

Ultrasonically Assisted Thiocyanation of Aromatic and Heteroaromatic Compounds Using Silica-Supported Bronsted Acids ($\text{HClO}_4\text{-SiO}_2$ and $\text{KHSO}_4\text{-SiO}_2$) as Reusable Catalysts

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ABSTRACT

When the HClO_4 and KHSO_4 were adsorbed on to the surface of silica gel grains, they will get high thermal and mechanical stabilities and these materials have been explored as a green catalyst for the thiocyanation reactions of aromatic, heteroaromatic compounds under conventional condition, and ultrasonically assisted conditions. In the ultrasonically assisted protocol, remarkable rate accelerations were exhibited and it offered selectivity in thiocyanation of aromatic compounds and heteroaromatic compounds with better yields. Moreover, these catalysts could be recycled using simple procedure up to five cycles with good catalytic efficiency. These developed protocols are also promising and comparable with the literature procedures.

Key words: $\text{SiO}_2\text{-HClO}_4$, $\text{SiO}_2\text{-KHSO}_4$, NH_4SCN , Thiocyanation, Ultrasonic assisted reactions.

1. INTRODUCTION

Among the first-generation catalysts, Bronsted acids and bases were found to be widely used catalysts for many organic transformations [1-6]. However, their usage associated with some issues such as high economy, volatility, toxicity, and hazardous laboratory/industry outlets is 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 [1-27]. A recent review published by Kaur *et al.* summarized that few of the most important silica-supported catalysts which were prepared using heteropoly acids such as fluoroboric acid, polyphosphoric acid, sulfuric acid, and perchloric acid [13]. All these catalysts have been utilized for many organic transformations to prepare desired compounds which are most important for the pharmaceutical and chemical industries. Silica-supported Bronsted acid catalysts can be easily isolated from the reaction mixture by simple filtration and they are reusable after the activation therefore all these processes become eco-friendly. In addition to this, silica-supported materials are found to be superior over traditional homogeneous catalysts and heterogeneous catalysts because of their high thermal and mechanical stabilities and large surface area, low toxicity, greater selectivity, high selectivity and simplicity in handling, and reusability. Wastages and by-products can be effectively reduced in these catalytic systems. Our interest toward the thiocyanated products is mainly connected to their wide range applications of antiparasitic, antitumor, antifungal, activities, and their important uses in organic synthesis as synthons, medicinal chemistry, pharmaceutical chemistry, and agriculture chemistry [28-36]. Over a period of time, certain regioselective efficient thiocyanation methods have been put forward [37-40], including few recent reports from our laboratory [41-44]. Literature survey reveals that many electrophilic

aromatic substitution protocols such as thiocyanation, nitration, sulfonation, and several other reactions have been reported using different catalysts under ultrasonic-assisted conditions including some recent reports from our laboratory [45-49] and silica-supported Bronsted acids were explored as efficient green and reusable catalysts for many electrophilic aromatic substitution reactions such as nitration and thiocyanation, sulfonation, and several other reactions under different reaction conditions such as conventional-reflux conditions, microwave-assisted conditions, and ultrasonic sound-assisted conditions, including few recent reports from our laboratory [50-53], however, silica-supported Bronsted acids such as $\text{SiO}_2\text{-KHSO}_4$ and $\text{SiO}_2\text{-HClO}_4$ have not been explored as heterogeneous reusable green catalysts so far for thiocyanation reactions under ultrasonic conditions.

Encouraged by these features, we wish to report here in a clean and environmentally friendly protocol for thiocyanation of aromatic compounds and heteroaromatic compounds with NH_4SCN within the sight of by utilizing silica upheld heterogeneous reusable impetuses $\text{SiO}_2\text{-KHSO}_4$ and $\text{SiO}_2\text{-HClO}_4$ under customary and ultrasonic waves helped conditions [54-60].

2. EXPERIMENTAL

General laboratory desktop chemicals are utilized in the present study, procured from Avra Synthesis (India), SD-Fine Chemicals (India), and Loba (India). Simple laboratory (1.5 L) Sonicator is used in this study.

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2.1. Preparation of $\text{SiO}_2\text{-HClO}_4$ and $\text{SiO}_2\text{-KHSO}_4$ Catalysts

Four grams (100–200 mesh graded) silica gel (SiO_2) was added to (20 mmol) HClO_4 in distilled water (25 ml), and this mixture was stirred for about 30 min at room temperature, since to the adsorption of KHSO_4 onto the surface of the silica gel grains. Then, the water was removed in vacuum the resultant powder was concentrated in an oven at 393 K temperature for 2–3 h to get $\text{SiO}_2\text{-HClO}_4$ catalyst. Same procedure is used for the preparation of $\text{SiO}_2\text{-KHSO}_4$ catalysts.

2.2. X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) Analysis of $\text{SiO}_2\text{-HClO}_4$ and $\text{SiO}_2\text{-KHSO}_4$ Catalysts

The as-prepared catalyst is characterized by XRD and SEM methods, its corresponding results are shown in Figures 1-4, SEM pictures of $\text{SiO}_2\text{-HClO}_4$ and $\text{SiO}_2\text{-KHSO}_4$ catalysts under different magnifications in the range of 50 μm –500 μm reveal non-uniformed morphologies are with flakes and polynomial cubic crystals were distributed in the grain like catalyst species. All these observations are conforming that the heterogeneous behavior of these $\text{SiO}_2\text{-HClO}_4$ and $\text{SiO}_2\text{-KHSO}_4$ catalyst.

