

Catalytic Dehydrofluorination of Hydrofluoroalkanes to Fluorinated Olefin Over Ni/AlF₃ Catalysts

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Abstract. The hydrofluoric acid-resisting aluminum compounds (AlF₃, AlPO₄, AlN) supported with Ni catalyst were prepared by the wetness impregnation and tested for dehydrofluorination of hydrofluoroalkane to synthesize fluoroolefins. It is found that Ni/AlF₃ catalyst has the best catalytic performance, CF₃CFH₂ conversion of 29.3% after the reaction at 430 °C for 30 h, CF₂HCH₃ conversion of 31.8% after the reaction at 250 °C for 30 h, respectively. Comparatively, dehydrofluorination temperature of CF₃CFH₂ is higher than CF₂HCH₃ over the aluminum compounds catalyst, and the activity of catalysts is related with Lewis acidity. For the aluminum compounds catalyst, addition of Ni had promoted the activity and stability of Lewis acidic catalysts, it is attributed to synergistic catalysis of Lewis acid sites and Ni.

1. Introduction

Fluorine-containing olefins are mainly used as monomer raw materials for fluoropolymer, such as vinyl fluoride for the PVF, vinylidene fluoride for the PVDF, and also as intermediates for the fluorine-containing fine chemicals such as trifluorobromoethylene, etc. Fluoroolefins are a kind of important fine chemicals, the synthesis route has been extensively studied in recent years. In many production methods of fluorine-containing olefins, dehydrofluorination (simplified to De-HF) of hydrofluorocarbons (HFCs) is simple and efficient. At present, there are three De-HF ways: pyrolysis [1-3], liquid alkali [4] and heterogeneous catalysis [5]. Pyrolysis usually needs a high temperature, rigorous equipment, many by-products. Liquid alkali way requires the use of strong alkali and produces large amount of by-product salts, those will bring about serious environmental problems. The catalytic De-HF with low temperature and high selectivity is focus on the synthesis of fluorine-containing olefins.

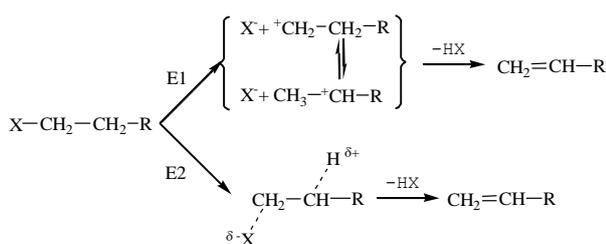
Most of the transition metal (such as Pd, Cu, Ni, Fe, Ir, Ru, etc.) has the role of activated C-H bond, so the transition metal and its supported catalyst in the catalytic dehydrogenation have a very important application. Pd/AlF₃ catalyst has the high reactivity for dehydrofluorination of 1, 1-difluorocyclohexane and 1, 1, 1, 3, 3-Pentafluoropropane [6,7], respectively. However, the noble metal catalyst due to its high price and gradually replaced by a large number of cheap non-noble

metal, which also meet the objectives of modern chemical sustainable development [8]. Relatively inexpensive Ni is considered to be one of a ideal metal for replacing noble metal. Alonso et al. [9] pointed out that nano-Ni particles can promote the H transfer reaction (such as alkane dehydrogenation, alcohol oxidation dehydrogenation, amine dehydrogenation). Shimizu et al. [8] studied the reaction mechanism of propanol dehydrogenation on Ni/Al₂O₃ catalyst, and believed that Ni can activate C-H bond and promote the dehydrogenation reaction with the acid-base site on Al₂O₃. Osaki et al. [10] reduced NiO-Al₂O₃ aerogels to obtain Ni/Al₂O₃ catalyst, TEM found that Ni particles with less than 6 nm were highly dispersed on the surface of Al₂O₃, which had a very good catalytic performance for CH₄ reforming. Aluminum compounds supported with Ni catalysts were investigated in the De-HF of HFCs in this paper.

