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Synthesis of a Zeolitic Imidazolate–Zinc Metal–Organic Framework and the Combination of its Catalytic Properties with 2,2,2-Trifluoroethanol for N-Formylation

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Abstract A novel protocol is reported for the N-formylation of amines with formic acid by using the nanoporous zeolitic imidazolate framework ZIF-8 as a heterogeneous catalyst in 2,2,2-trifluoroethanol.

Key words metal-organic frameworks, trifluoroethanol, zeolites, formylation, amines

Metal-organic frameworks (MOFs) are promising hvbrid materials for host-guest studies due to their high specific surface areas, defined pore sizes, and crystalline and tunable structures.¹ MOFs offer the advantages of easy separation of product, selectivity, and ready control of the time of contact with the catalyst.² Despite the benefits of heterogeneous catalysis, disadvantages also exist, such as deactivation of catalytic sites, formation of obstructing deposits within the particles, loss of catalytic material due to the formation of volatile species, and aggregation of catalyst crystallites,^{2,3} Zeolitic imidazole frameworks (ZIFs) are a subfamily of MOFs that consist of an imidazole linker and Zn⁺², and which are formed by a self-assembly approach.⁴ ZIFs have rapidly developed in terms of finding new structures, enhancement of their functionalities, expansion of their pore-size range, exploration of new sorption mechanisms for storage or separation of gases, and development of their catalytic properties.^{4,5} Among the ZIF family, nanocrystalline ZIF-8, which contains Zn⁺² ions and 2-methylimidazolate as a linker, is the most prominent representative.⁶

The use of ZIF-based catalysts for the transformation of organic molecules has received substantial attention in the recent years. For example, Seayad and co-workers reported the fabrication of Pd nanoparticles supported on ZIF-8 as an efficient heterogeneous catalyst for the aminocarbonylation

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of bromo- or iodoarenes under phosphine-free conditions.⁷ Miao et al. reported a novel core-shell-shell structured catalyst, Fe₃O₄@poly(4-vinylpyridine)@ZIF-8, as a heterogeneous recyclable catalyst for the Knoevenagel condensation reaction.⁸ Recently, Zahmakiran investigated the synthesis and characterization of iridium nanoparticles stabilized by the ZIF-8 framework and their catalytic use in the hydrogenation of cyclohexene and ethynylbenzene under mild conditions.⁹ Furthermore, ZIFs have recently been proposed as interesting candidates for various applications, such as a heterogeneous catalysts in organic transformations.

The amide functionality is one of the most fundamental chemical building blocks found in a wide variety of biological and synthetic structures, such as proteins, pharmaceuticals, or natural products. The most commonly used methods for the N-formylation of amines use formylating agents such as chloral,¹⁰ formic acid,¹¹ ammonium formate,¹² formic acetic anhydride,¹³ formate esters,¹⁴ N,N-dimethylformamide,¹⁵ formyl fluoride,¹⁶ formyl cyanide,¹⁷ or aldehydes.¹⁸ The use of MOF-based catalysts for the direct amidation of amines and carboxylic acids has received increased attention in recent years. Several novel MOF materials, such as the ionic [Et₄NBr]_{50%}-py covalent organic framework¹⁹ or Zr-azobenzene-4,4'-dicarboxylic acid,²⁰ have been reported to catalyze the N-formylation of amines by carboxylic acids. However, the development of a novel and mild method for N-formylation remains a desirable goal.

We recently reported the preparation of metal–organic frameworks of amines with MIL-53 (Al), and we used them in N-formylation in the absence of a solvent.²¹ We also developed catalytic applications of a copper-grafted nanoporous silica (SBA-15/En-Cu) in the presence of a base with water as a solvent for the conversion of aldehydes into amides.²²

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In recent years, fluorinated alcohol solvents such as 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) have been shown to have unique properties as solvents, co-solvents, or additives in organic synthesis.^{23,24} Bonnet-Delpon and co-workers investigated the use of fluorinated alcohols such as TFE and HFIP as reaction media or co-solvents in oxidation reactions.²⁴ Howard and coworkers showed that TFE can be used in the formation of helical elements in synthetic peptides.²⁵ Khaksar et al. reported an efficient method for the rapid synthesis of benzimidazole derivatives by using HFIP as a solvent.²⁶ We have recently succeeded in applying SBA-15/TFE.²⁷ SBA-15/NHSO₃H,²⁸ and HFIP/SBA-15⁹ as heterogeneous and recyclable catalysts in organic synthesis. However, to the best of our knowledge. N-formylation condensation reactions catalyzed by crystalline ZIF-8 in TFE as a co-solvent have not previously been reported.²⁶⁻²⁹ Here, we describe the preparation of crystalline ZIF-8 and the combination of its catalytic properties with those of TFE for N-formylation of amines in a recyclable procedure.³⁰ The pairing of ZIF-8 and TFE provides a simple and mild method for direct condensation of formic acid with amines.