2.3. Conventional Reflux Method for Synthesis of Thiocyanated Aromatic and Heteroaromatic Compounds Using $\text{SiO}_2\text{-HClO}_4$ and $\text{SiO}_2\text{-KHSO}_4$

Aromatic or heteroaromatic compound (10 mmol), NH_4SCN (10 mmol), and acetonitrile as dissolvable were taken into a cleaned and dried round base flask then, at that point add the ideal measure of the impetus $\text{SiO}_2\text{-HClO}_4$ or $\text{SiO}_2\text{-KHSO}_4$. Furthermore, mixed this response blend under reflux until the response is finished which is shown by thin-layer chromatography (TLC). After the total change, the impetus in the response blend was disconnected by straightforward filtration, and response combination is killed with aq. NaHCO_3 arrangement, and afterward added with ethyl acetate derivation. The natural organic layer was then isolated by utilizing isolating channel, and dried over Na_2SO_4 , decontaminated by section chromatography utilizing the combination of ethyl acetate derivation, hexane, and dried under vacuum to acquire the eventual outcome.

2.4. Ultrasonically Assisted Method for Synthesis of Thiocyanated Aromatic and Heteroaromatic Compounds Using $\text{SiO}_2\text{-HClO}_4$ and $\text{SiO}_2\text{-KHSO}_4$

For the ultrasonic-assisted thiocyanation aromatic or heteroaromatic compound (0.1 mol), the optimum amount of the catalyst ($\text{SiO}_2\text{-KHSO}_4$ or $\text{SiO}_2\text{-HClO}_4$) was added to the mixture followed by electrophile generating agent NH_4SCN (10 mmol) and 25 ml of dissolvable (acetonitrile) were taken in to a cleaned and dried round base carafe (RBF) and put into an ultrasonicator. Then, at that point, the response combination is sonicated at ordinary room temperature until the response was finished. Response was checked by TLC. After complete transformation as distinguished by TLC, then, at that point coming about response combination was extinguished with water, and is killed by aq. NaHCO_3 , and afterward added with ethyl acetate derivation. The natural organic layer was isolated by utilizing isolating pipe and dried over Na_2SO_4 and concentrated under vacuum, the subsequent items were separated by section chromatography utilizing the combination of ethyl acetic acid derivation and hexane as eluent to get unadulterated item. The mechanism behind the sonochemical effects in liquids is “the phenomenon of formation of acoustic cavitation.” The ultrasonic waves (with >20 kHz frequency) cause agitation, when these (US) waves are transmitted through liquid sample. These ultrasonic waves propagate into the liquid media and result high-pressure (compressions) and low-pressure (rarefactions)

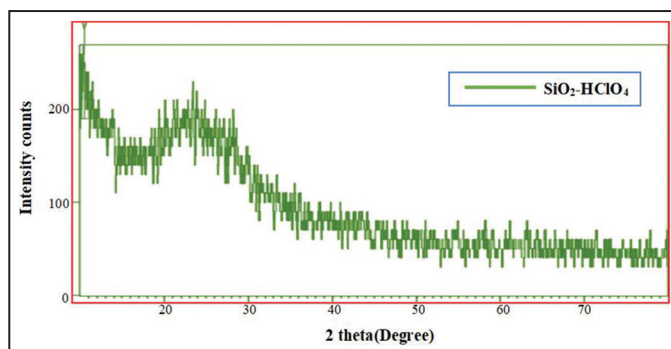


Figure 1: XRD - patterns of $\text{SiO}_2\text{-HClO}_4$ catalyst.

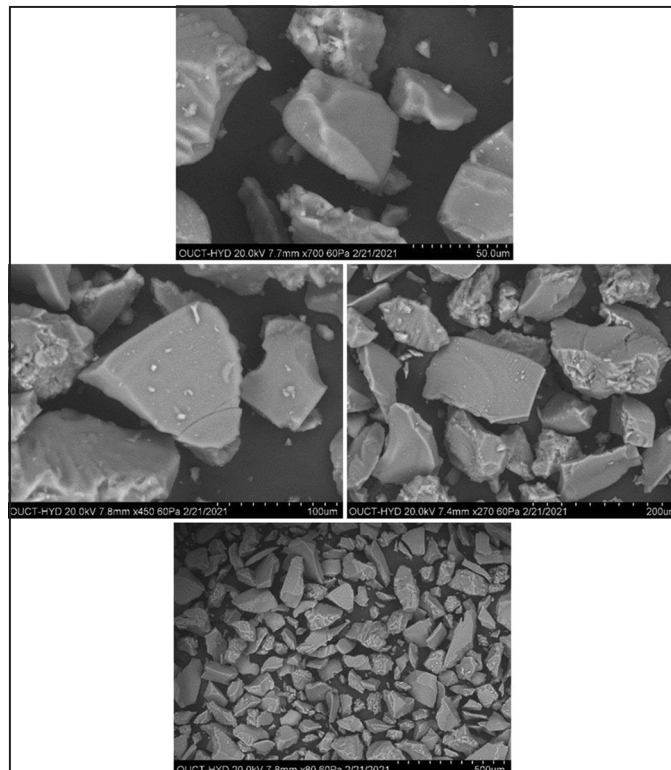


Figure 2: SEM Morphologies of $\text{SiO}_2\text{-HClO}_4$ catalyst.

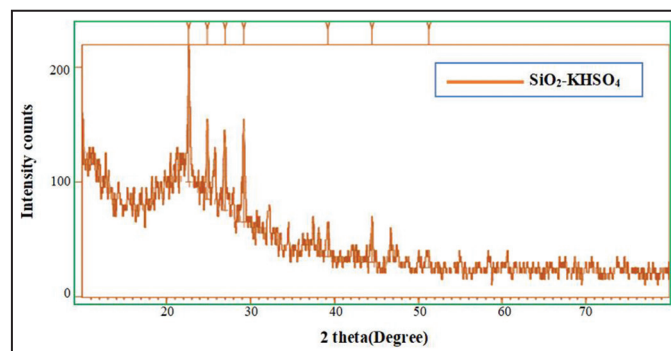


Figure 3: X-ray diffraction – patterns of $\text{SiO}_2\text{-KHSO}_4$ catalyst.

cycles alternatingly. During rarefactions, high intensive sound waves can generate very small vacuum cavities in the liquid, which were collapse violently (known as cavitation) during compression by releasing very high localized thermal energy, this energy causes for our desired chemical transformations.

