New Catalytic Performance of Immobilized Sulfuric Acid on Activated Charcoal for *N*-formylation of Amines with Ethyl Formate

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Summary: Simple and highly efficient procedure for *N*-formylation of various amines was carried out in the presence of the immobilized sufuric acid on activated charcoal as an efficient promoter system. All reactions were taken place in refluxing ethyl formate (54 °C) under mild reaction conditions. The product formamides were obtained in high to excellent yields (83–95%) within 4–80 min.

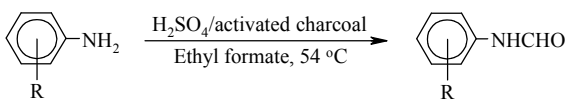
Keywords: Amines, Formylation, H_2SO_4/Activated charcoal, Ethyl formate.

Introduction

Protection of functional groups is a significant process in the synthesis of organic and industrial chemical compounds. In order to achieve high chemoselectivity in a subsequent chemical reaction, it is necessary to use protecting groups. The protection of amines by *N*-formylation reaction is one of the most important and extensively used transformations in organic synthesis [1]. Formamides have played a significant role in organic synthesis. They are also a highly useful class of intermediates in the synthesis of pharmaceutically important compounds such as fluoroquinolines [2], cancer chemotherapeutic agents [3], oxazilidones [4], Vilsmeier-Haake formylation reaction [5], nitriles [6], hydrosilylation of carbonyl compounds [7], 1-arylimi-dazole-5-carboxylates [8], 1-formyl-1,2-dihydroquinolines [9], nitrogen bridged heterocycles [10], fungicides [8, 11], isocyanates [12], formamidines [13] and allylation reaction [14].

Recently, a number of methods and reagents for *N*-formylation of various primary and secondary aromatic /aliphatic amines have been reported. Polymer supported formate [15], triethyl orthoformate [16, 17], $W(CO)_6$ [18, 19], Cl_3CCHO [20], HCO_2NH_4/nano Fe_3O_4/PEG-400 [21], NaOEt/$CHCl_3$ [22], HCO_2NH_4 [23], 2,2,2-trifluoroethyl formate [24], KF-Al_2O_3/$CHCl_3$ [25], pentafluorophenyl formate [26], HCO_2H/HCO_2Na [27], acetic formic anhydride [28], $NH_2OH{\cdot}HCl$ [29], I_2 [30], phenyl formate [31], DCC [32], $ZnCl_2$ [33], In [34], ZnO [35], γ-Fe_2O_3@HAp-SO_3H [36], $WO_4(SO_3H)_2$ [37], Fe(III)-exchanged sepiolite [38], TiO_2-P25 [39], Zr-MCM-41 [40], nanoceria [41], $NiFe_2O_4$@SiO_2-PPA [42], amberlite IR-120 [43], TBD-based ionic liquids [44], Brønsted acidic ionic liquid (RHA-[pmim]HSO_4) [45], PEG-400 [46], $HClO_4$/SiO_2 [47], silica sulfuric acid [48], ethyl formate in the presence of 2-(sulfooxy)propane-1,2,3-tricarboxylic acid/SiO_2 [49], silphos [$PCl_{3-n}(SiO_2)_n$] [50], disulfonamides polymers/microwave [51], $NaHSO_4{\cdot}H_2O$/activated charcoal [52], 2-chloro-4,6-dimethoxy-1,3,5-triazine [53], melamine trisulfonic acid [54], thiamine hydrochloride [55], hafnium(IV) bis(perfluoro-octanesulfonyl)imide complex supported on fluorous silica gel [56], ultrasound [57], ultrasound/[bmim]BF_4 [58], and ultrasound/nano CeO_2 [59] are some of the useful protocols which have been reported for the titled transformation. *N*-formylation of amines in the absence of a catalyst/promoter is very slow reaction and usually requires the particular reaction conditions or the prologed times to progress the reaction efficiently [60, 61]. Recently, *N*-formylation of amines has been extensively reviewed by Gerack *et al* [62].

Although most of the reported documents provided the useful synthetic methods, however, they generally suffer from disadvantages such as using expensive and unavailable reagents, organic solvents, thermal instability, and formation of side products, high reaction temperature, and excess amounts of formic acid, acidic reaction conditions and long reaction times. In order to overcome the mentioned drawbacks, we need to develop a better protocol for synthesis of formamides in terms of operational simplicity and economical viability. Herein, we wish to report a convenient and eco-friendly procedure subjecting the immobilized sulfuric acid on activated charcoal as a highly efficient promoter for *N*-formylation of various amines in refluxing ethyl formate (54 °C) under net conditions (Scheme-1).



Scheme-1: *N*-formylation of amines with H_2SO_4/activated charcoal system.

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Experimental

General

All reagents and substrates were purchased from commercial sources in high purity and they were used without further purification. Activated charcoal was obtained from Merck Company (art No 102186). FT-IR spectra were recorded on Thermo Nicolet Nexus 670 spectrophotometer using the KBr-pellet technique. Nuclear magnetic resonance spectra were obtained on a 300 MHz Bruker spectrometer using TMS as a standard. All products are known and were characterized by their ^{1}H, ^{13}C-NMR and FT-IR spectra followed by comparison with authentic data. The particle morphology was examined by measuring SEM using FESEM–TESCAN MIRA3. The N_2 adsorption-desorption isotherms was tested on Belsorp-max, BEL Japan. The specific surface area of sample was measured by the Brunauer-Emmett-Teller (BET) technique. The pore volume and pore size distribution were resulted from the desorption profiles of the isotherms using the Barrett–Joyner-Halanda (BJH) method. TLC was applied for the purity determination of the substrates, products and the reaction monitoring over silica gel 60 F_{254} aluminum sheet.

