Characterization of CrO$_x$-Y$_2$O$_3$ catalysts for fluorination of 2-chloro-1,1,1-trifluoroethane

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Received 21 July 2008; revised and accepted 13 March 2009

The fluorination of 2-chloro-1,1,1-trifluoroethane (CF$_2$CH$_2$Cl) to synthesize 1,1,1,2-tetrafluoroethane (CF$_3$CHF$_2$) has been carried out on various CrO$_x$-Y$_2$O$_3$ catalysts with different Cr loadings. The effect of Cr loading on the catalyst composition and structure has been investigated. X-ray diffraction and Raman results indicate that the CrO$_x$ species with high oxidation state (Cr(VI)) are well dispersed on the catalyst surface when the Cr loading was lower than 19.5 %. With increase in Cr loading, crystalline Cr$_2$O$_3$ and polymeric chromate are formed, which inhibit pre-fluorination of the catalysts. The catalysts are stable under the reaction conditions and the catalytic activity is strongly dependant on the pre-fluorinated CrO$_x$ content. The highest activity is obtained on a pre-fluorinated catalyst with a Cr loading of 19.5, with a 19 % CF$_3$ conversion at 320 °C, corresponding to a formation rate of 2.03 mmol h$^{-1}$ g$^{-1}$ cat, which is 3-fold higher than the best result obtained over a Cr/MgF$_2$ catalyst (0.68 mmol h$^{-1}$ g$^{-1}$ cat) under similar conditions. The Cr-Al$_2$O$_3$ catalyst has also been prepared and tested for the probe reaction in this study. The activity is lower as compared to that of the Cr-Y$_2$O$_3$ catalyst with the same Cr content. The higher activity of Cr-Y$_2$O$_3$ catalyst may be due to the higher degree of dispersion of the Cr(VI) species on the Y$_2$O$_3$ support than on other supports. It is also found that the CrF$_x$, CrO$_x$F$_y$ or Cr(OH)$_x$F$_y$ phases originating from higher oxidation state Cr(VI) species are the active sites for the fluorination reaction.

Keywords: Catalysts, Supported catalysts, Fluorination; Oxides, Chromium oxides; Yttrium oxide

IPC Code: Int. Cl. 8 B01J23/26; B01J37/26; B01J39/10; C07C17/00

Hydrofluorocarbons (HFCs) with zero ozone depletion potential and low global warming potential have been considered as the alternatives to chlorofluorocarbons (CFCs). 1,1,1,2-Tetrafluoroethane (CF$_3$CH$_2$F, HFC-134a) is one of the promising alternatives, which has been widely used as refrigerants, solvents and catalysts for fluorination of 2-chloro-1,1,1-trifluoroethane and dismutation of CCl$_2$F$_2$. Cho et al. prepared the CrO$_x$ catalysts on various supports and found that the activity of the catalyst decreases in the order of MgO>Al$_2$O$_3$>MgF$_2$>TiO$_2$>ZrO$_2$. Kim et al. have systematically studied chromium catalysts for the fluorination of 2-chloro-1,1,1-trifluoroethane (CF$_2$CH$_2$Cl, HCFC-133a). It was found that the catalytic activity over the CrF$_3$/MgF$_2$-AlF$_3$ catalysts was lower than that over the single support catalysts (CrF$_3$/MgF$_2$ and CrF$_3$/AlF$_3$) because of the formation of MgAlF$_5$.1.5H$_2$O. Furthermore, it was found that the highly dispersed chromium fluoride or oxyfluoride species are the active sites for the fluorination of HCFC-133a to HFC-134a. In another study, Adamczyk et al. found that all chromium oxyfluorides exhibited significantly higher catalytic activity than the pure CrF$_3$ or Cr$_2$O$_3$, in the fluorination of HCFC-133a and dismutation of CCl$_2$F$_2$. It has also been reported that CrO$_x$F$_y$ shows catalytic activity 20 times higher than that of CrF$_3$.H$_2$O for the fluorination of HCFC-133a. In a F/Cl exchange reaction (fluorination of CH$_2$Cl$_2$ to CH$_2$F$_2$), Quan et al. found that Cr species with higher oxidation state exhibits higher catalytic activity than Cr(III).

