

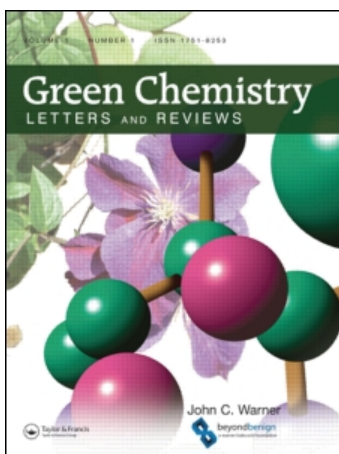
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Silica supported perchloric acid ($\text{HClO}_4\text{-SiO}_2$): a green, reusable, and highly efficient heterogeneous catalyst for the synthesis of thioethers under solvent-free conditions at room temperature

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RESEARCH ARTICLE

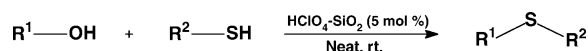
Silica supported perchloric acid (HClO₄-SiO₂): a green, reusable, and highly efficient heterogeneous catalyst for the synthesis of thioethers under solvent-free conditions at room temperature

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A highly efficient and clean procedure is described for the synthesis of thioethers with excellent yields under solvent-free conditions at room temperature using a catalytic amount of HClO₄-SiO₂. The catalyst is easily prepared, stable, and reusable without much loss of catalytic activity, and is efficient under the reaction conditions.



Keywords: silica supported perchloric acid; thioethers; solvent-free conditions; room temperature synthesis

Introduction

Synthetic chemists continue to explore new methods to carry out chemical transformations. One of these new methods is to run reactions on the surface of solids. Surfaces have properties that are not duplicated in the solution or gas phase, hence entirely new chemistry may occur. Even in the absence of new chemistry, a surface reaction may be more desirable than a solution counterpart, because the reaction is more convenient to run or a higher yield of the product is attained. For these reasons, surface synthetic organic chemistry is a rapidly growing field of study.

Thioethers have emerged as a prominent class of organic compounds; they have useful applications as key reagents in organic synthesis, in agro-chemicals, and in bioorganic, medicinal, and heterocyclic chemistry (1). Thioethers can also act as building blocks in the synthesis of various sulfur compounds, which can be used in many biological processes (2). Thioether linkage has been used to prepare cyclic analogues of acyclic polypeptides to restrict their conformation mobility and thus to increase their biological activity and stability against biodegradation (3,4). Numerous synthetic methods exist for synthesizing thioethers (5–10); such methods typically involve the condensation

of activated aryl halides with thiols under strongly basic conditions (11). Some of the most common approaches to the synthesis of thioethers are the S-alkylation of thiols under the conditions of Mitsunobu reaction (12), by the deoxygenation of sulphoxides (13,14), the displacement of leaving groups with sulphur nucleophile (15,16), the addition of thiols to carbonyl compounds followed by the in-situ reduction of the generated intermediate thionium ion (17), an anti-Markonikov addition of arenes and alkanethiols to alkenes (18,19), the metal mediated cross-coupling processes (20–22) or the metal-catalyzed hydrothiolation of alkynes (23). Undoubtedly, these methods are good in terms of reactivity. However, the synthetic scopes of the aforementioned reaction conditions are often hampered by prolonged reaction times, the use of expensive or commercially unavailable materials (24,25), high temperature, use of cumbersome bases or hazardous and corrosive compounds such as alkylating agents (26), strong reducing agents (27), harsh reaction conditions and tedious workup procedures (28,29), and low product yields. Moreover, the method invariably results in the formation of several by-products, which in turn results in lower yields. Recently, the synthesis of thioethers has been carried out using ZrCl₄-SiO₂ (30), Ni-nanoparticles (31), however, this method involves large amounts of

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catalyst, long reaction times, and the use of organic solvent as well as high temperature.

The toxic and volatile nature of many organic solvents, particularly chlorinated hydrocarbons that are widely used in organic synthesis have posed a serious threat to the environment. Consequently, methods that successfully minimize their use are the focus of much attention (32). In recent years, the use of catalysts immobilized on solid supports has received considerable attention. Such catalysts not only simplify the purification process but also help in preventing the release of reaction residues into the environment. Thus, the solvent-free conditions along with the supported catalyst provide a protocol for achieving environmentally friendly economical organic synthesis. Therefore, in this communication we report the $\text{HClO}_4\text{-SiO}_2$ (33) catalyzed efficient and convenient synthesis of thioethers from various alcohols with thiols in high yields under solvent-free conditions at room temperature (Scheme 1).

