

Supporting Information

Table S1 Conversion of CH₄ and CHF₃, rates of formation of products and mass losses as a function of temperature under condition 1 listed in Table 1.

T K	t s	Conv. %			Rate of formation, mmol/h						Mass loss [#] , %					
		CH ₄	CHF ₃	C ₂ F ₄	C ₂ H ₂ F ₂	CO ₂	C ₂ H ₄	C ₂ H ₂	C ₂ H ₃ F	C ₂ HF ₃	C ₃ F ₆	Others*	HF	C F H		
1023	0.32	0.17	1.46	0.040	0.020	0.002	---	0.008	---	---	---	---	0.10	0.27	0.68	0.18
1053	0.32	0.66	3.78	0.060	0.030	0.004	---	0.009	---	---	---	---	0.50	1.40	1.71	0.4
1073	0.31	1.15	9.12	0.270	0.053	0.005	---	0.010	---	---	---	---	1.23	2.47	2.87	0.67
1088	0.31	1.28	12.1	0.360	0.090	0.007	0.006	0.015	0.004	0.004	---	---	1.84	2.87	3.07	0.27
1103	0.30	2.14	15.8	0.510	0.182	0.008	0.008	0.029	0.009	0.018	---	---	2.48	3.02	2.96	0.37
1118	0.30	3.39	22.8	0.680	0.307	0.012	0.020	0.046	0.014	0.039	0.005	---	3.67	4.35	4.23	0.44
1133	0.30	5.57	31.2	0.840	0.506	0.034	0.030	0.071	0.023	0.075	0.010	0.058	5.40	5.69	4.84	2.82
1153	0.30	9.67	46.8	0.860	0.928	0.050	0.040	0.121	0.038	0.154	0.018	0.174	7.86	9.90	10.4	1.07
1173	0.29	15.3	59.8	0.785	1.390	0.100	0.050	0.149	0.045	0.238	0.025	0.469	11.0	12.7	11.3	1.01

[#]: Mass loss (%) = $\frac{\text{Element in the feed (mmol h}^{-1}) - \text{Element in the outlet stream (mmol h}^{-1})}{\text{Element in the feed (mmol h}^{-1})} \times 100\%$

*: C₂H₆, CH₂F₂, CHF₂CHF₂ and other unidentified species

---: below detection limit.

Table S2 Effect of input CH₄/CHF₃ ratio on the yield and selectivity to C₂H₂F₂ (T = 1153 K).

Reaction condition	Ratio of CH ₄ /CHF ₃	CH ₄ conv %	CHF ₃ conv %	Yield to C ₂ H ₂ F ₂ %	Selectivity to C ₂ H ₂ F ₂ %
1	1.1	9.67	46.8	7.2	15.4
2	2.1	7.75	48.0	11	22.4

