Supporting Information

Bifunctional Heterometallic Metal-organic Frameworks for Solvent-free Heterogeneous Cascade Catalysis

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Materials: $In(NO_3)_3 \cdot xH2O$, $Ga(NO_3)_3 \cdot xH2O$, VCl_3, $MnCl_2$, $FeCl_3 \cdot 6H_2O$, $InCl_3$, $Mg(OAc)_2 \cdot 4H2O$, $Sc(OAc)_3 \cdot xH_2O$, $Co(OAc)_2 \cdot 4H_2O$, N,N-dimethylacetamide (DMA), N,N-Diethylformamide (DEF) and HCl (37%, AR grade) were purchased from Aldrich Chemical Co. and used as received without further purification. 3,3′,5,5′-azobenzenetetracarboxylic acid (H_4ABTC) was prepared according to the methods previously reported[S1].

1. Synthesis of CPM200 MOFs

Synthesis of $[InMg_2(OH)(ABTC)_{1.5}(H_2O)_3]$ (CPM-200-In/Mg): In a 20 ml glass vial, 44 mg of $InCl_3$, 172 mg of $Mg(OAc)_2 \cdot 4H_2O$, and 71 mg of H_4ABTC were dissolved in a mixture of 8.0 g of DMA and 1.6 g of H_2O. After addition of 240 mg HCl, the vial was sealed and placed in a 90 ºC oven for 2 days. Pure yellow cubic crystals were obtained after cooling to room temperature. Pure sample was obtained by filtering and washing the raw product with DMA.

Synthesis of $[InCo_2(OH)(ABTC)_{1.5}(H_2O)_3]$ (CPM-200-In/Co): In a 20 ml glass vial, 44 mg of $InCl_3$, 200 mg of $Co(OAc)_2 \cdot 4H_2O$, and 71 mg of H_4ABTC were dissolved in a mixture of 8.0 g of DMA and 1.6 g of H_2O. After addition of 240 mg HCl, the vial was sealed and placed in a 90ºC oven for 3 days. Pure reddish-brown cubic crystals were obtained after cooling to room temperature. Pure sample was obtained by filtering and washing the raw product with DMA.

Synthesis of $[InMn_2(OH)(ABTC)_{1.5}(H_2O)_3]$ (CPM-200-In/Mn): In a 20 ml glass vial, 44 mg of $InCl_3$, 160 mg of $MnCl_2 \cdot 4H_2O$, and 71 mg of H_4ABTC were dissolved in a

mixture of 8.0 g of DMA and 1.6 g of H_2O. After addition of 240 mg HCl, the vial was sealed and placed in a 90°C oven for 1 days. Pure yellow cubic crystals were obtained after cooling to room temperature. Pure sample was obtained by filtering and washing the raw product with DMA.

Synthesis of [$FeMg_2(OH)(ABTC)_{1.5}(H_2O)_3$] (CPM-200-Fe/Mg): In a 20 ml glass vial, 54 mg of $FeCl_3 \cdot 6H_2O$, 172 mg of $Mg(OAc)_2 \cdot 4H_2O$, and 71mg of H_4ABTC were dissolved in a mixture of 8.0 g of DMA and 1.6 g of H_2O. After addition of 240 mg HCl, the vial was sealed and placed in a 90°C oven for 5 days. Pure yellow cubic crystals were obtained after cooling to room temperature. Pure sample was obtained by filtering and washing the raw product with DMA.

Synthesis of [$GaMg_2(OH)(ABTC)_{1.5}(H_2O)_3$] (CPM-200-Ga/Mg): In a 20 ml glass vial, 56 mg of $Ga(NO3)_3 \cdot x$H2O, 172 mg of $Mg(OAc)_2 \cdot 4H_2O$, and 71 mg of H_4ABTC were dissolved in a mixture of 8.0 g of DMA and 1.6 g of H_2O. After addition of 240 mg HCl, the vial was sealed and placed in a 90°C oven for 3 days. Pure yellow irregular polyhedral crystals were obtained after cooling to room temperature. Pure sample was obtained by filtering and washing the raw product with DMA.

Synthesis of [$VMg_2(OH)(ABTC)_{1.5}(H_2O)_3$] (CPM-200-V/Mg): In a 20 ml glass vial, 48 mg of VCl_3, 258 mg of $Mg(OAc)_2 \cdot 4H_2O$, and 106 mg of H_4ABTC were dissolved in a mixture of 12.0 g of DMA and 2.4 g of H_2O. After addition of 360 mg HCl, the vial was sealed and placed in a 90°C oven for 5 days. Pure yellow cubic crystals were obtained after cooling to room temperature. Pure sample was obtained by filtering and washing the raw product with DMA.