As mentioned above, although the chromium oxides catalysts for the fluorination reaction have been studied, the focus of research is on the transition metal oxide/fluoride supports. Very few studies on other supports has been reported. Also, the activities of these catalysts reported in the literature are usually low. In our previous study, we investigated the effect of...
calcination temperature on the CrO$_x$-Y$_2$O$_3$ catalysts structure and reactivity and found that low calcination temperature was beneficial to the dispersion of Cr(VI) species, which enhances the catalytic activity$^9$. We report herein the effect of Cr loading on the structure and the catalytic performance of the catalysts. The evolution of the active sites for this reaction is also discussed.

Materials and Methods

Catalyst preparation and activation

The CrO$_x$-Y$_2$O$_3$ catalysts were prepared by a deposition-precipitation method. A detailed process is as follows: an aqueous solution of Cr(NO$_3$)$_3$ was mixed with Y(OH)$_3$ powder and then an aqueous solution of (NH$_4$)$_2$CO$_3$ (1 M) was added to the mixture under stirring until a precipitated slurry was obtained. The resulting slurry was aged for 2 h and separated from the mother liquid, washed with deionized water and dried at 120 °C overnight. Finally, it was calcined at 400 °C for 4 h. The catalysts were denoted as CrYO-2.4, CrYO-9.8, CrYO-19.5, CrYO-46.5 and CrO$_x$, with the number indicating the Cr content in the catalyst, as determined by the inductively coupled plasma (ICP) technique. In addition, a Cr-Al$_2$O$_3$ sample with Cr loading 20 wt% (denoted as CrAlO-20) was prepared by the above method, and was employed as a reference catalyst.

Before the reaction, pre-fluorination was carried out in order to activate the catalyst. The pre-fluorination process was performed in a stainless steel tubular reactor (1 cm i.d. × 30 cm). The calcined CrYO catalyst (3 g) was loaded into the reactor and dried at 260 °C for 2 h and at 350 °C for 2.5 h under N$_2$ flow (30 cm$^3$ min$^{-1}$). Then the N$_2$ flow was stopped and a mixture of HF (80 cm$^3$ min$^{-1}$) and N$_2$ (20 cm$^3$ min$^{-1}$) was introduced at 260 °C for 2 h and subsequently at 350 °C for 2.5 h. The CrYO-2.4, CrYO-9.8, CrYO-19.5, CrYO-46.5, CrO$_x$ and CrAlO-20 catalysts after the activation process were denoted as CrYF-2.4, CrYF-9.8, CrYF-19.5, CrYF-46.5, CrF$_x$, and CrAlF-20, respectively.

Fluorination reaction

The fluorination reaction was carried out in the same reactor after catalyst activation, under atmospheric pressure. The pre-fluorinated catalyst (3 g) was loaded, corresponding to a catalyst volume of 3 cm$^3$. Flow rates of CF$_3$CH$_2$Cl and HF pre-heated at 30 °C were carefully controlled using mass flow controllers. The molar ratio of HF/CF$_3$CH$_2$Cl was 10 and the GHSV was 3000 h$^{-1}$. The gaseous products were analyzed by a gas chromatograph (Shimadzu GC-14C) equipped with a flame ionization detector (FID) and a HP GS-GASPRO capillary column (30 m × 0.32 mm).

Catalyst characterization

Surface areas of the catalysts were determined by the modified BET method from the N$_2$ sorption isotherms at 77 K on an Auto-sorb-1 apparatus. Scanning electron microscopy (SEM) images of the catalysts were obtained on a Hitachi S-4800 microscope equipped with an Energy Dispersion X-ray (EDX) attachment.

X-ray diffraction (XRD) patterns of the catalysts were collected on a Philips PW3040/60 powder diffractometer operating at 40 kV and 40 mA using Cu Kα radiation in the 20 range from 10 to 80° with a scan rate of 0.3° min$^{-1}$.

