Supporting information

Synergistic catalysis of carbon partitioned LaF_3-BaF_2 composite for the coupling of CH_4 with CHF_3 to VDF

Jinchao Wang,[a] Wenfeng Han,*[a,b,c] Shucheng Wang,[b,c] Haodong Tang,[a] Wucan Liu,[b,c] Ying Li,[a] Chunshan Lu, *[a] Jianjun Zhang,[b,c] Eric M. Kennedy, [d] Xiaonian Li *[a]

[a] Institute of Industrial Catalysis, Zhejiang University of Technology, Chaowang Road 18, Hangzhou 310014, Zhejiang, P. R. China.

[b] State Key Laboratory of Fluorinated Greenhouse Gases Replacement and Control Treatment, Tianmushan Road 387, Hangzhou 310032, Zhejiang, P. R. China.

[c] Zhejiang Research Institute of Chemical Industry, Tianmushan Road 387, Hangzhou 310032, Zhejiang, P. R. China.

[d] Process Safety and Environment Protection Research Group, School of Engineering, The University of Newcastle, Australia

Email: hanwf@zjut.edu.cn (W.F. Han); lcszjcn@zjut.edu.cn (C.S. Lu)

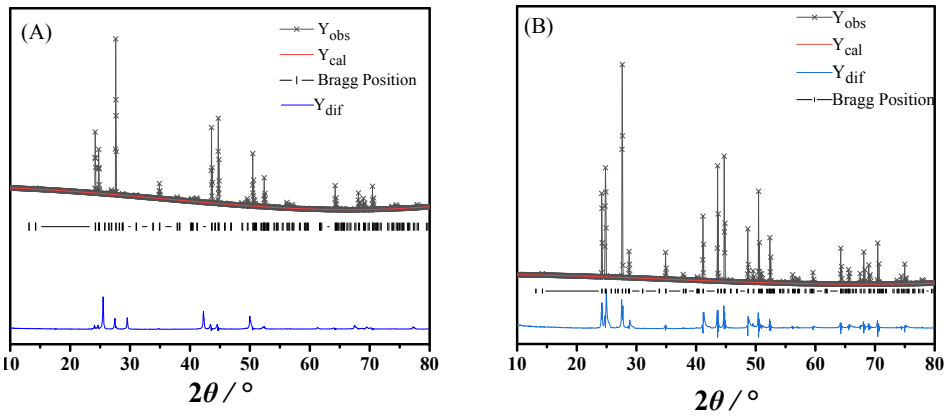

Fig. S1 Rietveld refinement analysis for the XRD patterns of (A) LaF_3-BaF_2 composites prepared by HF precipitation method (x=0.4) and (B) LaF_3-BaF_2 composites prepared by PVDF mediated calcination (x=0.6).

Table S1. The phase composition derived from the Rietveld refinement analysis in Fig. S1.

Catalyst	Elemental concentration, mass fraction%			
	LaF_3	BaF_2	LaOF	$Ba_{1-x}La_xF_{2+x}$
HF precipitation	34.11	7.66	11.65	46.58
PVDF mediated calcination	29.03	28.89	32.20	9.88

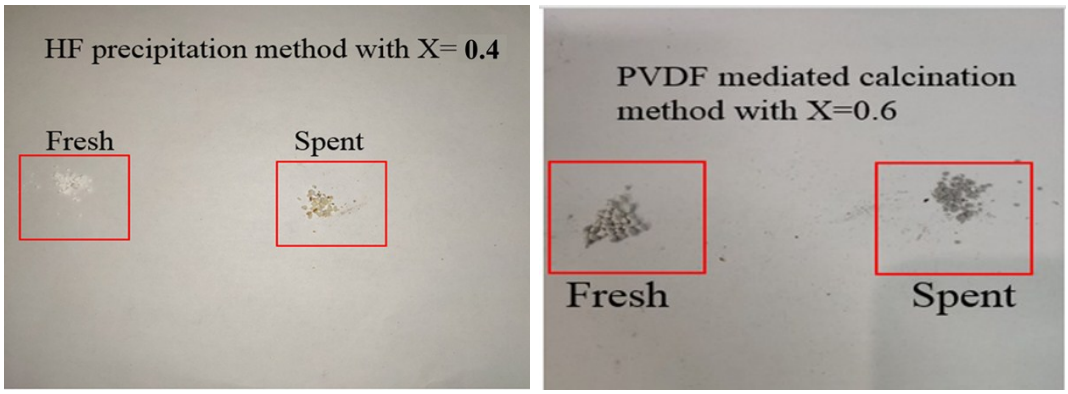

Fig. S2 photo images of fresh and spent catalysts prepared by HF precipitation and PVDF mediated calcination.

