JOURNAL OF CATALYSIS 56, 99–109 (1979)

X-Ray Photoelectron Spectroscopic Study of Unsupported Cobalt–Molybdenum Sulfide Catalysts

G. DELVAUX, P. GRANGE, AND B. DELMON

Groupe de Physico-Chimie Minérale et de Catalyse, Université Catholique de Louvain,
Place Croix du Sud 1, 1348 Louvain-la-Neuve, Belgium

Received November 10, 1977; revised June 19, 1978

X-Ray photoelectron spectroscopic (XPS) measurements have been made on unsupported, fully sulfided, cobalt–molybdenum catalysts which had previously operated catalytically until attainment of steady activity. Total sulfur content and intrinsic activity for hydrogenolysis of thiophene, for hydrogenation of cyclohexene and for isomerization of cyclohexane are also reported. The entire range of concentration $0.0 < r < 1.00$, where $r = \text{Co}/(\text{Co} + \text{Mo})$, has been investigated. There exists a good correlation between XPS and catalytic activity measurements. Two concentration domains can be distinguished. In the low cobalt concentration range there is an increase in the binding energy of the Mo $3d_{3/2}$, Mo $3d_{5/2}$, and S $2p_{3/2-1/2}$ levels. In the range of concentration where the catalysts exhibit a strong synergy for hydrogenolysis and isomerization, the binding energy of these levels decreases. Furthermore, the sulfur content is maximum. The formation of a reduced species with a charge between Mo^{4+} and Mo^{3+}, which could be involved in the active sites, has been postulated.

INTRODUCTION

We have previously shown that unsupported cobalt sulfide–molybdenum sulfide catalysts prepared by different methods present many similarities with the usual supported ones (*1–7*). By studying, in comparison with supported catalysts, the more simple system which unsupported sulfides represent, we have thus tried to elucidate some of the characteristics of a group of catalysts which is of prime importance in hydrodesulfurization and hydrotreating of petroleum fractions.

Electron spectroscopy has proved valuable for the physicochemical study of supported hydrodesulfurization catalysts (*8–17*). The method is extremely useful for indicating interactions between the active phases and the support. However, the features pertaining to the active phases themselves and their mutual interactions are blurred by those arising because of the presence of the support, especially because of the broadening of the lines. Preliminary results indicated that X-ray photoelectron spectroscopy (XPS) was able to provide particularly valuable information on unsupported catalysts (*18*).

This work concerns unsupported fully sulfided, cobalt–molybdenum catalysts. Special attention was given to the phenomena occurring in catalysts containing a small amount of cobalt [with atomic ratio $r = \text{Co}/(\text{Co} + \text{Mo}) < 0.10$] and in catalysts having the composition $0.15 < r < 0.50$ corresponding to the synergetic effect, namely, an important enhancement of the catalytic activity in hydrogenolysis of thiophene and in hydrogenation of unsaturated hydrocarbons. A distinctive feature of the present work is that the catalysts had been operating previously, until

0021-9517/79/010099-11$02.00/0

attainment of steady activity, in a model reaction and were then transferred without contact with the atmosphere to the ESCA equipment. Catalytic activities per unit surface area of the catalysts are also reported.

EXPERIMENTAL METHODS

1. Preparation of the Catalyst

The so-called "co-maceration method" was used for the preparation of the catalysts (*1*, *2*). Molybdenum oxide (MoO_3) and cobalt oxide (Co_3O_4) were co-digested in an aqueous ammonium sulfide solution for 6 hr at 70°C. The compounds obtained were subsequently heated under a H_2S–Ar atmosphere for 4 hr at 400°C before evacuation.

Nine catalysts were prepared covering the range of composition $r = \mathrm{Co}/(\mathrm{Co} + \mathrm{Mo})$ from 0 to 1. Compositions were confirmed by atomic absorption measurements.

2. Analyses of the Sulfur Content

The total sulfur content of the samples before they had operated catalytically was measured gravimetrically. The fresh catalysts were dissolved in aqua regia, where sulfur was transformed to sulfuric acid. The sulfate ions were precipitated in the form of $BaSO_4$ by $BaCl_2$ and weighed.

