Electronic Supplementary Material (ESI) for Catalysis Science & Technology


# Towards applications of metal-organic frameworks in catalysis: C-H direct activation of benzoxazole with aryl boronic acids using $Ni_2(BDC)_2(DABCO)$ as an efficient heterogeneous catalyst

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**Supporting information**

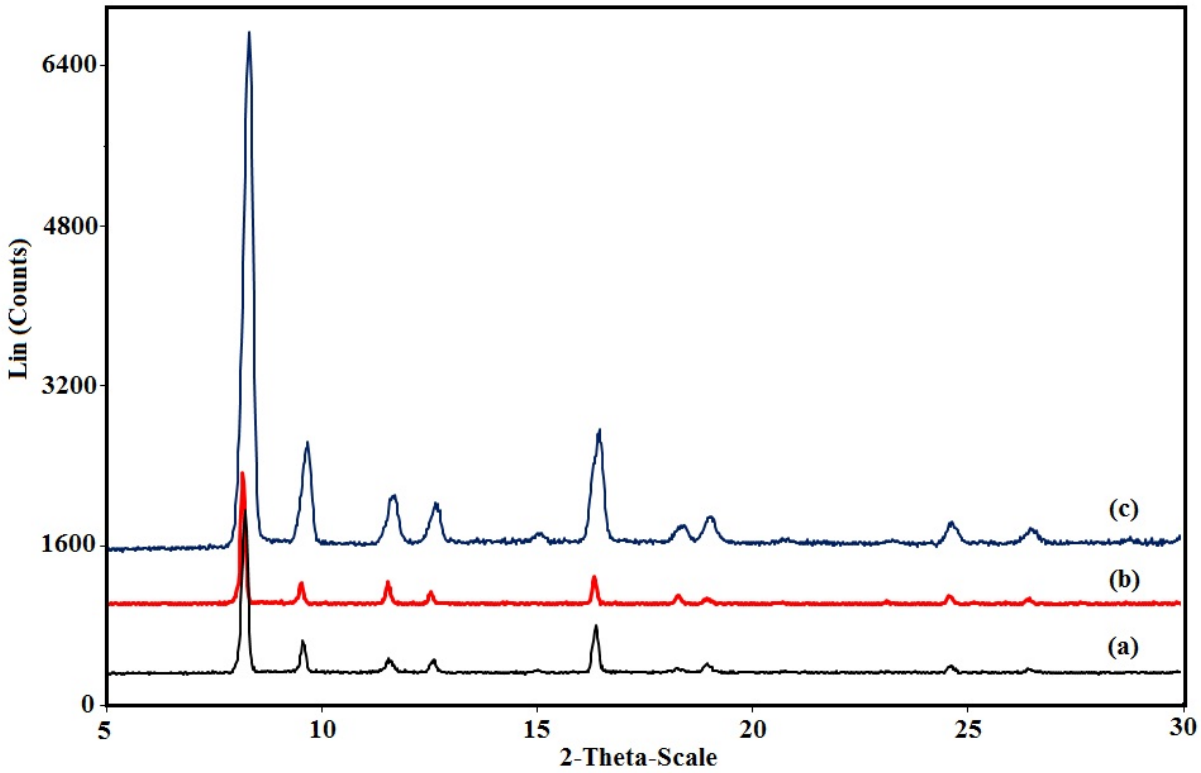


Fig. S1. X-ray powder diffractograms of the as-synthesized (a), $CH_3OH$-exchanged (b), and activated (c) $Ni_2(BDC)_2(DABCO)$.


Fig. S2. SEM micrograph of the $Ni_2(BDC)_2(DABCO)$.

