SUPPORTING INFORMATION

Sulfate-Modified MOF-808 as Superacid Catalysts: A Performance Evaluation of Zr(IV) and Hf(IV) Analogues in Acetalization Reactions

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1. Synthesis of precursors materials.

Synthesis of MOF-808-Zr and MOF-808-Hf. The materials were synthesized according to the published literature with a slight modification [1,2]. $ZrCl_4$ (0.2330 g; 1 mmol) was dissolved in a glass vial in 3.5 mL of DMF. In a second vial, the linker benzene-1,3,5-tricarboxylic acid (0.2101 g; 1 mmol) was dissolved in 3.5 mL of DMF. Both solutions were placed in a sonicator for 20 minutes. Subsequently, both vials were mixed and 7 mL of HCOOH were added. The mixture was heated at 100 °C for 24 hours. A powder white solid was collected and washed three times with 6.0 mL of DMF and three times with 6.0 mL of acetone, each one performed every six hours. Finally, the material was dried at room temperature with vacuum in a desiccator. MOF-808-Hf was synthesized following the same procedure, using $HfCl_4$ instead of $ZrCl_4$.

2. Characterization of materials

2.1. Powder X-ray diffraction pattern.

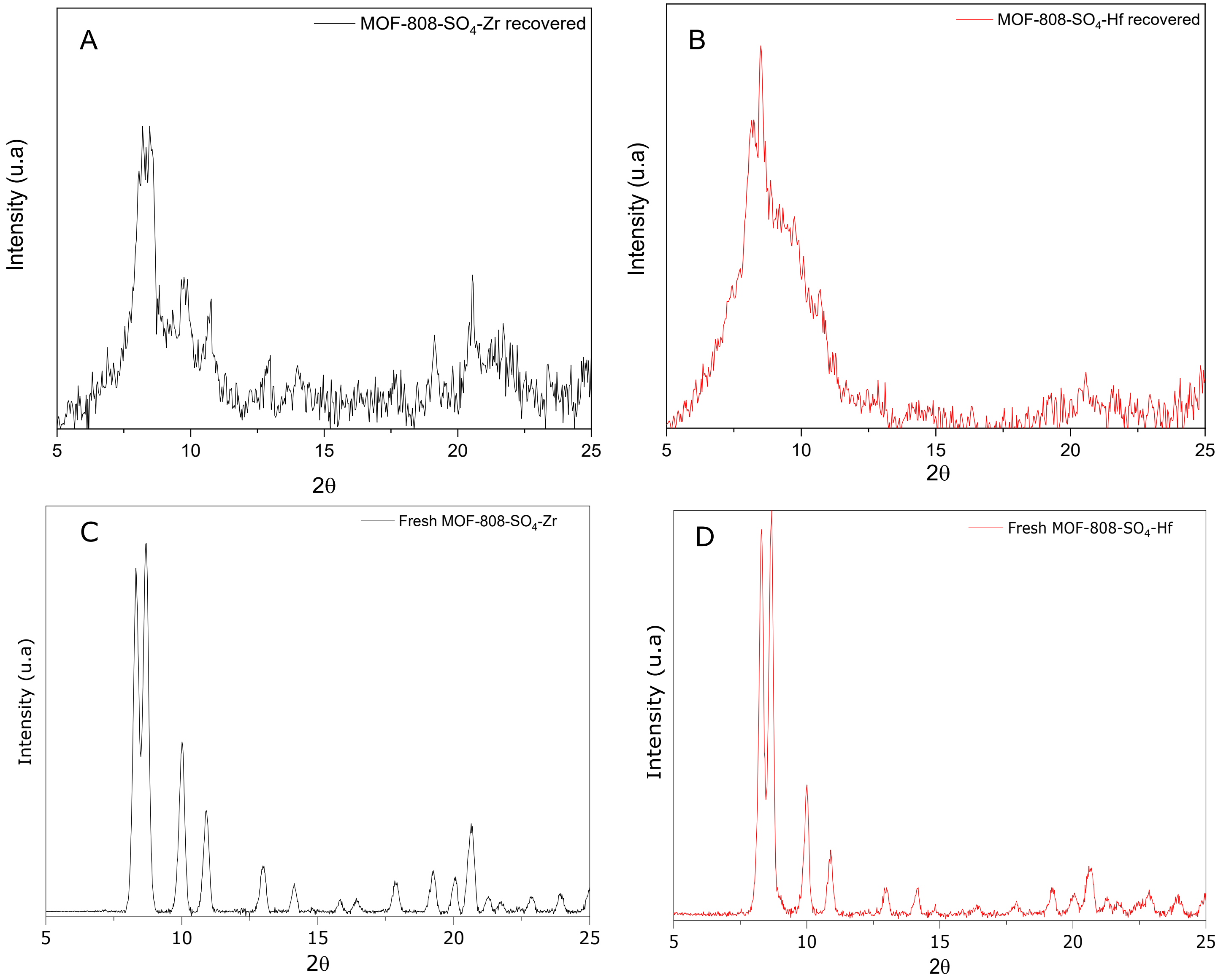


Figure S1. Diffraction patterns of MOF-808-SO_4-Zr (A) and MOF-808-SO_4-Hf (B) recovered post-catalysis. In addition, the diffraction patterns of each fresh MOF-808-SO_4-Zr (C) and MOF-808-SO_4-Hf (D) material are observed.

