Electronic Supplementary Material (ESI) for Catalysis Science & Technology

SUPPORTING INFORMATION

Towards acid MOFs: catalytic performance, deactivation and stability of sulfonic acid functionalized architectures

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Figure S1. CoKα Powder X-Ray diffraction patterns of HSO_3-MIL-101(Cr) samples synthesized with HCl or HF described in the experimental section.

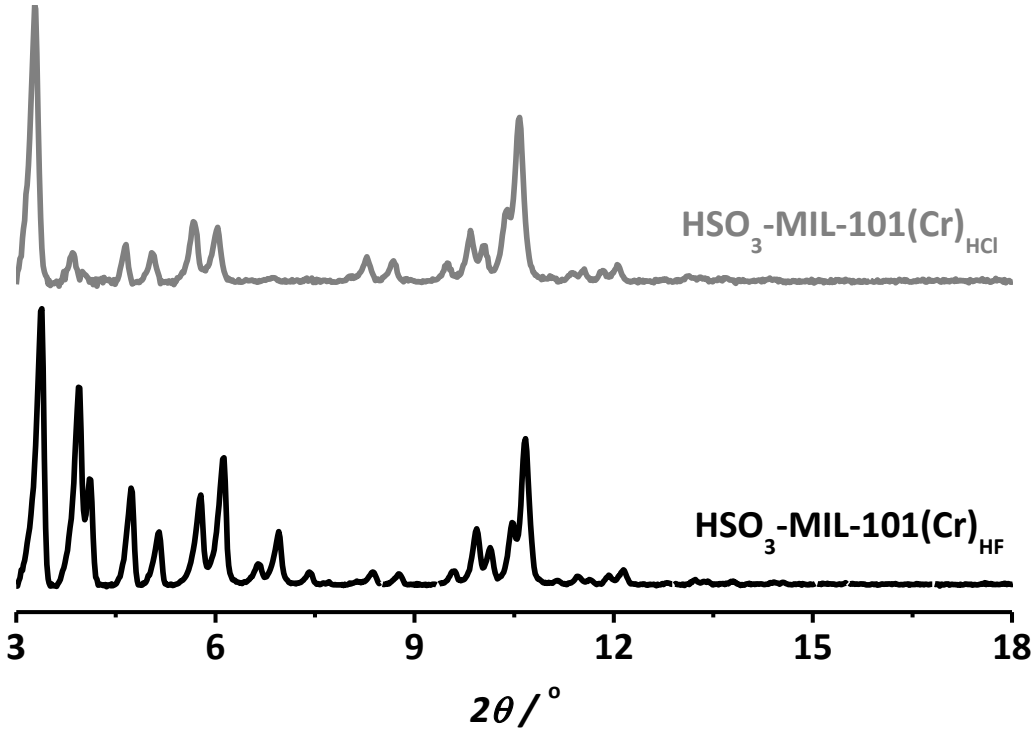


Figure S2. Nitrogen adsorption isotherms at 77 K of HSO_3-MIL-101(Cr) samples synthesized with HCl (*grey*) or HF (*black*) as described in the experimental section.

