

FORMYLATION OF AMINES AND ALCOHOLS USING AMINOPROPYLATED MESOPOROUS SBA-15 SILICA (APMS) AS AN EFFICIENT AND RECYCLABLE CATALYST

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Aminopropylated mesoporous SBA-15 silica (APMS) is introduced as a new, recyclable and efficient catalyst for the formylation of a variety of amines and alcohols by using readily available formic acid under solvent-free conditions.

Keywords: SBA-15; Solid bases; Formylation; Amines; Alcohols.

Formylation of amines to produce formamides is an important reaction in synthetic organic chemistry. Formamides have wide applications as intermediates in the preparation of pharmaceuticals such as fluoroquinolines¹, substituted aryl imidazoles², 1,2-dihydroquinolines³, nitrogen-bridged heterocycles⁴, oxazolidinones⁵ and cancer chemotherapeutic agents⁶. They constitute important precursors in the synthesis of fungicides and herbicides². Formamides are also Lewis base catalysts, which are known to catalyze reactions such as allylation⁷ and hydrosilylation⁸ of carbonyl compounds. In addition, formamides are very useful reagents in Vilsmeier formylation reactions⁹ as well as in the synthesis of formamidines and isocyanides¹⁰. Formamide has been also undergone reactions to create nucleic acid bases and simple base derivatives on a powdered TiO₂ surface¹¹. Alkynyl formamides have been subjected to the hydroamidation reaction in the presence of Rhodium catalyst in order to construct the synthetic intermediates of a proteasome inhibitor and salinosporamide A¹². Chemo-selective activation of formamide by a transition metal catalyst has been shown as an effective and attractive synthetic strategy in this synthesis.

Moreover, the formyl group is a useful amino-protecting group in peptide synthesis¹³. Acetic formic anhydride¹⁴ is a common formylating reagent for formylating the amines. This reagent is sensitive to atmospheric moisture and cannot be stored due to decomposing to acetic acid and carbon monoxide. Formylating reagents such as chloral¹⁵, activated formic acid¹⁶, activated formic acid esters¹⁷, KF/Al₂O₃¹⁸, ammonium formats¹⁹, CDMT²⁰ and solid supported reagents²¹ are the other reported formylating reagents. However, many of these reagents suffer from various drawbacks such as use of sluggish, thermally unstable or toxic formylating agents/catalysts, difficult accessibility to reagents or applicability only for the formylation of aromatic amines. Use of organic solvents, high temperature, long reaction time and formation of by-products are the other limitation of the reported methods.

Modified mesoporous silica by alkali metals or organic basic groups are important solid base catalysts in organic chemistry²². In recent years, aminopropylated mesoporous SBA-15 silica (APMS) which is easily prepared by the reaction of 3-aminopropyl(triethoxy)silane with SBA-15 has been attracted much attention by organic chemists, as a solid base catalyst for the promotion of organic transformations^{22a-22d}. These compounds were also applied as useful intermediates for further functionalization²³.

In conjunction of our interest in the development of new applications of recyclable solid catalysts²⁴, in this paper, we wish to introduce a simple, new and efficient protocol for the formylation of amines by formic acid in the presence of a catalytic amount of recyclable aminopropylated mesoporous SBA-15 silica as a solid base catalyst under solvent-free conditions.

EXPERIMENTAL

Chemicals were purchased from Merck and Fluka Chemical Companies. All of the products are known and were identified by their spectral data. IR spectra were run on a Perkin-Elmer 780 instrument. NMR spectra was recorded on a Bruker Avance DPX-400. Mass spectra was recorded on a Shimadzu GCMS-QP5050A. Elemental analysis for C, H and N was obtained by using a Elementar, Vario EL III. The purity of the products and the progress of the reactions were accomplished by TLC on silica-gel polygram SILG/UV₂₅₄ plates. X-ray diffraction (XRD; Bruker D8ADVACE) with Ni-filtered CuK α radiation (1.5406 Å) was investigated. Data was recorded with a speed of 2° min⁻¹ and a step of 0.05°. N₂ adsorption/desorption isotherms were determined at 77.40 K with a Quantachrome NOVA apparatus. Before measurements, SBA-15 sample was outgassed under vacuum at 150 °C for 12 h and APMS sample was outgassed under nitrogen at 90 °C for 12 h. Using the Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) analyses, the specific surface area and the pore size distributions were obtained from the desorption branch of the isotherms, respectively.