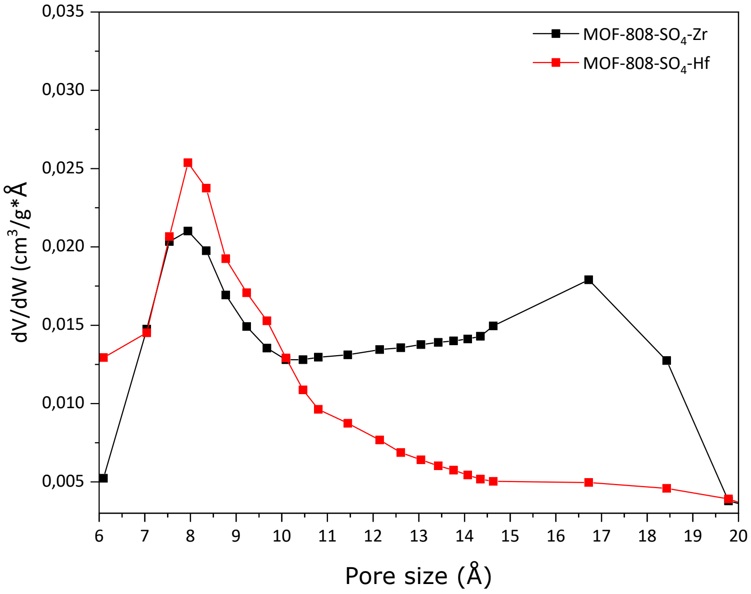


Figure S2: Pore size distribution of MOF-808-SO_4-Zr and MOF-808-SO_4-Hf materials using HK method (B).

Table S1. BET specific surface area and pore size distribution of the MOF-808-Zr and MOF-808-Hf precursor materials.

Materials	**$S_{(BET)}$ m^2g^{-1}**	**Pore size distribution (HK) (Å)**
MOF-808-Zr	1339	5.3 – 15
MOF-808-Hf	958	5.3 - 16

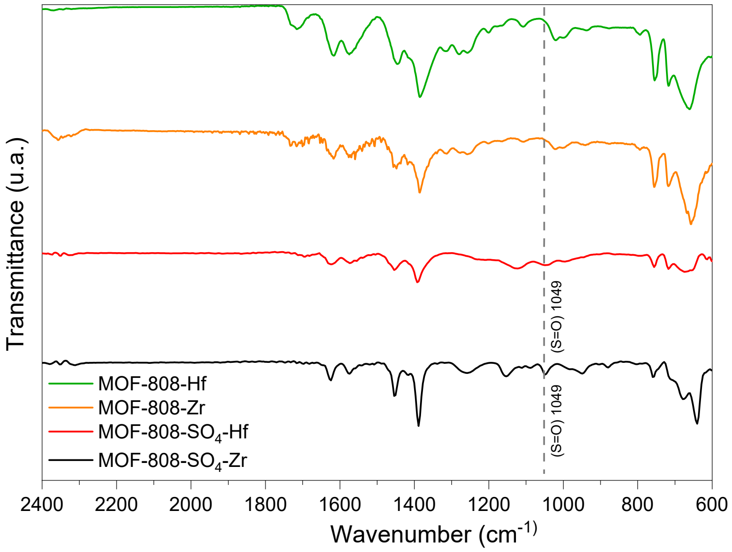


Figure S3. Infrared spectroscopy of MOF-808-SO_4-Zr and MOF-808-SO_4-Hf compared with their precursors MOF-808-Zr and MOF-808-Hf.

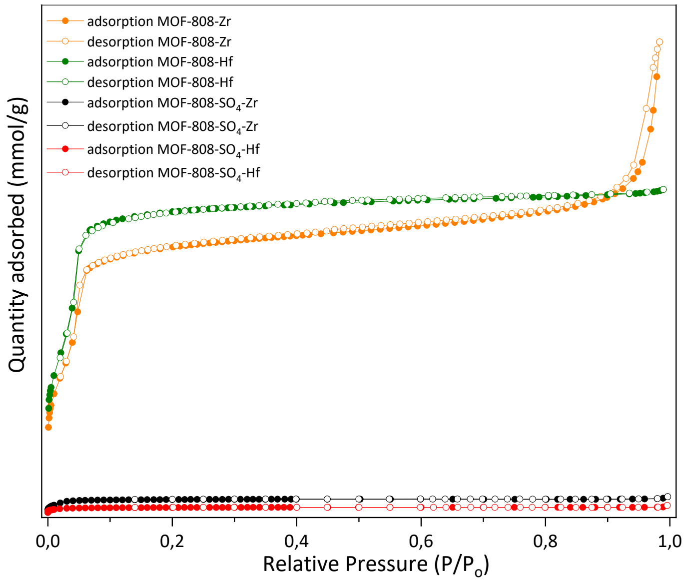


Figure S4. N_2 adsorption and desorption isotherm of MOF-808-SO$_4$-Zr and MOF-808-SO$_4$-Hf compared with their precursors.

