



Solvent-Free Synthesis of 1,2,4,5-Tetrasubstituted Imidazoles Using Nano $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-OSO}_3\text{H}$ as a Stable and Magnetically Recyclable Heterogeneous Catalyst

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ABSTRACT

Nano- Fe_3O_4 encapsulated-silica particles bearing sulfonic acid groups ($\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-OSO}_3\text{H}$) has been used as an efficient and magnetically separable heterogeneous catalyst for the synthesis of 1,2,4,5-tetrasubstituted imidazoles by one-pot, four-component reaction of benzil, aromatic aldehydes, primary amines, and ammonium acetate under neat conditions. The effect of various reaction parameters, such as reaction temperature, catalyst loading and solvent effect, were studied. The desired products are obtained in relatively short reaction times with high yields. Importantly, the catalyst could be easily separated from the reaction mixture by a permanent magnet and reused for several times without the significant loss of its activity.

Key words: $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-OSO}_3\text{H}$, Magnetically separable, Solvent-free conditions, 1,2,4,5-Tetrasubstituted imidazoles.

INTRODUCTION

In synthetic organic chemistry, the one-pot multicomponent reaction (MCR) strategy has become a powerful tool to improve the efficiency of a reaction wherein a reactant is subjected to successive chemical reactions in one vessel. This process consists of two or more synthesis steps which are carried out without isolation of any intermediate. The overall advantages of this strategy involve: i) use of commercially available starting

materials; ii) avoiding a lengthy separation of the intermediates; iii) saving time and resources; iv) achieving increase in the chemical yield¹⁻³. The development of new MCRs and improvement of known MCRs are therefore areas of considerable current interest. One such reaction is the synthesis of 1,2,4,5-tetrasubstituted imidazoles. The imidazole ring system is one of the most important substructure found in a large number of natural products and pharmacologically active compounds^{4,5}. Different substituted imidazoles

show variable biological activities such as antibacterial, anti-allergic, anti-inflammatory, antitumor analgesic, glucagon receptor antagonism therapeutic agents, and pesticides⁶⁻⁹. Also, some of them are known as inhibitors of P38 MAP¹⁰ kinase and B Raf kinase¹¹. Recent advances in green chemistry and organometallic catalysis has extended the application of imidazoles as ionic liquids¹²⁻¹⁴ and N-heterocyclic carbenes¹⁵.

Numerous methods for the synthesis of 1,2,4,5-tetrasubstituted imidazoles have been reported. They can be accessed by cyclization of α -(N-acyl-N-alkylamino- α -ketoamides in refluxing AcOH¹⁶, hetero-Cope rearrangement¹⁷, condensation of a 1,2-diketone with an aryl nitrile and primary amine under microwave irradiation¹⁸, and N-alkylation of trisubstituted imidazoles¹⁹. Another direct method involves a four-component condensation of 1,2-diketones or α hydroxyketones with aldehydes, primary amines, and ammonium acetate in the presence of a catalyst such as TFA in ionic liquid [Bpy]BF₄²⁰, montmorillonite K10 supported titanium²¹, L-proline²², InCl₃·3H₂O²³, BF₃·SiO₂²⁴, Brønsted acidic ionic liquid²⁵, carbon-based solid acid²⁶, K₅CoW₁₂O₄₀·3H₂O²⁷, *p*-dodecylbenzene sulfonic acid²⁸, FeCl₃/montmorillonite K10 under microwave irradiation²⁹, NH₄H₂PO₄/Al₂O₃³⁰, NaHSO₄/SiO₂³¹, and H₆P₂W₁₈O₆₂·24H₂O/SiO₂³². Each of these methods has its own merit, however, all of the reported methods (except for the reaction catalyzed by FeCl₃/montmorillonite K10 under microwave irradiation) require relatively prolonged reaction time. Also, some of these catalysts are expensive or having other problems like requirement of solvents for synthesis, and low yields of the products. Furthermore, the synthesis using homogeneous catalysts have major problem of catalyst recovery and reuse. To avoid these limitations, the discovery of a new and efficient catalyst with high catalytic activity, short reaction time, recyclability, and simple reaction work-up for the synthesis of 1,2,4,5-tetrasubstituted imidazoles is of prime interest.

