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Original Research article

Silica-supported HClO_4 and KHSO_4 as reusable green catalysts for sulfonation of aromatic compounds under solvent-free conditions

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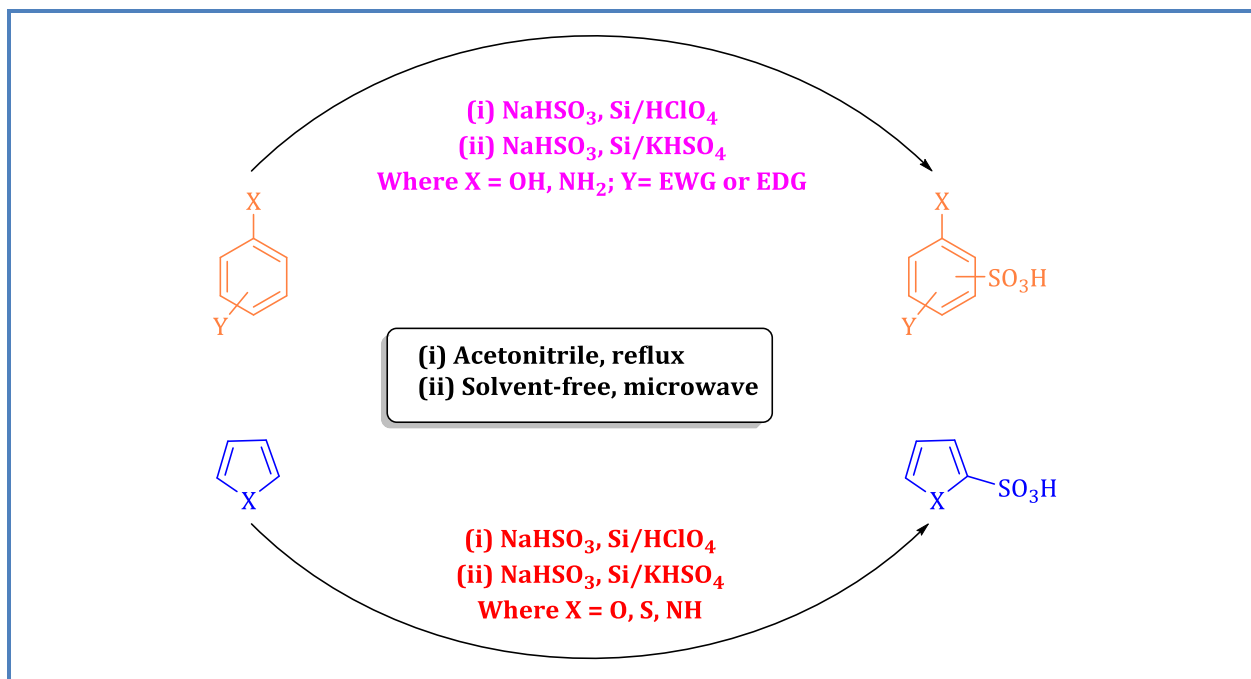
Sulfonation

Aromatic compounds

ABSTRACT

A green protocol is described for sulfonation of aromatic compounds that has been accomplished using sodium bisulfite (NaHSO_3) in the presence of reusable green heterogeneous $\text{SiO}_2/\text{HClO}_4$ and $\text{SiO}_2/\text{KHSO}_4$ (Silica-supported HClO_4 and KHSO_4 catalysts) under conventional and solvent-free microwave irradiation. The reactions afforded very good yields of products within 3 to 5 hour under conventional conditions. However, the reaction times in microwave-assisted protocol are drastically reduced to 3 to 5 minutes (from 3 to 5 hour under conventional conditions) followed by increasing product yields. Moreover, the developed silica-supported catalysts could be recycled for at least three to four times.