3. Surface Area Measurements

Surface area measurements were made by gravimetric nitrogen adsorption and the BET method.

4. XPS Measurements

Before the ESCA measurements, the catalysts were contacted with a model, sulfur-containing, hydrocarbon feed (see below, Section 5) under atmospheric pressure for 20 hr. Unfortunately, because of the necessity to transfer the catalyst to the ESCA equipment without contamination it was not possible to use the high pressure equipment, but only all-glass, atmospheric pressure equipment. However, except for the pressure, all conditions were equivalent to those used in the high pressure catalytic activity measurements. The length of the catalytic run (20 hr) was sufficient to reach a stable activity.

After the catalytic run, the catalysts were sealed off from the atmospheric pressure equipment under vacuum and transferred to a glove box attached to the ESCA apparatus.

The electron spectrometer was a Vacuum generators ESCA 2 instrument. The samples were gently ground under dry nitrogen in the glove box, placed on a platinum plate, and introduced into the measuring chamber. The exciting radiation was $\mathrm{Al}K\alpha$ ($h\nu = 1486.6$ eV). The electrostatic analyzer energy was set at 90 eV. Accumulation of the spectra was realized with Tracor Northern NS 560 equipment. Gold, evaporated onto the sample, was used as a reference. The reference line was Au $4f_{7/2}$ ($h\nu = 82.8$ eV). Spectra were registered before and after gold evaporation in order to check that the gold evaporation process did not modify the sample. Accumulation time depends on the samples and on the elements. It is approximately between 4 and 10 min for Au, 10 and 20 min for Mo and S, and 3 and 12 hr for Co. No change was observed among the intensities observed in successive scanning during the accumulation period for Au, Mo and S. Because of the much longer accumulation time for cobalt and the fact that accumulation took place during the night, we have no direct indication concerning cobalt, but we have verified that the spectra of the other elements are not altered after recording the Co spectrum.

The minimum number of hypotheses have been used for the decomposition of the spectra, which was carried out on an IBM computer with a special program. The only condition imposed for the Mo $3d_{\frac{3}{2}}$, Mo $3d_{\frac{5}{2}}$, and S $2p_{\frac{1}{2}}$ lines is that they have a Gaussian form, which is the case with the

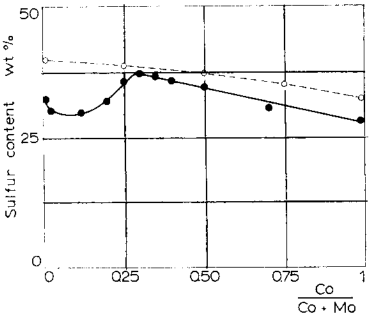

FIG. 1. Sulfur content as a function of catalyst composition. (○) Calculated on the basis of $MoS_2 + Co_9S_8$. (●) Experimental.

equipment used and the conditions of measurements. For S $2p_{\frac{3}{2}}$ and S $2p_{\frac{1}{2}}$, it was imposed that the peaks have the same width at half-height and be at a distance of 1.374 eV from each other. Each cobalt line has two strong satellites. The distance between the peaks is in agreement with the values previously reported (*8, 13, 14–17*). The value of the half-width depends on the apparatus used. They have been determined experimentally on pure Co_3O_4 (*17*). The same width at half-height was imposed to Co $2p_{\frac{1}{2}}$ and Co $2p_{\frac{3}{2}}$ and the half-height width of the second satellite was set at 1.44 times that of the first satellite. Distances of 6.46 and 6.16 eV were imposed between the satellites of Co $2p_{\frac{1}{2}}$ and Co $2p_{\frac{3}{2}}$, respectively. The baseline was determined by the integral method (*17*).

The position of the peak is given by the computer program as the position of the maximum of the Gaussian curve. Reproducibility of measurements with two different portions of the same sample and computer decomposition of the curves is better than 0.05 eV. This good reproducibility comes from the use of a platinum plate as a support for the sample.

The intensity of the line is the area under the Gaussian curve.

