Synthesis of 2,3,3,3-tetrafluoropropene by catalytic dehydrofluorination of 1,1,1,3,3-pentafluoropropane over Ni-Cr$_2$O$_3$ catalyst

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2,3,3,3-Tetrafluoropropene (HFO-1234yf) has been synthesized from 1,1,1,3,3-pentafluoropropane (HFC-245fa) by dehydrofluorination over a series of Ni-Cr$_2$O$_3$ catalysts. HFC-245fa could be readily dehydrofluorinated to HFO-1234yf and 1,3,3,3-tetrafluoropropene (HFO-1234ze) over these catalysts. Characterization results reveal that the Ni species in the catalysts is mainly metallic. Ammonia temperature-programmed desorption results indicate that the surface acidity is enhanced with increasing Ni contents in the catalysts, which is responsible for the increased selectivity towards HFO-1234yf. The formation of carbon during the reaction led to the coverage of surface acidic sites, which accounted for the decrease of the selectivity to HFO-1234yf.

Keywords: Catalysts, Nickel catalysts, Dehydrofluorination, Nickel, Nickel acetate, Chromium, Pentafluoropropane, Tetrafluoropropene

2,3,3,3-Tetrafluoropropene (HFO-1234yf) with zero ozone depletion potential and low global warming potential has been considered as a promising candidate as a substitute for 1,1,1,2-tetrafluoroethane (HFC-134a)\textsuperscript{1,2}. Due to its outstanding thermodynamic properties as well as nontoxicity to human, it has been widely used in cooling agents, foaming agents, buffing abrasive agents, displacement drying agents, gaseous dielectrics and power cycle working fluids\textsuperscript{3}.

The synthetic routes for synthesis of HFO-1234yf mainly includes addition/fluorination reaction route with halogenated methane and halogenated ethylene as raw materials\textsuperscript{4}, chlorine/fluorine exchange reaction route with 1,1,2,3-tetrachloropropene and 2-chloro-3,3,3-trifluoropropene (HCFC-1233xf) as raw material\textsuperscript{5,6}, dehydrohalogenation reaction route with 1,1,1,3,3-pentafluoropropane (HFC-245eb) or 1,1,1,2,2-pentafluoropropane (HFC-245cb) as raw material\textsuperscript{7,8} and isomerization reaction route with 1,3,3,3-tetrafluoropropane (HFC-1234ze) as raw material\textsuperscript{9}. Among these, the addition/fluorination reaction route and chlorine/fluorine exchange reaction route with halogenated methane and halogenated ethylene as raw materials\textsuperscript{4}, chlorine/fluorine exchange reaction route with 1,1,2,3-tetrachloropropene and 2-chloro-3,3,3-trifluoropropene (HCFC-1233xf) as raw material\textsuperscript{5,6}, dehydrohalogenation reaction route with 1,1,1,3,3-pentafluoropropane (HFC-245eb) or 1,1,1,2,2-pentafluoropropane (HFC-245cb) as raw material\textsuperscript{7,8} and isomerization reaction route with 1,3,3,3-tetrafluoropropane (HFC-1234ze) as raw material\textsuperscript{9}. Among these, the addition/fluorination reaction route and chlorine/fluorine exchange reaction route are complex; the raw materials (HFC-245eb and HFC-245cb) used in the dehydrohalogenation reaction are not economic. Although isomerization reaction is more selective, the raw material HFO-1234ze with higher cost is not suitable for industrial applications. Considering that it is easier to produce HFO-1234ze through catalytic dehydrofluorination of the more economical 1,1,1,3,3-pentafluoropropane (HFC-245fa)\textsuperscript{10}, the traditional synthetic routes of HFO-1234yf with HFC-245fa as raw material have been followed. In the first step, HFC-245fa was catalytically converted to HFO-1234ze by dehydrofluorination\textsuperscript{10}, in the second step, HFO-1234ze was catalytically converted HFO-1234yf by isomerization\textsuperscript{9}. If the first step and second step could be combined into one, which is HFC-245fa $\xrightarrow{\text{Cat.}}$ HFO-1234yf + HF, the reaction process would be simplified and more importantly, the energy consumption can be effectively controlled. Therefore, one-step synthesis from HFC-245fa to HFO-1234yf is a promising process. Unfortunately, this reaction is mainly reported in patents and very few published papers are available. For example, a patent\textsuperscript{11} reported a synthesis route for the production of trans-1,3,3,3-tetrafluoropropene (HFO trans-1234ze) by catalytically dehydrofluorination of 1,1,1,3,3-pentafluoropropane (HFC-245fa) to produce a mixture of cis-1,3,3,3-tetrafluoropropene and trans-1,3,3,3-tetrafluoropropene, which was then isomerized cis-1234ze to trans-1234ze.

