

Reusable silica supported perchloric acid and potassium bisulphate as green catalysts for thiocyanation of aromatic compounds under solvent free conditions

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Abstract

Reusable silica supported HClO_4 and KHSO_4 materials have been explored as green catalysts for thiocyanation of aromatic compounds under conventional and solvent free microwave assisted conditions. The microwave assisted protocol exhibited remarkable rate accelerations and offered selective thiocyanation of aromatic and heteroaromatic compounds with good yields. The developed protocols are also promising and comparable with the existing procedures.

Keywords: Silica supported potassium bisulfate; silica supported HClO_4 ; ammonium thiocyanate; selective thiocyanation; solvent free microwave assisted reactions; rate accelerations.

Introduction

Brønsted acids and bases which were probably the first generation catalysts were found to be used in a number of organic transformations [1]. But issues such as toxicity, volatility, high price and hazardous laboratory/industry outlets are the major limitations in their use as catalysts. However, catalysts adsorbed on silica gel were found beneficial to overcome these issues. This could be because of the voluntarily availability of silica gel, simple work-up procedure, long catalytic life and recyclability, eco-friendly nature and the capability to accelerate the reactions to afford good to excellent product yields [1-20]. A recent review published by Manpreet Kaur and co-workers describes some of the most

important silica supported catalysts which were prepared using heteropolyacids, polyphosphoric acid, perchloric acid, fluoroboric acid, and sulphuric acid [8]. These catalysts have been used in a number of organic reactions to yield compounds that are important in the chemical and pharmaceutical industries. Silica supported catalysts can be separated easily by filtration and reused after activation in order to make the process eco-friendly. In addition, silica supported materials are superior over conventional homogeneous and heterogeneous catalysts because of their large surface area, high mechanical and thermal stabilities, greater selectivity, low toxicity, reusability, high selectivity,

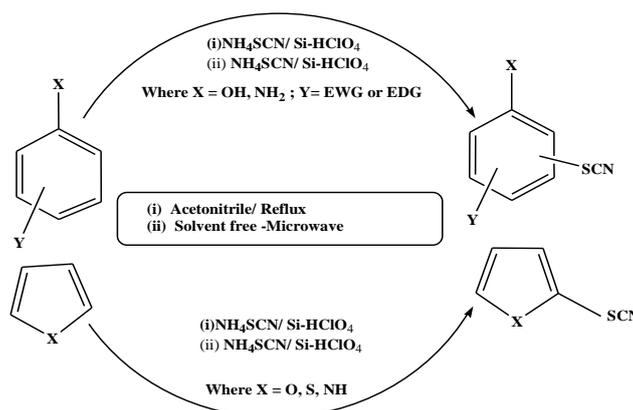
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and simplicity in handling. By-products and wastages can be effectively minimized in these catalytic systems. Interest in the thiocyanate products is connected mainly with their wide range of antifungal, antitumor, antiparasitic activities and their use as important synthons in organic, pharmaceutical, medicinal and agriculture chemistry [24-32]. Over a period of time, several efficient regioselective thiocyanation methods have been put forward [33-35] including few recent reports from our laboratory [36-38]. Literature survey,

however, reveals that silica supported Brønsted acids such as $\text{SiO}_2/\text{HClO}_4$, $\text{SiO}_2/\text{KHSO}_4$ have not been explored as catalysts so far for thiocyanation reactions. Encouraged by these features, we wish to report here in a clean and environmentally friendly protocol for thiocyanation of aromatic compounds using ammonium thiocyanate (NH_4SCN) in the presence of silica supported reusable heterogeneous catalysts $\text{SiO}_2/\text{HClO}_4$ and $\text{SiO}_2/\text{KHSO}_4$ under conventional and solvent-free microwave assisted conditions [2,3].



