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X-ray Photoelectron Spectroscopy of Chromium Trioxide and some of its Suboxides

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The present investigation is a systematic study of the X-ray photoelectron spectroscopy "ESCA" of CrO_3 and its suboxides, $CrO_{2.88}$, $CrO_{2.67}$, $CrO_{2.51}$, $CrO_{2.46}$, $CrO_{2.41}$, $CrO_{1.98}$ and $CrO_{1.5}$. The main peaks located at 581–574 eV and at 590–583 eV are for $Cr2p_{3/2}$ and $Cr2p_{1/2}$, respectively.

The change of binding energy of the Cr2*p* electrons of the investigated samples are attributed to the variation of the partial ionic character of the Cr–O bond, of the crystal structure, and of the oxidation state, Cr^{6+} to Cr^{3+}, of the chromium ions.

Dies ist eine systematische Untersuchung von CrO_3 und seiner Suboxide, $CrO_{2.88}$, $CrO_{2.67}$, $CrO_{2.51}$, $CrO_{2.46}$, $CrO_{2.41}$, $CrO_{1.98}$ und $CrO_{1.5}$ mittels "ESCA". Die Hauptsignale von 581–574 eV gehören zu $Cr2p_{3/2}$, die von 590–583 eV zu $Cr2p_{1/2}$.

Die Änderung der Bindungsenergie der Cr2*p*-Elektronen der untersuchten Proben werden der Veränderung des ionischen Anteils der Cr–O-Bindung, der Kristallstruktur und dem Oxidationszustand der Chrom-Ionen Cr^{6+}–Cr^{3+} zugeordnet.

1. Introduction

Recently, X-ray photoelectron spectroscopy, "XPS" techniques, have become an important tool in the field of chemical structure of inorganic materials. It is a useful technique for revealing bonding, core level binding energies, spin-orbit splittings, exchange splittings and qualitative differences in the oxidation states of the metal.

Chromium oxides are a good example of incomplete 3d orbitals which result in a wide variety of physical properties. "XPS" may serve as a convenient monitor for change in the oxidation states of compounds when passing from Cr_2O_3 to CrO_3.

Table 1. Different conditions of preparations of suboxides of chromium.

Oxide	Preparation temperature °C	Composition of the obtained sample
CrO_3	230	$CrO_{2.88}$
CrO_3	280	$CrO_{2.67}$
CrO_3	320	$CrO_{2.51}$
CrO_3	340	$CrO_{2.46}$
CrO_3	360	$CrO_{2.41}$
CrO_3	400	$CrO_{1,98}$
CrO_3	1000	$CrO_{1.50}$

Most of the previous work was restricted to definite compounds which had stable formulae such as CrO_3 [1], CrO_2 [2] and Cr_2O_3 [3]. As far as the authors are aware, no mention in the literature concerning the "XPS" is found with respect to chromium suboxides.

We have tried to correlate the "XPS" for CrO_3, $CrO_{2.88}$, $CrO_{2.67}$, $CrO_{2.51}$, $CrO_{2.46}$, $CrO_{2.41}$, $CrO_{1.98}$ and $CrO_{1.5}$ with calculations of the partial ionic character of the Cr−O bond in the above compounds, and to evaluate the extent of multiplet splitting of $Cr2p_{3/2}-Cr2p_{1/2}$. This work can be considered as continuation of previously measured physico-chemical properties of CrO_3 and its suboxides [4].

2. Experimental

Seven samples of composition CrO_{3-x} ($x = 0-1.5$) were prepared from the thermal decomposition of CrO_3 in a closed system of a stainless steel bomb designed by Kubota [5], to obtain single suboxides [6]. These oxides are CrO_3, $CrO_{2.88}$, $CrO_{2.67}$, $CrO_{2.51}$, $CrO_{2.46}$, $CrO_{2.41}$, $CrO_{1.98}$ and $CrO_{1.5}$. The different conditions of preparations are summarized in Table 1.

