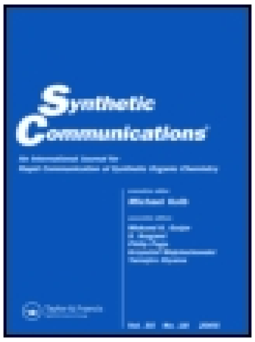

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Silica supported perchloric acid and potassium bisulphate as reusable green catalysts for nitration of aromatics under solvent free microwave conditions

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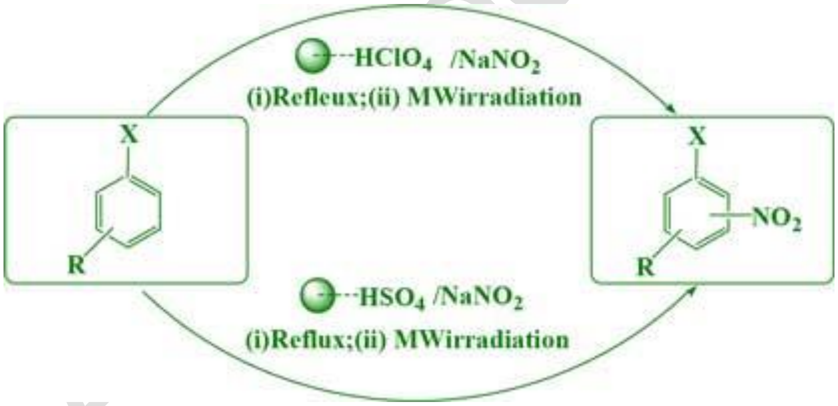
**Supplemental data (full experimental details, and spectroscopic data) are attached a separate file website

ABSTRACT

Silica supported perchloric acid and bisulfate (SiO2/HClO4 and SiO2/KHSO4) have been developed as reusable green catalysts for nitration of aromatic compounds using NaNO2in acetonitrile medium under conventional and solvent free microwave conditions. The reaction times under microwave irradiation are significantly shorter than conventional method even though the yields obtained in microwave assisted reactions are comparable with those obtained under reflux conditions.

GRAPHICAL ABSTRACT



KEYWORDS: aromatic compounds, microwave irradiation, NANO$_2$, nitration, rate acceleration, SIO$_2$/HCLO$_4$, SIO$_2$/KHSO$_4$

Introduction

Nitro aromatic compounds are important precursors for various industrial products such as pharmaceuticals, plastics and dyes. In spite of voluminous literature is reported for alternative protocols, many of the catalysts used could not be recycled. Therefore, Nitro aromatic compounds are yet, mainly produced by using mixed acid (nitric acid and sulfuric acid) for nitration.[1–3] However, this classical nitration protocol is not only hazardous, but also causes environmental pollution when the remaining (unused) nitration mixture is sent to the industry or laboratory drains. In order to eliminate and/reduce such environmental issues, there has been an upsurge in the development of environmentally safe chemistry protocols following Paul Anastas priciples.[4] Rajesh Vekariya and Hitesh Patel[5] summarized recent advances in the synthesis of nitrophenols following green chemistry approches.

On the other hand, design and synthesis of reusable heterogeneous catalysts received much more attention, because these catalysts can be removed easily by filtration and reused after completion of the reaction. This reusability makes the whole process eco-friendly, and thus plays a prominent role in organic chemistry due to environmental and economic considerations. In addition, heterogeneous and reusable catalysts are superior over homogeneous catalysts. Silica supported catalyst could be placed in the forefront because of its unique features such as high efficiency due to large surface area, high mechanical and thermal stabilities, greater selectivity, low toxicity, reusability, and simplicity of handling. Recently, potassium bisulphate immobilized on silica (SiO_2-$KHSO_4$) has been found to be an efficient, recyclable heterogeneous catalyst for synthesis of propargyl indoles.[6] Literature survey reveals that $NaHSO_4$ immobilized on silica (SiO_2-$NaHSO_4$) could also employed as efficient heterogeneous catalyst for various organic transformations.[9–16] On the other hand, silica supported perchloric acid ($SiO_2/HClO_4$) has also been accomplished as an eco-friendly heterogeneous catalyst for various types of organic reactions.[17–24] Encouraged by these features, we wish to report clean and environment friendly protocols for nitration of aromatic compounds using $NaNO_2$in presence of reusable heterogeneous green catalysts SiO_2-$HClO_4$ and SiO_2-$KHSO_4$ under reflux conditions. And we have also explored the same reactions under Microwave condition. Nevertheless, Heravi and other co-workers[25,26] recently reported the nitration of aromatic compounds using $NaNO_2$in presence of $KHSO_4$in acetonitrile medium under un-immobilized conditions.

