Solvent free Mortar-Pestle assisted Grinding (A Green) technique for the synthesis of aryl sulfonic acids with Sodium bisulfite using silica adsorbed HClO$_4$ and KHSO$_4$ as Catalysts.

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Abstract:
Aromatic and heteroaromatic compounds have been sulfonated with NaHSO$_3$ in presence of silica adsorbed Perchloric acid (HClO$_4$), and Potassium bisulfate (KHSO$_4$). Under conventional solvothermal and solvent free Mortar-Pestle grinding technique, these reactions provide their respective sulfonic acids as products in better yields within 2.5-4 hr. (HClO$_4$), 3.5-5 hr. (KHSO$_4$) in conventional solvothermal conditions. However, in the Mortar-Pestle grinding technique reaction times are strangely reduced to 8-10 min. (HClO$_4$), 9-12 min. (KHSO$_4$), and products yields also increased. Additionally, silica adsorbed perchloric acid, potassium bi sulfite catalysts could be re-used for at least three or four cycles.
Key Words: *Synthesis of aryl sulfonic acids; NaHSO$_3$; Silica adsorbed Perchloric acid, and Silica adsorbed Potassium bisulfate; Efficient green grind stone technique.*
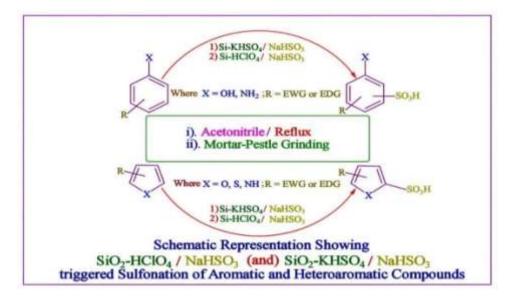

I.Introduction

Synthesis of aryl sulfonic acids is an organic reaction in which a -SO$_3$H$^+$ electrophile can replace a hydrogen atom on arene system [1]. The sulfonationofaromatic and heteroaromaticcompounds [2-13] has receivedhighattentionbecausemanyofthesulfonated aromatics and heteroaromaticshave been using asreactiveintermediates for the manufacturing ofpesticides,pharmaceuticals,polymersandseveralindustrialproducts.Sulfonationofaromatichydrocarbonsisgenerallyachievedbyusingsulfuricacid,sulfurtrioxide,orchlorosulfuricacid[13]. Among several sulfonating agents' H$_2$SO$_4$14, 15], oleumH$_2$S$_2$O$_7$ [16, 17] and SO$_3$ [18] are being used widely, but some of them have high reactivity and toxicity level therefore they cause to polymer chain degradation during the reaction. More diacids are formed in the presence of H$_2$S$_2$O$_7$ than the presence of H$_2$SO$_4$. Due to the high aggressiveness of SO3 (sulfonating agent) electrophile all the organic compounds with electron donating group are rapidly undergoes reaction with SO3. The sulfonation with SO$_3$ is rapid and highly exothermic therefore, it is very difficult to perform the sulfonation reactions using SO$_3$ as sulfonating agent on an industrial scale. Aperusalofliterature showsthatBronstedacidsandbasescouldalsobeusedascatalystsinanumberof (EAS)electrophilic aromatic substitution reactions, but few of them were also hazardous, volatile, toxic, expensive, and also difficult to perform the reactions with these catalysts. Laboratory biproducts and wastages of such hazardous acids and bases catalysts cause environmentalpollution. According to the recent past literature reports, to overcome these issues several silica and aluminum adsorbed acid catalysts are developed,whichaffordedbetteryieldsandproductivityincomparisontoconventional protocols [19-29], because solid supported catalysts can have long catalytic life time, consists large surface area of active sites, they can easily separate from the reaction mixture and recyclable which makes them eco-friendly, andprovidegoodtoexcellentyieldswithsimplework- upprocedure. Literaturesurvey, reveals that many electrophilic aromatic substitution protocols like thiocyanation, nitration, sulfonation, and several other reactions have been reported by using different catalysts usingmortar-pestle assisted grinding method including some recent reports from our laboratory [30-34].Silica supported Bronsted acids were explored as an efficient green and reusable catalysts for many electrophilic aromatic substitution reactions like nitration and thiocyanation, sulfonation, and several other reactions under different reaction conditions such as conventional-reflux conditions, microwave assisted conditions, ultrasonic sound assisted conditions[35-38].However, silica supportedBronsted acids such as SiO$_2$-KHSO$_4$, SiO$_2$-HClO$_4$ have not been explored as heterogeneous reusable

