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# Mesoporous silica SBA-15 functionalized with acidic deep eutectic solvent: A highly active heterogeneous *N*-formylation catalyst under solvent-free conditions

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Najmedin Azizi, Department of Green Chemistry, Chemistry and Chemical Engineering Research Center of Iran, P.O. Box 14335-186, Tehran, Iran. Email: azizi@ccerci.ac.ir Mesoporous silica SBA-15 functionalized with *N*-methylpyrrolidonium-zinc chloride based deep eutectic solvent (DES) is found to be a more efficient and reusable catalyst for a convenient *N*-formylation of a variety of amines at room temperature. *N*-Formylation of primary, secondary as well as heterocyclic amines have been carried out in good to excellent yields by treatment with formic acid in low loading of DES/SBA-15 an environmentally benign catalyst for the first time. The DES/SBA-15 catalyst, which possesses both Brønsted and Lewis acidities as well as an active SBA-15 support, makes this procedure quite simple, reusable, more convenient and practical. This catalyst was tolerant of a wide range of functional groups, and it can be reused for four runs without obvious deactivation.

#### **KEYWORDS**

acidic deep eutectic solvent, acidic support, amines, N-formylation, SBA-15

# **1 | INTRODUCTION**

Protecting groups play a pivotal role in organic synthesis, particularly in the multi-step synthesis of multifunctional targets and structurally complicated natural products.<sup>[1]</sup> Amines as well as amino acids moieties represent the most abundant functional groups in nature.<sup>[2]</sup> In this context, in the multistep organic synthesis, the protection of reactive amino groups is acute and unavoidable.<sup>[3]</sup> N-formylation by the formyl (CHO) group was one of the most common protection methods in organic synthesis due to their ease of formation. The formylation products are valuable intermediates in the construction of various important N-heterocyclic compounds.<sup>[4]</sup> Furthermore, they are useful reagents in Vilsmeier formylation reactions and the most common reagent for the preparation of isocyanide derivatives for isocyanide-based multicomponent reactions.<sup>[5]</sup> Owing to substantial capacity of formamide derivatives, several methods or reagents for the N-formylation of amines in the presence of catalysts or heating source have been reported during recent years.<sup>[6-15]</sup> Despite their own merits, many existing N-formylation methods require harsh reaction conditions, large amounts of expensive catalysts, difficulties in the preparation of catalyst, tedious purification, unstable reagents and inert atmosphere using rigorously dried solvents.

According to the principles of green chemistry, organic functional group transformation should be carried out at room temperature in the presence of more environmentally benign and efficient heterogeneous catalysts.<sup>[16-18]</sup> Nanostructured mesoporous silica matrices, in particular, SBA-15 are attractive candidates as heterogeneous catalysts for various organic transformations due to their large surface area, narrow pore size distribution and a tunable pore diameter.<sup>[19-24]</sup> On the other hands, adsorbed or covalently bonded organic functional groups, especially ionic liquids at the surface of nanostructured mesoporous silica matrices have been widely researched because of the many applications of these composite materials.<sup>[24–27]</sup> Deep eutectic solvents DESs are the most attractive and effective precursor for immobilization on the solid support for the several advantages such as ease of preparation, available from bulk renewable resources, and especially economic considerations.<sup>[28-35]</sup> DES is advanced ionic liquids in terms of a low vapor pressure and low flammability with additional advantages such as biodegradability, non-toxicity, and being inexpensive. Moreover, unlike ionic liquids, these green solvents do not require a preliminary purification step since one only has to mix natural and readily available starting materials.<sup>[36–42]</sup>

Based on the above information, our research group has been engaged mainly on the development of environmentally friendly organic synthesis in green reaction media such as water and DESs.<sup>[43–45]</sup> In our development efforts towards this important class of DESs, herein we report an alternative, recyclable, mild and highly effective catalytic system based DES that immobilized on nanoporous silica SBA-15 for the *N*-formylation of amine derivatives with formic acid under solvent-free conditions. Our key objective is to design novel SBA-15 nanocomposite with DES supported linear side chains with the simple manner without tedious synthetic procedure.