5. Catalytic Activity Measurements

Catalytic activity measurements were made, as previously, with a model feed containing cyclohexane 70% (by weight) and cyclohexene 30% (by weight), to which 5000 ppm thiophene were added. Pressure was 30 bar, with a space hourly velocity of 20. The H_2 (gas NTP)/hydrocarbons (liquid) ratio was 600 (*1*).

Catalytic activity is expressed as intrinsic (or real) activity, i.e., activity per unit surface area of the catalysts.

For preparation of the samples analyzed by XPS, the same conditions were used at atmospheric pressure.

RESULTS

1. Sulfur Content of the Fresh Catalysts

Figure 1 is a plot of the total sulfur analyses of the samples vs the Co/(Co + Mo) ratios. The dotted line corresponds to the theoretical content of a mixture of MoS_2 and Co_9S_8. The measured sulfur content is always below theoretical. There is a marked maximum for sulfur content in the composition range $0.25 < r < 0.50$.

2. Specific Surface Area

Specific surface area is plotted vs composition r in Fig. 2. Conspicuous features are the strong decrease in surface area with catalysts containing a small amount of cobalt and the maximum in the range $0.15 < r < 0.50$.

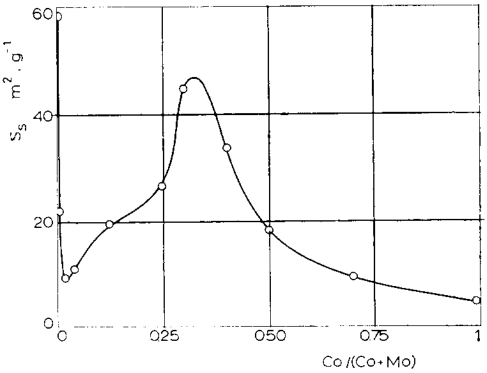

FIG. 2. Surface area as a function of catalyst composition.

3. XPS Results

XPS spectra indicate that no detectable contamination of the samples during their transfer from the catalytic reactor to the ESCA equipment has taken place. There is no line corresponding to the sulfate ion (*19*), the line which appears first in contaminated samples, nor is there a signal corresponding to the O line. Gold deposition brings about neither broadening of the lines of the other elements, nor detectable displacement of these lines with respect to one another. We are therefore led to conclude that gold deposition does not perturb the surface of the catalysts and that XPS data correspond really to the surface of the catalyst after they have operated.

Figure 3 shows an example of a typical spectrum. We have illustrated the spectrum of Mo, Co, and S recorded for the 0.30 catalyst. The two peaks Mo $3d_{5/2}$ and Mo $3d_{3/2}$ are well separated. It is the same for the Co $2p_{1/2}$ and Co $2p_{3/2}$ peaks but the resolution of the satellites of the second peak is not good. For the sulfur, the main peak is attributed to the S $2p_{3/2}$ level and the shoulder, to the S $2p_{1/2}$ peak.

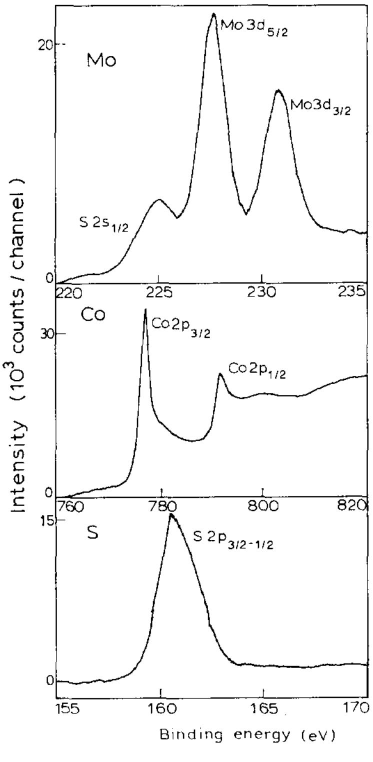

FIG. 3. XPS spectra of the sample $r = 0.30$ (254 channels for each scanning).

