High Resolution XPS Study of a Thin Cr$_2$O$_3$(111) Film Grown on Cr(110)

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Transition metal oxides are important materials in heterogenous catalysis, as supporting materials as well as active components. The catalytic activity of Cr$_2$O$_3$ for IE polymerization of olefines or hydrogenation of alkenes is well known and rather high. Therefore, it is important to get information on the surface electronic structure of Cr$_2$O$_3$. Here we report high resolution XPS measurements of a thin epitaxial Cr$_2$O$_3$(111) film grown on Cr(110). The oxide films have been prepared by in situ oxidation of a Cr(110) single crystal disk (12 mm diameter, 1.5 mm thickness, purity 5n) at elevated temperatures (540 K to 780 K) in an atmosphere of 10$^{-6}$ mbar of O$_2$. The oxygen doses have been typically in the range of a few thousand Langmuirs. Under these conditions a Cr$_2$O$_3$(111) layer [Cr$_2$O$_3$(0001) orientation in hexagonal notation] forms on the surface as confirmed via low energy electron diffraction IV analysis. The film thickness ranges from about 2.5 nm to 8.0 nm under the chosen preparation conditions, allowing electron spectroscopy to be performed without charge compensation. The studies of Cr$_2$O$_3$(111) have been performed as part of a project aimed at investigating idealized catalytic systems under ultrahigh vacuum conditions. © 1998 American Vacuum Society. [S1055-5269(96)00303-9]

Keywords: x-ray photoelectron spectroscopy; oxidation; chromium oxide

PACS: 79.60.Dp, 82.65.Jv, 81.65.Mq

SPECIMEN DESCRIPTION (Accession ##00317)

Host Material: Cr metal
CAS Registry #: 2440-47-3
Host Material Characteristics: homogeneous; solid; single crystal; conductor; metal; thin film
Chemical Name: chromium
Host Composition: Cr
Form: single crystal
Structure: (110) face centered cubic
As Received Condition: single crystal as grown (12 mm diameter, 1.5 mm thick, purity 5n)
Analyzed Region: (110) surface
Ex Situ Preparation/Mounting: single crystal cut in (110) direction and polished, then spot-welded to the manipulator
In Situ Preparation: The Cr(110) substrate was cleaned by cycles of neon sputtering ($E = 750$ eV, $T = 780$ K, 2 h) and annealing ($T = 1040$ K, some minutes) until the contaminant concentration (nitrogen) was below 3% according to XPS.
Charge Control: No charge control was necessary, as the host material was metallic.
Temp. During Analysis: 300 K
Pressure During Analysis: <$1 \times 10^{-7}$ Pa

SPECIMEN DESCRIPTION (Accession ##00318)

Host Material: Cr$_2$O$_3$
CAS Registry #: 2440-47-3

Host Material Characteristics: homogeneous; solid; single crystal; dielectric; inorganic compound; thin film
Chemical Name: chromium oxide
Host Composition: Cr, O
Form: thin film
Structure: Cr$_2$O$_3$(111)
History & Significance: Cr$_2$O$_3$ has been studied as part of a project aiming at modeling catalysts (especially supported catalysts) under ultrahigh vacuum (UHV) conditions. We have chosen to study a thin Cr$_2$O$_3$(111) film instead of a bulk crystal since this allows for electron spectroscopy to be performed without charging of the sample. The substrate for the oxide was a Cr(110) single crystal disk (12 mm diameter, 1.5 mm thick, purity 5n) with the main contaminant being nitrogen. For this film adsorption data as well as data for the electronic and geometric structure are available (Refs. 1 and 2).
As Received Condition: not specified
Analyzed Region: (111) surface
Ex Situ Preparation/Mounting: no additional preparation after oxidation
In Situ Preparation: Oxidation procedure: 10$^{-6}$ mbar O$_2$, 1 min annealing at 540 K, followed by 2 min at 780 K, then flash at 1140 K. This was repeated until the low energy electron diffraction (LEED) pattern exhibited sharp spots of Cr$_2$O$_3$(111) without visible spots of the Cr(110) substrate.
Charge Control: No charge control was necessary as the host material was metallic, and the oxide film was too thin for charging.
Temp. During Analysis: 300 K
Pressure During Analysis: $< 1 \times 10^{-7}$ Pa