Synthesis of SBA-15

SBA-15 was prepared according to the work of Zhao²⁵. Pluronic P123 triblock copolymer (2 g) dissolved in H₂O (15 ml). HCl (2 M, 60 ml) was added to the solution, followed by adding TEOS (4.25 g) at 313 K in 24 h. The molar composition of the mixture, TEOS/P123/HCl/H₂O, was 1:0.017:6:192. The resulting mixture was heated at 373 K under static conditions for another 24 h. The resulting solid product was filtered and washed with deionized water. The P123 template was reduced by calcining the material at 823 K in air for 6 h.

Synthesis of APMS by Grafting

APMS was prepared according to the procedure described previously with minor modification²⁶. SBA-15 (1 g) was carefully vacuum-dried at a temperature of 393 K and stored under nitrogen atmosphere prior to the addition of dry toluene (30 ml). Then 3-aminopropyltrimethoxysilane (2.5 ml) was added to the solution. The mixture was refluxed under stirring for 18 h. The sample was filtered and then cleaned by shoxhlet extraction in toluene for 12 h and dried at 80 °C for 24 h.

Formylation of Amines and Alcohols. General Procedure

APMS (0.08 g, 0.02 mmol) was added to the stirred mixture of amino alcohol (1 mmol) and formic acid 98% w/w (2–10 mmol) in an oil bath at 40 °C and stirred for an appropriate time (Tables II and III). CH₂Cl₂ (10 ml) was added to the cooled reaction mixture. The catalyst was filtered off, washed with CH₂Cl₂ (2 × 10 ml), dried at 100 °C for 1 h and reused for the similar reaction. Filtrate was washed by water (2 × 10 ml) and dried over anhydrous Na₂SO₄. The organic solvent was removed under reduced pressure and the resulting crude product was purified by column chromatography eluted with *n*-hexane–EtOAc (1:1).

N,N'-1,3-Phenylenebisformamide: Light yellow solid, m.p. 157–159 °C. ¹H NMR (400 MHz, DMSO): 10.22 bs, 2 H (NH); 8.26 s, 2 H (CHO); 7.93 s, 1 H (Ar); 7.30 d, 2 H, *J*(4,5) = 9.6 (H-4); 7.25 t, 1 H, *J*(5,6) = 8.4 (H-5). ¹³C NMR (100 MHz, DMSO): 160.0, 139.0, 129.7, 114.9, 110.4.

4-Morpholine carbaldehyde: Colorless oil. ¹H NMR (400 MHz, CDCl₃): 7.98 s, 1 H (CHO); 3.62 t, 2 H, *J*(2,3) = 4.4 (H-3); 3.58 t, 2 H, *J*(5,6) = 5.8 (H-5); 3.49 t, 2 H, *J*(2,3) = 4.8 (H-2); 3.33 t, 2 H, *J*(5,6) = 4.8 (H-6). ¹³C NMR (100 MHz, CDCl₃): 160.8, 67.1, 66.3, 45.7, 40.5.

RESULTS AND DISCUSSION

At first, aminopropylated mesoporous SBA-15 silica was synthesized by known methods²⁶ modified slightly. The percentage of the supported amino groups on SBA-15 (3.34%) was obtained by CHN analysis.

