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Nanosized $Mn(acac)_3$ Anchored on Amino Functionalized Silica for the Selective Oxidative Synthesis of 2-arylbenzimidazoles, 2-arylbenzothiazoles and Aerobic Oxidation of Benzoins in Water

Ravinderpal Kour Sodhi · Satya Paul

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Abstract Silica functionalized $Mn(acac)_3$ was prepared and employed for the one-pot oxidative synthesis of 2-arylbenzimidazoles, 2-arylbenzothiazoles; and oxidation of benzoins to benzils under air atmosphere using water as the reaction medium. Environmentally friendly procedure, chemoselectivity and excellent yields are main advantages of this procedure. In all the cases, the catalyst was found to be highly active and selective; passes hot filtration test successfully; and could be recycled several times with a slight loss of activity.

Keywords Silica functionalized $Mn(acac)_3$ · 2-arylbenzimidazoles · 2-arylbenzothiazoles · Benzils · Recyclable heterogeneous catalyst · Green procedure · Aqueous medium · Air atmosphere

1 Introduction

In recent times, the development of heterogeneous catalysts [1–6] for organic synthesis has taken lead over their homogeneous counterparts because of simplified recovery, recyclability and ease of handling, potential for incorporation in continuous reactors and microreactors; and more environmentally safe disposal. Among various solid supports commonly used for the preparation of heterogeneous catalysts, silica's have received more attention [1, 7–14]. Recently, water has been found to be a promising medium for heterogenised homogeneous catalysis. Catalysts heterogenised through covalent or non-covalent attachment to either inorganic or organic materials, particularly silica have been successfully employed in aqueous media [15].

Benzimidazole and benzothiazole functionality leads to highly active pharmaceuticals [16–20]. High profile biological activities of compounds containing benzimidazole and benzothiazole structures has attracted considerable attention for their synthesis. Commonly employed synthesis of benzimidazoles involve the reaction between 1,2-phenylenediamines and carboxylic acids or their derivatives (nitriles, amidates, orthoesters) in the presence of strong acids such as polyphosphoric acid [21] or mineral acids [22] and the thermal or acid promoted cyclization of *N*-(*N*-arylbenzimidoyl)-1,4-benzoquinoneimines [23]. The other popular strategies for their synthesis utilize *o*-nitroanilines as intermediates or resort to direct *N*-alkylation of an unsubstituted benzimidazole [24–27]. Recently, strategies have directed toward the synthesis of benzimidazoles involving cyclocondensation of 1,2-phenylenediamines with aldehydes under oxidative conditions [28–31]. In addition to various methodologies reported for the synthesis of benzothiazoles [32–39], the most common and convenient involve the cyclocondensation of *o*-aminothiophenols with aldehydes under oxidative conditions [28–31, 40, 41]. In many of the methods for the synthesis of benzimidazoles or benzothiazoles, stoichiometric amounts of oxidizing agents such as amino-acid based prolinium nitrate ionic liquid [42], $K_3Fe(CN)_6$ at 90 °C under basic conditions [43]; excess of $Mn(OAc)_3$ in AcOH at 110 °C for 4 h [44]; CAN–H_2O_2 [28]; $Cu_{3/2}PMo_{12}O_{40}/SiO_2$ [29]; $Fe(NO_3)_3$–H_2O_2 [30]; $ZrOCl_2 \cdot nH_2O$/montmorillonite K10 [31]; nano CuO in DMSO [45] etc. have been employed. Recently, Chakraborti et al. [46] have reported environmentally benign method for the synthesis of 2-arylbenzothiazoles in water at 110 °C.

R. K. Sodhi · S. Paul (✉)
Department of Chemistry, University of Jammu, Jammu
180 006, India
e-mail: paul7@rediffmail.com

The oxidation of benzoins to benzils is an important synthetic transformation in organic synthesis because of their applications as photosensitive and synthetic agents in organic and pharmaceutical chemistry [47–52]. The most straight forward method for the synthesis of benzils is the oxidation of benzoins. Numerous oxidizing reagents have been reported for the oxidation of benzoins to benzils in homogeneous and heterogeneous media [53, 54]. To overcome the problems associated with homogeneous catalysis, we have recently reported a series of silica functionalized metal catalysts for the selective oxidation of benzoins to benzils in toluene at 100 °C [54]. Thus, there is still a need to develop new method which utilizes water as solvent and hence contribute toward green chemistry.