Preparation of Immobilized H_2SO_4 on Activated Charcoal

In a round-bottom flask containing activated charcoal (0.1 g), concentrated sulfuric acid (0.1 g, 98%) was added and the mixture was stirred vigorously for 10 min at room temperature to afford the immobilized H_2SO_4 on activated charcoal.

A Typical Procedure for N-formylation of Amines with Ethyl Formate Promoted by H_2SO_4/Activated Charcoal System

In a round-bottom flask (10 mL) equipped with a magnetic stirrer and condenser, a solution of aniline (1 mmol, 0.093 g) in ethyl formate (2 mL, 0.025 mol) was prepared. The immobilized H_2SO_4 on activated charcoal (0.2 g) was then added and the reaction mixture was stirred under reflux conditions (54 °C) for 7 min. Progress of the reaction was monitored by TLC. When the reaction was completed, the mixture was passed through a short column of silica gel (200–400 mesh) and the eluted solvent was then evaporated under reduced pressure to afford the pure *N*-phenyl formamide in 95% yield (0.115 g, Table-2, entry 1).

Results and Discussion

Recently, *N*-formylation of amines with the immobilized $NaHSO_4 \cdot H_2O$ on activated charcoal as an efficient promoter system has been successfully reported by our research group [52]. This success encouraged us to further investigate the titled reaction with another acidic promoter system under green and mild reaction conditions. Activated charcoal with the surface up to 1500 m²/g is a microporous inert carbon and can be absorbed different structures of organic and inorganic molecules. The extensive distribution of materials on the surface of activated charcoal makes it more desirable for academic and industrial purposes [63-65]. In line with the outlined strategies, we therefore decided to incorporate acidic characteristic of sulfuric acid with microporosity of activated charcoal, and so using it as an efficient promoter system for *N*-formylation of amines by ethyl formate.

The issue was preliminary investiagted by preparation of the immobilized sulfuric acid on activated charcoal through the easy miscibility of 1:1 weight percentage of concentrated sulfric acid (0.1 g) and activated charcoal (0.1 g) at room temperature within 10 min. The impregnated sulfuric acid on activated charcoal was then characterized by infrared spectroscopy. Fig. 1 shows the FT-IR of the bare activated charcoal (a), and the immobilized H_2SO_4 on activated charcoal (b).

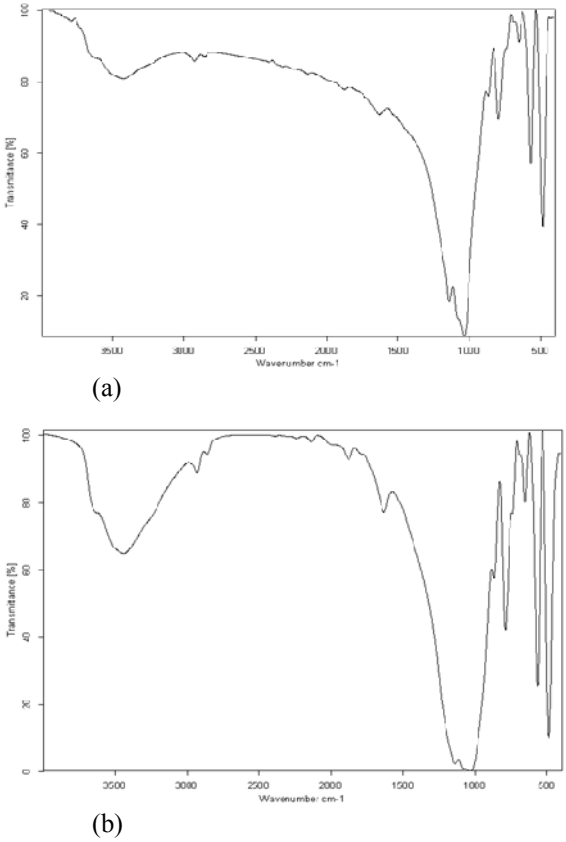


Fig. 1: FT-IR spectra of activated charcoal (a), and H_2SO_4/activated charcoal system (b).

Scanning electron microscopy (SEM) is a useful method that is used to determine the morphology and size distribution of particles in scales of micro to nano range. SEM images of the bare activated charcoal are displayed in Fig. 2. The images show that the size and morphology of particles are not uniform and both of micro and nano scale particles are observed in activated charcoal. In micro scale, the size of particles is ranged from 1–100 μm and in nano scale from 4–11 nm. SEM images of H_2SO_4/activated charcoal system are also shown in Fig. 3. The images show that by the immobilization of sulfuric acid on the surface of activated charcoal, shape, size and distribution of particles are changed to uniform. Particles in micro scale are ranged from 1–50 μm and in nano scale from 16–26 nm.

