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Reliable Method for Determining the Oxidation State in Chromium Oxides

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We show that an appropriate analysis of the electron energy loss spectra in relation to the Cr—O bonds gives a reliable methodology to obtain the oxidation state in chromium oxides. It is based on the energy difference between the Cr L_3 and O K edges, which acts as a measure of the binding energy difference between the Cr $2p_{3/2}$ and O 1s core levels.

Introduction

Improving our knowledge of materials on a micro- and nanoscale is becoming increasingly important to scientific exploration. Miniaturization, interface issues, and composite materials can only be understood by way of precise information about the local atomic and electronic structures. In this context, electron energy loss spectroscopy (EELS) in a transmission electron microscope (TEM) is of particular interest, since it gives us information on the local structure, oxidation state, and bonding of the different atoms that constitute the material, essentially at the single-crystal scale![1,2] The EELS technique has been widely used in determining the valence state and coordination environment of transition-metal cations: for instance, in titanates, manganates, and ferrites.[3−6] With regard to chromium compounds, the earliest attempt at solving this problem was carried out by means of XPS in 1976.[7] However, in the Cr compounds studied thus far, it has been rather difficult to unambiguously determine the valence and/or coordination number.[8,9] Daulton and Little demonstrated the intrinsic difficulty (in over 30 different chromium compounds) in establishing a correlation between the integrated L_3/L_2 peak intensity ratio and oxidation state of the chromium, which is the traditional approach in determining a cation's valence by EELS. Although the range of possible valences can be constrained, there is still not a precise method for the determination of a unique oxidation state.[8] It is interesting to note that other authors have remarked upon the importance of the O K edge in Cr(III) and Cr(IV) compounds.[9] They have shown that the differences between the CrO_2 and Cr_2O_3 EELS spectra are in the O K edge and not in the Cr $L_{2,3}$.

Herein we report a reliable method to conclusively evaluate the oxidation state in chromium oxides. The method is based on the energy difference between the Cr L_3 and O K edges, which acts as a measure of the binding energy difference of the Cr $2p_{3/2}$ and O 1s core levels. This approach for determining the oxidation state is unprecedented in chromium compounds, and its accuracy even reveals the chromium coordination environment.

In a recent publication, not only the use of photoemission core-level shifts (*chemical shifts*) to determine the physical charge of the transition metal ion was rejected but also the very idea of oxidation states.[10] However, a defense of this heuristic basic school concept was elegantly accomplished by Jansen and Wedig.[11] In this sense, EELS, representing the difference in energy between a core-level initial state and the lowest energy final state of an excited electron, is comparable to XPS.[12] Therefore, a shift in the TM L_3 spectra indeed reflects a change in the oxidation state.[13]

Experimental Section

The compounds used in this study were selected in order to cover a wide range of different structures in a variety of oxidation states of the chromium oxides. Thus, we have tested the following: $CrTa_2O_6$ (trirutile) with Cr^{2+};[14] β-$CaCr_2O_4$, β-$CdCr_2O_4$ ($CaFe_2O_4$ type structure),[15,16] $BiCrO_3$ (perovskite),[17] Cr_2O_3

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Table 1. Oxidation State, Oxygen Coordination, Energy Difference ($\Delta E_{\text{Cr-L}_3\text{-O-K}}$), Average Cr−O Distance, and Integrated Intensity Ratio between the L_3 and L_2 Edges for the Chromium Compounds Used