In recent times, transition-metal catalyzed oxidations using oxygen as green oxidant are highly desirable [55–58]. Among various transition metals, manganese is probably the most versatile in promoting or catalyzing oxidation reactions [59–65]. Various supported manganese complexes have been prepared and used for various oxidation reactions [66–71]. Recently, silica functionalized Mn(acac)$_2$ has been reported for the oxidation of limonene using *t*-BHP as an oxidant [72]. Most desirable oxidations are those which could be carried out under air atmosphere without using additional oxidant.

In this paper, we report the simple preparation of silica functionalized Mn(acac)$_3$ [SiO$_2$-Mn(acac)$_3$] and its application for the selective oxidative synthesis of 2-arylbenzimidazoles or 2-arylbenzothiazoles by the one-pot condensation of aromatic aldehydes and *o*-phenylenediamine or *o*-aminothiophenols, respectively; and selective oxidation of benzoins, under air atmosphere using water as the reaction medium.

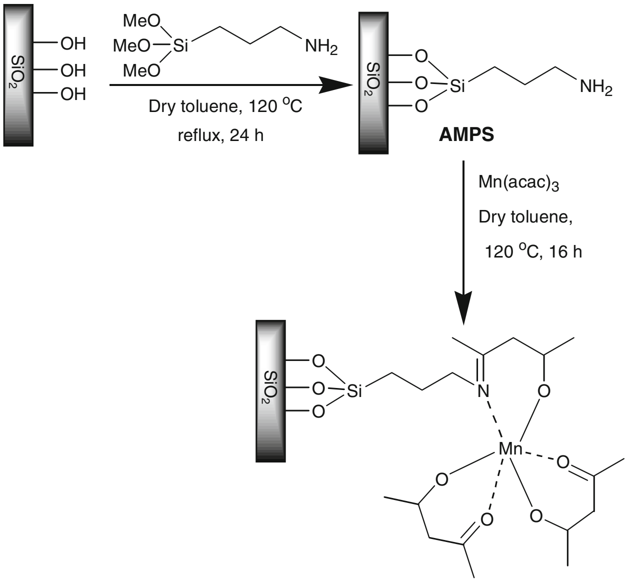
2 Experimental

2.1 General Remarks

The chemicals used were either prepared in our laboratories or purchased from Aldrich Chemical Company and Merck. The products were characterized by comparison of their physical data with those of known samples or by their spectral data. The ^{1}H NMR data were recorded in CDCl$_3$ or DMSO-d$_6$ on Bruker DPX 200 (200 MHz) spectrometer using TMS as an internal standard. The IR spectra were recorded on Perkin-Elmer FTIR spectrophotometer using KBr windows and mass spectra were recorded using Bruker Esquires 3000 (ESI). XRD spectra were recorded on Bruker AXSD8 X-ray diffraction spectrometer and scanning electron microscope (SEM) using Jeol make T-300 scanning electron microscope. Transmission electron micrographs (TEM) were recorded in a H7500 Hitachi. The amount of the manganese supported on silica was determined by stirring the sample in dil. HNO$_3$ and subjecting to AAS analysis on GBC Avanta-M atomic absorption spectrometer manufactured by GBC Scientific agencies.

2.2 Preparation of Silica Functionalized Mn(acac)$_3$ [SiO$_2$-Mn(acac)$_3$]

Silica (K100, 0.063–0.200 mm) was activated by refluxing in a mixture of conc. HCl and distilled water (1:1) for 12 h and then washed thoroughly with distilled water and dried at 110 °C for 12 h. Activated silica (10 g) was added to the solution of 3-aminopropyl(trimethoxy) silane (1.79 g, 10 mmol) in dry toluene (150 mL) and refluxed for 24 h. The 3-aminopropylsilica (AMPS) was filtered off, washed with hot toluene (100 mL) and dried at 110 °C for 5 h to give the surface bound amino groups (AMPS). For the preparation of SiO$_2$-Mn(acac)$_3$, a mixture of organically modified silica (AMPS, 5 g) and Mn(acac)$_3$ (0.85 g, 2.5 mmol) in dry toluene (100 mL) was stirred at 120 °C for 16 h. The catalyst was filtered off, washed with toluene (250 mL) till the washings were colourless and dried in a hot air oven at 110 °C for 5 h. In order to remove any physisorbed Mn(acac)$_3$, the catalyst was conditioned by refluxing for 12 h each in xylene at 130 °C (2 × 2 h), ethanol at 78 °C (2 × 2 h) and acetonitrile at 80 °C (2 × 2 h). Finally, the catalyst was dried in hot air oven at 110 °C for 5 h. The complete preparation procedure of SiO$_2$-Mn(acac)$_3$ is represented in Scheme 1.



