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

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High Resolution XPS Study of a Thin Cr₂O₃(111) Film Grown on Cr(110)

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Transition metal oxides are important materials in heterogeneous catalysis, as supporting materials as well as active components. The catalytic activity of Cr₂O₃ 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 Cr₂O₃. Here we report high resolution XPS measurements of a thin epitaxial Cr₂O₃(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 5*n*) at elevated temperatures (540 K to 780 K) in an atmosphere of 10⁻⁶ mbar of O₂. The oxygen doses have been typically in the range of a few thousand Langmuirs. Under these conditions a Cr₂O₃(111) layer [Cr₂O₃(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 Cr₂O₃(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

Accession #s 00317, 00318

Technique: XPS

Host Material: #00317: Cr metal;
#00318: Cr₂O₃

Instrument: Leybold-Heraeus EA 11

Major Elements in Spectrum: Cr, O

Minor Elements in Spectrum: none

Printed Spectra: 6

Spectra in Electronic Record: 6

Spectral Category: comparison

Original Submission: 8/24/95

Accepted for Publication: 6/17/97

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 5*n*)

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: Cr₂O₃

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: Cr₂O₃(111)

History & Significance: Cr₂O₃ 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 Cr₂O₃(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 5*n*) 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 O₂, 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 Cr₂O₃(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_{α} monochromatic

Source Energy: 1486.6 eV

Source Strength: 450 W

Analyzer Width: 3000 $\mu\text{m} \times 3000 \mu\text{m}$

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 $\mu\text{m} \times 10000 \mu\text{m}$

Incident Angle: 45°

Polar Angle: 45°

Azimuthal Angle: 0°

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_2O_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 $I_1/I_2 = \exp(-\delta/\lambda)$, 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, δ = film thickness, and λ = mean free electron path length.

ACKNOWLEDGMENTS

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REFERENCES

1. H. Kühlenbeck, C. Xu, B. Dillmann, M. Hassel, B. Adam, D. Ehrlich, S. Wohlrab, H.-J. Freund, U. A. Ditzinger, H. Neddermeyer, M. Neuber, and M. Neumann, *Ber. Bunsenges Phys. Chem.* **96**, 15 (1992).
2. F. Rohr, M. Beumer, H.-J. Freund, J. A. Mejias, V. Staemmler, S. Moeller, L. Hammer, and K. Heinz, *Surf. Sci. Lett.* **372**, L291 (1997).
3. M. P. Seah and W. A. Dench, *Surf. Interface Anal.* **1**, 1 (1979).

SPECTRAL FEATURES TABLE							
Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area	Sensitivity Factor	Concentration (at. %)	Peak Assignment
00318-02	Cr $2p_{3/2}$	576.6	2.5	...	...	...	Cr ₂ O ₃
00318-02	Cr $2p_{1/2}$	586.5	3.0	...	...	...	Cr ₂ O ₃
00318-02	Cr $2p_{1/2}$	583.1	...	...	...	...	Cr(110) metal (substrate)
00318-02	Cr $2p_{3/2}$	574	...	...	...	...	Cr(110) metal (substrate)
00318-03	O $1s$	530.7	1.1	...	...	...	Cr ₂ O ₃
00318-04	Cr $3s$	75.3	3.3	...	...	...	Cr ₂ O ₃
00318-04	Cr $3p$	43.9	3.0	...	...	...	Cr ₂ O ₃
00318-04	O $2s$	22.9	2.8	...	...	...	Cr ₂ O ₃
00318-04	valence band	4.7	7.0	...	...	...	Cr and O from Cr ₂ O ₃
00318-05	Cr $2s$	698.9	9.5	...	...	...	Cr ₂ O ₃

Footnote to Spectrum 00318-01: oxidized Cr(110) single crystal, Cr $2p$ region, showing structures due to Cr₂O₃(111) and small Cr $2p$ peaks due to the Cr(110) substrate (583.1 eV, 574 eV).

ANALYZER CALIBRATION TABLE						
Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
...	...	...	...	...	...	...

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

GUIDE TO FIGURES				
Spectrum (Accession) #	Sample Voltage*	Multiplier	Baseline	Comment #
317-1	0	1.000	0	1
318-1	0	1.000	0	2
318-2	0	1.000	0	2
318-3	0	1.000	0	2
318-4	0	1.000	0	2
318-5	0	1.000	0	2

* Sample voltage due to charging unless otherwise noted.

1. Clean Cr.

2. Cr₂O₃ peak energies were referenced to Fermi level of Cr metal which could be measured through thin oxide (see 318-5).

Accession #	00317-01
Host Material	Cr metal
Technique	XPS
Spectral Region	survey
Instrument	Leybold-Heraeus EA 11
Excitation Source	Al K_{α} monochromatic
Source Energy	1486.6 eV
Source Strength	450 W
Source Size	not specified
Analyzer Type	spherical sector
Incident Angle	45°
Emission Angle	0°
Analyzer Retard Ratio	4
Analyzer Resolution	0.125 eV
Total Signal Accumulation Time	not specified
Total Elapsed Time	330 s
Number of Scans	5
Comment	survey of the clean Cr single crystal

Accession #	00318-01
Host Material	Cr ₂ O ₃
Technique	XPS
Spectral Region	survey
Instrument	Leybold-Heraeus EA 11
Excitation Source	Al K _α monochromatic
Source Energy	1486.6 eV
Source Strength	450 W
Source Size	not specified
Analyzer Type	spherical sector
Incident Angle	45°
Emission Angle	0°
Analyzer Retard Ratio	4
Analyzer Resolution	0.125 eV
Total Signal Accumulation Time	not specified
Total Elapsed Time	330 s
Number of Scans	5
Comment	survey of the oxidized Cr single crystal

■ **Accession #:** 00318-02
 ■ **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.

■ **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_2O_3
Technique: XPS
Spectral Region: Cr 3s; Cr 3p;
 O 2s; Cr/O valence band
 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: 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_2O_3
Technique: XPS
Spectral Region: Cr 2s
 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: 100.8 eV
 Analyzer Resolution: 0.77 eV
 Emission Angle: 0°
 Total Signal Accumulation Time:
 not specified
 Total Elapsed Time: 930 s
 Number of Scans: 30
 Comment: oxidized Cr single
 crystal