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green catalysts so far for Sulfonation reactions under Mortar-Pestle grinding conditions. Recently we have explored silica adsorbed $HClO_4$ and $KHSO_4$ as reusable catalysts for thiocyanation of aromatic compounds under variousconditions [24]. Encouraged by striking applications of aryl sulfonic acids, silica-supportedcatalysts. And to make these reactions completely as greenery we have explored silica adsorbed Perchloric acid and Silica adsorbed Potassium bi sulfate as an efficient catalysts for synthesis of aryl sulfonic acids using mortar-pestle assisted grinding methods. In the present study (Scheme 1). The reactions under solvent free mortar-pestle assisted grinding are substantially decreases the reaction times and also increases the reaction yields.

Scheme 1: SiO_2-$KHSO_4$, SiO_2-$HClO_4$/$NaHSO_3$ mediated Synthesis of Aryl sulfonic acids under solvothermal and solvent free Mortar-Pestle assisted grinding conditions.

II. Experimental

All chemicals and solvents used in this work were purchased from Avra Chemicals, Aldrich, Merck, which were used without further purification.

2.1 General Procedure for the Preparation of SiO_2-$HClO_4$, and SiO_2-$KHSO_4$ Catalysts

To an aqueous solution of 20 mmol (25mL) $HClO_4$ /$KHSO_4$, (4 g, 100–200 mesh) silica gel was added and stirred continuously for about 30 to 40 minutes a room temperature to ensure adsorption of $HClO_4$/$KHSO_4$ on to the grains of silica gel (SiO_2). Resultant powder was separated under vacuum, and dried for about 3hr. at 120^oC to get crystalline powder, which was characterized by XRD, scanning electron microscopy (SEM), methods. Figure-2 shows adsorption of acids on Silica surface.
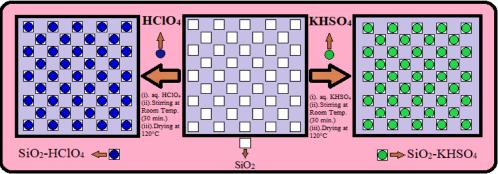

Figure-1: Schematic Representation of Preparation of SiO_2-$HClO_4$, SiO_2-$KHSO_4$ Catalysts.

2.3 General Procedure for the Preparation of Aryl Sulfonic acids Using SiO₂-HClO₄, SiO₂-KHSO₄ Catalysts under Conventional RefluxMethod

The optimum amounts of catalysts (SiO₂-HClO₄, SiO₂-KHSO₄) and 10 mmol aromatic compounds, NaHSO₃ (10 mmol) and 25ml of acetonitrile, were received into aclean RBF and stirred under reflux until the response is completed. Which is indicated by TLC. After the complete conversion, the SiO₂-HClO₄, SiO₂-KHSO₄ Catalysts war isolated by simple filtration, and then the remaining reaction mixture was quenched with water and then neutralized with NaHCO₃ solution, afterward added with Ethyl acetate. Then organic layer was isolated by using separating funnel, dried over Na₂SO₄, purified with column chromatography, using suitable eluent and concentrated under vacuum to obtain the final product.

2.4 General procedure for the Preparation of Aryl Sulfonic acids Using SiO₂-HClO₄, SiO₂-KHSO₄ Catalysts under Mortar-Pestle grinding assisted Method

Catalytic amounts of SiO₂-HClO₄, SiO₂-KHSO₄ (0.01mol percentage), electrophile generating agent (0.1 mol NaHSO₃), (0.1 mol) aromatic or heteroaromatic compound are received into a cleaned mortar and subjected to grinding without using any reaction media or solvent. Progress of the reaction is monitored with TLC. When the response is completed, as shown by TLC, the resulting products were isolated from the response mixture according to the procedure, as given in preceding sections. Rate enhancements in Mortar-Pestle grinding assisted reactions are explained as due to the conversion of mechanical/kinetic energy (exerted due to grinding) into thermal energy, which becomes driving force for bulk activation of reactive species.
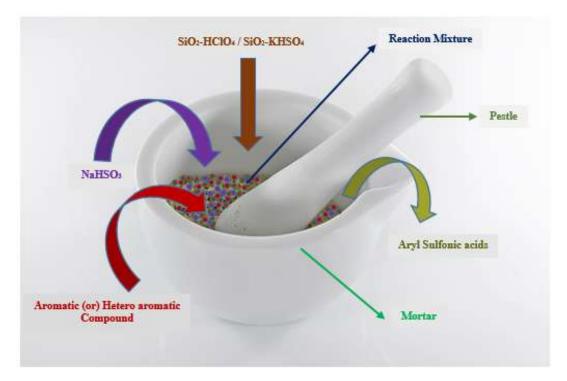