UV-visible diffuse reflectance spectra were recorded on a Thermo Evolution 500 spectrophotometer equipped with a labsphere RSA-UC-40. Raman spectra were obtained on a Renishaw RM1000 confocal microscope with an exciting wavelength of 514.5 nm under ambient conditions with the catalysts were as prepared without dehydration. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a VG ESCALAB MK2 system (Perkin-Elmer) with Al-Kα radiation (hv = 1486.6 eV). The pass energy was fixed at 20 eV to ensure sufficient sensitivity. Binding energies were calibrated by using the contaminant carbon (C1s = 284.6 eV). Electron paramagnetic resonance (EPR) measurements were recorded using Bruker Biospin GnbH EPR spectrometer at X-band frequencies at room temperature with 9.867 GHz field modulation.

Reducibility of the catalyst was measured by means of H$_2$ temperature programmed reduction (H$_2$-TPR) technique. The catalyst (20 mg) was placed in a quartz reactor, which was connected to a home made TPR apparatus. H$_2$ in N$_2$ (5 %) was introduced with a flow rate of 25 cm$^3$ min$^{-1}$. The catalyst was heated from 150-900 °C at a heating rate of 20 °C min$^{-1}$. The amount of H$_2$ uptake during the reduction was measured using a thermal conductivity detector (TCD). Water produced during the reduction was trapped with a 5A molecular sieve.
Contents of Cr in the catalysts were determined by the inductively coupled plasma (ICP) technique.

**Results and Discussion**

**Structural characterization**

Table 1 lists the BET surface areas of the catalysts. The surface areas of the CrYO catalysts were ~10 m² g⁻¹, except those of pure Y₂O₃, pure CrOₓ and CrAlO-20. After the pre-fluorination, the surface area of pure CrFₓ showed no obvious change as compared to the CrOₓ catalyst. However, the CrYF catalysts had higher surface areas than the corresponding CrYO catalysts while the CrAlF-20 catalyst showed the opposite change. Moreover, for the CrYF catalysts, the BET surface area first increased and then decreased with further increase in Cr content.

The microstructure of the representative catalysts CrYO-19.5 and CrYF-19.5 are presented in Fig. 1. It can be seen that the surface of CrYO-19.5 catalyst is very smooth while the CrYF-19.5 catalyst has some pores on its surface.

Figure 2 shows the XRD patterns of the CrYO and the CrYF catalysts. The CrYO catalysts are amorphous with the Cr content increasing from 0 to 19.5 %. However, a crystalline Cr₂O₃ phase emerges in the CrYO-46.5 catalyst and it is clearly observed in the pure CrOₓ and the CrAlO-20 catalysts. After the pre-fluorination, the support Y₂O₃ transformed to YF₃, and weak peaks due to the CrFₓ phase were observed in the catalysts with Cr content from 2.4 % - 46.5 %. The crystalline Cr₂O₃ phase was also observed in the CrYF-46.5 catalyst. The XRD patterns of the CrFₓ and the CrAlF-20 catalyst are nearly identical to that of the

| Table 1 — BET surface areas of CrYO and CrYF catalysts |
|-----------------|-----------------|
| Catalyst       | CrYO (m² g⁻¹)  | CrYF (m² g⁻¹) |
| Y₂O₃           | 4               | 11            |
| CrYO-2.4       | 11              | 30            |
| CrYO-9.8       | 13              | 65            |
| CrYO-19.5      | 11              | 61            |
| CrYO-46.5      | 13              | 27            |
| CrOₓ           | 20              | 18            |
| CrAlO-20       | 190             | 44            |

Fig. 1 — SEM images for (a) CrYO-19.5, and, (b) CrYF-19.5 catalysts.

Fig. 2 — XRD patterns of (a) CrYO, and, (b) CrYF catalysts.
CrO$_x$ and the CrAlO-20 catalysts, indicating that no obvious change occurred during the pre-fluorination process.

Figure 3 shows the UV-vis diffuse reflectance spectra of the catalysts. For the CrYO catalysts, all except the support Y$_2$O$_3$ show an absorption at about 370 nm, which is assigned to Cr$^{6+}$ (Refs 10 & 11). In addition, an absorption at about 610 nm assigned to Cr$^{3+}$ (Refs 12 & 13) is detected for the CrYO-46.5, the CrO$_x$ catalyst and the CrAlO-20 catalysts, indicating the formation of the crystalline Cr$_2$O$_3$. After pre-fluorination, the absorption at 370 nm due to the Cr$^{6+}$ was still observed for all the catalysts except for the YF$_3$. Besides, new absorptions at ~470 and 610 nm assigned to the Cr$^{3+}$ were observed for the CrYF catalysts; these two absorption bands became stronger for the CrAlF-20 catalyst.

