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X-Ray Photoelectron Spectrum of Cr_2O_5

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Synopsis. The X-ray photoelectron spectrum of the powder of Cr_2O_5 was measured and compared with those of the related chromium compounds. It is concluded that Cr_2O_5 is a mixed-valence compound having Cr^{3+} and Cr^{6+} ions, possibly with the ratio of 1:2.

We have previously studied the X-ray photoelectron spectra of CrO_2, and related Cr compounds which contain Cr^{3+}, Cr^{4+} and Cr^{6+}.[1)] One of the present authors (T. N.)[2)] found that the powder of Cr_2O_5 can be obtained as an intermediate product in the process of preparing the ferromagnetic fine powder of CrO_2 by the hydrothermal decomposition of CrO_3 under a high oxygen pressure. The chemical composition of this oxide suggests the possibility that Cr ions in this oxide are in the valency state of Cr^{5+}. Thus it seemed of great interest to see if Cr ions are actually in the state of Cr^{5+} or in a mixed-valence state. We examined the X-ray photoelectron spectrum of the powder of Cr_2O_5 and found that this oxide is a mixed-valence compound having Cr^{6+} and Cr^{3+} ions with a ratio of 2:1.

Experimental

The powder of Cr_2O_5 was prepared by the following method. The powder of CrO_3 was heated at 350 °C for 2 h in the ordinary atmosphere, and, after cooled, the product was suspended in water to remove water-soluble components and ferromagnetic component, the latter being removed by applying a magnetic field to the suspension. The resultant product Cr_2O_5 was filtered off from the suspension and dried. The powder thus obtained was confirmed to be Cr_2O_5 by means of X-ray diffraction.

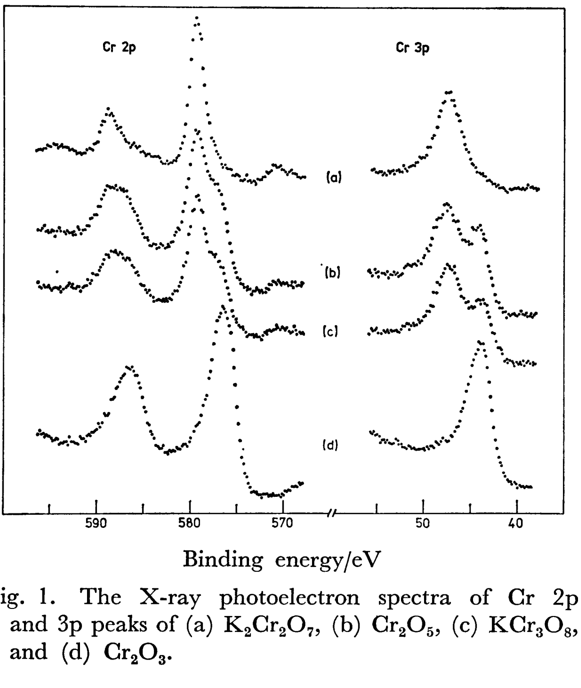

Fig. 1. The X-ray photoelectron spectra of Cr 2p and 3p peaks of (a) $K_2Cr_2O_7$, (b) Cr_2O_5, (c) KCr_3O_8, and (d) Cr_2O_3.

In the present study, we also measured the X-ray photoelectron spectra of Cr_2O_3, $K_2Cr_2O_7$, and KCr_3O_8. The first two compounds were commercially obtained and the last one was synthesized according to the literature.[3)]

X-Ray photoelectron spectra were measured with a McPherson ESCA 36 photoelectron spectrometer using Mg $K\alpha$ (1253.6 eV) as the stimulating radiation. All measurements were done on the powder samples pressed onto aluminium plates. Binding energies of photoelectron peaks were calibrated by using Au $4f_{7/2}$ peak (84.0 eV) of gold deposited on the sample.

In the case of Cr_2O_5, the X-ray photoelectron spectrum was found to change gradually with X-ray irradiation. Thus, we collected the photoelectron data only within a short measuring time on each fresh sample, and, repeating such measurements on many fresh samples, we summed up the data to obtain the spectrum which can be regarded as the one having been little affected by X-ray irradiation.

Results and Discussion

The Cr 2p and Cr 3p regions of the XPS spectrum of Cr_2O_5 are shown in Fig. 1 together with those of KCr_3O_8, $K_2Cr_2O_7$, and Cr_2O_3. The observed spectra are very much similar between Cr_2O_5 and KCr_3O_8. In these two cases, the Cr 3p peak exhibits a shape composed of two component peaks, the Cr $2p_{3/2}$ peak exhibits a shoulder at the low binding energy side of the main peak, again suggesting that two peaks are superimposed on each other, and the Cr $2p_{1/2}$ peak is very broad. All these facts indicate that Cr ions of two different valency states are contained in Cr_2O_5 as well as in KCr_3O_8, in other words, these materials are mixed-valence compounds. In effect, it is known from the X-ray crystal structure analysis that there are Cr^{6+} and Cr^{3+} sites with the ratio of 2:1 in the crystal lattice of KCr_3O_8.[4)] Thus one can regard that, in the XPS spectrum of KCr_3O_8, each core electron peak associated with Cr ions, is a superposition of the peaks due to Cr^{6+} and Cr^{3+}, respectively. This can be seen in Fig. 1 by comparing the spectrum of KCr_3O_8 with those of Cr_2O_3 and $K_2Cr_2O_7$: Cr_2O_3 contains only Cr^{3+} and $K_2Cr_2O_7$ contains only Cr^{6+}. The fact that the profiles of the Cr 2p and Cr 3p peaks of Cr_2O_5 are very much similar to those of the corresponding peaks of KCr_3O_8, suggests that Cr_2O_5 is also a mixed-valence compound having Cr^{6+} and Cr^{3+} sites with a ratio roughly the same as that