Figure-2: Mortar-Pestle Assisted Synthesis of Aryl sulfonic acids in presence of SiO₂-HClO₄ and SiO₂-KHSO₄ catalysts.

III. Results and Discussion
3.1 SEM (Scanning Electron Microscopy), and Powder XRD (Powder X-Ray Diffraction)-Analysis of SiO₂-HClO₄, SiO₂-KHSO₄ Catalysts
The as prepared catalyst was examined with different analytical methods like Scanning Electron Microscopy (SEM) using different magnifications their corresponding SEM images were shown in blow as figure 3, 4. And

these catalysts has also examined with powder X-Ray diffraction their corresponding XRD-patterns were shown in figure 5, 6.
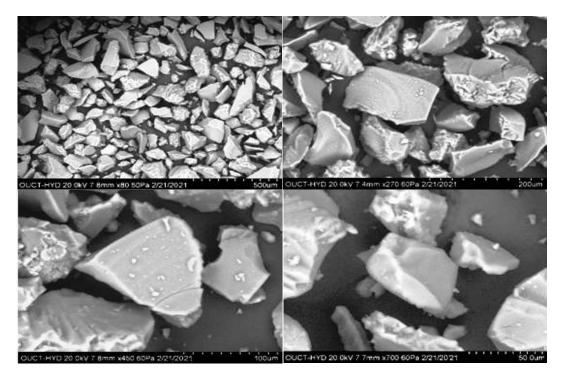

Figure-3: SEM images, and morphology of SiO_2-$HClO_4$ catalyst under different magnifications.
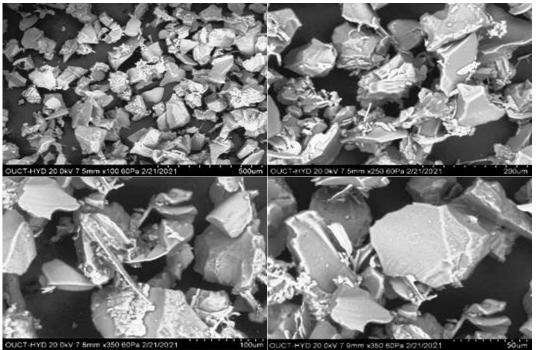

Figure-4: SEM images, and morphology of SiO_2-$KHSO_4$ catalyst under different magnifications.

Morphology recorded in the SEM images (Fig. 3 for SiO_2-$HClO_4$, and Fig. 4 for SiO_2-$KHSO_4$) clearly depicted that no-uniform polynomial cubic crystals, and flakes are spread over on the Silica surface. More so, the magnification under 50 μm (in Fig. 3 and Fig. 5) magnification depicted non-uniform flakes and polynomial cubic crystals of nano grain acid species are spread over the layers. These results are similar to the earlier findings of Zeba Siddiqui [29], and also by our research group in earlier publications.

3.2 Optimization of catalyst

Initially for the optimization of quantities of SiO_2-$KHSO_4$, and SiO_2-$HClO_4$ catalysts for sulfonation reactions, authors have done sulfonation by taking phenol as a representative substrate with $NaHSO_3$ in the presence and absence of SiO_2-$HClO_4$, and SiO_2-$KHSO_4$ catalysts using mortar-pestle grinding method under solvent free conditions. Sulfonation did not occur with $NaHSO_3$ alone in the absence of SiO_2-$HClO_4$, and SiO_2-$KHSO_4$ catalysts. Good yields are observed with 0.30 gm SiO_2-$HClO_4$/$NaHSO_3$ and 0.35 gm SiO_2-$KHSO_4$/$NaHSO_3$ (Table 1). These results reveal that SiO_2-$HClO_4$, is better catalyst over SiO_2-HSO_4, because $HClO_4$ is stronger protic acid than $KHSO_4$. According to the literature reports potassium bi sulphate ($KHSO_4$) is a weak acidic salt, here the acidic environment generated by the protolysis of HSO_4^- ion. But perchloric ($HClO_4$) acid (p^{Ka} = -15 to -10) is a stronger protic acid than (HNO_3) nitric acid, and (H_2SO_4) sulfuric acid, due to a minimal interference of weaker ClO_4^- nucleophile.