Synthesis of [$ScMg_2(OH)(ABTC)_{1.5}(H2O)_3$] (CPM-200-Sc/Mg): In a 20 ml glass vial, 45 mg of $Sc(NO_3)_3 \cdot xH_2O$, 172 mg of $Mg(OAc)_2 \cdot 4H_2O$, and 71 mg of H_4ABTC were dissolved in a mixture of 8.0 g of DEF and 1.6 g of H_2O. After addition of 240 mg HCl, the vial was sealed and placed in a 90 ºC oven for 5 days. Pure yellow cubic crystals were obtained after cooling to room temperature. Pure sample was obtained by filtering and washing the raw product with DEF.

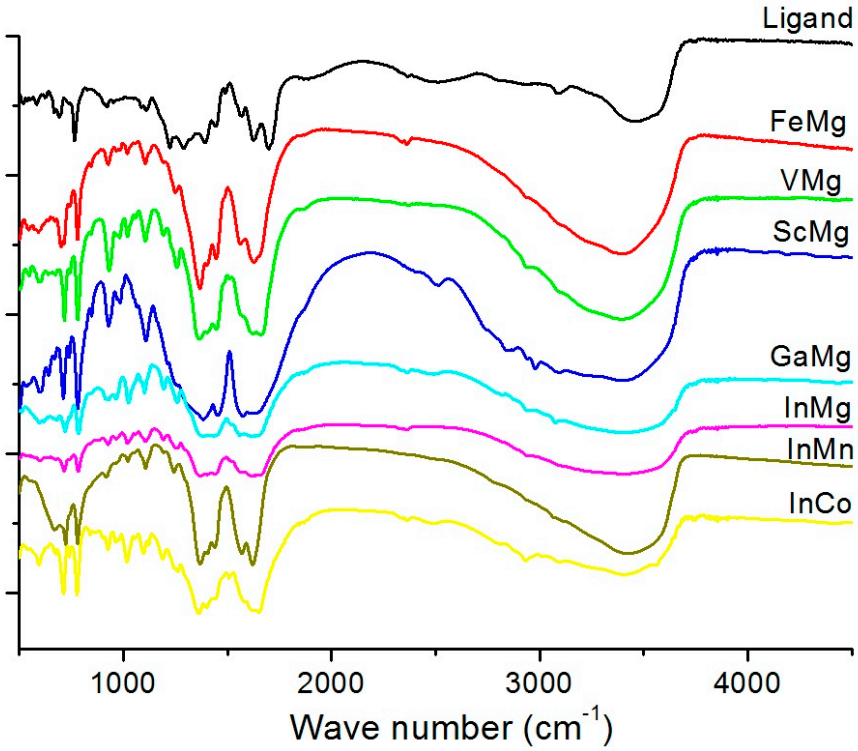

Fig. S1 FT-IR spectra for ligand and seven CH_2Cl_2-exchanged CPM200 MOFs

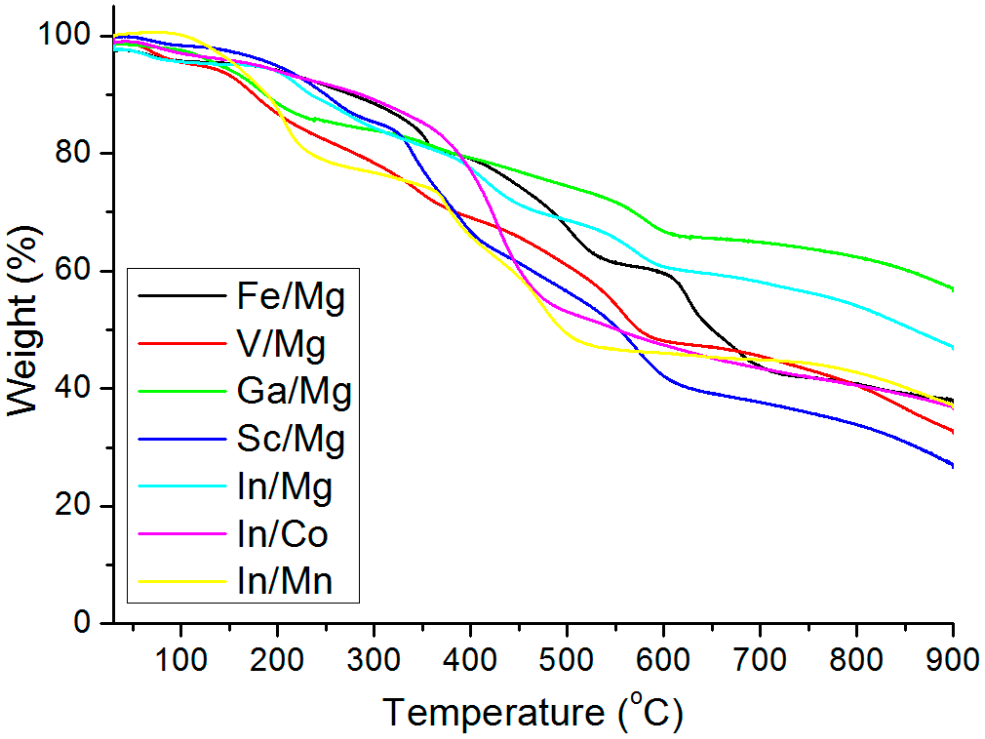

Fig.S2 TGA curves for CH_2Cl_2-exchanged CPM200 MOFs.

