



Mesoporous sBa-15 silica catalyst functionalized with phenylsulfonic acid groups (SbA-15-ph- SO_3H) as efficient nanocatalyst for chemoselective thioacetalization of carbonyl compounds

Alireza Sedrpoushan & Habibollah Ghazizadeh

To cite this article: Alireza Sedrpoushan & Habibollah Ghazizadeh (2017) Mesoporous sBa-15 silica catalyst functionalized with phenylsulfonic acid groups (SbA-15-ph- SO_3H) as efficient nanocatalyst for chemoselective thioacetalization of carbonyl compounds, Journal of Sulfur Chemistry, 38:1, 112-118, DOI: [10.1080/17415993.2016.1257929](https://doi.org/10.1080/17415993.2016.1257929)

To link to this article: <http://dx.doi.org/10.1080/17415993.2016.1257929>



Published online: 31 Dec 2016.



Submit your article to this journal [↗](#)



Article views: 4



View related articles [↗](#)



View Crossmark data [↗](#)

Mesoporous sBa-15 silica catalyst functionalized with phenylsulfonic acid groups (SbA-15-ph- SO_3H) as efficient nanocatalyst for chemoselective thioacetalization of carbonyl compounds

Alireza Sedrpoushan and Habibollah Ghazizadeh

Institute of Industrial Chemistry, Iranian Research Organization for Science and Technology (IROST), Tehran, Iran

ABSTRACT

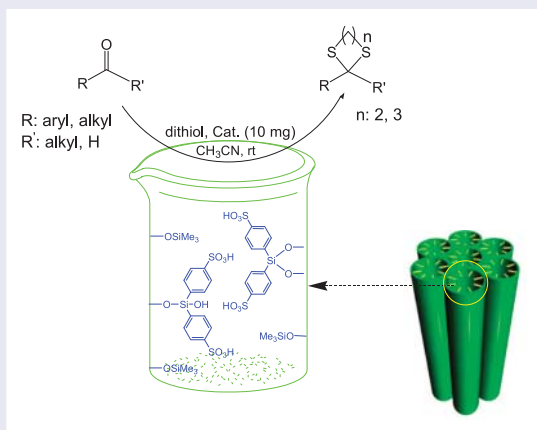
In this research a Nano acidic catalyst was prepared and its efficiency on thioacetalization of carbonyl compounds was examined. For this aim we used modified SBA-15 as support, which have been modified by phenolic and sulfonic acid. SBA-15 is a member of mesoporous. Mesostructures-based properties such as large specific surface, low specific weight, chemical and thermal resistance have been used in different fields such as catalyst, drug delivery, chromatography, microelectronic, separation and purification. Based on our knowledge mesopores are ideal catalysts and usually have been used as solid catalyst, which have been modified by organic groups and metal oxides. These types of application are based on the large dispersability of the modifier groups at mesopores.

