Inorganica Chimica Acta, 85 (1984) L57–L60

The Galena/Dichromate Solution Interaction and the Nature of the Resulting Chromium(III) Species

DALE L. PERRY*, LEON TSAO

Lawrence Berkeley Laboratory, University of California, Berkeley, Calif. 94720, U.S.A.

and J. ASHLEY TAYLOR

NSF Regional Instrumentation Facility for Surface Analysis, University of Minnesota, Minneapolis, Minn. 55455, U.S.A.

Received January 4, 1984

The reaction of aqueous sodium dichromate, $Na_2Cr_2O_7$, with galena (PbS) is one of the most commonly observed reactions in the froth flotation separation of galena from other metal sulfide ores, the sodium dichromate acting as a modifier in the process. Surface studies [1, 2] have shown that the resulting chemical species on the galena include both the chromium(VI) species and the reduced chromium(III) species. While the X-ray photoelectron data regarding the chromium(VI) species in these studies were consistent with $PbCrO_4$, the assignment of the chromium(III) species was not so unequivocal. One researcher [1] indicated that the Cr(III) probably was some type of oxidation product formed on the surface, while yet another team of investigators [2] speculated that it was $PbCr_2O_4$ (a combination of $Pb(OH)_2$ and Cr_2O_3) on the basis of binding energy data alone. This laboratory has re-investigated this reaction system, making detailed studies of the X-ray photoelectron spectra (XPS) of the reacted galena surfaces and comparing them to those of model chromium(III) compounds.

Experimental

A physical Electronics Model 555 X-ray photoelectron spectrometer equipped with a Mg K_α (1253.6 eV) anode source was used for obtaining all spectra. The energy scale of the spectrometer was calibrated using the Au $4f_{7/2}$ = 83.8 eV, Cu $2p_{3/2}$ = 932.4 eV, and Cu $3p_{3/2}$ = 74.9 eV photoelectron lines [3]. The adventitious carbon 1s = 284.6 eV line was used for charge referencing. All model compound samples were studied as fine powders mounted on polymer film-based adhesive tape with a metallic backing, while the galena samples were run as both powders and freshly cleaved chips.

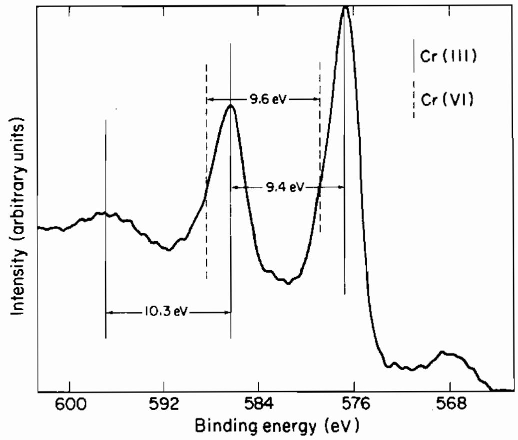

Fig. 1. The chromium $2p_{3/2,1/2}$ photoelectron spectrum of galena that has been reacted with an aqueous solution of $Na_2Cr_2O_7$ using the reaction conditions found in Refs. 1 and 2.

Galena samples were obtained from Ward's Natural History Establishment. Both chromium(III) and chromium(VI) standards were purchased as reagent grade materials and used without further purification, with the exception of $Cr(OH)_3$ and $Cr_2(CO_3)_3\cdot H_2O$. $Cr(OH)_3$ (possibly better formulated as $Cr_2O_3\cdot nH_2O$; please see below) was prepared [4] by completely precipitating $Cr(NO_3)_3\cdot 9H_2O$ from aqueous solution using NaOH, followed by washing with cold, distilled water after filtration through a Buchner funnel and air drying on the filter bed. $Cr_2(CO_3)\cdot nH_2O$ was prepared [5] by precipitating $Cr(NO_3)\cdot 9H_2O$ with Na_2CO_3 from aqueous solution, washing with cold, distilled water, and air drying on a Buchner funnel bed.

The galena samples were reacted with aqueous $Na_2Cr_2O_7$ solutions in a manner almost identical to those previously used [1, 2]. Instead of using an aqueous solution of SO_2 (H_2SO_3, or sulfurous acid) to remove any oxidation products on the surfaces of the galena samples [1], boiling water was used. The resulting samples yielded spectra which showed only the sulfide species; no traces of oxidation products such as sulfur or sulfate could be detected. An increase in the concentration of the $Cr_2O_7^{2-}$ in the reaction solution (while keeping the amount of galena fixed) above those used in [1] and [2] yielded spectra which were virtually identical; this is in agreement with results previously reported [2].