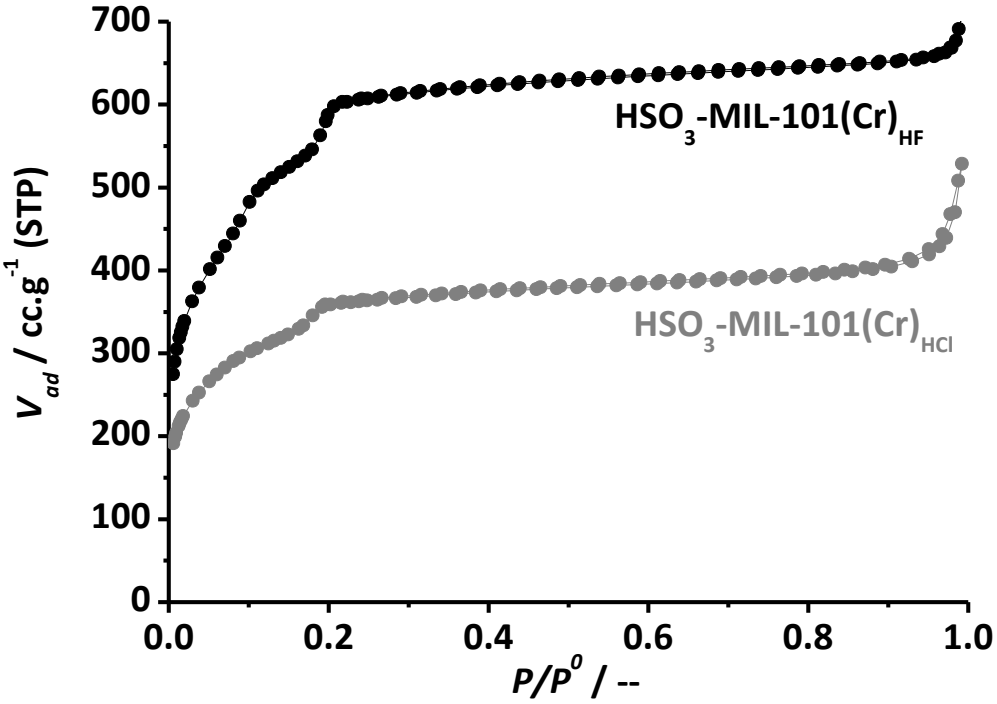


Figure S3. SEM images of HSO_3-MIL-101(Cr) samples.

(a) HCl (*left*) (b) HF (*right*)

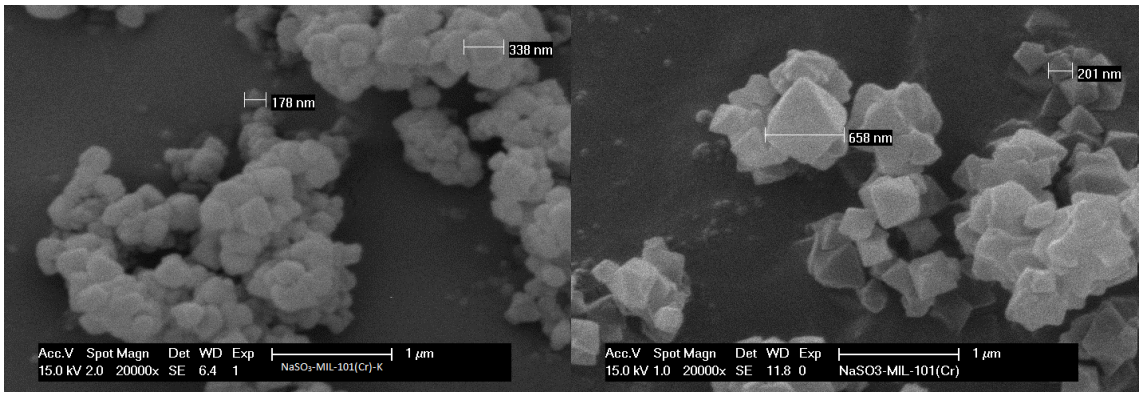


Figure S4. Thermo-gravimetric analysis of HCl (*grey*) or HF (*black*) synthesized HSO_3-MIL-101(Cr) samples.

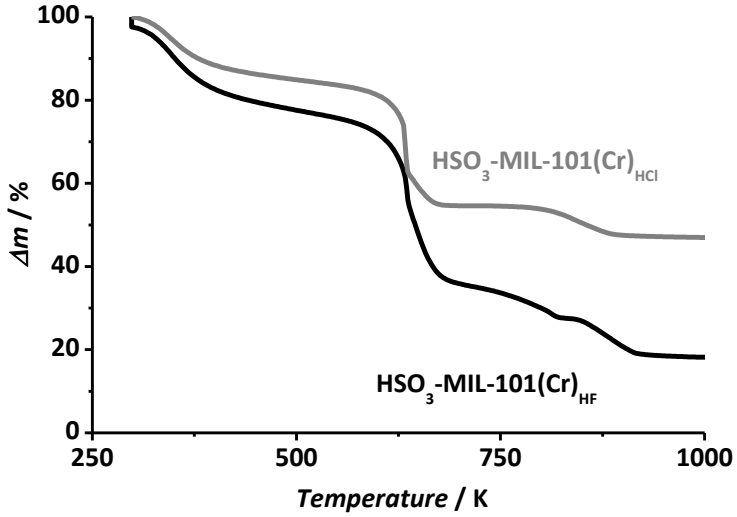


Figure S5. CoKα Powder X-Ray diffraction patterns of HSO_3-MIL-101(Cr) samples before (*black*) and after (*grey*) three reaction cycles.