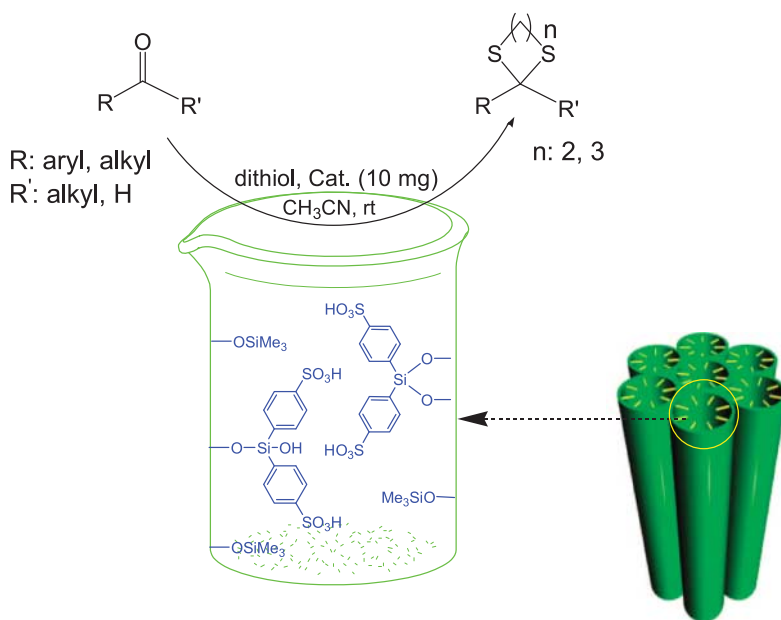
ARTICLE HISTORY

Revised 21 February 2016

KEYWORDS

Mesoporous material; solid acid catalyst; thioacetals; chemoselective





Scheme 1. Thioacetalization of carbonyl compounds using SBA-15-ph- SO_3H .

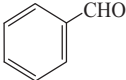
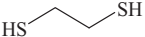
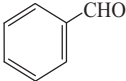

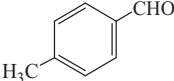
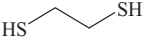
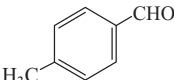

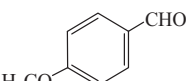
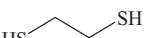
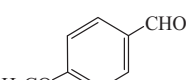

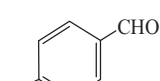

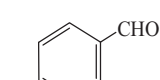

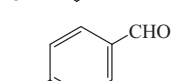
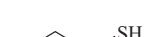
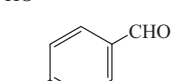

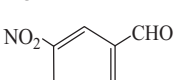
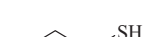
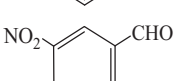

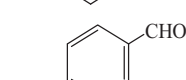
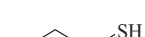
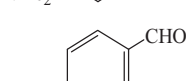

1. Introduction

The protection of carbonyl functionality as a dithioacetal is important in the total synthesis of complex natural and non-natural products [1,2]. Thioacetals are relatively stable toward a wide variety of reagents and are also useful in organic synthesis as acyl carbanion equivalents in C–C bond-forming reaction [3,4]. They are usually prepared by the condensation of carbonyl compounds with thiols or dithiols using a strong protic acid such as HCl [5] or Lewis acids such as $BF_3 \cdot OEt_2$ [6] or $ZnCl_2$ [7] as catalysts. Other Lewis acids, namely, $AlCl_3$ [8], WCl_6 [3], $InCl_3$ [9], P_2O_5/SiO_2 [10] and $[bmim]HSO_4$ [11]. A number of milder procedures employing lithium salts [12], $NiCl_2$ [13], trichloroisocyanuric acid [14], NBS [15], I_2 [16], microwave [17], HBF_4-SiO_2 [18], $Y(OTf)_3$ [19], $VO(OTf)_2$ [20], $ScCl_3$ [21], *N*-bromo sulfonamides [22], DBH [23], $CoCl_2$ [24], $Sc(OTf)_3$ [25], silica phenyl sulfonic acid [26] and silica functionalized sulfonic acid [27] have also been reported for this purpose. The regeneration of parent carbonyl compounds is not always a facile and straightforward process and therefore development of dethioacetalization protocols has engaged the attention of organic chemists over the years [28–30]. Unfortunately, many of these protocols suffer from the drawbacks such as a requirement for stoichiometric amounts of catalysts, long reaction times, the use of expensive reagents and/or chlorinated organic solvents, harsh reaction conditions, difficulties in work-up, and in some instances strong acidic reagents.

2. Result and discussions

In continuation of our ongoing research on the development of more efficient and environmentally friendly procedures for some important transformations in organic synthesis

Table 1. Thioacetalization of carbonyl compounds catalyzed by SBA-15-ph-SO₃H at ambient conditions.

| Entry | Substrate | Dithiol | Protection ^a | | Ref. |
|-------|---|---|-------------------------|-----------|------|
| | | | Time (min)(h) | yield (%) | |
| 1 |  |  | (30) | 96 | [13] |
| 2 |  |  | (30) | 90 | [13] |
| 3 |  |  | (40) | 92 | [16] |
| 4 |  |  | (45) | 90 | [16] |
| 5 |  |  | (15) | 96 | [13] |
| 6 |  |  | (20) | 90 | [13] |
| 7 |  |  | (25) | 96 | [16] |
| 8 |  |  | (30) | 96 | [11] |
| 9 |  |  | (35) | 90 | [13] |
| 10 |  |  | (45) | 90 | [13] |
| 11 |  |  | (90) | 85 | [16] |
| 12 |  |  | (90) | 80 | [16] |
| 13 |  |  | (50) | 90 | [18] |
| 14 |  |  | (60) | 90 | [18] |

(continued).

