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Catalytic dehydrofluorination of 1,1,1,2tetrafluoroethane to synthesize trifluoroethylene over a modified NiO/Al₂O₃ catalyst[†]

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A promising fluorinated NiO/Al₂O₃ catalyst for synthesizing trifluoroethylene through the catalytic dehydrofluorination of CF₃CFH₂ was prepared, and the relationship between the Lewis acid sites and activity was investigated. 20.1% conversion of CF₃CFH₂ was observed, and the selectivity to trifluoroethylene was observed to be 99% at 430 °C after 100 h.

Trifluoroethylene (CF2=CHF) is used as an important fluorine-containing monomer and biologically active compound,¹ which is generated through the hydrodechlorination of trichlorotrifluoroethane or chlorotrifluoroethene using supported Pd or Ru catalyst.²⁻⁵ Nevertheless, there are many difficulties involved during separation and purification; moreover, expensive raw materials and noble metal catalysts are required. Comparatively, the dehydrofluorination of 1,1,1,2tetrafluoroethane (CF₃CFH₂) to synthesize trifluoroethylene is a promising route. The raw CF₃CFH₂ has eventually been replaced by 2,3,3,3 tetrafluoropropene due to its high global warming potential (over 1300) as a new greenhouse gas.^{6,7} The transformation of CF₃CFH₂ to trifluoroethylene with high additional value resolved the excess capacity of CF3CFH2. Admittedly, it exhibits atom efficiency and has better potential in industrial application. However, the studies concerning the catalytic dehydrofluorination of CF₃CFH₂ are hardly reported in the form of professional research studies, and most of the presented works are limited to patents.8-10

The dehydrofluorination of hydrofluorocarbons (HFCs) is thermodynamically and kinetically hindered.^{11,12} To obtain a considerable yield of fluorinated olefin, it is necessary to develop highly efficient catalysts to accelerate the reaction rate. As claimed in the literature, $Mg_2P_2O_7$,^{13,14} AlF₃,¹⁵ Fe₂O₃– CdO–Al₂O₃ (ref. 16) and Pd/AlF₃ (ref. 17) catalysts were used for HFCs dehydrofluorination. In addition, NiO/Al₂O₃

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catalysts were applied industrially for methanation,^{18,19} steam reforming and pre-reforming of natural gas.²⁰ However, the NiO/Al₂O₃ catalysts used for the dehydrofluorination of HFCs have not been reported scientifically.

It was disclosed that the catalytic performance of dehydrohalogenation is closely related to Lewis acidity.^{13–15,21} Teinz *et al.* reported the dehydrohalogenation of 3-chloro-1,1,1,3tetrafluorobutane (CF₃CH₂CFClCH₃) over metal fluoride, and dehydrofluorination was selectively catalyzed by strong Lewis acid sites. For the dehydrofluorination of CF₃CH₃, the influence of the strength of the Lewis acid sites on the formation of CF₂==CH₂ was investigated by Li *et al.*^{13,14} Okazaki *et al.*¹⁵ assumed that the product distribution was dependent on the acidic strength of the catalysts. However, the relationships between the Lewis acid sites and activity for the dehydrofluorination of CF₃CFH₂ are not clarified to date.

Herein, NiO/Al₂O₃ catalysts activated by HF pretreatment were prepared for the dehydrofluorination of CF_3CFH_2 to synthesize trifluoroethylene. Moreover, the catalyst preparation, including the reaction conditions, was optimized. XRD, BET, SEM/EDX, TEM, py-IR and NH₃-TPD were employed to disclose the relationship between the catalyst structure and its activity. Moreover, the deactivation and regeneration of the catalyst were investigated.

 γ -Al₂O₃ was modified by a series of metal oxides such as alkalis, alkaline earth, rare-earth, and transition metals. The oxide catalysts activated by the pre-fluorination of HF gas were used for the dehydrofluorination of CF₃CFH₂ to synthesize trifluoroethylene under the same reaction conditions. The trifluoroethylene yields for fluorinated MO_x/Al₂O₃ catalysts are summarized in Table 1. The selectivity to trifluoroethylene for all catalysts is up to 99%, and the other few byproducts are CF₂HCF₃ and CF₂HCFH₂. From Table 1, it can be observed that the activities of NiO/Al₂O₃ and Ce₂O₃/Al₂O₃ catalyst showed high activity at a low-temperature range of 400– 450 °C. However, Cr₂O₃ and the related species as dopants in the catalyst are toxic to environment and human health.