Graphical Abstract



Introduction

For over 150 years, electrophilic aromatic substitution reactions such as sulfonation of aromatic compounds [1-12] received the attention of synthetic chemists because many of the sulfonated aromatic are useful reactive intermediates to prepare pesticides, pharmaceuticals, polymers and several industrial products. Sulfonation is the introduction of sulfonic acid group ($-\text{SO}_3\text{H}$) or SO_3 electrophile into an aromatic entity. Sulfonation of aromatic hydrocarbons is generally achieved by using sulfuric acid, sulfur trioxide, or chloro sulfuric acid [12]. Besides these, sulfonation could also be achieved by the reaction of organic halogen compounds with inorganic sulfites; and the oxidation of thiols, disulfides, and certain classes of organic sulfur compounds [13]. A perusal of literature shows that Brønsted acids and bases could also be used as catalysts in a number of electrophilic aromatic substitution reactions, but some of these catalysts are toxic, volatile, expensive, hazardous, and difficult to handle. Laboratory drains of such hazardous acids and bases cause environmental pollution.

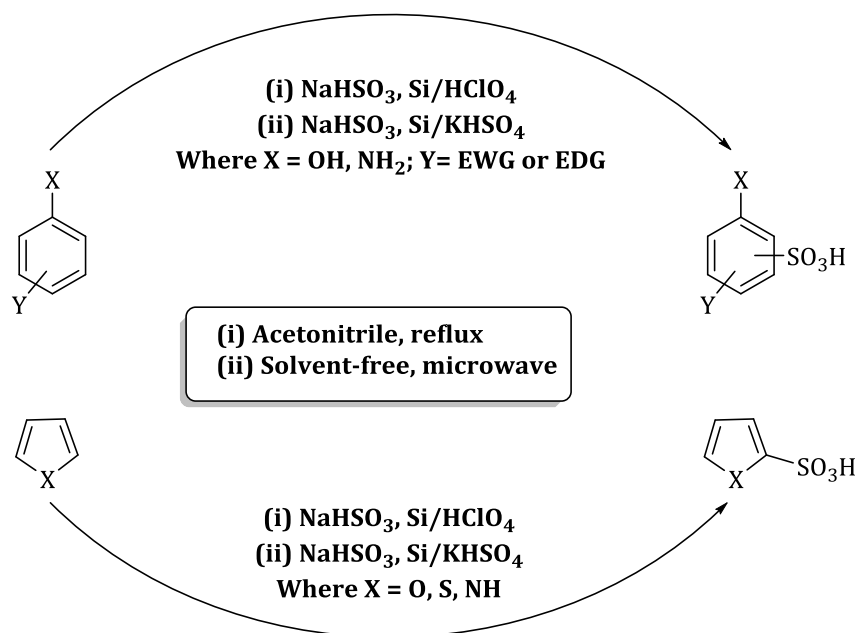
In recent past, several aluminium and silica-supported acid catalysts are developed to overcome these issues, which afforded better yields and productivity in comparison to conventional protocols [14-24], because solid supported catalysts possess high surface, long catalytic life, environment-friendliness, and provide good to excellent yields with simple work-up procedure.

We have recently explored silica supported HClO_4 and KHSO_4 materials as reusable green catalysts for thiocyanation of aromatic compounds under conventional and solvent-free microwave assisted conditions [24]. Stimulated by the noteworthy advantages of silica-supported catalysts, we have embarked on exploring silica supported HClO_4 and KHSO_4 as an efficient catalysts for sulfonation of aromatic compounds in the present study (Schem 1).

Experimental

Matreials and methods

Chemicals used in this study are reagent grade, which are purchased from Aldrich, SD-fine chemicals Avra, and used as such. Thin layer chromatography (TLC) experiments were carried out using Merck aluminum-backed 0.2 mm silica gel 60 F-254 plates. Merck silica gel 60 (230-400 mesh) was used to perform Column chromatography. Microwave-assisted (MWA) reactions were performed in a bench mate model microwave oven (CEM-908010, bench mate model, 300W laboratory microwave reactor) was used in this study. Method of the preparation, and characterization of Silica supported catalysts ($\text{SiO}_2/\text{KHSO}_4$ and $\text{SiO}_2/\text{HClO}_4$) is the same as reported in our recent publication [24].



