Electronic supplementary information

Catalytic dehydrofluorination of 1, 1, 1, 2-tetrafluoroethane to synthesize trifluoroethylene over the modified NiO/Al$_2$O$_3$ catalyst

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Experimental Section

1. Catalyst preparation

The MOx/Al$_2$O$_3$ catalysts were prepared by a wetness incipient impregnation in aqueous solution of metal nitrate (Ce(NO$_3$)$_3$ 6H$_2$O, Mg(NO$_3$)$_2$ 6H$_2$O, Ca(NO$_3$)$_2$ 4H$_2$O, Sr(NO$_3$)$_3$, La(NO$_3$)$_3$ 6H$_2$O, Cr(NO$_3$)$_3$ 9H$_2$O, Fe(NO$_3$)$_3$ 9H$_2$O, Ni(NO$_3$)$_3$ 6H$_2$O, Pd(NO$_3$)$_2$ 2H$_2$O, KNO$_3$, NaNO$_3$). For instance, commercial γ-Al$_2$O$_3$ (A. R., Sinopharm Chemical Reagent Co., Ltd) impregnated solution of Ni(NO$_3$)$_2$ 9H$_2$O (A. R., Aldrich) was dried at 100 ℃ for 12h and calcined at 500 ℃ for 3 h in air. The calcined NiO/Al$_2$O$_3$ catalyst was activated at 260 ^{o}C for 1 h and subsequently at 400 ^{o}C for 3 h, under the mixture gas of HF and N$_2$ (the molar ratio of N$_2$/HF = 1, total flow rate = 40 ml min^{-1}). The calcined samples were denoted as NiAlO-x catalyst, and x indicates the NiO weight content. The prefluorinated NiAlO-x catalyst was denoted as NiAlF-x catalyst.

2. Characterization

X-ray diffraction (XRD) patterns were collected on a Foucs D8 powder diffractometer operating at 40 kV and 30 mA with a Cu Kα X-ray radiation source (λ

= 0.154056 nm), in the 2θ range from 10 to 80° with a scan rate of 0.2° min^{-1}. BET

results were determined by N_2 sorption isotherms at 77 K on an NOVA 2200e, and

the samples were degassed at 200 $^{\circ}$C and 2×10^{-5} mbar for 12h. SEM (HitachiS-4700)

with an EDX attachment (Zeiss Supra55) was taken on a Hitachi S-4800, the catalyst

power was directly imbedded in conductive tapes, with the acceleration voltage of 20

kV.

NH$_3$-TPD was conducted using a set of automatic Altamira-100 apparatus. The

preheated (500 $^{\circ}$C) solid was absorbed with ammonia at 100 $^{\circ}$C. After the sample was

purged with nitrogen (30 ml min^{-1}, 30 min), the temperature was raised with 10 $^{\circ}$C

min^{-1} up to 600 $^{\circ}$C while the desorbed ammonia was recorded continuously via a TCD

detector. FT-IR spectra were obtained with a Perkin-Elmer 2000 FT-IR equipment and

a self-supported wafer of sample (ca.40 mg). Samples were pretreated at 400 $^{\circ}$C for 2

h under vacuum, and followed by adsorption of purified pyridine (Aldrich, 99+ %

grade) vapor at room temperature for 20 min. The system was then degassed and

evacuated at 100 $^{\circ}$C under a high vacuum, and the IR spectrum on a self-supported

wafer of sample was also recorded in the spectral range 1800–1400 cm^{-1} with 64

scans and at a resolution of 4 cm^{-1}.

Raman spectra were collected on a Renishaw RM1000 confocal microscope with

exciting wavelength of 514.5 nm under ambient conditions. TG experiments were

performed under the air atmosphere using a Netzsch STA 449C instrument, with a

heating rate of 1 $^{\circ}$C min^{-1}.

3. Dehydrofluorination of CF$_3$CFH$_2$

The dehydrofluorination of CF$_3$CFH$_2$ was carried out in a fixed bed reactor. 1.0 g

of catalyst was used for the reaction. The molar ratio of N$_2$/CF$_3$CFH$_2$ was 10 in a total

flow rate of 22.5 ml min^{-1}. To remove the product HF, the reaction effluent passed an

aqueous KOH solution, then, it was analyzed by a gas chromatograph (HP-5890)