In this study, the direct synthesis of HFC-1234yf using HFC-245fa as the raw material has been conducted through a dehydrofluorination reaction over Ni-Cr$_2$O$_3$ catalysts. The effects of Ni species
Materials and Methods

The Ni-Cr$_2$O$_3$ catalysts were prepared using a mechanical mixing method. The detailed process is as follows: Cr(NO$_3$)$_3$·9H$_2$O (analytical grade, Sinopharm Chemical Reagent Co., Ltd., China) was dissolved in distilled water, and an aqueous solution of NH$_3$·H$_2$O was added to the solution under stirring until a precipitated slurry was obtained. The resulting slurry was dried at 120 °C overnight to obtain Cr(OH)$_3$. Finally, the prepared Cr(OH)$_3$ and Ni(CH$_3$COO)$_2$·4H$_2$O (analytical grade, Sinopharm Chemical Reagent Co., Ltd., China) were mechanically mixed and calcined at 500 °C for 4 h in N$_2$ to obtain the xNi-Cr$_2$O$_3$ catalysts, where $x$ ($x = 0, 2, 5, 10, 15$ or $20\%$) refers to the molar percent of Ni in the xNi-Cr$_2$O$_3$ catalysts. For comparison, a catalyst consisting of mechanically mixed Ni and Cr$_2$O$_3$ was prepared. The detailed process is as follows: Cr(NO$_3$)$_3$·9H$_2$O (analytical grade, Sinopharm Chemical Reagent Co., Ltd., China) was dissolved in distilled water, and an aqueous solution of NH$_3$·H$_2$O was added to the solution under stirring until a precipitated slurry was obtained. The resulting slurry was dried at 120 °C overnight to obtain Cr(OH)$_3$. Then, it was calcined at 500 °C in N$_2$ for 4 h to yield Cr$_2$O$_3$. Further, Ni(CH$_3$COO)$_2$·4H$_2$O was calcined at 500 °C in N$_2$ for 4 h when Ni was obtained. Finally, Ni and Cr$_2$O$_3$ were mechanically mixed.

Specific surface areas of the catalysts were determined by the modified BET method from the adsorption isotherms at liquid nitrogen temperature (~195.7 °C) on a NOVA 40000c surface area & pore size analyzer. Before measurements, the samples were out-gassed at 300 °C for 4 h under vacuum. X-ray diffraction (XRD) patterns were recorded using a PANalytic XPert PW3040 diffractometer with Cu Kα radiation ($\lambda = 0.1542$ nm) operated at 40 kV and 40 mA. The patterns were collected in a 20 range from 10° to 90°, with a scanning step of 0.15°/s.

The reduction properties of Ni-Cr$_2$O$_3$ catalysts were measured by hydrogen temperature-programmed reduction (H$_2$-TPR), which was carried out in a fixed bed (i. d. = 6 mm) reactor containing 20 mg of catalyst. The sample was heated from 30 °C to 300 °C at a rate of 10 °C/min and kept at 300 °C for 30 min under a flow of N$_2$. After cooling down to 50 °C, the sample was heated from 50 °C to 700 °C with a heating rate of 10 °C/min under a mixture of 5% H$_2$-95% N$_2$ (20 mL/min). The amount of H$_2$ consumption was measured by a gas chromatograph with a thermal conductivity detector (TCD), which was calibrated by the quantitative reduction of a known amount of CuO powder.