Scheme 1 Synthesis of silica functionalized Mn(acac)$_3$ [SiO$_2$-Mn(acac)$_3$]

2.3 SiO_2-Mn(acac)$_3$ Catalyzed Oxidative Synthesis of 2-arylbenzimidazoles and 2-arylbenzothiazoles

A mixture of 1,2-phenylenediamine (0.8 mmol) [for entries 3, 6, 9, 10, 1,2-phenylenediamine (1 mmol) was used] or *o*-aminothiophenol (1 mmol), aromatic aldehyde (1 mmol) and SiO_2-Mn(acac)$_3$ (0.2 g, 6.8 mol% Mn) in water (7 mL) was stirred at 70 °C under air atmosphere for an appropriate time (Table 1). On completion (monitored by TLC), the reaction mixture was cooled to room temperature and filtered. The residue was washed with hot ethyl acetate (40 mL), followed by distilled water (200 mL). The organic layer was washed with water and dried over anhydrous Na_2SO_4. Finally, the product was purified by passing through column of silica gel and elution with EtOAc: pet ether.

Table 1 SiO_2-Mn(acac)$_3$-catalyzed selective oxidative synthesis of 2-arylbenzimidazoles[a] and 2-arylbenzothiazoles[b] in water at 70 °C under air atmosphere

Entry	R	X	Time (h)	Yield (%)[c]	m.p./Lit. m.p. (°C)
1	C_6H_5	NH	3	90	290–292/292 [82]
2	4-OMeC_6H_4	NH	3.5	95	225–226/226 [82]
3[d]	4-MeC_6H_4	NH	4	93	271–272/270 [82]
4	4-ClC_6H_4	NH	5	92	288–290/288–291 [82]
5[e]	4-ClC_6H_4	NH	8	90	288–290/288–291 [82]
6[d]	4-$NO_2C_6H_4$	NH	4	88	313–315/316 [82]
7	3-$NO_2C_6H_4$	NH	4	88	204–205/204–206 [82]
8	2-$NO_2C_6H_4$	NH	4	90	278–279/277–279 [83]
9[d]	$C_6H_5CH = CH$	NH	4..5	87	202-205/203-205 [82]
10[d]	2-Furyl	NH	5	89	285–287/288 [82]
11	C_6H_5	S	5	93	113–114/115–116 [41]
12	4-OMeC_6H_4	S	3	93	117–119/119–121 [41]
13	4-MeC_6H_4	S	5	93	84–85/86 [84]
14	4-OHC_6H_4	S	5	92	229–230/231–232 [85]
15[f]	4-ClC_6H_4	S	3.5	93	114–115/116.5 [86]
16	4-ClC_6H_4	S	8	92	114–115/116.5 [86]
17	4-BrC_6H_4	S	4	92	131/130–133 [87]
18	4-$NO_2C_6H_4$	S	3.5	92	224–225/224–226 [41]
19	3-$NO_2C_6H_4$	S	3.5	91	184–186/181–183 [41]
20	2-Furyl	S	3.5	94	104–105/106–107 [88]

[a] Reaction conditions: aldehyde (1 mmol), 1,2-phenylenediamine (0.8 mmol), SiO_2-Mn(acac)$_3$ (0.2 g, 6.8 mol% Mn), water (7 mL) and 70 °C as the reaction temperature

[b] Reaction conditions: aldehyde (1 mmol), *o*-aminothiophenol (1 mmol), SiO_2-Mn(acac)$_3$ (0.2 g, 6.8 mol% Mn), water (7 mL) and 70 °C as the reaction temperature

[c] Isolated yield by column chromatography

[d] Reaction conditions: in case of entries 3, 6, 9, 10, aldehyde (1 mmol), 1,2-phenylenediamine (1 mmol), SiO_2-Mn(acac)$_3$ (0.2 g, 6.8 mol% Mn), water (7 mL) and 70 °C as the reaction temperature

