Chromia Catalysts for Halogen Exchange Reactions: *In situ* Studies by Total Electron-Yield XAS

S.L.M. Schroeder, O. Boese[1], N. Weiher, B. Adamzcyk[1], T. Rayment[2] and E. Kemnitz[1]

Freie Universität Berlin, Institut für Physikalische & Theoretische Chemie
Takustr. 3, 14195 Berlin, Germany

[1]Humboldt-Universität zu Berlin, Institut für Allgemeine & Angewandte Chemie
Hessische Str. 1-2, 10115 Berlin, Germany

[2]University of Cambridge, Department of Chemistry
Lensfield Road, Cambridge CB2 1EW, United Kingdom

Catalysts based on chromia (Cr_2O_3) are effective for a range of halogen exchange reactions. They are not only employed in several technical processes for the manufacture of hydrofluorocarbons (HFCs) but have also been shown to exhibit considerable potential for the low-temperature destruction of chlorofluorocarbons (CFCs) harmful for the stratospheric ozone layer [1]. Very little is known about the molecular mechanisms underlying the halogen-exchange reaction over these materials. Most importantly, the chemical state and crystallographic composition of active chromia catalysts are unclear. By means of *in situ* X-ray diffraction (XRD) studies we have found that catalysts generated by thermal decomposition of $NH_4Cr_2O_7$ contain a considerable amount of XRD-amorphous phases (fig. 1). These phases are thermally stable in the temperature range employed for the catalytic reaction and have hitherto not been characterised with a view to their structural and electronic properties. Better insight into the properties of these phases is needed because their presence appears to be essential for the development of catalytic activity.

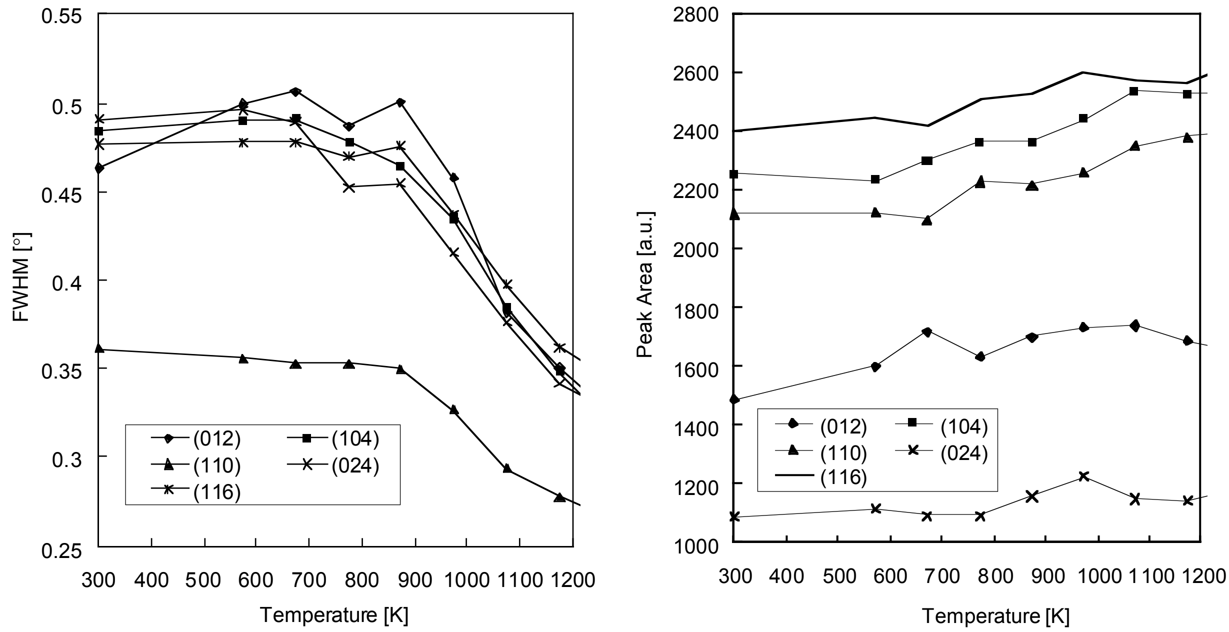

Figure 1: Selected results of *in situ* XRD measurements during thermal treatment of an active, partially XRD-amorphous chromia catalyst. As indicated by an increase in diffraction line intensities, thermal decomposition to (strongly disordered) Cr_2O_3 and of the amorphous components begins at temperatures above 700 K (right panel). Sintering to well ordered Cr_2O_3 begins at temperatures above 900 K, as indicated by a decrease in FWHM of the diffraction lines (left panel).