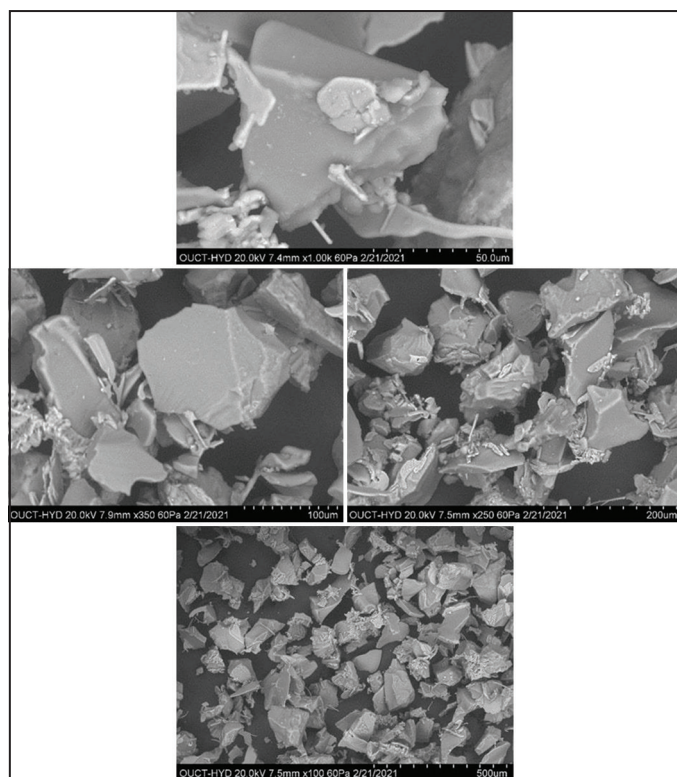


Figure 4: Scanning electron microscope morphologies of $\text{SiO}_2\text{-KHSO}_4$ catalyst.

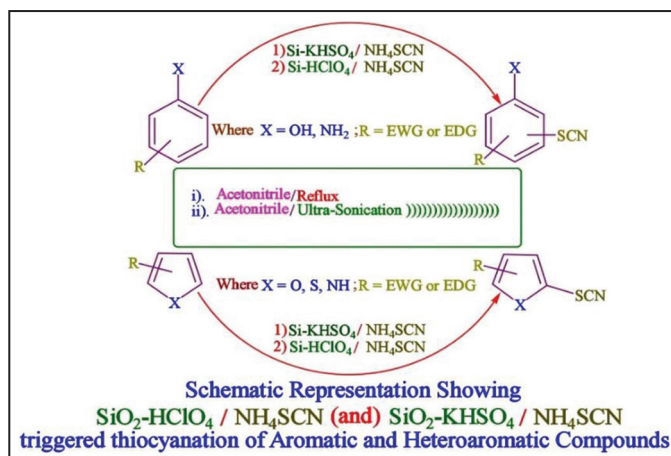
3. RESULTS AND DISCUSSION

3.1. Optimization of Catalysts

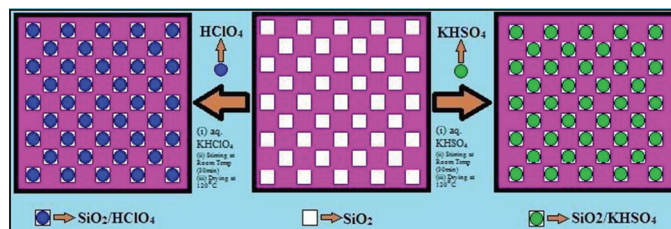
In this present work, we have reported thiocyanation of aromatic and heteroaromatic compounds with NH_4SCN using reusable silica-supported catalysts such as $\text{SiO}_2\text{-HClO}_4$ or $\text{SiO}_2\text{-KHSO}_4$ (Figure 5) under conventional conditions in acetonitrile solvent as well as ultrasonically assisted conditions (Scheme 1).

In the beginning, we optimized the catalyst ($\text{SiO}_2\text{-HClO}_4$ or $\text{SiO}_2\text{-KHSO}_4$) quantity for thiocyanation reaction. We accomplished the thiocyanation reactions using various quantities of $\text{SiO}_2\text{-HClO}_4$ and $\text{SiO}_2\text{-KHSO}_4$ catalysts (Scheme 2, Table 1). Data presented in Table 1 reveal that the maximum conversions occurred when 0.25 gm $\text{SiO}_2\text{-HClO}_4$ and 0.3 gm $\text{SiO}_2\text{-KHSO}_4$ are used as catalysts. A further increase in the catalyst quantity did not appreciably affect the conversion. Data given in Table 1 further denote that the best results were reported with $\text{SiO}_2\text{-HClO}_4$ over a $\text{SiO}_2\text{-KHSO}_4$ catalyst. This could be attributed to the fact that HClO_4 is a stronger acid than KHSO_4 . To check the reusability of the catalysts ($\text{SiO}_2\text{-HClO}_4$ and $\text{SiO}_2\text{-KHSO}_4$), the catalysts were isolated from the reaction mixture by simple filtration and washed with $\text{CH}_3\text{COOC}_2\text{H}_5$. After drying, the catalyst was activated under the same experimental conditions set and used again to verify the reactions. The catalyst is recycled for about 4–5 times showing a slight reduction of activity during the consecutive use of the recovered catalyst this data compiled in Table 2, and has graphically represented, as shown in Figure 1.

Perchloric corrosive is a very corrosive ($\text{pKa} = -15$ – -10), which is a productive corrosive than H_2SO_4 and HNO_3 acids. It can give solid causticity negligible obstruction since perchlorate is more fragile nucleophile. KHSO_4 produces an acidic climate by the total protolysis of the sulfate particle (HSO_4), without decay. Thiocyanation of sweet smelling and heteroaromatic intensifies continues smoothly with ammonium thiocyanate using silica-supported perchloric acid and



Scheme 1: Schematic representation showing synthesis of thiocyanated aromatic and heteroaromatic compounds using $\text{SiO}_2\text{-KHSO}_4$ and $\text{SiO}_2\text{-HClO}_4$.



