Experiment title: Thermal decomposition of chromium(VI) oxide; high resolution in-situ powder diffraction studies of mixed valence chromium oxides.

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<th><strong>Experiment number:</strong></th>
<th>01-01-263</th>
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<td><strong>Beamline:</strong></td>
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<td><strong>Date of experiment:</strong></td>
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<td>from: 14/9 2001 to: 19/9 2001</td>
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<td><strong>Date of report:</strong></td>
<td>7/3 2003</td>
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<td><strong>Local contact(s):</strong></td>
<td>Hermann Emerich</td>
</tr>
</tbody>
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Names and affiliations of applicants (* indicates experimentalists):
*Poul Norby, Deptartment of Chemistry, University of Oslo, N-0315 Oslo, Norway
*Helmer Fjellvåg, Deptartment of Chemistry, University of Oslo, N-0315 Oslo, Norway

Report:

CrO₃, chromium(VI) oxide, has a 1-dimensional crystal structure formed by infinite single chains of corner linked CrO₄-tetrahedra. When heated, CrO₃ will decompose through several steps to chromium(III) oxide, Cr₂O₃. The thermal decomposition of CrO₃ has been the topic of many studies, but the decomposition sequence and the structures and stoichiometry of the intermediate mixed valence chromium oxides are still not fully understood. The decomposition is strongly dependent on e.g. pressure, oxygen partial pressure and traces of moisture. Several mixed-valence compounds have been identified in the decomposition sequence. A compound known as Cr₃O₈ was shown by structure determination(1) to have the true composition Cr₈O₂₁. It is triclinic, \( a = 5.433, b = 6.557, c = 12.117 \text{Å}, \alpha = 106.36, \beta = 95.73 \) and \( \gamma = 77.96^\circ \) and contains chromium(III), chromate- and tetrachromate groups, and the composition can be given as \( \text{Cr(III)}(\text{Cr(VI)O}_4)_{12}(\text{Cr(VI)}_4\text{O}_{12}) \). The existence of one or more phases with composition \( \text{Cr}_2\text{O}_5(\text{Cr}_6\text{O}_{15}) \) has been reported, but no structural information is available. \( \text{Cr}_2\text{O}_{12} \) was synthesized at high pressure, and the structure has been determined. In \( \text{Cr}_5\text{O}_{13} \) chromium(III) is connected by chromate groups, and the composition can be given as: \( \text{Cr(III)}_2(\text{Cr(VI)}_2\text{O}_4) \). Thus the transformation sequence observed is:

\[
\text{CrO}_3 \to \text{Cr}_8\text{O}_{21} \to \text{Cr}_6\text{O}_{15}(\text{Cr}_2\text{O}_5) \to (\text{Cr}_5\text{O}_{12}) \to \text{Cr}_2\text{O}_3.
\]

When taking into account the appropriate oxidation states of chromium, the compounds are:

\[
\text{Cr(VI)}\text{O}_3 \to \text{Cr(III)}_2\text{Cr(VI)}_6\text{O}_{21} \to \text{Cr(III)}_2\text{Cr(VI)}_4\text{O}_{15} \to \text{Cr(III)}_2\text{Cr(VI)}_3\text{O}_{12} \to \text{Cr(III)}_2\text{O}_3.
\]
A systematic change in stoichiometry is observed. A couple of interesting missing stoichiometries are: \( \text{Cr}_7 \text{O}_{18} \) (\( \text{Cr}^{\text{III}}_2 \text{Cr}^{\text{VI}}_5 \text{O}_{18} \)) and \( \text{Cr}_4 \text{O}_8 \) (\( \text{Cr}^{\text{III}}_2 \text{Cr}^{\text{VI}}_2 \text{O}_8 \)). \( \text{Cr}_7 \text{O}_{18} \) has so far not been observed, but it could exist as a chromium chromate trichromate, \( \text{Cr}^{\text{III}}_3 \text{Cr}^{\text{VI}}_4 \text{O}_{10} \). \( \text{Cr}_4 \text{O}_8 \) does exist (\( \text{CrO}_2 \)); not as a mixed valence compound, but as a chromium(IV) oxide.

High resolution powder diffraction was used to follow the thermal decomposition of \( \text{CrO}_3 \) and \( \text{Cr}_8 \text{O}_{21} \) under various reaction conditions, such as different oxygen partial pressures. The aim was to identify new phases in the decomposition sequence, and to resolve the issue concerning the structure of \( \text{Cr}_6 \text{O}_{15} \) (\( \text{Cr}_2 \text{O}_5 \)).

The Figure shows an example of a series of powder diffraction patterns collected during heating of \( \text{Cr}_8 \text{O}_{21} \). The formation of an intermediate phase is clearly visible. During the experiments several different, but closely related, phases with assumed composition close to \( \text{Cr}_5 \text{O}_8 \) (\( \text{Cr}_6 \text{O}_{15} \)) were obtained. One of the phases has been indexed based on a triclinic unit cell, \( a = 6.561, b = 8.401, c = 8.951 \text{Å}, \alpha = 99.95, \beta = 73.16 \text{ and } \gamma = 89.06^\circ \). The structure determination is not yet completed.

1. P. Norby, A. Nørlund Christensen, H. Fjellvåg and M. Nielsen
"The crystal structure of \( \text{Cr}_8 \text{O}_{21} \) determined from powder diffraction data. Thermal transformation and magnetic properties of a chromium-chromate-tetrachromate."