The study related to De-HF mechanism of HFCs is few up to now. Kamiguchi et al. [11] gives a schematic representation of the typical dehydrohalogenation mechanism of HFCs, as shown in Scheme 1. It is generally believed that De-HF is carried out by the E1 mechanism. The reaction initial step is cleavage of C-F bond by activation. Usually, the fluorine of HFCs with strong electronegativity has partially negativity charged, it can be chemically adsorbed by Lewis acid sites and accelerate the cleavage of the C-F bond. Teinz et al. [12] argued that AlF₃ belonged to Lewis acid was an effective De-HF catalyst, and the interaction between Lewis acid sites and fluorine atom initiates the De-HF. Li et al. [13] suggested that the weak Lewis acid sites on the P₂O₇⁴⁻

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salt is the reaction center, it proposed that the carbonium-ion mechanism over the $Mg_2P_2O_7$ catalyst for De-HF of 1, 1, 1-trifluoroethane(CF_3CH_3) to vinylidene fluoride. Dehydrofluorination of HFCs should involve the cleavage of C-F and C-H bond. For the above studies, they focus the C-F bond activation, however, the synergistic activation of C-F and C-H bond is not proposed up to now. At present, there is no clear conclusion about De-HF mechanism for HFCs on the catalyst surface. In this paper, Aluminum compound supported Ni catalysts were used to catalytic De-HF of CF_3CFH_2 and CF_2HCH_3 , respectively. BET, XRD, NH_3 -TPD and FT-IR characterization were conducted to catalysts, and the relationship between activity and structure of catalyst was revealed. The synergistic catalysis mechanism of dehydrofluorination of HFCs was discussed.



Scheme 1 The De-HF mechanism of HFCs.

2. Materials and Methods

2.1 Catalyst preparation

The Ni/AlF_3 , Ni/AlN and $Ni/AlPO_4$ catalyst were prepared by the wetness impregnation in aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$. The raw materials included $Ni(NO_3)_2 \cdot 6H_2O$, AlF_3 , AlN and $AlPO_4$ were from the Aladdin. The aluminum compounds impregnated with nickel nitrate was dried at $100\text{ }^\circ\text{C}$ overnight. Finally, it was calcined at $500\text{ }^\circ\text{C}$ for 3 h at air. Then prepared catalyst was subject to reduction in H_2 flow (40 mL/min) at $500\text{ }^\circ\text{C}$ for 2 h. Prior to use, prefluorination was carried out in a stainless steel tubular reactor with a diameter of 3 cm and a length of 40 cm.

2.2 Dehydrofluorination of HFCs

Dehydrofluorination of HFCs (CF_3CFH_2 , CF_2HCH_3) was carried out in a continuous-flow fixed-bed metal reactor (15 mm i.d.) operated in the downflow mode at atmospheric pressure. The reaction temperature was determined with a thermocouple in contact with the 2.0 g catalyst. The flow rates of the gas HFCs and N_2 were carefully regulated by mass flow controllers. The molar ratio of $N_2/HFCs$ was 10 in a total flow rate of 22.5 ml min^{-1} and the gas hourly space velocity (GHSV) was 675 h^{-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 (I. D. $0.53\text{ mm} \times 50\text{ m}$) with a FID detector.

2.3 Characterization

Surface areas of the catalysts were determined by the modified BET method from the N_2 sorption isotherms at 77 K on an automatic NOVA 2200 apparatus.

X-ray diffraction (XRD) patterns were collected on a Focuss D8 powder diffractometer operating at 40 kV and 30 mA using $Cu-K\alpha$ radiation, in the 2θ range from 10 to 70° with a scan rate of $0.2^\circ\text{ min}^{-1}$.

Pyridine (Py) absorbed infrared spectrum (Py-IR) was also conducted at 200 and $400\text{ }^\circ\text{C}$, under a high vacuum. The IR spectrum a self-supported wafer of the sample was also recorded in the spectral range $1800\text{--}1400\text{ cm}^{-1}$ with 64 scans and at a resolution of 4 cm^{-1} .

Ammonia temperature-programmed desorption (NH_3 -TPD) was conducted on an automatic Altamira-100 Characterization System. 100 mg of catalysts was loaded into a quartz tubular reactor and was heated from room temperature to $500\text{ }^\circ\text{C}$ and kept for 30 min in a flow of N_2 (30 ml min^{-1}). Then it was cooled down to $50\text{ }^\circ\text{C}$. A flow of NH_3 (20 ml min^{-1}) was then introduced for 10 min. The gaseous or physical sorption NH_3 was removed by purging N_2 flow (30 ml min^{-1}) at $80\text{ }^\circ\text{C}$ for 1 h. Then the sample was heated to $600\text{ }^\circ\text{C}$ with a ramp of $10\text{ }^\circ\text{C min}^{-1}$. The desorbed NH_3 was monitored continuously via a TCD detector. The total amount of NH_3 desorbed was exactly determined by the adsorption with an excess of dilute HCl and following the titration with $NaOH$ solution. For the titration, the mixture indicator was adopted, containing 0.1% brom-cresol green ethanol solution and 0.2% methyl red ethanol solution.