Surface acidity of the catalysts was measured by ammonia temperature-programmed desorption (NH$_3$-TPD) which was carried out in a fixed-bed reactor (i. d. = 6 mm) containing 100 mg of catalyst. The sample was heated from 30 °C to 500 °C at a rate of 10 °C/min, kept at 500 °C for 30 min and cooled down to 50 °C under a flow of N$_2$. Then a flow of NH$_3$ (40 mL/min) was introduced to the reactor for 30 min. The gaseous or physical adsorption of NH$_3$ was removed by purging N$_2$ flow (40 mL/min) at 100 °C for 60 min. Then the sample was heated from 50 °C to 700 °C at a rate of 10 °C/min, and the profile was recorded using a gas chromatograph with a TCD detector.

Raman spectra were collected by a Renishaw RM1000 confocal microprobe under ambient conditions. The wavelength of the excitation laser was 514 nm. The scanning range was 200–2000 cm$^{-1}$.

The catalytic defluorination reaction was carried out in a fixed bed reactor (10 mm (i.d.)×300 mm), equipped with an electric heater. Ni-Cr$_2$O$_3$ catalysts (4.5 mL) was loaded into the reactor and dried at 100 °C for 60 min. Then the sample was heated from 50 °C to 700 °C at a rate of 10 °C/min, and kept at 500 °C for 1 h in N$_2$ with a flow rate of 30 mL/min. After the catalyst was dry, a mixture of N$_2$ and HFC-245fa with a molar ratio of N$_2$/HFC-245fa = 4 was introduced (total flow = 25 mL/min, space velocity = 333 h$^{-1}$). The products were analyzed by a gas chromatograph (Shimadzu GC-2014) equipped with a flame ionization detector (FID) and a GS-GASPRO capillary column (60 mx0.32 mm).

Results and Discussion

Figure 1 shows the XRD patterns of fresh and spent Ni-Cr$_2$O$_3$ catalysts. As shown in Fig. 1, diffraction peaks due to crystalline Cr$_2$O$_3$ are clearly observed in fresh and spent Ni-Cr$_2$O$_3$ catalysts. Also, with increasing Ni content in the catalyst, the diffraction peaks of Cr$_2$O$_3$ become weaker. This indicates that crystalline size of Cr$_2$O$_3$ decreases with increasing Ni content in the catalyst. In addition, diffraction peaks of metallic Ni in the Ni-Cr$_2$O$_3$ catalysts are also detected, probably due to the fact that Ni(CH$_3$COO)$_2$·4H$_2$O decomposes to metallic Ni in N$_2$ at 500 °C. Compared with the fresh Ni-Cr$_2$O$_3$ catalysts (Fig. 1a), the spent Ni-Cr$_2$O$_3$ catalysts (Fig. 1b) show diffraction peaks assigned to
crystalline NiF₂, which is formed by Ni species reacting with the HF formed by catalytic dehydrofluorination of HFC-245fa during the reaction H \text{HFC-245fa}\xrightarrow{\text{Cat.}}\text{HFO-1234yf (ze) + HF}.

Figure 2 shows the $\text{H}_2$-TPR profiles of the Ni-Cr₂O₃ catalysts. For the Cr₂O₃ catalyst, only one reduction peak ($\alpha$ peak) at 290 °C is observed. Considering that crystalline Cr₂O₃ can not be reduced below 800 °C in $\text{H}_2$ atmosphere, the reduction peak ($\alpha$ peak) of the catalyst is probably due to the reducible CrOₓ ($x > 1.5$) species \(^{12-14}\). The same reduction peaks ($\alpha$ peaks) are also observed in the Ni-doped catalysts. The hydrogen consumption of the $\alpha$ peaks (reducible CrOₓ ($x > 1.5$) species) in the Ni-Cr₂O₃ catalysts was calibrated with known amounts of CuO powder (0.20, 0.21, 0.18, 0.16, 0.08 and 0.06 mmol/g for Cr₂O₃, 2Ni-Cr₂O₃, 5Ni-Cr₂O₃, 10Ni-Cr₂O₃, 15Ni-Cr₂O₃ and 20Ni-Cr₂O₃, respectively). As can be seen, with increasing Ni content in the catalyst, the content of high-valent Cr species (CrOₓ, $x > 1.5$) species decreases but the area of reduction peak ($\beta$ peak at 550 °C) of the NiO in intimate contact with the oxide support \(^{15-17}\) gradually increases. When the content of Ni-doping is 20%, the hydrogen consumption of NiO is the highest (0.23 mmol/g). If one assumes that all the Ni species exist in the form of NiO, the calculated hydrogen consumption is 2.64 mmol/g. The much lower experimental hydrogen consumption compared with the theoretical value suggests that the Ni species of the catalyst surface exist mainly in the metallic state, which is consistent with the XRD results.