Results and Discussion

The chromium $2p_{3/2,1/2}$ spin–orbit doublet spectrum of the reacted galena is shown in Fig. 1. Each of the two photoelectron lines consists of obvious

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*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

TABLE I. X-Ray Photoelectron Data for the Galena/$Cr_2O_7^{2-}$ Reaction and Related Cr(III) Compounds.[a,b]

Sample	Cr $2p_{3/2}$	Cr $2p_{1/2}$	O1s	C 1s[c]	Cr ($2p_{1/2}$ − $2p_{3/2}$)	Cr 3s Splitting	Cr $2p_{1/2}$ Satellite[d]
Galena/$Cr_2O_7^{2-}$	577.0-Cr(III)	586.4-Cr(III)	530.9	288.0	9.4	4.1–4.3	10.3
	578.8-Cr(VI)	588.4-Cr(VI)			9.6		
Cr_2O_3	576.3	586.1	529.9		9.8	4.3	10.3
$Cr(OH)_3$[e]	576.6	586.4	530.8	288.0	9.8	4.1	10.3
$Cr_2(CO_3)_3 \cdot nH_2O$[f]	577.0	587.1	531.2	288.0	10.1	4.1	10.3

[a] All values in electron volts, eV. [b] Adventitious carbon 1s = 284.6 eV. [c] Carbon line attributable to the carbonate species. [d] Distance (to the high binding energy side) from the main $2p_{1/2}$ line. [e] Also formulated as $Cr_2O_3 \cdot nH_2O \cdot xCO_2$; please see text and Ref. 4. [f] Also formulated as $Cr_2O_3 \cdot nH_2O \cdot xCO_2$; please see text and Ref. 5.

doublets, one line in each doublet representing chromium(III) and the other line representing chromium(VI). Binding energies and spin–orbit splittings (Table I) for the chromium(VI) lines are in good agreement with an assignment of $PbCrO_4$ as previously reported [1]. The photoelectron data for both the hexa- and trivalent chromium species in that report are in excellent agreement with those in this study.

The chromium(III) portion of the spectrum, however, represents a much more complex situation, since chromium(III) with its $3d^3$ electronic paramagnetic configuration [as opposed to the diamagnetic $3d^0$ state of chromium(VI)] exhibits a broader 2p core line, associated 'shake-up' satellite lines to the high binding energy side of the main photoelectron lines, and multiplet splitting of the 3s core levels by the 3d valence electrons [6]. Additionally, spectra characteristics and parameters resulting from these effects can be altered by factors such as sample hydration.

The two chromium(III) lines shown in Fig. 1 have binding energies of 577.0 and 586.4 eV, respectively, for the $2p_{3/2}$ and $2p_{1/2}$ lines. These values are very similar to those exhibited by $Cr(OH)_3$ and hydrated $Cr_2(CO_3)_3$ shown in Table I as well as those previously reported for the natural mineral CrOOH [7], a hydrated chromium(III) oxide. The spin–orbit splitting between the Cr $2p_{3/2}$ and $2p_{1/2}$ lines is 9.4 eV, within experimental error also quite close to the splitting of 9.8 eV exhibited by the hydroxide and carbonate chromium(III) models in Table 1. The seeming discrepancy of 0.4 eV between the two values can probably be attributed to the inability to locate the exact centroids of the chromium(III) peaks accurately. While these splittings also compare favorably to that of 9.7 eV previously reported [8] for Cr_2O_3, it is highly unlikely that any Cr_2O_3 formed in an aqueous reaction medium would be anhydrous.