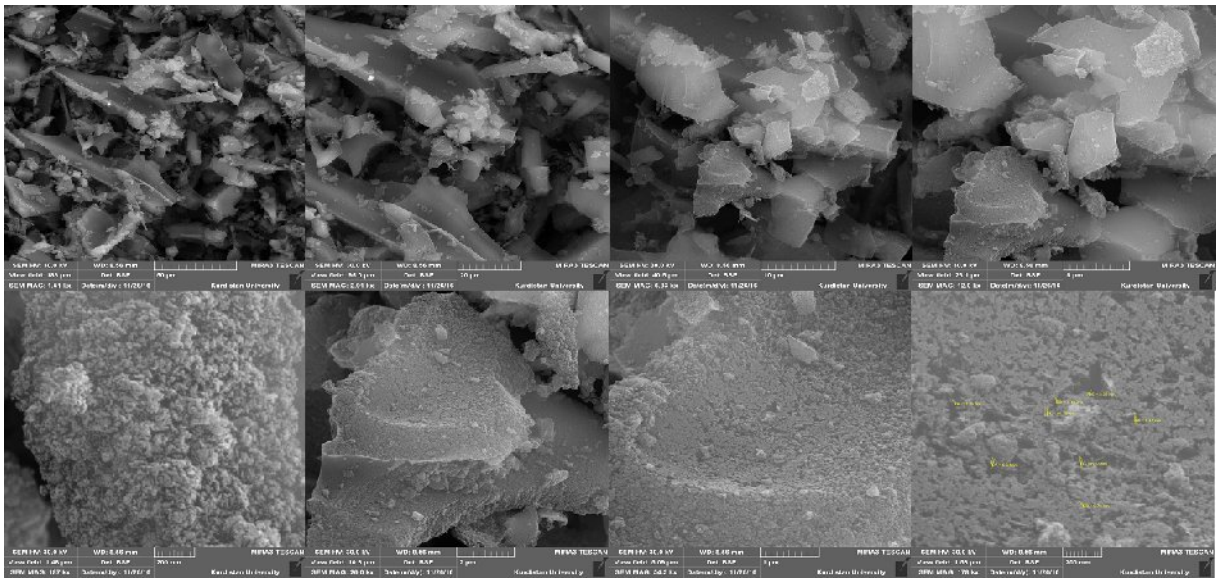


Fig. 2: SEM images of activated charcoal.

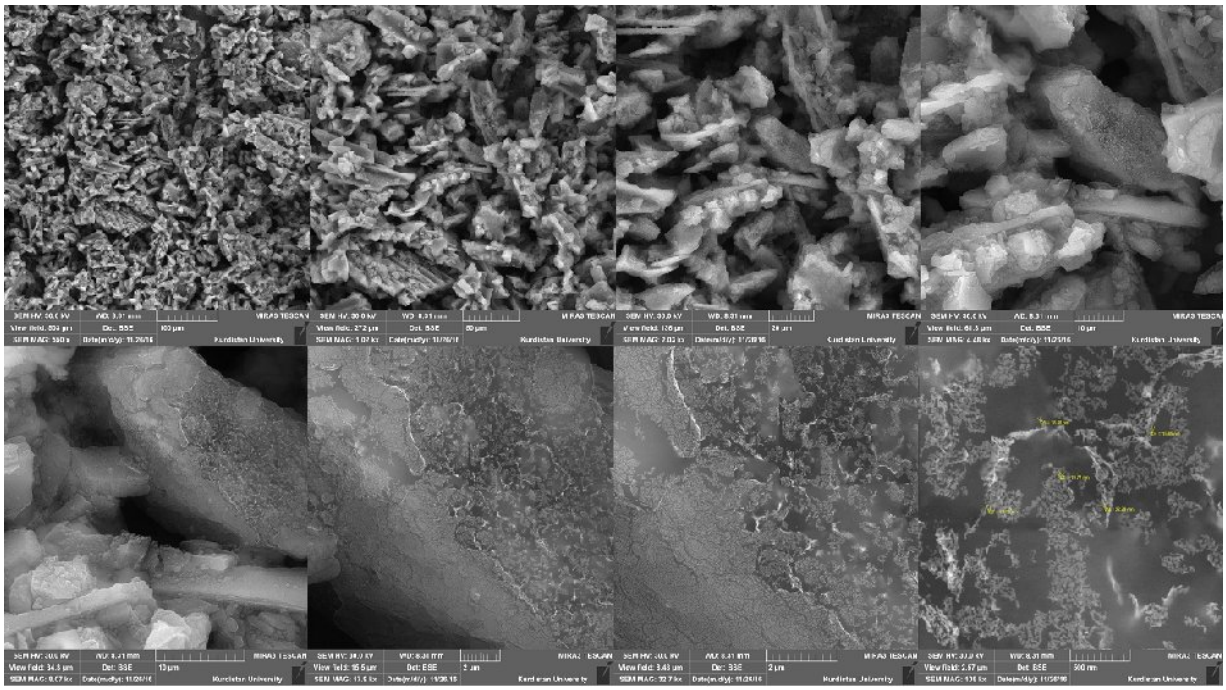
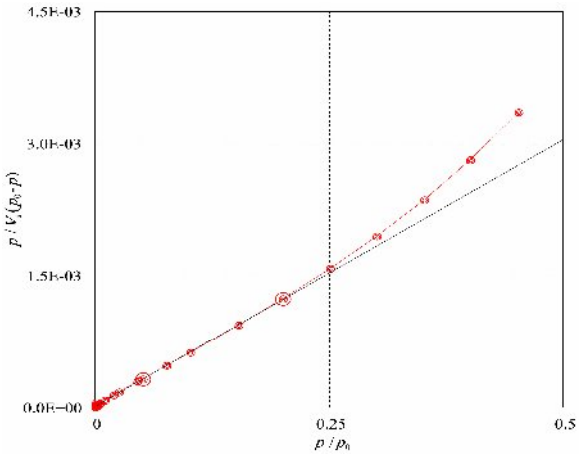
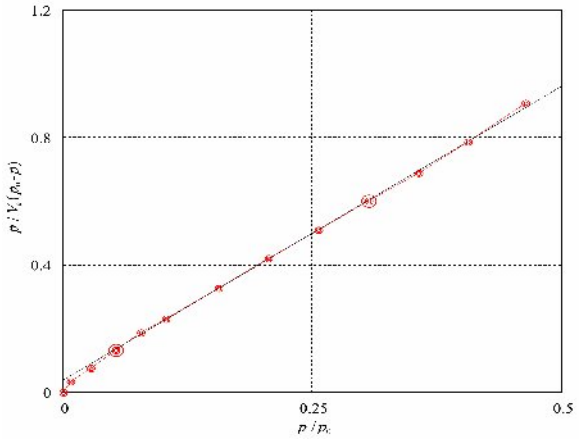