compd	oxidn state	Cr coord	$\Delta E_{\text{Cr L}_3\text{-O K}}$ ±0.2 (eV)	⟨Cr−O⟩ (Å)	$\int I_{L_3}/I_{L_2}$
$CrTa_2O_6$	2+	VI	45.1	2.133	1.78
$CrTaO_4$	3+	VI	46.7	1.988	1.67
β-$CaCr_2O_4$	3+	VI	46.6	2.006	1.59
β-$CdCr_2O_4$	3+	VI	46.4	2.012	1.58
Cr_2O_3	3+	VI	46.6	1.995	1.63
CrOOH	3+	VI	46.9	1.977	1.61
$BiCrO_3$	3+	VI	46.6	1.991	1.71
$CrNb_2O_6$	3+	VI	46.8	1.991	1.77
$CrNbO_4$	3+	VI	47.4	1.988	1.43
"$PbCrO_3$"	3.5+	VI	47.2	2.003	1.48
$(Sr_2O_2)(CrO_2)_{1.85}$	3.5+	VI	46.8	2.015	1.60
CrO_2	4+	VI	48.6	1.902	1.49
$CrSr_2GdCu_2O_8$	4+	VI	47.2	1.908	1.60
$CaCrO_3$	4+	VI	47.1	1.908	1.46
$SrCrO_3$	4+	VI	48.2	1.909	1.39
Sr_2CrO_4	4+	IV	48.0	1.817	1.49
$TmCrO_4$	5+	IV	50.6	1.650	1.37
$NdCrO_4$	5+	IV	50.2	1.711	1.41
$CaCrO_4$	6+	IV	52.0	1.569	1.39
$SrCrO_4$	6+	IV	51.8	1.626	1.32

(corundum),[18] CrOOH, $CrTaO_4$, $CrNb_2O_4$, and $CrNbO_4$ (rutiles) for Cr^{3+};[19−21] CrO_2 (rutile),[22] $CrSr_2GdCu_2O_8$ (Ru-1212 type),[23] $SrCrO_3$, $CaCrO_3$ (perovskites),[24,25] and Sr_2CrO_4 (β-K_2SO_4 type) for Cr^{4+},[26] $TmCrO_4$ (scheelite) and $NdCrO_4$ (zircon) for Cr^{5+};[27,28] $CaCrO_4$ and $SrCrO_4$ (monacite type) with Cr^{6+}.[29] Additionally, we included two structures that presumably present a combination of chromium oxidation states and have a nontypical Cr−O bond length (comparable to the longest Cr−O bond in Cr^{3+} compounds; Table 1) into the studied oxides: the misfit layer $(Sr_2O_2)(CrO_2)_{1.85}$ and the compositionally incommensurate modulated "$PbCrO_3$".[30,31]

The synthesis of the samples as well as their structural features have been described in previous publications.[14−31] For the acquisition of the EEL spectra we have used an ENFINA EELS system placed on a JEOL JEM 3000FEG microscope, operating at 300 keV in the diffraction mode with a collection semiangle of 8.9 mrad. Under these conditions, the product of the momentum transfer and the extent of the core electron wave function is sufficiently smaller than unity and the core-level energy loss spectra are well described by the dipole transition.[32] The background has been subtracted with an inverse power law fitting, and plural scattering contributions were removed using the Fourier-ratio deconvolution technique.[33] The measurement of the experimental L_3/L_2 ratio of integrated peak intensities has been made over a 5 eV integration width around the maxima of each peak after a background subtraction following Pearson's method.[34] The energy values for the different maxima are collected in the Supporting Information, accompanied by the spectra themselves.

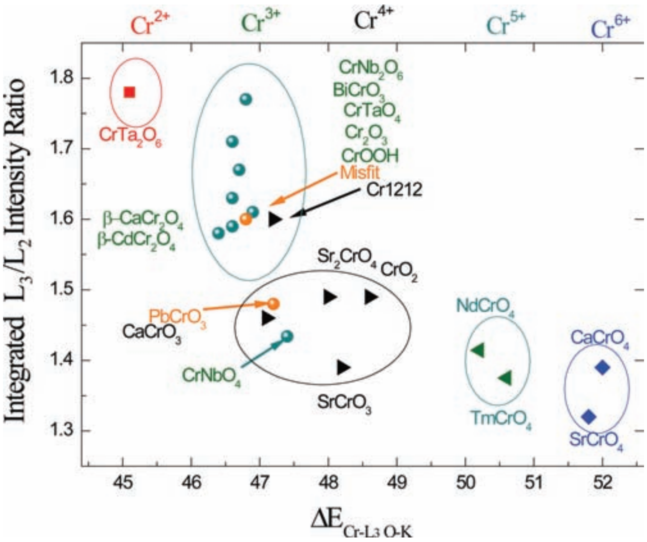

Figure 1. Correlation between L_3/L_2 ratios and ΔE with the different valences grouped.