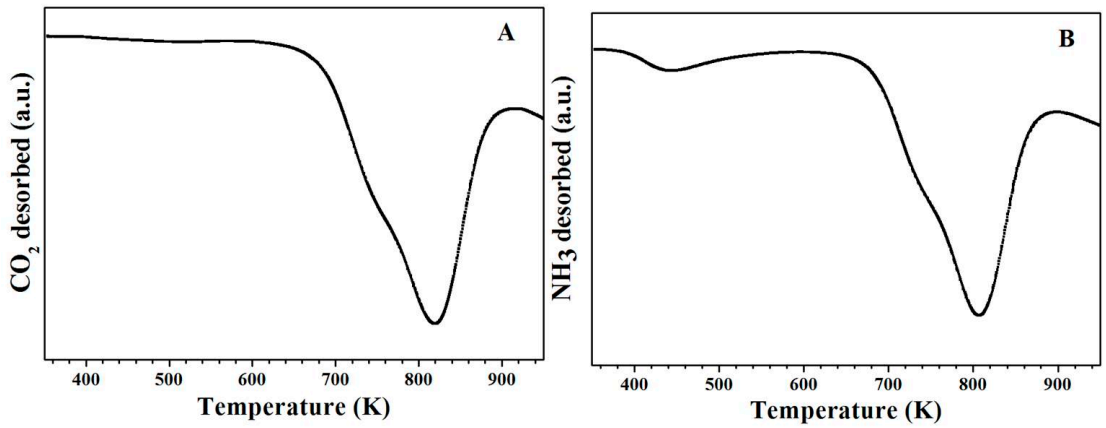

Fig. S3. CO_2-TPD (A) and NH_3-TPD (B) profiles of CPM200 V/Mg catalysts.

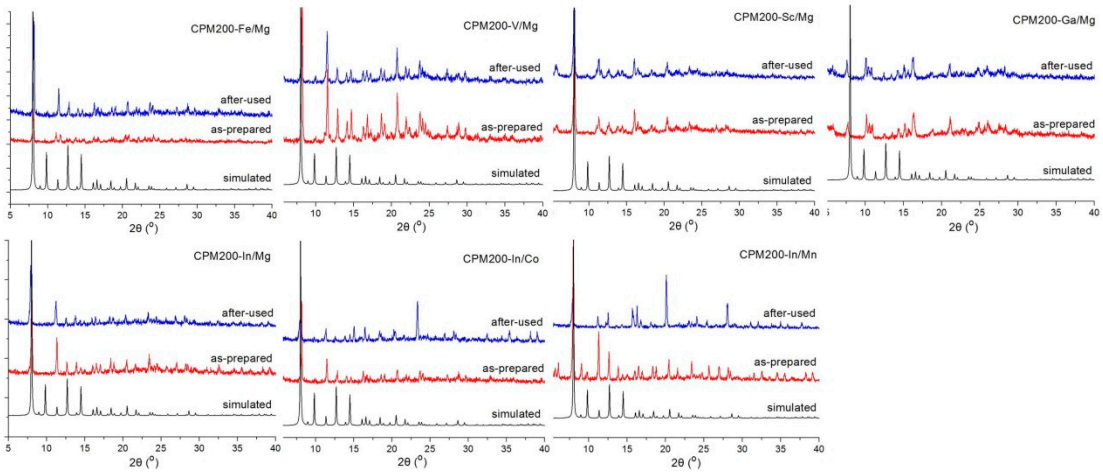

Fig. S4 Experimental PXRD patterns before and after used and simulated PXRD patterns for CPM-200 MOFs

Table S1 Summary of molecular weight, surface area and pore volume data for CPM-200 MOFs [S2].

CPM200	In/Mg	In/Co	In/Mn	In/Ni	Fe/Mg	V/Mg	Sc/Mg	Ga/Mg
Molecular weight	765.84	835.08	827.10	834.64	706.87	701.96	695.96	720.74
Surface area $_{BET}$ (m^2/g)	1347	1040	941	877	1459	1011	1041	1056
Pore volume (cm^3/g)	0.65	0.51	0.45	0.43	0.72	0.50	0.51	0.54

References

[S1] Wang, S.; Wang, X.; Li, L.; Advincula, R. C. *J. Org. Chem.* **2004**, *69*, 9073.

[S2] Zhai, Q. G.; Bu, X. H.; Mao, C. Y.; Zhao, X.; Feng, P. Y., J. Am. Chem. Soc. 2016, 138, 2524-2527