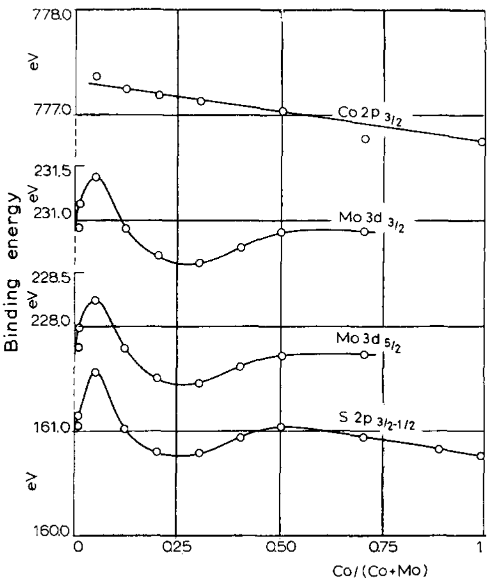

FIG. 4. Binding energy as a function of catalyst composition.

The values obtained correspond fairly well to those reported by various authors (*8–17*). However, very marked variations

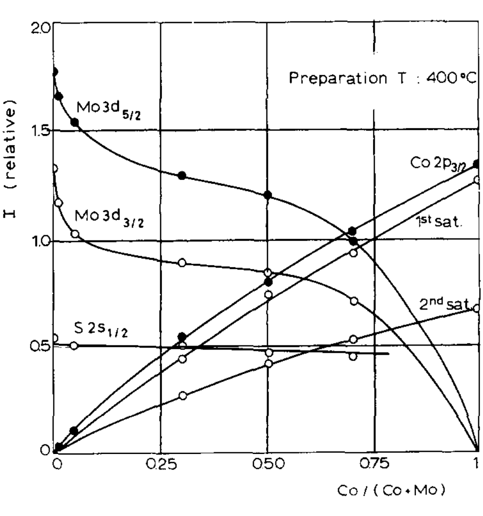

FIG. 5. Intensity of XPS peaks as a function of catalyst composition.

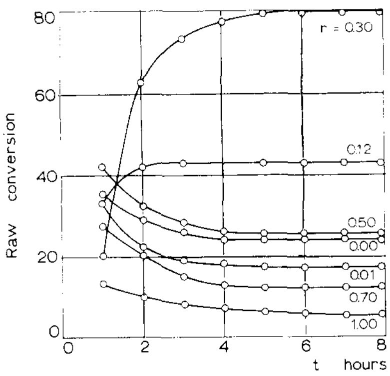

FIG. 6. Hydrogenolysis of thiophene as a function of time.

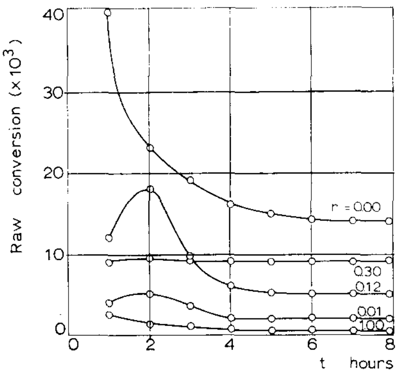

FIG. 8. Isomerization of cyclohexane as a function of time.

in the position of the lines with composition of the catalyst can be observed. Figure 4 indicates a gradual decrease in the binding energy of Co $2p_{3/2}$ and a more complicated variation in the binding energies of Mo $3d_{3/2}$, Mo $3d_{5/2}$, and S $2p_{3/2-1/2}$. A marked increase in the binding energies is observed on catalysts with small Co content, and a minimum is observed for $0.15 < r < 0.50$. Comparison of the intensities of the XPS lines is possible when taking the ratio of the surface area of a given peak to that of the S $2p_{3/2-1/2}$ peak. Figure 5 is the plot obtained for S $2s_{1/2}$, Mo $3d_{3/2}$, Mo $3d_{5/2}$, and Co $2p_{3/2}$ versus composition. There is no special feature concerning the latter line; one merely observes a regular increase with cobalt content. The figure suggests a slight decrease in the intensity of the S $2s_{1/2}$ line. We do not believe the results to be sufficiently accurate for giving a real significance to this observation. Actually, no such variation was observed on fully sulfided, supported catalysts [Ref. (*20*)]. The sigmoidal shape of the Mo lines deserves more attention.