Scheme 1. Thiocyanation of reactions using $\text{SiO}_2/\text{KHSO}_4$ and $\text{SiO}_2/\text{HClO}_4$

Experimental methods

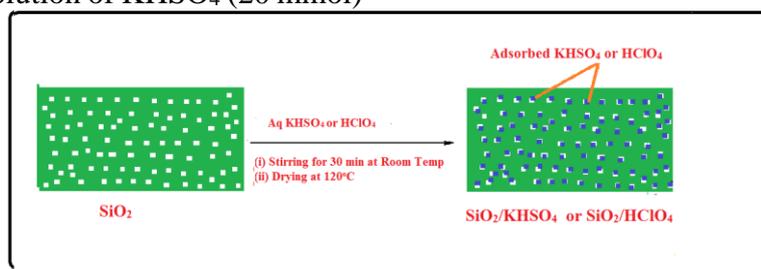
General

Laboratory desktop chemicals are used in this study, procured from Avra (India), SD-fine chemicals (India) or Loba (India). Bench mate model microwave oven (CEM-908010, 300W) was used as a microwave reactor in this study.

Preparation of $\text{SiO}_2/\text{KHSO}_4$ and $\text{SiO}_2/\text{HClO}_4$ catalysts

Silica gel (4 g, 100–200 mesh) was added to a solution of KHSO_4 (20 mmol)

in distilled water (25 mL), and stirred for about 30min at room temperature, for the adsorption of KHSO_4 onto the surface of the silica gel. Water was removed in vacuum, the resultant powder was dried in an oven at 120°C for 2-3 h to afford $\text{SiO}_2/\text{KHSO}_4$ catalyst. Procedure for the preparation of $\text{SiO}_2/\text{HClO}_4$ catalyst is same as mentioned in the previous section for the preparation of $\text{SiO}_2/\text{KHSO}_4$ catalyst.



Scheme 2. Adsorption of $\text{SiO}_2\text{-HClO}_4$ and $\text{SiO}_2\text{-KHSO}_4$