[e] The reaction was carried out using 4-chlorobenzaldehyde (20 mmol), 1,2-phenylenedimine (16.6 mmol), SiO_2-Mn(acac)$_3$ (2 g, 67.9 mol% Mn), water (30 mL) and 70 °C as the reaction temperature

[f] The reaction was carried out using 4-chlorobenzaldehyde (20 mmol), *o*-aminothiophenol (20 mmol), SiO_2-Mn(acac)$_3$ (2 g, 67.9 mol% Mn), water (25 mL) and 70 °C as the reaction temperature

Table 2 SiO_2-Mn(acac)$_3$ catalyzed selective oxidation of benzoins to benzils at 100 °C in water under air atmosphere

Entry	Ar	Time (min)	Yield (%)[a]	m.p./Lit. m.p. (°C)
1	C_6H_5	45	99	96–97/95 [89]
2	4-MeC_6H_4	45	97	103–104/104–105 [89]
3	4-MeOC_6H_4	60	97	134–135/135 [89]
4	4-ClC_6H_4	50	96	197–199/199 [89]
5	4-*t*-$C_4H_9C_6H_4$	50	94	103–104/104–104.5 [90]

Reaction conditions: benzoin (1 mmol), K_2CO_3 (1.5 mmol), SiO_2-Mn(acac)$_3$ (0.15 g, 5.1 mol% Mn), water (5 mL) and 100 °C as the reaction temperature

[a] Isolated yields

2.4 SiO_2-Mn(acac)$_3$ Catalyzed Oxidation of Benzoins to Benzils

A mixture of benzoin (1 mmol), K_2CO_3 (1.5 mmol) and SiO_2-Mn(acac)$_3$ (0.15 g, 5.1 mol% Mn) in water (5 mL) was stirred at 100 °C for an appropriate time (Table 2). On completion (monitored by TLC), the reaction mixture was cooled to room temperature and filtered. The residue was washed with hot ethyl acetate (30 mL), followed by distilled water (150 mL). The organic layer was washed with water and dried over anhydrous Na_2SO_4. Finally, the product was obtained after crystallization with EtOAc: pet ether.

The structures of the products synthesised were confirmed by FTIR, ^{1}H NMR, mass spectral data and comparison with authentic samples prepared according to literature procedures.

3 Results and Discussion

3.1 Catalyst Preparation and Characterization

SiO_2-Mn(acac)$_3$ was prepared by refluxing Mn(acac)$_3$ with (3-aminopropyl)silica in dry toluene (Scheme 1) following the procedure reported for the synthesis of MCM-41-Mn(acac)$_2$ with slight modification [72]. A similar methodology has also been reported for the preparation of MCM-41-L/Mn(acac)$_2$ [73] using EtOH and HCl in addition to toluene which we have used in our present procedure. The characterization of SiO_2-Mn(acac)$_3$ was done by FTIR, TGA, XRD, SEM, TEM and AAS analysis.

The FTIR of 3-aminopropylsilica (AMPS) displays characteristic –CH_2 stretching bands at 2939 and