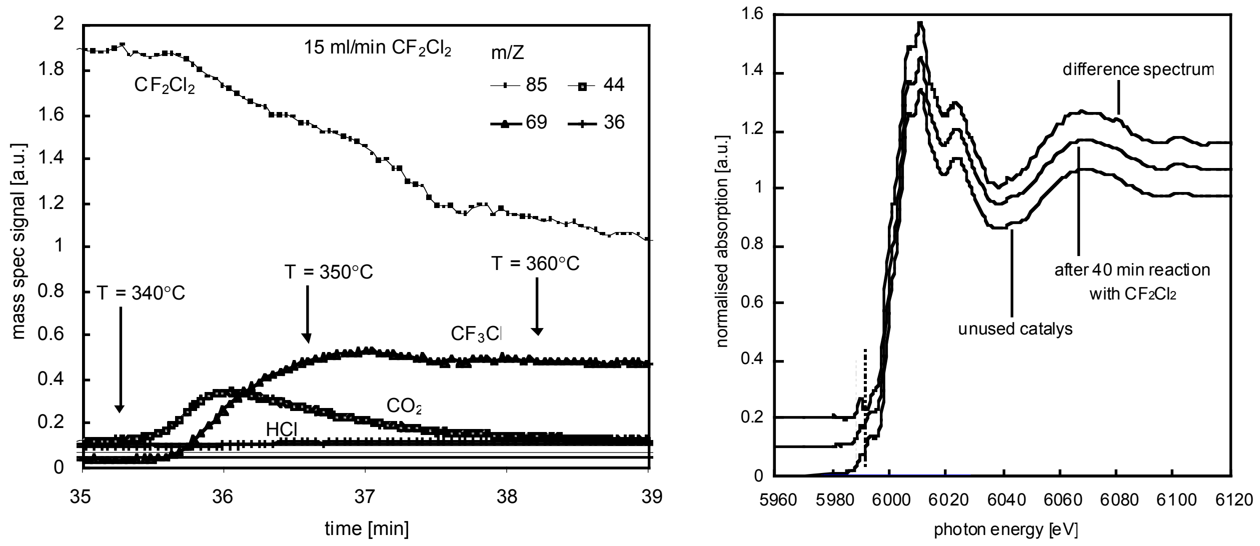

Figure 2: Left: Mass spectroscopic traces of reactant- and product-concentrations recorded during the catalytic reaction in the TEY XAFS cell. Right: XANES regions of the Cr K-edge spectra of the chromia catalyst before and after reaction. Note the small differences in the pre-edge region.

XAFS measurements at the Cr K-edge were performed by means of gas-flow toal electron-yield (TEY) detection employing a newly developed *in situ* cell. Spectra of active chromia catalysts (an example is presented in fig. 3) exhibit significant differences to spectra of crystalline, pure Cr_2O_3, confirming the presence of structurally and electronically different phases. Measurements before and after the catalytic reaction (fig. 2) did not reveal the formation of structurally and electronically different bulk phases, but small changes in the pre-edge region of the spectra might indicate the presence of small amounts of higher oxidation states of chromium after the catalytic reaction.

References

[1] E. Kemnitz and J.M. Winfield, in: *Advanced Inorganic Fluorides: Synthesis, Characterization and Applications*, edited by T. Nakajima, A. Tressaud & B. Zemva (Elsevier, Amsterdam 1999).

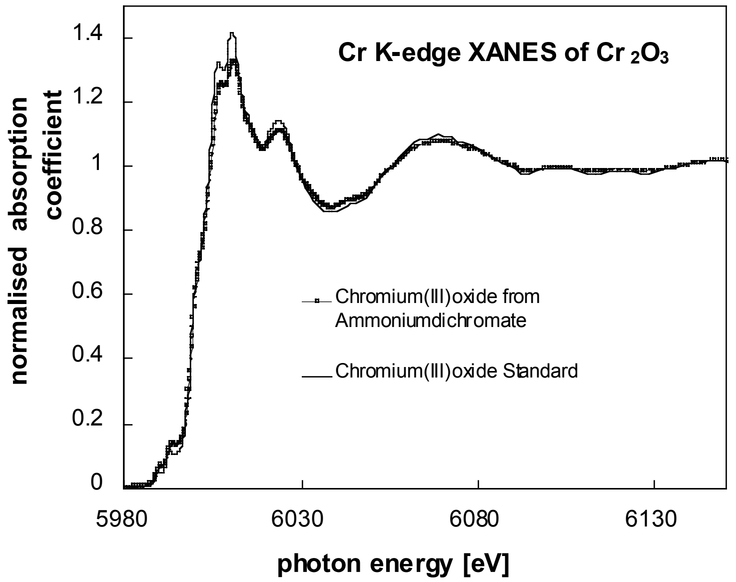

Figure 2: XANES regions of the Cr K-edge spectra of crystalline Cr_2O_3 and of a partially XRD-amorphous chromia catalyst for halogen exchange reactions.Note the reduced XAFS amplitudes.