



Fig. S1: ¹⁹F MAS NMR spectrum (v_{rot} = 20 kHz, D1=5s, NS=64) of CaF₂ prepared by CaO + EtOH + 2 HF_{EtOH}.



Fig. S2: ¹⁹F MAS NMR spectrum (rs-echo, v_{rot} = 20 kHz, L0=10, D1=5s, NS=64) of CaF₂ prepared by CaO + EtOH + 2 HF_{EtOH}.



Fig. S3: ¹⁹F MAS NMR spectrum (v_{rot} = 20 kHz, D1=5s, NS=64) of CaF₂-xerogel prepared by CaBr₂ · H₂O + EtOH + 2 HF_{EtOH} and dried at 40°C.



Fig. S4: ¹⁹F MAS NMR spectra of CaClF xerogel prepared by $CaCl_2 + EtOH + 1$ HF_{EtOH} dried at **a**) 600 °C in air (v_{rot} = 19 kHz, D1=5s, NS=64) respectively stored in a glove box after calcination (v_{rot} = 20 kHz, D1=5s, NS=64) and dried at **b**) 40 °C in air (v_{rot} = 20 kHz, D1=5s, NS=64) respectively stored in a glove box after drying (25 kHz, D1=5s, NS=64).



Fig. S5: 19 F NMR spectra of CaF₂-sols with different fluorine content. (Liquid NMR spectrometer)



Fig. S6: ¹⁹F MAS NMR spectra of CaF₂-xerogels prepared by CaCl₂ + H₂O + 2 HF_{aq} dried at room temperature in air (**a**) v_{rot} = 25 kHz, D1=5s, NS=64 and (**b**) rs-echo, v_{rot} = 20 kHz, L0=20, D1=5s, NS=256.



Fig. S7: TEM image of CaF₂ particles without 5 mol% of TMOS on a carbon-coated copper grid.



Fig. S8: TEM image of CaF₂ particles with 5 mol% of TMOS on a carbon-coated copper grid.