Scheme 2: Adsorption of HClO_4 or KHSO_4 on to the surface of silica gel grains (SiO_2).

Table 1: Optimization $\text{SiO}_2\text{-HClO}_4$ and $\text{SiO}_2\text{-KHSO}_4$ catalysts for thiocyanation of indole

| Entry | $\text{SiO}_2\text{-HClO}_4$ | | $\text{SiO}_2\text{-KHSO}_4$ | |
|-------|------------------------------|-----------|------------------------------|-----------|
| | Amt. of catalyst | Yield (%) | Amt. of catalyst | Yield (%) |
| 1 | 0.10 gm | 51 | 0.10 gm | 45 |
| 2 | 0.15 gm | 89 | 0.15 gm | 80 |
| 3 | 0.25 gm | 92 | 0.25 gm | 84 |
| 4 | 0.30 gm | 92 | 0.30 gm | 85 |
| 5 | ---- | ---- | 0.35 gm | 85 |

potassium bisulfate catalysts under reflux conditions in acetonitrile medium. Tables 3 and 4 clearly demonstrate that silica-supported perchloric acid is efficient over silica-supported potassium bisulfate in terms of the obtained reaction times and yields. $\text{SiO}_2\text{-HClO}_4$ triggered reaction was completed in 2.5–6 h time, while 3–8 h time was required for $\text{SiO}_2\text{-KHSO}_4$ catalyst. Phenol on thiocyanation gave 4-thiocyanato phenol. Similarly, other aromatic compounds (Entries 2–18) provided the corresponding thiocyanate products in good to achieve maximum conversion of substrates into products (Tables 3 and 4). The observed reaction times of all the studied thiocyanation reactions under reflux conditions are in between 2.5 h and 6 h with $\text{SiO}_2\text{-HClO}_4$ as a catalyst but in the case of $\text{SiO}_2\text{-KHSO}_4$ catalyst, the reaction times are 3 h–8 h. All the obtained thiocyanation products were confirmed by several spectroscopic analytical techniques [$\text{NMR}^{(13}\text{C}, ^1\text{H})$ and Mass] and compared with the literature. Under ultrasonic-assisted condition, reaction times of all the above reactions were reduced from 2.5 to 6 h (under reflux) to 12–35 min. The high reaction rates with ultrasonication could be occurred due to increase in number of activation reactive

species [54-60]. The phenomenon is occurred by rapid local heating and pressure's effect. When NH_4SCN is added to the reaction system,

SCN^+ electrophile is generated *in situ*, which, in turn, attacked by the arene (aromatic or heteroaromatic ring) nucleophile, to produce products the proposed mechanism shown in the Scheme 3.

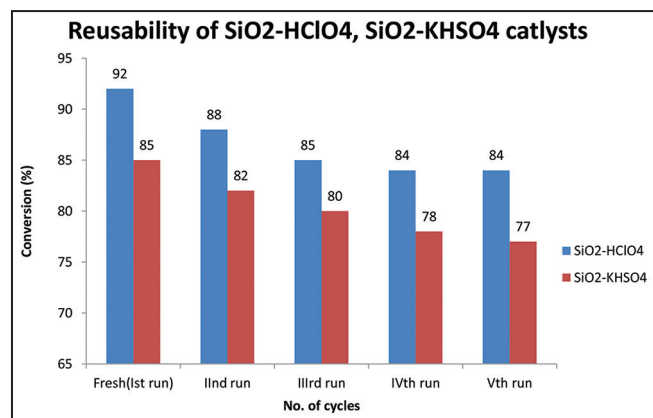


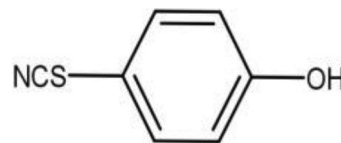
Figure 5: Bar diagram for recyclability $\text{SiO}_2\text{-HClO}_4$ and $\text{SiO}_2\text{-KHSO}_4$ catalysts (indole).

Table 2: Reusability of $\text{SiO}_2\text{-HClO}_4$ and $\text{SiO}_2\text{-KHSO}_4$ catalysts under ultrasonication-assisted thiocyanation at RT (room temperature)

| Reused cycle | $\text{SiO}_2\text{-HClO}_4$ | | $\text{SiO}_2\text{-KHSO}_4$ | |
|-----------------------------|------------------------------|-----------|------------------------------|-----------|
| | R. T. | Yield (%) | R. T. | Yield (%) |
| I st run (Fresh) | 15 min | 92 | 17 min | 85 |
| II nd run | 16 min | 88 | 18 min | 82 |
| III rd run | 18 min | 85 | 18 min | 80 |
| IV th run | 18 min | 84 | 19 min | 78 |
| V th run | 20 min | 84 | 20 min | 77 |

3.2. Spectroscopic Analytical Data for Few Typical Compounds

(1) 4-Thiocyanato phenol:



MP: 45–49°C.

IR (cm^{-1} , KBr): 833, 1099, 1171, 2160, 3421.

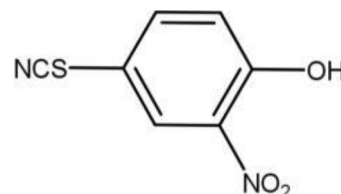
$^1\text{H-NMR}$ (400 MHz, CDCl_3): (ppm) 5.88(1H, s, OH), 6.87(2H, d, $J=8\text{Hz}$, H_2 , H_6), 7.45(2H, d, $J=8\text{Hz}$, H_3 , H_5).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): (ppm) 112.2 (SCN), 113.3 (C, C_4), 117.5 (CH_2 , C_2 , C_6), 134.1 (CH_2 , C_3 , C_5), 158.1 (C, C_1).

MS (70eV, EI): m/z (%) = 151 [M^+], 123, 95, 80, 71, 65.

Yields: 89% (With $\text{SiO}_2\text{-HClO}_4$), 84% (With $\text{SiO}_2\text{-KHSO}_4$).

