

Supporting Information

A fluorolytic sol-gel route to access an amorphous Zr fluoride catalyst: A useful tool for C-F bond activation

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ZrF₄ motif reproduced from literature

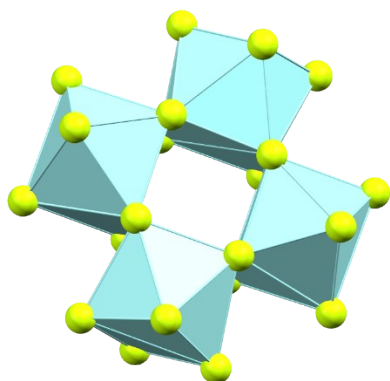


Figure S 1: ZrF₄ motif reproduced from Abrahams *et al.*¹

Reactivity studies using fluoropentane

15 mg of material were placed in a JYoung NMR tube and triethylsilane (0.2 mmol) was added. Subsequently, fluoropentane (0.2 mmol) and the respective solvent (C₆D₆ for testing Friedel-Crafts alkylation and C₆D₁₂ for testing dehydrofluorination reactions) were added. The products were analysed using ¹H and ¹⁹F NMR spectroscopy.

Table S1: Selected ¹H and ¹⁹F NMR resonances of the reactants and products of the catalytic reactions in C₆D₆.

Entry	Product/reagent	$\delta(^1\text{H NMR})$ in ppm	$\delta(^{19}\text{F NMR})$ in ppm
1	F(CH ₂) ₄ CH ₃	4.11 (dt, ² J(H,F) = 47.6 Hz, ³ J(H,H) = 6.2 Hz, 2H, CH ₂ F)	-217.2 (hept, ² J(F,H) = 23.5 Hz)
2	(E/Z)-pent-2-ene	5.41 (m, 2H, CH ₃ CH=CHCH ₂ CH ₃)	-
3	Et ₃ SiH	3.73 (hept. 1H)	-
4	pentylbenzene	2.5 (m)	-
5	Et ₃ SiF	-	-175.3 (m, ³ J(F,H) = 6.8 Hz)

Table S2: Selected ¹H and ¹⁹F NMR resonances of the reactants and products of the catalytic reactions in C₆D₁₂.

Entry	Product/reagent	$\delta(^1\text{H NMR})$ in ppm	$\delta(^{19}\text{F NMR})$ in ppm
1	F(CH ₂) ₄ CH ₃	4.32 (dt, ² J(H,F) = 47.6 Hz, ³ J(H,H) = 6.2 Hz, 2H, CH ₂ F)	-218.4 (hept, ² J(F,H) = 23.5 Hz)
2	(E/Z)-pent-2-ene	5.41 (m, 2H, CH ₃ CH=CHCH ₂ CH ₃)	-
3	Et ₃ SiH	3.88 (hept. 1H)	-
4	Et ₃ SiF	-	-175.5 (m, ³ J(F,H) = 6.8 Hz)