Results and Discussion

The first method that we used to obtain the oxidation state in chromium oxides by means of EELS was a modification of the traditional approach. We considered the well-stocked integrated L_3/L_2 intensity ratio method not only against the L_3 onset energy[1] but also against the energy difference between the Cr L_3 and O K edges: that is, the difference between Cr $2p_{3/2}$ and O 1s binding energies. Moreover, with this selection, we avoid different energy scale calibrations or alignments in the spectrometer, giving a more general character to the procedure.

A plot of the integrated L_3/L_2 intensity ratio against the $\Delta E_{\text{Cr L−O K}}$ value is shown in Figure 1. The data collected display a roughly linear decrement of the intensity ratio proportional to the increment in the $\Delta E_{\text{Cr L−O K}}$ energy difference. In addition, the data present a well-clustered behavior with respect to the oxidation state, and the scatter diminishes in comparison with previous works that only considered the traditional method.[8] However, there are two compounds that are "misplaced" in these oxidation-state clusters: $CrNbO_4$ (Cr^{3+}) and $CrSr_2GdCu_2O_8$ (Cr^{4+}). The misfit layer and the "$PbCrO_3$" perovskite, though, are situated within the bounds of +3 and +4, respectively. This shows that this methodology is inconclusive for the chromium oxides, although one can approximate the oxidation state.

To avoid these discrepancies, we test another method. Now, we consider the oxidation state only as a function of the $\Delta E_{\text{Cr L−O K}}$ energy difference (Figure 2a): it can be seen that the Cr^{4+} extends in a wider energy range than the other Cr

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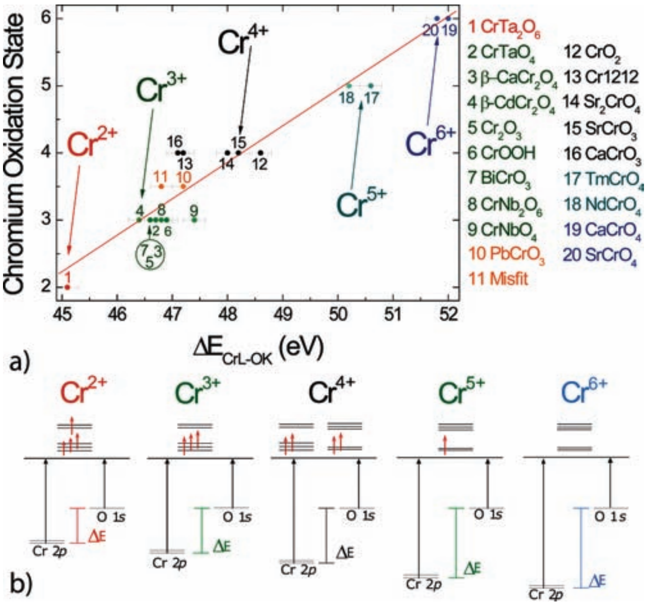

Figure 2. (a) Chromium oxidation state as a function of the energy difference (Cr L_3−O K). (b) Schematic representation of the electronic transitions and $\Delta E_{\mathrm{Cr\,L-O\,K}}$ for each of the chromium oxides and their qualitative energy level splitting. Cr^{2+} is represented in a high-spin configuration, as observed in $CrTa_2O_6$ and Cr^{4+} in both octahedral and tetrahedral splittings. For Cr^{2+}: (1) $CrTa_2O_6$. For Cr^{3+}: (2) $CrTaO_4$; (3) β-$CaCr_2O_4$; (4) β-$CdCr_2O_4$; (5) Cr_2O_3; (6) CrOOH; (7) $BiCrO_3$; (8) $CrNb_2O_6$; (9) $CrNbO_4$. For $Cr^{3.5+}$: (10) $PbCrO_3$; (11) $(SrO_2)(CrO_2)_{1.85}$. For Cr^{4+}: (12) CrO_2; (13) $CrSr_2GdCu_2O_8$; (14) Sr_2CrO_4; (15) $SrCrO_3$; (16) $CaCrO_3$. For Cr^{5+}: (17) $TmCrO_4$; (18) $NdCrO_4$. For Cr^{6+}: (19) $CaCrO_4$; (20) $SrCrO_4$.