Results and discussion

As part of our program aiming at developing new, selective, and environmentally friendly methodologies for the preparation of fine chemicals employing $\text{HClO}_4\text{-SiO}_2$ as a catalyst, we wish to describe herein a highly effective protocol for the synthesis of thioether from the reaction of alcohols with thiols under solvent-free conditions at room temperature (Scheme 1).

Initially, a systematic study was carried out for catalytic evaluation of $\text{HClO}_4\text{-SiO}_2$ for the condensation of benzyl alcohol (1 mmol) with thiophenol (1.1 mmol) under various conditions at room temperature (Table 1). After many studies, we found that when less than 5 mol% of $\text{HClO}_4\text{-SiO}_2$ was applied, lower yields of the corresponding product (Table 1, entries 3–6) resulted, whereas use of 5 mol% $\text{HClO}_4\text{-SiO}_2$ gives excellent results in terms of yield and time required for completion of the reaction (Table 1, entry 7). However, use of more than 5 mol% of catalyst did not improve the yield (Table 1, entries 8–9). When attempts were made to carry out this reaction not only in the absence of $\text{HClO}_4\text{-SiO}_2$ but also in the presence of silica the substrate was recovered almost quantitatively (Table 1, entries 1, 2).

Next, we studied the effect of various solvents and the results of the reaction of benzyl alcohol (1 mmol)



Scheme 1. Synthesis of thioether using silica supported perchloric acid ($\text{HClO}_4\text{-SiO}_2$) under solvent-free conditions at room temperature.

Table 1. A catalytic study of $\text{HClO}_4\text{-SiO}_2$ during the reaction of benzyl alcohol (1 mmol) and thiophenol (1.1 mmol) at room temperature under solvent-free conditions.

Entry	$\text{HClO}_4\text{-SiO}_2$ (mol%)	Time min/[h]	Yield (%)
1	—	[05]	—
2	Silica	60	—
3	1	25	30
4	2	20	45
5	3	18	65
6	4	15	87
7	5	10	95
8	6	10	95
9	7	10	95

with thiophenol (1.1 mmol) using 5 mol% $\text{HClO}_4\text{-SiO}_2$ at room temperature, shown in Table 2.

When organic solvents such as dichloromethane (DCM), chloroform, nitromethane, tetrahydrofuran (THF), and acetonitrile were used for this reaction, the desired product was obtained in low yields (Table 2, entries 2–6). Whereas, an excellent yield of the desired product was obtained when the reaction was carried out at room temperature under solvent-free conditions (Table 2, entry 1). These results led to the suggestion that solvent-free conditions are best suited for this reaction.

To evaluate the scope and generality of the catalyst, the reactions of alcohols with thiols under solvent-free conditions at room temperature were conducted. The results are summarized in Table 3. It is important to mention that all aliphatic, aromatic, and cyclic thiols underwent the reaction smoothly. It was noted that electronic factors played an important role in these reactions. Aromatic alcohols substituted with electron-donating groups reacted faster than those substituted with electron withdrawing groups and provided thioethers in higher yield (Table 3). Primary and secondary alcohols did not react with thiols in the presence of $\text{HClO}_4\text{-SiO}_2$ and remained mostly intact even after 24 h of stirring (Table 3, entries 15, 16). Under the present conditions, all reactions were clean and free from any by-product.

Table 2. Investigation of various solvents.

Entry	Solvent	Time (min)	Yield (%)
1	neat	5	95
2	DCM	30	40
3	CHCl_3	45	30
4	MeNO_2	30	35
5	THF	60	10
6	CH_3CN	10	60

Table 3. HClO₄-SiO₂ catalyzed formation of thioethers.