(a) HCl (*left*) (b) HF (*right*)

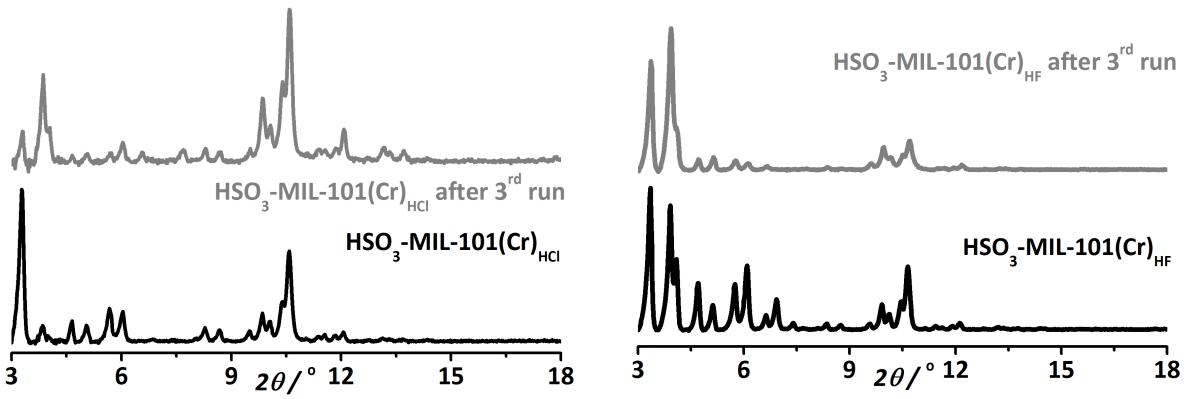
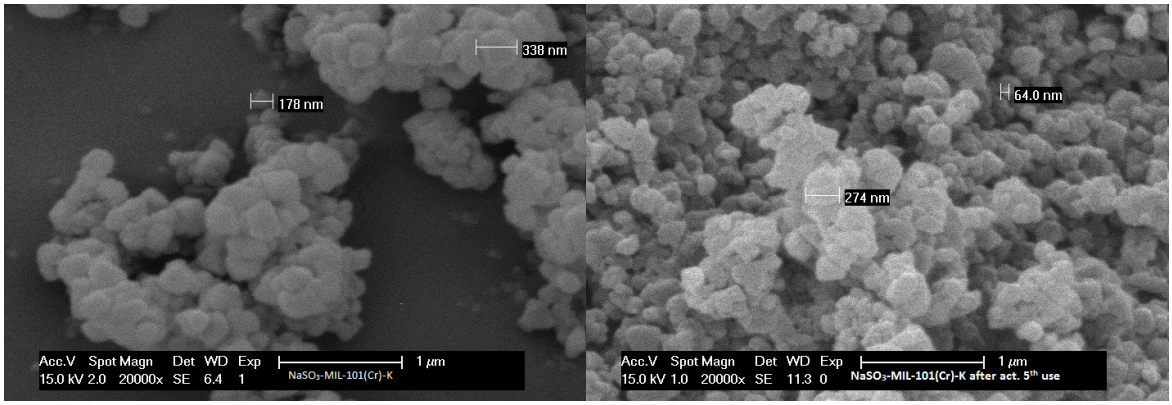


Figure S6. SEM images of HSO_3-MIL-101(Cr) samples before (*left*) and after (*right*) three reaction cycles.