In the structure of ZIF-8, the zinc atoms are connected to nitrogen atoms by 2-methylimidazolate (MeIM) linkers, creating a nanoporous structure containing four-, six-, eight-, and twelve-membered-ring Zn_4N tetrahedral clusters.³¹ This structure is similar to that of conventional aluminosilicate zeolites, where the Zn^{+2} ions play the role of silicon and the MeIM linkers form bridges that mimic the role of oxygen in zeolites.³² The morphology of crystalline ZIF-8 was examined by scanning electron microscopy and energy-dispersive X-ray spectroscopy, and it was found to have a typical octahedral shape with particle sizes ranging from 2 to 4µm.

The catalytic activity of ZIF-8 in N-formylation was assessed by examining the formylation of aniline with formic acid as a model reaction. To highlight the advantages of using this zinc-based MOF as a heterogeneous catalyst, it was compared with other MOFs [OMS-Cu(BDC), nanobelt Cu-BTC, OMS-MIL-100(Fe), and Cu(BDC)(DABCO)] (Figure 1). The direct N-formylation reaction in TFE at 50 °C in the presence of 3 mol% ZIF-8 catalyst gave a >99% yield after 90 min. The other MOFs exhibited poorer catalytic activity in this transformation. The catalytic activity of ZIF-8 was also compared with that of homogeneous catalysts [Zn(NO₃)₂, Zn(OAc)₂, ZnCl₂, CuCl₂, and FeCl₃] (Figure 1). Notably, Zn(NO₃)₂, the inorganic compound used to prepare ZIF-8, exhibited a lower catalytic activity than ZIF-8.

Compared with other polar and nonpolar nonfluorinated alcohol solvents, TFE has specific properties resulting from the presence of the trifluoromethyl group. The electron-withdrawing character of the CF₃ group of TFE confers a high activity on the hydrogen of the hydroxy group ($pK_a =$ 12.4), and it can form strong hydrogen bonds in comparison

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Figure 1 Reactivity of heterogeneous and homogeneous catalysts in an N-formylation reaction. *Reaction conditions*: $PhNH_2$ (1 mmol), HCO_2H (2 mmol), catalyst (3 mol%), TFE (3 mL), 50 °C.

with other nonfluorinated solvents such as toluene, MeOH, CH_2Cl_2 , or DMF. In the model reaction of aniline with formic acid, TFE exhibited the best performance among the various solvents tested, giving a >98% yield in 90 minutes (Figure 2).²⁴



Figure 2 Effect of solvent on the yield of the model reaction. Reaction conditions: $PhNH_2$ (1 mmol), HCO_2H (2 mmol), ZIF-8 (5 mg), solvent (3 mL), 40 °C, 90 min.

When the reaction was carried out in the absence of the catalyst, the yield decreased to less than 30%, even after 120 minutes (Table 1, entry 1). The best yield was obtained when the reaction was carried out in the presence of 5 mg of ZIF-8 in 3 mL of TFE at 40 $^{\circ}$ C (entry 5). The effects of polar nonfluorinated solvents (DMF and MeOH) on the progress of the reaction progress were also examined (entries 2 and 3).

After examining the effects of various conditions on the reaction progress, we explored the general applicability of the catalyst with various amines containing electron-with-drawing or electron-donating substituents and with formic or acetic acid (Table 2). All the formylated derivatives were isolated in good to excellent yields.

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 Table 1
 Optimization of the Reaction Conditions for the N-Formvla tion of Aniline^a

	N	H ₂ 0 + H 0H	ZIF-8/	TFE tions		н
Entry	Solvent	Substrate ratio ^b	ZIF-8 (mg)	Time (min)	Temp (°C)	Yield ^c (%)
1	TFE	1:3	-	120	25	<30
2	DMF	1:3	5	120	50	78
3	MeOH	1:3	5	120	50	84
4	TFE	1:2	5	120	25	>92
5	TFE	1:2	5	90	40	>99
6	-	1:2	5	150	50	88

^a Reaction conditions: PhNH₂ (1 mmol), HCO₂H, ZIF-9, solvent (3 mL).

^b Substrate ratio: aniline/formic acid.

^c Isolated yield.

