SO$_3$H-functionalized metal organic frameworks: an efficient heterogeneous catalyst for the synthesis of quinoxaline and derivatives

RADOELIZO S. Andriamitantsoa, a Jingjing Wang, a Wenjun Dong, a Hongyi Gao, a Ge Wang *
a Beijing Key Laboratory of Function Materials for Molecule & Structure Construction, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, P.R China.

Corresponding Author: gewang@mater.ustb.edu.cn

Experimental

Synthesis of UiO-66-Zr-NH$_2$

UiO-66-Zr-NH$_2$ was synthesized according to the previously reported method. Typically, ZrCl$_4$ (1.6 g, 6.8 mmol), 2-aminoterephtalic acid (1.2 g, 6.8 mmol) and acetic acid (11.4 mL, 3.4 mol) were mixed with 150.0 mL DMF in a round-bottomed flask. Then, water (0.5 mL, 0.028 mmol) was added to the solution under ultrasound at 60 ºC. Finally, the mixture solution was further kept in a bath at 120 ºC. After 24 h reaction, the solution was cooled to room temperature and the precipitate was collected by centrifugation. The obtained solid was washed with DMF (2 x 20.0 mL), ethanol (3 x 20.0 mL) and dried in vacuum (80 ºC, 3 h).

Post-synthetic modification of UiO-66-Zr-NH$_2$ to UiO-66-Zr-NH-RSO$_3$H

UiO-66-NH$_2$ (1.5 g, 0.85 mmol based on molecular weight of 1766 g/mol) was dispersed in 20.0 mL of CHCl$_3$. Then, 2 equiv. of 1,3-propanesultone (207 mg, 1.7 mmol) was added into the mixture. The mixture was stirred slowly at 25 ºC for 12 h. After the solution was decanted, and the sample was washed with 10.0 mL of DMF then soaked in 10 mL DMF for three days, with fresh DMF every 24 h. After three days of soaking the sample was rinsed once a day with 10 mL CHCl$_3$ for two days. Finally, the crystals were dried under vacuum at 40 ºC.

Synthesis of the sulfonated-polystyrene (SPS) microspheres

Commercial polystyrene (PS) spheres were purchased from Sigma-Aldrich. The SPS was prepared as follows: 1.0 g of PS particles was dispersed in 100 mL concentrated sulfuric acid in a 250 mL
three-necked flask equipped with a mechanical stirrer, and the mixed solution was heated to 55 ºC and stirred for 6 h. Then the products were separated by centrifugation, washed with ethanol and deionized water, and subsequently dried by lyophilization.
Fig. S1. SEM images of: (a) UiO-66-Zr-NH$_2$ and (b) UiO-66-Zr-NH-RSO$_3$H.

Fig. S2. XRD patterns of: (a) UiO-66-Zr-NH$_2$ and (b) UiO-66-Zr-NH-RSO$_3$H.
Fig. S3. Nitrogen adsorption-desorption isotherms of UiO-66-Zr-NH$_2$.

Fig. S4. FT-IR spectra of PS and the SPS catalyst.
Fig. S5. Plausible mechanism for the condensation of benzene-1,2-diamine with benzil.

Fig. S6. XRD spectra of: (a) fresh MIL-101-Cr-NH-RSO₃H and (b) MIL-101-Cr-NH-RSO₃H catalyst after the fifth run.
Fig. S7. FT-IR spectra of: (a) fresh MIL-101-Cr-NH-RSO_3H and (b) MIL-101-Cr-NH-RSO_3H catalyst after the fifth run.

Selected Spectral Data

2,3-diphenylquinoxaline (Yield 93%)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.06 (m, 2H), 8.01 (m, 2H), 7.53 (m, 4H), 7.41 (m, 6H); IR (KBr) ($\nu$ max, cm$^{-1}$): 3055, 1542, 1495, 1448, and 1355.

2,3-dimethylquinoxaline (Yield 91%)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.02 (m, 2H), 7.70 (m, 2H), 2.78 (s, 6H); IR (KBr) ($\nu$ max, cm$^{-1}$): 3065, 1441, 1395, 768.

2,3-bis(4-fluorophenyl)quinoxaline (Yield 85%)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.15-8.09 (dd, 2H), 7.81-7.76 (dd, 2H), 7.35 (d, 4H), 7.22(d, 4H); IR (KBr) ($\nu$ max, cm$^{-1}$): 3031, 2958, 1617, 1517, 1448, 1355.

2,3-bis(4-methoxyphenyl)quinoxaline (Yield 87%)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.14(s, 1H), 7.92(d, 4H), 7.72(s, 1H), 7.52(d, 1H), 6.96(m, 4H), 6.88(d, 1H), 3.83(s, 6H); IR (KBr) ($\nu$ max, cm$^{-1}$): 3056, 2957, 1617, 1517, 1448, 1355.

6-Methyl-2,3-diphenylquinoxaline (Yield %)
$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.12-8.07 (d, 1H), 7.96 (1s, 1H), 7.64-7.58 (d, 1H), 7.57-7.53 (m, 4H), 7.35 (m, 6H), 2.65 (s, 3H); IR (KBr) (v max, cm$^{-1}$): 3083, 3054, 3026, 1619, 1484, 1445, 1345, 1201, 1138, 1060, 1023, 979, 833, 775, 695, 595, 545.

(2,3-Diphenylquinoxalin-6-yl)(phenyl)methanone (Yield %)

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.45 (s, 1H), 8.23-8.18 (d, 2H), 7.88-7.84 (d, 2H), 7.55-7.46 (m, 7H), 7.33-7.28. (m, 6H); IR (KBr) (v max, cm$^{-1}$): 3057, 3035, 1733, 1660, 1598, 1446, 1402, 1346, 1309, 1265, 1198, 1124, 1057, 1022, 980, 890, 846, 770, 696, 600, 542.

[2,3-Bis(4-fluorophenyl)quinoxaline-6-yl](phenyl)methanone (Yield %)

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.60 (s, 1H), 7.39 (s, 2H), 7.02-7.00 (d, 2H), 6.79-6.73 (m, 1H), 6.70-6.58 (m, 6H), 6.50-6.42 (m, 4H); IR (KBr) (v max, cm$^{-1}$): 3066, 1651, 1594, 1492, 1447, 1408, 1334, 1270, 1199, 1177, 1092, 1052, 978, 893, 833, 788, 594, 540.

Notes and references