In recent years economic and environmental concerns encourage the application of heterogeneous catalysts to carry out various organic transformations³³⁻³⁶. These catalysts make the processes clean, safe, high-yielding and

inexpensive. In recent years, the use of heterogeneous nanocatalysts have been receiving growing attention, because they have high catalytic activities due to their large specific surface area^{37,38}. Recently, nano-Fe₃O₄ encapsulated-silica particles bearing sulfonic acid groups (Fe₃O₄@SiO₂-OSO₃H) have been prepared and used as an efficient acid catalyst in some organic reactions³⁹⁻⁴². They can be readily separated from the reaction mixture by a permanent magnet and reused several times. The process is more effective than filtration and centrifugation in preventing loss of the solid catalyst. However, there are no reports on the use of Fe₃O₄@SiO₂-OSO₃H as an acidic heterogeneous catalyst for the synthesis of 1,2,4,5-tetrasubstituted imidazoles.

As a consequence of our interest in developing new efficient synthetic methodologies⁴³⁻⁴⁷ for the synthesis of bioactive molecules and owing to the biological significance of 1,2,4,5-tetrasubstituted imidazoles, we wish to report herein a solvent-free synthesis of 1,2,4,5-tetrasubstituted imidazoles catalyzed by Fe₃O₄@SiO₂-OSO₃H, as a green and effective magnetically recyclable heterogeneous catalyst (Scheme 1).

EXPERIMENTAL

All chemicals were available commercially and used without additional purification. The melting points were recorded using a Stuart SMP3 melting point apparatus. The IR spectra of the products were obtained with KBr disks, using a Tensor 27 Bruker spectrophotometer. The ¹H NMR (400 & 500 MHz) spectra were recorded using Bruker 400 & 500 spectrometers.

General Procedure for the Synthesis of 1,2,4,5-Tetrasubstituted Imidazoles 5a-m Using Fe₃O₄@SiO₂-OSO₃H as Catalyst

A mixture of benzil **1** (1 mmol), an aromatic aldehyde **2** (1 mmol), a primary amine **3** (1 mmol), ammonium acetate **4** (1 mmol), and Fe₃O₄@SiO₂-OSO₃H (0.10 g) was heated in the oil bath at 130 °C for 15-60 min. The reaction was monitored by thin-layer chromatography (TLC). Upon completion, hot ethanol was added to the reaction mixture and the catalyst was separated using an external magnet (Fig 1.). The catalyst was washed with a small portion

of hot ethanol (10 mL). The combined filtrate was concentrated by half and allowed to stand at r.t.. The precipitated solid was collected by filtration, and recrystallized from ethanol 96% to give compounds **5a-m** in high yields.

RESULTS AND DISCUSSION

For our investigations, the catalyst $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$ was prepared according to the literature procedure^{39,40}. The FT-IR spectrum of the catalyst (Fig. 2a) exhibits the Fe-O vibration^{39,40} at 587 cm^{-1} . The bands at 1091 cm^{-1} , 797 cm^{-1} and 463 cm^{-1} were attributed to the Si-O-Si asymmetric and symmetric stretching vibrations as well as bending vibration, respectively⁴⁰. The spectrum also shows the SO_2 symmetric and asymmetric stretching modes in $1100\text{-}1250\text{ cm}^{-1}$ that were covered by a stronger absorption of Si-O bond^{40,43} at 1091 cm^{-1} . Also, the absorption band at 1637 cm^{-1} and the broad band at around $3000\text{-}3700\text{ cm}^{-1}$ were

attributed to stretching vibration of the adsorbed water^{40,41}. The density of the SO_3H groups was measured using KOH (0.01 mol L^{-1}) as titrant by acid-base potentiometric titration. The amount of SO_3H in the catalyst was 1.5 mmol/g .

In the effort to develop an efficient and environmentally benign method for synthesis of 1,2,4,5-tetrasubstituted imidazoles we initiated our studies by adding a catalytic amount of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$ to a mixture of benzil (1 mmol), benzaldehyde (1 mmol), aniline (1 mmol), and ammonium acetate (1 mmol), as model reaction, in different solvents and under solvent-free conditions (Table 1). We were pleased to see that the reaction was efficiently catalyzed by $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$ under solvent-free conditions at elevated temperature leading to a high yield of product **5a**. The reaction conditions were then optimized by conducting the reaction at different temperatures and using different amounts of catalyst. The results

Table 1: Synthesis of compound 5a in the presence of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$ catalyst under different reaction conditions