Results and Discussion

Initially, we have prepared Si-adsorbed catalyst (SiO_2-$HClO_4$ and SiO_2-$KHSO_4$) and characterized by SEM and XRD data. As shown in Figures 1 and 2. These observations are largely similar to those reported by Zeba Siddiqui,[27] confirming the heterogeneous nature of catalysts which comprise adsorbed $KHSO_4$ and $HClO_4$ on silica. We have optimized the quantity of the prepared catalyst required for nitration reaction using phenol as a model substrate, and varied amounts of catalysts as shown in **Table 1**. Accordingly we used the optimized amount of catalyst in the conventional and microwave assisted nitration reactions. It is also important to note that no nitro product was observed in the absence of the catalyst.

The data compiled in **Table 1** revealed that optimum quantity of SiO_2-$HClO_4$ catalyst for nitration reaction is 0.2gms where as SiO_2-$KHSO_4$ catalyst is 0.25gms. 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 best results are obtained with SiO_2-$HClO_4$ over SiO_2-$KHSO_4$ catalyst because $HClO_4$ is stronger acid than $KHSO_4$ (Perchloric acid is a superacid with very low pKa, and HSO_4^- with pKa = 1.92; or $K_a = 1.2 \times 10^{-2}$).[28] 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^-. Scheme 2 shows a general conversion of aromatic compound to nitroarene.

To examine the reusability of the catalysts (SiO_2-$HClO_4$ and SiO_2-$KHSO_4$) 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 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, as shown in **Figure 3**.

Nitration of aromatic compounds proceeds smoothly with $NaNO_2$in presence of SiO_2-$HClO_4$ and SiO_2-$KHSO_4$ under reflux conditions in acetonitrile medium. Data presented in **Tables 2** and **3** clearly demonstrate that silica supported Perchloric acid is efficient over silica supported bisulfate in terms of reaction times and yields obtained. The reaction with phenol was completed in 1.5hours in presence of SiO_2-$HClO_4$ and where as 2.5hours in case of SiO_2-$KHSO_4$. In both the cases 2-nitro phenol and 4-nitro phenols were obtained as products. Similarly, other aromatic compounds (entries 2-12) provided the corresponding nitro products in good to excellent yields under similar reaction conditions. The reaction times for all the studied reactions under conventional reflux condition are in the range of 1.5hours to 3.5hours in presence of SiO_2-$HClO_4$, where as in the case of SiO_2-$KHSO_4$ is 2.5 to 5hours . The products obtained were identified by spectroscopic methods and compared with literature reports.[29] In order to decrease the reaction times and avoid the use of solvent, reactions were conducted under microwave (MW) irradiation. Reaction times reduced from 1.5-5hours (under reflux) to 1-4min in MW assisted reactions. Rate enhancements under microwave could be attributed due to bulk activation phenomenon,[29] which is achieved due to rapid heating and pressure effects. On the basis of observed results, a plausible mechanism for SiO_2-$HClO_4$ and SiO_2-$KHSO_4$ catalyzed nitration could be proposed as shown in Scheme 2. The reactions in presence of silica supported catalysts with $NaNO_2$ gives HNO_2in the first step, due to acidic nature of silica catalysts. Nitrous acid thus formed might convert to nitric acid under reflux temperature. Ultimately, NO_2 + electrophile is generated due to the reaction between HNO_3 and silica catalysts, which then interact with aromatic compound to afford nitro compound, and catalyst is regenerated as shown in mechanistic pathway of Scheme 3.

