2002; Khazaei et al., 2012; Hu et al., 2014; Karimi and Vafaezadeh, 2013; Rostamnia and Xin, 2014; Rostamnia and Doustkhah, 2014a).

Recently, immobilization of the ILs into the mesoporous of SBA-15 (IL@SBA-15) has gained increasing attention in replacement of the conventional mineral amorphous silica materials based on their high surface area, high thermal and mechanical stability (Rostamnia et al., 2013a, 2014a, 2014b, 2015a; Rostamnia and Xin, 2013; Yang et al., 2009; Rostamnia and Pourhassan, 2013; Rostamnia and Doustkhah, 2014a). One exceptional advantage is that the location of organic groups of ILs in the pores of SBA-15 allows for molecular-level fine-tuning of the host microenvironment. It is especially advantageous for water-medium organic synthesis since the hydrophobic support microenvironment could concentrate the substrates and decrease diffusion limitation to facilitate the reaction processes (Rostamnia et al., 2013a, 2014a, 2014b, 2015a; Rostamnia and Xin, 2013; Yang et al., 2009; Rostamnia and Pourhassan, 2013; Rostamnia and Doustkhah, 2014a; Kowalski et al., 2005; Das and Chakraborty, 2010; Sato et al., 2001).

Recently, to aim green chemistry, we synthesized a series of organic-inorganic hybrid heterogeneous systems, which displayed comparable activity and selectivity to those of homogenous system in a wide range of water medium organic reactions (Rostamnia et al., 2012b, 2013a, 2013b, 2013c, 2014a, 2014b, 2014c, 2015a; Rostamnia and Xin, 2013; Yang et al., 2009; Rostamnia and Pourhassan, 2013; Rostamnia and Doustkhah, 2014a, 2014b; Kowalski et al., 2005; Das and Chakraborty, 2010; Sato et al., 2001; Rostamnia and Morsali, 2014; Rostamnia and Zabardasti, 2012; Rostamnia, 2011; Rostamnia and Amini, 2014). Encouraged by these successful efforts and aiming to develop a stable and highly active porous solid H⁺-catalyst, herein we aimed to synthesis and examine the catalytic activity of IL-HSO₄@SBA-15 in the oxidation of sulfides based on their pharmaceutical activities and synthetic intermediate volatility (Kowalski et al., 2005; Das and Chakraborty, 2010; Sato et al., 2001). For oxidation of sulfides to furnish sulfoxides, one of the problems encountered with this method is over oxidation of sulfoxides to produce sulfones. And also, another problem is the absence of selectivity which sometimes lead to undesired compounds. However, our proposed catalytic system has surpassed this method and the drawback is resolved. This system was accomplished under heavy metal and metal-free conditions with high selectivity toward

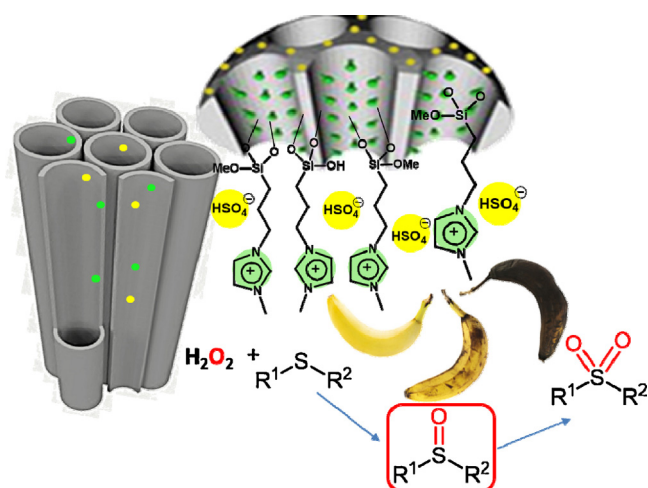


Fig. 1 – IL-HSO₄@SBA-15 for green oxidation of sulfides.

sulfoxides. And owing to its heterogeneity and efficiency, it was recoverable and reusable at least for 14 runs. Simplicity, high efficiency, ease of work-up, and its mild reaction conditions are the other aspects of this system (Fig. 1).

2. Experimental

2.1. Chemicals and apparatus

Tetraethoxysilane (TEOS), 3-(chloropropyl)trimethoxysilane ((MeO)₃SiPrCl), triblock copolymer P123 (EO₇₀PO₂₀EO₇₀) and other reagents were obtained from Aldrich, Merck (Germany) and Fluka (Switzerland) and used as received. Melting points were measured on an Electrothermal 9100 apparatus. The IR spectra were determined using a FT-IR Bruker-Vector 22.

2.2. Synthesis of IL-HSO₄@SBA-15

SBA-15 was synthesized according to our previous reported procedure (Rostamnia et al., 2013a). The obtained mesoporous silica of SBA-15 was then incorporated with imidazolium hydrogensulfate as [MPIIm][HSO₄]-SBA-15 (IL-HSO₄@SBA-15). The IL-HSO₄@SBA-15 was synthesized by taking *N*-methylimidazole (1 mmol) and chloropropyl silane ((MeO)₃SiPrCl) in 1:1 molar ratio by keeping it at 110 °C for 24 h under nitrogen atmosphere. The obtained IL of trimethylsilylpropyl methylimidazole [TmspMIm]Cl was dissolved in 100 mL toluene at room temperature followed by addition

Table 1 – Optimized reaction conditions for the oxidation of sulfides.^a

Entry	R ¹	R ²	Time (min)	Yield (%) ^b
1	C ₆ H ₅ -	C ₆ H ₄ CH ₂ -	60	96
2	C ₆ H ₅ -	C ₆ H ₅ -	120	84
3	4-Br-C ₆ H ₄	C ₆ H ₄ CH ₂ -	60	97
4	C ₆ H ₅ -	CH ₃ -	30	100
5	C ₆ H ₅ -	2-Py	40	92
6	3-NO ₂ -C ₄ H ₄	3-NO ₂ -C ₄ H ₄	90	95
7	C ₆ H ₅ -	3-MeO-C ₄ H ₄	120	80
8	3-MeO-C ₄ H ₄	3-MeO-C ₄ H ₄	160	82
9	C ₆ H ₄ CH ₂ -	C ₆ H ₄ CH ₂ -	20	100
10	4-NO ₂ -C ₄ H ₄ -CH ₂	4-NO ₂ -C ₄ H ₄ -CH ₂	20	100
11	4-Br-C ₄ H ₄	4-MeO-C ₄ H ₄	60	90

^a Reaction conditions: sulfide (1 mmol), H₂O₂ (4 mmol).

^b Yields based on GC analysis.

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