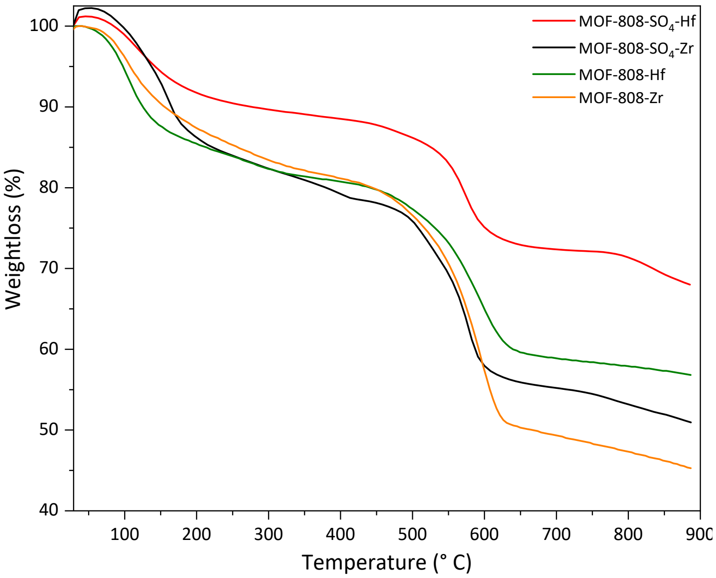


Figure S5. Thermogravimetric analysis of MOF-808-SO$_4$-Zr and MOF-808-SO$_4$-Hf compared with their precursors.