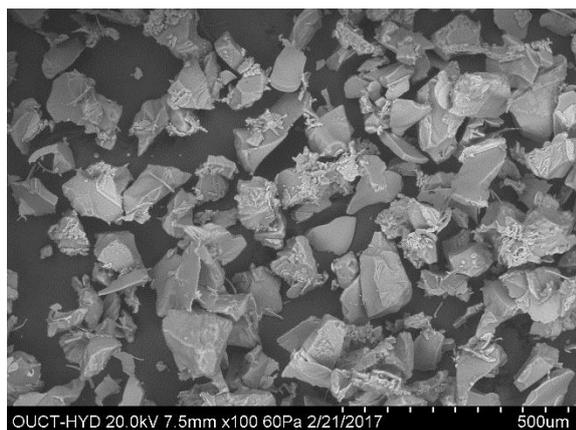


Figure 1a. SEM with 500 μm magnification

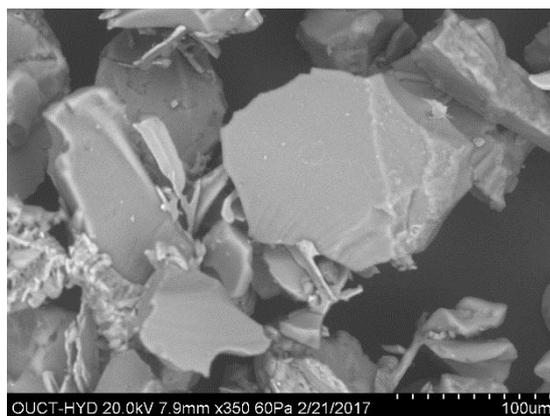


Figure 1d. SEM with 100 μm magnification

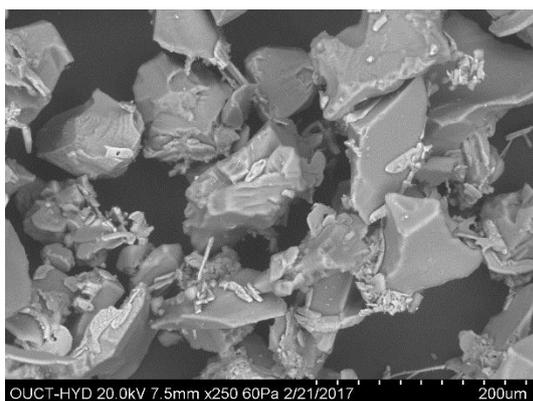


Figure 1b. SEM with 200 μm magnification

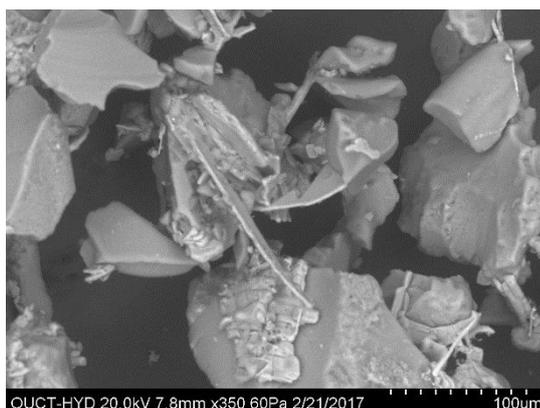


Figure 1e. SEM with 100 μm magnification

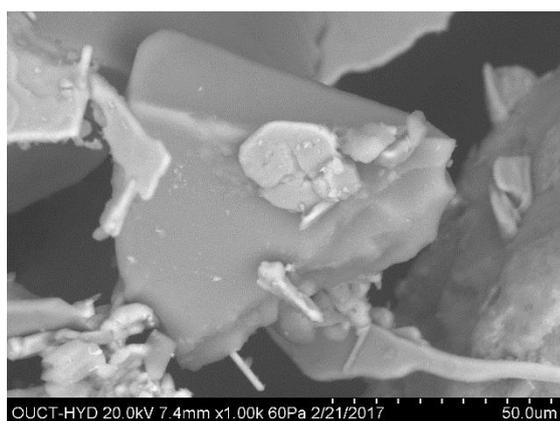


Figure 1c. SEM with 200 μm magnification

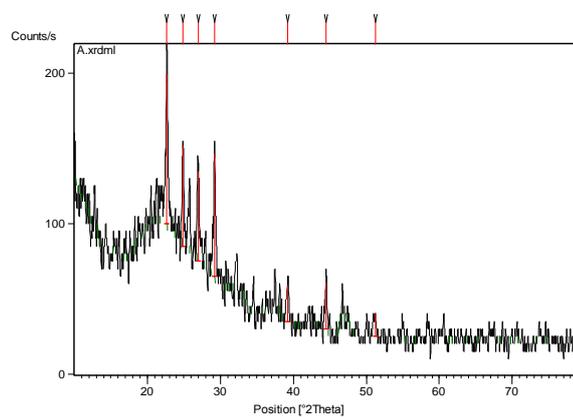


Figure 1f. XRD analysis of SiO₂/KHSO₄ catalyst

Figure 1. SEM and XRD analysis of Silica adsorbed KHSO₄ catalyst

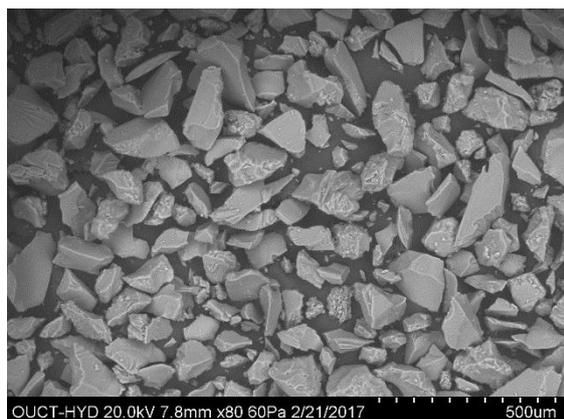


Figure 2a. SEM with 500 μm magnification

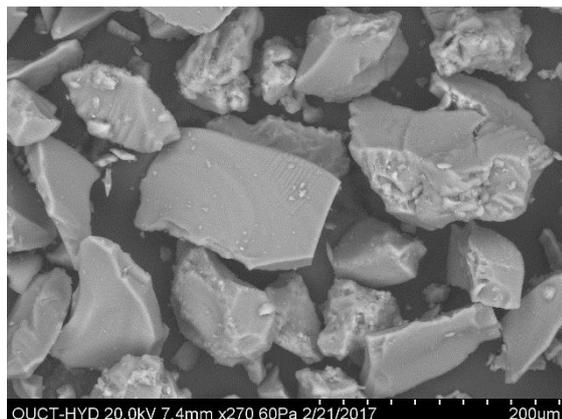


Figure 2d. SEM with 200 μm magnification

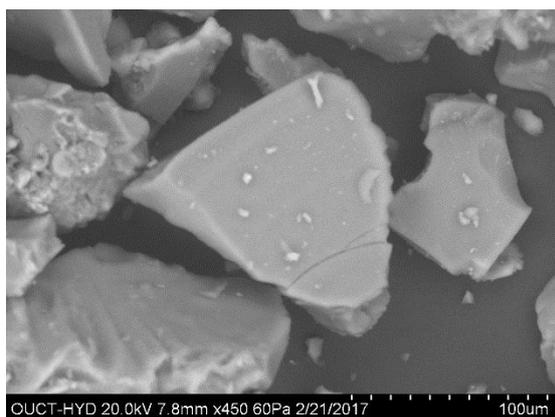


Figure 2b. SEM with 100 μm magnification

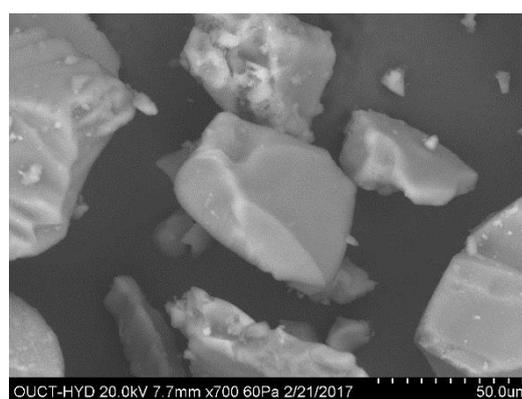


Figure 2e. SEM with 50 μm magnification