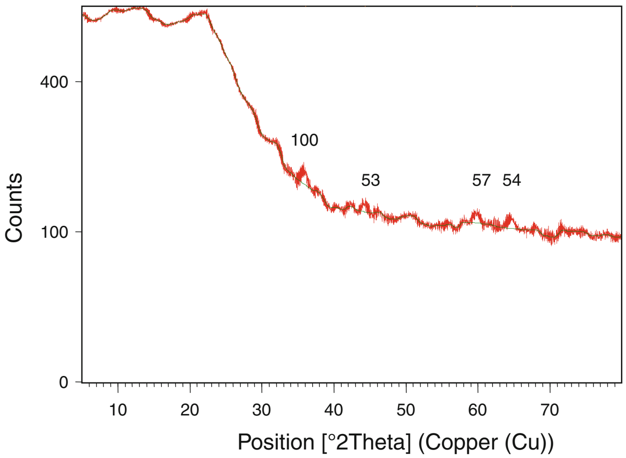


Fig. 1 XRD diffraction patterns of SiO$_2$-Mn(acac)$_3$

Fig. 2 SEM image of SiO$_2$-Mn(acac)$_3$

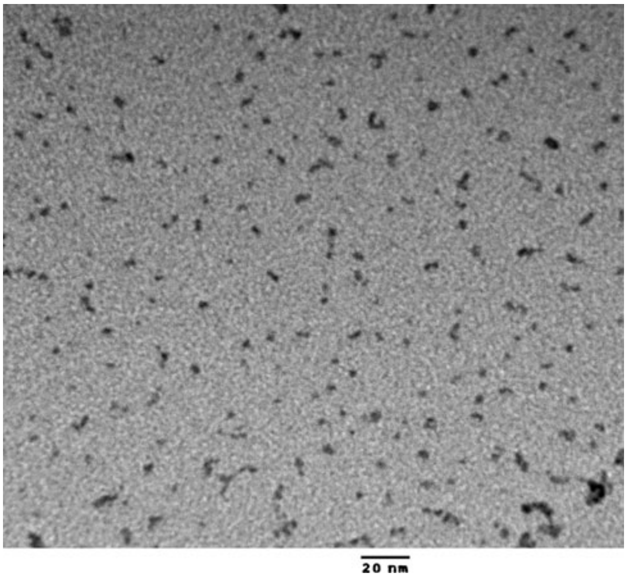


Fig. 3 TEM image of SiO$_2$-Mn(acac)$_3$

2970 cm^{-1}. After schiff condensation, the –CH$_2$ stretching band shifted to 2928 cm^{-1} and the characteristic band due to C = N bond appears at 1637 cm^{-1}.

The stability of SiO$_2$-Mn(acac)$_3$ was determined by thermal analysis. The TGA curve showed an initial weight loss up to 110 °C which may be attributed to loss of the residual solvent and water trapped onto the surface of silica. Further, weight loss occurred from 195 to 550 °C, which was due to the loss of organic functionality. Thus, the catalyst is stable up to 195 °C and it is safe to carry out the reaction at 70 or 100 °C under heterogeneous conditions.

The powdered XRD patterns for SiO$_2$-Mn(acac)$_3$ showed the peaks in the pattern which were indexed on the basis of crystallographic data for the known structure of silica (Fig. 1). Four major reflection patterns were found in the XRD pattern corresponding to $2\theta = 36°$, 44°, 59° and 64°. The microstructure and morphology was studied using the SEM. The surface of SiO$_2$-Mn(acac)$_3$ was found to be fine homogeneous powder with porous structure (Fig. 2). The TEM images provide a direct observation of the morphology and distribution of manganese onto SiO$_2$-Mn(acac)$_3$. The regular arrangement of the pores can be clearly observed. The Mn is uniformly distributed with average diameter of 7.5 nm (Fig. 3). Further, no bulk aggregation of the metal occurred indicating that the Mn was finely dispersed onto the surface of silica.

The amount of the manganese supported onto silica was determined by AAS analysis. It was found that 0.0173 g of Mn per g of SiO$_2$-Mn(acac)$_3$ was present.

3.2 Catalyst Testing for the Synthesis of 2-arylbenzimidazoles and 2-arylbenzothiazoles

To test the activity of SiO$_2$-Mn(acac)$_3$ as completely heterogeneous catalyst for the one-pot synthesis of 2-arylbenzimidazoles (Scheme 2), 4-methoxybenzaldehyde and 1,2-phenylenediamine were selected as the test substrates. After carrying out series of reactions under different set of conditions, the optimized conditions selected are: aldehyde (1 mmol), 1,2-phenylenediamine (0.8 mmol), SiO$_2$-Mn(acac)$_3$ (0.2 g, 6.8 mol% Mn), water (7 mL) and 70 °C as the reaction temperature. In the cyclocondensation of aldehydes with 1,2-phenylenediamine, there are possibilities of two products, [43, 74, 75], 2-arylbenzimidazoles and 1,2-disubstituted benzimidazoles. The present procedure gives 2-arylbenzimidazoles selectively and no 1,2-disubstituted benzimidazoles have been detected.