Conclusions

In summary, we have demonstrated that nitration of aromatic compounds using $NaNO_2$in presence of $SiO_2/HClO_4$ and $SiO_2/KHSO_4$ (Silica supported) catalysts proceeds smoothly under reflux and solvent free microwave conditions, with high yields, short reaction times, The chosen catalysts could be recycled easily, showing that the developed protocols could also be included as good examples of green chemistry methods and advantageous over several protocols.

Experimental Details

Preparation of $SiO_2/KHSO_4$ and $SiO_2/HClO_4$ catalysts

Silica gel (4g, 100–200 mesh) was added to a solution of $KHSO_4$ (20 mmol) in distilled water (25ml), 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 to give a powder which was dried in an oven at 120°C for 2-3hrs to afford a $SiO_2/KHSO_4$ catalyst. Procedure for the preparation of $SiO_2/HClO_4$ catalyst is same as mentioned in the previous section for the preparation of $SiO_2/KHSO_4$ catalyst.

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

Scanning electron microscopic pictures of $SiO_2/KHSO_4$ and $SiO_2/HClO_4$ catalysts (Figures 1 and 2) under different magnifications in the range of 50 to 200µm revealed non-uniform morphologies with polynomial cubic crystals and flakes embedded with grain and spike like species. XRD analysis of the samples (Figure 1d) and **Figure 2d**) probably indicate amorphous nature of the catalysts. Broad peaks 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,[27] confirming the heterogeneous nature of catalysts which comprise adsorbed $KHSO_4$ and $HClO_4$ on silica.

Nitration of aromatics using SiO2/KHSO4 under conventional conditions

The optimum amount of the catalyst (**$SiO_2/KHSO_4$** or **$SiO_2/HClO_4$)** was added to the mixture of aromatic compound (10 mmol), $NaNO_2$ (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 reaction, the catalyst was separated by filtration, and the reaction mixture is treated with $NaHCO_3$ solution, followed by the addition of ethyl acetate. Organic layer was then separated, dried over Na_2SO_4, purified with column chromatography and evaporated under vacuum to get final product. Products thus obtained were characterized spectroscopically and obtained data were confirmed with earlier reports.[30] Nitration of phenol in the present study afforded 2-NO_2 phenol as major product and 4-NO_2 phenol as minor component respectively.

2-NO_2 Phenol: (yellow crystalline solid) ^{1}HNMR (300MHz, $CDCl_3$): δ 9.52 (s, 1H, OH), 8.15 (dd, 1H, J = 8.5Hz, *J* = 8Hz), 8.12 (d, 1H, *J* = 8Hz) 7.55 (dd, 1H, *J* = 8Hz J = 7.5Hz) 6.95

(d, 1H, *J* = 8.5Hz); ^{13}C NMR (75MHz, $CDCl_3$): δ 155.2, 137.6, 133.8, 125.1, 120.2, 119.9; mp = 43-48^{o}C; HRMS (EI) Calcd. M, 139.1088, Found: 139.0272

4-NO_2 Phenol: (yellow powder), ^{1}HNMR (300MHz, $CDCl_3$): δ 9.95 (s, 1H, OH), 6.95 (d, 2H, *J* = 8Hz), 8.15 (d, 2H, *J* = 8Hz); ^{13}C NMR (75MHz, $CDCl_3$): δ 161.7, 141.3, 126.3, 115.8; mp = 111-113^{o}C; HRMS (EI) Calcd. M, 139.1086, Found: 139.0274

Microwave assisted nitration of aromatics under solvent free conditions

For the purpose of microwave assisted nitration of aromatics Aromatic compound (10 mmol), $NaNO_2$ (10 mmol) and optimum quantity of the catalyst (**$SiO_2/KHSO_4$** or **$SiO_2/HClO_4$)** 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 and is washed with $NaHCO_3$ solution. Organic layer was then separated, dried over Na_2SO_4, purified with column chromatography and evaporated under vacuum to get final product as mentioned above.