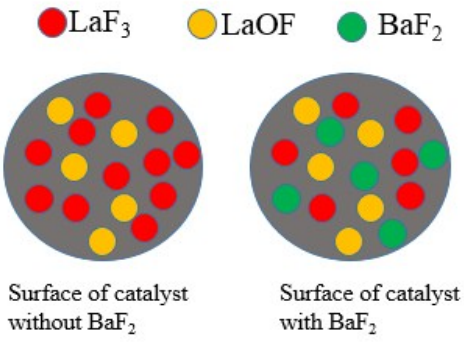

Fig. S3 Schematic illustration for the promotion effect of BaF_2 on LaF_3-BaF_2 composite catalyst.

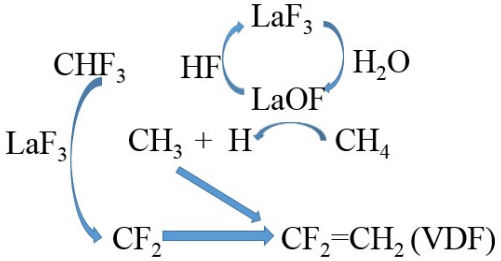

Fig. S4 Proposed reaction mechanism over LaF_3-BaF_2 composite catalyst.

Table S2. The phase composition derived from the Rietveld refinement analysis in Fig. S5 and S6.

Catalyst	Elemental concentration, mass fraction%			
	LaF_3	BaF_2	LaOF	$Ba_{1-x}La_xF_{2+x}$
HF precipitation	36.03	3.23	2.21	58.53
PVDF mediated calcination	38.58	21.05	27.61	12.76

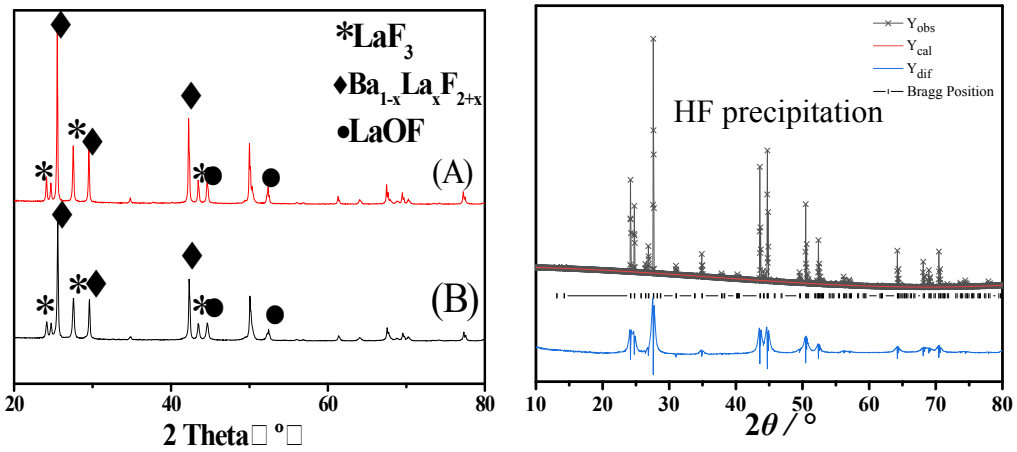

Fig. S5 XRD patterns and Rietveld refinement analysis of catalyst prepared by HF precipitation (x=0.4). (A) fresh catalyst and (B) spent catalyst. Reaction conditions: 15 h, T of 700℃, GHSV of 900h^{-1} and feeding $CHF_3/CH_4/O_2/N_2$=1:1:0.06:9.

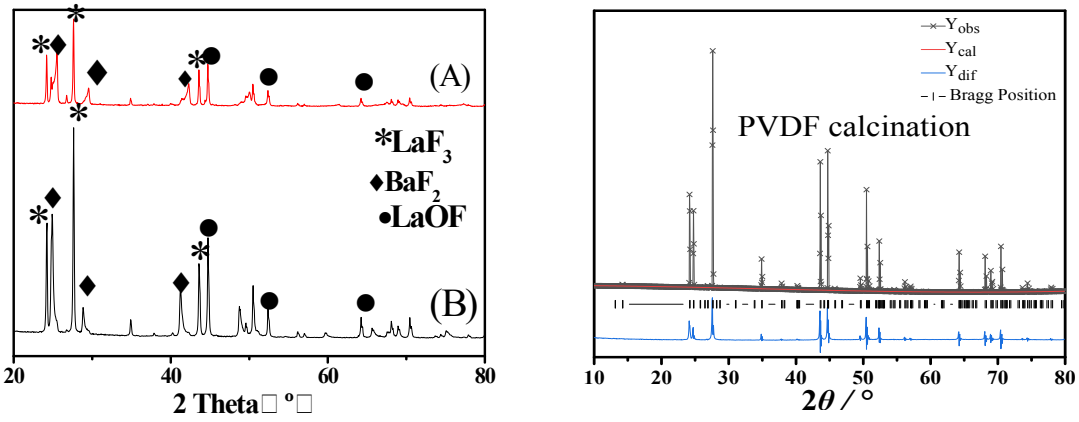

Fig. S6 XRD patterns and Rietveld refinement analysis of catalyst prepared by PVDF mediated calcination (x=0.6). (A) fresh catalyst and (B) spent catalyst. Reaction conditions: 15 h, T of 700℃, GHSV of 900h^{-1} and feeding $CHF_3/CH_4/O_2/N_2$=1:1:0.06:9.