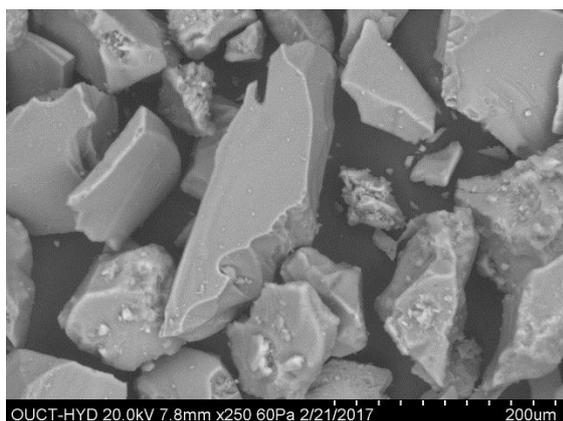


Figure 2c. SEM with 200 μm magnification

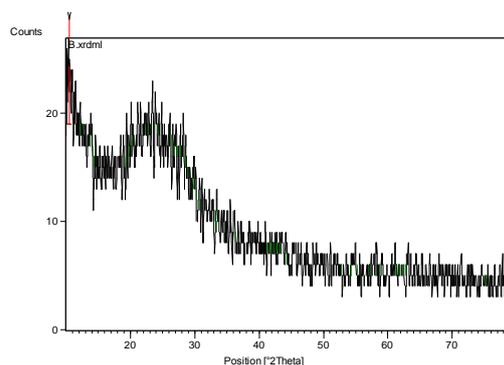


Figure 2f: XRD analysis of SiO₂/ HClO₄

Figure 2. SEM and XRD analysis of Silica adsorbed HClO₄ catalyst

SEM and XRD Analysis of SiO₂/KHSO₄ and SiO₂/HClO₄ catalysts

Scanning electron microscopic pictures of SiO₂/KHSO₄ and SiO₂/HClO₄ catalysts (Figures 1 and 2) under different magnifications in the range of 50 to 200 μm revealed non-uniform morphologies with polynomial cubic crystals and flakes embedded with grain like species. XRD analysis of the samples (Figures 1(f) and 2(f)) probably indicate amorphous nature of the catalysts. Broad peaks which were observed around 23 and 25 respectively (on 2θ scale) could be attributed to silica. These observations are largely similar to those reported by Zeba Siddiqui [39], confirming the heterogenous nature of catalysts which comprise adsorbed KHSO₄ and HClO₄ on silica.