First, DES/SBA-15 composite was synthesized by simple and rapid two-step method based on physical adsorption of DES onto the surface of SBA-15 as shown in Figure 1.<sup>[43]</sup> [HNMP]ZnCl<sub>3</sub>-based DES was prepared using a reported procedure from the literature with some modifications *via* 



FIGURE 1 Simple procedure for immobilization of DES on SBA-15

two-step synthesis process.<sup>[25]</sup> First, N-methyl-2а pyrrolidinone (NMP) reacted with hydrochloric acid (HCl) to form [HNMP]Cl, then ZnCl<sub>2</sub> was added to form the final DES following the procedure outlined in literature.<sup>[20]</sup> [HNMP]ZnCl<sub>3</sub> based DES was immobilized on calcined SBA-15 by dissolving certain amount of the prepared DES in ethanol with constant stirring at 60 °C overnight. The resulting suspension was then used to immobilize SBA-15 with DES content of 50 wt %. After the immobilization, the sample was dried at 60 °C under vacuum for 12 h and the catalyst was labeled as DES/SBA-15. The new concept of supported DES catalysis (Figure 1) is very simple and easy preparation which does not require tethering or complicated synthetic modification of SBA-15 and therefore, the characteristics of the material are dependent solely on the DES and SBA-15 dopant. The addition of an additional linker for immobilization is not required, and the catalyst was prepared by dissolving the biodegradable DES after immobilization on the SBA-15 at room temperature.

The morphology and crystalline properties of the DES/ SBA-15 nanocomposites were characterized by the thermal gravimetric analysis (TGA), fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and Brunauer–Emmett–Teller (BET) surface analysis.

The SEM image used in this experiment is shown in Figure 2. The SEM image of mesoporous SBA-15 shows a uniform particle distribution and morphology with some structural twisting (Figure 2a). Considering the BET surface analysis data and the distribution of pore size, this spatial torsion does not have substantial effect on the mesostructure in terms of surface area, pore size and pore diameter. It should be noted that after the immobilization of DES on the SBA-15 surface, the irregular small and large particles shaped (Figure 2b). However, there is not a clear explanation for the deep eutectic solvent effect on the SBA-15 surface but according to the N<sub>2</sub> adsorption/desorption isotherms for DES/SBA-15, the mesostructures still remained in the catalyst but the surface area and the morphological structure altered dramatically.

According to infrared spectrum of SBA-15 (Figure 3) there is an asymmetric stretching vibration of Si-O-Si bond in 1078 cm<sup>-1</sup>. Moreover, the peaks at 463 cm<sup>-1</sup> and 801 cm<sup>-1</sup> both were attributes to symmetric stretching vibration of Si-O-Si bonds. The observed broad absorption in the region of 3445 cm<sup>-1</sup> represents silanol groups at the surface of mesoporous structure. In addition to symmetric and asymmetric fluctuations stretching associated with the Si-O-Si bonds and silanol surface groups on SBA-15 mesostructure, in DES/SBA-15 infrared spectrum the stretching vibrations in 1638 cm<sup>-1</sup> and 2967 cm<sup>-1</sup> are associated with the carbonyl group and methyl alkanes respectively.





**FIGURE 2** The SEM image of mesoporous SBA-15 (a) and DES/SBA-15 (b)

Elemental analysis data of mesoporous silica SBA-15 indicates the presence of oxygen (57.51%) and Silicon (42.49%) percentage by weight in the mesoporous structure. Based on the obtained results for DES/SBA-15 in Figure 4, the zinc, chlorine, silicon, nitrogen, oxygen, and carbon atoms percentage by weight are in agreement with those used for the preparation of the mesoporous SBA-15 immobilized with deep eutectic solvent.

The  $N_2$  adsorption–desorption isotherms for both SBA-15 and DES/SBA-15 obtained by BET analysis showed WILEY Organometallic 3 of 10 Chemistry

hysteresis loop similar to the standard type IV isotherm for mesoporous materials (Figure 5). The surface area for SBA-15 was 520 m<sup>2</sup>/g with the total pore volume of 0.50 g/cm<sup>3</sup>, and an average pore diameter of 5 nm. Based on the BJH chart in the region of 1 to 100 nm, after impregnation of DES on to the mesoporous SBA-15 material, the surface area and the total pore volume considerably decreased to 150 m<sup>2</sup>/g and 0.21 cm<sup>3/</sup>g respectively and the average pore diameter obtained to about 4.5 nm (Figure 6). In this regard it can be concluded that the mesoporous structure of SBA-15 and DES/SBA-15 in terms of morphology and pores distribution are similar to each other.