The XRD patterns of calcined SBA-15 and APMS were also studied (Fig. 1). The X-ray diffraction pattern of SBA-15 showed three well resolved peaks corresponding to the reflections (1 0 0), (1 1 0) and (2 0 0), associated with p6mm space group and hexagonal symmetry of SBA-15 (Fig. 1a). A similar XRD pattern was observed for APMS, which revealed that SBA-15 still had

a high degree of hexagonal mesoporous organization in APMS structure (Fig. 1b). A decrease in the peak intensities with a slightly forward shift in XRD pattern of APMS showed that amine groups placed inside of the SBA-15 channels.

N_2 adsorption/desorption isotherms and the pore-size distribution of calcined SBA-15 and APMS are shown in Fig. 2. The specific surface areas were estimated from the adsorption branch of isotherms using the Barrett-

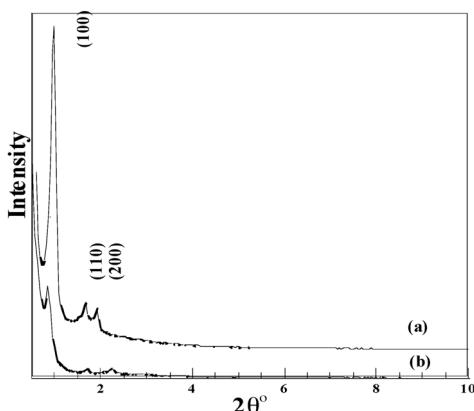


FIG. 1
The powder XRD patterns of calcined SBA-15 (a) and APMS (b)

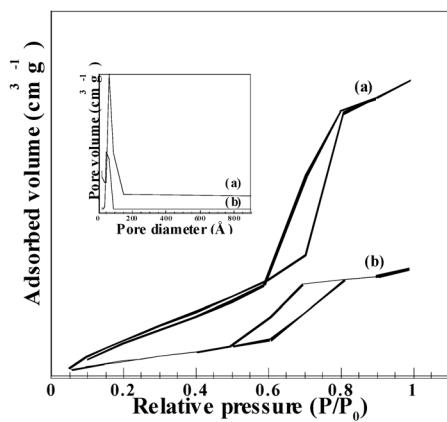


FIG. 2
Nitrogen adsorption/desorption isotherms incorporated with pore size distribution profiles at the inset for calcined SBA-15 (a) and APMS (b)

Emmett–Teller (BET) technique. Pore size distributions were calculated from the desorption branch of isotherms via the Barrett–Joyner–Halenda (BJH) model. The results in Fig. 2 presented typical IV isotherm with H1-type hysteresis loop at high relative pressure according to the IUPAC classification for mesoporous materials²⁷ with uniform pore size distributions. Corresponded textural parameters are also listed in Table I. As shown in Table I, only the wall thickness of APMS is increased in comparison with SBA-15. Other parameters such as specific surface area, pore volume and pore diameter are decreased. These observations are contributed to incorporation of aminopropyl groups onto SBA-15. In a comparison with Zeleňák's procedure²⁶ for APMS synthesis, an increasing in surface area and a slight decreasing in amine groups loading are clearly observed in the present method for the synthesis of APMS (Table I).

TABLE I

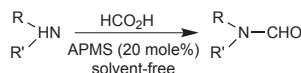
Physicochemical properties of catalysts: S_{BET} , specific surface area ($\text{m}^2 \text{ g}^{-1}$); V_{BJH} , pore volume ($\text{cm}^3 \text{ g}^{-1}$); D_{BJH} , pore diameter (nm); A_o , cell parameters (nm); D_{100} , interplanar spacing (nm); W , wall thickness (nm); V_{MI} , micropore volume ($\text{cm}^3 \text{ g}^{-1}$), amine loading (mmol g⁻¹)

Material	S_{BET}	V_{BJH}	D_{BJH}	A_o	D_{100}	W	V_{MI}	Amine loading
SBA-15	890.4 (687) ²⁶	1.27	6.063	10.4164	8.854	4.3534	0.06968	–
APMS	242.4 (134) ²⁶	0.4573	4.606	12.083	10.2706	7.477	0.003197	2.38 (2.72) ²⁶

^a Calculated from the desorption branch. ^b $W = A_o - D_{\text{BJH}}$ ($A_o = 2D_{100}/\sqrt{3}$).