The composition of all samples was determined by chemical analysis [7] (Table 1). This work was carried out on a photoelectron spectrophotometer "550 ESCA/SAM", (Physical Electronics). The Mg ($K\alpha_{1,2}$) X-ray radiation of 1254 eV photon energy was used to excite the photoelectron [8]. The samples were mounted on an aluminium holder in the form of pellets. At least three runs for of the same composition were taken. Only the reproducible peaks are analysed "with ± 0.1 eV". To account for differential sample charging, all binding energies reported here have reference to the ClS peak (at 285 eV), due to the adventitious hydrocarbon contamination present on the surface of each sample [9].

3. Results and discussion

X-ray photoelectron spectra of $Cr2p_{3/2}$ and $Cr2p_{1/2}$ electrons of chromium oxides in the energy range 570−595 eV are shown in Fig. 1 and listed in

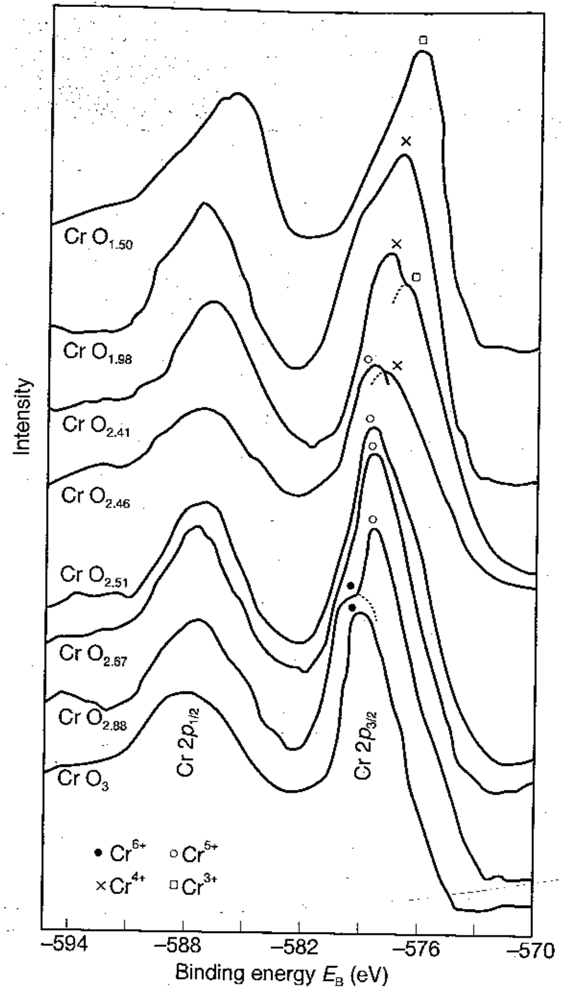

Fig. 1. Chromium $2p_{1/2}$ and $2p_{3/2}$ peaks in various chromium oxides CrO_{3-x} ($x = 0-1.5$)

Table 2. It is of interest to note that binding energy values "E_B" are in good agreement with those obtained by different authors for CrO_3, CrO_2 and Cr_2O_3 [1−3]. Generally, the "E_B" values decrease with decreasing oxygen content from CrO_3 to $CrO_{1.5}$.

Different authors [10, 11] concluded that changes in the binding energy of core electrons of chromium oxides may be due to differences in:

1. Partial ionic character of the Cr−O bond.
2. Crystal structure.
3. Valencies Cr^{6+} to Cr^{3+}.

Table 2. Binding energies "E_B" (eV) of Cr in chromium oxides and pure chromium metal (±0.1 eV).