(a) HCl



(b) HF

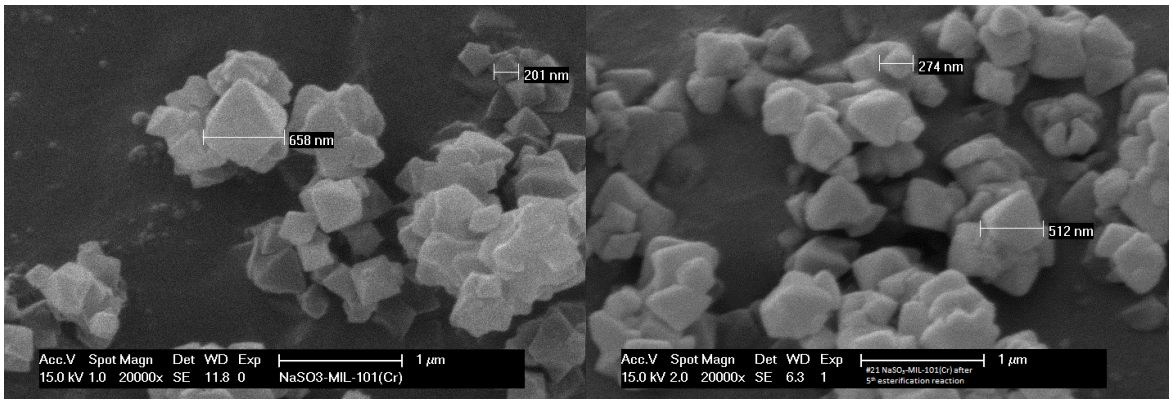
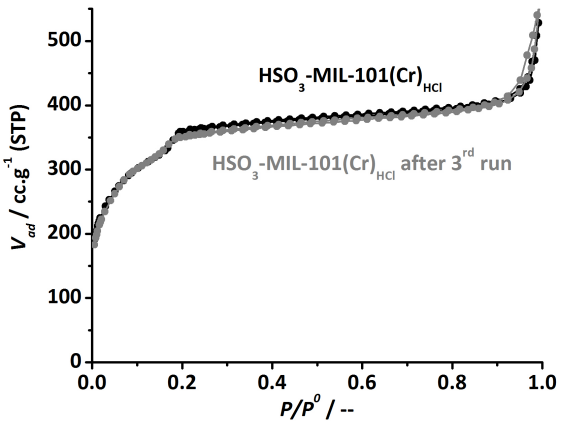


Figure S7. Nitrogen adsorption isotherm at 77 K of HSO_3-MIL-101(Cr) samples before (*black)* and after (*grey*) three reaction cycles.

(a) HCl



(b) HF

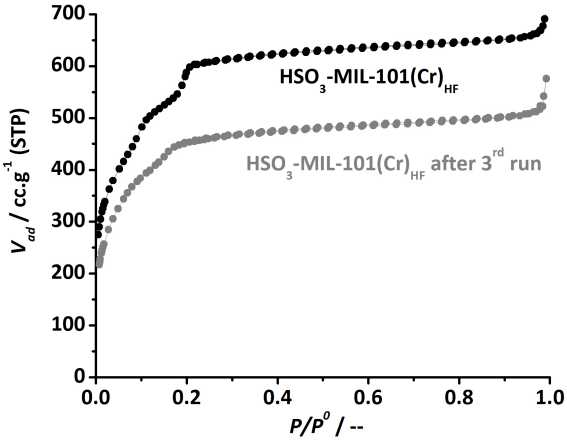


Figure S8. XRD and Nitrogen adsorption isotherms (77 K) of 50%HSO_3-MIL-101(Cr) (*grey*) compared with full HSO_3-MIL-101(Cr) (*black*).