Scheme 1. Sulfonation of aromatic compounds using $\text{SiO}_2/\text{HClO}_4$ and $\text{SiO}_2/\text{KHSO}_4$ catalysts
Sulfonation of aromatics using $\text{SiO}_2/\text{KHSO}_4$ under conventional reflux conditions

The catalyst (0.30 g of $\text{SiO}_2/\text{KHSO}_4$ or $\text{SiO}_2/\text{HClO}_4$) was added to the mixture of aromatic compound (10 mmol), NaHSO_3 and acetonitrile, were taken in a previously cleaned round bottom

flask and stirred under reflux conditions. The progress of the reaction was monitored by TLC. After the completion of the reaction, the catalyst was separated and the reaction mixture was treated with NaHCO_3 solution, followed by the addition of ethyl acetate. The organic layer was separated, dried over Na_2SO_4 and evaporated under vacuum, purified with column chromatography to get pure product. The products of the reactions are characterized by spectroscopic methods.

Microwave-assisted sulfonation of aromatics under solvent-free conditions

For aromatic sulfonation, the contents such as aromatic compound (10 mmol), NaHSO_3 and optimum quantity (0.30 g) of the catalyst ($\text{SiO}_2/\text{KHSO}_4$ or $\text{SiO}_2/\text{HClO}_4$) were taken in a previously cleaned beaker, mixed thoroughly and placed in micro-wave oven. The progress of the reaction was monitored by TLC. After the completion of reaction, the reaction mixture was filtered and is treated with NaHCO_3 solution and followed the same procedure as mentioned above.

Results and discussion

In order to optimize the reaction conditions, sulfonation was carried out with varied concentrations of silica-supported catalyst, and the results are presented in Table 1. The data compiled in Table 1 revealed that optimum quantity of $\text{SiO}_2/\text{HClO}_4$ catalyst for nitration reaction is 0.2 g whereas $\text{SiO}_2/\text{KHSO}_4$ catalyst is 0.25 g. Further increase of catalyst amount did not appreciably affect the yield of the product. The conversion yields of the nitration of phenol presented in Table 1 also indicate that the best results are obtained with $\text{SiO}_2/\text{HClO}_4$ over $\text{SiO}_2/\text{KHSO}_4$ catalyst. This is because HClO_4 is a stronger acid than KHSO_4 (Perchloric acid is a superacid with $\text{pK}_a = -10.0$ to 15.0 , while pK_a of $\text{HSO}_4^- = 1.8$); and it is also a stronger acid than either sulfuric ($\text{pK}_a = -10.0$ from sulfuric to bisulfuric) or nitric acid ($\text{pK}_a = -2.0$). Thus, HClO_4 provides strong acidity with minimal interference because perchlorate is weakly nucleophile, whereas KHSO_4 creates an acidic environment due to the complete protolysis of the ion HSO_4^- . Acidity (pK_a) of both HSO_4^- and HSO_3^- is almost equal to one another ($\text{pK}_a = 1.8$). Bisulfite (HSO_3^-) is the conjugate base of sulfurous acid, H_2SO_3 :



^{17}O NMR spectroscopy provided evidence that solutions of sulfurous acid and protonated sulfites contains a mixture of isomers, which is in equilibrium:

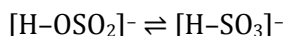


Table 1. Effect of Catalyst and on the sulfonation of aromatic compounds

Entry	SiO ₂ /HClO ₄		SiO ₂ /KHSO ₄	
	Amount of catalyst (g)	Yield (%)	Amount of catalyst (g)	Yield (%)
1	0.1	50	0.1	45
2	0.15	70	0.15	62
3	0.20	87	0.20	68
4	0.25	94	0.25	75
5	0.3	95	0.3	80
6	-	-	0.4	81

Data presented in Table 2 show that benzene did not undergo sulfonation, but other substituted benzenes underwent sulfonation smoothly in 2 to 4 hours, under conventional heating followed by constant stirring), and afforded corresponding sulfonic acids as ascertained by spectroscopic studies. Sulfonation of toluene (Table 1, entry 1) gave 4-methyl benzene sulfonic acid as major part, (o:m:p ratio: 10:0:90) with isolated 90% yield. However, all the other aromatic hydrocarbons (Table 2, entries: 2-11) afforded only para derivatives. In an attempt to avoid refluxing the reaction mixtures at elevated temperatures, we have carried out the experiments under microwave irradiation, using an a microwave oven.