Figure 4 shows the Raman spectra of the as-prepared catalysts. From Fig. 4a, it can be seen that no signals are observed for the Y$_2$O$_3$ under the ambient conditions. For the catalysts with low Cr content, the main bands at 350 and 800-900 cm$^{-1}$ assigned to Cr$^{6+}$ were observed$^{14-16}$. As the Cr loading increased up to 46.5 %, the Raman band at 887 cm$^{-1}$ shifted to a lower frequency 853 cm$^{-1}$. Besides, a weak band at 537 cm$^{-1}$ due to the crystalline Cr$_2$O$_3$ was also observed. Furthermore, for the pure CrO$_x$ catalyst, new bands at 300, 342, 537 and 1344 cm$^{-1}$ corresponding to the crystalline Cr$_2$O$_3$ were observed. Also, the CrAlO-20 catalyst showed nearly identical Raman signals as the CrYO-46.5 catalyst.

For the CrYF catalysts (Fig. 4b), the band at 849 cm$^{-1}$ assigned to the oligomeric chromate$^{17,18}$ was observed for the catalyst with Cr content 2.4-46.5 %.

![Fig. 3 — UV-vis diffuse reflectance spectra of (a) CrYO, and, (b) CrYF catalysts.](image-url)

![Fig. 4 — Raman spectra of (a) CrYO, and, (b) CrYF catalysts.](image-url)
For the CrYF-19.5 and the CrYF-46.5 catalysts, another Raman band at 537 cm$^{-1}$ due to the crystalline Cr$_2$O$_3$ was observed. No obvious difference in the Raman signals between the CrFx, the CrAlF-20 and the CrO$_x$, the CrAlO-20 catalysts was detected.

Figure 5 shows the Cr 2P XPS spectra of the CrYO-19.5, CrYO-46.5, CrYF-19.5 and CrYF-46.5 catalysts. The CrYO catalysts show two peaks at 576.8 and 579.4 eV, which are assigned to the Cr$^{3+}$ and Cr$^{6+}$, respectively$^{19,20}$. After the pre-fluorination, the Cr 2p$_{3/2}$ core level shows three peaks at 579.4, 577.9 and 575.9 eV. The peak at 579.4 eV is assigned to CrF$_3$, and the peak at 577.9 eV may be attributed to the formation of Cr(OH)$_x$F$_y$ by fluorination of CrO$_x$, while the peak at 575.9 eV is assigned to Cr$_2$O$_3$ phase$^{21}$.

EPR studies$^{22,23}$ on Cr(VI)/SiO$_2$, Cr(VI)/Al$_2$O$_3$ and Cr(VI)/TiO$_2$ catalysts have shown that three different chromium signals are observed depending on the Cr loading, treatment conditions and support. These signals referred to the γ, β, δ signals, are ascribed to the Cr$^{5+}$, Cr$_2$O$_3$ like clusters and dispersed Cr$^{3+}$, respectively. EPR spectra of CrYO-19.5 catalyst shows a weak isotropic resonance around $g = 1.9$ assigned to the γ-signal and a relatively broad resonance around $g = 2.1$ due to Cr$_2$O$_3$. Besides, a weak peak at higher $g$ values (around 4.1) ascribed to the dispersed Cr$^{3+}$ was also observed$^{24}$. However, for the CrYF-19.5 catalyst, all the γ, β and δ-signals disappeared with another peak emerging at around 3400 Gauss probably assigned to the CrF$_x$ (ref. 25).

