

SURFACE CHEMISTRY OF COBALT IN CALCINED COBALT-KAOLINITE MATERIALS

Key Words— CoAl_2O_4 , Cobalt, Diffuse reflectance spectroscopy, Kaolinite, X-ray photoelectron spectroscopy.

INTRODUCTION

The analysis of metal ion bonding and the identification of surface species on mineral and clay surfaces is important in understanding adsorption phenomena and in developing methods for the preparation of materials with established surface chemistry. X-ray photoelectron spectroscopy (XPS) is a surface-sensitive analysis technique that may provide information on metal coordination geometry and oxidation state (Koppelman and Dillard, 1979; Bancroft *et al.*, 1979). XPS studies have been successful in describing the chemical nature of cobalt oxides and cobalt adsorbed on a variety of substrates. Tewari and Lee (1975) and McIntyre and Tewari (1977) identified $\text{Co}(\text{OH})_2$ on the surface of ZrO_2 and Al_2O_3 following the interaction of $\text{Co}^{2+}(\text{aq})$ with ZrO_2 and Al_2O_3 . Lunsford *et al.* (1978) detected $\text{Co}(\text{III})$ on a zeolite Y sample prepared by the adsorption of $\text{Co}(\text{NH}_3)_6^{3+}$ on zeolite Y and heating the treated sample to 400°C . Declerck-Grimee *et al.* (1978) suggested from a detailed analysis of XPS spectra that Co_9S_8 is the active cobalt-containing component in cobalt/molybdate hydrodesulfurization catalysts. The Co 2p XPS spectra for $\text{Co}(\text{II})$ adsorbed on MnO_2 (Murray and Dillard, 1979) were interpreted to indicate the formation of $\text{Co}(\text{III})$ on the surface.

Recent studies of X-ray-induced Auger processes (Wagner *et al.*, 1979; Dillard and Koppelman, 1982; Harvey and Linton, 1981) demonstrated that speciation of surface components is practical using XPS. To provide speciation information, core-binding energy data (CBE) and Auger kinetic-energy results (AKE) must be compared. Such a comparison reveals that unique values for CBE and AKE are found for a series of metal compounds. The results are then related to the electron density at the atom of interest and thus provide speciation of surface species.

To demonstrate the surface analytical potential of XPS, calcined cobalt-kaolinite samples have been prepared to contain CoAl_2O_4 . In these samples CoAl_2O_4 has been confirmed by X-ray powder diffraction measurements, and tetrahedral $\text{Co}(\text{II})$ has been identified by means of visible diffuse reflectance spectroscopy. The present study illustrates the utility of using XPS binding energy data, core-electron satellite features, and X-ray-induced Auger processes for the identification of surface species. Such results provide a powerful characterization scheme for the analysis of clay surfaces where bulk techniques such as X-ray powder diffraction are ineffective.

EXPERIMENTAL

Calcined cobalt-kaolinite materials were prepared by heating mixtures of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ with kaolinite Hydrite PX in air. The Hydrite PX sample was obtained from Georgia Kaolin company from their well-crystallized kaolin deposits in central Georgia. It was fractionated with centrifugal assistance to obtain a particle size distribution with 90% of the clay particles having an equivalent spherical diameter of $<2 \mu\text{m}$. The clay was flocculated with acid during its processing resulting in a clay-water dispersion (20% solid) with $\text{pH} \sim 4.5$. The cation-exchange capacity of the clay is 3 meq/100 g and the BET surface area is $13 \text{ m}^2/\text{g}$. The compositions of the mixtures and the temperatures and duration of calcination are summarized in Table 1. Cobalt oxides and hydroxides and CoAl_2O_4 were obtained from commercial suppliers.

The structural integrity of the commercial materials was confirmed by X-ray powder diffraction (XRD) analysis (Table 1).

XPS spectra were measured using a DuPont model 650 electron spectrometer (Murray and Dillard, 1979; Koppelman *et al.*, 1980). An Al anode was used ($h\nu = 1486 \text{ eV}$) to measure the Co 2p binding energies and a Mg anode ($h\nu = 1254 \text{ eV}$), to determine the Auger kinetic energies. These anodes and conditions were necessary because interferences from the oxygen KVV Auger occur in the Co 2p region when using a Mg anode and the Fe 2p levels interfere in the Co Auger region when an Al anode is used. The solids for XPS analysis were prepared by placing an acetone or aqueous suspension of the sample on a brass probe and allowing the liquid to evaporate at room temperature in air. The XPS binding energies were calibrated using background carbon or silicon in the clay. The precision of the binding energy measurements is $\pm 0.1 \text{ eV}$, whereas that for the Co L_{3VV} Auger kinetic energies is $\pm 0.3 \text{ eV}$. The spectra were measured using the MCA (multi-channel analyzer) mode of operation.