Figure 3 shows the α_s plot for the SBA-15 and APMS samples. The α_s plot is obtained based on the standard nitrogen adsorption isotherm (Fig. 2). Micropore volume (V_{MI}) is determined by intercept of adsorption axis (Table I).

In the next step, *N*-formylation of different types of amines with formic acid was studied in the presence of APMS in order to find a new application of APMS as a catalyst in organic synthesis. Finding the best reaction conditions, a series of reactions of aniline with formic acid catalyzed by different molar ratios of APMS under solvent-free conditions were investigated. The best yield of *N*-phenylformamide was obtained with 2 equivalents of formic acid in the presence of 20 mole % of APMS at 40 °C. Then, the optimized reaction conditions were used for the formylation of various amines with formic acid catalyzed by APMS (Scheme 1, Table II).



SCHEME 1
Formylation of amines with formic acid catalyzed by APMS

TABLE II
APMS catalyzed formylation of amines with formic acid under solvent-free conditions

Entry ^{ref.}	Substrate	HCO ₂ H, mmol	Time, min	Yield ^a , %
1 ^{16a}	aniline	2	15	95
2 ^{16a}	<i>p</i> -anisidine	2	120	95
3 ^{16b}	3-aminophenol	2	60	95
4 ^{16a}	4-methylaniline	2	60	80
5 ^{16b}	3-bromoaniline	2	5	95
6 ^{16b}	4-aminobenzoic acid	2	180	95
7 ^{16a}	4-nitroaniline	3	600	70
8 ²⁸	<i>p</i> -phenylenediamine	6	420	95
9 ²⁹	<i>m</i> -phenylenediamine	4	30	95
10 ^{16b}	ethanolamine	2	10	90
11 ³⁰	cyclooctylamine	2	5	95
12 ³¹	benzylamine	2	30	80
13 ^{16b}	butylamine	2	5	95
14 ³²	<i>iso</i> -propylamine	2	5	95
15 ^{16a}	<i>tert</i> -butylamine	2	5	95
16 ^{16a}	diphenylamine	10	30 ^b	95
17 ³³	dibutylamine	2	5	95
18 ^{16a}	imidazole	2	30 ^b	80
19 ^{16a}	morpholine	2	30	80
20 ³¹	piperidine	2	15	95
21 ³²	isoleucine	2	15	90

^a Yields refer to those of pure isolated products characterized by comparison of their spectroscopic data with those of authentic samples. Reaction temperature 40 °C. ^b Reaction temperature 70 °C.

As indicated in Table II, formylation of anilines substituted with different electron-donating and electron-withdrawing groups proceeded well and the corresponding *N*-phenylformamides were obtained in 70–95% yields (entries 1–7). Under the similar reaction conditions, both amino groups in diamines underwent formylation reaction (entries 8 and 9). Aliphatic amines and benzyl amine which normally show poor yields^{16f,34}, were formylated in 80–95% yields by employing a catalytic amount of APMS (entries 10–17). It is worth to mention that excellent chemoselectivity was observed for substrates with hydroxyl functionalities providing *N*-formyl derivatives as the sole product without side reactions (entries 3 and 10). Furthermore, formylation reaction of heterocyclic amines and isoleucine as an α -aminoacid gave the corresponding products in good to high yields (entries 18–21).

After performing formylation reaction of aniline, under the conditions described in Table II, CH_2Cl_2 was added to the reaction mixture and the catalyst was filtered off and reused for the similar reaction. This process was carried out for five runs without noticeable reduction in the catalytic activity of the catalyst. The average isolated yield for five consecutive runs was 93.8%, which clearly demonstrates the practical reusability of the catalyst (Fig. 4). This reusability demonstrates the high stability and turnover of APMS under the employed conditions. It is worth noting that the recyclability test was stopped after five runs.