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Classification	Catalyst	Trifluoroethylene yields/%				
		500 °C	475 °C	450 °C	425 °C	400 °C
Parent	Al_2O_3	40.7	36.4	23.2	16.5	9.8
Transition	NiO/Al ₂ O ₃	60.3	43.6	32.2	22.9	14.4
	Cr_2O_3/Al_2O_3	37.6	34.3	29.2	21.9	14.0
	PdO/Al ₂ O ₃	26.3	28.4	20.9	14.4	9.7
	Fe ₂ O ₃ /Al ₂ O ₃	15.6	9.5	6.0	3.8	2.3
Rare-earth	Ce_2O_3/Al_2O_3	48.4	35.8	26.0	17.8	11.5
	La ₂ O ₃ /Al ₂ O ₃	27.5	20.7	15.4	10.9	7.7
Alkaline-earth	MgO/Al ₂ O ₃	5.5	3.7	2.3	1.4	1.0
	CaO/Al ₂ O ₃	3.5	2.5	1.7	1.0	0.6
	SrO/Al ₂ O ₃	2.9	2.1	1.4	0.9	0.5

Most of the transition and rare-earth metals added in the Al_2O_3 could not enhance its activity, and the activity of catalysts with alkaline-earth and alkalis was drastically low. Comparatively, NiO/Al₂O₃ catalyst shows an environmentally friendly and high catalytic activity.

Table 1 Catalytic performance of fluorinated catalysts for the dehydrofluorination of $CF_3CFH_2^{a}$

We modified Al_2O_3 with nickel nitrate and investigated the effect of NiO loading on its activity (Fig. S1†). It can be observed in Fig. S1 (ESI†) that with increasing NiO loading from 0 to 25 wt.%, the activity of NiAlF-12.8 catalyst reached the highest value, then decreased with a further increase in NiO contents over 12.8 wt.%. Moreover, the activity of NiAlF-16.7 and NiAlF-25 catalyst was lower than the parent Al_2O_3 (NiAlF-0). This indicated that the modification of the appropriate Ni species could enhance the catalytic activity.

The stability test was carried out over the optimal NiAlF-12.8 catalyst at 430 °C (Fig. 1). With a GHSV of 675 h⁻¹ and a CF₃CFH₂/N₂ molar ratio of 10, the conversion of CF₃CFH₂ slowly decreased, and then remained over 20.0%. However, trifluoroethylene selectivity did not change obviously during the on-stream time of 100 h. The activity of NiAlF-12.8 nearly remained stable after 78 h, showing good stability at a proper reaction temperature.

The deactivation of NiAlF-12.8 catalyst was accelerated in the dehydrofluorination process under high temperature conditions, high GHSV and low ratio of N_2 to CF_3CFH_2 . The regeneration of the deactivated NiAlF-12.8 catalyst was performed by a temperature-programmed calcination with an increasing rate of 2 °C min⁻¹ to 550 °C for 2 h in a mixed flow of nitrogen containing 10% oxygen. The regenerated NiAlF-12.8 catalyst needs to be pre-fluorinated again before the reaction. The results are listed in Table S1.† It was found that the reactivity could be recovered by more than 94% of the fresh catalyst, indicating that NiAlF-12.8 catalyst has an excellent regeneration capability.

Fig. 2 shows the XRD patterns of a) NiAlO and b) NiAlF catalysts. In Fig. 2a, the diffraction peaks of Al₂O₃ phase can be observed for all NiAlO catalysts. No diffraction peaks due to NiO phase are observed for the NiAlO-6 and NiAlO-12.8 catalysts.²² With increasing NiO content, the intensities of the NiO diffraction peaks appeared and became stronger, whereas the Al₂O₃ diffraction peaks weakened. For the NiAlO-25 catalyst, the peaks with strong intensity were attributed to the bulk NiO crystalline.²³ After the prefluorination of NiAlO catalysts, the characteristic peaks due to AlF₃ and NiF₂ phases are observed, as shown in Fig. 2b. The intensity of the diffraction peaks of AlF₃ at 25.3° due to (012) plane first increased, and reached the maximum with 12.8% of NiO content. The low content of Ni species could accelerate the crystal growth of AlF₃ crystalline particles under fluorination, initially causing the intensity of the AlF₃ peak to increase. In



Fig. 1 The stability of NiAlF-12.8 catalyst at 430 °C.