(a) XRD (b) Nitrogen adsorption isotherms

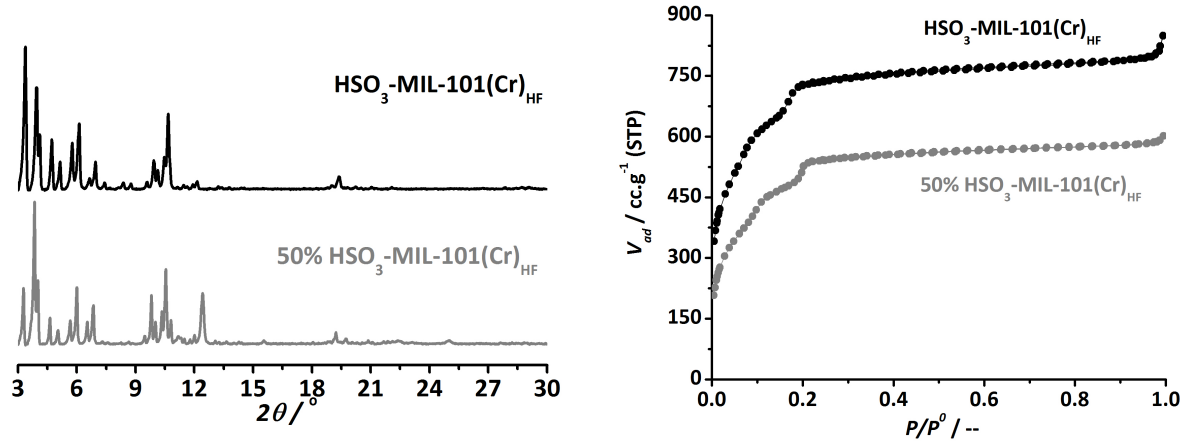


Figure S9. XPS survey spectra of HSO_3-MIL-101(Cr) full sulfonic linker and mixture of 50% with TBD. Zoom in at the F 1*s* and S 2*p* core-levels.