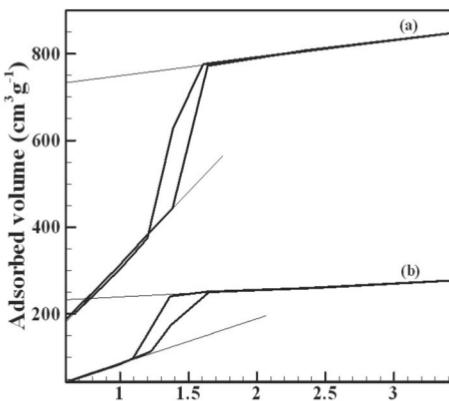


FIG. 3
The α_s plot for samples of SBA-15 (a) and APMS (b)

Formylation of the hydroxyl groups is considered as one of the most widely used transformations in organic chemistry³⁵, because deformylation can be affected selectively in the presence of acetate or other ester protect-

TABLE III
APMS catalyzed formylation of alcohols with formic acid under solvent-free conditions

Entry ^{ref.}	Substrate	Time, min	Yield ^a , %
1 ^{16d}	benzyl alcohol	30	95
2 ^{16d}	4-methoxybenzyl alcohol	5	95
3 ^{16d}	4-chlorobenzyl alcohol	30	90
4 ³⁸	1-phenyl ethanol	15	90
5 ³⁸	2-phenyl ethanol	15	90
6 ³⁹	<i>n</i> -butyl alcohol	5	95
7 ^{16c}	2-octanol	30	90
8 ^{16c}	menthol	30	90
9 ³⁸	cyclohexanol	5	90
10 ⁴⁰	<i>tert</i> -butyl alcohol	30	80

^a Yields refer to those of pure isolated products characterized by comparison of their spectroscopic data with those of authentic samples. Reaction conditions: HCO_2H (10 equivalents), reaction temperature 40 °C.

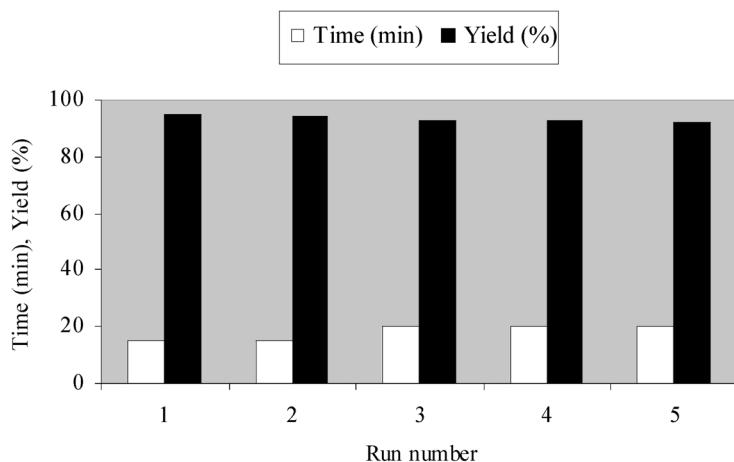
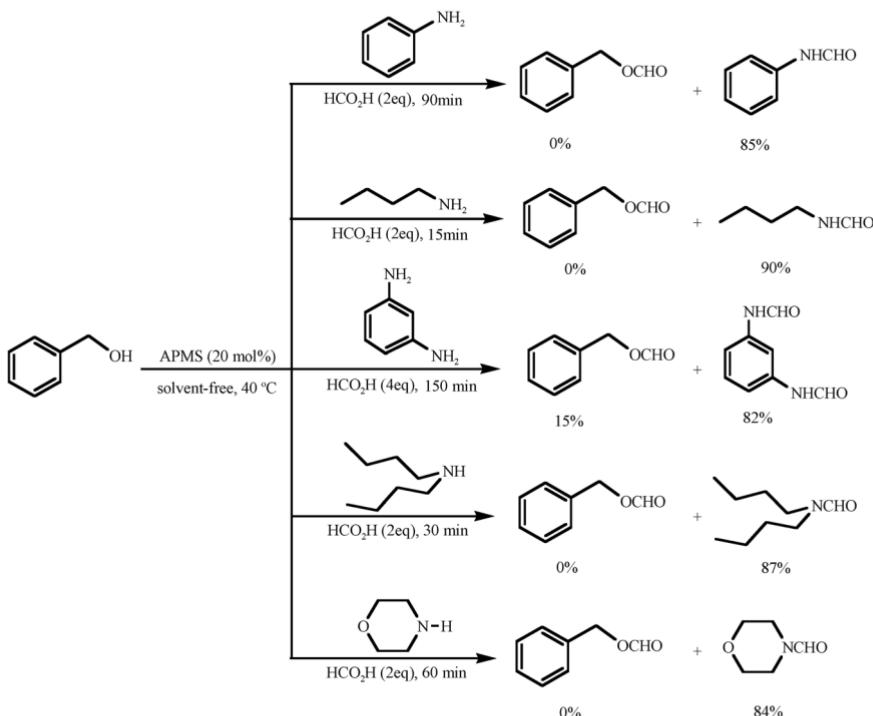