If one examines the region of the spectrum to the high binding energy side of the chromium $2p_{1/2}$ peak, the similarities between the spectra of the dichromate-treated galena and the $Cr(OH)_3$ and $Cr_2(CO_3)_3 \cdot nH_2O$ compounds are even more striking. The 'shake-up' satellites of each spectrum, due to electronic configuration interactions [6] which are most pronounced in paramagnetic ions such as chromium(III), are identical, found at a value of 10.3 eV to the high binding energy side of the main $2p_{1/2}$ photoelectron line. Indeed, the chromium 2p spectra (and associated 'shake-up' satellites) of the dichromate-treated galena and these two model compounds exhibit profiles which are virtually identical; with the exception of the small differences in binding energies, the spectra are superimposable on one another. The profile of the chromium 2p spectrum of the other model compound in Table I – Cr_2O_3 – is also identical to that of the dichromate-treated galena surface. The line width (FWHM, or full width at half maximum) of the chromium 2p lines of all of these compounds is approximately 3.1 eV, virtually identical to that reported (3.0 eV) for Cr_2O_3 [8]. The intensity ratio of the satellite at 10.3 eV to the higher binding energy side of the Cr $2p_{1/2}$ line and the line itself is 0.18; this, too, is virtually identical to the value of 0.16 reported for Cr_2O_3 [6], strongly indicating that all of the model compounds and the chromium(III) complex on the dichromate-treated galena surface are related to Cr_2O_3.

The oxygen 1s binding energies reported in Table I give further evidence for the chromium(III) species being derived from some form of hydrated chromium(III) oxide such as $Cr(OH)_3$. The binding energies for this photoelectron line are 530.9, 530.8, and 531.2 eV for the dichromate-treated galena, $Cr(OH)_3$, and $Cr_2(CO_3)_3 \cdot nH_2O$, respectively. This represents a range of only 0.4 eV for the three samples, in fairly close agreement with one another. The three values are, however, a full volt higher than Cr_2O_3, further indicating that the chromium(III) species on the galena surface cannot be the simple, anhydrous Cr_2O_3. Since the degree of hydration of metal oxide has been shown by other workers [8–10] to strongly influence the oxygen 1s binding energies, it is not surprising that the binding energy here for the O 1s line is this high. One worker [8] has shown that hydrating chromium oxides can increase the binding energy up to 2 eV. This would be consistent with the present observations if one assumes that the chromium(III) species on the galena surface is some type of hydrated Cr_2O_3 or derived from hydrated Cr_2O_3.

The chromium 3s multiplet splitting [6] exhibited by the dichromate-treated galena is approximately 4.1 eV for all but one of the samples examined, the multiplet splitting in that sample being 4.3 eV. Again, this is in excellent agreement with 4.1 eV reported in Table I for $Cr_2(CO_3)_3 \cdot nH_2O$ and $Cr(OH)_3$; the lower end of the range of values is also extremely close to that of 3.9 eV reported for CrOOH [7]. A small range of 0.3 eV in the splitting of different galena samples is not surprising in light of still other recent results in an investigation of hydrated iron(III) oxides which have shown the 3s multiplet splitting to vary almost 2 eV due to the *extent* of the hydration of the oxides [10]. Also, it is extremely difficult to assign an exact splitting of the 3s level in the present case due to the rather low intensity of the two 3s lines in the spectrum of the galena surface, thus yielding a slightly different splitting for the same compound which apparently differs slightly from sample to sample.

An examination of the carbon 1s line reveals not only the adventitious carbon line at 284.6 eV but also a line at 288.0 eV for the dichromate-treated galena sample, $Cr(OH)_3$, and $Cr_2(CO_3)_3 \cdot nH_2O$. This line indicates the presence of the carbonate species, which undoubtedly results from chemisorption (and subsequent reaction) of CO_2 from the reaction solution with the hydrated chromium oxide. This reaction, forming a mixed hydrated oxide/carbonate complex, has been documented for several other metal oxide (and 'hydroxide') systems, including lead [11], uranium [9], and plutonium [12]. While one cannot assign the carbonate species to the chromium(III) exclusively, such an association is reasonable in light of the chemisorption of CO_2 by all the anhydrous Cr_2O_3 samples prepared and studied in this investigation. Previous workers [2] have indicated that Cr_2O_3 often has a coating of $Cr(OH)_3$, or CrOOH, on its surface which would act as a reaction substrate for CO_2; also, Allen *et al.* [8] have shown the effects on the XPS spectra of aging Cr_2O_3 in open air. The extreme similarities in the XPS spectral parameters of Cr_2O_3 and CrOOH have also been compared previously [7]. Strong evidence has been observed for the presence of the analogous lead(II) hydroxide/carbonate complex [11] on the galena surface on the basis of the lead core photoelectron lines.