Fig. 3: SEM images of H_2SO_4/activated charcoal system.

The pore properties of activated charcoal were determined by nitrogen adsorption–desorption system. The calculated specific surface areas using the BET for activated charcoal (Fig. 4a) was 715.50 $m^2 \cdot g^{-1}$. The pore volume was 0.645 $cm^3 \cdot g^{-1}$. The corresponding pore size distribution was determined to be 3.61 nm using the Barrett–Joyner–Halenda (BJH), indicating activated charcoal is mesoporous (2 $<D_v<$50 nm). The BET analysis was also carried out for the immobilized sulfuric acid on activated charcoal (Fig. 4b). The corresponding data for the immobilized system is noted as: calculated specific surface areas (2.31 $m^2 \cdot g^{-1}$), pore volume (0.023 $cm^3 \cdot g^{-1}$) and pore size distribution (39.89 nm).



(a)



(b)

Fig. 4: BET–plots for activated charcoal (a), and H_2SO_4/activated charcoal system (b).

After synthesis and characterization, potentiality of the prepared H_2SO_4/activated charcoal system for *N*-formylation of amines was examined by the reaction of aniline with ethyl formate under different reaction conditions. The results of these examinations are summarized in Table-1. Formylation of aniline in the absence of sulfuric acid and activated charcoal did not any take place (entry 1), however, the reaction of 1 mmol of aniline with the alone H_2SO_4 (0.1 g) in refluxing ethyl formate (2 mL) was carried out with low efficiency (45%, entry 2). The result showed a moderate influence of sulfuric acid to accelerate the rate of reaction. In continuation, the synergic influence of sulfuric acid and microporosity of activated charcoal was more studied (entries 4–8). The experiments resulted that the immobilization of 0.1 g H_2SO_4 on 0.1 g activated charcoal dramatically accelerated *N*-formylation of aniline with ethyl formate leading to complete the reaction within 7 min. Therefore, the conditions mentioned in entry 8 were selected as the optimums.

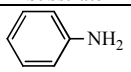
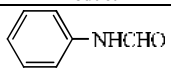
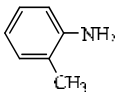
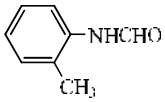
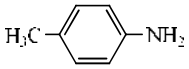
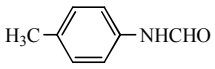
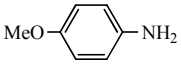
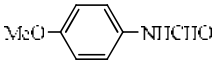
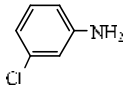
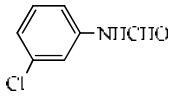
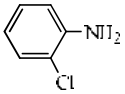
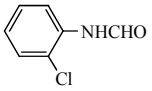
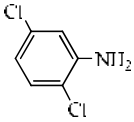
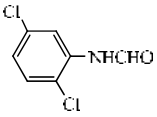
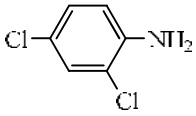
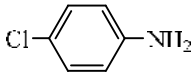
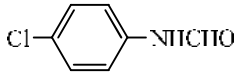
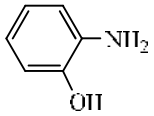
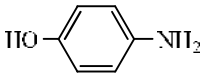
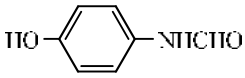
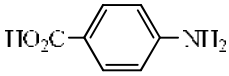
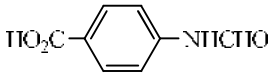
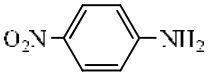
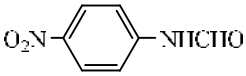
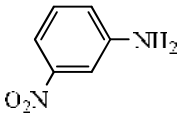
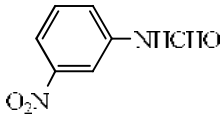
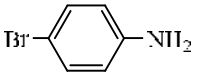
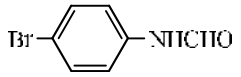
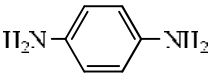
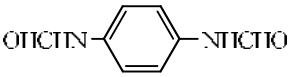
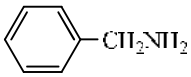
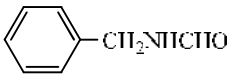
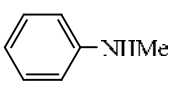
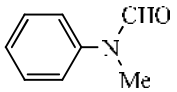
Table-1: Optimization experiments for N-formylation of aniline with ethyl formate in the presence of H2SO4/activated charcoal system[a].