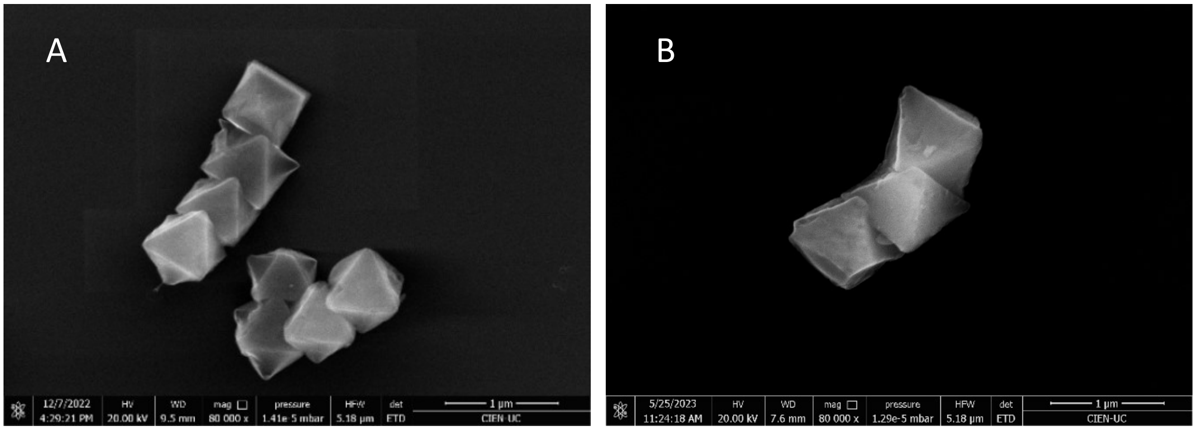
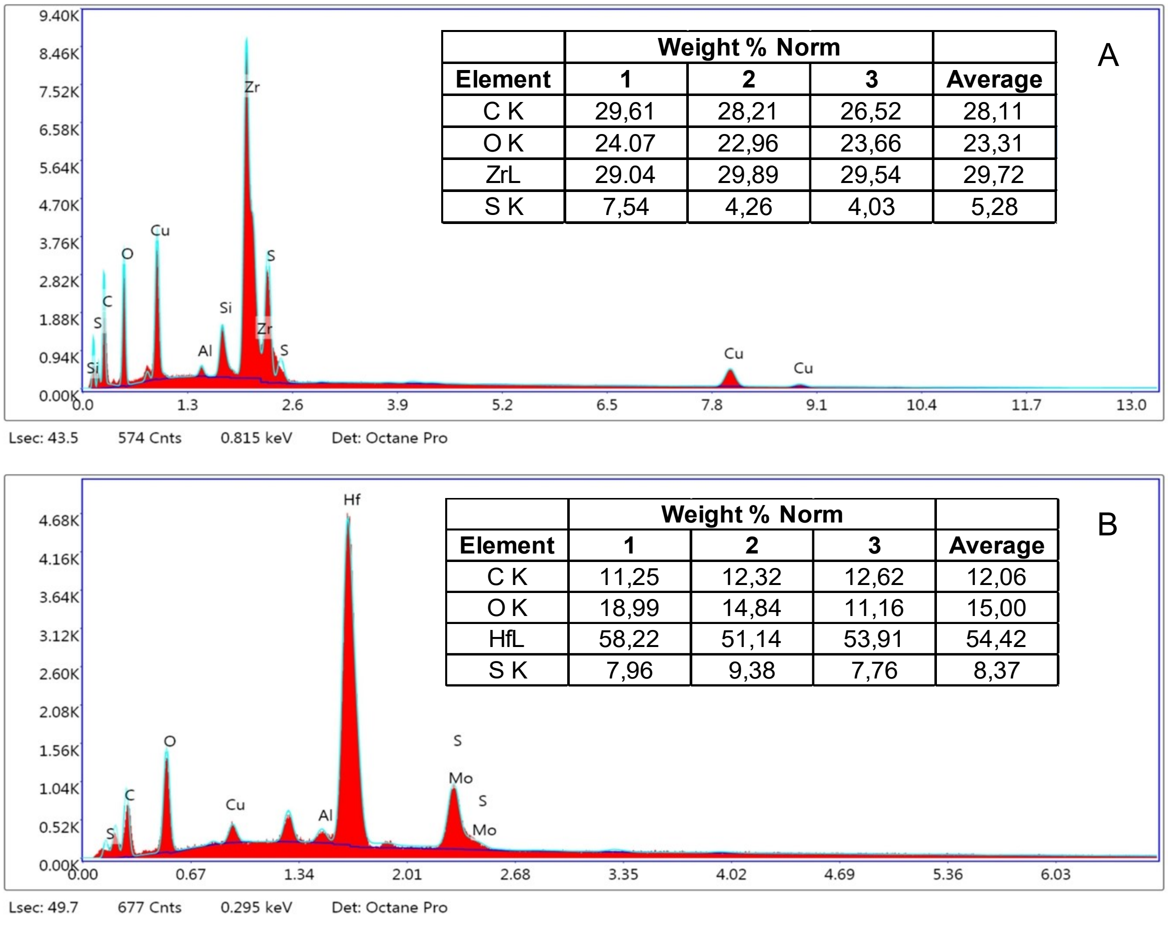


Figure S6. SEM images of MOF-808-M materials. MOF-808-Zr (A) and MOF-808-Hf (B) with a magnitude of 80,000.



	Weight % Norm			
Element	1	2	3	Average
C K	29,61	28,21	26,52	28,11
O K	24.07	22,96	23,66	23,31
ZrL	29.04	29,89	29,54	29,72
S K	7,54	4,26	4,03	5,28

	Weight % Norm			
Element	1	2	3	Average
C K	11,25	12,32	12,62	12,06
O K	18,99	14,84	11,16	15,00
HfL	58,22	51,14	53,91	54,42
S K	7,96	9,38	7,76	8,37

Figure S7. EDS for the materials MOF-808-SO_4-Zr (A) and MOF-808-SO_4-Hf (B).

Table S2. Hammett indicators and acidity of MOF-808-SO_4-Zr y MOF-808-SO_4-Hf.

Indicators	**pKa**	**MOFs**	
		MOF-808-SO_4-Zr	**MOF-808-SO_4-Hf**
4-nitrotoluene	-11.4	+	+
Anthraquinone	-8.1	+	+
2,4-dinitroaniline	-4.4	+	+
4-nitrodiphenylamine	-2.4	+	-
2-nitroaniline	-0.2	+	-