High resolution transmission electron microscopy (HRTEM) of the sample was obtained on a JEOL JEM 2100F equipment with a field emissive gun, operating at 200 kV and with a point resolution of 0.24 nm .

3. Results and discussion

3.1. Reactivity

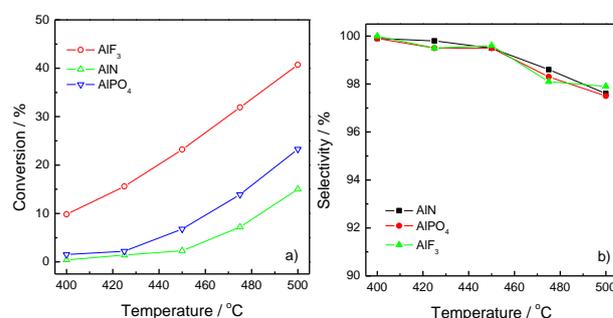


Figure 1 a) Conversion and b) selectivity of AlF_3 , AlN and $AlPO_4$ catalysts for De-HF of CF_3CFH_2 .

Since the HF with strong corrosion produced during dehydrofluorination (De-HF) of hydrofluorocarbons (HFCs), choice of catalyst is harsh. Generally, fluorides, phosphates and nitrides have the hydrofluoric acid-resistance. It is selected the AlF_3 , AlN and $AlPO_4$ catalysts for De-HF of HFCs and investigated their

catalytic performance. 1, 1-difluoroethane (CF_2HCH_3) and 1, 1, 1, 2-tetrafluoroethane (CF_3CFH_2) are considered as typical HFCs molecular for De-HF reaction. Figure 1a) is the activity results of the AlF_3 , AlN and AlPO_4 catalyst in the reaction temperature range of 400~500 °C. It is found that the activity of AlF_3 is higher than that of the AlN and AlPO_4 . The AlN and AlPO_4 have little catalytic activity when the reaction temperature is less than 425 °C. Fig.1b) is the relationship between selectivity to trifluoroethylene and reaction temperature. At 480 °C, selectivity of three catalysts is not much different, all above 98%. From Figure 1b), the selectivity of three catalysts to trifluoroethylene is gradually decreased as the reaction temperature increases, due to presence of by-product $\text{CFH}=\text{CFH}$, CF_2HCF_3 and CF_2HCFH_2 derived from the cracking or isomerization of CF_3CFH_2 under the high temperature [14,15]. The temperature is also an important factor affecting the performance of the catalyst. Among the three catalysts, AlF_3 catalyst has a good catalytic performance for De-HF of CF_3CFH_2 .

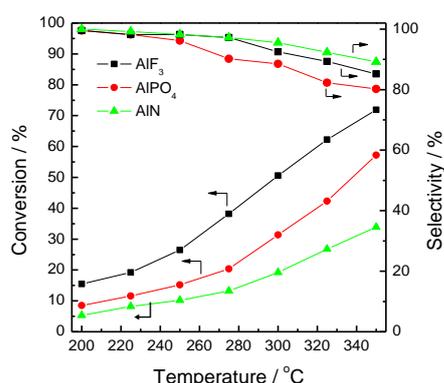


Figure 2 Reactivity of AlF_3 , AlN and AlPO_4 catalyst for dehydrofluorination of CF_2FCH_3 .

Then, the AlF_3 , AlN and AlPO_4 catalysts used to dehydrofluorination of CF_2HCH_3 to vinyl fluoride. It can be seen from the Figure 2 that AlF_3 has the highest activity for De-HF of CF_2HCH_3 , compared with the AlPO_4 and AlN catalysts. When the temperature is low (200~250 °C), the selectivity of the three catalysts to vinyl fluoride is not very different (close to 100%). When the reaction temperature is more than 280 °C, selectivity (S) of three catalysts is: $S_{\text{AlN}} > S_{\text{AlF}_3} > S_{\text{AlPO}_4}$. Similarly, the temperature has a significant effect on De-HF of CF_2HCH_3 , and the AlF_3 catalyst has a high activity.

Table 1. Dehydrofluorination of CF_3CFH_2 , CF_2HCH_3 .