using a HP-PLOT/Al_2O_3 column (0.53 mm $\times$ 50 m) and FID detector.
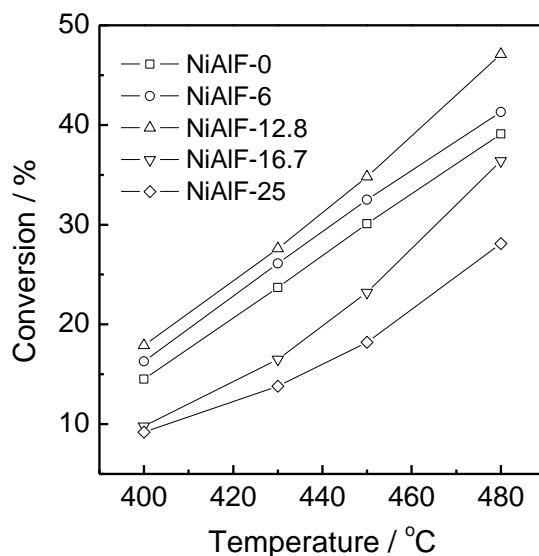
Supporting Figures and Tables

Fig. S1 Activity of NiAlF catalysts, N_2/CF_3CFH_2=10, P=1 atm, catalyst: 1.0 g.
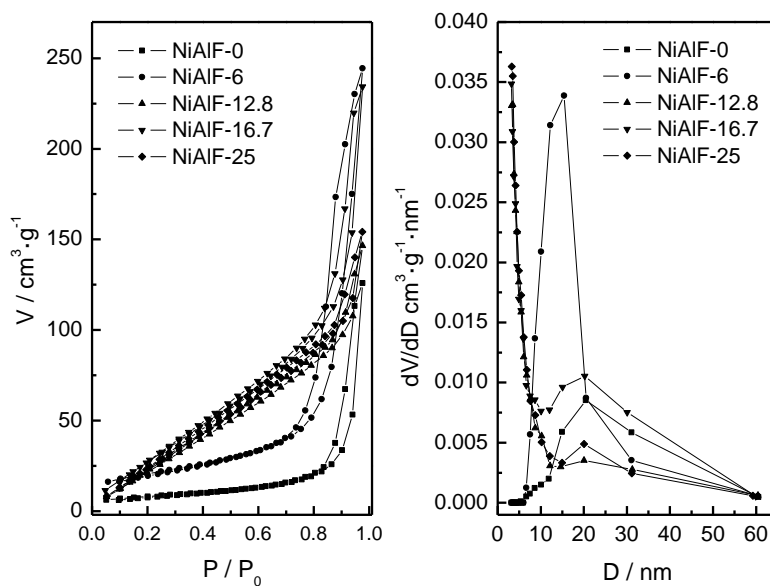
Fig. S2 N_2 adsorption isotherms (a) and pore diameters (b) of the NiAlF catalysts.

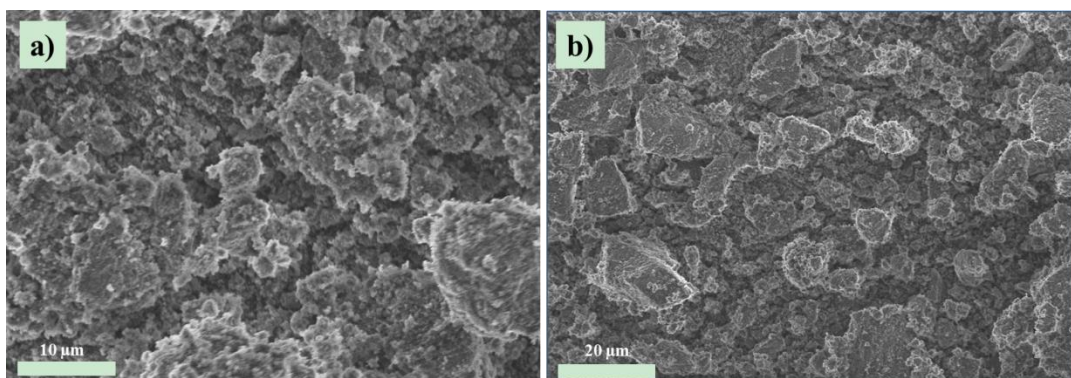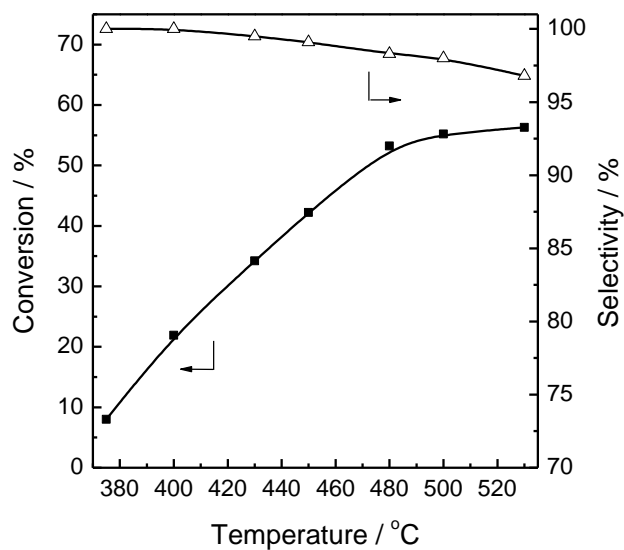Fig. S3 SEM images of catalysts. SEM: a) NiAlO-12.8 and b) NiAlF-12.8 catalyst.