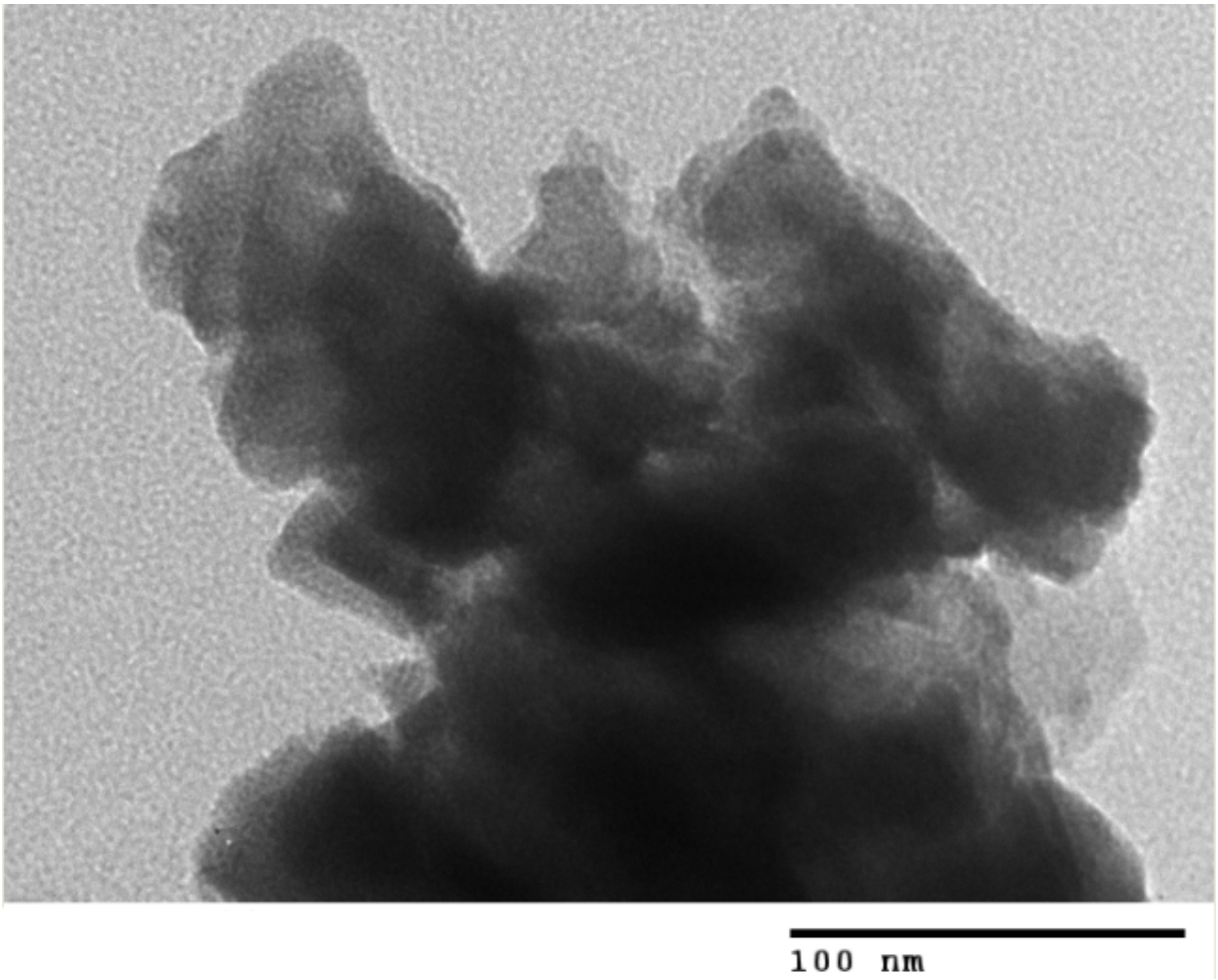


Fig. S3. TEM micrograph of the $Ni_2(BDC)_2(DABCO)$.