Entry	Charcoal (g)	H_2SO_4 (g)	Condition	Time (min)	Yield (%)
1	–	–	reflux	480	0
2	–	0.1	reflux	480	45
3	0.1	–	reflux	480	30
4	0.025	0.025	reflux	360	60
5	0.05	0.025	reflux	180	70
6	0.05	0.05	reflux	80	80
7	0.1	0.05	reflux	40	90
8	0.1	0.1	reflux	7	100

[a]All reactions were carried out with 1 mmol of aniline in ethyl formate (2 mL).

The generality of this synthetic protocol was further studied with *N*-formylation of various aromatic primary amines with ethyl formate at the optimized reaction conditions. Table-2 shows the general trend and versatility of this synthetic method. As seen, all types of aromatic amines having electron-releasing or withdrawing groups were easily converted to their *N*-formyl derivatives in the presence of sulfuric acid (0.1 g)/activated charcoal (0.1 g) system within 4–80 min. The table also shows that amines possessing electron-releasing groups accelerated the rate of *N*-formylation reaction (entries 3 and 4), whereas amines with electron withdrawing groups required longer reaction times. During the formylation reaction, functionality of alkyl, nitro, halogen and carbonyl remained intact. It is notable that under the experimental conditions or the prolonged reaction times, *O*-formylation of phenols did not any take place. So, molecules containing phenolic and amino groups chemoselectively were carried out *N*-formylation of amino group versus phenolic one (entries 11 and 12). More examinations also resulted that in the case of benzylic and aromatic secondary amines such as benzylamine and *N*-methylaniline, the protocol was also efficient and produced the corresponding formamides in 88–90 % yields (entries 18 and 19).

Table-2: *N*-formylation of amines with ethyl formate in the presence of H_2SO_4/activated charcoal system[a].

Entry	Substrate	Product	Time (min)	Yield (%)	M.p. (°C)	Ref.
1			7	95	46-48	[56]
2			19	90	60-62	[56]
3			4	90	52-54	[56]
4			5	91	81-82	[21]
5			19	89	56-57	[66]
6			14	87	77-80	[56]
7			30	92	149-151	[56]
8			22	88	56-58	[46]
10			22	90	100-102	[56]
11			5	88	129-131	[21]
12			12	89	135-137	[21]
13			45	88	256-258	[45]
14			48	92	194-195	[56]
15			42	90	134-135	[66]
16			22	89	118-120	[56]
17			21	83	210-212	[45]
18			38	88	60-62	[56]
19			80	90	123-124	[21]

[a]All reactions were carried out with 1 mmol of amines in the presence of H_2SO_4 (0.1 g)/activated charcoal (0.1 g) system in refluxing ethyl formate (2 mL).
[b]Yields refer to isolated pure products.

Table-3: Comparison of *N*-formylation of aniline with H_2SO_4/activated charcoal system and other reported reagents.

Entry	Catalyst	Mol%	Conditions	Time (min)	Yield (%)	Ref.
1	H_2SO_4/activated charcoal	0.2 g	C_2H_5OCHO/reflux (54 °C)	7	95	[a]
2	$NaHSO_4 \cdot H_2O$/activated charcoal	0.3 g	C_2H_5OCHO/reflux (54 °C)	25	92	[52]
3	Without catalyst and solvent	–	HCO_2H/80 °C	25	90	[67]
4	SiO_2-$HClO_4$	2.5	HCO_2H/r.t.	15	96	[47]
5	Silphos [$PCl_{3-n}(SiO_2)n$]	1 g	C_2H_5OCHO/r.t	75	92	[50]
6	γ-Fe_2O_3@Hap-SO_3H	0.9	HCO_2H/r.t.	20	97	[36]
7	TiO_2-P25	0.1 g	HCO_2H/r.t.	45	99	[39]
8	$ZnCl_2$	10	HCO_2H/70 °C	10	96	[33]
9	2-(sulfooxy)propane-1,2,3-tricarboxy-lic acid/SiO_2	0.13 g	C_2H_5OCHO/r.t.	450	90	[49]
[a]Current protocol.						

In order to highlight the versatility of H_2SO_4/activated charcoal system, we compared the result of *N*-formylation of aniline with those of reported for other reagents (Table-3). The results exhibit that in terms of non-acidic characteristic of formylating agent (ethyl formate), mild reaction conditions and a short reaction time, the present protocol is more efficient or comparable with other methodologies.

Conclusions

In this study, we have introduced the immobilized sulfuric acid (0.1 g) on activated charcoal (0.1 g) as a highly efficient promoter system for easy *N*-formylation of various amines with ethyl formate. All reactions were carried out successfully using the immobilized system in refluxing ethyl formate (54 °C) within 4–80 min. The product formamides were obtained in high to excellent yields. Easy preparation, inexpensive and availablity of the immobilized system, simple procedure, high yields and the benefits of using solvent-free conditions are the advantages which make this protocol a synthetically useful addition to the existing methodologies.