X-ray diffraction of postfluorinated xerogels listed in Table 1

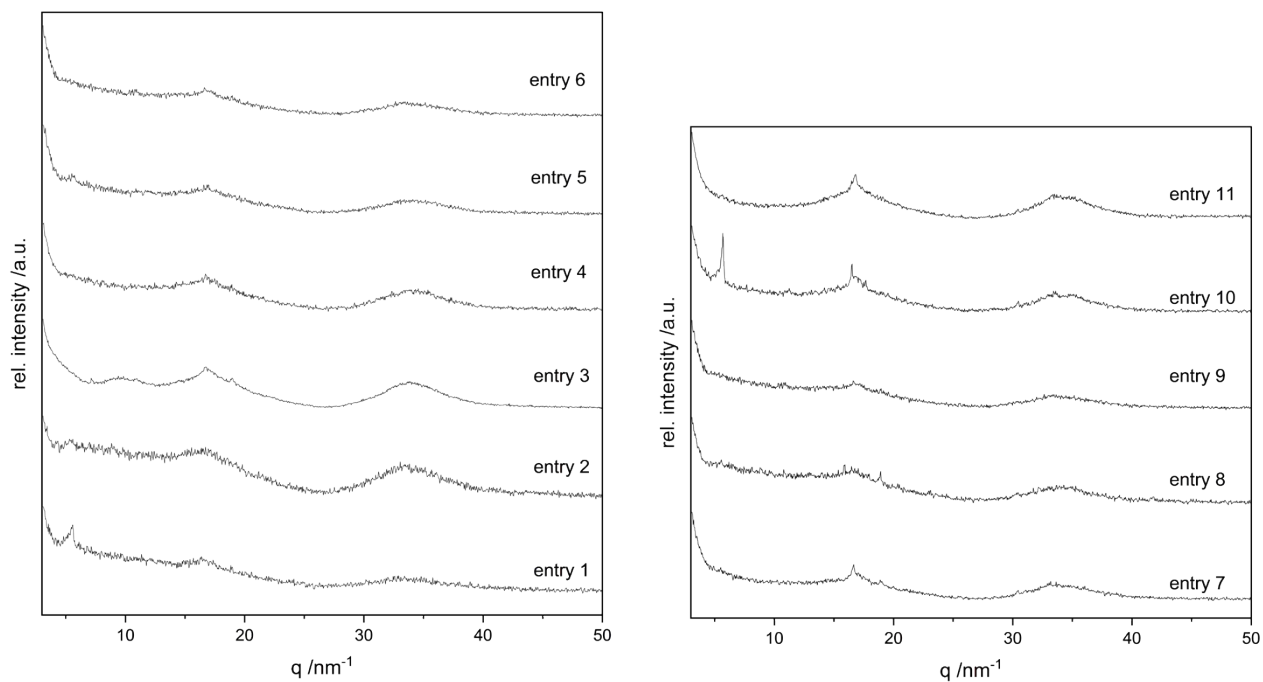


Figure S2: XRD patterns obtained from the postfluorinated materials listed in Table 1 according to their entry number.

Under-stoichiometric fluorination of $Zr(acac)_4$

$Zr(acac)_4$ was weighed in under atmospheric conditions and placed under vacuum for 1h in the reaction vessel before the procedure was continued. 250 mL of $iPrOH$ were then added to the reagent. The mixture was refluxed for 1h and allowed to cool down. The solution obtained from $Zr(acac)_4$ appeared to be a stable milky suspension as soon as the temperature dropped below 40 °C. Subsequently, an HF solution in $iPrOH$ (21.5 M, 1-3 eq) was added dropwise but rapidly. The solvent was removed under vacuum, after the mixture was aged overnight under vigorous stirring. The product was stored under Ar in a Glovebox. If one equivalent was used the mixture became transparent. If two equivalents were used then the mixture became transparent directly during HF addition and colourless threads were observed after complete addition. The synthesis of the under-stoichiometric xerogel with three equivalents of HF did not result in any other observation than the xerogel described in the methods section of the article. The xerogel described here are designated as $ZrF_{x1}-OH^{(acac)}$, $ZrF_{x2}-OH^{(acac)}$, $ZrF_{x3}-OH^{(acac)}$. The index at the fluorine atom is changed to "x". The number indicates the employed amount of HF.

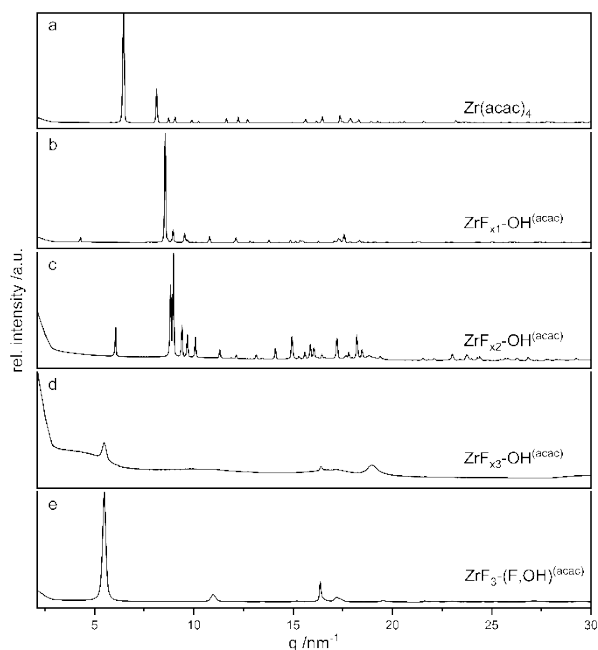


Figure S3: Ex-situ XRD patterns of xerogels synthesised on using various equivalents((b) 1, (c) 2, (d) 3, (e) 4 of HF. The pattern of the Zr-source $Zr(acac)_4$ (a) is displayed as a reference.