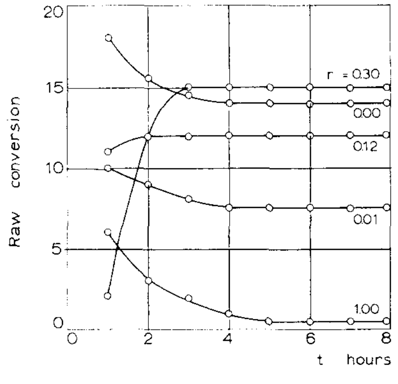

FIG. 7. Hydrogenation of cyclohexene as a function of time.

4. Catalytic Activity

Figures 6, 7, and 8 give typical activity variations for catalysts with different compositions versus time in the hydrogenolysis of thiophene, the hydrogenation of cyclohexene, and the isomerization of cyclohexane (high pressure equipment).

Activities stabilize after a few hours, 5 hr in the most unfavorable cases. Stable intrinsic (per unit surface area) activities measured after 8 hr are plotted in Figs. 9, 10, and 11 versus composition of the catalyst.

DISCUSSION

A general remark is that all types of measurements on cobalt-molybdenum sulfide catalysts point to the two conspicuous ranges of composition which we had already investigated, namely, the low concentration range ($r < 0.10$) and the synergetic range ($0.15 < r < 0.50$). Almost invariably, anomalies are observed in these composition ranges.

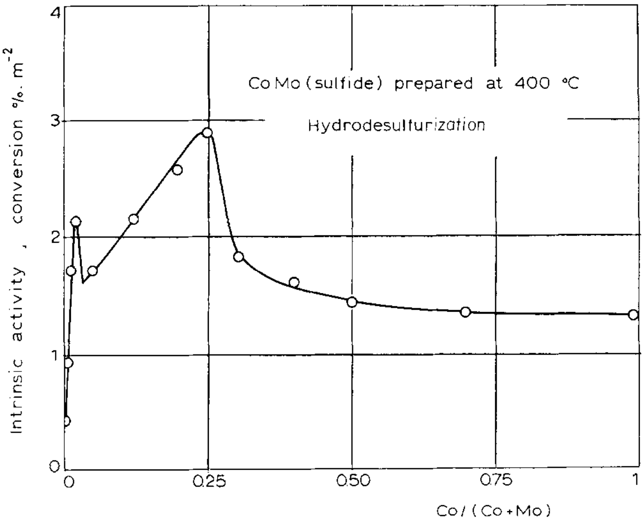

FIG. 9. Stable intrinsic activities in the hydrogenolysis of thiophene.

Our results concerning sulfur content were obtained on fresh samples which had not been specially protected against contact with air. Although we have no indication of any loss of SO_2 (usually, the formation of sulfate ions is observed in ESCA on samples contacted with air, and these sulfate ions would be weighed together with those resulting from reaction with aqua regia), some slight error may exist in our results. However, this error should be similar in all the samples and the shape of the curve in Fig. 1 would not be altered. Nevertheless not too much emphasis should be put on these results, because we presume that an important change in sulfur content takes place during catalysis. For that reason, the corresponding discussion will be short.

It need only be mentioned that both the decrease in sulfur content for low cobalt concentrations and the increase in the