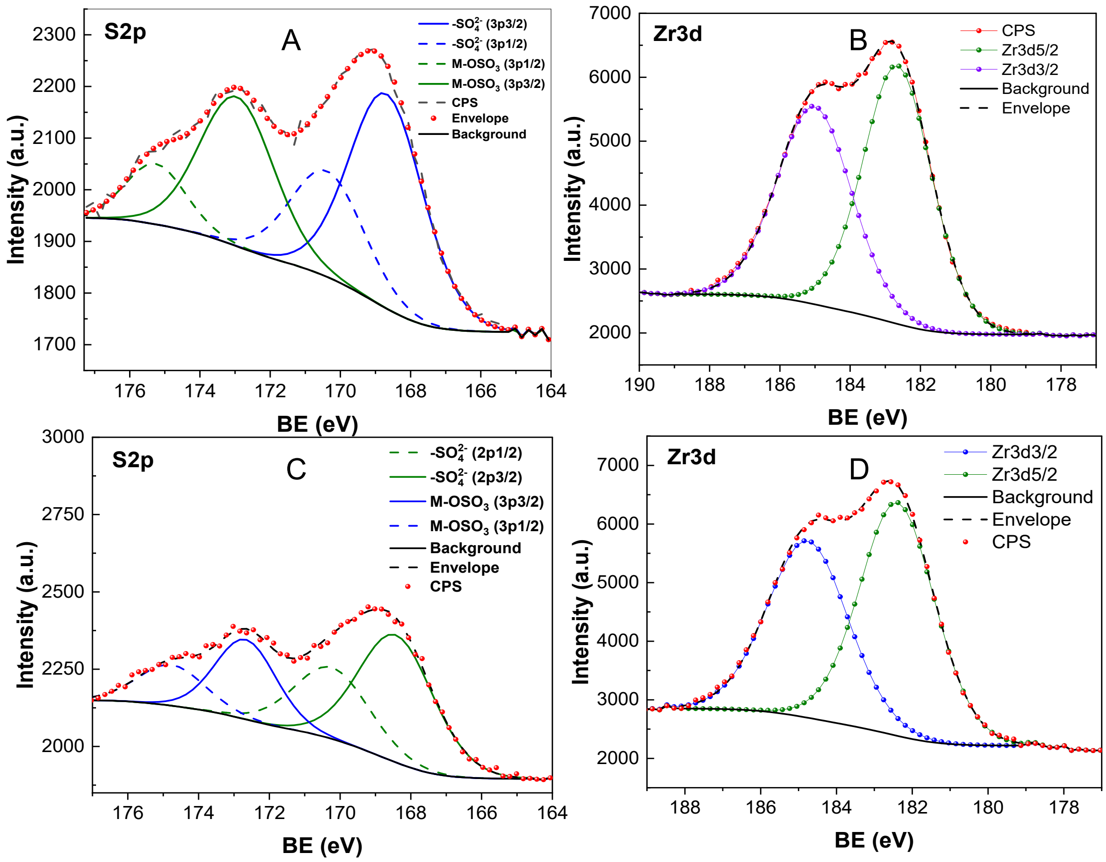


Figure S8. XPS corresponding to MOF-808-SO_4-Zr before catalysis (A-B) and after catalysis (C-D).

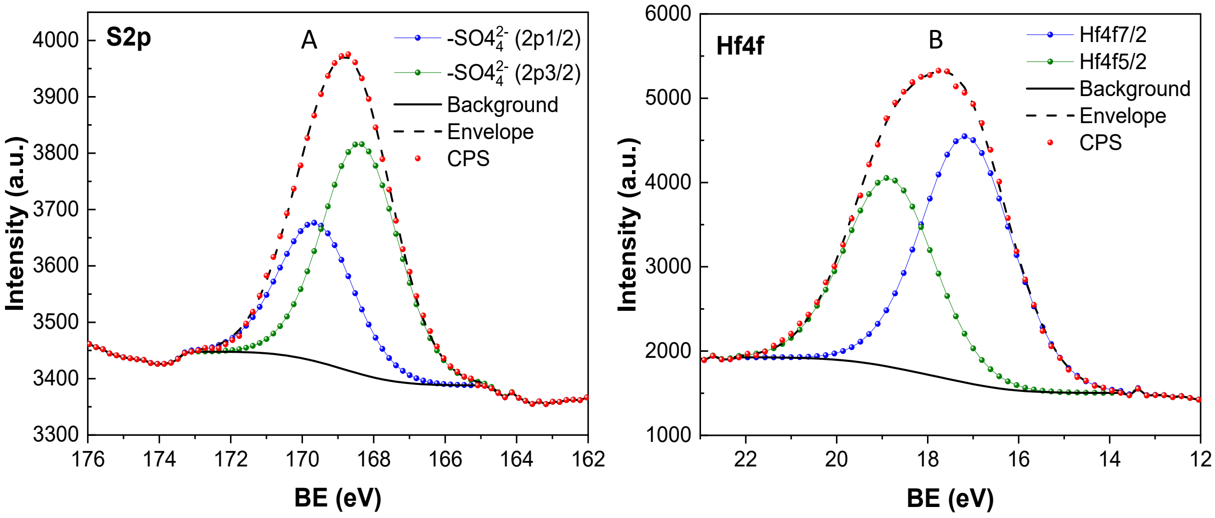


Figure S9. XPS corresponding to MOF-808-SO$_4$-Hf before catalysis (A-B).

