Static TOF-SIMS Surface Analysis of a CCl$_2$F$_2$ Activated Chromia Catalyst Used for a Cl/F Exchange Reaction

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Static TOF-SIMS results strongly underpin earlier conclusions from ESCA, XANES, and tracer studies that the accumulation of fluorine and chlorine at the surface of chromia by a heterogeneous reaction with a chlorofluorocarbon compound results in the formation of mixed chromium oxide halide species and not in the nucleation of CrCl$_3$ and/or CrF$_3$ phases.

TOF-SIMS is a highly sensitive surface analytical technique that probes only the (three) outermost layers of a sample. In the so-called static mode of SIMS, the measured signal originates only from a virgin surface. Therefore, the respective SIMS spectrum then comprises a strongly correlated fragmentation pattern of the original surface lattice.[1]

It is well known that chromia needs to be halogenated before it becomes catalytically active in halogen exchange reactions. In several publications,[2−5] it was concluded from ESCA, XANES, XRD, and tracer studies that, most probably, neither CrCl$_3$ nor CrF$_3$ but *"chromium (III) oxide fluoride chloride"* species are the catalytically active ones. However, additional independent experimental proof is required to underpin these conclusions.

In this study, static TOF-SIMS was used for the first time to answer the question of whether there are CrCl$_3$ and/or CrF$_3$ phases existing at the surface of chromia halogenated by exposure to CCl$_2$F$_2$. Activated chromia as well as reference samples were analyzed by static TOF-SIMS.[2]

Cr$_2$O$_3$ was synthesized by a volcano reaction of (NH$_4$)$_2$Cr$_2$O$_7$. The primary reaction product was boiled in distilled water for 4 h, filtered, washed with distilled water, dried in air, and then heated at 400 °C for 3 h under N$_2$. XRD proofed a structure according to PDF 38-1479.[6] CrCl$_3$ was a commercial sample (Aldrich) delivered under Ar. XRD proofed a structure according to PDF 32-279.[6] α-CrF$_3$ was a commercial sample (Aldrich) delivered under Ar. XRD proofed a structure according to PDF 16-44.[6] A halogenated but inactive catalyst was obtained after drying Cr$_2$O$_3$ in a 10 mL/min N$_2$ flow at 400 °C for 3 h and subsequent exposure to N$_2$ (10 mL/min) + CCl$_2$F$_2$ (2 mL/min) at 390 °C for 1 min in a tubular flow reactor. A halogenated and active catalyst was obtained after exposing dried chromia to N$_2$ (10 mL/min) + CCl$_2$F$_2$ (2 mL/min) at 390 °C for 120 min. A catalytically activated dismutation reaction of CCl$_2$F$_2$ was proofed by GC. The XPS surface compositions are found to be CrO$_{1.59}$F$_{0.04}$Cl$_{0.06}$ and CrO$_{1.26}$F$_{0.13}$Cl$_{0.17}$ for 1- and 120-min activated samples, respectively.[2] After exposure to CCl$_2$F$_2$, halogenated chromia samples were taken from the reactor in a glovebox to avoid air exposure. They were transported to the TOF-SIMS instrument in an evacuated desiccator.

During transfer to the SIMS UHV spectrometer chamber, the samples were quickly exposed to air (a few seconds).

Static SIMS spectra were obtained by a TOF-SIMS IV instrument (Ion-Tof GmbH, Münster, Germany) with a pulsed Ga$^+$ primary ion beam (15 keV, 0.80 pA). This ion beam was digitally scanned over an analysis area of $200 \times 200 \ \mu$m^2. Total acquisition times were fixed to 50 s. Thus, the total ion dose was less than 6.0×10^{11} ions/cm^2 (i.e., well below the static limit of SIMS ($\sim 1.0 \times 10^{13}$ ions/cm^2 [1])). Because of charging, low-energy electrons were used to stabilize the surface potential of the samples during analysis. The mass resolution at CrCl$_4$$^-$ was ca. 7300. For more experimental details, see ref 2.