In case of 2-arylbenzothiazoles, the reaction was carried out using 4-methoxybenzaldehyde (1 mmol), *o*-aminothiophenol (1 mmol), SiO$_2$-Mn(acac)$_3$ (0.2 g, 6.8 mol% of Mn), deionized water (7 mL) and atmospheric air as the

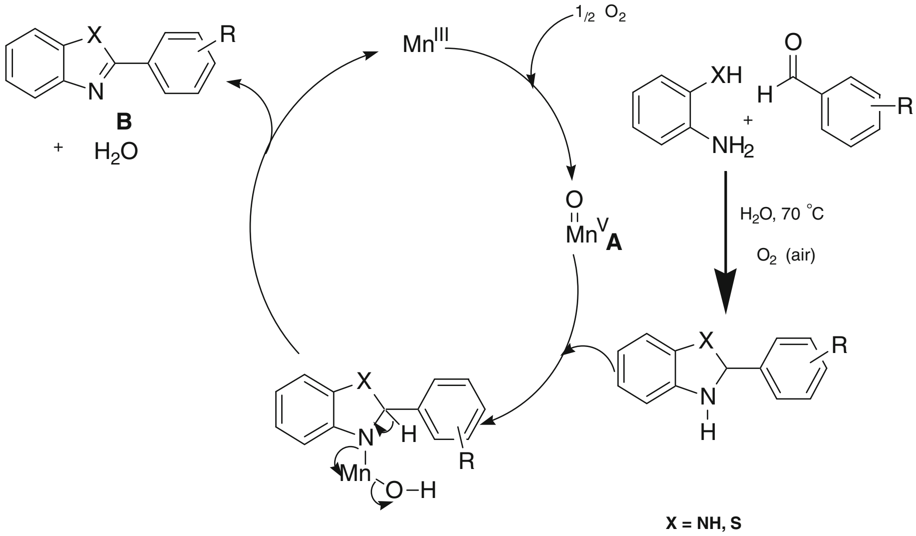


Fig. 4 Proposed mechanism for the SiO_2-Mn(acac)$_3$ catalyzed oxidative synthesis of 2-arylbenzimidazoles and 2-arylbenzothiazoles

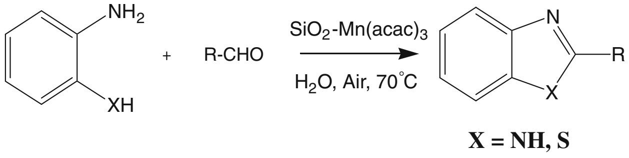
source of oxygen under stirring at 70 °C for 3 h (Scheme 2). It was found that 2-(4-methoxyphenyl)benzothiazole was obtained in 93% isolated yield. Since thiols are good nucleophiles and SET agents, but no substitution of the halogen atom (4-chloro and 4-bromobenzaldehyde) or the nitro group (4-nitrobenzaldehyde), dealkylation (4-methoxybenzaldehyde) or reduction of nitro group took place, which demonstrated high chemo-selectivity of the reactions. No competitive dithioacetal formation was observed under the present conditions, though dithioacetal formation is the common reaction of aldehydes with thiols. No disulfide formation was observed, which clearly indicates the high selectivity of the procedure.

To demonstrate the versatility of the catalytic system for the synthesis of 2-substituted benzimidazoles and benzothiazoles, aldehydes substituted with various electron-withdrawing and electron-donating groups were chosen and excellent results were obtained (Table 1). Heterocyclic aldehydes also worked well and corresponding products were obtained in excellent yields (Table 1, entries 10, 20).

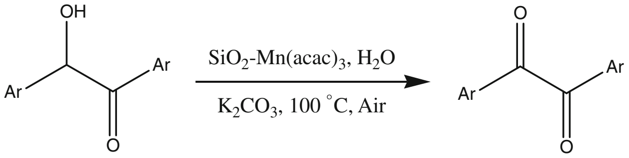
To scale-up the reaction conditions, the reactions were carried out by stirring a mixture of 1,2-phenylenediamine (1.79 g, 16.6 mmol in case of benzimidazoles) and *o*-aminothiophenol (2.5 g, 20 mmol in case of benzothiazoles), 4-chlorobenzaldehyde (2.72 g, 20 mmol), SiO_2-Mn(acac)$_3$ (2 g, 67.9 mol% Mn) and water (30 mL) at 70 °C for 8 h. After the usual work-up, 2-(4-chlorophenyl)benzimidazole was obtained in 90% isolated yield (Entry 5, Table 1) and 2-(4-chlorophenyl)benzothiazole was obtained in 92% isolated yield (Table 1, entry 16).