Table-1: Optimization of Catalyst for Sulfonation of Phenol

Entry	SiO_2-$HClO_4$		SiO_2-$KHSO_4$	
	Quantity of reagent (gm)	Yield (%)	Quantity of reagent (gm)	Yield (%)
1	0.10	48	0.10	44
2	0.15	65	0.15	60
3	0.20	79	0.20	66
4	0.25	85	0.25	75
5	0.30	90	0.30	78
6	0.35	90	0.35	80

3.3 Reusability of catalyst

It is of interest to note that both the catalysts (SiO_2-$HClO_4$, and SiO_2-$KHSO_4$) could be recycled with a slight reduction in the yield of products. Once the first batch of reaction is completed, the catalyst is filtered from the reaction mixture, treated with ethyl acetate to remove organic traces, and concentrated by using a hot air oven at 120^oC up to two to three hours. The as-activated catalyst is reused for another batch of experiments. Similar procedure is adopted for four to five cycles to reusability of the catalyst, and related observations are compiled shown in **table -2.**

Table-2: Reusability of SiO_2-$HClO_4$, SiO_2-$KHSO_4$ catalysts in Mortar-Pestle Grinding assisted synthesis of aryl sulfonic acids at room temperature.

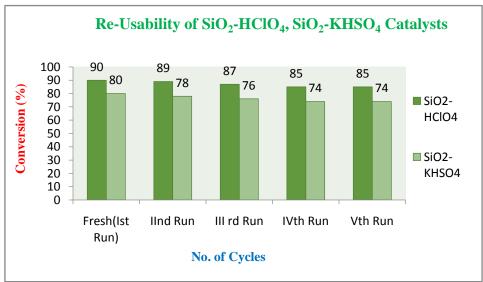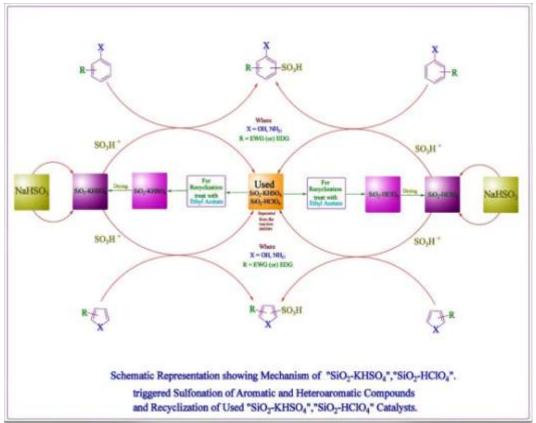| Reused cycle	SiO_2-$HClO_4$		SiO_2-$KHSO_4$	
	R. T. (min)	Yield (%)	R. T. (min)	Yield (%)
Fresh (I[st] run)	15	90	17	80
IInd run	17	89	18	78
IIIrd run	18	87	19	76
IVth run	19	85	19	74
V[th] run	20	85	20	74

Figure-5: Bar diagram for recyclability SiO$_2$-HClO$_4$ and SiO$_2$-KHSO$_4$ catalysts (Phenol).

Scheme-2: SiO$_2$-KHSO$_4$, SiO$_2$-HClO$_4$ / NaHSO$_3$ mediated Synthesis of aryl sulfonic acids under solvothermal and solvent free mortar-Pestle grinding assisted conditions. And Recyclization of used Catalyst.

After the optimization catalyst we have taken up the synthesis of certain aryl sulfonic acids with optimum quantities of both catalysts under conventional, mortar-pestle grinding assisted methods. The observed outputs of the current study are here in compiled in tables 2, and 3.