Fig. 2 XRD patterns of a) NiAlO and b) NiAlF catalysts. The NiO loading is 1) 0%, 2) 6.0%, 3) 12.8%, 4) 16.7%, and 5) 25.0%.

addition, the diffraction peaks of NiF₂ gradually became stronger. It was indicated that the extended exposure of NiO/Al₂O₃ catalyst to fluorinating gases at elevated temperatures led to the complete conversion of Al₂O₃ and NiO to AlF₃ and NiF₂, respectively.

The N₂ adsorption isotherms and pore size distributions of NiAlF catalysts are shown in Fig. S2.† All the isotherms are type IV, according to the IUPAC classification. Other parameters, such as surface area, pore volume, and pore size, are summarized in Table S2.† There is an increase in the surface area with the amount of nickel (from 0 to 12.8 wt.%). Fig. S3† shows the SEM images of catalysts. The NiAlO-12.8 catalyst is disordered in Fig. S3a,† and most of the bulk grains are crystalline AlF₃ formed by fluorination, as shown in Fig. S3b.†

First, the acidic amounts and strengths of NiAlF catalysts were measured using NH₃-TPD techniques. Fig. 3 shows the NH₃-TPD profiles of NiAlF catalysts with different NiO loading. The acidic amount was also calculated, and is listed in Fig. 3 (inset). The broad peaks around 170 °C and 315 °C could be ascribed to the NH₃ adsorbed on the weak acidic and strong acidic sites,²⁴ respectively. With increasing content of Ni species, the acidic amount increases, then declines drastically, and reaches the maximum for the NiAlF-12.8 catalyst. The acidic amounts of NiAlF-12.8 (0.43 mmol g⁻¹) and NiAlF-6 catalysts (0.37 mmol g⁻¹) are larger than that of the NiAlF-0 (AlF₃, 0.34 mmol g⁻¹) catalyst. However, NiAlF catalysts with high Ni species loading (>12.8 wt.%) show weak acidity.

Pyridine adsorption experiments were conducted to determine the properties of the acidic sites. Obviously, two characteristic bands at $v_{19b} = 1448$ and $v_{8a} = 1612 \text{ cm}^{-1}$ due to the Lewis acid sites^{25,26} on AlF₃ catalysts are observed in Fig. 4a. For the NiAlF-12.8 catalyst, the v_{8a} feature includes peaks at 1622 and 1616 cm⁻¹ associated with the strong and weak Lewis acid sites,^{27,28} respectively. However, the catalyst without Ni additive (NiAlF-0) has only one type of Lewis acid at 1612 cm⁻¹. This indicates that the NiF₂ plays an important role in the acidity of NiAlF catalyst. The NiAlF-12.8 catalysts adsorbed pyridine at room temperature. They were outgassed at 100 or 300 °C, and their py-IR spectra were obtained,



which are presented shown in Fig. 4b. The band shifts were observed with an increase in the desorption temperature on the NiAlF-12.8 catalyst, as shown in Fig. 4b. This shift in temperature shows the higher acidic strength. M. Wojciechowska *et al.*²⁴ reported that new Lewis acid sites appeared on the surface of the MgF₂ catalyst-doped appropriate NiF₂, which originated from the coordinatively unsaturated Ni²⁺ ions. These facts agreed with our findings in which new Lewis acid sites were observed in the NiF₂/AlF₃ catalyst (Fig. 3). It is considered that the Ni content plays an important role in the number of acid sites on the NiAlF catalyst.

Carmichael group et al.^{29,30} reported the cleavage of C-F in the dehydrofluorination of CF₃CH₃ and CF₂HCH₃. In general, C-F cleavage (the dissociation energy is 522.0 ± 8.4 kJ mol⁻¹) needs high activation energy, accompanied by high reaction temperature. It is well known that the Lewis acid sites are considered to activate C-F bond. Li et al.13 reported the dehydrofluorination of CF₃CH₃ into CF₂H₂ over the Lewis acidic Mg₂P₂O₇ catalyst. Teinz et al.²¹ reported that C-F bond activation over Lewis acid sites was the initial step of dehydrohalogenation. Therefore, Lewis acid sites play a key role in the dehydrofluorination of CF₃CFH₂. Fig. 5 shows the relationship between Lewis acid sites and the activity of the NiAlF catalysts. Interestingly, it is found that the number of Lewis acid sites is closely proportional to the conversion of CF₃CFH₂ (Fig. 5). The NiAlF-12.8 catalyst exhibited high activity, attributed to its large Lewis acidic amount. In conclusion, it is undoubtedly suggested that Lewis active sites are the