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Table 2 Reactions of Various Amines and Carboxylic Acids in the Presence of ZIF-8/TFE^a



2	$4-O_2NC_6H_4$	Н	Me	3b	120	86
3	Ph	Н	Me	3c	90	>96
4	2-pyridyl	Н	Me	3d	120	92
5	Ph	Ph	Н	3e	90	95
6	Ph	Ph	Me	3f	90	93
7	$2-EtO_2CC_6H_4$	Н	Me	3g	150	84
8	6-methyl-2-pyridyl	Н	Me	3h	150	85
9	1-naphthyl	Н	Me	3i	90	92
10	$4-O_2NC_6H_4$	Н	Н	3j	120	89
11	1-naphthyl	Н	Н	3k	90	93

^a Reaction conditions: amine (1 mmol), carboxylic acid (2 mmol), ZIF-8 (5 mg), TFE (3 mL), 40 °C.

We next investigated the reusability of the ZIF-8 for the model reaction under solvent-free conditions in the presence of TFE over ten successive runs. For both systems, the yield decreased slightly over eight runs, and more sharply over the ninth and tenth runs (Figure S3).

The chemoselectivity of our method was also tested by treating an equimolecular mixture of piperidine (1 mmol) and aniline (1 mmol) with formic acid (4 mmol) under the optimized conditions. Analysis of the mixture after 90 minutes showed that the yield of piperidine-1-carbaldehyde (1b) was 64%, whereas phenylformamide (2b) was present only in a trace amount and N-formyl-N-phenylformamide (3a') was isolated in 19% yield (Scheme 1).





In summary, crystalline ZIF-8 was successfully synthesized and, in the presence of TFE, was found to be an efficient and recyclable catalyst for N-formylation and Nacetylation reactions. The catalyst could be separated from the reaction mixture by filtration and reused in subsequent runs without a significant loss of its catalytic activity.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610159.

References and Notes

- (1) (a) Ghose, A. K.; Viswanadhan, V. N.; Wendoloski, J. J. J. Comb. Chem. 1999, 1, 55. (b) Yang, Q.; Xu, Q.; Jiang, H.-L. Chem. Soc. Rev. 2017, 46, 4774. (c) Wang, C.; Liu, D.; Lin, W. J. Am. Chem. Soc. 2013, 135, 13222. (d) Hu, M.-L.; Safarifard, V.; Doustkhah, E.; Rostamnia, S.: Morsali, A.: Nouruzi, N.: Beheshti, S.: Akhbari, K. Microporous Mesoporous Mater. 2018, 256, 111.
- (2) Augustine, R. L.; O'Leary, S. T. J. Mol. Catal. A: Chem. 1995, 95, 277
- (3) Cremer, E. Adv. Catal. 1955, 7, 75.
- (4) Chen, B.; Yang, Z.; Zhu, Y.; Xia, Y. J. Mater. Chem. A 2014, 2, 16811.
- (5) (a) Park, K. S.; Ni, Z.; Côté, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. Proc. Natl. Acad. Sci. U. S. A. 2006, 103, 10186, (b) Wu, H.: Zhou, W.: Yildirim, T. J. Am. Chem. Soc. 2007, 129, 5314.
- (6) Chokbunpiam, T.; Chanajaree, R.; Remsungnen, T.: Saengsawang, O.; Fritzsche, S.; Chmelik, C.; Caro, J.; Janke, W.; Hannongbua, S. Microporous Mesoporous Mater. 2014, 187, 1.
- (7) Dang, T. T.; Zhu, Y.; Ngiam, J. S.; Ghosh, S. C.; Chen, A.; Seavad, A. M. ACS Catal. 2013, 3, 1406.
- (8) Miao, Z.; Yang, F.; Luan, Y.; Shu, X.; Ramella, D. J. Solid State Chem. 2017. 256. 27.
- (9) Zahmakiran, M. Dalton Trans. 2012, 41, 12690.
- (10) Blicke, F.; Lu, C.-J. J. Am. Chem. Soc. 1952, 74, 3933.
- (11) Chen, F. M.; Benoiton, N. L. Synthesis 1979, 709.
- (12) Reddy, P. G.; Kumar, G. K.; Baskaran, S. Tetrahedron Lett. 2000, 41,9149.
- (13) Strazzolini, P.; Giumanini, A. G.; Cauci, S. Tetrahedron 1990, 46, 1081.
- (14) Hill, D. R.; Hsiao, C.-N.; Kurukulasuriya, R.; Wittenberger, S. J. Org. Lett. 2002, 4, 111.