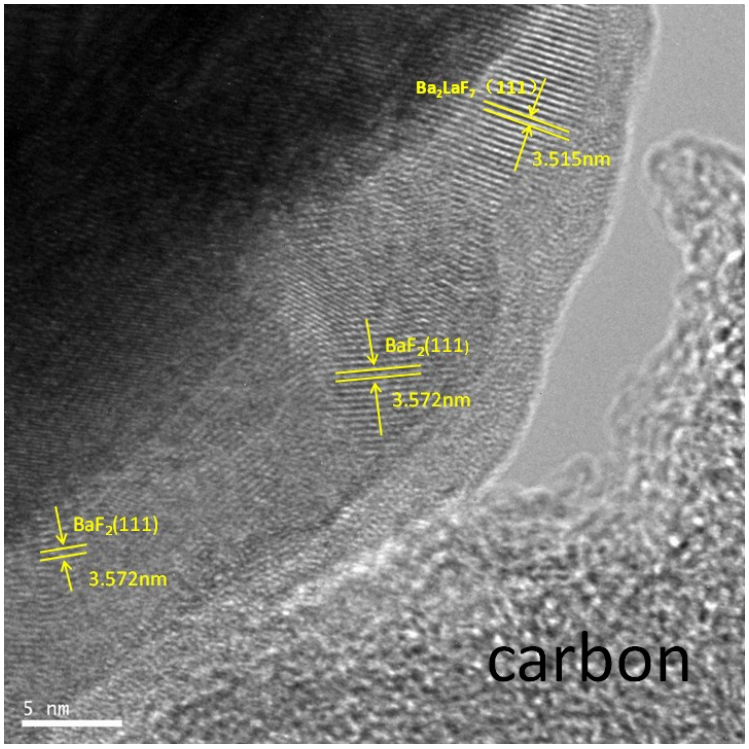

Fig. S7 TEM image of spent catalyst (x of 0.6, prepared by mediated calcination, TOS of 15 h). Reaction conditions: 15 h, *T* of 700℃, GHSV of 900h^{-1} and feeding $CHF_3/CH_4/O_2/N_2$=1:1:0.06:9.

Table S3 Surface elemental composition of fresh and spent catalysts prepared by HF precipitation method with x of 0.4(determined by XPS analysis).

Catalyst	Elemental concentration, %					F/（3*La+2*Ba）
	C	O	F	La	Ba	
Fresh	19.58	18.33	49.33	13.35	6.55	0.93
Spent	27.73	11.24	46.65	12.08	6.33	0.95

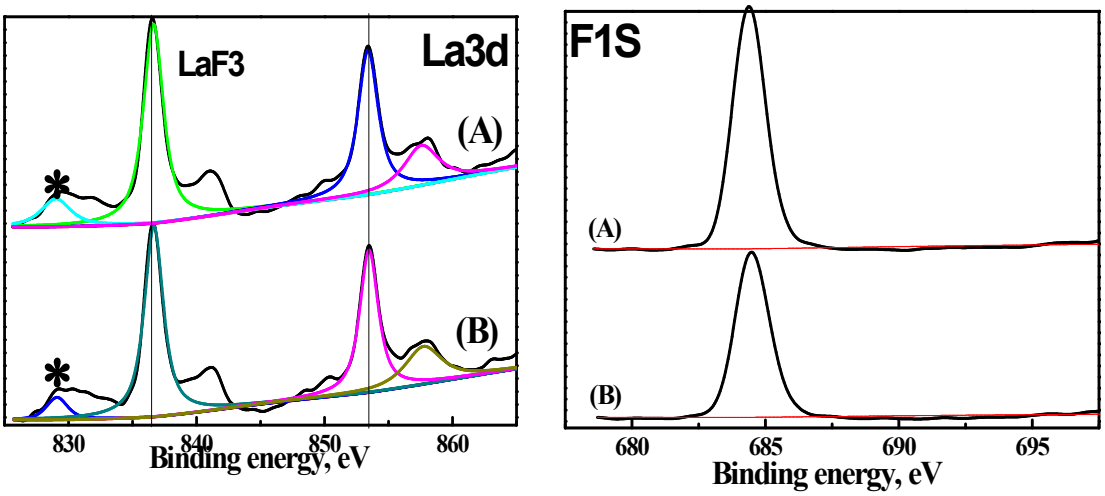

Fig. S8 XPS characterization of catalyst prepared by HF precipitation method with X=0.4.(A): before reaction;(B) after reaction . the highlight is the F(KLL) Auger transition.

Table S4 Surface elemental composition of LaF_3 catalyst prepared by HF precipitation method and PVDF mediated calcination （determined by XPS analysis）

Catalyst	Elemental concentration, %				F/La	O/La
	C	O	F	La		
HF Precipitation	17.16	9.16	52.16	21.16	2.47	0.43
PVDF mediated calcination	18.67	15.47	46.02	19.3	2.38	0.80