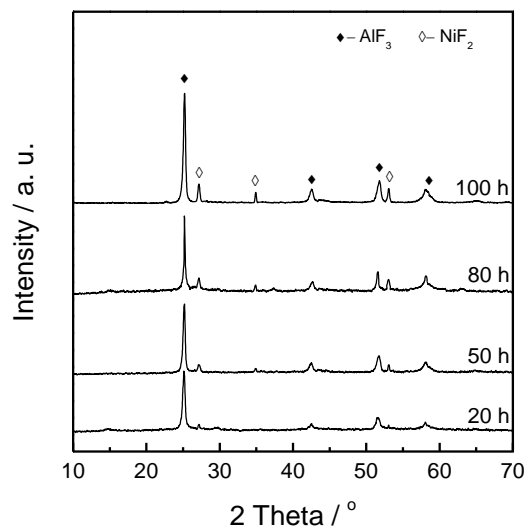Fig. S4 Influence of temperature on the catalytic performance. N_2/HFC-134a=10, GHSV = 675 h^{-1}.

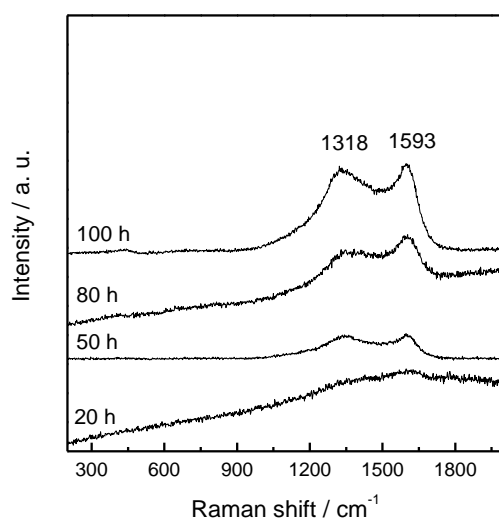Fig. S5 XRD patterns of NiAlF-5 catalyst after different reaction time.

Fig. S6 Raman spectra of NiAlF-12.8 catalyst after different reaction time.
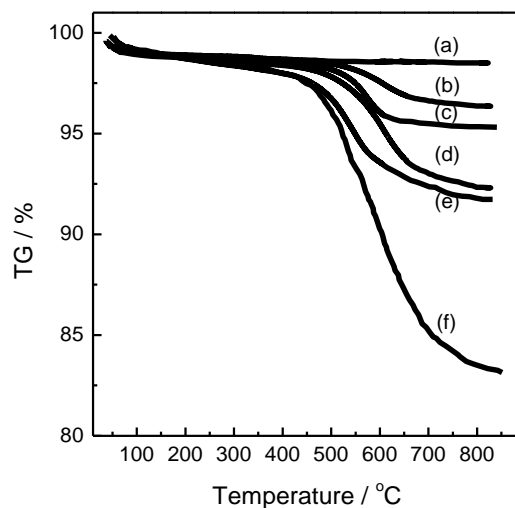
S5

Fig. S7 TG curves of NiAlF catalyst. (a) fresh catalyst, (b) 20 h, (c) 50 h, (d) 80 h, (e) 100 h, (f) deactivated catalyst.

Table S1 Catalytic reactivity of the catalyst before and after regeneration

Catalyst	Conversion / %	Selectivity / %	Yield / %
Fresh	28.1	99.9	28.0
Deactivated	8.4	99.6	8.3
After regeneration	26.5	99.8	26.4

Table S2 Physical properties of the NiAlO and NiAlF catalysts.

Catalysts	S_{BET} / $m^2\,g^{-1}$	Volume / $cm^3\,g^{-1}$	Averge poresize / nm	Total acidic amount / $mmol\,g^{-1}$
NiAlF-0	27.925	0.195	19	0.326
NiAlF-6.0	72.534	0.378	20	0.307
NiAlF-12.8	130.945	0.227	3-20	0.388
NiAlF-16.7	139.345	0.363	3-20	0.206
NiAlF-25.0	134.628	0.239	3-20	0.128
NiAlO-12.8	314.212	0.558	10	n/a