The thermal stability and compositional analysis of the DES/SBA-15 was further investigated using TGA and is shown in Figure 7. TGA studies suggested that an abrupt weight loss occurs from 210 to 500 °C due to decomposition of DES part of catalyst. There is a 2% weight loss around 200 °C which can be attributed to water elimination from the DES/SBA-15. Therefore, the DES/SBA-15 is stable around this temperature and could be show catalytic activity.

After preparation and characterization of DES/SBA-15 nanocomposites, the applicability and efficiency of the nanocomposite in the N-formylation was validated by aniline and formic acid as a model reaction (Table 1). First, our investigation focused on finding the best reaction condition to maximize the yield in a model system and a set of reactions were carried out under different catalytic conditions (catalyst loading, reaction time, and solvent). Due to the environmentally friendly benefit of the solvent free reactions, the model reaction was first carried out under solvent-free condition. As shown in Table 1, when the reaction was carried out with 1.5 equiv. of formic acid in the presence of DES/SBA-15 (20 mg) at room temperature within 50 min., a single product was obtained in 97% isolated yield after simple workup without flash chromatography (Table 1, entry 5). Encouraged with this initial result, we decided to monitor the time required for completion of model reaction (Figure 8). After varying time we found that the model reaction did not proceed for completion at short reaction times. Upon lowering the catalyst loading to 10 mg, the yield decreased to 76%, (Table 1, entry 7) whereas an increasing in catalyst concentration to 50 mg did not shorten the reaction time. Furthermore, results showed that no desired product could be detected when the model reaction was conducted in the absence of DES/SBA-15, and only the starting materials were recovered (Table 1, entry 9), indicating that DES/ SBA-15 were absolutely necessary for this procedure. However, it is worth noting that the use of SBA-15 for N-formylation affords 35% yield after 50 min. (Table 1, entry 10), while the N-formylation in the presence of large



FIGURE 3 The FT-IR spectra of SBA-15, DES, and DES/SBA-15



FIGURE 4 The EDS analysis for mesoporous silica SBA-15 and DES/SBA-15



FIGURE 5 The  $N_2$  adsorption–desorption isotherms for SBA-15 and DES/SBA-15

amount of DES (100 mg) gives 85% yield (Table 1 entry 11). In addition, the DES/SBA-15 nanocomposite showed superior activities compared to DES or SBA-15 alone due to the synergistic effect and facilitates the separation of the high viscose DES from the reaction mixture and reducing the cost and the amount of DES.

Having identified the most effective optimized reaction conditions, to demonstrate the versatility of the method, the N-formylation reactions between formic acid and a variety of aromatic and aliphatic amines were screened, and the results are shown in Table 2. Structurally diverse anilines containing both electron-donating and electronwithdrawing groups underwent N-formylation with formic acid under mild reaction conditions and the products were isolated in good to excellent yields. Anilines containing electron-donating groups underwent the conversion smoothly and give the excellent yields at short reaction times. Anilines containing electron-withdrawing groups such as chloro, fluoro, bromo and iodo gave the good yields with longer reaction times. In contrast, strong electron-withdrawing group such as nitro and carbonyl and deactivated amines (Table 2, entries 15, 16) gave the slightly lower yield with longer reaction times. Furthermore, different functional groups in the aromatic amines such as alkyl, nitro, halogens and carbonyl remained intact (Table 2). The procedure is equally effective for secondary aromatic amines and N-ethyl aniline that gave good yields. For a variety of sterically hindered amines and heterocyclic amines, the catalyst showed good results without any significant influence of their structures on the product yields. Primary and secondary aliphatic amines can also be used as starting components to synthesize



**FIGURE 6** The BJH chart in the region of 1 to 100 nm for SBA-15 and impregnated DES/SBA-15

corresponding n-formylamine under optimized reaction conditions. When 1,2-phenylenediamine as aromatic diamine was used, instead of *N*-formylation reaction, benzimidazole as a sole cyclization product was obtained. Chemoselectivity of the DES/SBA-15 catalyst was also investigated by performing formylation of amines with a hydroxy group in the side chain as a bifunctional compound (Table 2, entry 13). Excellent chemoselectivity was observed for substrates with hydroxy functionalities, providing selective *N*-formylation in high yields without side reactions.