50 45 NiAIF-12.8 NiAIF-6 NiAIF-6 NiAIF-6 NiAIF-0 35 30 NiAIF-25 25 0.12 0.18 0.24 0.30 0.36 0.42 Lewis acid sites / mmol g⁻¹

Fig. 5 Dependence of the conversion of CF_3CFH_2 on the amount of Lewis acid sites, N₂/CF₃CFH₂ = 10, *P* = 1 atm, catalyst: 1.0 g.

main active sites of the catalysts for the dehydrofluorination of $\mathrm{CF}_3\mathrm{CFH}_2$.

According to the thermodynamic parameter of CF_3CFH_2 dehydro-fluorination reaction¹¹ [$\triangle_r G^{\theta}$ (298 K) = 70.3 kJ mol⁻¹; $\triangle_r H^{\theta}$ (298 K) = 128.6 kJ mol⁻¹], this reaction favors a high temperature. The influence of temperature from 375 to 530 °C on the NiAlF catalyst has been shown in Fig. S4.† With an elevation in the reaction temperature, the selectivity to trifluoroethylene decreased from 100% to 96.8%, accompanied with the formation of CFH=CFH, CF₂HCF₃ and CF₂HCFH₂. The byproducts were derived from the pyrolysis and isomerization^{31,32} of CF₃CFH₂ at high temperature. When the dehydrofluorination of CF₃CFH₂ was conducted at high temperatures (\geq 480 °C), the used catalysts turned black in a short time, indicating that serious coke or polymerization occurred over the catalysts. Therefore, a proper reaction temperature should be selected in the range of 400–480 °C.

As can be seen from Fig. 1, the deactivation behavior of the catalysts was investigated. Fig. S5† shows the XRD patterns of the used NiAlF-5 catalyst with different reaction times. Only the AlF₃ and NiF₂ phases were observed in the NiAlF-5 catalyst for 100 h, and the peak intensity increased with time on steam. It is indicated that the crystalline sizes of AlF₃ and NiF₂ increased with the reaction time on steam, and the catalyst was slowly sintered. Fig. S6† shows the Raman spectra of the used NiAlF-12.8 catalyst for different reaction times. Other intense broad bands located at 1318 and 1593 cm⁻¹ in the Raman spectra are attributed to the A_{1g} vibration mode and the E_{2g} vibration mode of the carbon,³³ respectively. The intensity of the Raman peak due to the carbon species increased with reaction time, demonstrating that the level of formed coke increased with the time on steam.

TG experiments were conducted to further illustrate the amount of coke generated for the deactivated NiAlF-12.8 catalyst during the reaction process, as shown in Fig. S7.† An obvious weight loss was observed below 100 °C in all the used NiAlF-12.8 catalysts, attributed to the loss of the physically adsorbed H_2O . In addition, a main weight loss was observed around the broad range from 500–590 °C, which was undisputedly assigned to the combustion of deposited carbon on the used NiAlF catalysts.³⁴ It is found that the weight loss of the used catalysts increased with the reaction time on steam. It was further confirmed that the coke resulted in the decline of catalytic activity, in agreement with the results obtained from Raman spectroscopy (Fig. S6†). It can be implied that the deposition over the catalysts.

In summary, a fluorinated NiO/Al₂O₃ catalyst was developed for a promising process on the catalytic dehydrofluorination of CF₃CFH₂ for synthesizing trifluoroethylene. The optimized NiAlF catalyst with 12.8 wt.% NiO shows an excellent performance, giving 20% conversion and 99% selectivity with a good stability. The relationship between the number of Lewis acid sites and the activity of NiAlF catalysts is closely linear regression relation. In addition, the slow deactivation is mainly attributed to coke deposition over the catalyst, and the deactivated catalyst can be easily regenerated by heating at 550 °C. More importantly, the fluorinated NiO/Al₂O₃ catalyst with an excellent defluorination performance could be applied to the dehydrofluorination of other HFCs, such as the dehydrofluorination of CF₂HCH₃ (HFC-152a) for synthesizing vinyl fluoride (a very important fluoride monomer).

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