The reduction properties of the CrYO catalysts were studied. The TPR profile of CrYO-2.4 catalyst shows a major peak at 660 °C with a shoulder peak at 520 °C. The former is related to the less easily reducible monochromate and the latter to the more reducible oligomeric chromate$^{18}$. With increasing Cr loading, the major reduction peak gradually shifted to lower temperature (610 °C), with a weak shoulder peak at 680 °C for the CrYO-19.5 catalyst. With further increase in Cr loading, the shift of the peak became more obvious, and the reduction peak for the CrO$_x$ was observed at about 370 °C. With the increasing Cr loading, the amount of H$_2$ consumption first increased and then decreased; the largest amount of H$_2$ consumption was obtained on the CrYO-19.5 catalyst (3.3 mmol H$_2$ g Cr$^{-1}$).

Catalytic activity

Figure 6 shows the catalytic activity over the catalysts with different Cr loadings. Note that the selectivity to CF$_3$CH$_2$F is not given since it was higher than 98 %. It can be seen that the Cr loading has great influence on the catalytic activity. As the Cr loading increased from 2.4 to 19.5 %, the conversion of the HCFC-133a increased under all the reaction temperatures except at 340 °C. Conversion of 19 % was achieved at 320 °C over the CrYF-19.5 catalyst. However, the catalytic activity decreased with the further increase in Cr loading up to 46.5 %. Much lower conversion (3 %) was obtained over the CrFx.

Fig. 5 — Cr 2P XPS spectra of the (a) CrYO-19.5, (b) CrYO-46.5, (c) CrYF-19.5, and, (d) CrYF-46.5.
catalyst at 320 °C. However, the activity of the CrAlF-20 catalyst (conversion of 10 % at 320 °C) is lower compared to the CrYF-19.5 with the same Cr content. The stability of the pre-fluorinated CrYO-19.5 catalyst (CrYF-19.5) was tested at 320 °C under reaction conditions. The catalyst was quite stable during the reaction period of 50 h and the conversion was kept at about 19 %.

**Effect of Cr loading on the catalyst structure**

As the chromium oxide species strongly depend on the support and the surface chromium content, the features of the chromium oxides on the catalyst surface were investigated in the current work. The surface area data (Table 1) reveal that the CrF catalysts, except pure CrF_{x} and the CrAlF-20, have larger surface areas than those of the corresponding CrYO catalysts. This suggests that the structure of the CrYO catalysts has changed after the reaction with HF. The structural change revealed by the SEM results (Fig. 1) indicates that the more porous structure of the CrYF catalyst may have originated from the reaction of HF with the CrYO catalyst. However, a small increase in surface area was observed on the CrYF-46.5 catalyst, implying that it is difficult for the CrYO catalysts with higher Cr loading to be fluorinated. This can also be verified from the XRD (Fig. 2) and Raman (Fig. 4) spectra; no obvious change was observed between the CrO_{x} and CrF_{x}, either in the XRD pattern or in the Raman spectrum.

XRD (Fig. 2a) and the UV-vis (Fig. 3a) data reveal the distribution of the chromium oxides on the surface of Y_{2}O_{3} as a function of the Cr content. For the low Cr content catalysts, the chromium oxides were well dispersed on the support surface and mainly existed in the higher oxidation state of Cr(VI). The increase in the Cr content results in poorly dispersed chromium cluster or crystalline Cr_{2}O_{3}. In both the XRD pattern and the UV-vis spectrum, crystalline Cr_{2}O_{3} or poorly dispersed Cr^{3+} was observed with Cr content of 46.5 %. Therefore, it suggests that the oxidation state of CrO_{x} species transformed from high oxidation state to the lower with increase in Cr content. The distribution of the chromium oxides on the Y_{2}O_{3} surface is quite consistent with earlier reports by Yim et al.^{18} that the chromium oxides are well dispersed on the surface of TiO_{2} and Al_{2}O_{3} with the Cr content up to 16.8 %. However, the CrAlO-20 catalyst prepared in the current study has poorer Cr dispersion as compared to that in CrYO-19.5 catalyst with the same Cr content, as indicated by XRD (Fig. 2) and UV-vis (Fig. 3) data. The difference between the present CrAlO-20 catalyst and that reported in literature^{18} is probably due to the different preparation methods.