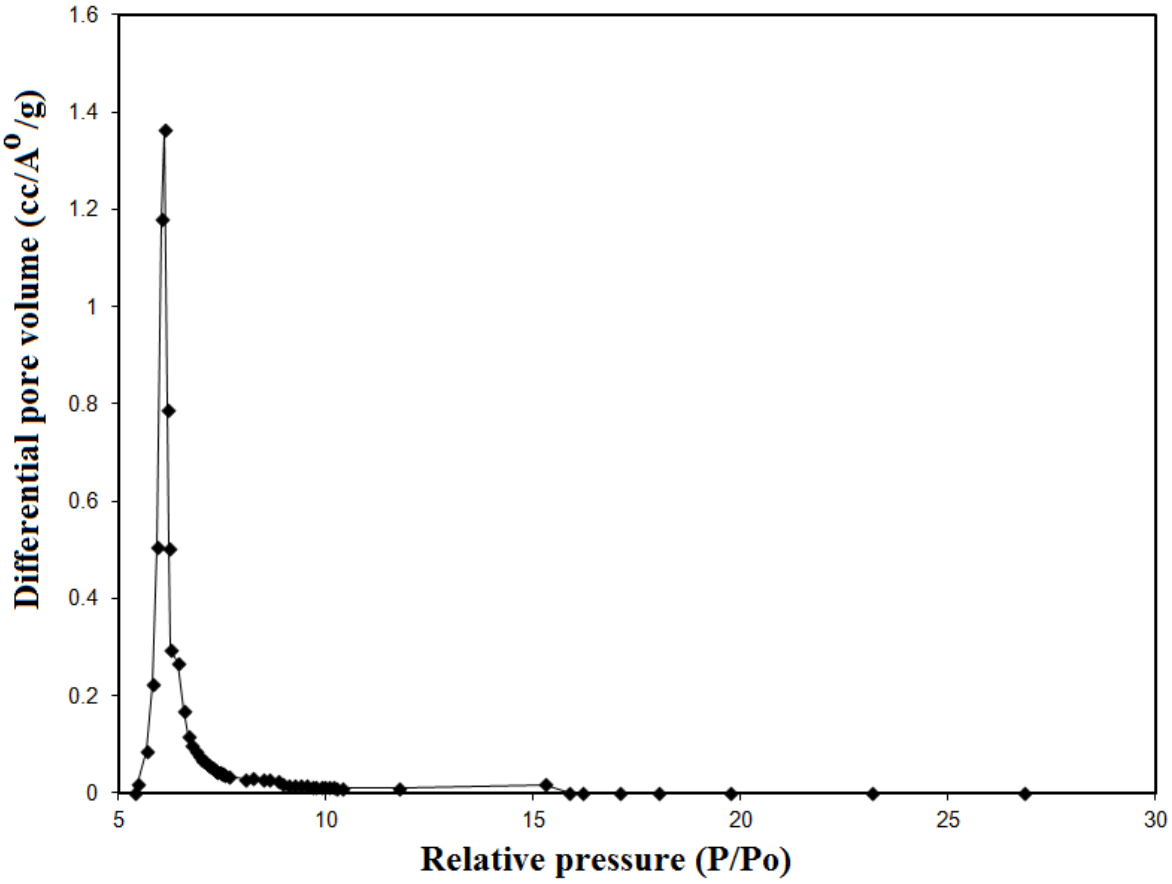


Fig. S4. Pore size distribution of the fresh $Ni_2(BDC)_2(DABCO)$.

**Pore size distribution measurement parameters**

Sample Mass: 0.0275 g

Cold Free Space: 48.9336 cm³

Ambient temperature: 22.00 °C

Automatic Degas: Yes

Analysis Adsorptive: N2

Analysis Bath Temp.: 77.300 K

Thermal Correction: No

Warm Free Space: 16.6957 cm³ Measured

Equilibration Interval: 5 s

Low Pressure Dose: None

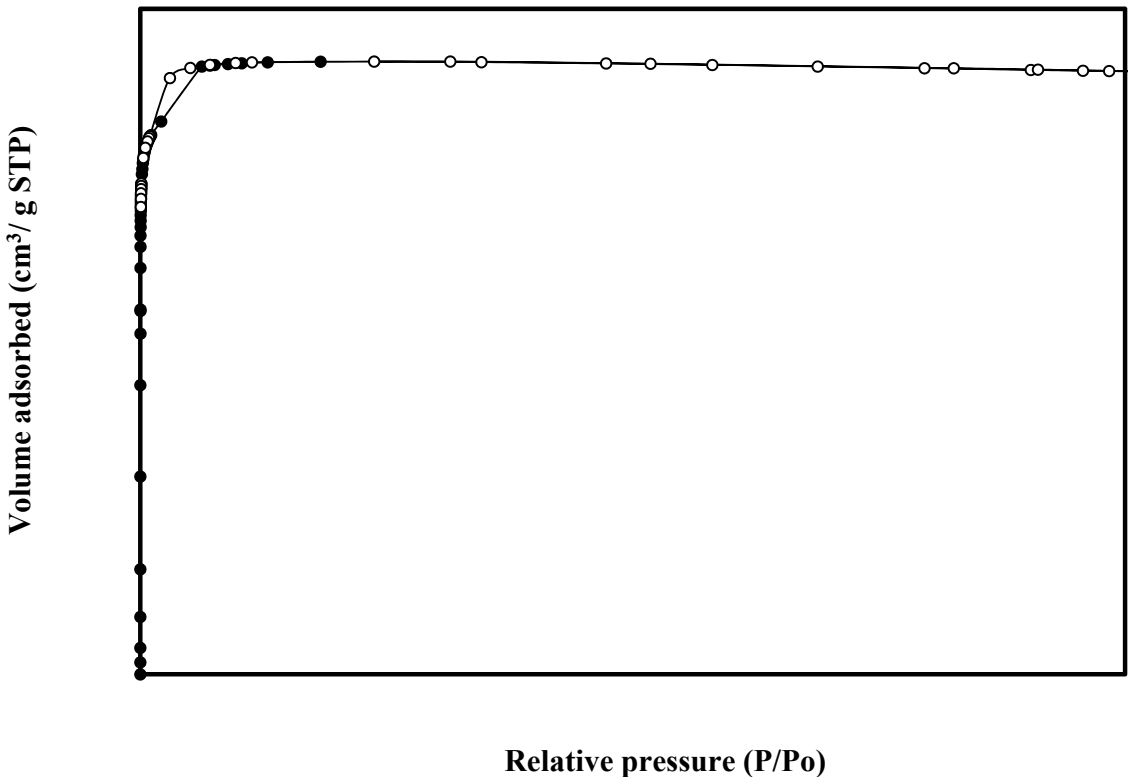


Fig. S5. Nitrogen adsorption/desorption isotherm of the $Ni_2(BDC)_2(DABCO)$. Adsorption data are shown as closed circles and desorption data as open circles.