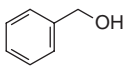
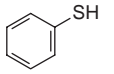
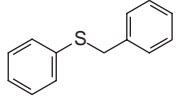
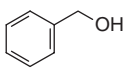
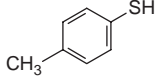
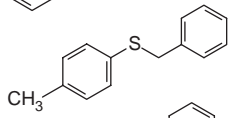
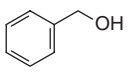
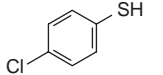
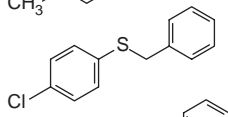
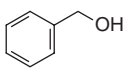
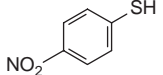
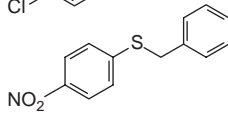
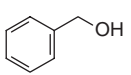
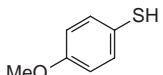
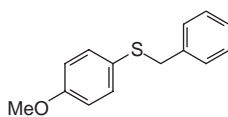
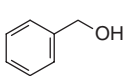
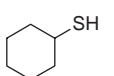
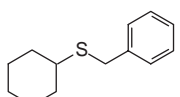
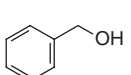
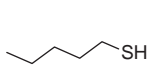
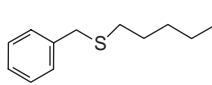
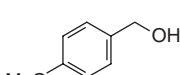
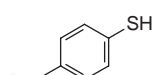
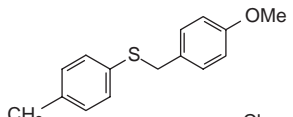
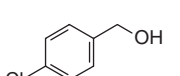
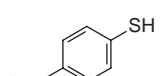
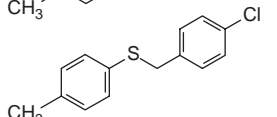
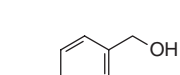
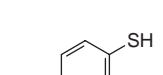
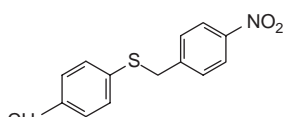
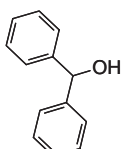
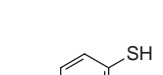
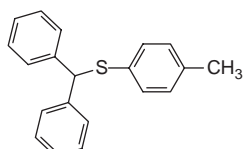
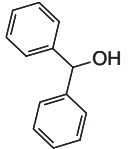
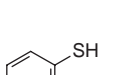
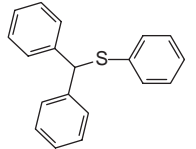
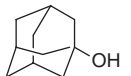
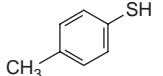
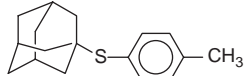

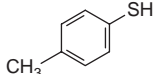
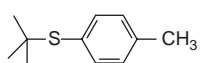
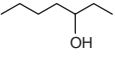
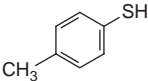
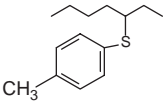
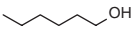
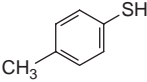
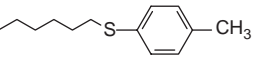
Entry	Alcohol	Thiol	Product ^a	Time (min)	Conversion	Isolated yield (%) ^b
1				10	100	95
2				5	100	96
3				15	95	89
4				20	93	85
5				18	85	79
6				12	96	91
7				18	89	78
8				2	100	95
9				20	100	95
10				75	76	62
11				5	100	96
12				12	100	92
13				10	100	95
14				7	100	89

Table 3 (Continued)

Entry	Alcohol	Thiol	Product ^a	Time (min)	Conversion	Isolated yield (%) ^b
15				120	10	–
16				180	15	–

^aconfirmed by comparison with authentic samples (FT-IR, TLC, mp, bp).

^bYield of isolated pure products.

Table 4 compares our results (time, yield, and reaction conditions) with results obtained by other groups. As can be seen, our method is simpler, more efficient, and uses no toxic solvents.

The advantage of the use of a heterogeneous catalyst for this transformation is the ease of catalyst/substrate separation. In our process, when the catalytic reaction was completed, $\text{HClO}_4\text{-SiO}_2$ could be recovered conveniently from the reaction mixture and be used further for the next cycle without activation, only through filtration and subsequent washing with ethyl acetate. Efforts were then made to examine the reusability of $\text{HClO}_4\text{-SiO}_2$ by using benzyl alcohol (1 mmol) with thiophenol (1.1 mmol) under solvent-free conditions at room temperature as a model substrate and the results are described. It was observed that, with the increasing number of cycles of the reaction, the catalytic activity of the $\text{HClO}_4\text{-SiO}_2$ decreases and it was nearly lost after seven cycles. The graphical presentation of the relation between the number of cycles of the reaction and the catalytic activity in terms of yield is presented in Figure 1.