Thiocyanation of aromatic compounds using SiO₂/KHSO₄ under conventional reflux conditions

The optimum amount of the catalyst (SiO₂/KHSO₄ or SiO₂/HClO₄) was added to the mixture of aromatic compound (10 mmol), NH₄SCN (10 mmol) and acetonitrile, in a previously cleaned round bottom flask and stirred under reflux till the reaction is completed. Progress of the reaction was monitored by TLC. After the completion of the reaction, the catalyst was separated by filtration, reaction mixture is treated with NaHCO₃ solution, followed by the addition of ethyl acetate.

The organic layer was then separated, dried over Na₂SO₄, purified by column chromatography and evaporated under vacuum to get the final product.

Microwave assisted thiocyanation of aromatic compounds under solvent free conditions

For microwave assisted thiocyanation, aromatic compound (10 mmol), NH₄SCN (10 mmol) and optimum quantity of the catalyst (SiO₂/KHSO₄ or SiO₂/HClO₄) were taken in a previously cleaned beaker, mixed thoroughly and placed in micro-wave oven (CEM-908010, bench mate model, 300W laboratory microwave reactor), till the reaction is completed. Progress of the reaction was monitored by TLC. After the completion, the reaction mixture is treated with ethyl acetate, catalyst is separated by filtration. The filtrate is washed with NaHCO₃ solution. The organic layer was then separated, dried over Na₂SO₄, purified by column chromatography and evaporated under vacuum to get the final product as mentioned above.

Results and discussion

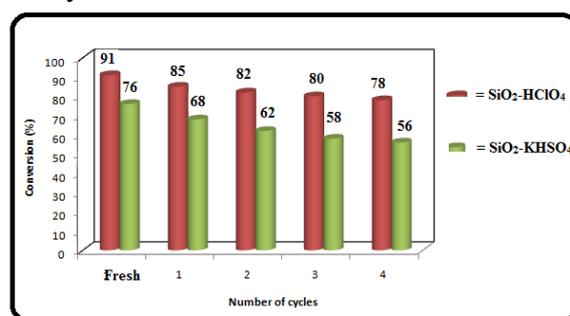
Present work describes thiocyanation of aromatic and heterocyclic compounds using NH₄SCN in presence of reusable Si-supported catalysts SiO₂/HClO₄ or SiO₂/KHSO₄ under conventional conditions in acetonitrile solvent, as well microwave assisted solvent-free conditions (Scheme 2).

Table 1. Catalyst optimization for thiocyanation of Phenol

Entry	SiO ₂ /HClO ₄		SiO ₂ /KHSO ₄	
	Amount of catalyst (gms)	Yield (%)	Amount of catalyst (gms)	Yield (%)
1	0.1	52	0.1	46
2	0.20	91	0.20	64
3	0.25	92	0.25	76
4	0.3	92	0.3	77
5	-	-	0.4	78

Initially, we optimized the catalyst (SiO₂/HClO₄ or SiO₂/KHSO₄) quantity for thiocyanation reaction. We performed the reactions using different quantities of SiO₂/HClO₄ and SiO₂/KHSO₄ catalysts (Tables 1 and 2). Data compiled in Table 1 reveals that the maximum conversion occurred when 0.2gm SiO₂/HClO₄ or SiO₂/KHSO₄ is used as catalyst. A further increase in the catalyst quantity did not appreciably affect the conversion. Data presented in Table 1 further indicates that the best results were obtained with SiO₂/HClO₄ over a SiO₂/KHSO₄ catalyst. This could

be attributed to the fact that HClO₄ is a stronger acid than KHSO₄. To check the reusability of the catalysts (SiO₂/HClO₄ and SiO₂/KHSO₄), the catalysts were separated from the reaction mixture by simple filtration and treated with ethyl acetate. After drying, the catalyst was activated under the same set of experimental conditions and used again to verify the reactions. The catalyst is recycled for about four to five times showing a slight reduction of activity during the consecutive use of the recovered catalyst, as shown in Figure 1.