The negative static SIMS spectra of Cr$_2$O$_3$, CrCl$_3$, and α-CrF$_3$ are displayed in Figures 1−3. Characteristic fragment ion patterns are obtained. Strong intensity was obtained for CrO$_2$$^-$ and CrO$_3$$^-$ with Cr$_2$O$_3$, for CrCl$_3$$^-$ and CrCl$_4$$^-$ with CrCl$_3$, and for CrF$_3$$^-$ and CrF$_4$$^-$ with CrF$_3$. There are SIMS data for Cr$_2$O$_3$ in the literature[1,7,8] reporting a very similar fragment CrO$_x$$^-$ secondary ion pattern such as that in Figure 1. In the spectra of CrCl$_3$ and CrF$_3$, some Cr$_x$O$_y$X$_z$$^-$ (X = Cl, F) secondary ions are found that might be due to the original existence of oxides in traces at the surface or/and due to partial hydration followed by hydrolysis of the samples during rapid exposure to air by the preparation. It should be mentioned that although all reference samples are characterized by Cr atoms octahedrally coordinated to their ligands the characteristic fragment ion patterns are somewhat different. These differences are due to the complexity of the secondary cluster ion formation process in SIMS. It is known that individual secondary ion emission probabilities and stabilities provide a substantial matrix effect in SIMS.[1]

Negative TOF-SIMS spectra of Cr$_2$O$_3$ samples activated with CCl$_2$F$_2$ at 390 °C for 1 and 120 min are displayed in Figures 4 and 5, respectively. First, the high yields of CrX$_4$$^-$ leading fragment ions found with the CrCl$_3$ and CrF$_3$ reference samples were not obtained for the activated chromia samples. The other CrX$_n$$^-$ fragments (n < 4) are found again but with rather low yields. Moreover, secondary fragment ions such as Cr$_2$Cl$_5$$^-$, Cr$_2Cl_6$$^-$, Cr$_2Cl_7$$^-$, Cr$_3Cl_7$$^-$, Cr$_3Cl_8$$^-$, Cr$_2F_5$$^-$, Cr$_2F_6$$^-$, and Cr$_2F_7$$^-$, which were detected in the negative TOF-SIMS spectra of CrCl$_3$ and CrF$_3$, respectively, were not observed in the activated chromia samples. These observations clearly indicate that separated CrCl$_3$ and/or CrF$_3$ phases are not present in significant

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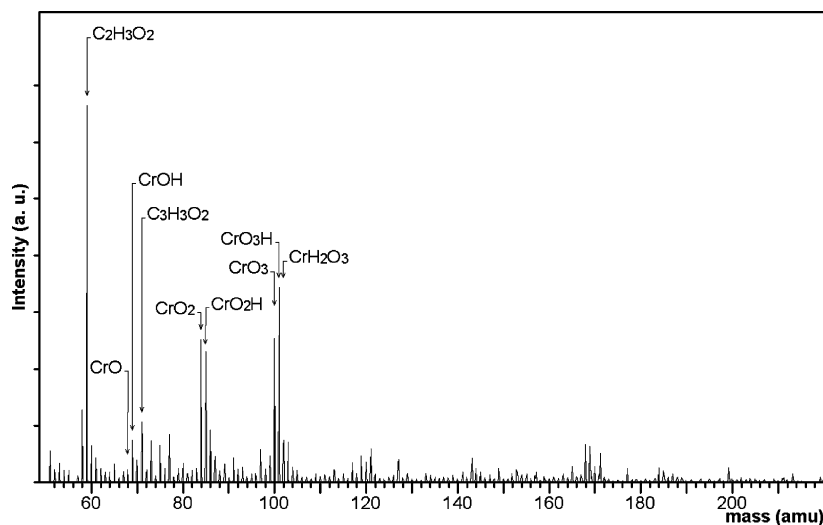‡ Bundesanstalt für Materialforschung und -prüfung.

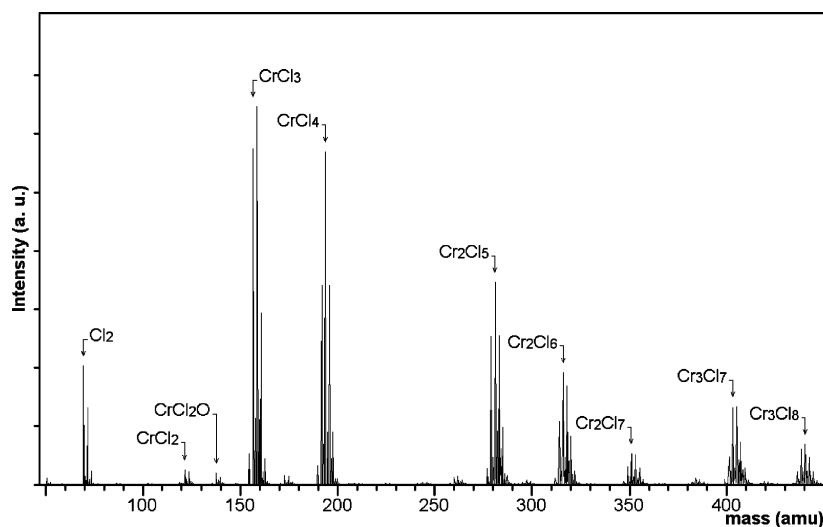**Figure 1.** Negative TOF-SIM spectrum of Cr_2O_3.