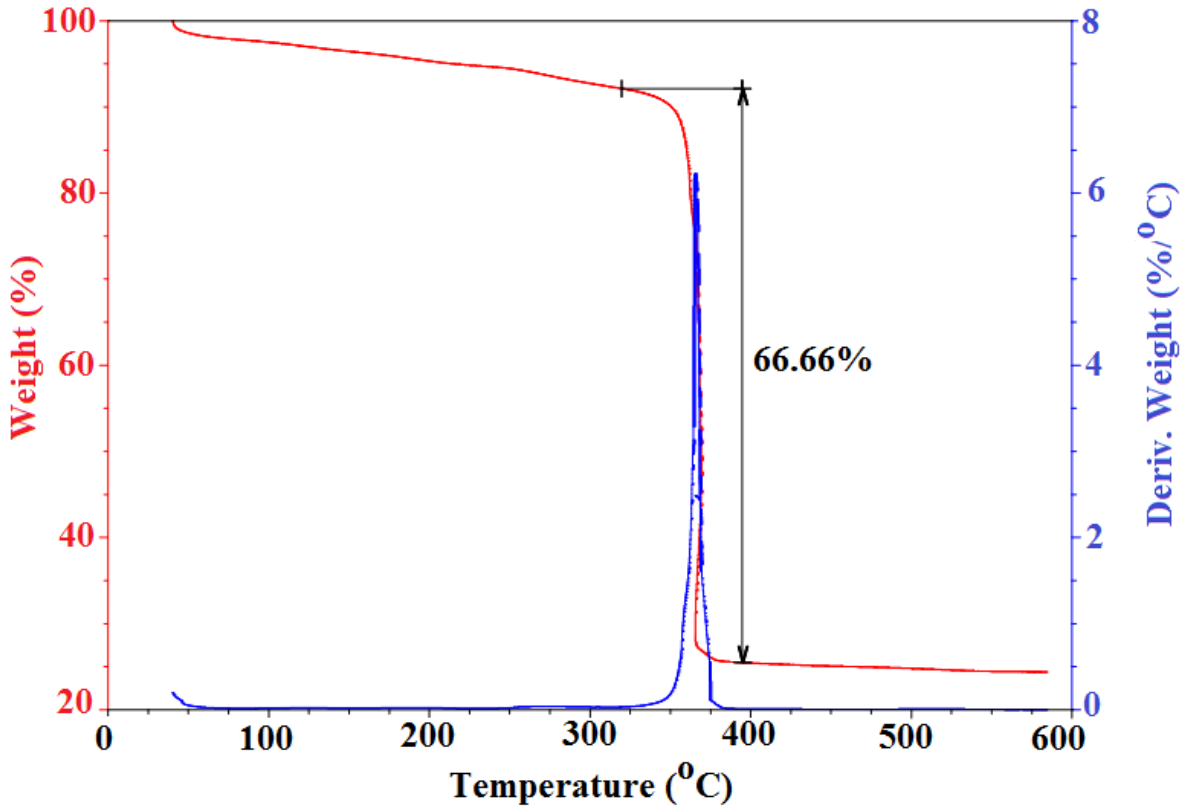


Fig. S6. TGA analysis of the $Ni_2(BDC)_2(DABCO)$.