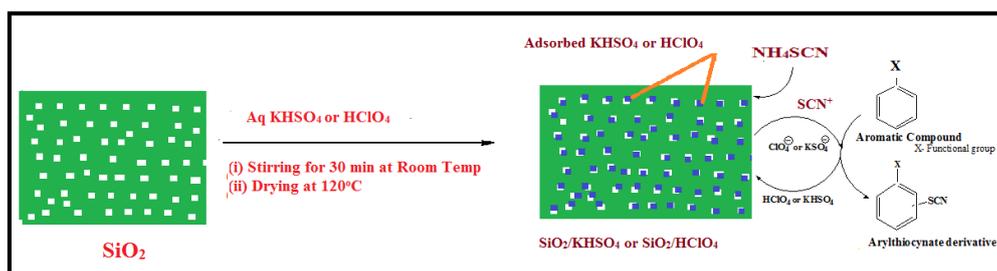
**Figure 3.** Bar diagram for recyclability SiO₂/HClO₄ and SiO₂/KHSO₄ catalysts

Perchloric acid is a super acid (pKa = -10 to -15), which is a stronger acid than sulfuric and nitric acids. It provides strong acidity with minimal interference because perchlorate is weakly nucleophilic. KHSO₄ creates an acidic environment due to the complete

protolysis of the ion HSO₄⁻, without decomposition. Thiocyanation of aromatic compounds proceeds smoothly with NH₄SCN in the presence of SiO₂/HClO₄ and SiO₂/KHSO₄ under reflux conditions in acetonitrile medium. Tables 3 and 4 clearly demonstrate that

silica supported perchloric acid is efficient over silica supported bisulfate in terms of the obtained reaction times and yields. $\text{SiO}_2/\text{HClO}_4$ triggered reaction was completed in 1.5 h while 2.5 hours was required for $\text{SiO}_2/\text{KHSO}_4$ system. Phenol upon thiocyanation gave 4- thiocyanato phenol. Similarly, other aromatic compounds (Entries 2-14) provided the corresponding thiocyanate products in good to achieve maximum conversion of substrates into products (Table 5). The reaction times for all the studied reactions under conventional reflux condition are in the range of 1.5 h to 3.5 hours in the presence of $\text{SiO}_2/\text{HClO}_4$, where as in the case of

$\text{SiO}_2/\text{KHSO}_4$ is 2.5 to 5 h. All the obtained products were identified by spectroscopic methods (NMR and mass spectra) and compared with the literature. Under microwave condition, reaction times were reduced from 1.5-5 h (under reflux) to 1-5 min. Rate enhancements under microwave could be attributed due to bulk activation [40-45] phenomenon which is achieved due to rapid heating and pressure effects. When NH_4SCN is added to the reaction system SCN^+ electrophile is generated *in situ*, which in turn attacks the benzene ring, to afford products as shown in Scheme 3.



Scheme 3. Thiocyanation of aromatic compounds in presence of $\text{SiO}_2/\text{HClO}_4$ and $\text{SiO}_2/\text{KHSO}_4$

Table 2. Comparison of the isolated yields for the thiocyanation of Aniline to 4-thiocyanato aniline with reported classical methods

Catalyst	Reaction conditions	R.T. (min)	Yield (%)	Reference
$\text{SiO}_2/\text{HClO}_4$	(Solvent-free) MW assisted reaction	1.0	85	Present Work
$\text{SiO}_2/\text{KHSO}_4$	(Solvent-free) MW assisted reaction	25	80	Present Work
Zeolite-H-SDUSY/ NH_4SCN	USAR in MeCN	90	78	36
$\text{NH}_4\text{VO}_3/\text{NH}_4\text{SCN}/\text{KHSO}_4$	USAR in MeCN	(35-40)	79	37
Copper powder/ NH_4SCN	-----	-----	56	38
Aryldiazonium salt/ NH_4SCN	-----	-----	80	39

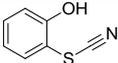
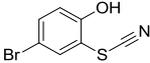
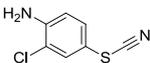
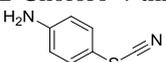
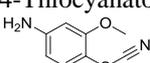
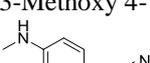
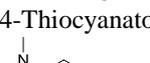
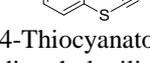
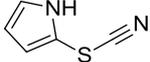
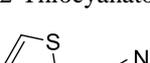
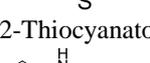
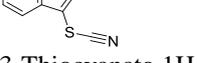
Table 3. Thiocyanation of aromatic compounds in presence of SiO₂/HClO₄ catalyst