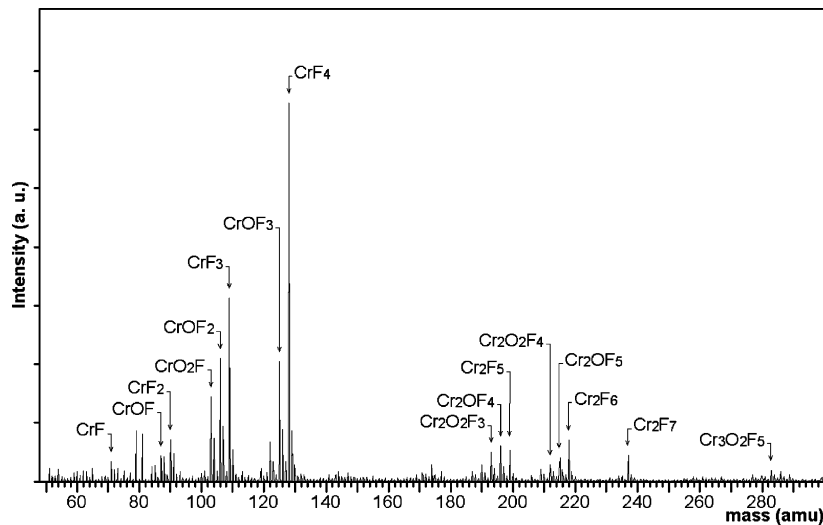**Figure 2.** Negative TOF-SIM spectrum of $CrCl_3$.

Figure 3. Negative TOF-SIM spectrum of CrF_3.

amounts on the surface. Instead, the results indicate that a mixed chromium oxide halide compound is formed during the activation process (e.g., by the exchange of some of the chromia oxygen atoms in the outermost layer with Cl and F atoms), in agreement with previous ESCA, XANES, and tracer studies.[2-5] This interpretation is now strongly supported by our new SIMS results because we found mixed secondary fragment ions such as $CrClOF^-$, $CrClF_2^-$, $CrCl_2F^-$, and $Cr_2ClO_2F^-$ exclusively in the spectra of activated chromia samples. These fragment ions are to be expected in a static SIMS experiment with a chromia surface where oxygen is statistically substituted by F and Cl, providing a neighborhood for Cr with O, Cl, and F.
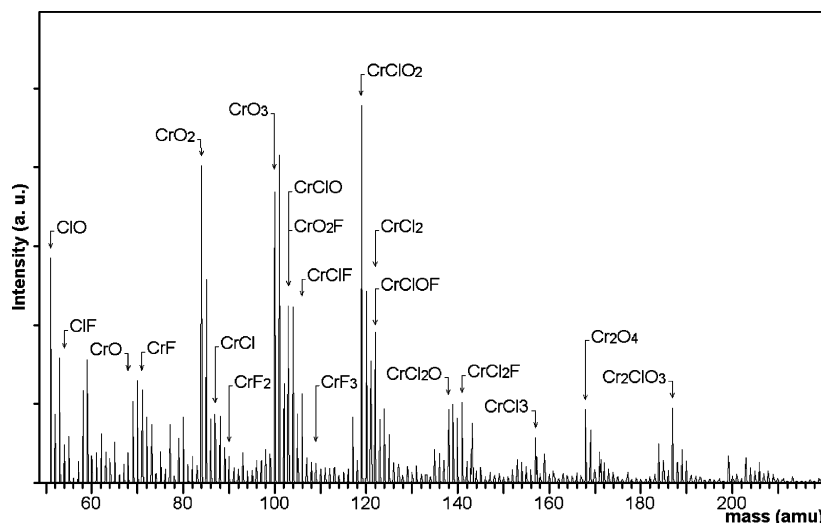
Figure 4. Negative TOF-SIM spectrum of Cr_2O_3 after 1 min of activation in CCl_2F_2 at 390 °C.
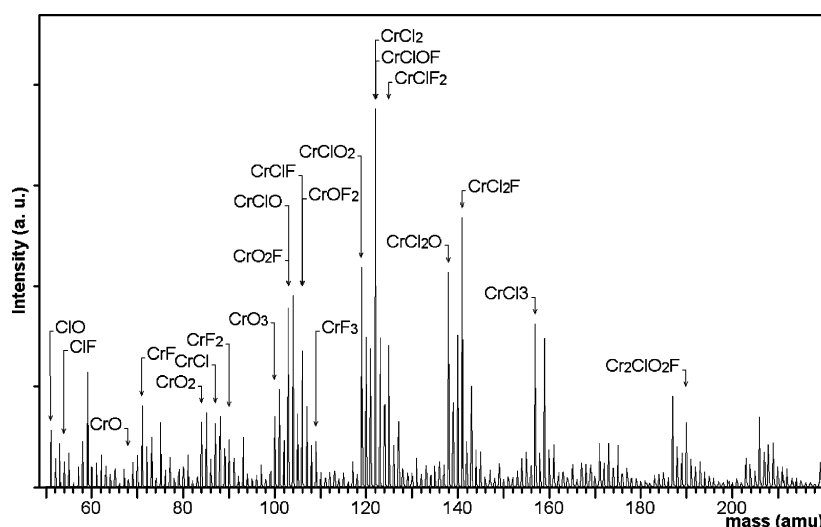