(2) 2-Nitro 4-Thiocyanato phenol:



MP: 70–74°C.

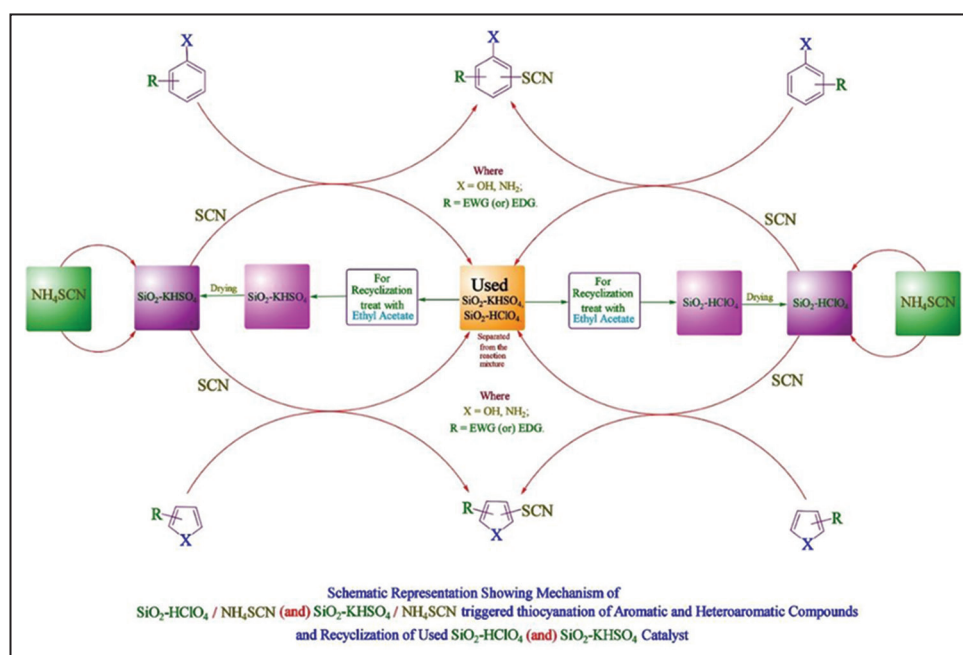
IR (cm^{-1} , KBr): 848, 893, 1258, 1418, 1524, 2155, 3265.

Table 3: $\text{SiO}_2\text{-HClO}_4$ catalyzed thiocyanation of aromatic compounds under reflux and ultrasonic conditions

| Entry | Substrate | Product | Conventional | | Ultrasonication | |
|-------|------------------------|------------------------------------|--------------|----------|-----------------|----------|
| | | | R. T. | Yield(%) | R. T. | Yield(%) |
| 1 | Phenol | 4-Thiocyanato phenol | 4.5 h | 82 | 22 min | 89 |
| 2 | <i>o</i> -Nitro Phenol | 2-Nitro 4-thiocyanato phenol | 3.5 h | 78 | 20 min | 86 |
| 3 | Catechol | Thiocyanato benzene 1,2 diols | 2.5 h | 82 | 21 min | 88 |
| 4 | 3-Methyl phenol | 3-Methyl 4-thiocyanato phenol | 3 h | 76 | 12 min | 86 |
| 5 | 3-Methoxy phenol | 3-Methoxy 4-thiocyanato phenol | 2.5 h | 80 | 13 min | 88 |
| 6 | Aniline | 4-Thiocyanato aniline | 3 h | 79 | 15 min | 84 |
| 7 | 2-Nitro Aniline | 2-Nitro 4-Thiocyanato aniline | 3 h | 74 | 18 min | 78 |
| 8 | 3-Methoxy Aniline | 3-Methoxy 4-thiocyanato aniline | 2.5 h | 86 | 15 min | 90 |
| 9 | N, N- dimethylaniline | 4-Thiocyanato N, N-dimethylaniline | 3.5 h | 72 | 19 min | 85 |
| 10 | Diphenyl amine | 4-Thiocyanato diphenylamine | 6 h | 70 | 25 min | 87 |
| 11 | Pyrrole | 2-Thiocyanato 1H-pyrrole | 3.5 h | 82 | 23 min | 86 |
| 12 | Furan | 2-Thiocyanato furan | 3.5 h | 80 | 21 min | 88 |
| 13 | Thiophene | 2-Thiocyanato thiophene | 3 h | 84 | 17 min | 90 |
| 14 | Indole | 3-Thiocyanato 1H-indole | 3 h | 82 | 14 min | 92 |
| 15 | N-Methyl indole | 3-thiocyanato N-Methyl indole | 3.5 h | 76 | 22 min | 85 |
| 16 | 2-Methyl indole | 2-Methyl 3-thiocyanato indole | 3.5 h | 77 | 20 min | 86 |
| 17 | 5-Methoxy indole | 5-Methyl 3-thiocyanato indole | 3 h | 83 | 19 min | 88 |
| 18 | 5-Br indole | 5-Bromo 3-thiocyanato indole | 4 h | 73 | 20 min | 84 |

Table 4: SiO₂-KHSO₄ catalyzed thiocyanation of aromatic compounds under reflux and ultrasonic conditions