Table 1. Continued.

| Entry | Substrate | Dithiol | Protection ^a | | Ref. |
|-------|---------------|---------|-------------------------|-----------|------|
| | | | Time (min)(h) | yield (%) | |
| 15 | | | [2] | 85 | [13] |
| 16 | | | [3] | 80 | [13] |
| 17 | Cinamaldehyde | | [1.5] | 85 | [16] |
| 18 | Cinamaldehyde | | [1.5] | 75 | [16] |
| 19 | | | [3] | 75 | [18] |
| 20 | | | [4] | 70 | [18] |
| 21 | | | [4] | 65 | [16] |
| 22 | | | [5] | 55 | [16] |

^aProducts were characterized from their physical properties, comparison with authentic samples by spectroscopic methods.

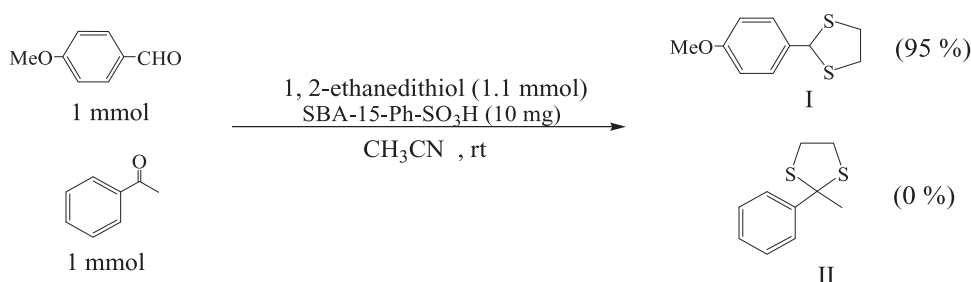
[31–36], herein we wish to report a mild and highly chemoselective procedure for the conversion of aldehydes in presence of ketones into 1,3-dithiolanes and 1,3-dithianes using SBA-15-Ph-SO₃H as a solid acid heterogeneous nanocatalyst under almost neutral reaction conditions (Scheme 1).

First the reaction of benzaldehyde with 1,2-ethanedithiol in the presence of SBA-15-Ph-SO₃H [10 mg] at room temperature using different solvents such as CH₂Cl₂, CHCl₃, CCl₄, CH₃CN and EtOH was carried out. The results show that CH₃CN is a better solvent.

To test the generality and versatility of this procedure in the thioacetalization, we examined a number of aromatic, aliphatic and α,β -unsaturated aldehydes and ketones using the optimized conditions (Table 1). As shown in Table 1, various types of aromatic aldehydes with electron-donating and electron-withdrawing groups were cleanly and rapidly converted to the corresponding dithianes and dithiolanes in the presence of catalysts. However, aromatic and aliphatic ketones were slowly converted to their corresponding S,S-acetals (Table 1, Entries 19–22).

The difference in reactivity of the SBA-15-Ph-SO₃H toward aldehydes and ketones gave us impetus to study chemoselective reactions (Scheme 2).

To compare SBA-15-Ph-SO₃H with previously published methods for the thioacetalization of carbonyl compounds with benzaldehyde and *p*-chlorobenzaldehyde, we carried out the following studies, as shown in Table 2. This clearly demonstrates that SBA-15-Ph-SO₃H is a good catalyst for the thioacetalization of carbonyl compounds.



Scheme 2. Chemoselective activity of the SBA-15-ph-SO₃H toward aldehydes and ketones.