Entry	Substrate	Product	Conventional		Microwave	
			R. T (hr)	Yield (%)	R. T (min)	Yield (%)
1	Aniline	4-Thiocyanatoaniline	3	76	1	85
2	<i>o</i> -Cl aniline	2-Chloro 4-Thiocyanatoaniline	2.5	80	1	90
3	<i>m</i> -OMe aniline	3-Methoxy 4-Thiocyanatoaniline	3	82	1	90
4	N-Methyl aniline	4-Thiocyanato N-methylaniline	3.5	75	1	88
5	N, N dimethyl aniline	4-Thiocyanato N, N-dimethyl aniline	3.5	72	1	86
6	Diphenyl amine	4-Thiocyanato diphenylamine	6	70	2	90
7	Phenol	2-Thiocyanato phenol	4.5	78	2	90
8	<i>p</i> -Cl Phenol	4-Chloro 2-thiocyanatophenol	3.5	80	2	94
9	Pyrrole	2-Thiocyanato 1H-pyrrole	3.5	82	2	90
10	Furan	2-Thiocyanato furan	3.5	82	2	88
11	Thiophene	2-Thiocyanato thiophene	3	84	1	92
12	Indole	3-Thiocyanato 1H-indole	3	82	1	90
13	5-Br indole	5-Bromo 3-thiocyanato indole	4	72	2	85
14	N-Methyl indole	3-thiocyanato N-Methyl- indole	3.5	76	2	90

Table 4. Thiocyanation of aromatic compounds in presence of SiO₂/KHSO₄ catalyst

Entry	Substrate	Product	Conventional		Microwave	
			R. T (hrs)	Yield (%)	R. T (min)	Yield (%)
1	Aniline	4-Thiocyanatoaniline	4	70	2	80
2	<i>o</i> -Cl aniline	2-Chloro 4-Thiocyanatoaniline	4	72	1	82
3	<i>m</i> -OMe aniline	3-Methoxy 4-Thiocyanatoaniline	4.5	75	2	84
4	N-Methyl aniline	4-Thiocyanato N-methylaniline	5	68	2	78
5	N, N dimethyl aniline	4-Thiocyanato N, N-dimethyl aniline	4.5	65	2	76
6	Diphenyl amine	4-Thiocyanato diphenylamine	8	62	5	74
7	Phenol	2-Thiocyanato phenol	6	72	3	80
8	<i>p</i> -Cl Phenol	4-Chloro 2-thiocyanatophenol	5.5	75	4	85
9	Pyrrole	2-Thiocyanato 1H-pyrrole	5	78	2	85
10	Furan	2-Thiocyanato furan	5	76	4	90
11	Thiophene	2-Thiocyanato thiophene	4.5	82	2	90
12	Indole	3-Thiocyanato 1H-indole	5	85	2	92
13	5-Br indole	5-Bromo 3-thiocyanato indole	6	68	3	75
14	N-Methyl indole	3-thiocyanato N-Methyl- indole	5.5	72	2	78