$$\text{Yield of C}_2\text{H}_2\text{F}_2 = \frac{f}{f} \times 100\%$$

$$\text{Selectivity of C}_2\text{H}_2\text{F}_2 = \frac{f}{f - f} \times 100\%$$

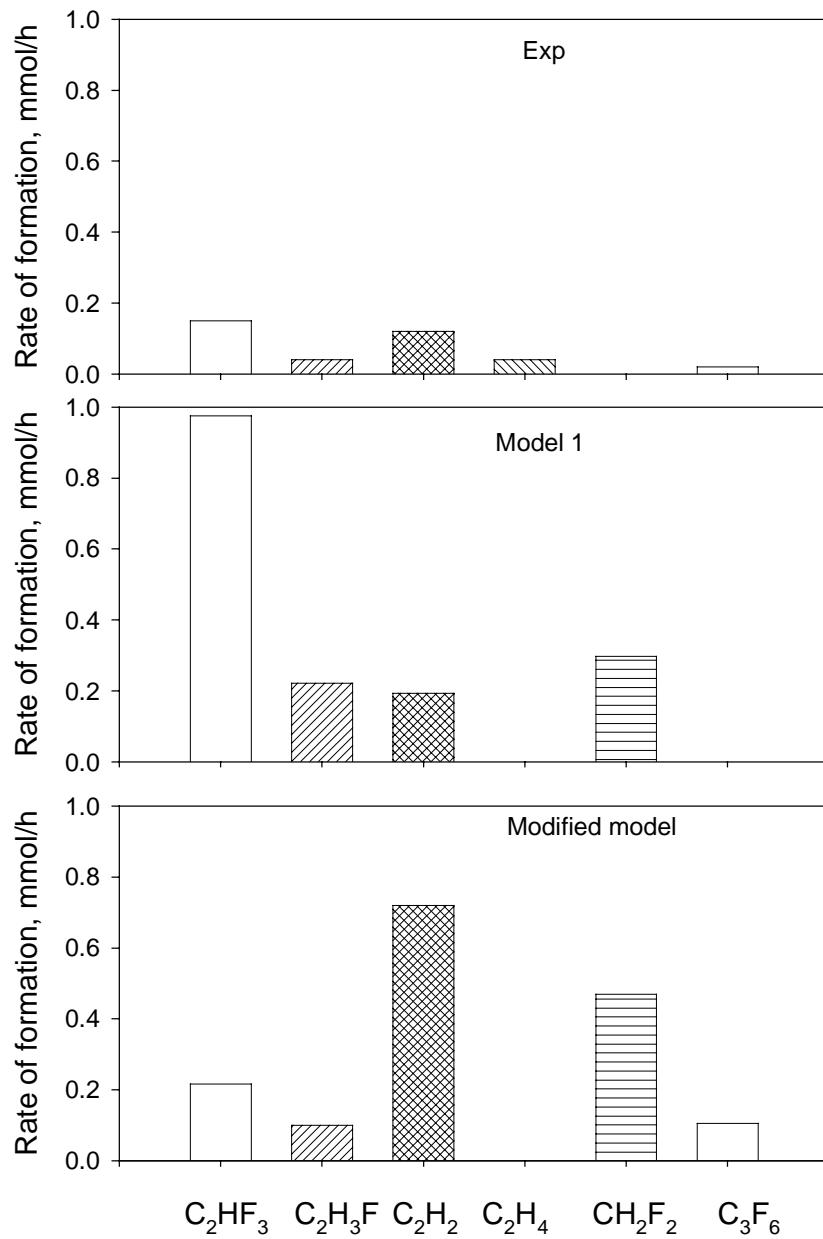


Figure S1 Comparison of rates of formation of other important products at 1153 K under condition 1 (see Table 1).