Table-3: Synthesis of aryl sulfonic acids with NaHSO₃ using SiO2-HClO₄ Catalyst**.**

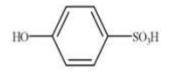| Entry	Substrate	Product	Salvo-Thermal assisted		Mortar-Pestle Grinding	
			R. T. (hr.)	Yield (%)	R. T. (min.)	Yield (%)
1	Phenol	4-hydroxybenzene sulfonic acid	2.5	91	8	90
2	Catechol	3,5-di hydroxybenzene sulfonic acid	2.5	74	10	76
3	4-Nitro phenol	5-hydroxy 2-nitrobenzene sulfonic acid	3	88	10	85
4	Cl-Benzene	4-chlorobenzene sulfonic acid	3.5	78	9	79
5	Br-Benzene	4-bromobenzene sulfonic acid	3	69	8	70
6	Anisole	4-methoxybenzene sulfonic acid	2.5	75	8	75
7	2-methylphenol	4-hydroxy 3-meythylbenzene sulfonic acid	2.5	74	10	75
8	3-methylphenol	4-hydroxy 2-methylbenzene sulfonic acid	3.5	75	9	77
9	4-methylphenol	2-hydroxy 5-methylbenzene sulfonic acid	3	74	9	75
10	Aniline	4-aminobenzene sulfonic acid	3	80	8	78
11	Toluene	4-methylbenzene sulfonic acid	4	69	9	72
12	2-Toludine	4-amino 5-methylbenzene sulfonic acid	2.5	76	10	75
13	4-Toludine	2-amino 5-methylbenzene sulfonic acid	2.5	78	8	79
14	Furan	Furan 2-sulfonic acid	3	80	9	80
15	1H-Pyrrole	Pyrrole 4-sulfonic acid	3.5	70	8	75

Table-4: Synthesis of aryl sulfonic acids with NaHSO₃ using SiO₂-KHSO₄ Catalyst.

Entry	Substrate	Product	Salvo-Thermal assisted		Mortar-Pestle Grinding	
			R. T. (hr.)	Yield (%)	R. T. (min.)	Yield (%)
1	Phenol	4-hydroxybenzene sulfonic acid	3.5	82	10	80
2	Catechol	3,5-di hydroxybenzene sulfonic acid	4	77	10	79
3	4-Nitro phenol	5-hydroxy 2-nitrobenzene sulfonic acid	4	75	10	77
4	Cl-Benzene	4-chlorobenzene sulfonic acid	4.5	76	12	75
5	Br-Benzene	4-bromobenzene sulfonic acid	4	65	9	66
6	Anisole	4-methoxybenzene sulfonic acid	4	73	9	73
7	2-methylphenol	4-hydroxy 3-meythylbenzene sulfonic acid	4	70	10	72
8	3-methylphenol	4-hydroxy 2-methylbenzene sulfonic acid	4	73	9	75
9	4-methylphenol	2-hydroxy 5-methylbenzene sulfonic acid	3.5	72	9	74
10	Aniline	4-aminobenzene sulfonic acid	4	76	9	76
11	Toluene	4-methylbenzene sulfonic acid	4	65	9	67
12	2-Toludine	4-amino 5-methylbenzene sulfonic acid	3.5	73	10	75
13	4-Toludine	2-amino 5-methylbenzene sulfonic acid	4	74	10	75
14	Furan	Furan 2-sulfonic acid	4	77	9	78
15	1H-Pyrrole	Pyrrole 4-sulfonic acid	4	65	10	70

The resulting product yields are fairly good. Additionally, the reaction rate enhancements were observed and reaction times were also substantially decreased with mortar-pestle grinding assisted reactions. These enhanced reaction rates accelerations explained suitably caused by the bulk activation of reactive species, during the grinding of the reactants in a mortar with a pestle kinetic energy converted to very high localized heat(thermal) energy This causes bulk activation of reactive species compared to conventional methods.The resulted products were detected by spectroscopic methods, such as ^{1}HNMR, and C[13]NMR. The products obtained are comparable to earlier reported results in the literature, spectroscopic data for some of the products obtained has given below.
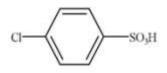
3.4 Spectral Data of CertainCompounds

1. 4-Hydroxy Benzene Sulfonic Acid:

^{1}H-NMR (DMSO-d₆):δ (ppm) 7.23 (dd, J = 6.5 Hz, J = 1.5 Hz, 1H), 7.27(dd, J = 8.0 Hz, J = 2.0 Hz, 1H), 7.78(dd, J = 7.5 Hz, J = 9.0 Hz, 1H), 7.94(dd, J = 7.5 Hz, J = 2.0 Hz, 1H), 10.05(s, 1H, OH);
*^{13}C-NMR (DMSO-d₆):δ (ppm)*157.98, 135.87, 126.88, 113.90.