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Venkateswarlu, M.; Venkanna, P.; Saiprakash, P. K. *Synth. Comm.* 2015, *45*, 251–2258; (e) Srinivas, P.; Rajanna, K. C.; Satish Kumar, M.; Rajendar Reddy, K. *Synth. React. Inorg. Metal-Org. Nano-Met. Chem.* 2014, 44, 364–370.

Table 1. Catalyst optimization for nitration of Phenol.

Entry	Phenol (mmol)	Amount of catalyst (gms)			
		SiO2-HClO4	Yield (%)	SiO2-KHSO4	Yield (%)
1	10	0.1	50	0.1	48
2	10	0.15	65	0.15	58
3	10	0.20	91	0.20	67
4	10	0.25	92	0.25	76
5	10	0.3	92	0.3	76
6	10	–	–	0.4	77

Table 2. Nitration of aromatic compounds in presence of SiO2/HClO4 catalyst.

S. No	Substrate	Product	Conventional		Microwave	
			R. T (hrs)	Yield (%)	R. T (min)	Yield (%)
1	Phenol	2- NO2:4- NO2 Phenol	1.5	75:16	1	78:20
2	β- Napthol	1-NO2-2-naphthol	3	82	2	90
3	Anisole	4- NO2:2- NO2 Anisole	2	74:15	2	85:12
4	Toulene	4- NO2:2- NO2 Toulene	2	70:20	1	82:15
5	p-Cresol	4-Me-2-NO2 Phenol	1.5	82	2	94
6	o-Cresol	2-Me-4-NO2 Phenol	2.5	76	2	85
7	Chloro benzene	4- NO2:2- NO2 Cl benzene	3	65:18	2	72:18
8	Indole	3-NO2 Indole	2.5	80	1	92
9	Napthalene	2-NO2:1-NO2Napthalene	3	64:15	2	72:16
10	Benzoic acid	3- NO2 Benzoic acid	3.5	72	2	80
11	Thiophene	2-NO2 Thiophene	3	74	2	85
12	Furan	2- NO2 furan	2	75	2	82

Table 3. Nitration of aromatic compounds in presence of SiO2/KHSO4 catalyst.

S. No	Substrate	Product	Conventional		Microwave	
			R. T (hrs)	Yield (%)	R. T (min)	Yield (%)
1	Phenol	2- NO2:4- NO2 Phenol	2.5	64:12	2	68:15
2	β- Napthol	1-NO2-2-naphthol	5	62	4	70
3	Anisole	4- NO2:2- NO2 Anisole	3	65:15	4	70:16
4	Toulene	4- NO2:2- NO2 Toulene	3	58:20	2	60:22
5	p-Cresol	4-Me-2-NO2 Phenol	3	75	3	82
6	o-Cresol	2-Me-4-NO2 Phenol	3.5	70	3	74
7	Chloro benzene	4- NO2:2- NO2 Cl benzene	4	54:15	3	62:18
8	Indole	3-NO2 Indole	2.5	78	2	85
9	Napthalene	2-NO2:1-NO2Napthalene	4	50:16	3	62:15
10	Benzoic acid	3- NO2 Benzoic acid	4	68	4	75
11	Thiophene	2-NO2 Thiophene	3.5	65	4	70
12	Furan	2- NO2 furan	3	70	3	75

Figure 1. (a) SEM of *Si-KHSO4* with 100μm magnification. (b): XRD analysis of SiO2/ KHSO4 catalyst.