Figure 3 shows the NH₃-TPD profiles of the Ni-Cr₂O₃ catalysts, as well as the calculated amounts
of acidic sites. NH₃ desorption peaks (400–600 °C) observed in the Ni-Cr₂O₃ catalysts. Also, with increasing Ni content in the catalyst, NH₃ desorption peak shifts toward lower temperature and the area of NH₃ desorption peak gradually increases, which indicates that the acid strength gradually weakens and surface acid sites gradually increase. The acid sites on the catalyst surface were calibrated with the amount of desorbed NH₃. The amounts of acid sites on Cr₂O₃, 2Ni-Cr₂O₃, 5Ni-Cr₂O₃, 10Ni-Cr₂O₃, 15Ni-Cr₂O₃ and 20Ni-Cr₂O₃ catalysts are 16.4, 79.3, 97.3, 117.1, 155.9 and 188.3 µmol/g, respectively. It is clear that Ni has remarkable effects on the acid strength and the surface acid sites.

Cr₂O₃ is known for its Lewis acidity as reported in the literature. In addition, the Lewis acidity of Cr₂O₃ has been detected by pyridine absorption experiment in our previous work. Therefore, in the current work also, the acid sites of Ni-Cr₂O₃ catalysts should be assigned as Lewis acid sites.

Table 1 shows the surface acid sites, specific surface areas and surface acid densities of Ni-Cr₂O₃ catalysts. As shown in Table 1, the surface Lewis acid sites gradually increase but the specific surface areas decrease slightly with increasing Ni content in the Ni-Cr₂O₃ catalysts. Based on the amounts of surface Lewis acid sites and the surface areas of the catalysts, the surface acid densities of the Cr₂O₃, 2Ni-Cr₂O₃, 5Ni-Cr₂O₃, 10Ni-Cr₂O₃, 15Ni-Cr₂O₃ and 20Ni-Cr₂O₃ catalysts are calculated to be 0.30, 1.76, 3.04, 4.34, 6.00 and 8.97 µmol/m², respectively. It is clearly shown that with increasing Ni content in the catalyst, the surface acid density gradually increases.

Figure 4 shows the catalytic behavior of the Ni-Cr₂O₃ catalysts for catalytic dehydrofluorination of HFC-245fa at 400 °C. The conversion of HFC-245fa is > 99% for all the catalysts (Fig. 4a). With increasing Ni content in the Ni-Cr₂O₃ catalysts, the selectivity to HFO-1234yf gradually increases. However, the selectivity to HFO-1234yf gradually decreases during the reaction (Fig. 4b). When the Ni content is 2–10%, the selectivity to HFO-1234yf is relatively stable (14.1–12.3%) during 3–10 h reaction time. Interestingly, the decline of the selectivity to HFO-1234yf is accompanied by an increase in the selectivity to HFO-1234ze (Fig. 4c). Further, the catalytic behavior of the previous Ni-Cr₂O₃ was compared to that of a catalyst consisting of mechanically mixed Ni and Cr₂O₃ (Fig. 5).

Table 1 — The surface acid sites, specific surface areas and surface acid densities of Ni-Cr₂O₃ catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface acid sites (µmol/g)</th>
<th>Specific surface area (m²/g)</th>
<th>Surface acid density (µmol/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂O₃</td>
<td>16.4</td>
<td>54</td>
<td>0.30</td>
</tr>
<tr>
<td>2Ni-Cr₂O₃</td>
<td>79.3</td>
<td>45</td>
<td>1.76</td>
</tr>
<tr>
<td>5Ni-Cr₂O₃</td>
<td>97.3</td>
<td>32</td>
<td>3.04</td>
</tr>
<tr>
<td>10Ni-Cr₂O₃</td>
<td>117.1</td>
<td>27</td>
<td>4.34</td>
</tr>
<tr>
<td>15Ni-Cr₂O₃</td>
<td>155.9</td>
<td>26</td>
<td>6.00</td>
</tr>
<tr>
<td>20Ni-Cr₂O₃</td>
<td>188.3</td>
<td>21</td>
<td>8.97</td>
</tr>
</tbody>
</table>