Yields:
With SiO_2- $HClO_4$ = 91 %(Conventional), 90 %(Mortar-Pestle),
With SiO_2-$KHSO_4$= 82 %(Conventional), 80 %(Mortar-Pestle).
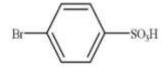
2. *4-ChloroBenzeneSulfonicAcid:*

^1H- NMR   (DMSO-d_6):δ   (ppm)   8.68(dd,J=8.0Hz,J=1.0Hz,   1H),7.79(dd,J=   7.5Hz,J=1.0Hz, 1H),7.86(dd,J=7.5Hz,J=1.0 Hz, 1H);
^{13}C-NMR (DMSO-d_6):δ (ppm)141.89, 138.02, 129.70, 128.06.
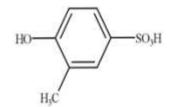*Yields:*
With SiO_2- $HClO_4$ = 78 %(Conventional), 79 %(Mortar-Pestle),
With SiO_2-$KHSO_4$= 76 %(Conventional), 75 %(Mortar-Pestle).

3. *4-Bromo Benzene Sulfonic Acid:*

^1H NMR (DMSO-d_6):δ (ppm)7.55 (dd, J = 7.5, Hz J = 0.5 Hz, 1H), 7.65 (dd, J = 8.0 Hz, J = 0.5 Hz, 1H), 7.73 (dd, J = 7.5 Hz, J = 0.5 Hz, 1H), 7.85(dd, J = 8.0 Hz, J = 0.5Hz, 1H);
^{13}C NMR (DMSO-d_6):δ (ppm)138.77, 134.96, 129.95, 128.03.
Yields:
With SiO_2- $HClO_4$ = 69 %(Conventional), 70 %(Mortar-Pestle),
With SiO_2-$KHSO_4$= 65 %(Conventional), 66 %(Mortar-Pestle).
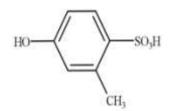
4. *4-Hydroxy-3-methylbenzenesulfonic Acid:*

^1HNMR (DMSO-d_6):δ (ppm)3.01(s, 3H),7.04(dd,J=7.5Hz,J=1.0Hz, 1H), 7.11 (dd, J = 7.5 Hz, J = 1.5 Hz, 1H), 7.89 (dd, J = 1.5 Hz, J = 1.0 Hz, 1H);
^{13}C NMR (DMSO-d_6):δ (ppm)155.98, 135.83, 127.99, 125.04, 122.76, 114.06, 15.07.
Yields:
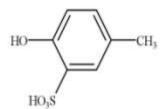With SiO_2- $HClO_4$ = 74 %(Conventional), 75 %(Mortar-Pestle),
With SiO_2-$KHSO_4$= 70 %(Conventional), 72 %(Mortar-Pestle).
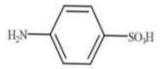
5. 4-Hydroxy-2-methylbenzenesulfonic Acid:

*^{1}HNMR (DMSO-d$_6$):δ (ppm)*2.35(s, 3H), 7.02 (dd, J = 3.0 Hz J = 1.0 Hz, 1H),7.04(dd,J=8.0Hz,J=3.0Hz, 1H), 7.96 (dd, J = 7.5 Hz, J = 1.0 Hz, 1H);
^{13}C NMR (DMSO-d$_6$):δ (ppm) 158.36, 134.28, 125.26, 128.76, 125.65, 113.92, 20.82.
Yields:
With SiO$_2$- HClO$_4$ = 75 %(Conventional), 77 %(Mortar-Pestle),
With SiO$_2$-KHSO$_4$= 73 %(Conventional), 75 %(Mortar-Pestle).