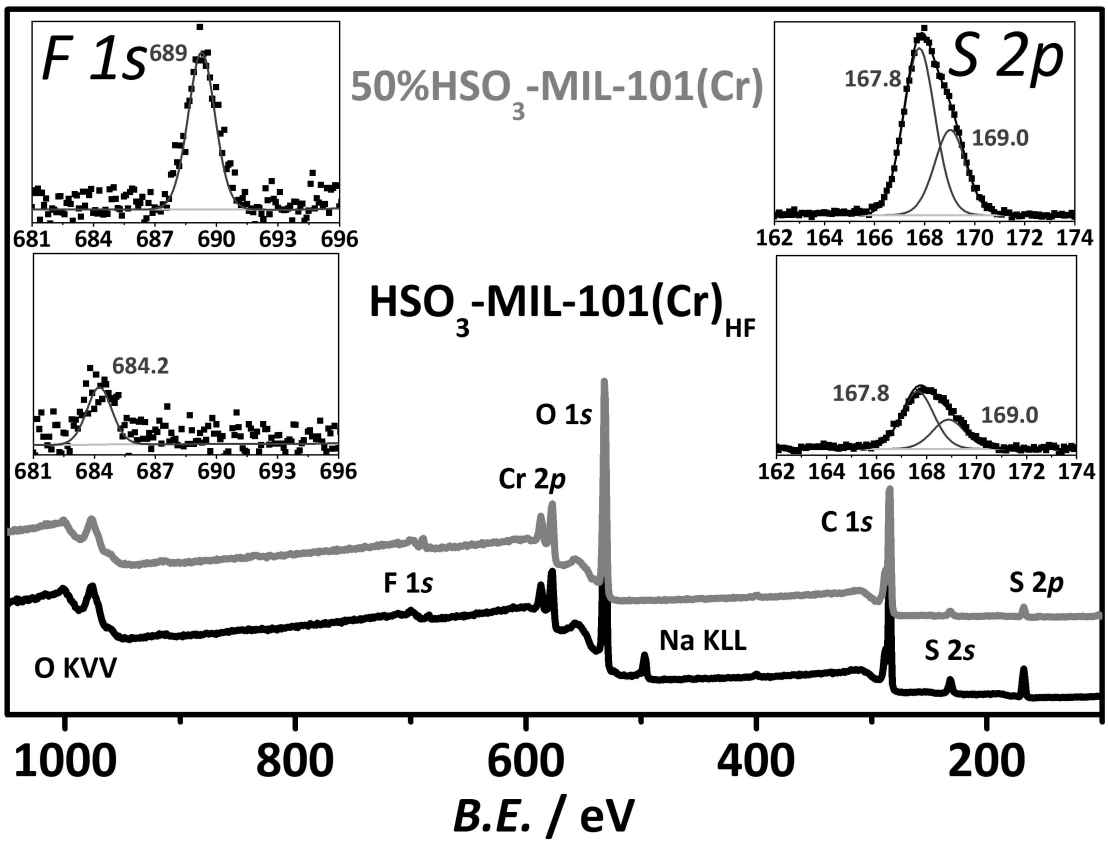


Figure S10. Structure pattern profile refinement of HSO_3-ZrMOF (*R*wp = 0.0495). Data collected on ID31 (ESRF), λ= 0.79989 Å. Cubic setting, space group *Im-3m*, *a* = 41.5331(2) Å.

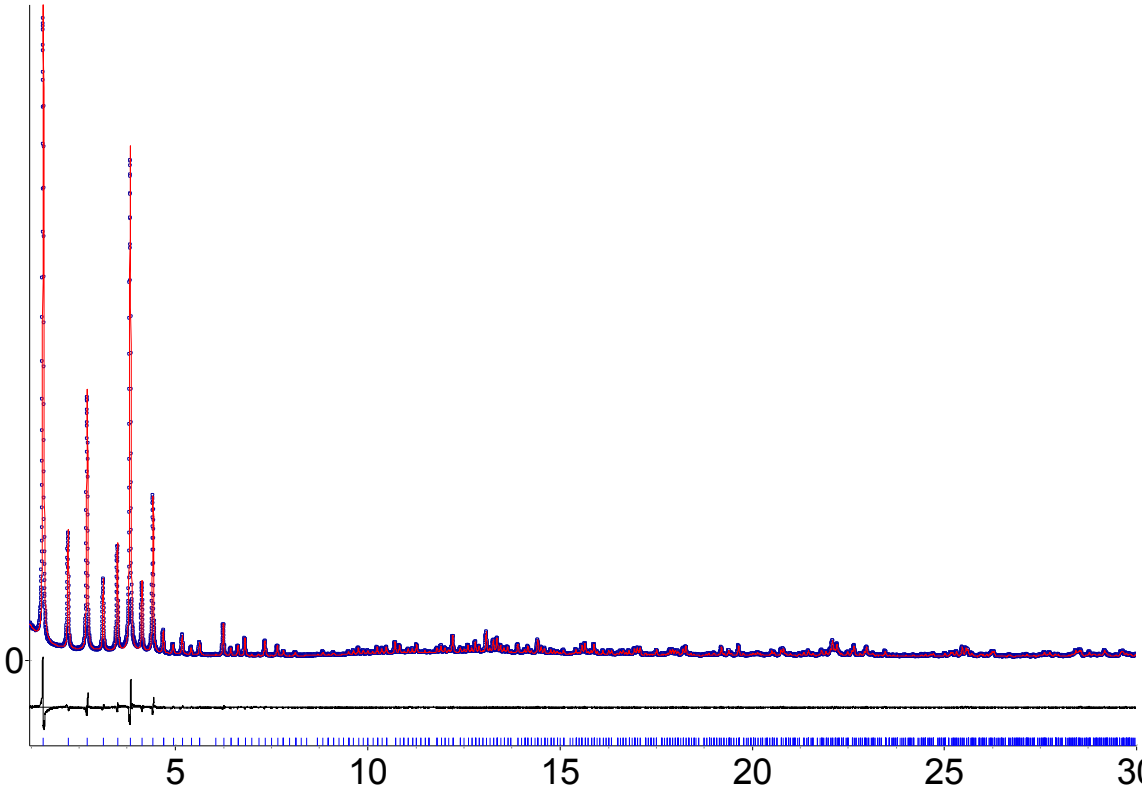


Figure S11. Partial structural model of the HSO3-Zr MOF: location of the Zr6 clusters (yellow balls, black bonds) within the unit-cell (in grey).