Visible diffuse reflectance spectra were measured using a Cary 14 spectrophotometer. The dry powdered samples were placed in standard 10-mm quartz cuvettes and MgO was placed in the reference beam. XRD patterns were obtained using a General Electric model XRD-6 diffractometer and Ni-filtered $\text{CuK}\alpha$ radiation.

RESULTS AND DISCUSSION

The measured binding energies for the Co 2p core levels and the Co L_{3VV} Auger kinetic energies are summarized in Table 2 along with XPS results for selected cobalt compounds. Characteristic Co 2p core-level spectra are presented in Figure 1 for CoAl_2O_4 and for the 10% $\text{Co}(\text{NH}_3)_6\text{Cl}_3/\text{kaolinite}$ product, sample 3. Co 2p XPS spectra for the calcined cobalt(II)-kaolinite samples (samples 1, 2) are similar to those shown in Figure 1. The diffuse visible reflectance spectra for CoAl_2O_4 and for sample 2 are presented in Figure 2. Similar reflectance spectra are recorded for samples 1 and 3.

The XRD results for the calcined samples suggest the presence of CoAl_2O_4 , cristobalite, $\delta\text{-Al}_2\text{O}_3$, and mullite. However,

Table 1. Preparation of calcined cobalt/kaolinite samples.

Sample	Cobalt compound ¹	Wt. kaolinite ² (g)	Temperature (°C)	Time (hr)	Product ³
1	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	90	1050	1.0	CoAl_2O_4 , mullite
2	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	90	1200	2.0	CoAl_2O_4 , mullite, cristobalite
3	$\text{Co}(\text{NH}_3)_6\text{Cl}_3$	90	1050	1.0	CoAl_2O_4 , mullite, $\delta\text{-Al}_2\text{O}_3$

¹ 10.0 g.

² Hydrite PX.

³ X-ray powder diffraction characterization.

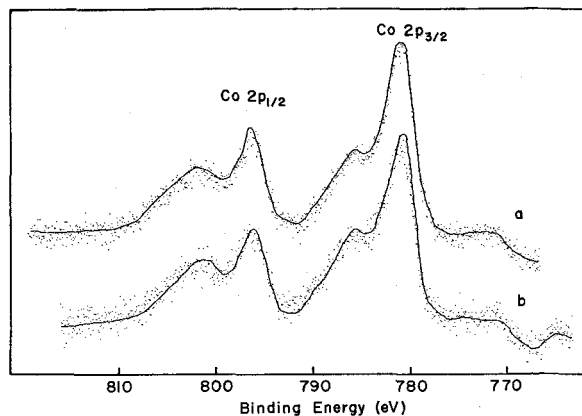


Figure 1. X-ray photoelectron Co 2p spectra: (a) CoAl_2O_4 ; (b) Sample 3.

no attempt was made to quantify the estimates on any of the crystalline phases because of the relatively poor quality of the XRD patterns. The important result is that all cobalt-kaolinite samples contained discrete CoAl_2O_4 .

The visible reflectance spectra (Figure 2) for a calcined sample and for CoAl_2O_4 are indicative of Co(II) in tetrahedral coordination. The absorption maxima correspond to the ${}^4\text{A}_g(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ transition (Figgis, 1966) and are in good agreement with the results for tetrahedral Co(II) in CoAl_2O_4 (Ashley and Mitchell, 1968) and Co(II) in $\text{CoMo}/\text{Al}_2\text{O}_3$ catalysts, where CoAl_2O_4 was produced by calcination (Gajardo *et al.*, 1980). That identical reflectance spectra were obtained for the samples indicates that tetrahedral Co(II) is present in all calcined cobalt-kaolinite materials.

The energy separations and satellite structure of the XPS spectra for Co $2p_{1/2}$ -Co $2p_{3/2}$ and the Co $2p_{3/2}$ binding energies indicate that the chemical environment about cobalt is equivalent in all samples (Figure 1). The intense satellite structure on the high binding-energy side of the main photopeak demonstrates that cobalt is present as Co(II). The Co $2p_{1/2}$ -Co $2p_{3/2}$ splitting of 15.7 eV compares favorably with the value of 16 eV reported by Brinen and Armstrong (1978) for Co(II) in CoAl_2O_4 . That Co(II) is high spin can be shown by examination of the Co $2p_{1/2}$ -Co $2p_{3/2}$ energy difference and Co 2p peak shapes.