| Entry | Substrate | Product | Conventional | | Ultrasonication | |
|-------|------------------------|------------------------------------|--------------|----------|-----------------|----------|
| | | | R. T. | Yield(%) | R. T. | Yield(%) |
| 1 | Phenol | 4-Thiocyanato phenol | 6 h | 78 | 25 min | 84 |
| 2 | <i>o</i> -Nitro Phenol | 2-Nitro 4-thiocyanato phenol | 5.5 h | 72 | 23 min | 78 |
| 3 | Catechol | Thiocyanato benzene 1,2 diols | 3 h | 80 | 22 min | 85 |
| 4 | 3-Methyl phenol | 3-Methyl 4-thiocyanato phenol | 3.5 h | 76 | 18 min | 83 |
| 5 | 3-Methoxy phenol | 3-Methoxy 4-thiocyanatophenol | 3 h | 86 | 18 min | 88 |
| 6 | Aniline | 4-Thiocyanato aniline | 4 h | 74 | 18 min | 79 |
| 7 | 2-Nitro Aniline | 2-Nitro 4-Thiocyanatoaniline | 5 h | 68 | 20 min | 69 |
| 8 | 3-Methoxyaniline | 3-Methoxy 4-thiocyanatoaniline | 3 h | 85 | 17 min | 85 |
| 9 | N, N- dimethylaniline | 4-Thiocyanato N, N-dimethylaniline | 4.5 h | 65 | 21 min | 74 |
| 10 | Diphenyl amine | 4-Thiocyanato diphenylamine | 8 h | 62 | 35 min | 73 |
| 11 | Pyrrole | 2-Thiocyanato 1H-pyrrole | 5 h | 78 | 26 min | 86 |
| 12 | Furan | 2-Thiocyanato furan | 4 h | 80 | 22 min | 85 |
| 13 | Thiophene | 2-Thiocyanato thiophene | 4.5 h | 82 | 19 min | 88 |
| 14 | Indole | 3-Thiocyanato 1H-indole | 5 h | 85 | 17 min | 85 |
| 15 | N-Methyl indole | 3-thiocyanato N-Methyl indole | 5.5 h | 72 | 24 min | 76 |
| 16 | 2-Methyl indole | 2-Methyl 3-thiocyanato indole | 4.5 h | 77 | 25 min | 84 |
| 17 | 5-Methoxy indole | 5-Methyl 3-thiocyanato indole | 3.5 h | 82 | 20 min | 84 |
| 18 | 5-Br indole | 5-Bromo 3-thiocyanato indole | 6 h | 68 | 22 min | 73 |

**Scheme 3:** Mechanism of showing recyclization of used SiO₂-HClO₄ and SiO₂-KHSO₄ catalysts in thiocyanation reaction.

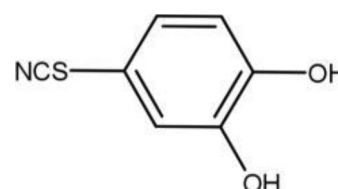
¹H-NMR (400 MHz, CDCl₃): (ppm) 7.32 (1H, d, J=8.6 Hz, H₆), 7.78 (1H, dd, J=8.7, 2.3 Hz, H₅), 8.38(1H, d, J= 2.2, 4.1Hz, H₃), 10.69 (1H, s, OH).

¹³C-NMR (100 MHz, CDCl₃): (ppm) 108.9 (SCN), 114.7 (C, C₄), 121.8 (CH₂, C₆), 129.1 (CH₂, C₃), 132.8 (C, C₂), 138.7 (CH₂, C₅), 155.7 (C, C₁).

MS (70eV, EI): *m/z* (%) = 196 [M⁺], 178, 169, 151, 137, 124.

Yields: 86% (With SiO₂-HClO₄), 78% (With SiO₂-KHSO₄).

(3) Thiocyanatobenzene-1, 2 diols:



MP: 140–145°C.

IR (cm⁻¹, KBr): 1280, 1511, 2163, 3298.



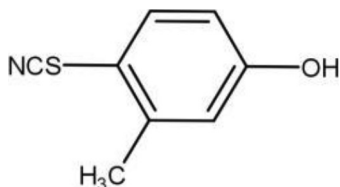
¹H-NMR (400 MHz, CDCl₃): (ppm) 6.82 (1H, d, J=8.2 Hz, H₆), 6.89 (1H, dd, J=8.1, 3.9 Hz, H₅), 6.93 (1H, d, J= 3.9 Hz, H₃), 9.62 (2H, s, OH).

¹³C-NMR (100 MHz, DMSO -d₆): (ppm) 111.1 (C, C₄), 113.2 (SCN), 116.8 (CH₂, C₆), 119.2 (CH₂, C₃), 124 (C, C₅), 145.9 (C, C₂), 146.7 (C, C₁).

MS (70eV, EI): *m/z* (%) = 167 [M⁺], 142, 133, 121, 110, 95, 85, 69, 52.

Yields: 88% (With SiO₂- HClO₄), 85% (With SiO₂-KHSO₄).

(4) 3-Methyl 4-thiocyanatophenol:



MP: 65–70°C.

IR (cm⁻¹, KBr): 1240, 1571, 2163, 3318.

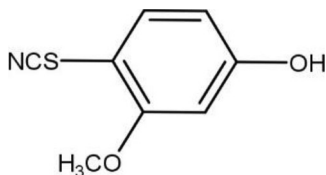
¹H-NMR (400 MHz, CDCl₃): (ppm) 2.45 (3H, s, CH₃), 6.05 (1H, s, OH), 6.7 (1H, dd, J=8.2, 2.7 Hz, H₆), 6.78 (1H, d, J= 2.6 Hz, H₂), 7.44 (1H, d, J= 8.6 Hz, H₅).

¹³C-NMR (100MHz, CDCl₃): (ppm) 20.5 (CH₃), 110.8 (SCN), 111.9 (C, C₄), 115.2 (CH₂, C₆), 117.8 (CH₂, C₂), 135 (CH₂, C₅), 142.9 (C, C₃), 157.9 (C, C₁).

MS (70eV, EI): *m/z* (%) = 165 [M⁺], 147, 136, 120, 110, 95, 85, 68, 51.

Yields: 86% (With SiO₂- HClO₄), 83% (With SiO₂-KHSO₄).

(5) 3-Methoxy 4-thiocyanatophenol:



MP: 138–142°C.

IR (cm⁻¹, KBr): 797, 858, 1202, 2153, 3358.

¹H-NMR (400 MHz, DMSO -d₆): (ppm) 3.91 (3H, s, OCH₃), 6.45 (1H, dd, J= 8.1-3.9 Hz, H₆), 6.56 (1H, d, J= 4.1 Hz, H₂), 7.38 (1H, d, J= 7.8 Hz, H₅), 9.92 (1H, s, OH).