FIG. 4
Reusability of APMS as a catalyst for the formylation of aniline. Time, min (white), Yield, % (black)

ing groups. Furthermore, if the alcoholic group is planned to be oxidized later in the synthetic processes, the formylated alcoholic group does not need to be deprotected and direct oxidation, under Oppenauer conditions, can be realised³⁶. Moreover, formate esters serve as useful synthetic reagents and intermediates³⁷. In order to show the general applicability of this method, we have also tried formylation reaction of hydroxyl functional groups in alcohols with formic acid. The results showed that the reactions involving benzylic and primary/secondary/tertiary aliphatic alcohols worked well and the expected O-formylated products smoothly achieved in 80–95% yields (Table III). Comparison of formylation of alcohols with N-formylation reaction reveals that more amount of formic acid is required for the O-formylation reaction.

Showing the catalytic effect of APMS in the formylation of alcohols, reaction of 4-methoxybenzyl alcohol with formic acid in the absence of any catalyst was examined. However, this reaction remained incomplete and



SCHEME 2
Selective formylation of amines in the presence of benzyl alcohol

only 40% of the desired product was obtained after 24 h. A similar reaction in the presence of SBA-15 led to the formation of the desired product in 90% yield after 2 h. The results of this study showed that APMS, which is one of the organic-inorganic hybrid materials not only acted as a solid base catalyst, but also had an interaction with formic acid. This kind of interaction is known in the literature⁴¹ and fascinates the formylation reaction. To determine the selectivity of the method, formylation of benzyl alcohol in the presence of different amines was studied (Scheme 2). It was observed that the method was highly selective for the formylation of different types of amines such as aniline and primary/secondary amines versus alcohols. Both amino groups in 1,3-diaminobenzene underwent formylation reaction in the presence of benzyl alcohol with good selectivity and produced the desired product in 85% yield.

CONCLUSION

In conclusion, APMS was prepared according to the procedure described previously with minor modification from SBA-15. The incorporation of aminopropyl groups onto SBA-15 was shown by XRD and BET methods. The synthesized APMS was used as a new, re-usable and efficient solid base catalyst for formylating a wide variety of aliphatic and aromatic amines and alcohols by using readily available formic acid under solvent-free conditions. Ease of recovery and catalyst reusability makes this method an economic, benign and waste-free chemical process for the formylation of amines and alcohols. Use of water tolerant and thermally stable catalyst, simple reaction setup, not requiring specialized equipment, high product yields and short reaction times are the other advantages of the presented protocol.

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