Reaction times in microwave-assisted reactions are at least four to eight times less than conventional thermal method followed by substantial increase of product yields. It is interesting to note that the sulfonation of toluene under sonication not only reduced the reaction time but also the para derivative (4-methyl benzene sulfonic acid; Table 2, entry 1) is further increased (o:m:p) ratio from (10:0:90) to (5:0:95) with isolated yield from 90% to 95%. In all the other cases (Table 2, entries 2-11), the product yield is largely increased from 2 to 5%. Inspired by the green chemistry principles [25, 26], we have conducted the reactions under microwave irradiation.

Observed dramatic rate accelerations in microwave assisted reactions could be attributed to bulk activation of molecules due to direct thermal and uniform heating during course of microwave irradiation [27-31], as explained in earlier literature reports (Table 3).

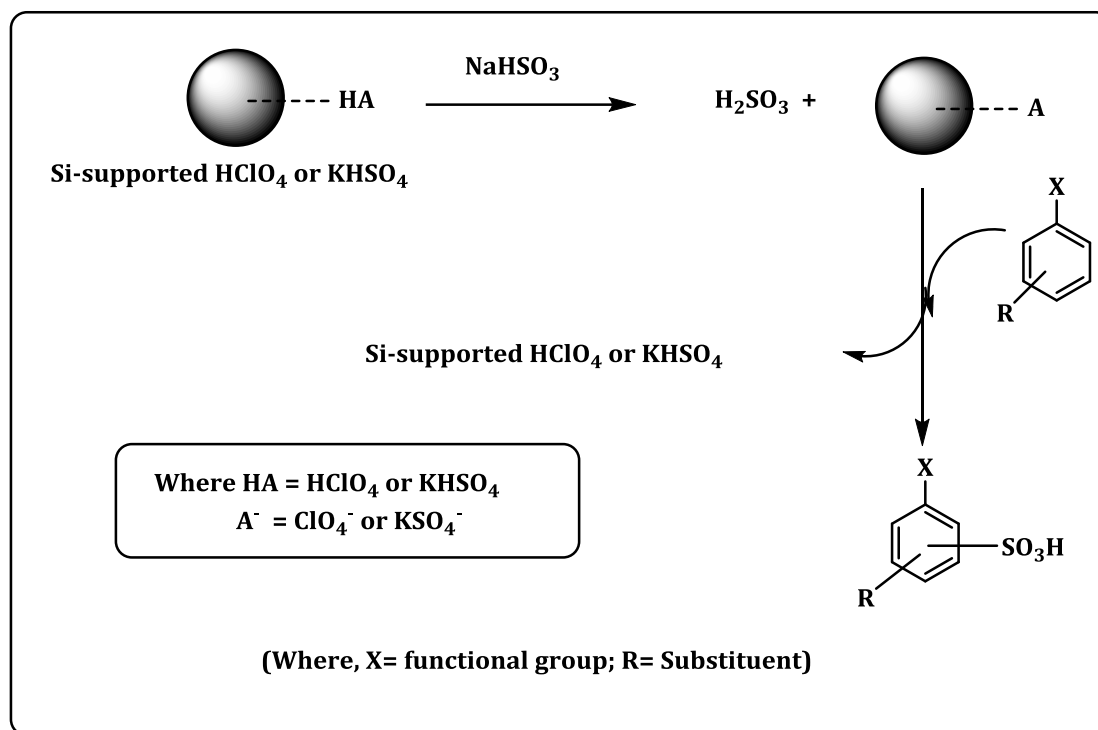
Mechanism of silica-supported KHSO₄ and HClO₄ induced sulfonation could be explained by considering their interaction with NaHSO₃ in the first step to give sulfurous acid (H₂SO₃). In the second step, π -electron enriched aromatic hydrocarbon captures bisulphite (HSO₃)⁺ electrophile from sulfuric acid to afford aryl sulfonic acids, favored by soft-soft interactions between electrophile (a soft acid) and aromatic hydrocarbon (a soft base) as shown in Scheme 2.