Core electron (2p) spectra for low spin (Co(II)) have a Co $2p_{1/2}$ -Co $2p_{3/2}$ splitting of approximately 15.0–15.3 eV and satellite structure of low intensity (Frost *et al.*, 1974; Briggs and Gibson, 1974). For low-spin Co(II) the main $2p_{3/2}$ photopeak is broadened and shows (Frost *et al.*, 1974; Briggs and Gibson, 1974) evidence of two peaks in the $2p_{3/2}$ region arising from multiplet splitting. The features characteristic of low spin Co(II) are not prominent in the Co 2p spectra measured for the calcined cobalt-kaolinite materials (Figure 1). The XPS Co 2p splitting data are consistent with the presence of high-spin Co(II) where the Co(II) environment is tetrahedral and similar to that in CoAl_2O_4 .

In a study of CoAl_2O_4 , McIntyre and Cook (1975) measured a binding energy of 780.6 eV for the Co $2p_{3/2}$ level, whereas Gajardo *et al.* (1980) reported a value of 781.0 eV for a catalyst which contains CoAl_2O_4 . The good agreement for the Co $2p_{3/2}$ binding energies and similar appearance of the satellite features for calcined cobalt-kaolinite materials with those published for CoAl_2O_4 by McIntyre and Cook (1975) and Gajardo *et al.* (1980) support the conclusion that CoAl_2O_4 is present in the cobalt-kaolinite samples.

The shake-up satellite structure for cobalt is associated with

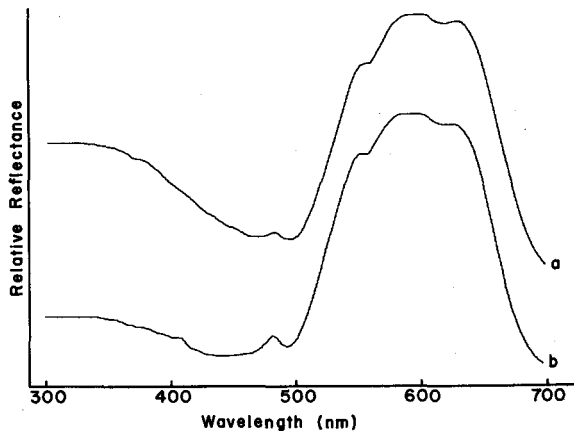


Figure 2. Visible reflectance spectra: (a) Sample 2; (b) CoAl_2O_4 .

charge-transfer excitation of the type, ligand \rightarrow metal (Frost *et al.*, 1974; Kim, 1975; Brisk and Baker, 1975). The energy separation between the satellite peak and the main 2p photopeak is related to the bonding nature of cobalt. Frost *et al.* (1974) found a general decrease in satellite separation as the bonding becomes more covalent for CoF_2 , CoCl_2 , CoBr_2 , and CoI_2 . In the calcined cobalt-kaolinite samples the satellite separation for the $2p_{3/2}$ level (Table 2) is approximately 4.7 eV for each material. The separation is less than that reported by Kim (1975) for CoO (6.3 eV) and by Koppelman and Dillard (1978) for Co adsorbed on chlorite (5.2 eV), but is in good agreement with the value reported by McIntyre and Cook (1975) for CoAl_2O_4 . These data indicate that cobalt bonding in the cal-

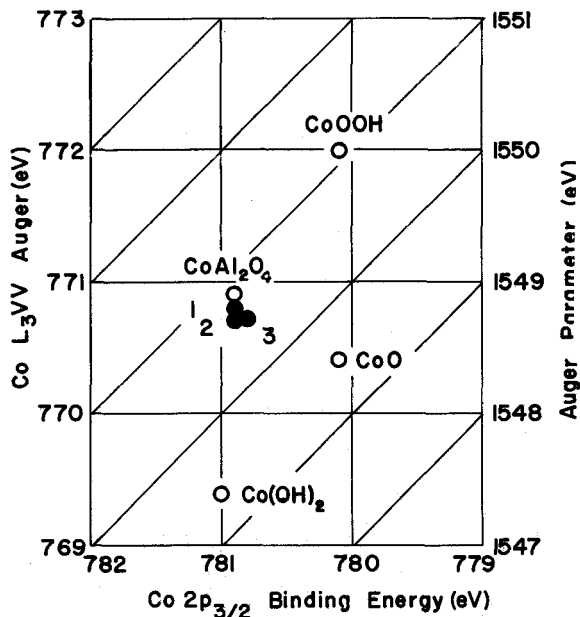


Figure 3. Wagner chemical-state plot: Co $2p_{3/2}$ binding energy vs. Co L_{3VV} Auger energy. Open circles = reference compounds, closed circles = calcined cobalt-kaolinite samples.