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References

1. J. Otera and J. Nishikido, *Esterification, Methods, Reactions and Applications*, 2th ed.; Wiley-VCH, Weinheim, 2010.
2. A. Jackson and O. Meth-Cohn, A New Short and Efficient Strategy for the Synthesis of Quinolone Antibiotics, *Chem. Commun*., **13**, 1319 (1995).
3. G. Pettit, M. Kalnins, T. Liu, E. Thomas and K. Parent, Notes-Potential Cancerocidal Agents. III. Formanilides, *J. Org. Chem.*, **26**, 2563 (1961).
4. B. B. Lohray, S. Baskaran, B. S. Rao, B. Y. Reddy and I. N. Rao, A Short Synthesis of Oxazolidinone Derivatives Linezolid and Eperezolid: A New Class of Antibacterials, *Tetrahedron Lett.,* **40**, 4855 (1999).
5. I. M. Downie, M. J. Earle, H. Heaney and K. F. Shuhaibar, Vilsmeier Formylation and Glyoxylation Reactions of Nucleophilic Aromatic Compounds Using Pyrophosphoryl Chloride, *Tetrahedron*, **49**, 4015 (1993).
6. D. Arlt and G. Klein, Preparation of Nitriles from Formamides, *U.S. Pat*., **4**, 297 (1983).
7. S. Kobayashi, M. Yasuda and I. Hachiya, Trichlorosilane-Dimethylformamide (Cl_3SiH-DMF) as an Efficient Reducing agent. Reduction of Aldehydes and Imines and Reductive Amination of Aldehydes under Mild Conditions Using Hypervalent Hydridosilicates, *Chem. Lett*., **25**, 407 (1996).
8. H. G. Grant and L. A. Summers, Synthesis of *N*-methyl-*N*-(2,2,2-trichloro-1-arylaminoethyl) tormamides and Related-Compounds as Potential Fungicides, *Aust. J. Chem.,* **33**, 613 (1980).
9. M. K. Faraj, Synthesis of Isocyanate Precursors from Primary Formamides, *U.S. Pat*., **5**, 686 (1997).
10. A. Kakehi, S. Ito, S. Hayashi and T. Fujii, Preparation of New Nitrogen-Bridged Heterocycles. 40. Synthesis of 1,4-Dihydropyrido(2,3-b)indolizin-4-one Derivatives, *Bull. Chem. Soc. Jpn.,* **68**, 3573 (1995).
11. B. C. Chen, M. S. Bednarz, R. Zhao, J. E. Sundeen, P. Chen, Z. Shen, A. P. Skoumbourdis and J. C. Barrish, A New Facile Method for the Synthesis of 1-Arylimidazole-5-carboxylates, *Tetrahedron Lett*., **41***,* 5453 (2000).
12. K. Kobayashi, S. Nagato, M. Kawakita, O. Morikawa and H. Konishi, Synthesis of 1-Formyl-1,2- dihydro-quinoline Derivatives by a Lewis Acid-Catalyzed Cyclization of *o*-(1-Hydroxy-2-alkenyl) Phenyl Isocyanides, *Chem. Lett*., **24**, 575 (1995).
13. Y. Han and L. Cai, An Efficient and Convenient Synthesis of Formamidines, *Tetrahedron Lett*.,