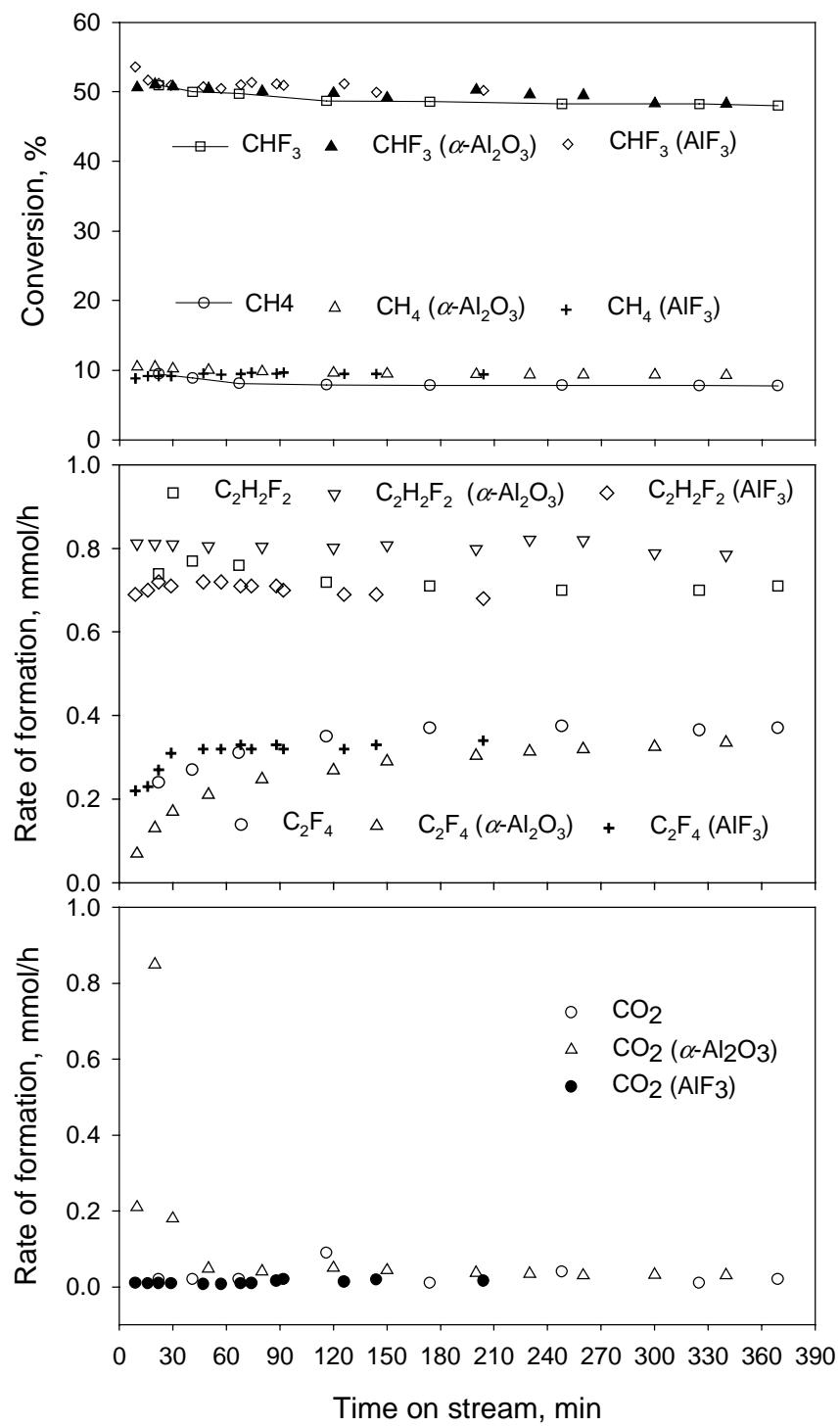


Figure S2 Conversion of CH_4 and CHF_3 and rates of formation of C_2F_4 , $\text{C}_2\text{H}_2\text{F}_2$ and CO_2 as a function of time on stream under condition 2 in Table 1.

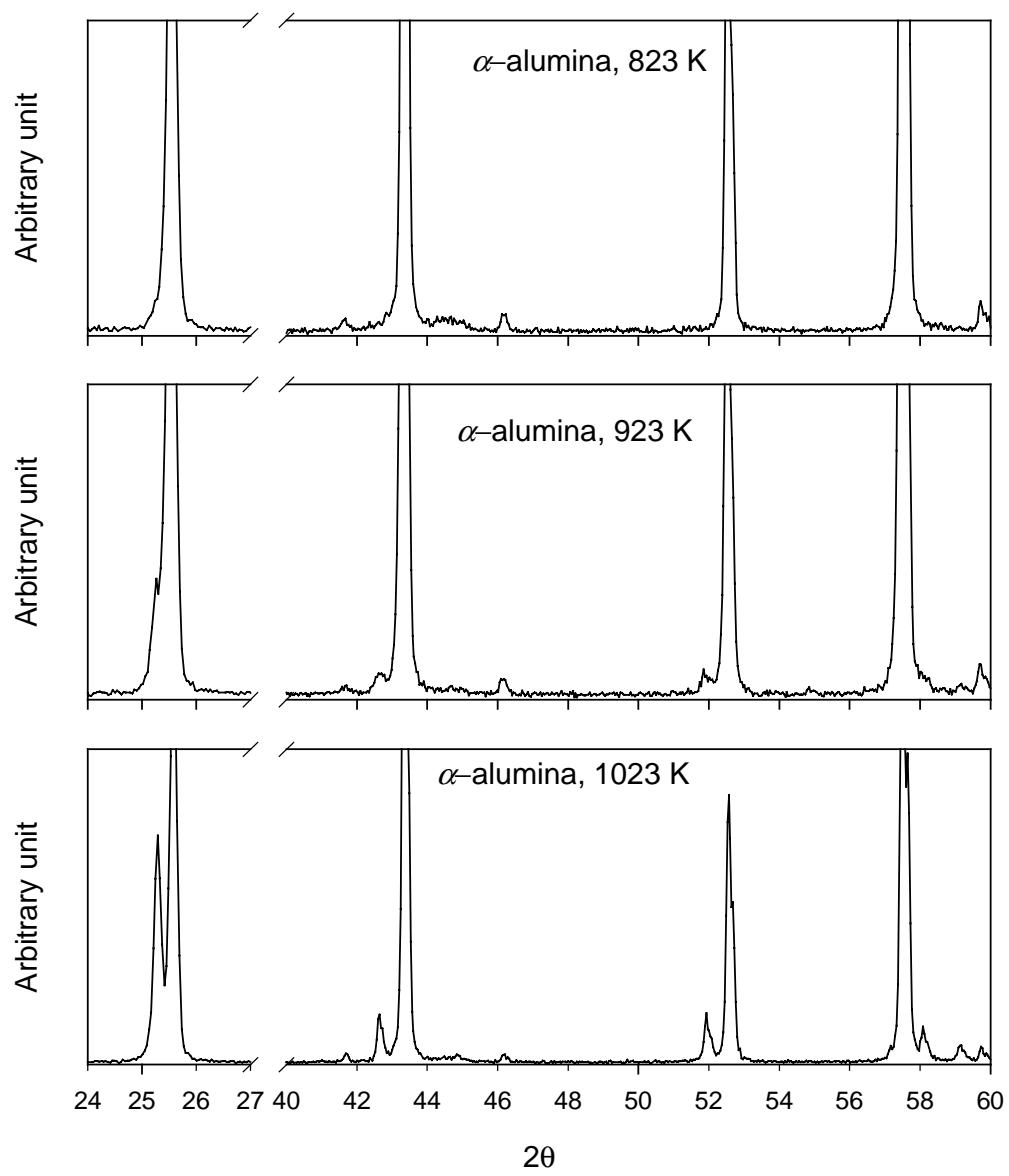


Figure S3 XRD spectra of α -alumina used in the pyrolysis of CHClF_2 under condition 5 in Table 1.