Fig. 4 — The conversion of HFC-245fa (a), the selectivity to HFO-1234yf (b) and the selectivity to HFO-1234ze (c) versus time on stream at 400 °C.
It has been recognized that the Lewis acid sites are the active sites for both dehydrohalogenation reactions and isomerization reactions. The high conversion of HFC-245fa is for all the catalysts at 400 °C (> 99.0 %) implies that the conversion is not sensitive for Lewis acid sites. However, with increasing Ni content, the selectivity to HFO-1234yf gradually increases at the beginning of the reaction (1 h reaction time), which is probably related to surface Lewis acid sites of the catalyst. As shown in Fig. 6, with increasing surface Lewis acid sites in the Ni-Cr$_2$O$_3$ catalysts, the selectivity to HFO-1234yf gradually increases after 1 h reaction time. This indicates that the increase of surface Lewis acid sites is conducive to the formation of HFO-1234yf. However, as the reaction progresses, the selectivity to HFO-1234yf gradually decreases while the selectivity to HFO-1234ze increases.

In order to further explain the experimental phenomena of the selectivity to HFO-1234yf and HFO-1234ze versus time on stream, the spent samples were characterized. In the Raman spectra of fresh and spent 10Ni-Cr$_2$O$_3$ catalysts, bands at 550 cm$^{-1}$ assigned to Cr$_2$O$_3$ species are observed for both catalysts (Fig. 7) which is consistent with the XRD results. However, Raman bands at 1350 cm$^{-1}$ and 1592 cm$^{-1}$ assigned to carbon deposit are observed only for the spent catalyst. This indicates that there is formation of carbon during the reaction. The formation of the carbon deposit is probably due to polymerization of the olefin products such as

![Fig. 5](image1.png)  
(a) Conversion of HFC-245fa, (b) selectivity to HFO-1234yf and (c) selectivity to HFO-1234ze versus time on stream at 400 °C.

![Fig. 6](image2.png)  
Relationship between selectivity to HFO-1234yf after 1 h reaction and surface acid sites of Ni-Cr$_2$O$_3$ catalysts.

![Fig. 7](image3.png)  
Raman spectra of fresh and spent 10Ni-Cr$_2$O$_3$ catalysts.
Ni-Cr

Conclusions

leads to decrease of selectivity to HFO-1234yf. carbon results in a decrease of Lewis acid sites, which significantly decreases as compared with the fresh result of

acid sites for the spent 10Ni-Cr catalyst, which is consistent with the result of Raman spectra (Fig. 7). The deposited carbon results in a decrease of Lewis acid sites, which leads to decrease of selectivity to HFO-1234yf.

Figure 8 shows the NH$_3$-TPD profiles of fresh and spent 10Ni-Cr catalysts. It is found that the Lewis acid sites for the spent 10Ni-Cr$_3$O$_3$ catalyst significantly decreases as compared with the fresh 10Ni-Cr$_3$O$_3$ catalyst, which is consistent with the result of Raman spectra (Fig. 7). The deposited carbon results in a decrease of Lewis acid sites, which leads to decrease of selectivity to HFO-1234yf.

Fig. 8 — NH$_3$-TPD profiles of fresh and spent 10Ni-Cr$_3$O$_3$ catalysts.

HFO-1234yf and HFO-1234ze, as also concluded by Lee et al.,

in fluorination of CF$_3$CH$_2$Cl.

This work demonstrates the promoting effect of Ni-Cr$_3$O$_3$ catalysts for catalytic dehydrofluorination HFC-245fa for synthesis of HFO-1234yf. The results showed that with increasing Ni-doping in the Ni-Cr$_3$O$_3$ catalysts, the initial selectivity to HFO-1234yf gradually increased, which is related to the increase of Lewis acid sites (surface acid density). As the reaction progressed, there was formation of carbon on the catalyst surface, as a result of which there is a decrease of Lewis acid sites, leading to decrease of selectivity to HFO-1234yf. When Ni doping was 2–10%, the catalysts contained the appropriate surface acid density, which made the selectivity to HFO-1234yf relatively stable during 3–10 h reaction.

Acknowledgement

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References