JOURNAL OF CATALYSIS 44, 335–337 (1976)

Some Remarks Concerning the X-Ray Photoelectron Spectra of the Co–Mo–Al_2O_3 Hydrodesulfurization Catalyst System[1]

The recent application of X-ray photoelectron spectroscopy (XPS) to the characterization of Co–Mo–Al_2O_c hydrodesulfurization catalysts has produced several interesting results (*2–6*). From the measurement of the Mo 3*d* binding energies of the oxidized catalysts, it is clear that molybdenum is present as Mo(VI). Hydrogen reduction of these catalysts at 400°C leads to the formation of lower oxidation state species, probably Mo(V) and Mo(IV) (*3, 4, 6*), a result which is also characteristic of the MoO_3/γ-Al_2O_3 system (*4, 7*). Reduction and sulfiding of the catalyst shifts the Mo 3*d* peaks to lower energies (*2, 3, 6*), the magnitude of this shift being consistent with the formation of MoS_2 (*3, 6, 8*). While this is a perfectly reasonable interpretation, it is interesting to note that in view of the relatively small spread of Mo 3*d* binding energies within the series of thioanions MoS_4^{2-}, $MoOS_3^{2-}$, and $MoO_2S_2^{2-}$ (*9*), the presence of mixed molybdenum oxysulfide species on the catalyst surface cannot be ruled out.

In contrast to the general agreement on the interpretation of the Mo 3*d* chemical shifts associated with the molybdenum component of the Co–Mo–Al_2O_3 catalysts, related measurements (*3, 5*) of the Co 2*p* binding energies permit less clear-cut assignments as to the nature of the cobalt. Thus, Friedman *et al.* (*3*) observed a single Co $2p_{3/2}$ peak in the XPS of the oxidized Co–Mo–Al_2O_3 catalyst, while Ratnasamy (*5*) reported the presence of three Co $2p_{3/2}$ peaks. These data, together with related results for other relevant cobalt–oxygen phases, are summarized in Table 1. When necessary, the literature data have been "corrected" so that the binding energies are quoted relative to the commonly accepted (*10*) Au $4f_{7/2}$ or C 1*s* binding energy standards of 83.8 and 285.0 eV, respectively.

Although differences in surface charging effects make a direct comparison of measured Co $2p_{3/2}$ binding energies from different sources of questionable value, it is useful to consider the individual sets of results. Friedman *et al.* (*3*) consider that the 782.0 eV peak (Table 1) arises from a close coincidence of the Co $2p_{3/2}$ binding energies of $CoAl_2O_4$ and some other (as yet unidentified) cobalt(II) species which is the source of the "active" cobalt sites during the sulfiding process. The higher energy peak at 786.7 eV, which is always present in the XPS spectra of these catalysts but which was not previously assigned (*3*), must be due to a shake-up satellite, arising from the charge transfer excitation O(2*p*) → Co(3*d*) (*11*). For CoO (*12, 13*), $CoAl_2O_4$ (*13*), and other cobalt(II) compounds (*13, 14*), satellite structure is usually located at ~5 eV to the high binding energy side of the primary photoionization peak.

Ratnasamy (*5*) has assigned the 786.9 eV binding energy (Table 1) to "Co^{2+} ions in coordination with strongly bound water molecules." This interpretation is clearly in error since in studies on the Co 2*p*

TABLE 1

Cobalt $2p_{3/2}$ Binding Energies (in eV) of Co–Mo–Al_2O_3 Catalysts and Related Systems

Phase	Co $2p_{3/2}$	Satellite	Reference source
Co–Mo–Al_2O_3	782.0^a	786.7^a	*3*^{c}
	782.5,^{b} 783.4^b	786.9^b	*5*
$CoAl_2O_4$	783.2^b		*5*
CoO	780.0^a	786.3^a	*12*
	780.3^b	785.8^b	*13*
Co_3O_4	779.6^b	789.1^b	*13*
Co_2O_3	779.4^b	788.3^b	*13*

[a] Relative to Au $4f_{7/2} = 83.8$ eV.

[b] Relative to C $1s = 285.0$ eV of carbon contaminant.