Table 2. XPS binding energy and Auger results.

Sample	Binding energy (BE)Co 2p _{3/2} (eV)	ΔBE (Co 2p _{1/2} -Co 2p _{3/2}) (eV)	ΔE (Co 2p _{3/2} (sat)-main) (eV)	Co (L ₃ VV) Auger kinetic energy (eV)
1	780.9	15.7	4.7	770.8
2	780.9	15.7	4.7	770.7
3	780.8	15.7	4.6	770.7
CoAl ₂ O ₄	780.9	15.6	4.7	770.9
CoO	780.1	15.9	6.3 ¹	770.4
Co(OH) ₂	781.0	16.0	5.8	769.4
CoOOH	780.1	15.0		772.0

¹ Kim, 1975.

calcined sample is similar in covalency to that in CoAl₂O₄ and that tetrahedral cobalt is bound more covalently than octahedral cobalt in CoO or than Co(II) adsorbed on clays.

A comparison of the XPS results can be made also with the results for tetrahedral cobalt(II) in Co₃O₄. From the XPS spectrum of Co₃O₄, Chuang *et al.* (1976) reported a Co 2p_{1/2}-Co 2p_{3/2} energy separation, of 15.3 eV, a Co 2p_{3/2} binding energy of 780.7 eV, and a satellite-main Co 2p_{3/2} peak separation of 8.8 eV for tetrahedral Co(II). The results of Chuang *et al.* (1976) may be compared with our corresponding values of 15.7 eV, 780.7 eV, and 4.7 eV for the spectral parameters for the calcined cobalt-kaolinite samples. For cobalt-kaolinite materials the satellite intensity is greater than for Co₃O₄ (Chuang *et al.*, 1976). This result is related to the smaller satellite to main 2p photopeak separation (4.7 eV) in that the ligand (oxygen) to metal charge transfer occurs at a lower energy and also has a greater transition probability (Kim, 1975; Frost *et al.*, 1974; Brisk and Baker, 1975). Thus, cobalt in calcined cobalt-kaolinite is more covalently bonded than tetrahedral Co in Co₃O₄ as indicated by greater satellite intensity and smaller satellite-main peak separation. That the calcined cobalt-kaolinite XPS data are not equal to those for Co₃O₄ also demonstrates that Co₃O₄ was not formed in the materials prepared in this study.

Wagner *et al.* (1979) suggested the use of the Auger parameter for identifying chemical species. An advantage of studying Auger processes is that the shifts in Auger kinetic energy among a given group of compounds are commonly greater than the shifts in core-level binding energies, and the Auger processes involving valence electrons are expected to be strongly influenced by alterations in the mode of bonding (Wagner *et al.*, 1979). The Co L₃VV Auger kinetic energy and the Co 2p core-electron binding-energy data are presented in Figure 3 in the format suggested by Wagner *et al.* (1979) to aid in identifying the dominant surface species. The positions for the calcined cobalt-kaolinite samples are in the region characteristic of CoAl₂O₄. Recognizing that the precision for determining the Auger kinetic energy is ±0.3 eV, and that other results presented herein are characteristic of high-spin tetrahedral Co(II), as in CoAl₂O₄, it is concluded that the cobalt-containing surface species is CoAl₂O₄.

In summary, the data indicate that the Co XPS spectra for calcined cobalt-kaolinite materials are characteristic of high-spin tetrahedral Co(II). The Co L₃VV Auger, Co 2p binding energies, and satellite features are supportive of surface cobalt in a covalent, electron-rich bonding environment when compared to selected Co(II) model compounds. The XPS data correspond closely to the results obtained for CoAl₂O₄ and suggest that surface CoAl₂O₄ is present on calcined cobalt-kaolinite materials.

ACKNOWLEDGMENT

We thank the Office of Water Resources and Technology for partial support of this work under Grant No. B-119 VA.

Department of Chemistry
Virginia Polytechnic Institute
and State University
Blacksburg, Virginia 24061

JOHN G. DILLARD
CATHERINE V. SCHENCK
MITCHELL H. KOPPELMAN¹

¹ Present address: Georgia Kaolin Company, Springfield, New Jersey 07081.