Table 5. NMR spectroscopic data for representative compounds

S.N.	Compound	NMR data
1.	 2-Thiocyanato phenol	$^1\text{H NMR}$ (CDCl_3): δ 7.14 (d, $J = 8.1$ Hz, 1H), 6.73 (m, $J = 7.9$ Hz, 2H), 6.54 (d, $J = 8.1$ Hz, 1H), 4.83 (s, 1H). $m/z = 151$.
2.	 4-bromo-2-thiocyanato-phenol	$^1\text{H NMR}$ (CDCl_3): δ 7.22 (s, 1H), 7.03 (d, $J = 8.1$ Hz, 1H), 6.53 (d, $J = 8.1$ Hz, 1H), 4.84 (s, 1H). $m/z = 230$.
3.	 2-Chloro-4-thiocyanatoaniline	$^1\text{H NMR}$ (CDCl_3): δ 7.52 (d, $J = 8.2$ Hz, 2H), 7.26 (dd, $J = 8.1$ Hz, 1H), 6.76 (d, $J = 8.2$ Hz, 1H), 4.37 (brd s, 2H). $m/z = 184$ (m.p. 59–61°C).
4.	 4-Thiocyanatoaniline	$^1\text{H NMR}$ (CDCl_3): δ 7.38 (d, $J = 8.7$ Hz, 2H), 6.66 (d, $J = 8.7$ Hz, 2H), 3.94 (brd s, 2H), $^{13}\text{C NMR}$ (75 Hz, CDCl_3): δ 148.7, 134.3, 116.1, 112.3, 109.5, $m/z = 150$ (m.p. 51–54°C.)
5.	 3-Methoxy 4-Thiocyanatoaniline	$^1\text{H NMR}$ (CDCl_3): δ 7.29 (d, $J = 8.3$ Hz, 1H), 6.28 (dd, $J = 8.3$ Hz, 1H), 6.24 (d, $J = 8.2$ Hz, 1H), 3.98 (s, 2H), 3.87 (s, 3H). $m/z = 180$ (m.p. 99–101°C)
6.	 4-Thiocyanato N-methylaniline	$^1\text{H NMR}$ (CDCl_3): δ 7.37 (d, $J = 8.64$ Hz, 2H), 6.59 (d, $J = 8.68$ Hz, 2H), 4.11 (brd s, 1H), 2.85 (s, 3H). $m/z = 164$.
7.	 4-Thiocyanato N,N-dimethylaniline	$^1\text{H NMR}$ (CDCl_3): δ 7.44 (d, $J = 8.8$ Hz, 2H), 6.66 (d, $J = 8.8$ Hz, 2H), 3.02 (s, 6H), $^{13}\text{C NMR}$ (75 MHz, CDCl_3): 151.5, 134.3, 113.2, 112.9, 106.4, 40.2. $m/z = 178$ (m.p. 72–74°C).
8.	 2-Thiocyanato 1H-pyrrole	$^1\text{H NMR}$ (CDCl_3): δ 6.27 (dd, $J = 3$ Hz, $J = 6.3$ Hz), 6.64 (m, 1H, $J = 1.5$ Hz, $J = 3.6$ Hz, $J = 3.9$ Hz), 6.96 (m, 1H, $J = 1.5$ Hz, $J = 3$ Hz, $J = 4.5$ Hz), 8.9 (s, 1H), $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 124.3, 120.1, 111.1, 110.9, 102.8. $m/z = 124$.
9.	 2-Thiocyanato thiophene	$^1\text{H NMR}$ (CDCl_3): δ 7.45–8.10 (m, 3H).
10.	 3-Thiocyanato 1H-indole	$^1\text{H NMR}$ (CDCl_3): δ 7.30 (m, 2H, $J = 9.9$ Hz, $J = 6.9$ Hz), 7.42 (m, 1H, $J = 9.9$ Hz, $J = 7.2$ Hz), 7.48 (d, 1H, $J = 3.0$ Hz), 7.09 (dd, 1H, $J = 5.7$ Hz, $J = 3$ Hz), 8.72 (br s, 1H), $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 135.9, 131.1, 127.4, 123.7, 121.8, 118.5, 112.3, 112.1, 91.53. $m/z = 174$. (mp 72–73°C).
11.	 5-Bromo 3-thiocyanato indole	$^1\text{H NMR}$ (CDCl_3): δ 8.87 (br s, 1H), 7.92–7.15 (m, 5H). $^{13}\text{C NMR}$ (CDCl_3): δ 134.6, 132.2, 129.3, 123.1, 121.2, 115.4, 113.7, 111.9, 102.2 ($m/z = 251$ (M-1), 253 (M+2) (mp 126–127°C).
12.	 4-Thiocyanato diphenylamine	$^1\text{H NMR}$ (CDCl_3): δ 7.43 (d, $J = 8.1$ Hz, 2H), 7.34 (t, $J = 8.2$ Hz, 2H), 7.14 (d, $J = 8.1$ Hz, 2H), 7.08 (t, $J = 8.2$ Hz, 1H), 7.03 (d, $J = 8.2$ Hz, 2H), 5.94 (brd s, 1H). $m/z = 226$ (m.p. 62–63°C).

Conclusion

We have demonstrated here thiocyanation of aromatic compounds using NH_4SCN in presence of $\text{SiO}_2/\text{HClO}_4$ and $\text{SiO}_2/\text{KHSO}_4$ (Silica supported) catalysts under reflux and solvent free microwave conditions. High yields, short reaction times and green conditions are the advantages of these protocols.

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