Infrared spectra of postfluorinated xerogels listed in Table 1

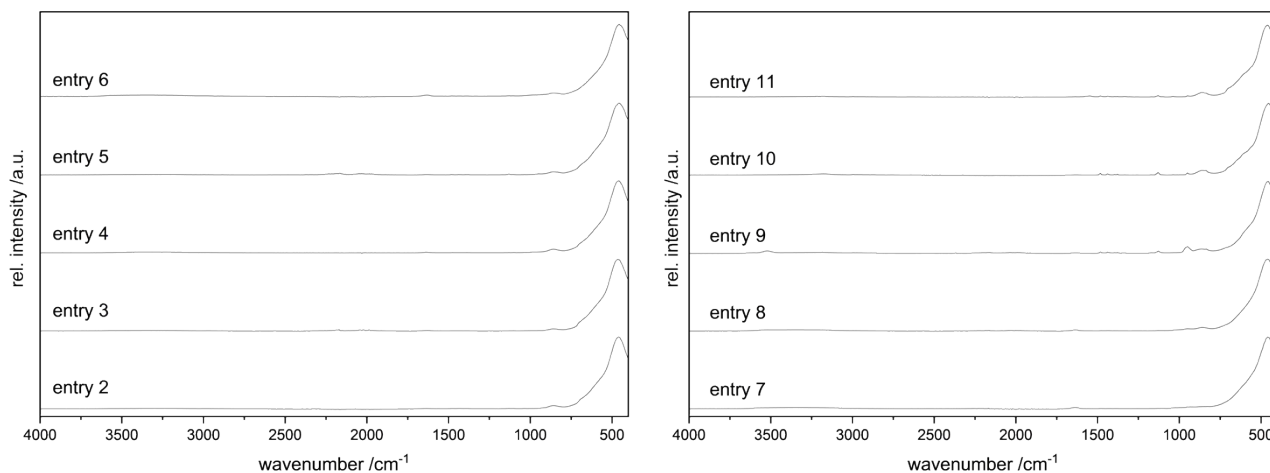


Figure S 4: IR spectra obtained from the postfluorinated materials listed in Table 1 according to their entry number.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) traces of the postfluorinated xerogels from the different precursors listed in Table 1

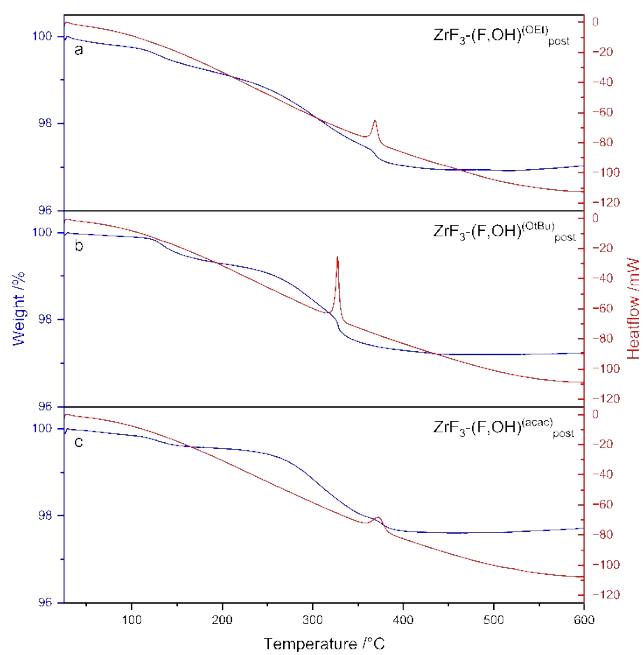


Figure S5: TGA (blue)/DSC (red) traces from the postfluorinated Xerogels obtained from the respective Zr-precursor complex: (a) Zr(OEt)₄; (b) Zr(OBu)₄; (c) Zr(acac)₄.

References

1 C. R. Ross, B. L. Paulsen, R. M. Nielson and S. C. Abrahams, *Acta Crystallogr. B*, 1998, **54**, 417–423.