¹³C-NMR (100MHz, DMSO -d₆): (ppm) 55.8 (OCH₃), 97.9 (C, C₄), 99.8 (CH₂, C₂), 108.8 (C, C₆), 112.1 (SCN), 136 (CH₂, C₅), 158.9 (C, C₃), 163 (C, C₁).

MS (70eV, EI): *m/z* (%) = 181 [M⁺], 165, 156, 137, 123, 112, 95, 78, 68.

Yields: 88% (With SiO₂- HClO₄), 88% (With SiO₂-KHSO₄).

(6) 4-thiocyanato aniline:



MP: 50–54°C.

IR (cm⁻¹, KBr): 822, 1179, 1384, 1496, 2147, 3348, 3419.

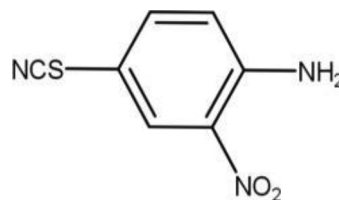
¹H-NMR (400 MHz, CDCl₃): (ppm) 3.95 (2H, s, N-H), 6.65 (2H, d, J= 8.6 Hz, H₂, H₆), 7.37 (2H, d, J= 8.6 Hz, H₃, H₅).

¹³C-NMR (100MHz, CDCl₃): (ppm) 110.3 (C, C₄), 113.2 (SCN), 115.6 (CH₂, C₂, C₆), 134.6 (CH₃, C₃, C₅), 148.8 (C, C₁).

MS (70eV, EI): *m/z* (%) = 150 [M⁺], 123, 95, 80, 71, 65.

Yields: 84% (With SiO₂- HClO₄), 79% (With SiO₂-KHSO₄).

(7) 2-Nitro 4-thiocyanato aniline:



MP: 105–110 °C.

IR (cm⁻¹, KBr): 823, 892, 1341, 1508, 2155, 3360, 3478.

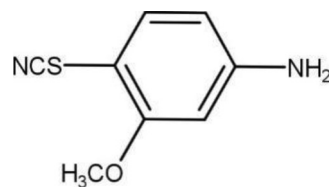
¹H-NMR (400 MHz, CDCl₃): (ppm) 6.36 (2H, s, N-H), 6.89 (1H, d, J= 8.7 Hz, H₆), 7.57 (1H, dd, J= 8.6, 2.3 Hz, H₅), 8.39 (1H, d, J=2.5 Hz, H₃).

¹³C-NMR (100MHz, CDCl₃): (ppm) 109.9 (C, C₄), 111.5 (SCN), 121.6 (CH₂, C₆), 130.9 (CH₂, C₃), 131.8 (C, C₂), 137.8 (CH₂, C₅), 144.9 (C, C₁).

MS (70eV, EI): *m/z* (%) = 195 [M⁺], 168, 149, 136, 121, 105.

Yields: 78% (With SiO₂- HClO₄), 69% (With SiO₂-KHSO₄).

(8) 3-methoxy 4-thiocyanato aniline:



MP: 98–101°C.

IR (cm⁻¹, KBr): 825, 1019, 1212, 1333, 1629, 2148, 2917, 3377, 3444.

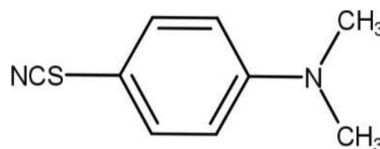
¹H-NMR (400 MHz, CDCl₃): (ppm) 3.88 (3H, s, OCH₃), 6.39 (2H, m, N-H), 6.44 (1H, dd, J= 7.8-4.1 Hz, H₆), 6.48 (1H, d, J=3.9 Hz, H₂), 7.38 (1H, d, J= 7.6 Hz, H₅).

¹³C-NMR (100MHz, CDCl₃): (ppm) 55.96 (OCH₃), 97.81 (C, C₄), 99.03 (CH₂, C₂), 108.05 (CH₂, C₆), 112.15 (SCN), 135.36 (CH₂, C₅), 151.01 (C, C₃), 159.75 (C, C₁).

MS (70eV, EI): *m/z* (%) = 180 [M⁺], 153, 134, 121, 116, 95.

Yields: 90% (With SiO₂- HClO₄), 85% (With SiO₂-KHSO₄).

(9) N, N-dimethyl 4-thiocyanato aniline:



MP: 71–75°C.

IR (cm⁻¹, KBr): 808, 1069, 1221, 1373, 1602, 2148, 2917, 3424.

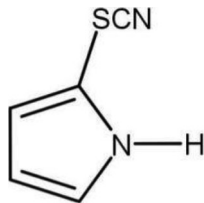
¹H-NMR (250 MHz, CDCl₃): (ppm) 3.05 (6H, s, CH₃), 6.68 (2H, d, J=10 Hz, H₂, H₆), 7.44 (2H, d, J= 9.8 Hz, H₃, H₅).

¹³C-NMR (100MHz, CDCl₃): (ppm) 41.01 (C, C₄), 107.6 (SCN), 111.9 (CH₂, C₂), 113.1 (CH₂, C₆), 134.4 (CH₂, C₃), 135.7 (CH₂, C₅), 150.97 (C, C₁).

MS (70eV, EI): m/z (%) = 178 [M^+], 153, 135, 121 115, 95.

Yields: 85% (With $\text{SiO}_2\text{-HClO}_4$), 74% (With $\text{SiO}_2\text{-KHSO}_4$).

(10) 2-Thiocyanato 1H-pyrrole:



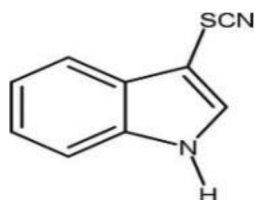
IR (KBr, cm^{-1}): 736, 1022, 1123, 1230, 1368, 1424, 1709, 2158, 3677.