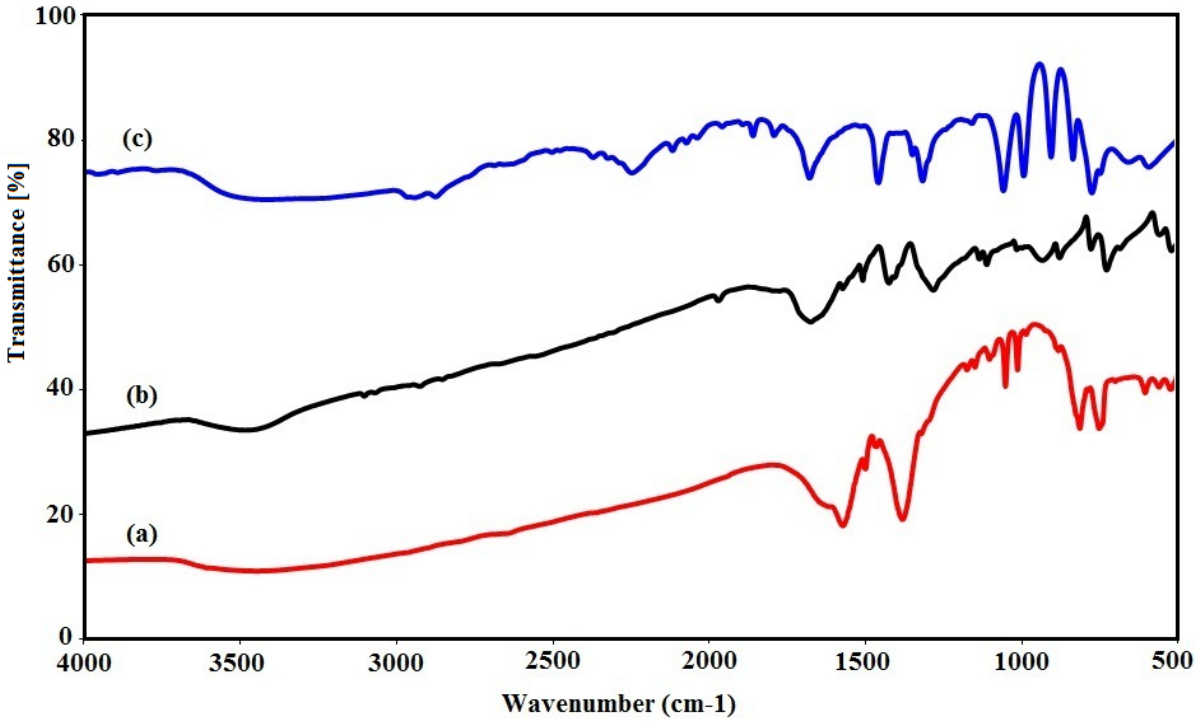


Fig. S7. FT-IR spectra of the $Ni_2(BDC)_2(DABCO)$ (a), 1,4-benzenedicarboxylic acid (b), and 1,4-diazabicyclo[2.2.2]octane (c).

| | Effect of temperature | Effect of solvents | Effect of bases | Effect of ligands | Effect of different nickel salts | Effect of different MOFs |
|---|---|---|---|---|---|---|
| Temperature (oC) | 80; 90; **100;** 120 | 100 | 100 | 100 | 100 | 100 |
| Solvent (5 ml) | DMAc | **DMAc**, DMF, DEF, NMP, DMSO, dioxane, toluene | DMAc | DMAc | DMAc | DMAc |
| Molar ratio A/B | 1:2 | 1:2 | 1:2,5 | 1:2,5 | 1:2,5 | 1:2,5 |
| Catalyst (10 mol%) | $Ni_2(BDC)_2$ (DABCO) | $Ni_2(BDC)_2$ (DABCO) | $Ni_2(BDC)_2$ (DABCO | $Ni_2(BDC)_2$ (DABCO) | **$Ni_2(BDC)_2(DABCO)$** $NiNO_3$ $NiSO_4$ $NiCl_2$ $Ni(OAc)_2$ | **$Ni_2(BDC)_2(DABCO)$** $Co_2(BDC)_2(DABCO)$ $Cu_2(BDC)_2(DABCO)$ $Ni_2(BTC)_2$ Ni(HBTC)(BIPY) |
| Base (2 eqv) | $K_3PO_4$ | $K_3PO_4$ | **$K_3PO_4$** $K_3CO_3$ $Na_2CO_3$ DBU *t*BuOK piperidine $CH_3COONa$ | $K_3PO_4$ | $K_3PO_4$ | $K_3PO_4$ |
| Ligand (20 mol%) | 2,2'-bipy | 2,2'-bipy | 2,2'-bipy | **2,2'-bipy** 1,10-phen acac EDA PPh3 | 2,2'-bipy | 2,2'-bipy |

Table S1. Summarizing the all catalyst, reaction conditions, additives have been tried in our study (texts in bold indicate the best conditions)

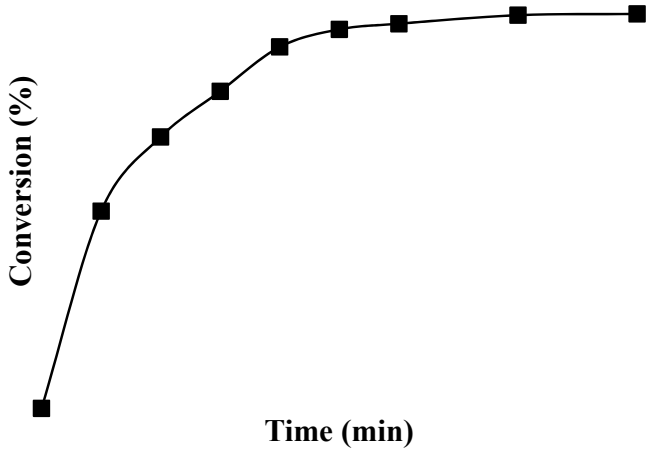


Fig. S8. Reaction with longer time (5 hours)

Reaction conversions stay unchanged after 3 hours. Specifically, 86 % and 87 % conversions were obtained at 3 hours and 5 hours, respectively.

***Procedure for the synthesis of $Cu_2(BDC)_2(DABCO)$, $Co_2(BDC)_2(DABCO)$, Ni(HBTC)(BIPY), $Ni_3(BTC)_2$:***

**$Cu_2(BDC)_2(DABCO)$**: A solid mixture of $H_2BDC$ ($H_2BDC$ = 1,4-benzenedicarboxylic acid; 0.332 g, 2 mmol), DABCO (DABCO = 1,4-diazabicyclo[2.2.2]octane; 0.112 g, 1 mmol), and $Cu(NO_3)_2.6H_2O$ (0.59 g, 2 mmol) was dissolved in DMF (DMF = *N,N'*-dimethylformamide; 15 ml). The resulting solution was distributed to two 20 ml vials. The vials were then heated at 100 $^oC$ in an isothermal oven for 48 h. After cooling the vials to room temperature, the solid product was removed by decanting with mother liquor and washed in DMF (3 x 10 ml) for 3 days. Solvent exchange was carried out with methanol (3 x 10 ml) at room temperature for 3 days. The material was then evacuated under vacuum at 140 $^oC$ for 6 h, yielding 0.381 g of $Cu_2(BDC)_2(DABCO)$ in the form of blue crystals (67% yield).