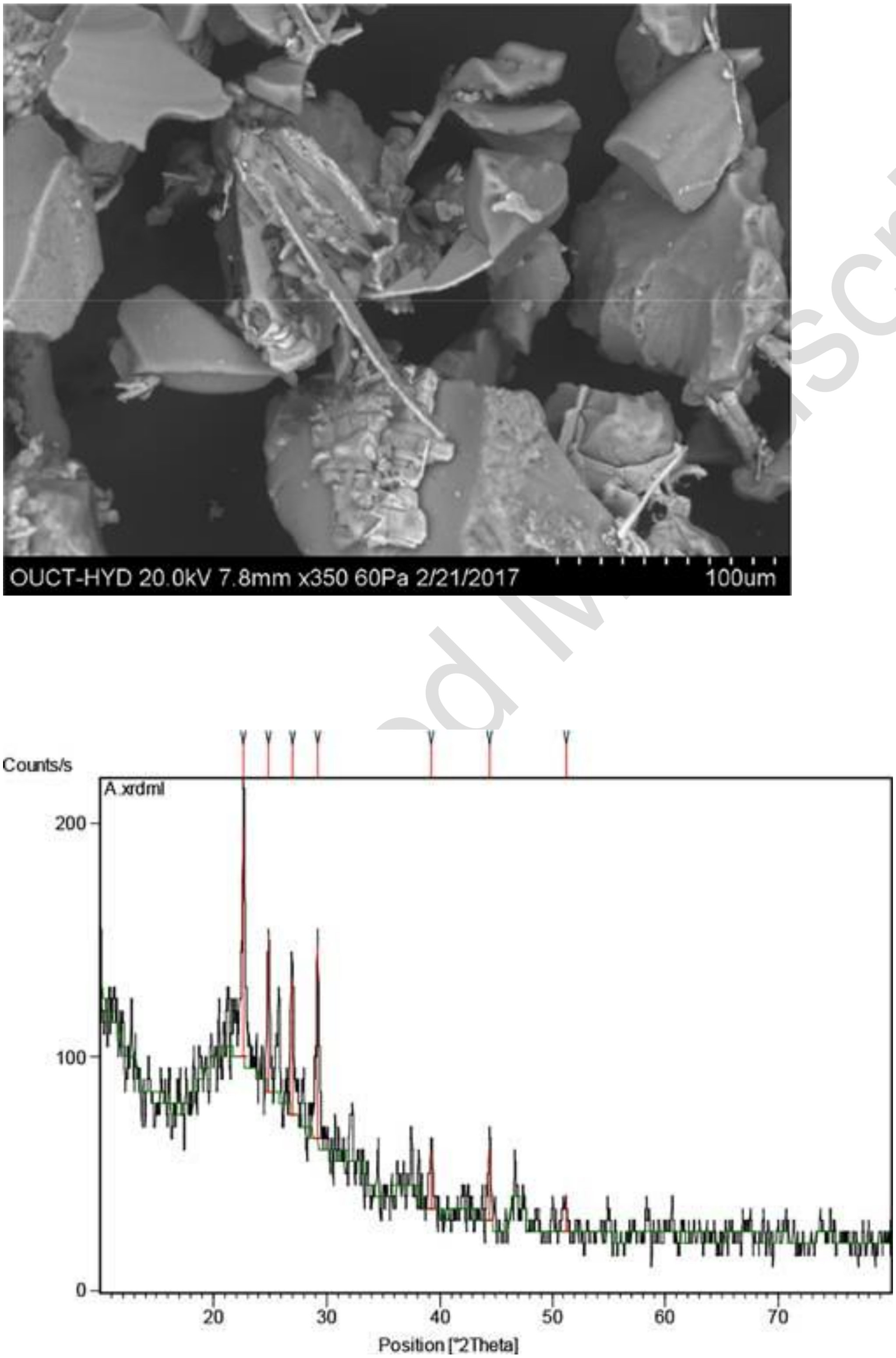


Figure 2 (a): SEM of *Si-HClO4* with 100μm magnification. (b): XRD analysis of Si-HClO4 catalyst.