Table 2. Sulfonation of aromatic compounds in presence of $\text{SiO}_2/\text{HClO}_4$ catalyst

Entry	Substrate	Product	Conventional		Microwave	
			R. T (h)	Yield (%)	R. T (min)	Yield (%)
1	Phenol	4-hydroxybenzene sulfonic acid	3	79	2	74
2	Aniline	4-aminobenzene sulfonic acid	2.5	81	3	87
3	Anisole	4- methoxybenzene sulfonic acid	2	74	1	79
4	Quinol	2,5 dihydroxybenzene sulfonic acid	1.5	68	2	72
5	<i>p</i> -nitro phenol	5-hydroxy 2-nitrobenzene sulfonic acid	2	80	4	93
6	<i>p</i> -amino phenol	2-amino 5-hydroxybenzene sulfonic acid	3	76	3	81
7	<i>p</i> -cresol	5-hydroxy 2-methylbenzene sulfonic acid	2.5	71	2	71
8	Catechol	3,4-dihydroxybenzene sulfonic acid	2	78	2	93
9	m-Chloro phenol	2-chloro 4-hydroxybenzene sulfonic acid	3	66	3	76
10	Chloro benzene	2-chloro 4-hydroxybenzene sulfonic acid	3.5	65	4	73
11	Toluene	4-methyl benzene sulfonic acid	3	68	3	75
12	Indole	1H-indole-4-sulfonic acid	4	76	2	84
13	Pyrrole	1H-pyrrole-4-sulfonic acid	3.5	71	2	86
14	Furan	Furan-2-sulfonic acid	2.5	79	3	87

Table 3. Sulfonation of aromatic compounds in presence of $\text{SiO}_2/\text{KHSO}_4$ catalyst

Entry	Substrate	Product	Conventional		Microwave	
			R. T (h)	Yield (%)	R. T (min)	Yield (%)
1	Phenol	4-hydroxybenzene sulfonic acid	4	69	3	71
2	Aniline	4-aminobenzene sulfonic acid	5	73	5	77
3	Anisole	4- methoxybenzene sulfonic acid	3.5	61	4	76
4	Quinol	2,5 dihydroxybenzene sulfonic acid	4	59	4	62
5	<i>p</i> -nitro phenol	5-hydroxy 2-nitrobenzene sulfonic acid	3.5	78	1	59
6	<i>p</i> -amino phenol	2-amino 5-hydroxybenzene sulfonic acid	4.5	77	4	84
7	<i>p</i> -cresol	5-hydroxy 2-methylbenzene sulfonic acid	2.5	55	3	68
8	Catechol	3,4-dihydroxybenzene sulfonic acid	3.5	88	5	83
9	m-Chloro phenol	2-chloro 4-hydroxybenzene sulfonic acid	4	56	4	61
10	Chloro benzene	2-chloro 4-hydroxybenzene sulfonic acid	3.5	70	4	78
11	Toluene	4-methyl benzene sulfonic acid	3	68	3	75
12	Indole	1H-indole-4-sulfonic acid	2.5	69	5	73
13	Pyrrole	1H-pyrrole-4-sulfonic acid	3.5	68	4	71
14	Furan	Furan-2-sulfonic acid	5.0	73	2	69



Scheme 2. Mechanism of sulfonation of aromatic

To examine the reusability of the catalysts (SiO₂/HClO₄ and SiO₂/KHSO₄) after completion of the reaction, the catalysts were separated from the reaction mixture by simple filtration, treated with ethyl acetate, and dried. The catalyst thus obtained was reused under otherwise similar conditions (same set of experimental conditions were used in initially) and used again to corroborate the results obtained earlier. The recycled catalysts were found to be active up to four or five cycles, with a slight reduction of catalytic activity.

Conclusion

In summary, in the present work, we have developed 2, 4, 6-trichloro-1, 3, and 5-triazine / KHSO₄ (TCTA-KHSO₄) reagent for selective sulfonation of aromatic hydrocarbons under conventional reflux conditions with continuous stirring. Typical supports include various kinds of carbon, alumina, and silica. The support is generally inert and does not participate in the catalytic reactions. Solid-supported reagents/catalysts are easily removed from reactions by filtration. After due purification, it can be recycled for another batch reactions. Thus, the supported catalysts are not only economical and efficient, but also environmentally-sound. Reagents on solid-support react differently, mostly more selectively, than their unbound counterparts. The reactions afforded very good yields of sulfonated products with good selectivity.

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