While not totally obvious initially, the model compounds $Cr(OH)_3$ and $Cr_2(CO_3)_3 \cdot nH_2O$ are indeed very much related chemically. $Cr(OH)_3$ probably is not a true hydroxide but rather a hydrated chromium(III) oxide of the type $Cr_2O_3 \cdot nH_2O$ [4, 13]. Similarly, $Cr_2(CO_3)_3 \cdot nH_2O$ cannot be considered a true carbonate but rather hydrated Cr_2O_3 with a chemisorbed layer of CO_2 [5]. This can best be generally formulated as $Cr_2O_3 \cdot nH_2O \cdot xCO_2$, a mixture of both chromium(III) oxide and carbonate. Both compounds are thus essentially chemical modifications of Cr_2O_3, with their exact chemical composition varying as a function of the degree of hydration and carbonation.

On the basis of the present X-ray photoelectron data, the reaction between galena and an aqueous solution of sodium dichromate yields both chromium(III) and chromium(VI) species. The chromium(III) complex is actually hydrated chromium(III) oxide, $Cr_2O_3 \cdot nH_2O$, with a layer of chemisorbed CO_2 on the surface, thus forming a mixed complex of the type $Cr_2O_3 \cdot nH_2O \cdot xCO_2$. This product is a result of the hydration of chromium(III) oxide which in turn adsorbs (and subsequently reacts with) CO_2. There is, however, no way of determining the amount of carbon dioxide adsorbed from the air during handling.

Acknowledgements

This research was supported by the U.S. Department of Energy under Contract Number DE-AC03-76SF00098 and by the University of Minnesota NSF Regional Instrumentation Facility for Surface Analysis, Grant No. NSF CHE-7916206. One of the authors (D.L.P.) also wishes to acknowledge support from the Director's Development Fund, Lawrence Berkeley Laboratory, and from the Office of Basic Energy Sciences through the Advanced Research Concepts Program of the Division of Engineering, Mathematics and Geosciences.

References

1 R. K. Clifford, K. L. Purdy and J. D. Miller, *AICHE Symp. Series, 71 (150),* 138 (1975).
2 V. I. Nefedov, Y. V. Salyn, P. M. Solozhenkin and G. Y. Pulatov, *Surf. Interface Anal., 2,* 170 (1980).
3 C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder and G. E. Muilenberg, 'Handbook of X-Ray Photoelectron Spectroscopy', Perkin-Elmer Corp., Eden Prairie, Minnesota (1979).
4 C. L. Rollinson, in 'Comprehensive Inorganic Chemistry', A. F. Trotman-Dickenson, Ed., Vol. III, Pergamon Press, New York, p. 666, 667 (1973).
5 M. J. Udy, Chromium, Vol. I, 'ACS Monograph Series', Reinhold Publishing Corp., New York, p. 210 (1956).
6 G. A. Vernon, G. Stucky and T. A. Carlson, *Inorg. Chem., 15,* 278 (1976).
7 I. Ikemoto, K. Ishii, S. Kinoshita, H. Kuroda, M. A. A. Franco and J. M. Thomas, *J. Sol. State Chem., 17,* 425 (1976).
8 G. C. Allen, M. T. Curtis, A. J. Hooper and P. M. Tucker, *J. Chem. Soc. Dalton,* 1675 (1973).

9 D. L. Perry, L. Tsao and H. G. Brittain, *Inorg. Chem.*, in press.

10 D. L. Perry and J. A. Taylor, 185th Natl. Meet. ACS, Seattle, Abstract INOR 107 (1983).

11 J. A. Taylor and D. L. Perry, *J. Vac. Sci. Tech.*, in press.

12 L. M. Toth and H. A. Friedman, *J. Inorg. Nucl. Chem.*, *40*, 807 (1978).

13 The hydrolysis of a chromium(III) salt results in a hydrated oxide which can be represented by formulas of the type $Cr(OH)_3$ or CrOOH, which are analogous to the iron(III) hydrated oxides [14]. While often referred to as '$Fe(OH)_3$', they are not hydroxides in the true chemical sense but rather hydrated ferric oxides, $Fe_2O_3 \cdot nH_2O$, which exhibit different structural modifications such as represented by α-, β-, and γ-FeOOH [14, 15].

14 D. T. Harvey and R. W. Linton, *Anal. Chem.*, *53*, 1684 (1981).

15 J. M. Gonzalez-Calbet, M. A. Alario-Franco and M. Gayoso-Andrade, *J. Inorg. Nucl. Chem.*, *43*, 257 (1981).