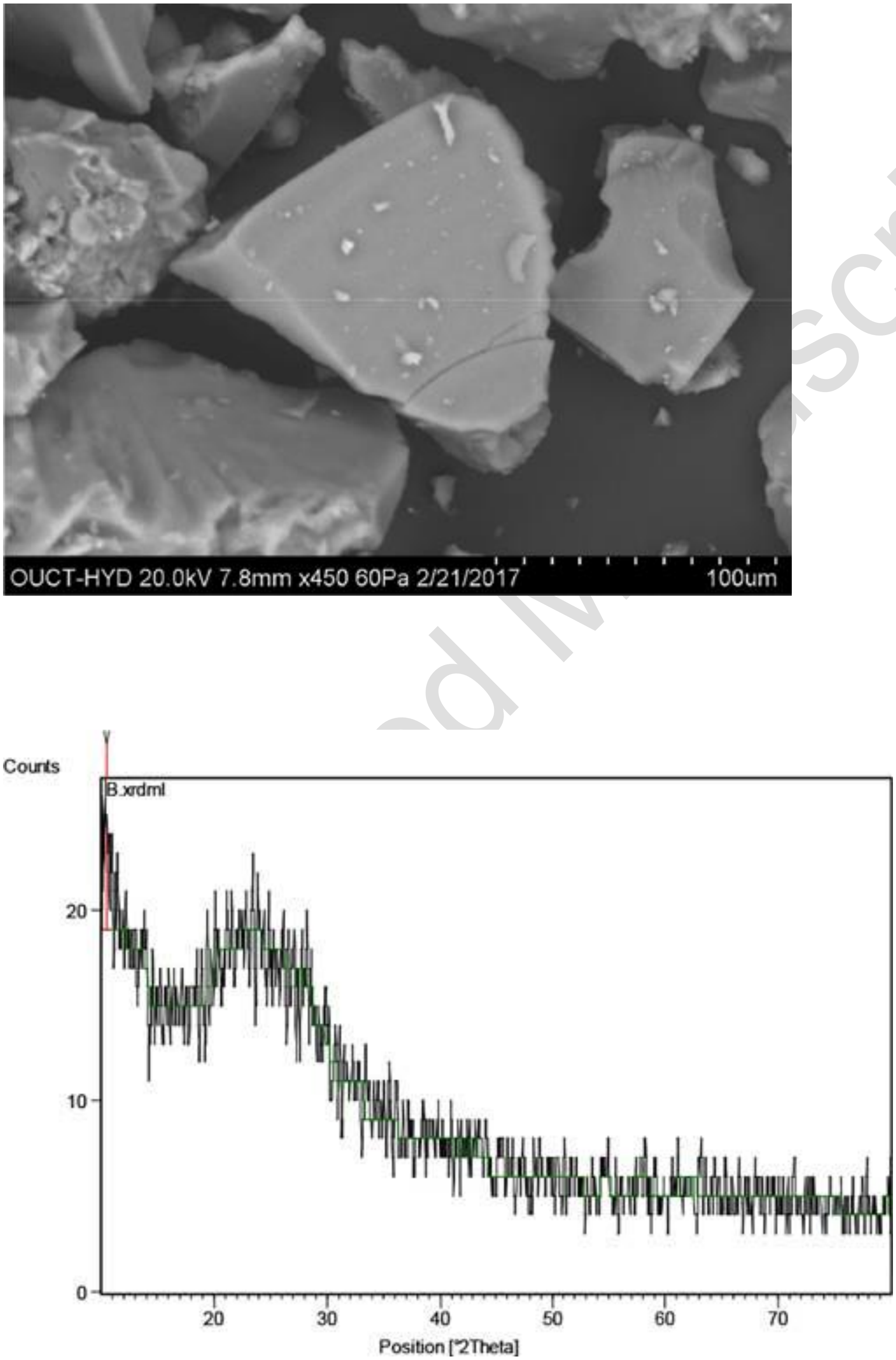
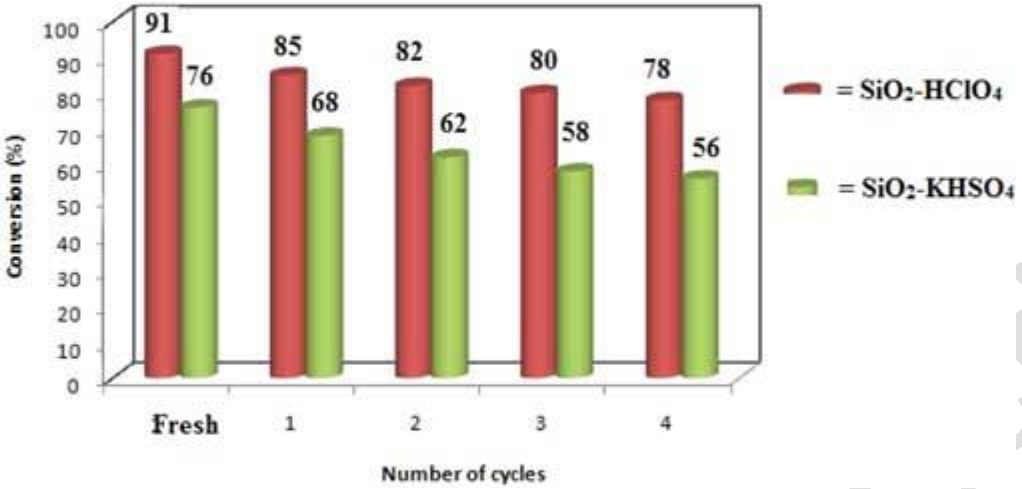
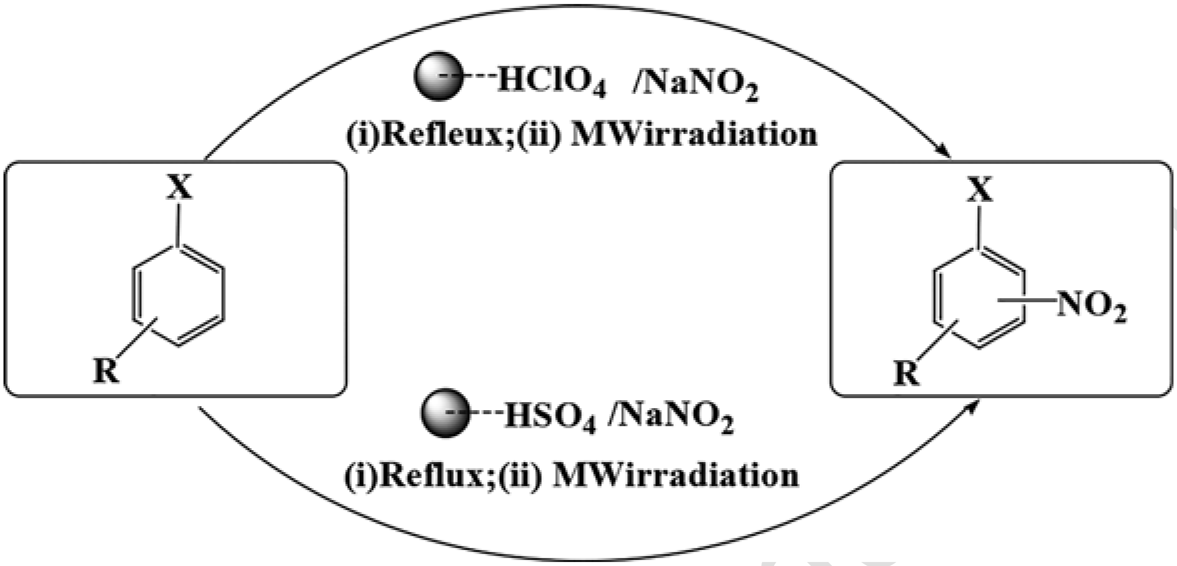


Figure 3. Bar diagram for recyclability SiO2-HClO4 and SiO2-KHSO4 catalysts.



Scheme 1. Nitration of aromatic compounds using Si-supported HClO4 and KHSO4 as catalysts in presence of NaNO2.



Scheme 2. Adsorption of HClO4 and KHSO4 on SiO2 to get SiO2-HClO4 and SiO2-KHSO4.

Scheme 3. Mechanism of nitration in presence of SiO2-HClO4 and SiO2-KHSO4.