**INSTRUMENT DESCRIPTION**

Manufacturer and Model: Leybold-Heraeus EA 11
Analyzer Type: spherical sector
Detector: 2 multichannel plates

**INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA**

- **Spectrometer**
  Analyzer Mode: constant pass energy
  Throughput ($T = E^{N}$): $N = -1$
  Excitation Source Window: 1.5 μm Al window
  Excitation Source: Al $K\alpha$ monochromatic
  Source Energy: 1486.6 eV
  Source Strength: 450 W
  Analyzer Width: 3000 μm $\times$ 3000 μm
  Signal Mode: multichannel direct

- **Geometry**
  Incident Angle: 45°
  Source to Analyzer Angle: 45°
  Emission Angle: 0°
  Specimen Azimuthal Angle: 0°
  Acceptance Angle from Analyzer Axis: 1.5°
  Analyzer Angular Acceptance Width: 3° $\times$ 3°

- **Ion Gun**
  Manufacturer and Model: Leybold-Heraeus IQE 12/38
  Energy: 500 eV
  Current: 10 μA
  Current Measurement Method: biased stage
  Sputtering Species: Ne
  Raster Size: 10000 μm $\times$ 10000 μm
  Incident Angle: 45°

**DATA ANALYSIS METHOD**

Energy Scale Correction: energy scale calibration to Fermi level of Cr metal

Quantitation Method: The thickness of the layer has been calculated from the intensity ratio of the Cr $2p_{3/2}$ levels of the Cr(110) substrate with and without oxide film using an empirical mean free path length for the electrons of 1.8 nm. The latter value has been calculated for Cr$_2$O$_3$ according to a procedure given by Seah and Dench (Ref. 3). Due to the limited accuracy of this value the error of the estimated layer thickness may be some 10%. Apart from this the film thickness is also strongly dependent on the oxygen dose and the oxidation temperature. Therefore the film thicknesses may vary for different films. For the preparation conditions chosen in our experiments we estimate the film thicknesses to range from about 2.5 nm to 8.0 nm. The equation used for calculating the film thickness was $I_1/I_2 = \text{exp}(-\delta/\lambda)$, where $I_1$ = intensity of the Cr $2p_{3/2}$ level of Cr(110) with oxide, $I_2$ = intensity of the Cr $2p_{3/2}$ level of Cr(110) without oxide, $\delta$ = film thickness, and $\lambda$ = mean free electron path length.

**ACKNOWLEDGMENTS**

We are grateful to the Deutsche Forschungsgemeinschaft, the Bundesministerium fur Forschung und Technologie, and the Ministerium fur Wissenschaft und Forschung des Landes NRW for funding our research.

**REFERENCES**

### SPECTRAL FEATURES TABLE

<table>
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<tr>
<th>Spectrum ID #</th>
<th>Element/Transition</th>
<th>Peak Energy (eV)</th>
<th>Peak Width FWHM (eV)</th>
<th>Peak Area</th>
<th>Sensitivity Factor</th>
<th>Concentration (at. %)</th>
<th>Peak Assignment</th>
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<tbody>
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<td>Cr $2p_{3/2}$</td>
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<td>Cr $2s$</td>
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Footnote to Spectrum 00318-01: oxidized Cr(110) single crystal, Cr $2p$ region, showing structures due to Cr$_2$O$_3$(111) and small Cr $2p$ peaks due to the Cr(110) substrate (583.1 eV, 574 eV).