Sample	O/Cr	$Cr2p_{3/2}$	$Cr2p_{1/2}$
$CrO_{3.00}$	3.00	581.6	588.0
$CrO_{2.88}$	2.88	578.2 581.8	587.1
$CrO_{2.67}$	2.67	578.2	586.5 587.6
$CrO_{2.51}$	2.51	578.5	586.7
$CrO_{2.46}$	2.46	577.5 578.8	586.7
$CrO_{2.41}$	2.41	576.8 577.5	585.8 586.1
$CrO_{1.98}$	1.98	576.5	586.2
$CrO_{1.50}$	1.50	575.3	585.2
Cr(metal)	—	574.1	583.5

Table 3. The ionic character "I" in CrO_3 and its suboxides.

Sample	O/Cr	I (%)
$CrO_{3.00}$	3.00	89.5
$CrO_{2.88}$	2.88	88.0
$CrO_{2.67}$	2.67	85.6
$CrO_{2.51}$	2.51	83.4
$CrO_{2.46}$	2.46	82.7
$CrO_{2.41}$	2.41	81.9
$CrO_{1.98}$	1.98	73.6
$CrO_{1.50}$	1.50	60.0

Discussing the effect of ionic character of Cr−O in CrO_3 and its suboxides, the following equation was used:

$$\text{Ionic character } I = 1 - \exp^{-[1/4(X_a - X_b)]}$$

where X_a and X_b are the values of electronegativities of the cationic and anionic atoms, respectively. The values of X for chromium and oxygen atoms are taken from Pauling measurements [12]. The calculated values of "I" are listed in Table 3. It is clear that the ionic part of the Cr−O bond decreases on going from CrO_3 to $CrO_{1.5}$ which is also the direction of decreasing "E_B" (Table 2).

The relation between the change of the ionic character "I" of the Cr−O bond and the binding energy of the Cr2p electrons of the investigated samples can be explained in the light of the fact that Cr atom loses some electronic charge in the bonding and, consequently, becomes positively charged. The result is a slight contraction of the electron distribution about the nucleus or increase in binding energy. This contraction decreases from CrO_3 to $CrO_{1.5}$, and the ionic character decreases in the same direction. Consequently, the binding energies "E_B" of the Cr2*p* electrons decrease from CrO_3 to $CrO_{1.5}$. These results are in harmony with those obtained by the present authors [13] for "XPS" of bismuth chalcogenides.

The second factor, namely the difference in crystal structure, consequently of the coordination parameters of CrO_3 and its suboxides, may also have an effect on the change of binding energy "E_B".

According to X-ray diffraction patterns [14], the crystal lattices of the investigated samples are as follows:

1. CrO_3, $CrO_{2.88}$, $CrO_{2.67}$, $CrO_{2.51}$, $CrO_{2.46}$ and $CrO_{2.41}$ (orthorhombic).
2. $CrO_{1.98}$ (tetragonal).
3. $CrO_{1.50}$ (hexagonal).

One may exclude an effect of the crystal structure of the chromium oxides $CrO_3-CrO_{2.41}$, as these compounds exhibit the same orthorhombic system.

It is worthy to state that CrO_3 is orthorhombic and the chromium ion tetrahedrally coordinated [11], while $CrO_{1.5}$ exhibits an hexagonal structure and octahedral coordinations. Binding energy values "E_B" of the above two oxides possess a difference of 2−3 eV which may be due to differences in the crystal structure (Table 2).

Different authors [15−18] found that the binding energy values "E_B" of Cr2*p* decrease as the oxidation states of the chromium ion decrease. Discussing the present values of "E_B" in the light of the above views, it is clear from Table 2, that the binding energies are smaller for $CrO_{1.5}$ (Cr^{3+}) than for CrO_3 (Cr^{6+}). These results are in harmony with those obtained by Allen *et al.* [16, 17]. They stated that the binding energy values of $Cr2p_{3/2}$ and $Cr2p_{1/2}$ in Cr^{6+} compounds are 589 and 579.8 eV, while in Cr^{3+} compounds they are 586 and 575 eV, respectively. Asami and Hashimoto [18] stated that the peak binding energies of 2*p* electrons of Cr in CrO_3 and Cr_2O_3 show the largest valency dependence. Thus, the third factor which can effect "E_B" is the valency of Cr in CrO_3 to $CrO_{1.5}$.