Table 2. Reaction times and yield for previously published methods.

| Substrate | Condition | Time (min) | Yield % | Ref. |
|-----------------------------|--|------------|---------|-----------|
| Benzaldehyde | NBS, 1,2-ethanedithiol, CH ₂ Cl ₂ , rt | 40 | 80 | [15] |
| Benzaldehyde | NiCl ₂ , 1,2-ethanedithiol, CH ₂ Cl ₂ -MeOH, rt | 165 | 96 | [13] |
| Benzaldehyde | CoCl ₂ , 1,2-ethanedithiol, CH ₃ CN, rt | 300 | 89 | [24] |
| Benzaldehyde | Trichloroisocyanuric acid, 1,2-ethanedithiol, CHCl ₃ , rt | 60 | 95 | [14] |
| Benzaldehyde | SBA-15-Ph-SO ₃ H, 1,2-ethanedithiol, CH ₃ CN, rt | 30 | 96 | This work |
| <i>p</i> -(Cl)-benzaldehyde | NBS, 1,3-propanedithiol, CH ₂ Cl ₂ , rt | 30 | 78 | [15] |
| <i>p</i> -(Cl)-benzaldehyde | CoCl ₂ , 1,3-propanedithiol, CH ₃ CN, rt | 30 | 88 | [24] |
| <i>p</i> -(Cl)-benzaldehyde | Trichloroisocyanuric acid, 1,3-propanedithiol, CHCl ₃ , rt | 120 | 94 | [14] |
| <i>p</i> -(Cl)-benzaldehyde | Sc(OTf) ₃ , 1,3-propanedithiol, CH ₂ Cl ₂ , rt | 40 | 90 | [25] |
| <i>p</i> -(Cl)-benzaldehyde | SBA-15-Ph-SO ₃ H, 1,3-propanedithiol, CH ₃ CN, rt | 30 | 96 | This work |

3. Conclusion

In conclusion, in this study we have introduced a new and useful application of Mesoporous SBA-15 silica catalyst functionalized with phenylsulfonic acid groups (SBA-15-Ph-SO₃H) as an efficient solid acid heterogeneous nanocatalyst for the thioacetalization of aldehydes and ketones under mild reaction conditions. The method is highly chemoselective for protection of aldehydes in the presence of ketones. Moreover, the method has advantages in terms of high yields of products, short reaction times, operational simplicity and easy work up of products.

4. Experimental

All commercially available chemicals were obtained from Merck and Fluka companies, and used without further purifications unless otherwise stated. ¹H NMR (nuclear magnetic resonance) spectra were recorded on a Jeol 90 MHz FT NMR spectrometer using tetramethylsilane as the internal standard and chemical shift are in δ (ppm). Infrared (IR) was conducted on a Perkin Elmer GX FT-IR spectrometer. All yields refer to isolated products.

4.1. General procedure for thioacetalization catalyzed by SBA-15-Ph-SO₃H in CH₃CN

To a stirred solution of substrate (1 mmol) and SBA-15-Ph-SO₃H (10 mg) in CH₃CN (3 mL) was added 1, 2-ethanedithiol or 1, 3-propanedithiol (1.1 mmol) at room temperature. The mixture was stirred for an appropriate time (Table 1). After completion of reaction as indicated by thin-layer chromatography, the organic solvent was filtrated, and

the catalyst was removed. The filtrate was evaporated under reduced pressure to achieve crude products. The crude products were purified by recrystallization from ethanol or column chromatography using *n*-hexane/acetone (10:1) as the eluent system.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

We are thankful to Iranian research Organization for Science and Technology for partial support of this work.