Catalyst	Conversion of CF_3CFH_2 / % (430 °C)				Conversion of CF_2HCH_3 / % (250 °C)			
	Time on stream / h				Time on stream / h			
	5	10	20	30	5	10	20	30
AlF_3	25.6	25.2	24.3	22.5	27.8	27.7	25.2	24.3
AlN	3.8	3.7	3.6	3.4	10.2	10.1	9.5	9.2
AlPO_4	8.6	8.5	8.4	8.2	15.2	15.0	14.5	14.1
Ni/AlN	5.2	5.1	5.0	4.8	13.4	13.2	12.5	12.1
Ni/AlF_3	30.2	29.8	29.2	29.3	32.5	32.1	31.5	31.8
Ni/AlPO_4	11.8	11.3	10.5	11.2	17.5	17.4	16.2	16.7

Supported Ni has a high activity for alkyl dehydrogenation, ammonia selective oxidation, alkylated steam reforming [16], etc., which has attracted much

attention in the field of heterogeneous catalysis. The Ni/AlF_3 , Ni/AlN and Ni/AlPO_4 catalysts used to De-HF of CF_3CFH_2 and CF_2HCH_3 , respectively, and the reactivity results are shown in Table 1. As seen from Table 1 that the activity of the AlF_3 , AlN and AlPO_4 catalysts has decreased with the reaction time for De-HF of HFCs (CF_3CFH_2 and CF_2HCH_3). It is found that activity of three catalysts is improved after 2%Ni supported on the AlF_3 , AlN and AlPO_4 catalysts. Although the activity of catalyst supported Ni also slows down, the decrease rate is obviously lower. So, the addition of Ni can improve activity for De-HF of HFCs. Dehydrofluorination temperature of CF_3CFH_2 is significantly higher than that of CF_2HCH_3 , which is due to CF_3CFH_2 molecules with more strong electron-withdrawing F and higher dissociation of the C-F bond.

3.2 Characterization

The surface area, pore diameter, pore volume of catalysts listed in Table 2. Surface area of the AlF_3 , AlPO_4 and AlN is $52 \text{ m}^2 \text{ g}^{-1}$, $29 \text{ m}^2 \text{ g}^{-1}$, $85 \text{ m}^2 \text{ g}^{-1}$, respectively. After supported Ni, their surface areas have little decrease, with no difference of pore diameter and volume. AlN catalyst has the low activity, it may due to the small surface area ($29 \text{ m}^2 \text{ g}^{-1}$).

Table 2 Physical properties of Al-based and Ni/AlF_3 catalyst.

Catalyst	$S_{\text{BET}} / \text{m}^2 \cdot \text{g}^{-1}$	Pore diameter / nm	Pore volume / $\text{cm}^3 \cdot \text{g}^{-1}$	Acid sites / $\text{mmol} \cdot \text{g}^{-1}$
AlF_3	52.0	9.0	0.646	0.326
AlPO_4	85.0	17.9	0.483	0.154
AlN	29.0	25.8	0.563	0.048
Ni/AlN	20.0	26.5	0.545	0.041
Ni/AlF_3	50.0	14.4	0.226	0.322
Ni/AlPO_4	64.0	13.2	0.046	0.147

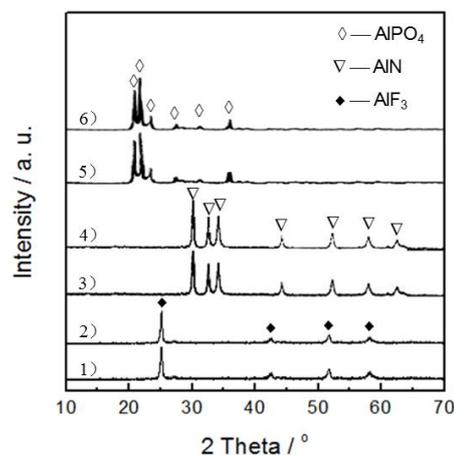


Figure 3 XRD patterns. 1) AlF_3 , 2) Ni/AlF_3 , 3) Ni/AlN , 4) AlN , 5) AlPO_4 , 6) Ni/AlPO_4

Figure 3 shows the XRD results of catalysts, AlF_3 (PDF: 44-0231), AlN (PDF: 25-1133) and AlPO_4 (PDF: 45-0177). As seen from Fig. 3 that the addition of Ni in the AlF_3 , AlN and AlPO_4 catalyst has no obvious change in the XRD diffraction peak. No peaks of Ni shown in the

Figure 3, this indicates that Ni present in the catalyst in the form of highly dispersion.