In order to test the robustness and practical applicability of this procedure, a relatively large-scale reaction of aniline (20 mmol) and formic acid (30 mmol) in the presence of DES/SBA-15 (200 mg) was performed. The reaction was completed in 60 min. With 86% isolated yield after simple work-up. After completion of the reaction, the mixture was



FIGURE 7 Thermogravimetric analysis (TGA) of DES/SBA-15

extracted with ethyl acetate (20 ml) and purified with the standard procedure to give the pure products.

The recycling of the catalyst is substantial in the largescale industrial application. The reusability of DES/SBA-15 in the model reaction of aniline with formic acid in 10 mmol scale was examined. After completion, the product was extracted with ethyl acetate (15 ml) and the insoluble

**TABLE 1** Optimization of *N*-formylation model reaction between aniline and formic acid

	PhNH <sub>2</sub> + HCOOH -	Catalyst Ph rt H	O ↓ H
Entry	Catalyst (20 mg)	Time (min)	Yield (%) <sup>a</sup>
1	Des/SBA-15	10	45
2	Des/SBA-15	20	60
3	Des/SBA-15	30	65
4	Des/SBA-15	40	80
5	Des/SBA-15	50	97
6	Des/SBA-15	60	97
7 <sup>b</sup>	Des/SBA-15	50	76
8 <sup>c</sup>	Des/SBA-15	40	97
9	-	50	10
10 <sup>d</sup>	SBA-15	50	35
11 <sup>e</sup>	DES	50	85

<sup>a</sup>Isolated yields.

<sup>b</sup>10 mg DES/SBA-15.

<sup>c</sup>50 mg DES/SBA-15.

<sup>d</sup>20 mg SBA-15.

e100 mg DES.

DES/SBA-15 catalyst was separated. The recovered DES/ SBA-15 was dried under vacuum washed with ethyl acetate (10 ml) used for another cycle of reaction. After four times no appreciable loss in its catalytic activity was observed (Scheme 1).

The possible reaction mechanism was proposed in Figure 6. We presume that the reaction proceeds via acid–base complexation of catalyst with the formic acid, and the SBA-15 part of catalyst could provide an excellent cooperative capability in the case of creating stability and bringing aniline and formic acid closer due to the high pore volume and narrow pore size distribution. The nucle-ophilic attack of aniline to the activated carbonyl carbon of formic acid and then dehydration gives the final products (Figure 9).

Finally, comparison of the DES/SBA-15 catalyzed nformylation of amines under solvent free conditions with a range of other methodologies demonstrated the high



FIGURE 8 The effect of reaction time on the N-formylation reaction

#### TABLE 2 N-formylation of a variety of aromatic and aliphatic amines in the presence of DES/SBA-15

	ArNH <sub>2</sub> + HCOOH $\frac{\text{DES/S}}{\text{rt, 4}}$	$\xrightarrow{\text{SBA-15 (20 mg)}}_{\text{40-120 min.}} \xrightarrow{\text{Ar}}_{\text{H}} \xrightarrow{\text{O}}_{\text{H}}_{\text{H}}$	
Entry	Substrate	Yield <sup>a</sup> (%)	References
1	NH <sub>2</sub>	97	[46]
2	CH <sub>3</sub> NH <sub>2</sub> CH <sub>3</sub>	78	[47]
3		97	[48]
4	NH NH	90	[46]
5	H <sub>3</sub> CO-NH <sub>2</sub>	97	[46]
6	CI NH2	90	[46]
7		98	[49]
8	$\sim NH_2$	74	[46]
9		88	[47]
10	Br-NH <sub>2</sub>	92	[46]
11		82	[49]
12	NH <sub>2</sub>	80	[47]
13		78	[50]
14 <sup>b</sup>		74	[51]
15	O <sub>2</sub> N-NH <sub>2</sub>	72	[51]
16		78	[46]

<sup>a</sup>Isolated yields.

<sup>b</sup>benzimidazole as product

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Run	1	2	3	4	5				
Yields	(%) 97	97	93	90	90	l			

SCHEME 1 The reusability of DES/SBA-15 catalyst



**FIGURE 9** The proposed reaction mechanism for N-formylation of aniline with formic acid

yields, short reaction times, low loading of catalyst and eco-friendly nature of the protocol (Table 3).