References

- [1] Greene TW, Wuts PGM. Protective groups in organic synthesis. 3rd ed. New York, NY: Wiley; 1999.
- [2] Greene TW. Protective groups in organic synthesis. New York, NY: Wiley; 1981.
- [3] Yu H, Dong D, Ouyang Y, et al. Chemoselective thioacetalization with odorless 2-(1,3-dithian-2-ylidene)-3-oxobutanoic acid as a 1,3-propanedithiol equivalent. *Can J Chem*. 2005;83:1741–1745.
- [4] Battaglia L, Pinna F, Strukul G. Thioacetalization of aldehydes and ketones in the presence of hydroxo complexes of platinum(II): an example of Lewis acid catalytic activity. *Can J Chem*. 2001;79:621–625.
- [5] Bulman Page PC, Prodger JC, Westwood D. Diastereoselectivity in the addition of Grignard reagents to ketones controlled by the 1,3-dithiane 1-oxide asymmetric building block. *Tetrahedron Lett*. 1993;49:10355–10368.
- [6] Nakata T, Nagao S, Mori S, et al. Total synthesis of (+)-pederin. 1. Stereocontrolled synthesis of (+)-benzoylpedamide. *Tetrahedron Lett*. 1985;26:6461–6464.
- [7] Evans DV, Truesdale LK, Grimm KG, et al. Stereochemical consequences of hydrogen exchange as a result of tritium atom reactions on solid aliphatic amino acids. *J Am Chem Soc*. 1977;99:5009–5017.
- [8] Ong BC. A simple and efficient method of thioacetal – and ketalization. *Tetrahedron Lett*. 1980;21:4225–4228.
- [9] Muthusamy S, Babu SA, Gunanathan C. Indium(III) chloride as an efficient, convenient catalyst for thioacetalization and its chemoselectivity. *Tetrahedron Lett*. 2001;42:359–362.
- [10] Mirjalili BF, Zolfigol MA. An efficient procedure for acetalization of carbonyl compounds with P₂O₅/SiO₂. *Phosphorus Sulfur Silicon Relat Elem*. 2004;179:1397–1401.
- [11] Gupta N, Goverdhan SL, Singh J. Acidic ionic liquid [bmim]HSO₄: An efficient catalyst for acetalization and thioacetalization of carbonyl compounds and their subsequent deprotection. *Catal Commun*. 2007;8:1323–1328.
- [12] Firouzabadi H, Iranpoor N, Karimi B. Lithium bromide-catalyzed highly chemoselective and efficient dithioacetalization of α,β -unsaturated and aromatic aldehydes under solvent-free conditions. *Synthesis*. 1999;1999:58–60.
- [13] Khan TH, Mondal E, Sahu PR, et al. Nickel(II) chloride as an efficient and useful catalyst for chemoselective thioacetalization of aldehydes. *Tetrahedron Lett*. 2003;44:919–922.
- [14] Firouzabadi H, Iranpoor N, Hazarkhani H. Trichloroisocyanuric acid as a mild and efficient catalyst for thioacetalization and transthiio-acetalization reactions. *Synlett*. 2001;2001:1641–1643.
- [15] Kamal A, Chouhan G. Mild and efficient chemoselective protection of aldehydes as dithioacetals employing N-bromosuccinimide. *Synlett*. 2002;2002:474–476.
- [16] Firouzabadi H, Iranpoor N, Hazarkhani H. Iodine catalyzes efficient and chemoselective thioacetalization of carbonyl functions, transthiioacetalization of O,O- and S,O-acetals and acylals. *J Org Chem*. 2001;66:7527–7529.