$^1\text{H-NMR}$ (250 MHz, CDCl_3): (ppm) 6.33 (1H, s, H_4), 6.68 (1H, s, H_3), 7.05 (1H, s, H_5), 8.66 (1H, brs, N-H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): (ppm) 102.94 (CH , C_4), 110.99 (CH , C_3), 111.99 (SCN), 120.20 (CH , C_5), 124.43 (C , C_2).

Yields: 86% (With $\text{SiO}_2\text{-HClO}_4$), 86% (With $\text{SiO}_2\text{-KHSO}_4$).

(11) 3-Thiocyanato 1H-indole:



MP: 72–74°C.

IR (cm^{-1} , KBr): 744, 1238, 1455, 2158, 3117, 3404.

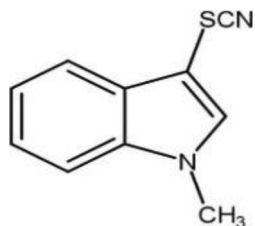
$^1\text{H-NMR}$ (400 MHz, CDCl_3): (ppm) 7.22–7.28 (2H, m, H_5 , H_6), 7.33–7.38 (1H, m, H_7), 7.39 (1H, d, $J = 4$ Hz, H_2), 7.69–7.75 (1H, m, H_4), 8.70 (1H, s, N-H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): (ppm) 91.8 (C , C_3), 112.1 (CH_2 , C_7), 113.4 (SCN), 117.8 (CH_2 , C_5), 122.1 (CH_2 , C_6), 122.9 (CH_2 , C_4), 128.2 (C , C_{3a}), 131.1 (CH_2 , C_2), 135.8 (C , C_{7a}).

MS (70eV, EI): m/z (%) = 174 [M^+], 141, 121, 136 91, 77.

Yields: 92% (With $\text{SiO}_2\text{-HClO}_4$), 85% (With $\text{SiO}_2\text{-KHSO}_4$).

(12) 1-Methyl 3-Thiocyanato 1H-indole:



MP: 74–78°C.

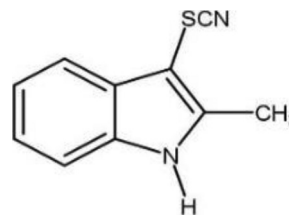
IR (cm^{-1} , KBr): 666, 758, 1245, 1516, 2152, 2925, 2948.

$^1\text{H-NMR}$ (250 MHz, $\text{DMSO-}d_6$): (ppm) 3.36 (3H, s, CH_3), 7.25–7.35 (2H, m, C_5 , C_6), 7.59 (1H, d, $J = 7.6$ Hz, C_4), 7.67 (1H, d, $J = 7.3$ Hz, C_7), 7.98 (1H, s, H_2).

$^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$): (ppm) 33.3 (C , C_3), 88.4 (CH_2 , C_7), 111.5 (CH_2 , C_5), 112.8 (SCN), 118.4 (CH_2 , C_6), 121.9 (CH_2 , C_4), 123.7 (CH_3 , C_1), 128.6 (C , C_{3a}), 137.1 (CH_2 , C_2), 137.3 (C , C_{7a}).

Yields: 85% (With $\text{SiO}_2\text{-HClO}_4$), 76% (With $\text{SiO}_2\text{-KHSO}_4$).

(13) 2-Methyl 3-Thiocyanato 1H-indole:



MP: 97–100°C.

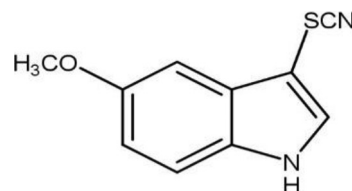
IR (cm^{-1} , KBr): 656, 744, 1235, 1298, 1406, 2153, 3328.

$^1\text{H-NMR}$ (250 MHz, CDCl_3): (ppm) 2.54 (3H, s, CH_3), 7.15–7.20 (2H, m, C_5 , C_6), 7.40 (1H, t, C_4), 7.55 (1H, t, C_7), 11.95 (1H, s, N-H).

$^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$): (ppm) 12.1 (C , C_3), 87.4 (CH_2 , C_7), 112.5 (CH_2 , C_5), 112.5 (SCN), 118.1 (CH_2 , C_6), 121.4 (CH_2 , C_4), 122.7 (CH_3), 128.6 (C , C_{3a}), 136.1 (C , C_2), 143.3 (C , C_{7a}).

Yields: 86% (With $\text{SiO}_2\text{-HClO}_4$), 84% (With $\text{SiO}_2\text{-KHSO}_4$).

(14) 5-Methoxy 3-Thiocyanato 1H-indole:



MP: 120–125°C.

IR (cm^{-1} , KBr): 623, 710, 804, 921, 1238, 1292, 1456, 1488, 2155, 3138, 3293.

$^1\text{H-NMR}$ (250 MHz, CDCl_3): (ppm) 3.88 (3H, s, CH_3), 6.94 (1H, d, $J = 10$ Hz, H_6), 7.17 (1H, s, H_4), 7.25 (1H, d, $J = 10$ Hz, H_7), 7.41 (1H, s, H_2), 8.30 (1H, s, brs, N-H).

$^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$): (ppm) 55.5 (C , C_3), 89.4 (CH_2 , C_7), 99.9 (CH_2 , C_6), 112.9 (SCN), 113.5 (C , C_5), 114.4 (CH_2 , C_4), 128.8 (OCH_3), 131.5 (C , C_{3a}), 133.8 (CH_2 , C_2), 155.2 (C , C_{7a}).

Yields: 88% (With $\text{SiO}_2\text{-HClO}_4$), 84% (With $\text{SiO}_2\text{-KHSO}_4$).

4. CONCLUSION

We have revealed here thiocyanation of aromatic and heteroaromatic compounds with NH_4SCN by utilizing $\text{SiO}_2\text{-HClO}_4$ and $\text{SiO}_2\text{-KHSO}_4$ (silica upheld Bronsted acids) impetuses under reflux and ultrasonically helped conditions. High item yields and shortening of response times are the major advantages of these protocols.

5. CONFLICTS OF INTEREST

All the authors declare that they do not have any conflicts of interest.

6. ACKNOWLEDGMENTS

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