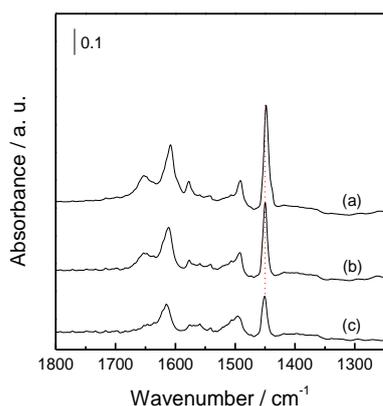


Figure 4 Py-IR spectra of (a) AlF₃, (b) AlPO₄ and (c) AlN

In this paper, Py-IR technique was used to detect the surface acid types of the AlF₃, AlN and AlPO₄ catalysts. Figure 4 shows the Py-IR results of the AlF₃, AlN and AlPO₄ catalysts. The vibrational peaks are attributed to Lewis acids at 1450 cm⁻¹, 1608 cm⁻¹ and 1652 cm⁻¹ (ν_{19b} and ν_{8a}, respectively), and 1540 cm⁻¹ (ν_{19b}) attributed to Brönsted acid [17,18]. It can be seen from Figure 4 that the vibration peaks (ν_{19b}) of the AlF₃, AlN and AlPO₄ catalysts appear at 1450 cm⁻¹, indicating that the surface of these catalysts is predominantly Lewis acid. After Ni was loaded, the surface acid types of the Ni/AlF₃, Ni/AlN and Ni/AlPO₄ catalysts did not change significantly.

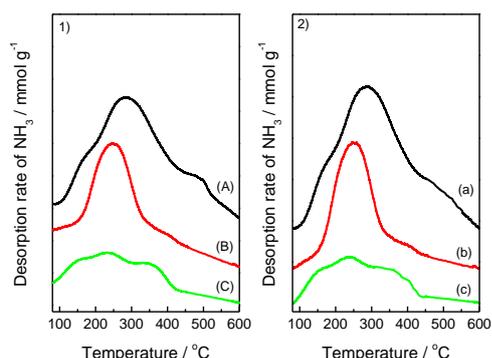


Figure 5 NH₃-TPD profiles. 1): (A) AlF₃, (B) AlPO₄ and (C) AlN; 2): (a) Ni/AlF₃, (b) Ni/AlPO₄ and (c) Ni/AlN.

In Figure 5.1) is the NH₃-TPD curve for the AlF₃, AlN and AlPO₄ catalysts. Compared with three catalysts, the AlN₃ has the largest NH₃ desorption peak area, followed by the AlPO₄, that of AlN is the smallest, so the acidity (A) order of the three catalyst is: A_{AlF₃} > A_{AlPO₄} > A_{AlN}, the acid amounts are listed in Table 2. Figure 5.2) is the NH₃-TPD results for the Ni/AlF₃, Ni/AlPO₄ and Ni/AlN catalysts. By comparing the catalyst doped and undoped Ni from Figure 5, it was found that the distribution of acid sites (NH₃ desorption peak position) and the peak area were not obviously different. Their acidity results are shown in Table 2. The acid amount of the catalyst before and after the loading of Ni did not

change significantly. Thus, the loading Ni did not significantly alter the Lewis acid properties of catalysts.

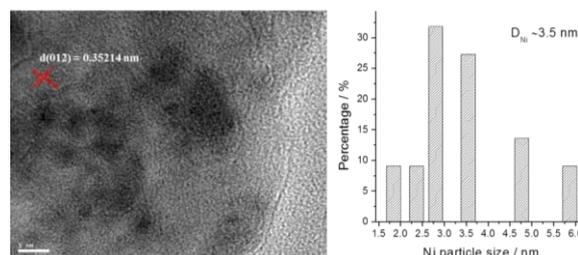


Figure 6 TEM images of Ni/AlF₃ catalyst

As can be seen from Table 1, the addition of Ni improved the activity of catalysts. As the Ni/AlF₃ catalyst has good activity for De-HF of HFCs, Ni supported on the catalyst surface are characterized by TEM, as shown in Figure 6. The lattice spacing of AlF₃ was calculated to be 0.35214 nm, which was attributed to the 012 crystal plane of AlF₃ according to the standard card of XRD. Distribution of Ni Particle Size As shown in the histogram in Figure 6, the size of Ni particles on the surface is mainly distributed at about 3 nm, which perform the excellent activity for De-HF of HFCs in this region of Ni particles.