[c] Data reported very recently in Ref. *6* closely resemble those reported earlier in Ref. *3*.

energies of $[Co(H_2O)_6]Cl_2$, $Co(OH)_2$, and CoO, it has been shown (*14*) that the Co $2p_{3/2}$ energies occur within a few tenths of an eV of one another. The weak 786.9 eV peak must therefore be a shake-up satellite (*11*) which is associated with one of the primary photoionization peaks at ~783 eV (Table 1). While the assignment (*5*) of the 783.4 eV binding energy (Table 1) to the $CoAl_2O_4$ component of the catalyst is not unreasonable, the origin of the lowest energy peak at 782.5 eV remains something of a mystery. There is no evidence from the XPS studies to support the suggestion by Ratnasamy (*5*) that it is due to the presence of CoO. Indeed, it has previously been shown (*13*) that it is very difficult to distinguish the oxide phases CoO, Co_2O_3, and Co_3O_4 from the value of the Co $2p_{3/2}$ energy alone. However, the shake-up satellite associated with the Co $2p_{3/2}$ peak of CoO is located at between 5.5 and 6.3 eV to higher energy of the primary peak (*12*), whereas a much larger separation (~9 eV) is characteristic of Co_2O_3 and Co_3O_4 (*13*). Consequently, without this additional information it is not justified to make such specific assignments of surface species from XPS alone.

In the reduction and sulfiding stage of treatment of the Co–Mo–Al_2O_3 catalyst, the appearance of a Co $2p_{3/2}$ peak to the low binding energy side of the peak due to the unreactive $CoAl_2O_4$ phase was attributed (*3*) to some cobalt species which had been both reduced and sulfided by the H_2/H_2S treatment. It should be noted that the Co $2p_{3/2}$ chemical shift between CoO and CoS is -2.4 eV (*14*), a value which is almost identical to the related shift of the Co $2p_{3/2}$ energy which occurs upon "reducing and sulfiding" the Co–Mo–Al_2O_3 catalyst (*3*). Consequently, it can be argued that from the XPS results there is no evidence that the cobalt(II) has been reduced. Recent work on the XPS of the MoS_2–Co_9S_8 system (*15*) adds a further complication, since no Co peaks were observed in the spectrum. This once again emphasizes one of the disadvantages of the XPS technique, namely, its failure to detect species which are no longer present on the "surface."

ACKNOWLEDGMENTS

Support from the National Science Foundation (Grant No. CHE 74-12788A02) and the NSF-MRL Program (DMR72-03018A04) is gratefully acknowledged.

REFERENCES

1. Part I of a series entitled the "The X-Ray Photoelectron Spectra of Heterogeneous Catalysts."
2. Armour, A. W., Mitchell, P. C. H., Folkesson, B., and Larson, R., *J. Less-Common Metals* **36**, 361 (1974).
3. Friedman, R. M., Declerck-Grimee, R. I., and Fripiat, J. J., *J. Electron Spect. Relat. Phenom.* **5**, 437 (1974).
4. Cimino, A., and De Angelis, B. A., *J. Catal.* **36**, 11 (1975).
5. Ratnasamy, P., *J. Catal.* **40**, 137 (1975).
6. Patterson, T. A., Carver, J. C., Leyden, D. E., and Hercules, D. M., *Spect. Lett.* **9**, 65 (1976).
7. Aptekar', E. I., Chudinov, M. G., Alekseev, A. M., and Krylov, O. V., *React. Kinet. Catal. Lett.* **1**, 493 (1974).
8. Stevens, G. C., and Edmonds, T., *J. Catal.* **37**, 544 (1975).

9. Muller, A., Jørgensen, C. K., and Diemann E., *Z. Anorg. Chem.* **391**, 38 (1972).
10. Johansson, G., Hedman, J., Berndtsson, A., Klasson, M., and Nilsson, R., *J. Electron Spect. Relat. Phenom.* **2**, 295 (1973).
11. Kim, K. S., *J. Electron Spect. Relat. Phenom.* **3**, 217 (1974).
12. Kim, K. S., *Phys. Rev.* **B11**, 2177 (1975).
13. Okamoto, Y., Nakano, H., Imanaka, T., and Teranishi, S., *Bull. Chem. Soc. Japan* **48**, 1163 (1975).
14. Frost, D. C., McDowell, C. A., and Woosley, I. S., *Mol. Phys.* **27**, 1473 (1974).
15. Canesson, P., and Grange, P., *C. R. Acad. Sci., Ser. C*, **281**, 757 (1975).

R. A. Walton

Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Received April 28, 1976