**$Co_2(BDC)_2(DABCO)$**: $H_2BDC$ ($H_2BDC$ = 1,4-benzenedicarboxylic acid; 0.332 g, 2 mmol), DABCO (DABCO = 1,4-diazabicyclo[2.2.2]octane; 0.112 g, 1 mmol), and $Co(NO_3)_2.6H_2O$ (0.58 g, 2 mmol) was dissolved in DMF (DMF = *N,N'*-dimethylformamide; 15 ml). The resulting solution was distributed to two 20 ml vials. The vials were then heated at 100 $^oC$ in an isothermal oven for 48 h. After cooling the vials to room temperature, the solid product was removed by decanting with mother liquor and washed in DMF (3 x 10 ml) for 3 days. Solvent exchange was carried out with methanol (3 x 10 ml) at room temperature for 3 days. The material was then evacuated under vacuum at 140 $^oC$ for 6 h, yielding 0.407 g of $Co_2(BDC)_2(DABCO)$ in the form of purple crystals (73% yield).

Structural analysis of $Cu_2(BDC)_2(DABCO)$ and $Co_2(BDC)_2(DABCO)$ were previously reported (ref. 42, ref. 43). It's worth to mention that compared to $Ni_2(BDC)_2(DABCO)$, these two MOFs don't have open metal sites, which prohibit the nucleophiles in attacking metal centers.

**Ni(HBTC)(BIPY)**: A solid mixture of $H_3BTC$ ($H_3BTC$ = **Benzene-1,3,5-tricarboxylic acid**; 0.442 g, 2 mmol), 4,4'-bipyridyl (0.318 g, 2 mmol), and $Ni(NO_3)_2.6H_2O$ (0.58 g, 2 mmol) was dissolved in DMF (DMF = *N,N'*-dimethylformamide; 15 ml). The resulting solution was distributed to two 20 ml vials. The vials were then heated at 100 $^oC$ in an isothermal oven for 48 h. After cooling the vials to room temperature, the solid product was removed by decanting with mother liquor and washed in DMF (3 x 10 ml) for 3 days. Solvent exchange was carried out with dichloromethane (3 x 10 ml) at room temperature for 3 days. The material was then evacuated under vacuum at 140 $^oC$ for 6 h, yielding 0.592 g of Ni(HBTC)(BIPY) in the form of light blue crystals (70% yield).

**$Ni_3(BTC)_2$**: a solid mixture of $H_3BTC$ ($H_3BTC$ = **Benzene-1,3,5-tricarboxylic acid**; 0.663 g, 3 mmol), 2-methyl imidazole (0.0734 g, 0.9 mmol), and $Ni(NO_3)_2.6H_2O$ (0.58 g, 2 mmol) was dissolved in DMF (DMF = *N,N'*-dimethylformamide; 15 ml). The resulting solution was distributed to two 20 ml vials. The vials were then heated at 85 $^oC$ in an isothermal oven for 48 h. After cooling the vials to room temperature, the solid product was removed by decanting with mother liquor and washed in DMF (3 x 10 ml) for 3 days. Solvent exchange was carried out with dichloromethane (3 x 10 ml) at room temperature for 3 days. The material was then evacuated under vacuum at 100 $^oC$ for 6 h, yielding 0.084 g of $Ni_3(BTC)_2$ in the form of light green crystals (21 % yield).