Figure 5. Negative TOF-SIM spectrum of Cr_2O_3 after 120 min of activation in CCl_2F_2 at 390 °C.

Considering the SIMS spectrum of the chromia sample exposed to CCl_2F_2 for 1 min, high yields of CrO_2^- and CrO_3^- fragment ions can still be found. These high yields are also very characteristic of untreated chromia. They are substantially reduced in the spectrum of the 120-min activated chromia sample (i.e., vs increasing reaction time and halogenation). The conclusion is that at least after 1 min of activation in CCl_2F_2 nonreacted Cr_2O_3 regions still seem to exist at the sample's surface. These regions are consumed step by step by the heterogeneous halogenation reaction providing mixed CrO_xCl_y-F_z species. Obviously, the secondary $CrClOF^-$ fragment ion seems to be the "key SIMS fragment" characteristic of these species. Accordingly, the $CrClOF^-$ yield increases with respect to increasing halogenation.

From the TOF-SIMS results presented in this communication, it can be concluded that the accumulation of fluorine and chlorine at the surface of chromia by a heterogeneous reaction with a chlorofluorocarbon results in the formation of chromium oxide halide species and not in the nucleation of $CrCl_3$ or CrF_3 phases. The observation of $CrO_xCl_yF_z^-$ and $CrCl_xF_y^-$ secondary fragment ions for the activated samples in a static TOF-SIMS experiment is taken as a proof of that. The formation of separated CrX_3 (X = Cl, F) phases is not very probable because

the characteristic fragment ion patterns of these phases cannot be identified in the static TOF-SIMS spectra of activated chromia.

References and Notes

(1) Vickerman, J. C. In *TOF-SIMS: Surface Analysis by Mass Spectrometry*; Vickerman, J. C., Briggs, D., Eds., IM Publications and Surface Spectra Limited: Chichester, U.K., 2001.

(2) Ünveren, E. Thesis, Humboldt-Universität zu Berlin, 2004. http://dochost.rz.hu-berlin.de/dissertationen/uenveren-ercan-2004-04-23/PDF/Uenveren.pdf.

(3) Kemnitz, E.; Kohne, A.; Grohmann, I.; Lippitz, A.; Unger, W. E. S. *J. Catal.* **1996**, *159*, 270.

(4) . Kemnitz, E.; Winfield, J. M. In *Advanced Inorganic Fluorides*; Nakajima, T., Zemva, B., Tressaud, A., Eds.; Elsevier: Lausanne, Switzerland, 2000; pp 367–401.

(5) Rowley, L.; Webb, G.; Winfield, J.; McCulloch, A. *Appl. Catal., A* **1989**, *52*, 69.

(6) Powder Diffraction File. *PDF-2 Database*, Sets 1–45, ICDD A6, Dataware Technologies Inc.: 1995.

(7) Poels, K.; Van Vaeck, L.; Gijbels, R. *Anal. Chem.* **1998**, *70*, 504.

(8) Cuynen, E.; Van Vaeck, L.; Van Espen, P. *Rapid Commun. Mass Spectrom.* **1999**, *13*, 2287.