Entry	Catalyst (g)	Solvent	T (°C)	Time (min)	Isolated yield (%)
1	-	-	130	120	22
2	0.02	-	110	80	56
3	0.02	-	130	70	59
4	0.04	-	110	80	61
5	0.04	-	130	70	67
6	0.06	-	110	80	73
7	0.06	-	130	60	83
8	0.06	-	150	60	84
9	0.08	-	110	70	78
10	0.08	-	130	60	88
11	0.08	-	150	60	88
12	0.10	-	110	60	89
13	0.10	-	130	50	94
14	0.10	-	150	60	93
15	0.12	-	130	50	93
16	0.10	$\text{CH}_3\text{CH}_2\text{OH}$	Reflux	180	30
17	0.10	CH_3OH	Reflux	180	22
18	0.10	H_2O	Reflux	180	16
19	0.10	CH_3CN	Reflux	180	15
20	0.10	CHCl_3	Reflux	180	18
21	0.10	$\text{CH}_3\text{CO}_2\text{Et}$	Reflux	180	12

Reaction conditions: benzil (1 mmol), benzaldehyde (1 mmol), aniline (1 mmol), ammonium acetate (1 mmol).

are summarized in Table 1. Low yield of the product was obtained in the absence of the catalyst at 130 °C after 120 min (entry 1) indicating that the catalyst is necessary for the reaction. The best result was

obtained when the reaction was run at 130 °C in the presence of 0.10 g $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$ under solvent-free conditions (entry 13).

Table 2: $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$ catalyzed synthesis 1,2,4,5-tetra substituted imidazoles 5a-m under the optimized conditions

Entry	R	Ar	Product	Time (min)	Isolated yield (%)	Melting point (°C)	
						Found	Reported
1	C_6H_5	C_6H_5	5a	50	94	217-219	216-218 ²⁴
2	C_6H_5	4-Cl C_6H_4	5b	25	95	150-152	149-151 ²⁴
3	C_6H_5	4-Me C_6H_4	5c	50	89	189-191	189-190 ³⁰
4	C_6H_5	4- $\text{O}_2\text{NC}_6\text{H}_4$	5d	20	97	190-192	192-194 ²⁸
5	C_6H_5	2-thienyl	5e	15	95	240-242	248-250 ²⁹
6	$\text{C}_6\text{H}_5\text{CH}_2$	4-Br C_6H_4	5f	60	87	174-176	172-175 ³⁰
7	$\text{C}_6\text{H}_5\text{CH}_2$	4-Cl C_6H_4	5g	60	88	161-162	162-165 ²⁴
8	$\text{C}_6\text{H}_5\text{CH}_2$	4-Me C_6H_4	5h	45	92	166-168	167-168 ²²
9	$\text{C}_6\text{H}_5\text{CH}_2$	4-MeOC C_6H_4	5i	60	87	160-162	161-162 ³⁰
10	4-Cl C_6H_4	4-Cl C_6H_4	5j	40	92	190-193	187-189 ²⁷
11	4-Me C_6H_4	4-Me C_6H_4	5k	55	91	190-192	188-191 ²⁷
12	Me	4-Br C_6H_4	5l	60	87	203-205	202-203 ³⁰
13	Me	4-Me C_6H_4	5m	60	88	223-225	222-223 ²²

Reaction conditions: benzil 1 (1 mmol), aromatic aldehyde 2 (1 mmol), primary amine 3 (1 mmol), ammonium acetate 4 (1 mmol), $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$ (0.10 g), 130 °C, solvent-free.

Table 3: Comparison of the efficiencies of various catalysts for the synthesis of 1,2,4,5-tetrasubstituted imidazoles

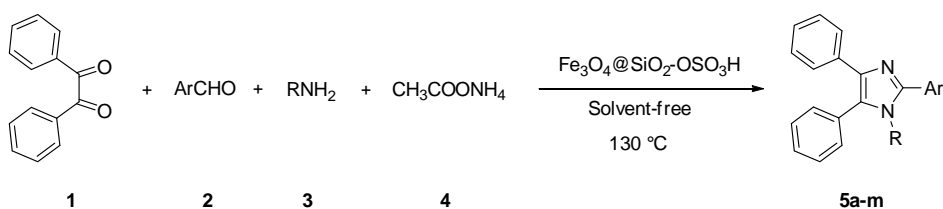
Catalyst	Conditions			Time (min)	Yield (%)	Ref.
	Solvent	T/°C	Other			
TFA	[Bpy]BF ₄	80	-	90-180	56-90	20
Montmorillonite K10 supported titanium	-	120	-	120-240	68-84	21
L-Proline	MeOH	reflux	-	510-600	76-88	22
InCl ₃ ·3H ₂ O	MeOH	r.t.	-	360-540	49-84	23
BF ₃ ·SiO ₂	-	140	-	120	80-93	24
Brønsted acidic ionic liquid	-	140	-	120-150	85-95	25
Carbon-based solid acid	-	130	-	60-120	86-94	26
K ₅ CoW ₁₂ O ₄₀ ·3H ₂ O	-	140	-	120-150	80-95	27
<i>p</i> -Dodecylbenzenesulfonic acid	H ₂ O	reflux	-	240	73-86	28
FeCl ₃ /montmorillonite K10	-	80	MW	3-4	78-89	29
NH ₄ H ₂ PO ₄ /Al ₂ O ₃	-	130	-	90-180	80-91	30
NaHSO ₄ /SiO ₂	-	140	-	120	85-92	31
H ₆ P ₂ W ₁₈ O ₆₂ ·24H ₂ O/SiO ₂	-	140	-	120	82-91	32
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$	-	130	-	15-60	87-97	this work