- [17] Bez G, Gogoi D. A rapid and efficient method for 1,3-dithiolane synthesis. *Tetrahedron Lett.* **2006**;47:5155–5157.
- [18] Kamble VT, Bandgar BP, Muley DB, et al. An expedient and efficient chemoselective protection of carbonyl compounds and transthioacetalization of O,O- and S,O-acetals catalyzed by $\text{HBF}_4 \cdot \text{SiO}_2$. *J Mol Catal A Chem.* **2007**;268:70–75.
- [19] De SK. Yttrium triflate as an efficient and useful catalyst for chemoselective protection of carbonyl compounds. *Tetrahedron Lett.* **2004**;45:2339–2341.
- [20] De SK. Vanadyl triflate as an efficient and recyclable catalyst for chemoselective thioacetalization of aldehydes. *J. Mol Catal A Chem.* **2005**;226:77–79.
- [21] De SK. Scandium chloride-catalyzed chemoselective thioacetalization of aldehydes. *Synthesis.* **2004**;6:828–830.
- [22] Veisi H, Ghorbani-Vaghei R, Akbari Dadamahaleh S. Poly(N-bromobenzene-1,3- disulfonamide) and N,N,N,N'-Tetrabromobenzene-1,3-disulfonamide as a mild and efficient catalyst for chemoselective thioacetalization of carbonyl functions and transthioacetalization reactions. *J Heterocyclic Chem.* **2011**;48:699–705.
- [23] Veisi H, Amiri M, Hamidian AH, et al. 1,3-Dibromo-5,5- dimethylhydantoin (DBH) as a mild and efficient catalyst for chemoselective thioacetalization of carbonyl compounds and dethioacetalization under mild conditions. *Phosphorus Sulfur Silicon.* **2010**;185:689–696.
- [24] De SK. Cobalt(II)chloride catalyzed chemoselective thioacetalization of aldehydes. *Tetrahedron Lett.* **2004**;45:1035–1036.
- [25] Kamal A, Chouhan G. Scandium triflate as a recyclable catalyst for chemoselective thioacetalization. *Tetrahedron Lett.* **2002**;43:1347–1350.
- [26] Veisi H, Sedrpoushan A, Zolfigol MA, et al. Silica phenyl sulfonic acid as a solid acid heterogeneous catalyst for chemoselective thioacetalization of carbonyl compounds and dethioacetalization under mild conditions. *J. Heterocyclic Chem.* **2013**;50:E204–E206.
- [27] Karimi B, Khalkhali M. Silica functionalized sulfonic acid as a recyclable interphase catalyst for chemoselective thioacetalization of carbonyl compounds in water. *J Mol Catal A Chem.* **2007**;271:75–79.
- [28] Komatsu N, Uda M, Suzuki H. Bismuth(III) halides and sulfate as highly efficient catalyst for the sulfonylation of carbonyl and related compounds. *Synlett.* **1995**;1995:984–986.
- [29] Moghadam FM, Boeini HZ. N-Benzyl-DABCO-tribromide as an efficient and mild reagent for deprotection of dithioacetals. *Synth Commun.* **2006**;36:1093–1096.
- [30] Hajipour AR, Mallakpour SE. Solid state deprotection of acetals and thioacetals using benzyl-triphenylphosphonium peroxymonosulfate. *Molecules.* **2002**;7:674–680.
- [31] Veisi H, Sedrpoushan A, Faraji AR, et al. A mesoporous SBA-15 silica catalyst functionalized with phenylsulfonic acid groups (SBA-15-Ph- SO_3H) as a novel hydrophobic nanoreactor solid acid catalyst for a one-pot three-component synthesis of 2H-indazolo[2,1-b]phthalazine-triones and triazolo[1,2-a]indazole-triones. *RSC Adv.* **2015**;5:68523–68530.
- [32] Veisi H, Sedrpoushan A, Zolfigol MA, et al. Synthesis and application of silica phenyl sulfonic acid as a solid acid heterogeneous catalyst for one-pot synthesis of 2-aryl-1-arylmethyl-1H-1,3-benzimidazoles and bis(indolyl)methanes in water. *J Heterocyclic Chem.* **2011**;48:1448–1454.
- [33] Veisi H, Sedrpoushan A, Maleki B, et al. Palladium immobilized on amidoximefunctionalized magnetic Fe_3O_4 nanoparticles: a highly stable and efficient magnetically recoverable nanocatalyst for Sonogashira coupling reaction. *Appl Organomet Chem.* **2015**;29:834–839.
- [34] Veisi H, Sedrpoushan A, Hemmati S. Palladium supported on diaminoglyoximefunctionalized Fe_3O_4 nanoparticles as a magnetically separable nanocatalyst in Heck coupling reaction. *Appl Organomet Chem.* **2015**;29:825–828.
- [35] Mohanazadeh F, Veisi H, Sedrpoushan A, et al. A very useful and mild method for the deoxygenation of sulfoxide to sulfide with silica bromide as heterogeneous promoter. *J Sulfur Chem.* **2014**;35:7–13.
- [36] Mohanazadeh F, Zolfigol MA, Sedrpoushan A, et al. Synthesis of silica bromide as heterogeneous reagent and its application to conversion of alcohols to alkyl bromides. *Lett Org Chem.* **2012**;9:598–603.