Table 1. XPS Core-level binding energies of chromium compounds

	Binding energy/eV			
	$K_2Cr_2O_7$	Cr_2O_5	KCr_3O_8	Cr_2O_3
Cr $2p_{1/2}$	588.9	588.6	588.3	
		587.1	586.7	586.5
Cr $2p_{3/2}$	579.6	579.3	579.4	
		577.0	577.2	576.6
Cr 3p	47.4	47.7	47.3	
		44.1	43.5	43.8
O 1s	530.3	529.8	530.2	530.6

in KCr_3O_8.

Using the profiles of the Cr 2p and Cr 3p peaks of Cr_2O_3 as those characteristic of Cr^{3+} ion, and the profiles of the corresponding peaks of $K_2Cr_2O_7$ as those characteristic of Cr^{6+} ion, we tried to decompose the observed Cr 2p and Cr 3p peaks of KCr_3O_8 and Cr_2O_5 into the component peaks due to Cr^{6+} and Cr^{3+} ions, respectively. The procedure used here is the same as the one which we have adopted in the XPS study of organic mixed-valence compounds.[5)]

The binding energies of the decomposed peaks are listed in Table 1 together with those of the corresponding peaks of Cr_2O_3 and $K_2Cr_2O_7$. In principle, one could determine the Cr^{6+}/Cr^{3+} ratio from this peak profile analysis. The analysis of the Cr 3p peak profile of KCr_3O_8 gave the Cr^{6+}/Cr^{3+} ratio as 2:1 in agreement with the ratio known from the crystal structure. In comparison with this, the Cr^{6+}/Cr^{3+} ratio obtained from the analysis of the Cr $2p_{3/2}$ peak of KCr_3O_8 was found to be rather anomalous, it being 1:1 in significant disagreement with the expected ratio. It should be noted that, in the obtained Cr $2p_{3/2}$ peak, the main peak corresponds to Cr^{6+} and its low-binding-energy shoulder correspond to Cr^{3+}, and the intensity ratio of the Cr^{6+} component to the Cr^{3+} component will be estimated to be 2—2.5 if we decompose the observed peak into the two components naively assuming the same peak width for the two components. On the other hand, it becomes 1:1 as we have mentioned when we use the Cr $2p_{3/2}$ peak profile of $K_2Cr_2O_7$ for the Cr^{6+} component and that of Cr_2O_3 for the Cr^{3+} component, the peak width of the former being significantly smaller than the latter. Seemingly it is inadequate to use the peak shapes of $K_2Cr_2O_7$ and Cr_2O_3 for decomposing the observed peak profile of a mixed valence compound. Probably we should better assume that the peaks of the Cr^{6+} and Cr^{3+} components are of nearly the same width. The situation will be the same in the case of Cr_2O_5. Since the observed profile of the Cr $2p_{3/2}$ peak of Cr_2O_5 is almost exactly the same as that of KCr_3O_8, one may conclude that the Cr^{6+}/Cr^{3+} ratio in Cr_2O_5 is also 2:1 as in KCr_3O_8. The observed profile of the Cr 3p peak of Cr_2O_5 is slightly different from that of KCr_3O_8 although they should be the same if the Cr^{6+}/Cr^{3+} ratio is identical between the two compounds as we have concluded from the Cr $2p_{3/2}$ peak shape. This may be due to the situation that, in the case of Cr_2O_5, it is rather hard to obtain the true Cr 3p peak profile without having been affected by X-ray irradiation since a considerably long measuring time is necessary to record Cr 3p peak while Cr_2O_5 is damaged with X-ray irradiation. Since Cr $2p_{3/2}$ peak is much stronger than Cr 3p peak, the observed 2p peak of Cr_2O_5 is likely to be more free from the radiation damage as compared with the Cr 3p peak.

In conclusion, the XPS data of Cr_2O_5 indicate that the chromium ions in Cr_2O_5 is not in the state of Cr^{5+} but in a mixed-valence state consisting of Cr^{6+} and Cr^{3+}, presumably with the ratio of 2:1.

References

1) I. Ikemoto, K. Ishii, S. Kinoshita, H. Kuroda, M. A. A. Franco, and J. M. Thomas, *J. Solid State Chem.*, **17**, 425 (1976).

2) T. Namikawa and M. Satou, *Nippon Kagaku Kaishi*, **1975**, 52.

3) J. J. Foster and A. N. Hambly, *Aust. J. Chem.*, **29**, 2137 (1976).

4) K. A. Wilhelmi, *Acta Chem. Scand.*, **12**, 1965 (1958).

5) I. Ikemoto, M. Yamada, T. Sugano, and H. Kuroda, *Bull. Chem. Soc. Jpn.*, **53**, 1871 (1980).