6. 2-Hydroxy-5-methylbenzenesulfonic Acid:

^{1}HNMR (DMSO-d$_6$): δ(ppm) 3.0(s, 3H),6.94(dd,J=7.5Hz,J=0.5Hz, 1H), 7.0 (dd, J = 7.5 Hz, J = 1.0 Hz, 1H), 7.75 (dd, J = 10 Hz, J = 0.5Hz, 1H);
^{13}C NMR (DMSO-d$_6$):δ(ppm) 147.25, 128.35, 126.52, 122.83, 120.35, 117.56, 18.42.
Yields:
With SiO$_2$- HClO$_4$ = 74 %(Conventional), 75 %(Mortar-Pestle),
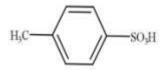With SiO$_2$-KHSO$_4$= 72 %(Conventional), 74 %(Mortar-Pestle).

7. 4-Amino Benzene Sulfonic Acid:

^{1}H NMR (DMSO-d$_6$):δ(ppm) 7.04(dd,J=8.0Hz,J=1Hz, 1H),7.21(dd,J= 7.5Hz,J=0.5Hz, 1H),7.88 (dd, J = 7.5 Hz, J = 1.0 Hz, 1H), 7.92(dd,J=7.5Hz,J=1.0 Hz, 1H), 9.68 (s, 1H, OH) 9.99 (s, 2H, NH);
*^{13}CNMR (DMSO-d$_6$):δ(ppm)*145.88, 132.05, 127.05, 121.79.
Yields:
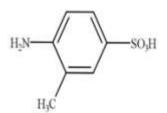With SiO$_2$- HClO$_4$ = 80 %(Conventional), 78 %(Mortar-Pestle),
With SiO$_2$-KHSO$_4$= 76 %(Conventional), 76 %(Mortar-Pestle).

8. 4-methylbenzene Sulfonic Acid:

^{1}H NMR (DMSO-d$_6$):δ(ppm) 1.68 (s, 3H), 6.59(dd,J=7.5Hz,J=0.5Hz, 1H),7.02(dd,J=7.5Hz,J=0.5Hz, 1H),7.08(dd, J = 7.5 Hz, J = 05 Hz, 1H), 7.12(dd,J=7.5Hz, J = 0.5 Hz, 1H);
*^{13}CNMR (DMSO-d$_6$)**: δ(ppm)* 142.05, 138.95, 128.90, 125.05, 19.99.
Yields:

With SiO_2- $HClO_4$ = 69 %(Conventional), 72 %(Mortar-Pestle),
With SiO_2-$KHSO_4$= 65 %(Conventional), 67 %(Mortar-Pestle).

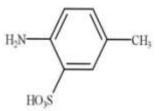### 9. 4-amino 5-methylbenzene Sulfonic Acid:

^{1}H NMR (DMSO-d_6):δ(ppm) 3.05 (s, 3H),7.09(dd,J=8.0Hz,J=0.5Hz, 1H),7.12(dd,J= 1.5 Hz J = 0.5 Hz, 1H), 7.99(dd,J=7.5Hz,J=2.0Hz, 1H);
*^{13}C NMR (DMSO-d_6):δ(ppm)*145.96, 132.06, 131.08, 127.90, 123.70, 121.90, 17.07.
Yields:
With SiO_2- $HClO_4$ = 76 %(Conventional), 75 %(Mortar-Pestle),
With SiO_2-$KHSO_4$= 73 %(Conventional), 75 %(Mortar-Pestle).

10.   2-amino 5-methylbenze Sulfonic Acid:

*^{1}H NMR (DMSO-d_6):δ(ppm)*2.89 (s, 3H), 7.09 (dd, J = 8.0 Hz, J = 0.5 Hz, 1H), 7.45 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H), 7.69 (dd, J = 1.5 Hz, J = 1.0 Hz, 1H);
*^{13}C NMR (DMSO-d_6):δ(ppm)*140.25, 138.08, 130.95, 128.10, 124.90, 123.82, 21.01.
Yields:
With SiO_2- $HClO_4$ = 78 %(Conventional), 79 %(Mortar-Pestle),
With SiO_2-$KHSO_4$= 74 %(Conventional), 75 %(Mortar-Pestle).

IV.Conclusions

Here we have evolved a simple eco-friendly methodology, for the preparation of aryl sulfonic acids from aromatic and hetero aromatic compounds, with $NaHSO_3$ using Nano grains of SiO_2-$HClO_4$, SiO_2-$KHSO_4$ as catalysts under Solvent free Mortar-Pestle Grinding assisted and conventional solvothermal methods. The evolved methodology provides various advantages those are easy to handling, rate enhancements and also increase in the reaction yields with simple work upprocedure.

References

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