3.3 Catalyst Testing for the Oxidation of Benzoins to Benzils

The most common method for the synthesis of benzils involves the oxidation of benzoins. However, the important aspects for this oxidation include selectivity, toxicity of oxidants and environmentally friendly procedure. Recently, we have reported [54] a selective method for the oxidation of benzoins in air atmosphere using covalently anchored Pd, Co and Ni complexes onto silica using toluene as solvent. To make the procedure still more green, the activity of SiO_2-Mn(acac)$_3$ was also tested for the oxidation of benzoins in air using deionized water as solvent (Scheme 3). Benzoin was selected as the test substrate and reaction was carried out under different set of conditions with respect to different solvents, temperatures and amounts of the catalyst. After carrying out series of reactions, the optimum conditions selected are: benzoin (1 mmol), SiO_2-Mn(acac)$_3$ (0.15 g, 5.1 mol% Mn), K_2CO_3 (1.5 mmol), water (5 mL) and 100 °C as the reaction temperature.



Scheme 2 SiO_2-Mn(acac)$_3$ catalyzed selective oxidative synthesis of 2-arylbenzimidazoles and 2-arylbenzothiazoles under air atmosphere in water



Scheme 3 SiO_2-Mn(acac)$_3$ catalyzed selective oxidation of benzoins to benzils under air atmosphere in water

Table 3 Effect of the catalyst on the SiO$_2$-Mn(acac)$_3$ catalyzed synthesis of 2-arylbenzimidazoles, 2-arylbenzothiazoles and benzils under air atmosphere using water as a solvent

Entry	Catalyst	2-Arylbenzimidazoles[a]		2-Arylbenzothiazoles[b]		Benzils[c]	
		Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)
1	No catalyst	10	No reaction	10	20	8	96
2	Activated SiO$_2$	10	Traces	10	25	8	97
3	AMPS	10	Traces	10	25	7.5	98
4	SiO$_2$-Mn(acac)$_3$	3	95	3	93	0.75	99

[a] Reaction conditions: 4-methoxybenzaldehyde (1 mmol), 1,2-phenylenediamine (0.8 mmol), activated silica or AMPS or SiO$_2$-Mn(acac)$_3$ (0.2 g), water (7 mL) and 70 °C as the reaction temperature

[b] Reaction conditions: 4-methoxybenzaldehyde (1 mmol), *o*-aminothiophenol (1 mmol), activated silica or AMPS or SiO$_2$-Mn(acac)$_3$ (0.2 g), water (7 mL) and 70 °C as the reaction temperature

[c] Reaction conditions: benzoin (1 mmol), K$_2$CO$_3$ (1.5 mmol), activated silica or AMPS or SiO$_2$-Mn(acac)$_3$ (0.15 g), water (5 mL) and 100 °C as the reaction temperature

To demonstrate the generality and versatility of the procedure, benzoins substituted with different groups at C-4/C-4′ possessing both electron-withdrawing and electron-donating groups were subjected to oxidation under the selected conditions and excellent results were obtained (Table 2).

Our catalytic system in water is advantageous to some of the earlier reported methods. For example, Yang et al. [76] have reported the synthesis of 2-arylbenzothiazoles at 100 °C using CTAB; Azizi et al. [77] used PTSA at 100 °C; Chakraborti et al. [46] carried out the reaction without using any catalyst at 110 °C. Very few catalytic systems have been reported for the synthesis of 2-arylbenzimidazoles in water. For example, Bahrami et al. [78] used H$_2$O$_2$/HCl in water at 80 °C and more recently, using SDS micelles at 25 °C [79]; Mukhopadhyay et al. [80] have used boric acid and glycerol at 80 °C. However, our catalytic system is successful at 70 °C with similar or higher yields and moreover, recyclable under the reaction conditions.

3.4 Heterogeneous Catalysis and Recyclability

When using a supported metal catalyst, two important issues need to be addressed to qualify this as purely heterogeneous catalyst. One is the possibility that some active metal migrates from the solid to the liquid phase and that this leached manganese would become responsible for a significant part of the catalytic activity. To rule out the contribution of homogeneous catalysis in the results shown in Table 1, one reaction in case of entry 2 was carried out in the presence of SiO$_2$-Mn(acac)$_3$ until the conversion was 37% and at that point, SiO$_2$-Mn(acac)$_3$ was filtered off at the reaction temperature after 1 h. The liquid phase was then filtered to another flask and allowed to react, but no further significant conversion was observed. This indicates that no active species was present in the supernatant (determined by AAS analysis).