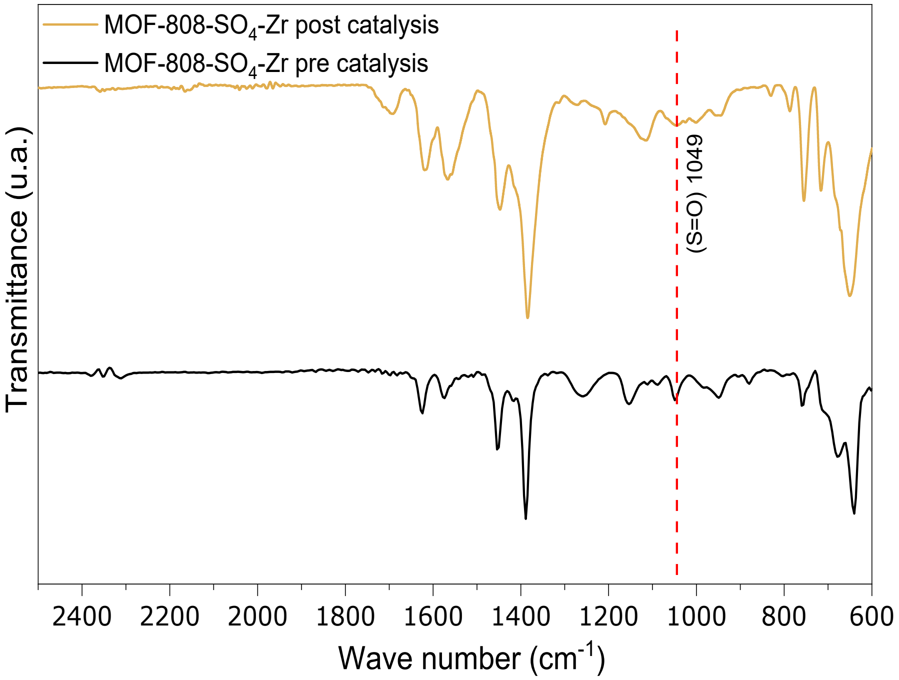


Figure S10. FT-IR of fresh MOF-808-SO$_4$-Zr (black color) and MOF-808-SO$_4$-Zr recovered after catalytic cycles (brown color).

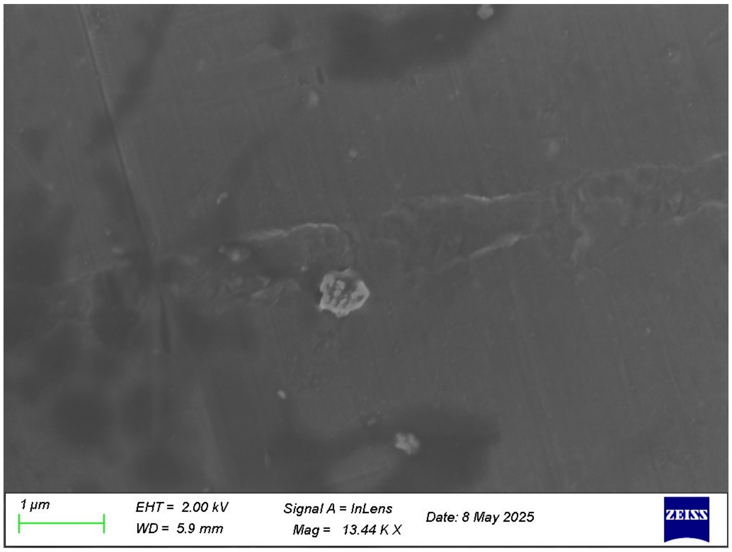


Figure S11. SEM analysis of MOF-808-SO_4-Zr post catalytic cycles.

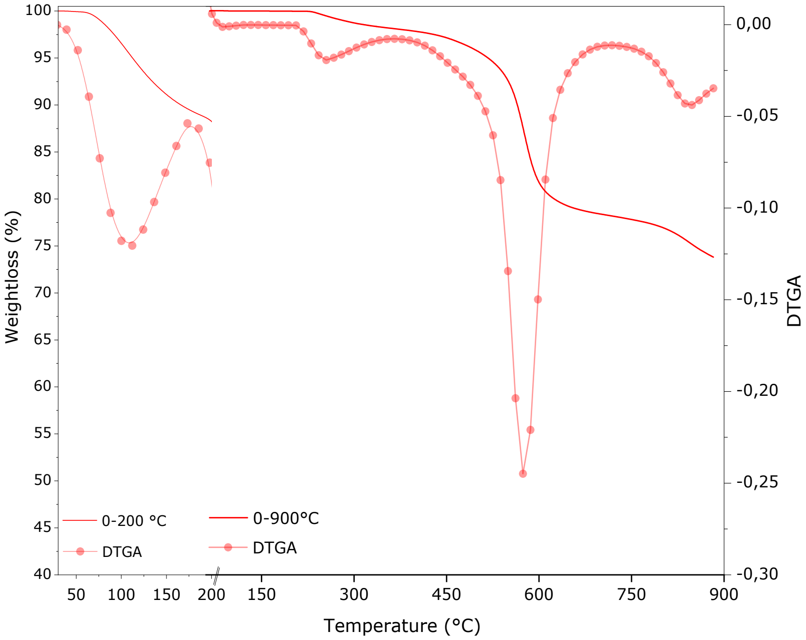


Figure S12. TGA MOF-808-SO_4-Hf from 0-200 °C (left) and 0-900 °C (right).