REFERENCES

- Ashley, J. H. and Mitchell, P. C. H. (1968) Cobalt-molybdenum-alumina hydrodesulfurization catalysts. Part 1. A spectroscopic and magnetic study of the fresh catalyst and model compounds: *J. Chem. Soc. A*, 2821-2827.
- Bancroft, G. M., Brown, J. R., and Fyfe, W. S. (1979) Advances in, and applications of, X-ray photoelectron spectroscopy (ESCA) in mineralogy and geochemistry: *Chem. Geol.* **25**, 227-243.
- Briggs, D. and Gibson, V. A. (1974) Direct observation of multiplet splitting in 2p photoelectron peaks of cobalt complexes: *Chem. Phys. Lett.* **25**, 493-496.
- Brinen, J. S. and Armstrong, W. D. (1978) Surface chemistry of activated hydrodesulfurization catalysts by X-ray photoelectron spectroscopy: *J. Catal.* **54**, 57-65.
- Brisk, M. A. and Baker, A. D. (1975) Shake-up satellites in X-ray photoelectron spectroscopy: *J. Electron Spectrosc. Relat. Phenom.* **7**, 197-213.
- Chuang, T. J., Brundle, C. R., and Rice, D. W. (1976) Interpretation of the X-ray photoemission spectra of cobalt oxides and cobalt oxide surfaces: *Surface Sci.* **59**, 413-429.
- Declercq-Grimee, R. I., Canesson, P., Friedman, R. M., and Fripiat, J. J. (1978) An X-ray photoelectron spectroscopy study of various CoMo/Al₂O₃ hydrodesulfurization catalysts: *J. Phys. Chem.* **82**, 889-894.
- Dillard, J. G. and Koppelman, M. H. (1982) X-ray photoelectron spectroscopic (XPS) surface characterization of cobalt on the surface of kaolinite: *J. Colloid Interface. Sci.* (in press).
- Figgis, B. N. (1966) *Introduction to Ligand Fields*: Wiley Interscience, New York, p. 239.
- Frost, D. C., McDowell, C. A., and Woolsey, I. S. (1974) X-ray photoelectron spectra of cobalt compounds: *Mol. Phys.* **27**, 1473-1489.
- Gajardo, P., Grange, P., and Delmon, B. (1980) Structure of oxide CoMo/γ-Al₂O₃ hydrodesulfurization catalysts: an XPS and DRS study: *J. Catal.* **63**, 201-216.
- Harvey, D. T. and Linton, R. W. (1981) Chemical characterization of hydrous ferric oxides by X-ray photoelectron spectroscopy: *Anal. Chem.* **53**, 1684-1688.
- Kim, K. S. (1975) X-ray photoelectron spectroscopic studies of the electronic structure of CoO: *Phys. Rev.* **B 11**, 2177-2185.
- Koppelman, M. H. and Dillard, J. G. (1978) An X-ray photoelectron spectroscopic (XPS) study of cobalt adsorbed on the clay mineral chlorite: *J. Colloid Interface Sci.* **66**, 345-351.
- Koppelman, M. H. and Dillard, J. G. (1979) The application of X-ray photoelectron spectroscopy (XPS or ESCA) to the study of mineral surface chemistry: in *Proc. Int. Clay Conf., Oxford, 1978*, M. M. Mortland and V. C. Farmer, eds., Elsevier, Amsterdam, 153-166.
- Koppelman, M. H., Emerson, A. B., and Dillard, J. G. (1980)

- Adsorbed Cr(III) on chlorite, illite, and kaolinite: an XPS study: *Clays & Clay Minerals* **28**, 119–124.
- Lunsford, J. H., Hutta, P. J., Lin, M. J., and Windhorst, K. A. (1978) Cobalt nitrosyl complexes in zeolites A, X, and Y: *Inorg. Chem.* **17**, 606–610.
- McIntyre, N. S. and Cook, M. G. (1975) X-ray photoelectron studies on some oxides and hydroxides of cobalt, nickel, and copper: *Anal. Chem.* **47**, 2208–2213.
- McIntyre, N. S. and Tewari, P. H. (1977) Comments on “adsorption of Co(II) . . .”: *J. Colloid Interface Sci.* **59**, 195–196.
- Murray, J. W. and Dillard, J. G. (1979) The oxidation of cobalt(II) adsorbed on manganese dioxide: *Geochim. Cosmochim. Acta* **43**, 781–787.
- Tewari, P. H. and Lee, W. (1975) Adsorption of Co(II) at the oxide-water interface: *J. Colloid Interface Sci.* **52**, 77–88.
- Wagner, C. D., Gale, L. H., and Raymond, R. H. (1979) Two dimensional chemical state plots: a standardized data set for use in identifying chemical states by X-ray photoelectron spectroscopy: *Anal. Chem.* **51**, 466–482.

(Received 24 August 1981; accepted 15 April 1982)