It is well known that Raman spectra can elucidate the molecular structure of Cr on inorganic oxides. In the current study, it has been shown that the chromium oxides species were mainly present as a monochromate for the low Cr loading (2.4-19.5 %) catalysts (Fig. 4). Note that the Raman band for the CrYO-2.4 is hardly observed due to low Cr content. The Raman bands at 853 cm^{-1} are observed with the increase in Cr loading up to 46.5 %, indicating the formation of the polymeric chromium oxide, for example, CrO_{x} trimers or tetramers and the decrease in the interaction between the CrO_{x} with the Y_{2}O_{3} support. This result is consistent with the results reported in another study on CrO_{x} supported on Al_{2}O_{3}, SiO_{2} and TiO_{2} supports. Also, the band for Cr_{2}O_{3} (545 cm^{-1}) appeared in the catalyst with 46.5 % Cr content and only crystalline Cr_{2}O_{3} species were observed for the pure CrO_{x} catalyst. Therefore, the Raman spectra again confirm that the high Cr loading leads to an increase in the Cr(III) content on the catalyst surface by the formation of poorly dispersed crystalline Cr_{2}O_{3} or CrO_{x} cluster. However, for the reference CrAlO-20 catalyst, the crystalline Cr_{2}O_{3} was formed on the Al_{2}O_{3} surface, indicating that the dispersion of the CrO_{x} also depends on the nature of the support.
The XPS (Fig. 5) and the EPR spectra show the existence of the dispersed Cr\(^{3+}\) and crystalline Cr\(_2\)O\(_3\) in the CrYO-19.5 catalyst. However, this was not observed in the XRD, Raman or UV-vis spectra, probably because either the Cr\(^{3+}\) was finely dispersed or some Cr\(^{3+}\) was incorporated into the Y\(_2\)O\(_3\) lattice. Besides, the \(\gamma\)-signal assigned to the isolated Cr\(^{5+}\), in most cases was observed in the EPR spectra. However, it has also been assigned to the mixed valence trimers of the type “Cr(VI)-O-Cr(III)-O-Cr(VI)” in which the average oxidation state of the chromium is +5 in the Cr\(_2\)O\(_3\)/Al\(_2\)O\(_3\) catalyst\(^{23}\). In the current study, the catalyst preparation does not favour formation of the unstable isolated Cr\(^{5+}\) species, hence we have attributed the \(\gamma\)-signal to the trimolecular cluster pseudo Cr\(^{5+}\), which is consistent with the XPS result (Fig. 5).

The TPR results show that with the increase in Cr loading, the reduction peak shifts to lower temperature, which indicates that the chromium oxides change from the monochromate to the polymeric chromate. This polymerization of chromate weakens the interaction between the CrO\(_x\) and the support Y\(_2\)O\(_3\), resulting in lower reduction temperature. The highest degree of polymerization was found in the pure CrO\(_x\) catalyst. Also, the amount of H\(_2\) consumption is maximum in the CrYO-19.5 catalyst, indicating that the highest distribution of monochromate in this catalyst.

**Active sites for the fluorination reaction**

As mentioned earlier, the CrYO catalysts were pre-fluorinated with HF before the fluorination reaction. Therefore, the investigation on the CrYF catalysts is more important since it may provide relevant information regarding the active sites for the fluorination reaction.

Phase composition of the CrYF catalyst can also be confirmed by the XRD, the UV-vis and the Raman data. The CrF\(_3\)-H\(_2\)O phase was observed for all the CrYF catalysts except the pure CrF\(_x\) catalyst (Fig. 2b). Consequently, the CrF\(_3\)-H\(_2\)O may have originated from the highly dispersed and high oxidation state Cr\(^{6+}\) species. However, in the UV-vis spectra (Fig. 3b), the Cr\(^{3+}\) absorption bands at 470 and 610 cm\(^{-1}\) were observed for all the catalysts and the band due to the Cr\(^{6+}\) was still present, suggesting that the fluorination process accelerates the formation of the crystalline Cr\(_2\)O\(_3\), which was transformed from part of the highly dispersed CrO\(_x\). The Raman results indicate that the fluorination process makes the chromium oxides polymeric and the polymeric chromates are difficult to be fluorinated. Also, part of the CrO\(_x\) was transformed to the crystalline CrO\(_2\). Comparison of the XRD and the Raman spectra of the CrF\(_x\) catalyst with those of the CrO\(_x\) catalyst showed that there was little change in the features, indicating that the CrO\(_x\) catalyst is very stable during the fluorination process.