Experimental

General

All chemicals were purchased from Sigma-Aldrich and Merck Chemical Companies. All reactions were

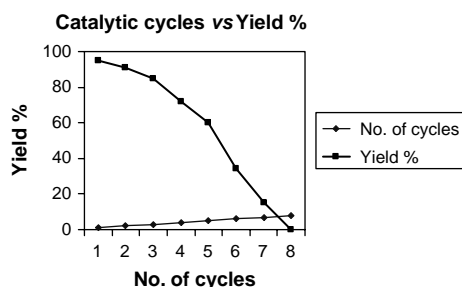


Figure 1. Effect of catalytic cycles on product yield using 5 mol% of $\text{HClO}_4\text{-SiO}_2$ at room temperature.

monitored by thin layer chromatography (TLC) using aluminum plates coated with silica gel (Merck) using 10% ethyl acetate and 90% hexane as eluent. The silica gel (230–400 mesh) for column chromatography was purchased from Spectrochem Pvt. Ltd., India. The products were characterized by comparison of their spectral and physical data with those of authentic samples. All authentic thioethers were prepared from the corresponding thiols according to the method described in Vogel (34). IR spectra were recorded on Nicolet (impact 400D model) FTIR Spectrometer. ^1H NMR spectra were recorded on a Bruker DRX-300 AVANCE at 300 MHz instrument using TMS as internal standard and $\text{DMSO-}d_6$ or CDCl_3 as solvent. Mass spectra was obtained by

Table 4. Comparison of our results with results obtained by other groups.^a

Catalyst	Catalyst loading (%)	Solvent	Temperature (°C)	Reaction time min (h)	Reusability of catalyst	Yield (%)	References
Ni-nanoparticles	10 mol	CH_3CN	rt.	22.2	5	95	31
$\text{ZrCl}_4\text{-SiO}_2$	0.5 mmol	—	50	15	0	90	30
$\text{HClO}_4\text{-SiO}_2$	0.05 mmol (5 mol)	—	rt.	10	6	95	–

^aBased on reaction between benzyl alcohol (1 mmol) with thiophenol (1.1 mmol).

using a GC-MS Hewlett Packard (EI, 20 eV) instrument. All yields refer to isolated ones.

Preparation of $\text{HClO}_4\text{-SiO}_2$ catalyst

A 70% aqueous perchloric acid (1.8 g, 12.5 mmol) was added to a suspension of SiO_2 (230–400 mesh, 23.7 g) in ether (70 ml). The mixture was concentrated and the residue was heated at 100°C for 72 h under vacuum to give $\text{HClO}_4\text{-SiO}_2$ (0.5 mmol/g) as free flowing powder (50 mg = 0.025 mmol of HClO_4).

Typical experimental procedure

A mixture of benzyl alcohol (1 mmol) and thiophenol (1.1 mmol) was stirred at room temperature in the presence of a catalytic amount of $\text{HClO}_4\text{-SiO}_2$ (100 mg, 0.05 mmol, 5 mol%) for an appropriate time (Table 3). After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with ethyl acetate (5 mL) and the catalyst was allowed to settle. The supernatant ethyl acetate was decanted off, washed with ethyl acetate (5 mL) and the combined organic solvent was evaporated under reduced pressure to afford crude product, which was purified by column chromatography (Silica gel: 230–400 mesh, petroleum ether (40–60°C): ethyl acetate = 9:1) to afford pure product.

Conclusion

We described herein perchloric acid adsorbed on silica gel ($\text{HClO}_4\text{-SiO}_2$) catalyzed highly efficient protocol for the synthesis of thioether by the condensation of alcohols with thiols under solvent-free conditions at room temperature in excellent yields. The remarkable catalytic activity that $\text{HClO}_4\text{-SiO}_2$ exhibited is convincingly superior to other recently reported catalytic methods with respect to high conversions, operational simplicity, enhanced reaction rates, cleaner reaction profiles, and ease of isolation of products. Inexpensive, and ready availability of the catalyst makes the procedure an attractive alternative to the existing methods for the synthesis of thioether.

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