### **2** | EXPERIMENTAL

#### 2.1 | General

Melting and boiling points were determined on a Buchi melting point B-545 apparatus. FTIR spectra were taken on a Bruker Vector-22 spectrometer in KBr pellets and reported in cm<sup>-1</sup>. <sup>1</sup>H NMR spectra were recorded at 500 MHz on a Bruker Avance-500 spectrometer in CDCl<sub>3</sub> as solvent with chemical shifts given in ppm relative to TMS as an internal standard. All chemicals such as amine, formic acid, DES and SBA-15 components were obtained from commercial suppliers and used without further purification. Water and Other solvent were distilled before use. All the reactions were monitored by GC or thin layer chromatography (TLC) with UV light as detecting agents.

#### 2.2 | Preparation of DES/SBA-15 nanocomposite

In a separate 100-mL, three-necked flask equipped with a magnetic stirring bar and a reflux condenser was charged with a N-methyl-2-pyrrolidone (7.22 ml, 75 mmol). After cooling down the reaction mixture to 0 °C in ice bath, the equimolar HCl 32% was added dropwise over a 1 h period and subsequently the reaction temperature was raised to 45 °C and was stirred for 24 h. Then, the water was removed by rotary evaporation and the white solid product was washed several times with ethyl acetate to remove any unreacted starting materials and dried under vacuum by rotary evaporator. In the next step, [HNMP]Cl mixed with equimolar ZnCl<sub>2</sub> and heated under constant stirring at 100 °C for 12 h under N<sub>2</sub> atmosphere. The [HNMP]ZnCl<sub>3</sub> was then dried under vacuum for 12 h and honey like brown viscose liquid was obtained. Finally, in 100 ml flask containing 2 g calcined SBA-15 in 20 ml ethanol HNMP/ZnCl<sub>3</sub> (2 g) was added and the reaction mixture was stirred at 60 °C overnight. The final DES/SBA-15 nanocomposite was obtained by removing the solvent under vacuum by rotary evaporator.[25,43]

#### 2.3 | General procedure

In the dried test tube with a magnetic stir bar, amine (1 mmol), formic acid (1.5 mmol) and DES/SBA-15 (20 mg) were added. The mixture was stirred vigorously at room temperature and the progress of the reaction was monitored by TLC or GC. After completion, the mixture was extracted with ethyl acetate (10 ml) and washed with water (10 ml), and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the ethyl acetate with a rotary

Entry Time (h) Yields (%) Ref. Catalyst Solvent Temp. (°C) [52] DMA 50 15 1 Thiazolium carbine (7.5 mol%) 53 [9] 2 ZnCl<sub>2</sub> (10 mol%) Solvent-free 70 0.16 96 [11] 3 Reflux 11 CH<sub>3</sub>CN 96 \_ [46] 4 **PEG400** 70 0.5 97 Nano-Fe<sub>3</sub>O<sub>4</sub> (10 mol%)) [47] 5 Pd(OAC)<sub>2</sub>/bpy,PivOH/BF<sub>3</sub>.Et<sub>2</sub>O (0.01 mmol) Toluene 120 24 93 [48] 6 Solvent-free 70 86 FSG-Hf(NPf<sub>2</sub>)<sub>4</sub> (1 mol%) 1 [49] 7 SBA-15/PrEn-NHSO3 (1 mol%) Solvent-free 50 4 97 [50] 8 [Cp\*RhCl<sub>2</sub>]<sub>2</sub>, KI (1.6 mmol) DMSO 100 20 69 [51] 9 [Ch-SO<sub>3</sub>H]<sub>3</sub>W<sub>12</sub>PO<sub>40</sub> (20 mg) Solvent-free Rt 0.08 99 10 DES/SBA-15 (20 mg) Solvent-free Rt 97 0.66 This work

TABLE 3 Comparison of DES/Sba-15 catalyst with previous procedure in the n-formylation reaction

evaporator, the residue was purified by column chromatography on silica gel to obtain the pure *N*-formyl amine derivatives. All compounds were known and were confirmed by FTIR, <sup>1</sup>H NMR and melting point.

In summary, the greener protocol developed in this paper offers an efficient catalytic system for *N*-formylation of amines in the presence of DES/SBA-15 as a novel heterogeneous catalyst under solvent-free conditions at room temperature. The application of DES/SBA-15 to the *N*-formylation of a wide variety of primary and secondary amines provides a green method for the synthesis of formamide derivatives in good to excellent yields. The methodology was shown to be fast, economic and environment friendly, and it involved a simple work-up.

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