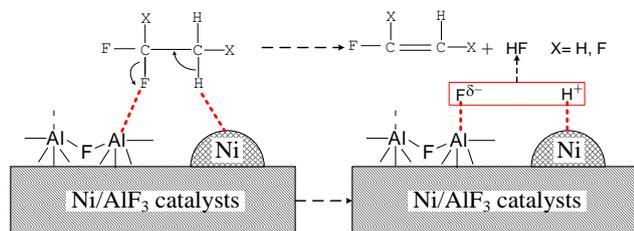
3.3 Effect of Lewis acid sites and Ni

The Lewis acid sites play an important role to dehydrofluorination (De-HF) of hydrofluorocarbons (HFCs). De-HF of HFCs requires more stringent conditions of reaction, such as high temperatures. The dissociation energy of C-F is 522.0 ± 8.4 kJ mol⁻¹, which is the higher than 414 kJ mol⁻¹ of C-H, so the cleavage of C-F bond is considered to be a key step of catalytic De-HF of HFCs. It is well known that Lewis acid are the reactivity centers of the activated C-X (X=F, Cl, Br, I) bonds [12]. AlF₃ catalyst has a high activity for De-HF of HFCs due to the fact that AlF₃ has large number of Lewis acid sites (0.326 mmol g⁻¹). For the AlF₃, AlN and AlPO₄ catalyst, it was also found that Lewis acid sites were proportional to activity of De-HF, the same results reported in our previous works [19].

According to the result of Table 1, for the AlF₃ catalyst, conversion of CF₂HCH₃ is 22.5% at 430 °C, conversion of CF₃CFH₂ is 24.3% at 250 °C. For the Ni/AlF₃ catalyst, conversion of CF₂HCH₃ is 29.3% at 430 °C, conversion of CF₃CFH₂ is 31.8% at 250 °C. The addition of Ni in the AlF₃, AlN and AlPO₄ catalyst improved the De-HF activity of HFCs (CF₂HCH₃ or CF₂HCH₃). Besides, the stability of AlF₃ catalyst obviously improved by addition of Ni as seen from the Table 1. The activity of AlF₃ catalyst decline with time on stream, the long-chain fluorocarbons and/or coke coving the Lewis acid centres might result in deactivation of catalysts. The long-chain fluorocarbons and coke derived from the coupling and cracking of carbon-positive ion intermediates [13], carbon-positive ion intermediate generated by cleavage of C-F bond over strong Lewis acid sites which considering as the first step

[12]. The Ni/AlF₃ catalysts possessed good activity and stability, it may be due to the fact that Ni restrain the formation of carbon-positive ion intermediate through the synergistic catalysis.

Scheme 3 shows the De-HF process of HFCs to fluoroolefins over the bi-functional Ni/AlF₃ catalyst. Carmichael Group [20,21] proposed two De-HF mechanisms of CF₃CH₃ and CF₂HCH₃, which is the homolytic and heterolytic cleavage in the C-F and C-H bond fracture. For the AlF₃ catalyst, the catalytic mechanism due to the carbon-positive ion (heterolytic cleavage), the activation of C-F bond over Lewis acid sites is the initial step. However, for the Ni/AlF₃ catalyst, the synergistic catalysis took place on the surface of catalyst (homolytic cleavage), the synergetic activation of C-F and C-H bond by Lewis acid sites and Ni showed in schematic diagram (Scheme 3). So, in the E2 elimination mechanism of HFCs, Lewis acid sites and Ni activated C-F and C-H bond, respectively. This mechanism could avoid the carbon-positive ion intermediates as much as possible. That may be main reason that Ni/AlF₃ catalyst has a good catalytic performance.



Scheme 3 Reaction mechanism of De-HF of HFCs over the Ni/AlF₃ catalyst.

4. Conclusion

Catalytic performance of AlF₃, AlN and AlPO₄ catalyst were investigated for dehydrofluorination of CF₃CFH₂ and CF₂HCH₃, respectively. By the IR and NH₃-TPD characterization, the activity of AlF₃, AlN and AlPO₄ catalyst were related to their Lewis acid sites. After additive Ni in the three Al catalysts, catalytic performance of catalysts were improve obviously, and of that Ni/AlF₃ catalyst is the best, the Ni particle is about 3 nm. The dehydrofluorination of HFCs to fluoroolefin over the Ni/AlF₃ catalyst were subjected to a synergistic catalysis of Lewis acid sites and Ni.

Acknowledgments

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