In order to find out the role of SiO$_2$-Mn(acac)$_3$ as the heterogeneous catalyst, the reaction with test substrates (entry 2, Table 1 for 2-arylbenzimidazoles; entry 12, Table 1 for benzothiazoles; and entry 1, Table 2 for benzoins) was also carried out in the presence of activated silica, 3-aminopropyl silica (AMPS) and without using any catalyst. The results are summarised in Table 3. It is clear that SiO$_2$-Mn(acac)$_3$ catalyzes the reactions.

In case of oxidation catalysis, the most important point is the deactivation and recyclability of the catalyst. To test this, a series of five consecutive runs were carried out with the same catalyst by the cyclocondensation of 1,2-phenylenediamine and 4-methoxybenzaldehyde [in case of 2-(4-methoxyphenyl)benzimidazole]; *o*-aminothiophenol and 4-methoxybenzaldehyde [in case of 2-(4-methoxyphenyl)benzothiazole]; and oxidation of benzoin to benzil. The results are shown in Fig. 4. Thus, there is no change in the activity of the catalyst up to fifth use. Further, there is no change in the amount of Mn in SiO$_2$-Mn(acac)$_3$ after fifth use (as determined by AAS analysis).

A cyclic mechanism has been proposed for the oxidative synthesis of 2-arylbenzimidazoles and 2-arylbenzothiazoles using SiO$_2$-Mn(acac)$_3$ in the presence of atmospheric air (Fig. 5). An oxygen molecule from air reacts with manganese to form oxo complex ‘**A**’ which deprotonate 2,3-dihydrobenzimidazole or 2,3-dihydrobenzothiazole yielding the product ‘**B**’. Mn^{III} is regenerated back with the elimination of water molecule. The formation of oxo complex ‘**A**’ from Mn^{III} and O$_2$ has already been reported elsewhere [81]. A similar mechanism as reported earlier [54] has been proposed for the oxidation of benzoins to benzils using SiO$_2$-Mn(acac)$_3$.

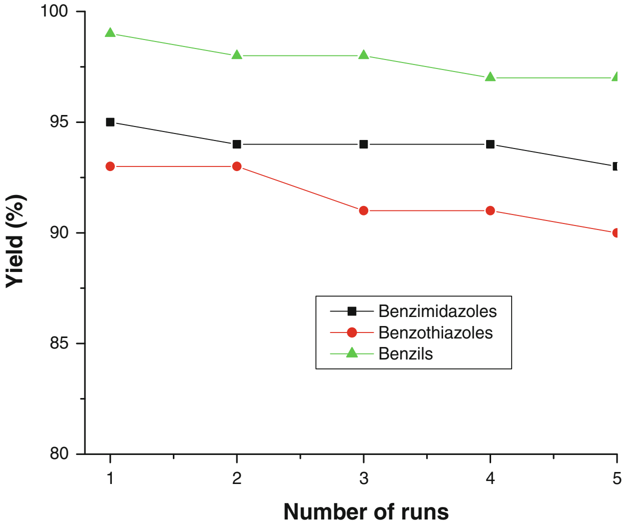


Fig. 5 Recyclability of SiO_2-Mn(acac)$_3$. Reaction conditions: Benzimidazoles-1,2-phenylenediamine (0.8 mmol), 4-methoxybenzaldehyde (1 mmol), SiO_2-Mn(acac)$_3$ (0.2 g, 6.8 mol% Mn), water (7 mL) at 70 °C for 3.5 h; benzothiazoles-*o*-aminothiophenol (1 mmol), 4-methoxybenzaldehyde (1 mmol), SiO_2-Mn(acac)$_3$ (0.2 g, 6.8 mol% Mn), water (7 mL) at 70 °C for 3 h; benzils–benzoin (1 mmol), SiO_2-Mn(acac)$_3$ (0.15 g, 5.1 mol% Mn), K_2CO_3 (1.5 mmol), water (5 mL) at 100 °C for 45 min

4 Conclusion

In conclusion, we have reported a novel heterogeneous SiO_2-Mn(acac)$_3$ for the selective oxidative synthesis of 2-arylbenzimidazoles and 2-arylbenzothiazoles; and selective oxidation of benzoins to benzils under air atmosphere in water. The salient features of our catalytic system includes high selectivity, mild reaction conditions, molecular oxygen from air as oxidant, recyclability, high yield of products and water as the reaction medium.

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