oxides that cluster tightly together. The two particular structures, "$PbCrO_3$" and the misfit layer, in a first approximation can be considered to be in a 3.5+ oxidation state in accordance with previous works.[30,31] This oxidation state is consistent with the trend followed in Figure 2a. The $\Delta E_{\mathrm{Cr\,L-O\,K}}$ energy difference values appear to fall within a limited energy range from 45.1 ($Cr^{2+}Ta_2O_6$) to 52.0 eV ($CaCr^{6+}O_4$), and a simple linear correlation between the oxidation state and the energy difference can be established. From it, we obtain a gradient of 1.7(1) eV per oxidation state.

$CaCrO_3$ and $CrSr_2GdCu_2O_8$, which contain Cr^{4+} ions, present a $\Delta E_{\mathrm{Cr\,L-O\,K}}$ energy difference somewhat smaller than is expected. Thus, this second approach lacks precision to be a fully predictive tool, as the Cr in $CaCrO_3$ and $CrSr_2GdCu_2O_8$ have been proven to be in the 4+ oxidation state.[35−37] Moreover, the $CrNbO_4$ rutile is also separated from the Cr^{3+} cluster, unlike $CrNb_2O_6$. This is an expected result, though; as the oxidation state of Nb changes from 4+ to 5+, the O K edge shifts to lower energy.[38] This increases the $\Delta E_{\mathrm{Cr\,L-O\,K}}$ energy difference from $CrNb_2O_6$ to $CrNbO_4$.

The $\Delta E_{\mathrm{Cr\,L-O\,K}}$ energy trend for all the compounds can be explained easily as well. A Cr ion in a higher oxidative environment will require more energy to excite its 2p core electrons as they are strongly bound to the less-screened nucleus, as schematized in Figure 2b. In other words, the trend is caused by a progressive increase of the effective charge of the nucleus. Since we are dealing with the same Z ($Z = 24$), there is more binding energy on a more charged ion.

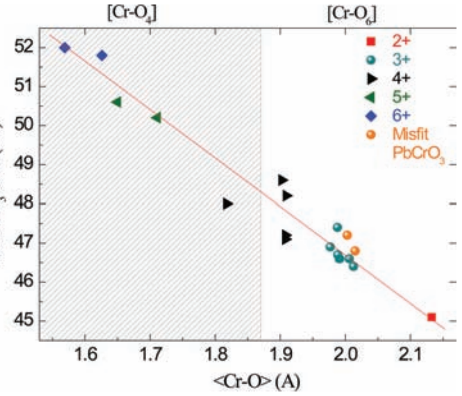

Figure 3. $\Delta E_{\mathrm{Cr\,L_3-O\,K}}$ energy difference as a function of the ⟨Cr−O⟩ bonds for each oxidation state. The shaded region represents the compounds with chromium having tetrahedral oxygen coordination, whereas the white region shows chromium octahedrally coordinated with oxygen.