It is clear form Fig. 1 and Table 2 that the binding energies of $Cr2p_{3/2}$ electrons in the different samples increase in the direction $Cr_2O_3-CrO_3$. These results are in good agreement with those obtained by Lavielle and Kessler [11]. They concluded that a more highly oxidized species gives rise to higher binding energies, while a more reduced species shows the opposite effect. Thus, the binding energy values for Cr2*p* levels increase with the oxidation number of chromium.

It can be seen that the "XPS" peaks of $Cr2p_{3/2}$ and $Cr2p_{1/2}$ for $CrO_{2.88}$, $CrO_{2.46}$, and $CrO_{2.41}$ (Fig. 1) cannot be due to a single phase. The dashed

Table 4. The separation "Δ" (eV) between $Cr2p_{1/2}$ and $Cr2p_{3/2}$ of $CrO_3-CrO_{1.5}$ samples.

Sample	O/Cr	$Cr2p_{1/2}-Cr2p_{3/2}$ "Δ"
$CrO_{3.00}$	3.00	6.4
$CrO_{2.88}$	2.88	8.9
$CrO_{2.67}$	2.67	8.3
$CrO_{2.51}$	2.51	8.2
$CrO_{2.46}$	2.46	9.2
$CrO_{2.41}$	2.41	9.0
$CrO_{1.98}$	1.98	9.7
$CrO_{1.50}$	1.50	9.9
Cr	–	9.4

curves for these oxides represent a mixed oxidation state of Cr in a trace amount. These results are in good agreement with those obtained by infrared [14] and diffuse reflectance [6] measurements. Infrared studies displayed that the samples CrO_3 and $CrO_{2.88}$ represent valency six, Cr^{6+}, at 906 cm^{-1}. Valency five, Cr^{5+}, is quite clear from the absorption bands of $CrO_{2.46}$ at 534 and 790 cm^{-1}. Infrared spectra, previously obtained on solid $CrO_{1.98}$ and $CrO_{1.50}$, show that the infrared bands are due to Cr^{4+} and Cr^{3+}, respectively [14]. The reflectance spectra of CrO_3 and $CrO_{2.88}$ show bands at 3.14, 2.25 and 3.39, 2.29 eV, respectively, which correspond to the transition of electrons of the valence band to the conduction one of Cr^{6+}. For samples $CrO_{2.67}$, $CrO_{2.51}$, $CrO_{2.41}$ and $CrO_{1.98}$ the spectra indicate that these samples contain Cr^{5+} and Cr^{4+}. Sample $CrO_{1.50}$ shows peaks at 2.68, 2.10 and 1.65 eV, corresponding to Cr^{3+}.

In conclusion, from the infrared and diffuse reflectance measurements [6, 14], it can be concluded that CrO_3 and Cr_2O_3 are the more stable forms of chromium oxides, while suboxides represent impure oxides which contain different valencies of chromium ions. These results are in harmony with those obtained in the present investigation.

The separations "Δ" between $Cr2p_{1/2}$ and $Cr2p_{3/2}$ of the investigated samples are represented in Table 4. Generally, these values increase from CrO_3 to $CrO_{1.5}$. Lavielle and Kessler [11] concluded that the separation "Δ" increases with the number of unpaired 3*d* electrons in chromium compounds. Thus, the unpaired 3*d* electrons in Cr oxides increase from CrO_3 up to $CrO_{1.5}$, and, consequently, the "Δ" values increase in the same direction.

In conclusion, one may state that X-ray photoelectron spectroscopy confirmed that the binding energy of chromium 2*p* electrons in $CrO_3-CrO_{1.5}$ is dependent primarily on the partial ionic character of the Cr–O bond and the oxidation state of the chromium ions, a minor contributing factor is the change in the crystal structure.

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