38, 5423 (1997).
14. S. Kobayashi and K. Nishio, Facile and Highly Stereoselective Synthesis of Homoallylic Alcohols Using Organosilicon Intermediates, *J. Org. Chem*., **59**, 6620 (1994).
15. B. Desai, T. N. Danks and G. Wagner, Thermal and Microwave-Assisted *N*-formylation Using Solid-Supported Reagents, *Tetrahedron Lett.*, **46**, 955 (2005).
16. R. A. Swaringen, J. F. Eaddy and T. R. Henderson, Reaction of Ortho Esters with Secondary Amines, *J. Org. Chem.,* **45**, 3986 (1980).
17. B. Kaboudin and M. Khodamorady, Organic Reactions in Water: a Practical and Convenient Method for the *N*-formylation of Amines in Water, *Synlett,* 2905 (2010).
18. J. E. McCusker, J. Logan and L. McElwee-White, Oxidative Carbonylation of Primary Amines to Ureas Using Tungsten Carbonyl Catalysts, *Organometallics,* **17**, 4037 (1998).
19. J. E. McCusker, A. D. Main, K. S. Johnson, C. A. Grasso and L. McElwee-White, $W(CO)_6$-Catalyzed Oxidative Carbonylation of Primary Amines to *N,N'*-Disubstituted Ureas in Single or Biphasic Solvent Systems. Optimization and Functional Group Compatibility Studies, *J. Org. Chem.,* **65**, 5216 (2000).
20. F. F. Blicke and C. J. Lu, Formylation of Amines with Chloral and Reduction of the *N*-Formyl Derivatives with Lithium Aluminum Hydride, *J. Am. Chem. Soc*., **74**, 3933 (1952).
21. Z. G. Wang and M. Lu, Highly Efficient *N*-formylation of Amines with Ammonium Formate Catalyzed by Nano-Fe_3O_4 in PEG-400, *RSC Adv*., **4**, 1234 (2014).
22. L. A. Shastri, S. L. Shastri, C. D. Bathula, M. Basanagouda and M. V. Kulkarni, Mild, Simple, and Efficient Method for *N*-formylation of Secondary Amines via Reimer-Tiemann Reaction, *Synth. Commun.,* **41**, 476 (2009).
23. R. P. Ganapati, G. D. Kishore Kumar and S. Baskaran, A Convenient Method for the *N*-formylation of Secondary Amines and Anilines Using Ammonium Formate, *Tetrahedron Lett*., **41**, 9149 (2000).
24. D. R Hill, C. N. Hsiao, R. Kurukulasuriya and S. J. Wittenberger, 2,2,2-Trifluoroethyl Formate: a Versatile and Selective Reagent for the Formylation of Alcohols, Amines, and *N*-hydroxylamines, *Org. Lett.,* **4**, 111 (2002).
25. M. Mihara, Y. Ishino, S. Minakata and M. Komatsu, Convenient *N*-formylation of Secondary Amines: KF-Al_2O_3-Promoted Synthesis of Formamide Derivatives via Dichlorocarbene Generated from Chloroform, *Synthesis*, 2317 (2003).
26. L. Kisfaludy and J. L. Ötvös, Rapid and Selective Formylation with Pentafluorophenyl Formate, *Synthesis*, 510 (1987).
27. G. Brahmachari and S. Laskar, A Very Simple and Highly Efficient Procedure for *N*-formylation of Primary and Secondary Amines at Room Temperature under Solvent-Free Conditions, *Tetrahedron Lett*., **51**, 2319 (2010).
28. S. Krishnamurthy, A Highly Efficient and General *N*-monomethylation of Functionalized Primary Amines via Formylation-Borane:Methyl Sulfide Reduction, *Tetrahedron Lett.*, **23**, 3315 (1982).
29. A. Deepali, A. Akansha, B. Anamika and K. V. Kumar, Hydroxylamine Hydrochloride as an Effective Catalyst for Formamide Derivative Synthesis and Their DPPH Scavenging Activity, *Res. J. Chem. Sci*., **4**, 54 (2014).
30. J. G. Kim and D. O. Jang, Facile and Highly Efficient *N*-formylation of Amines Using a Catalytic Amount of Iodine under Solvent-Free Conditions*, Synlett*, 2093 (2010).
31. H. Yale, Formylation of Amines with Phenyl Formate, *J. Org. Chem.*, **36**, 3238 (1971).
32. M. Waki and J. Meienhofer, Efficient Preparation of N^{α}-formylamino acid *tert*-Butyl Esters, *J. Org. Chem.*, **42**, 2019 (1977).
33. A. C. Shekhar, A. R. Kumar, G. Sathaiah, V. L. Paul, M. Sridhar and P. S. Rao, Facile *N*-formylation of Amines Using Lewis Acids as Novel Catalysts, *Tetrahedron Lett.,* **50**, 7099 (2009).
34. J. G. Kim and D. O. Jang, Indium-Catalyzed *N*-formylation of Amines under Solvent-Free Conditions, *Synlett*, 1231 (2010).
35. M. Hosseini-Sarvari and H. Sharghi, ZnO as a New Catalyst for *N*-formylation of Amines under Solvent-Free Conditions, *J. Org. Chem.*, **71**, 6652 (2006).
36. L. Ma'mani, M. Sheykhan, A. Heydari, M. Faraji and Y. Yamini, Sulfonic Acid Supported on Hydroxyapatite-Encapsulated-γ-Fe_2O_3 Nanocrystallites as a Magnetically Brønsted Acid for *N*-formylation of Amines, *Appl. Catal. A*., **377**, 64 (2010).
37. S. P. Pathare, R. V. Sawant and K. G. Akamanchi, Sulfated Tungstate Catalyzed Highly Accelerated *N*-Formylation, *Tetrahedron Lett.*, **53**, 3259 (2012).
38. B. Eren, R. Aydin and E. Eren, Catalysis and Reaction Mechanisms of *N*-formylation of Amines Using Fe(III)-exchanged Sepiolite, *Chem. Papers*, **68**, 584 (2014).