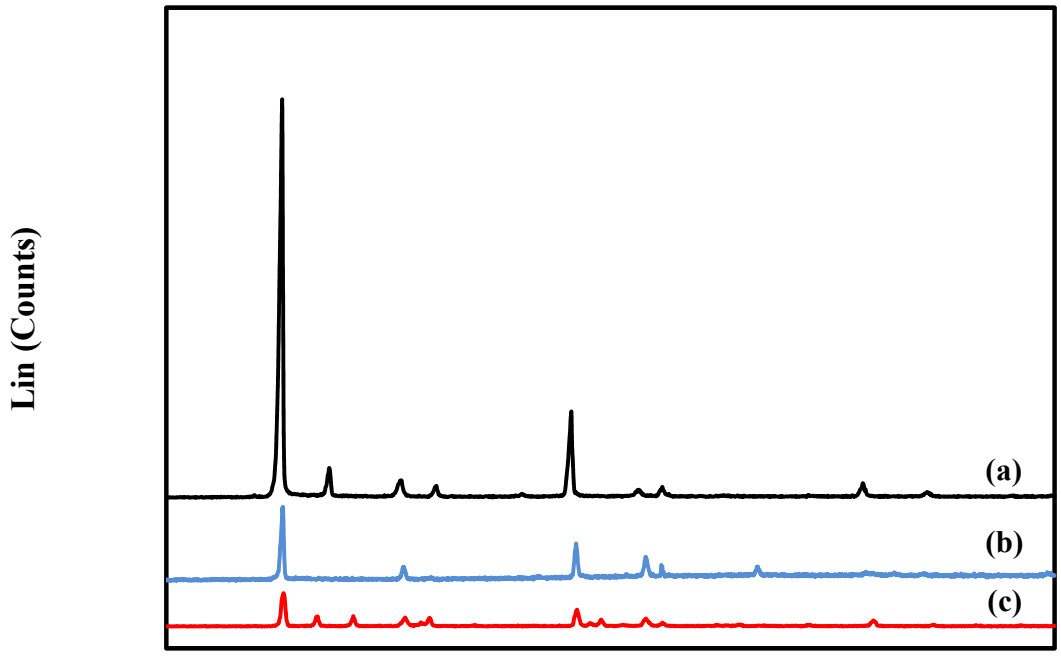


Fig. S9. X-ray powder diffractograms of the $Ni_2(BDC)_2(DABCO)$ (a), $Co_2(BDC)_2(DABCO)$ (b) and the $Cu_2(BDC)_2(DABCO)$ (c).

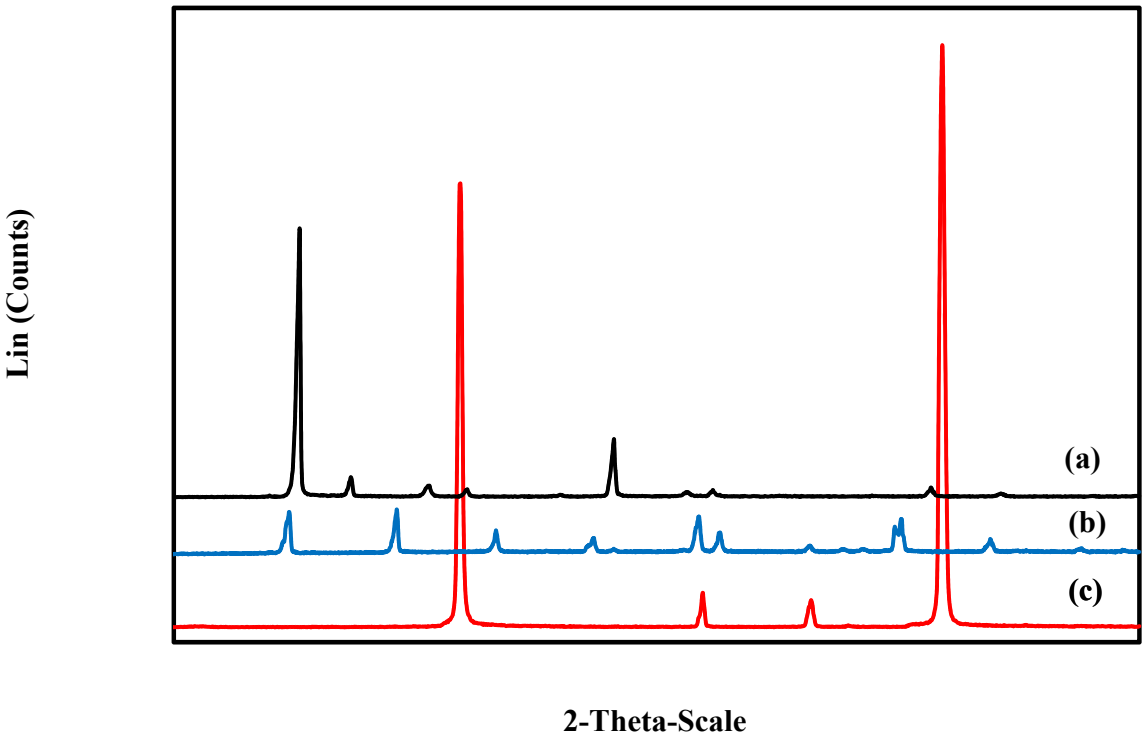


Fig. S10. X-ray powder diffractograms of the $Ni_2(BDC)_2(DABCO)$ (a), Ni(HBTC)(BIPY) (b) and the $Ni_3(BTC)_2$ (c).