The XPS result (Fig. 5) of the CrYF-19.5 catalyst reveals the existence of CrF\(_3\), CrF\(_x\)(OH)\(_y\) and Cr\(_2\)O\(_3\) species, and hence it may be concluded that these species was originated from the highly dispersed Cr(VI) species on the catalyst surface. The disappearance of the \(\gamma, \beta, \delta\)-signals with emergence of the CrF\(_x\) signal in the EPR spectra of the CrYF-19.5 catalyst indicates that the well dispersed Cr(VI)-O-Cr(III)-O-Cr(VI), Cr\(^{3+}\) and cluster Cr\(^{3+}\) has been changed to another chromium compounds, for example CrF\(_x\).

Figure 6 clearly shows that the catalytic activity strongly depends on the Cr content of the catalyst. With increasing Cr loading, the catalytic activity first increased and then decreased. The highest conversion obtained on the CrYF-19.5 catalyst was about 19\% at 320 \(^\circ\)C (HF/C\(_2\)F\(_2\)Cl \(= 10, \) GHSV=3000 h\(^{-1}\), corresponding to a formation rate of 2.03 mmol h\(^{-1}\)g\(^{-1}\)cat, which is much higher than the results reported in other studies under similar conditions. For example, on a Cr/MgF\(_2\) catalyst prepared by Lee et al.\(^5\), the best initial catalytic activity was 0.68 mmol h\(^{-1}\)g\(^{-1}\)cat at 340 \(^\circ\)C (HF/C\(_2\)F\(_2\)Cl \(= 8\)). In another study\(^7\), the Cr/MgO catalyst showed the best catalytic activity of 0.53 mmol h\(^{-1}\)g\(^{-1}\)cat at 320 \(^\circ\)C (HF/C\(_2\)F\(_2\)Cl \(= 8\)). In order to further illuminate the effect of the Cr content on the catalytic activity, the turnover frequency (TOF) of the reaction was calculated based on the total Cr content in the catalyst. It was observed that the TOF decreased dramatically with the increasing Cr loading, implying that the proportion of the active sites for the reaction decreased with increasing Cr content. Other researches too have pointed out that for the Cr based catalysts, the catalytic activity is greatly affected by the surface chromium species and support properties.\(^{14,26,27}\)

Cho et al.\(^{13}\) found that the chromium catalysts supported on MgO and Al\(_2\)O\(_3\) show higher catalytic activity than that supported on ZrO\(_2\) and TiO\(_2\). One of the reasons is that crystalline Cr\(_2\)O\(_3\) was formed on the Cr/ZrO\(_2\) and CrTiO\(_2\) catalysts while only amorphous Cr\(^{6+}\) existed on the Cr/MgO catalyst, implying that the Cr\(^{6+}\) species are responsible for the high activity. In the
current study, it was found that the Cr species (Cr(VI)) in the catalyst are amorphous and isolated (monochromate) when the Cr loading was lower than 19.5% (Fig. 2a), which can be easily fluorinated. However, the CrYO-46.5 catalyst with high Cr loading has crystalline CrO$_3$ or polymeric chromate, which is difficult to be fluorinate. Also, crystalline Cr$_2$O$_3$ was formed on the reference catalyst CrAlO-20, which led to lower activity than the CrYO-19.5 catalyst. Therefore, the higher activity obtained over the CrO$_3$-Y$_2$O$_3$ catalysts than on the Cr/MgO, Cr/MgF$_2$ or Cr/Al$_2$O$_3$ catalyst is probably due to the higher degree of dispersion of the Cr(VI) species on the Y$_2$O$_3$ support as compared to that on the MgO, Al$_2$O$_3$ or MgF$_2$ supports.

Acknowledgement
This work is financially supported by the Zhejiang Provincial Nature Science Foundation of China (No. Y407179). We also thank Dr. Jian-yong Mao (Zhejiang University) for carrying out the EPR experiment.

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