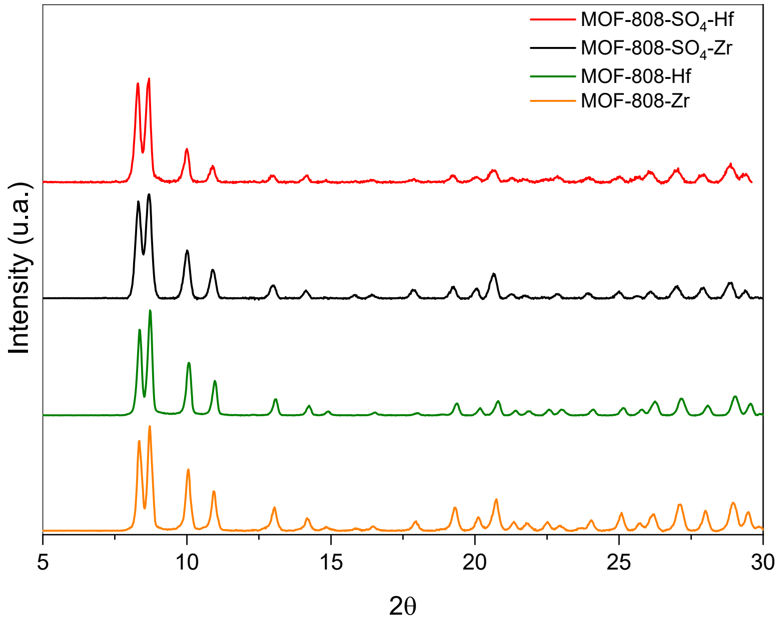


Figure S13. Powder X-ray diffraction patterns of MOF-808-SO$_4$-Zr and MOF-808-SO$_4$-Hf compared with its precursors.

3. Computational study.

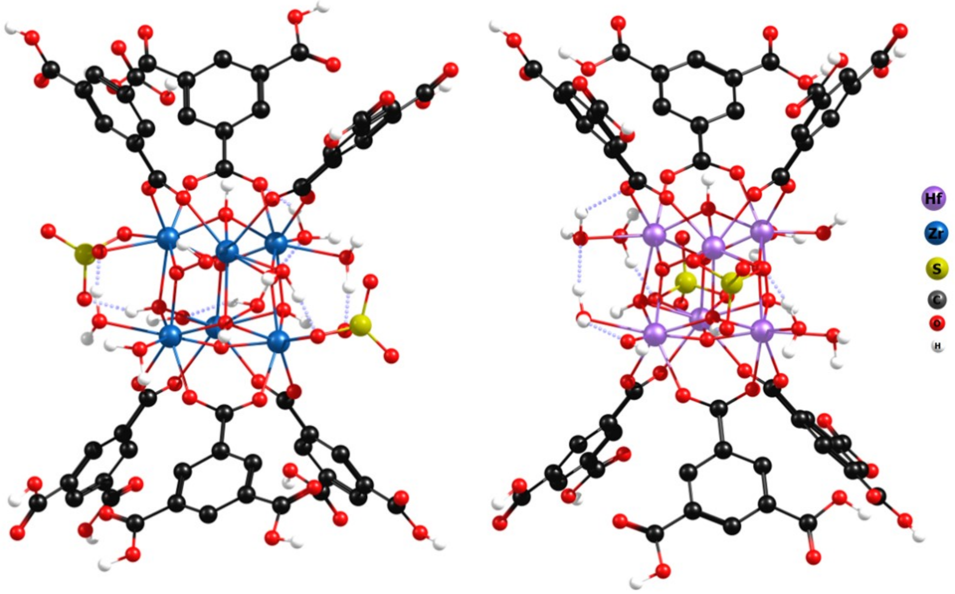


Figure S14. Visualization of the cluster model using the calculations, MOF-808-SO$_4$-Zr (left) and MOF-808-SO$_4$-Hf (right). All H atoms attached to carbon atoms were hidden for clarity.