39. B. Krishnakumar and M. Swaminathan, A Convenient Method for the *N*-formylation of Amines at Room Temperature using TiO_2-P25 or Sulfated Titania, *J. Mol. Catal. A Chem.*, **334**, 98 (2011).
40. M. Sadeghpour, A. Olyaei, Z. Derikvand, R. Razeghi and M. Vaziri, Zr-MCM-41 Nanoreactors: a Highly Efficient, Reusable and Novel Catalyst for the Synthesis of *N*-heteroaryl Formamides Under Solvent-Free Conditions, *J. Basic. Appl. Sci. Res.,* **3**, 125 (2013).
41. U. B. Patil, A. S. Singh and J. M. Nagarkar, Nanoceria-Catalyzed Highly Efficient Procedure for *N*-Formylation of Amines at Room Temperature under Solvent-Free Conditions, *Chem. Lett.*, **42**, 524 (2013).
42. A. Khojastehnezhad, M. Rahimizadeh, F. Moeinpour, H. Eshghi and M. Bakavoli, Polyphosphoric Acid Supported on Silica-Coated $NiFe_2O_4$ Nanoparticles: An Efficient and Magnetically Recoverable Catalyst for *N*-formylation of Amines, *Comp. Rend. Chim.*, **17**, 459 (2014).
43. M. R. Muthukur Bhojegowd, A. Nizam and M. A. Pasha, Amberlite IR-120: A Reusable Catalyst for *N*-Formylation of Amines with Formic Acid Using Microwaves, *Chin. J. Catal.*, **31**, 518 (2010).
44. S. M. Baghbanian and M. Farhang, Protic [TBD][TFA] Ionic Liquid as a Reusable and Highly Efficient Catalyst for *N*-formylation of Amines Using Formic Acid Under Solvent-Free Condition, *J. Mol. Liq.*, **183**, 45 (2013).
45. F. Shirini, M. Seddighi and M. Mamaghani, Brønsted Acidic Ionic Liquids Supported on Rice Husk Ash (RHA-[pmim]HSO_4): a Highly Efficient and Reusable Catalyst for the Formylation of Amines and Alcohols, *RSC Adv.*, **4**, 50631 (2014).
46. B. Das, M. Krishnaiah, P. Balasubramanyam, B. Veeranjaneyulu and D. N. Kumar, A Remarkably Simple *N*-formylation of Anilines Using Polyethylene Glycol, *Tetrahedron Lett.,* **49**, 2225 (2008).
47. M. I. Ansari, M. K. Hussain, N. Yadav, P. K. Gupta and K. Hajela, Silica Supported Perchloric Acid Catalyzed Rapid *N*-formylation under Solvent-Free Conditions, *Tetrahedron Lett.*, **53**, 2063 (2012).
48. D. Habibi, P. Rahmani and Z. Akbaripanah, *N*-formylation of Anilines with Silica Sulfuric Acid under Solvent-Free Conditions, *J. Chem.*, 1 (2013), (Article ID 972960).
49. A. Ghorbani-Choghamarani and Z. Akbaripanah, 2-(Sulfooxy)propane-1,2,3-tricarboxylic Acid as Novel and Versatile Catalyst for the Formylation of Alcohols and Amines Using Ethyl Formate under Neat Conditions, *Chin. Chem. Lett.*, **23**, 450 (2012).
50. N. Iranpoor, H. Firouzabadi and A. Jamalian, Silphos $[PCl_{3-n}(SiO_2)_n]$: a Heterogeneous Phosphine Reagent for Formylation and Acetylation of Alcohols and Amines with Ethyl Formate and Acetate, *Tetrahedron Lett.*, **46**, 7963 (2005).
51. R. Ghorbani-Vaghei, H. Veisi and M. Amiri, Poly(*N,N′*-dichloro-*N*-ethyl-benzene-1,3-disulfonamide, *N,N,N′,N′*-tetrachlorobenzene-1,3-disulfonamide, Poly(*N,N′*-dibromo-*N*-ethylbenzene-1,3-disulfonamide, and *N,N,N′,N′*-tetrabromobenzene-1,3-disulfonamide Catalyzed Formylation of Amines and Alcohols Using Ethyl Formate under Microwave Irradiation, *J. Iran. Chem. Soc.*, **6**, 761 (2009).
52. B. Zeynizadeh and M. Abdollahi, The Immobilized $NaHSO_4 \cdot H_2O$ on Activated Charcoal: a Highly Efficient Promoter System for *N*-formylation of Amines with Ethyl Formate, *Curr. Chem. Lett*., **5**, 51 (2016).
53. L. De Luca, G. Giacomelli, A. Porcheddu and M. Salaris, A New, Simple Procedure for the Synthesis of Formyl Amides, *Synlett*, 2570 (2004).
54. X. J Yang and Y. S. Zhang, Melamine Trisulfonic Acid-Catalyzed *N*-formylation of Amines under Solvent-Free Conditions, *Res. Chem. Intermed*., **39**, 2843 (2013).
55. M. Lei, L. Ma and L. Hu, A Convenient One-Pot Synthesis of Formamide Derivatives Using Thiamine Hydrochloride as a Novel Catalyst, *Tetrahedron Lett.*, **51**, 4186 (2010).
56. M. Hong and G. Xiao, Hafnium(IV) Bis(perfluorooctanesulfonyl)imide Complex Supported on Fluorous Silica Gel Catalyzed *N*-formylation of Amines Using Aqueous Formic Acid, *J. Fluor. Chem.,* **146**, 11 (2013).
57. D. Habibi and M. Nasrollahzadeh, An Ultrasound-Promoted Green Approach for the *N*-formylation of Amines under Solvent and Catalyst-Free Conditions at Room Temperature, *Compt. Rend. Chim*., **16**, 1008 (2013).
58. V. T. Kamble, G. M. Bondle and P. M. Pisal, Ultrasonic Promoted Catalyst-Free *N*-formylation of Amines in Neutral Ionic Liquid 1-Butyl-3-methylimidazolium Tetrafluoroborate, *Arab. J. Chem.*, 2013, 6 (DOI: doi:10.1016/j.arabjc.2013.09.007).
59. S. M. Sajadi, M. Maham and A. Rezaei, An Eco-friendly *N*-formylation of Amines Using Nano Cerium Oxide as a Recyclable Catalyst under Solvent-Free and Ultrasound Irradiation Conditions at Room Temperature, *Lett. Org.*

Chem., **11**, 49 (2014).

60. S. H. Jung, J. H. Ahn, S. K. Park and J. -K. Choi, A Practical and Convenient Procedure for the *N*-formylation of Amines Using Formic acid, *Bull. Korean Chem. Soc*., **23**, 149 (2002).
61. K. P. Dhake, P. J. Tambade, R. S. Singhal and B. M. Bhanage, An Efficient, Catalyst- and Solvent-Free *N*-formylation of Aromatic and Aliphatic Amines, *Green Chem. Lett. Rev.*, **4**, 151 (2011).
62. C. J. Gerack and L. McElwee-White, Formylation of Amines, *Molecules*, **19**, 7689 (2014).
63. H. Marsh and F. Rodríguez-Reinoso, *Activated Carbon*, Elsevier, Amsterdam (2006).
64. T. J. Bandosz, *Activated Carbon Surfaces in Environmental Remediation*, Elsevier, Amsterdam (2006).
65. J. F. Kwiatkowski, *Activated Carbon: Classifications, Properties and Applications*, Nova Science, New York (2011).
66. R. H. DeWolf and R. C. Newcomb, Hydrolysis of Formanilides in Alkaline Solutions, *J. Org. Chem.*, **36**, 3870 (1971).
67. M. Rahman, D. Kundu, A. Hajra and A. Majee, Formylation Without Catalyst and Solvent at 80 °C, *Tetrahedron Lett.*, **51**, 2896 (2010).