Using these optimized reaction conditions, and in order to evaluate the generality of this model reaction, we extended the reaction of benzil and ammonium acetate with a range of other aromatic aldehydes and primary amines (Table 2). As shown, in all cases, the expected products were obtained in high yields over relatively short reaction times. Easy separation of obtained products from the catalyst makes this method useful for the synthesis of 1,2,4,5-tetrasubstituted imidazoles.

In order to know the catalytic efficiency of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$, the data reported in the literature for the synthesis of 1,2,4,5-tetrasubstituted imidazoles using different type of the catalysts was compared with $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$. As shown in Table 3, our reaction conditions gave a shorter

reaction time than all the other conditions (except for the reaction catalyzed by $\text{FeCl}_3/\text{montmorillonite K10}$ under microwave irradiation) and gave high yields of the desired products with very simple work-up procedure.

In view of environmental friendly methodologies, recovery and reuse of the catalyst is highly preferable. Upon completion of the reaction, hot ethanol was added and the catalyst was recovered from the reaction mixture simply by applying an external permanent magnet. The recovered catalyst was washed with hot ethanol and then dried under vacuum at 50°C for 1 h before being reused in the same reaction. The catalyst could be used at least five times with only slight reduction in the catalytic activity. The yields



Scheme 1: $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$ catalyzed synthesis of 1,2,4,5-tetrasubstituted imidazoles



Fig. 1: The reaction mixture in the synthesis of 5a after adding hot ethanol in the presence of a magnetic field

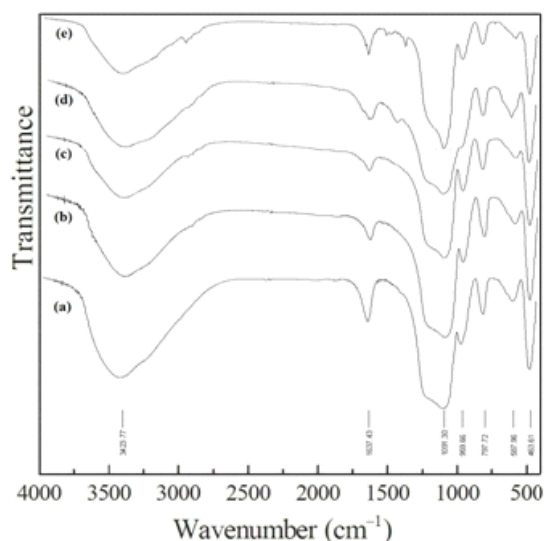


Fig. 2: FT-IR spectra of fresh catalyst $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-OSO}_3\text{H}$ (a, first run), and recovered catalysts (b-e, second to fifth run, respectively) for synthesis of compound 5a in model reaction

obtained were from 94, 93, 93, 91 and 90% in the first, second, third, fourth and fifth run respectively. Furthermore, retention of the structure of the catalyst was confirmed by comparing the FT-IR spectra of the recovered catalysts (Fig. 2b-e) with that of the fresh catalyst (Fig. 2a), for model reaction. As shown, these spectra are almost identical.

CONCLUSION

In summary, in this paper a highly efficient, neat and green method with a simple work-up procedure for the synthesis of 1,2,4,5-tetrasubstituted imidazoles via one-pot, four-component reaction of benzil, aromatic aldehydes, primary amines, and ammonium acetate has been

reported. The catalyst could be readily recovered using a simple external magnet and reused several times without any significant loss in activity. Other attractive features of this protocol are high yields, relatively short reaction times, avoiding the use of harmful organic solvents in the reaction and reusability of the catalyst. The catalyst can be used at least five times without substantial reduction in its catalytic activity.

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