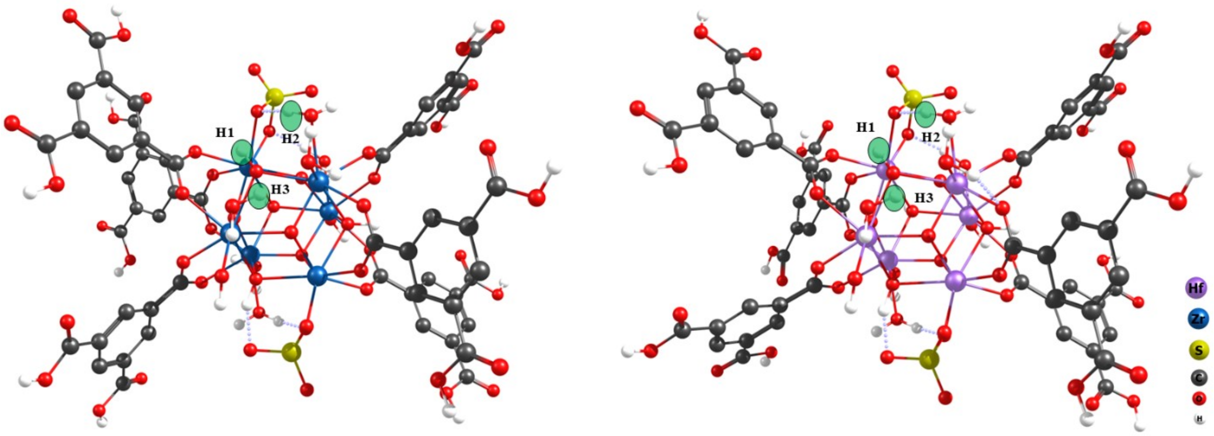


Figure S15. Visualization of the three types of hydrogen atoms involve on proton affinities (PAs) analysis, MOF-808-SO_4-Zr (left) and MOF-808-SO_4-Hf (right). All H atoms attached to carbon atoms were hidden for clarity.

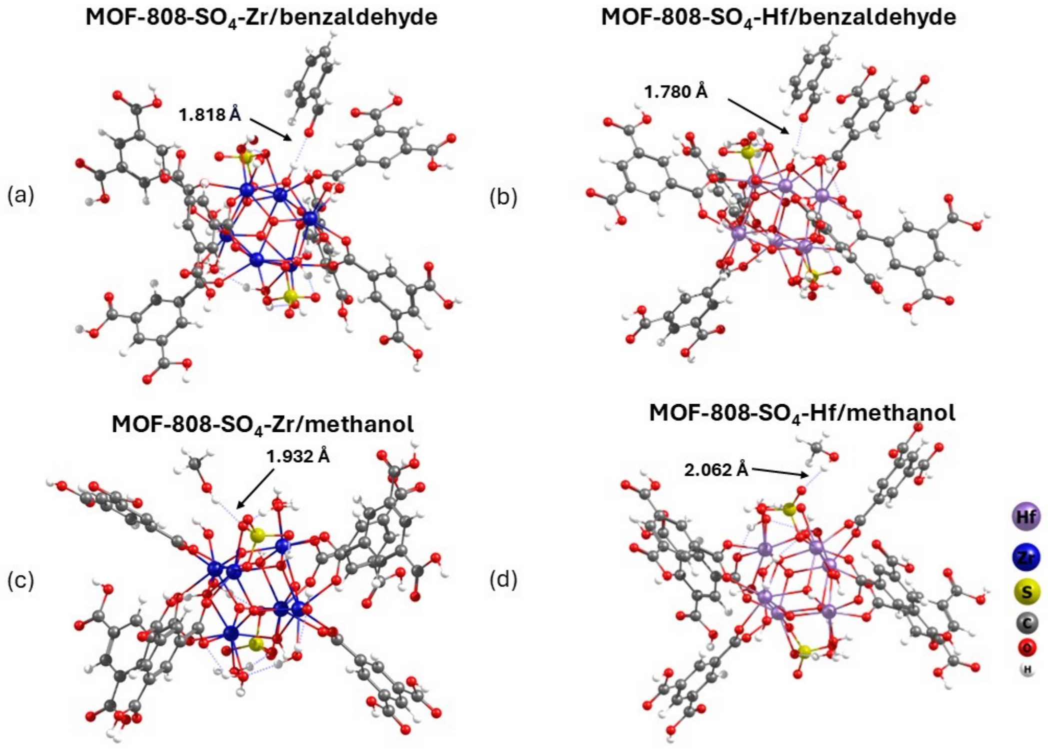


Figure S16. Optimized structures corresponding to the S0 electronic states of MOF-808-SO$_4$-M/ benzaldehyde and MOF-808-SO$_4$-M methanol, intermolecular interaction lengths are presented in Å

References

1. Hu, Z. *et al.* Modulated hydrothermal synthesis of highly stable MOF-808(Hf) for methane storage. *ACS Sustain Chem Eng* **8**, 17042–17053 (2020).

2. Li, M., Chen, J., Wu, W., Fang, Y. & Dong, S. Oxidase-like MOF-818 Nanozyme with High Specificity for Catalysis of Catechol Oxidation. *J Am Chem Soc* **142**, 15569–15574 (2020).