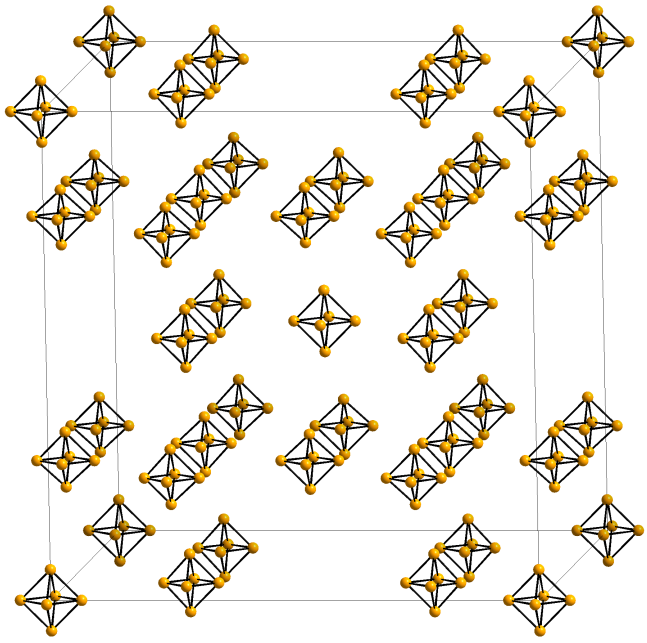


Figure S12. DRIFT spectra of HSO_3-ZrMOF before (*black*) and after (*grey*) use in the esterification reaction.

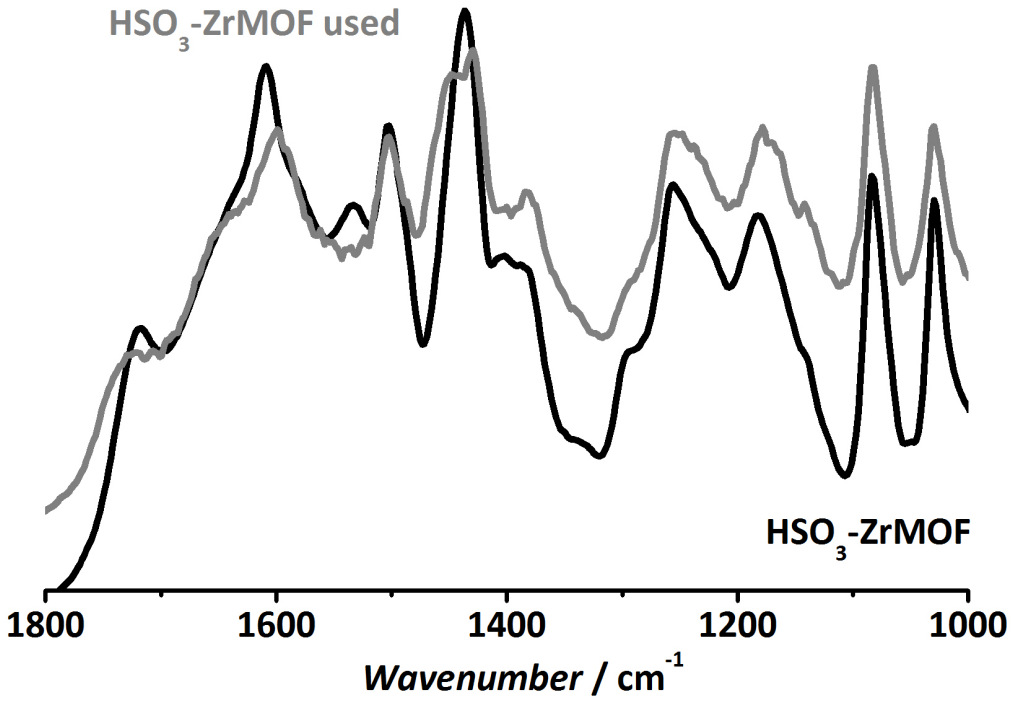


Table S1. Elemental analysis of chromium and sodium measured by ICP-OES from the different HSO_3-MIL-101(Cr) samples.

	Cr (wt.%)	Na (wt.%)	$Na^+/SO3^-$
HSO_3-MIL-101(Cr)$_{HF}$	15.1	2.75	0.41
HSO_3-MIL-101(Cr)$_{HCl}$	7.24	1.28	0.30