Therefore, a combination of these two methods, the integrated L_3/L_2 intensity ratio and the $\Delta E_{\mathrm{Cr\,L-O\,K}}$ energy difference, gives us an approximate manner to evaluate the chromium oxidation states in oxides. However, we still have discrepancies in our results. In order to improve the method, we compare the $\Delta E_{\mathrm{Cr\,L-O\,K}}$ value with a basic piece of these structures, the ⟨Cr−O⟩ bond. A plot of the energy difference as a function of the average ⟨Cr−O⟩ distance is shown in Figure 3. As the average formal oxidation state increases, the ⟨Cr−O⟩ bond length decreases, and one can observe a tight clustering of these ΔE difference energies for each oxidation state. The ⟨Cr−O⟩ distance of 1.91(1) Å for the formally +4 "chromates" in an octahedral oxygen environment are about 0.1 Å shorter than in the formally +3 chromium systems (1.99(2) Å), which in turn is approximately 0.1 Å shorter than the ⟨Cr−O⟩ bond in $Cr^{2+}Ta_2O_6$ trirutile (2.13 Å).

In the compounds with chromium in a tetrahedral oxygen environment, a similar trend is observed. For the 6+ chromium compounds the average ⟨Cr−O⟩ distance is 0.1 Å shorter than that observed for the 5+ oxides, and again this is smaller than that of Sr_2CrO_4 (1.59(3), 1.68(3), and 1.817 Å, respectively). These data are consistent with what has been observed by Shannon and Prewitt[39] and support the trend of a decrease in the bond length with increasing oxidation state and concomitant covalency, thus demonstrating that the core-level shifts reflect oxidation state changes. Even more, this method also distinguishes between different Cr^{4+} coordinations as well.

The "$PbCrO_3$" and misfit compound are placed within the 3+ cluster. This is because of their large ⟨Cr−O⟩ bond. We cannot pinpoint their oxidation state. In the first method (considering the integrated intensity L_3/L_2 ratio and the $\Delta E_{\mathrm{Cr\,L-O\,K}}$ energy difference), the "$PbCrO_3$" and the misfit seemed to present Cr^{4+} and Cr^{3+}, respectively. Using the $\Delta E_{\mathrm{Cr\,L-O\,K}}$ energy difference method alone, a 3−3.5+ oxidation state for both compounds could be assigned and finally, taking the structural information into account, we obtained a 3+ oxidation state for both. Thus, we have to take special

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care of the "complicated" structures (where an unusual ⟨Cr−O⟩ bond is found). For the remaining chromium oxides used in this study, there were no problems in assigning the correct oxidation state using the $\Delta E_{\mathrm{Cr\,L-O\,K}}$ energy difference as a function of their ⟨Cr−O⟩ bonds.

Although this methodology is new in EELS spectroscopy, it has its counterpart in platinum and niobium oxides with related spectroscopy such as ESCA and XPS, respectively.[38,40] However, the clear advantage over those methods is the high selectivity at a nanoscale level. Moreover, this study was applied to chromium oxides, but it is obviously of interest for a more general scope considering other cations and in such diverse forms as thin films, heterogeneous catalysts, glasses, and device components, provided they can be studied in an "EELS dotted TEM".

Summarizing, we have developed a new approach to determine the oxidation state in chromium oxides, considering the $\Delta E_{\mathrm{Cr\,L-O\,K}}$ energy difference of an EELS spectrum as function of the ⟨Cr−O⟩ bonds. However, there are two cases in which this method is inconclusive: the case of the misfit layer compound $(Sr_2O_2)(CrO_2)_{1.85}$ and the incommensurate modulated "$PbCrO_3$". Both structures could present a mixed-valence chromium status and have larger than usual ⟨Cr−O⟩ bonds, thus explaining why this method fails. Notwithstanding, in all the other compounds the oxidation state of Cr can be unambiguously established.

On a final note, although the oxidation state is not linearly related to a "loss" of electrons by the respective atoms but rather to the formation and length of covalent bonds, the determination of oxidation states is imperative. It is clear that oxidation state can be obtained by a judicious use of adequate techniques such as EELS/ELNES. From such data it is certainly possible to predict the oxidation state of an element in a variety of compounds.

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Supporting Information Available: Figures giving experimental spectra and tables giving the maxima values as well as a comparison with XPS data from the NIST. This material is available free of charge via the Internet at http://pubs.acs.org.

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