### ANALYZER CALIBRATION TABLE

<table>
<thead>
<tr>
<th>Spectrum ID #</th>
<th>Element/Transition</th>
<th>Peak Energy (eV)</th>
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<th>Sensitivity Factor</th>
<th>Concentration (at. %)</th>
<th>Peak Assignment</th>
</tr>
</thead>
</table>

Comment to Analyzer Calibration Table: The energy scale was calibrated by determining the Fermi edge of the Cr(110) substrate.

### GUIDE TO FIGURES

<table>
<thead>
<tr>
<th>Spectrum (Accession) #</th>
<th>Sample Voltage*</th>
<th>Multiplier</th>
<th>Baseline</th>
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* Sample voltage due to charging unless otherwise noted.
1. Clean Cr.
2. Cr$_2$O$_3$ peak energies were referenced to Fermi level of Cr metal which could be measured through thin oxide (see 318-5).
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<thead>
<tr>
<th>Accession #</th>
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<td>Host Material</td>
<td>Cr metal</td>
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<td>XPS</td>
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<td>Spectral Region</td>
<td>survey</td>
</tr>
<tr>
<td>Instrument</td>
<td>Leybold-Heraeus EA 11</td>
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<tr>
<td>Excitation Source</td>
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<tr>
<td>Source Energy</td>
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<tr>
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<tr>
<td><strong>Technique</strong></td>
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**Host Material:** Cr_2O_3  
**Technique:** XPS  
**Spectral Region:** Cr 2p\_1/2; Cr 2p\_3/2  
Instrument: Leybold-Heraeus EA 11  
Excitation Source: Al K\_α monochromatic  
Source Energy: 1486.6 eV  
Source Strength: 450 W  
Source Size: not specified  
Incident Angle: 45°  
Analyzer Type: spherical sector  
Analyzer Pass Energy: 12.6 eV  
Analyzer Resolution: 0.1 eV  
Emission Angle: 0°  
Total Signal Accumulation Time: not specified  
Total Elapsed Time: 8250 s  
Number of Scans: 150  
Comment: See footnote below the Spectral Features Table.

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**Accession #:** 00318-03  
**Host Material:** Cr_2O_3  
**Technique:** XPS  
**Spectral Region:** O 1s  
Instrument: Leybold-Heraeus EA 11  
Excitation Source: Al K\_α monochromatic  
Source Energy: 1486.6 eV  
Source Strength: 450 W  
Source Size: not specified  
Incident Angle: 45°  
Analyzer Type: spherical sector  
Analyzer Pass Energy: 25.2 eV  
Analyzer Resolution: 0.3 eV  
Emission Angle: 0°  
Total Signal Accumulation Time: not specified  
Total Elapsed Time: 600 s  
Number of Scans: 20  
Comment: oxidized Cr single crystal
**Accession #**: 00318-04  
**Host Material**: Cr$_2$O$_3$  
**Technique**: XPS  
**Spectral Region**: Cr 3s; Cr 3p; O 2s; Cr/O valence band  
Instrument: Leybold-Heraeus EA 11  
Excitation Source: Al K$_\alpha$ monochromatic  
Source Energy: 1486.6 eV  
Source Strength: 450 W  
Source Size: not specified  
Incident Angle: 45°  
Analyzer Type: spherical sector  
Analyzer Pass Energy: 100.8 eV  
Analyzer Resolution: 0.77 eV  
Emission Angle: 0°  
Total Signal Accumulation Time: not specified  
Total Elapsed Time: 560 s  
Number of Scans: 10  
Comment: oxidized Cr single crystal

---

**Accession #**: 00318-05  
**Host Material**: Cr$_2$O$_3$  
**Technique**: XPS  
**Spectral Region**: Cr 2s  
Instrument: Leybold-Heraeus EA 11  
Excitation Source: Al K$_\alpha$ monochromatic  
Source Energy: 1486.6 eV  
Source Strength: 450 W  
Source Size: not specified  
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Analyzer Type: spherical sector  
Analyzer Pass Energy: 100.8 eV  
Analyzer Resolution: 0.77 eV  
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Total Signal Accumulation Time: not specified  
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Number of Scans: 30  
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