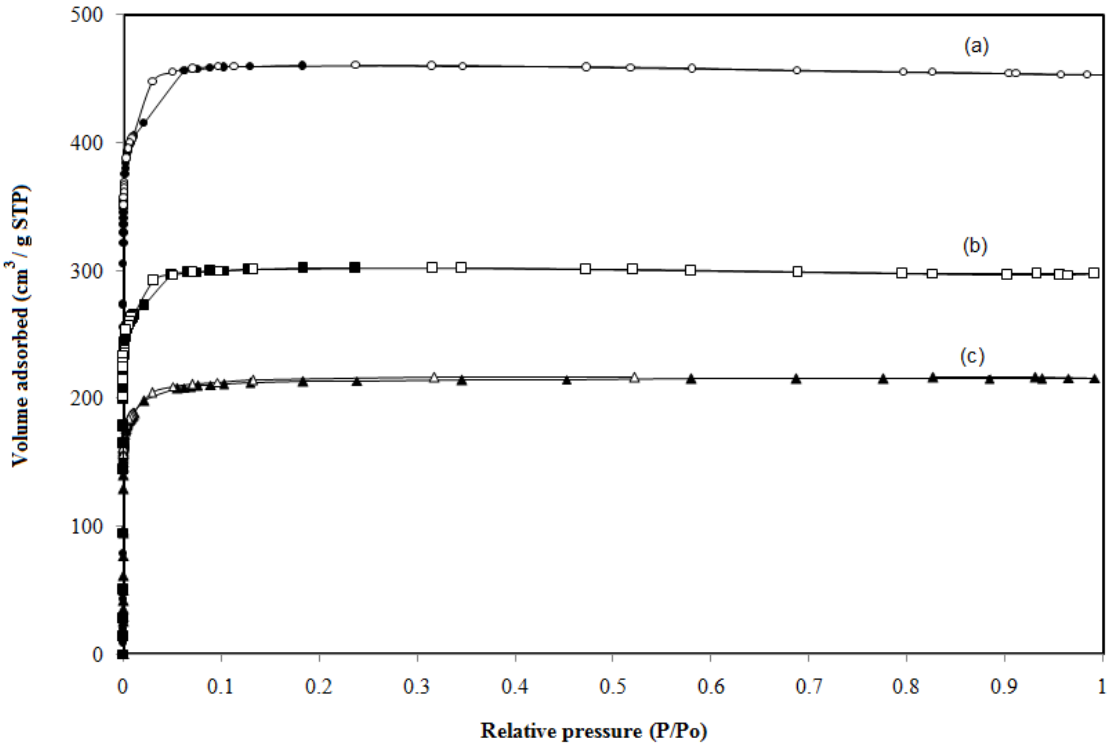


Fig. S11. Nitrogen adsorption/desorption isotherm of the fresh $Ni_2(BDC)_2(DABCO)$ (a), after reaction at 100 $^oC$ (b) and after reaction at 120 $^oC$ (c)

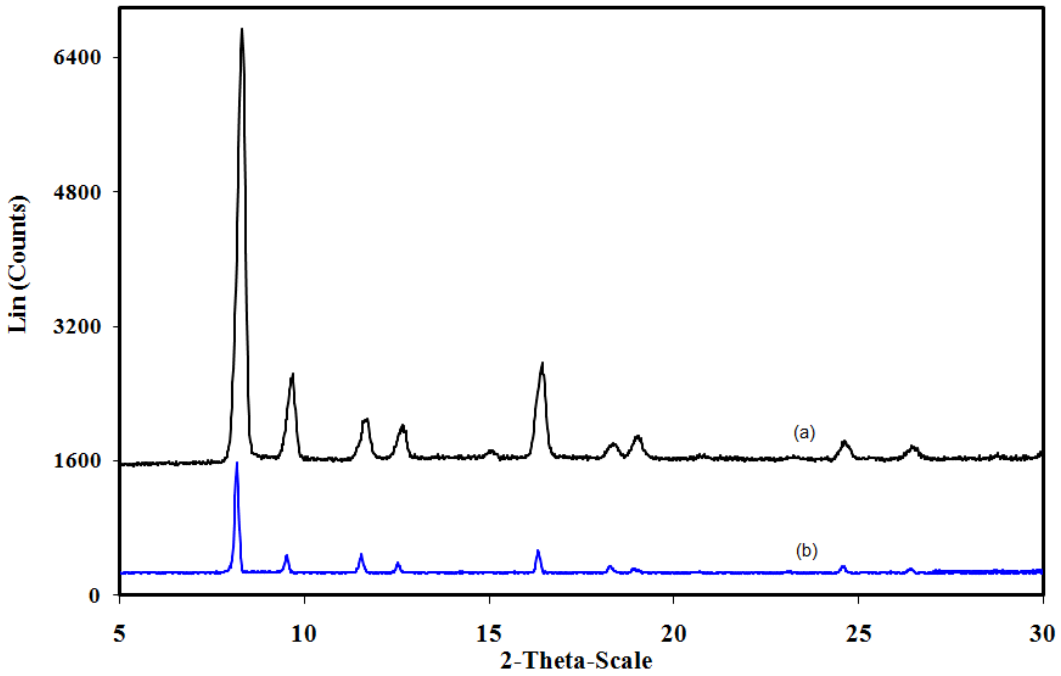


Fig. S12. X-ray powder diffractograms of the fresh (a) and reused (b) $Ni_2(BDC)_2(DABCO)$ catalyst (after reaction under 120 $^oC$).