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- (15) (a) Djuric, S. W. J. Org. Chem. 1984, 49, 1311. (b) Pettit, G.;
 Kalnins, M.; Liu, T.; Thomas, E.; Parent, K. J. Org. Chem. 1961, 26, 2563.
- (16) Olah, G.; Kuhn, S. J. Am. Chem. Soc. 1960, 82, 2380.
- (17) Soleymanifard, B.; Heravi, M. M.; Shiri, M.; Zolfigol, M. A.; Rafiee, M.; Kruger, H. G.; Naicker, T.; Rasekhmanesh, F. *Tetrahedron Lett.* **2012**, 53, 3546.
- (18) Pasqua, A. E.; Matheson, M.; Sewell, A. L.; Marquez, R. Org. *Process Res. Dev.* **2011**, *15*, 467.
- (19) Dong, B.; Wang, L.; Zhao, S.; Ge, R.; Song, X.; Wang, Y.; Gao, Y. *Chem. Commun.* **2016**, *52*, 7082.
- (20) Hoang, L. T.; Ngo, L. H.; Nguyen, H. L.; Nguyen, H. T.; Nguyen, C. K.; Nguyen, B. T.; Ton, Q. T.; Nguyen, H. K.; Cordova, K. E.; Truong, T. Chem. Commun. 2015, 51, 17132.
- (21) Rostamnia, S.; Karimi, Z. Inorg. Chim. Acta 2015, 428, 133.
- (22) Rostamnia, S.; Nouruzi, N.; Xin, H.; Luque, R. *Catal. Sci. Technol.* **2015**, *5*, 199.
- (23) (a) Eberson, L.; Hartshorn, M. P.; Persson, O.; Radner, F. Chem. Commun. 1996, 2105. (b) Eberson, L.; Hartshorn, M. P.; Persson, O. J. Chem. Soc., Perkin Trans. 2 1995, 1735.
- (24) Bégué, J.-P.; Bonnet-Delpon, D.; Crousse, B. Synlett **2004**, 2004, 18.
- (25) Povey, J. F.; Smales, C. M.; Hassard, S. J.; Howard, M. J. J. Struct. *Biol.* **2007**, *157*, 329.
- (26) Khaksar, S.; Heydari, A.; Tajbakhsh, M.; Vahdat, S. M. J. Fluorine Chem. **2010**, 131, 1377.
- (27) (a) Rostamnia, S.; Doustkhah, E. Tetrahedron Lett. 2014, 55, 2508. (b) Rostamnia, S.; Zabardasti, A. J. Fluorine Chem. 2012, 144, 69.

- (28) Rostamnia, S.; Doustkhah, E. Synlett 2015, 26, 1345.
- (29) Rostamnia, S.; Doustkhah, E.; Nuri, A. J. Fluorine Chem. 2013, 153, 1.

(30) N-Formylation: General Procedure

The appropriate amine (1 mmol), HCO_2H (3 mmol), and ZIF-8 (5 mg, 3 mol%) were added to TFE (3 mL), and the mixture was stirred at 40 °C for the appropriate time (Table 2). When the reaction was complete (TLC), the catalyst was recovered by centrifugation, and the TFE was recovered by distillation (bp 78 °C). The resulting mixture was then purified by column chromatography (silica gel) to provide the desired product. The structures of all products were confirmed by ¹H and ¹³C NMR spectroscopy (see Supporting Information).

N-Phenylformamide (3a)

White solid; yield: 120 mg (>99%); mp 45 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.28 (m, 3 H, CH of Ar), 7.57 (d, ³*J*_{HH} = 8.4 Hz, 2 H), 8.33 (s, 1 H, H of CHO), 9.15 (br s, 1 H, NH).

N,N-Diphenylacetamide (3f)

White solid; yield: 196 mg (93%); mp 101 °C. ¹H NMR (300 MHz, CDCl3): δ = 2.09 (s, 3 H, CH3), 6.96–7.37 (m, 10 H, CH of Ar).

- (31) (a) Venna, S. R.; Jasinski, J. B.; Carreon, M. A. J. Am. Chem. Soc. **2010**, 132, 18030. (b) Procházková, D.; Bejblová, M.; Vlk, J.; Vinu, A.; Štěpnička, P.; Čejka, J. Chem. Eur. J. **2010**, 16, 7773.
- (32) (a) Moggach, S. A.; Bennett, T. D.; Cheetham, A. K. Angew. Chem. **2009**, *121*, 7221. (b) Fairen-Jimenez, D.; Moggach, S.; Wharmby, M.; Wright, P.; Parsons, S.; Düren, T. J. Am. Chem. Soc. **2011**, *133*, 8900.

