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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Experimental

Chemicals and apparatus

All the chemicals were obtained commercially from Sigma-Aldrich, Merck (Germany) and Fluka (Switzerland), they were used without further purification. Fourier transform infrared (FT-IR) spectra were obtained using a Shimadazu IR-640 spectrometer, absorbencies are repotted in cm⁻¹. Melting points were measured on an Electrothermal 9100 apparatus. The crystalline phases of the nanostructure were recognized by Philips X-ray diffractometer (model PW1800). The ¹H and ¹³C NMR spectra were measured (CDCl₃) with a Bruker AVANCE 300 spectrometers at 300.13 and 75.46 MHz respectively. Tin liner chromatography (TLC, mesh 60) was monitoring the reaction completion.

Synthesis of ZIF-8 nanocrystals

Synthesis of crystalline ZIF-8 was carried out following the room temperature synthesis method reported in the literature ²⁹ with some minor modification. In typical method, a solution of Zn(NO₃)₂.6H₂O (1 mmol = 0.297 gr) in 20 mL methanol is added in to solution of
2-methyl imidazole (MeIM) (8 mmol = 0.656 gr) in 20 mL methanol under stirring for 24 h. After synthesis, the solids were separated from the milky colloidal dispersion by centrifugation at 3400 rpm for 15 min. After repeated wash with methanol by centrifugation the white crystals were dried at 40 °C in air. Finally, ZIF-8 was then activated in an oven/vacuum at 100 °C for 12 h.

**General procedure for N-formylation condensation reaction**

In typical run, amine (1 mmol), formic acid (3 mmol) and ZIF-8 (5 mg, 3 mol%) were added to 3 ml of TFE and reaction mixture was stirred at 40 °C for appropriate time (Table 2). After completion of the reaction (monitored by TLC), the catalyst was completely recovered from the residue by centrifuge, and residual TFE was also recovered with simple distillation (B.P. of TFE is 78 °C). The reaction mixture was then subjected to column chromatography using silica gel to provide the desired products. The structure of the product obtained has been confirmed by physical properties and ¹H and ¹³C NMR spectroscopy.

**Selected NMR data:**

2.3.1. N-phenylformamide (3a). ¹H NMR (300 MHz, CDCl₃): δ 7.28 (3 H, m, CH of Ar), 7.57 (2 H, d, ³JHH 8.4), 8.33 (1 H, s, H of CHO), 9.15 (1 H, broad, NH).

2.3.2. N-(4-nitrophenyl)acetamide (3b). ¹H NMR (300 MHz, CDCl₃): δ 3 (3 H, s, CH₃), 7.49 (1 H, broad, NH), 7.70 (2 H, d, ³JHH 8.7 Hz, CH of Ar), 8.22 (2 H, d, ³JHH 8.7 Hz, CH of Ar).

2.3.3. N-phenylacetamide (3c). ¹H NMR (300 MHz, CDCl₃): δ 2.16 (3 H, s, CH₃), 7.09 (1 H, t, ³JHH 7.2 Hz, CH of Ar), 7.29 (2 H, t, ³JHH 7.2 Hz, CH of Ar), 7.517 (2 H, d, ³JHH 7.8, CH of Ar), 8.14 (1 H, broad, NH).

2.3.4. N-(pyridine-2-yl)acetamide (3d). ¹H NMR (300 MHz, CDCl₃): δ 2.20 (3 H, s, CH₃), 7.03 (1 H, t, ³JHH 6.3, CH of Ar), 7.73 (1 H, t, ³JHH 7.2 Hz, CH of Ar), 8.21 (2 H, m, CH of Ar), 9.79 (1 H, broad, NH).

2.3.5. N,N-diphenylformamide (3e). ¹H NMR (300 MHz, CDCl₃): δ 7.13 (4 H, d, ³JHH 7.8 Hz, CH of Ar), 7.33 (4 H, t, ³JHH 7.8 Hz, CH of Ar), 7.56 (2 H, d, ³JHH 7.8 Hz, CH of Ar), 8.34 (1 H, s, CH of CHO).
2.3.6. *N,N*-diphenylacetamide (3f). H NMR (300 MHz, CDCl₃): δ 2.09 (3H, s, CH₃), 6.96-7.37 (10H, m, CH of Ar)

2.3.7. Ethyl2-(acetylamino)benzoate (3g). ¹H NMR (300 MHz, CDCl₃): δ 1.40 (3H, t, ³JHH7.2 Hz, CH of CH₂CH₃), 2.23 (3H, s, CH of COCH₃), 4.37 (2H, q, ³JHH7.2 Hz, CH of CH₂CH₃), 7.06 (1H, t, ³JHH7.5 Hz, CH of Ar), 7.53 (1H, t, ³JHH7.5 Hz, CH of Ar), 8.03 (1H, d, ³JHH7.8 Hz, CH of Ar), 8.69 (1H, d, ³JHH7.8 Hz, CH of Ar), 11.10 (1H, s, NH).

2.3.8. N-(6-methyl-2-pyridyl)acetamide (3h). ¹H NMR (300 MHz, CDCl₃): δ 2.20 (3H, s, CH of COCH₃), 2.53 (3H, s, CH₃), 6.90 (1H, d, ³JHH7.5 Hz, CH of Ar), 7.63 (1H, t, ³JHH7.8 Hz, CH of Ar), 8.04 (1H, d, ³JHH8.1 Hz, CH of Ar), 8.79 (1H, broad, NH).

2.3.9. N-(1-naphthyl)acetamide (3i). ¹H NMR (300 MHz, CDCl₃): δ 2.33 (3H, s, CH₃), 7.45-7.52 (4H, m, CH of Ar), 7.72 (1H, broad, NH), 7.85-7.88 (3H, m, CH of Ar).

2.3.10. N-(4-nitrophenyl)formamide (3j). ¹H NMR (300 MHz, CDCl₃): δ 7.40 (1H, s, CH of CHO), 7.74(2H, d, ³JHH8.1 Hz, CH of Ar), 8.24 (2H, d, ³JHH8.7 Hz, CH of Ar), 8.49 (1H, broad, NH).

2.3.11. N-(1-naphthyl)formamide (3k). ¹H NMR (300 MHz, CDCl₃): δ 7.32-8.03(7H, m, CH of Ar), 8.28(1H, broad, NH), 8.61(1H, s, CH of CHO).

Fig. S1. PXRD patterns of as-synthesized (a) and simulated (b) ZIF-8.
Fig. S2. FT-IR spectrum of TFE (blue), ZIF-8 (black) and ZIF-8/TFE (red).

Fig. S3. Reusability of the model reaction over the ZIF-8 and ZIF-8/TFE (a) and SEM of the ZIF-8 after 9th run (b).