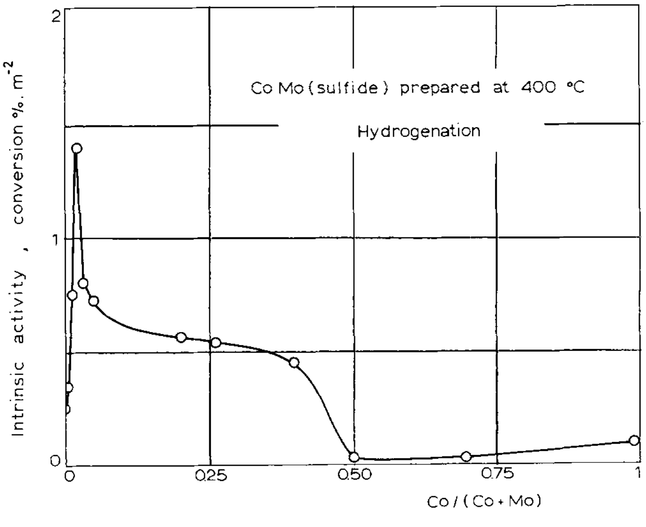

FIG. 10. Stable intrinsic activities in the hydrogenation of cyclohexene.

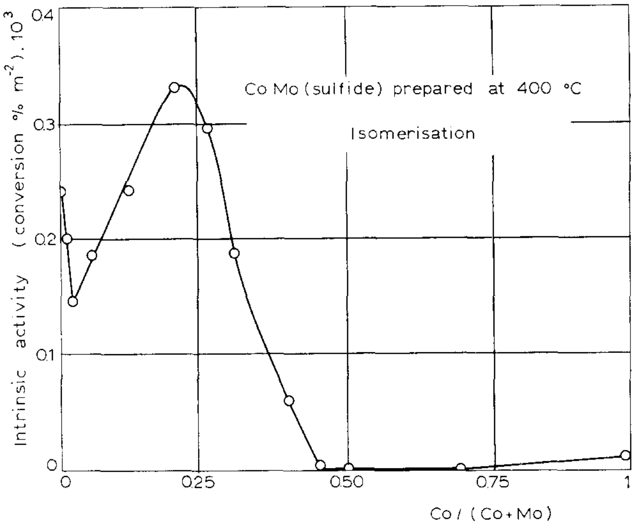

FIG. 11. Stable intrinsic activities in the isomerization of cyclohexene.

synergetic range agree with the observations of Furimsky and Amberg (*20*) on unsupported sulfide catalysts prepared by another method. The observations are related only to the genesis of the sulfide mixtures. We have no indications, from our investigations, on the solid-state chemistry of the genesis of the mixed catalysts which could explain the sulfur content anomalies.

The subsequent discussion will consider, separately, the cobalt low concentration range and the synergetic range.

Low Cobalt Concentration

The cobalt low concentration range is characterized by a strong decrease in specific surface area, strong anomalies in *intrinsic* activity, and an increase in ESCA binding energies of the Mo and S signals.

Whereas the raw catalytic activities (per weight of catalyst) always decrease when small amounts of cobalt are present, the feature is more complicated when intrinsic activities (per unit surface area) are considered. There is a maximum in the hydrogenolysis activity, a strong maximum in hydrogenation, and a decrease in isomerization. This indicates that different functions, or possibly sites, are involved and that the addition of cobalt changes differently the balance of the various reactions. The observation of a strong maximum in hydrogenation compares with a similar increase mentioned by Farragher and Cossee (*22*) on WS_2/Ni. The results presented by these authors during the discussion of their papers as well as our previous results (*24*) suggest that catalysts prepared at higher temperatures no longer exhibit the strong maximum of the hydrogenating activity in the cobalt low concentration range, but rather a modest increase followed by a strong maximum in the synergetic range. Thus, the shape of the hydrogenation curve is extremely sensitive to the preparation temperature.

On the other hand, the hydrogenolysis activity in the low concentration range is well below that in the synergetic range (Fig. 9).

The drastic decrease in surface area in the low concentration range (Fig. 2) corresponds to the increased crystallinity of MoS_2 previously mentioned (*2*) and also indicated by other authors (*22*). Similar results are obtained with all systems active in hydrodesulfurization, i.e., MoS_2 or WS_2 associated with Co, Ni, or Fe (*23, 24*). The decrease in surface area, however, does not agree with observations of other authors on unsupported systems prepared by another method (*22*).

The decrease in the relative intensity of the Mo XPS lines indicates that the surface area developed by MoS_2 decreases with respect with the total surface area of the catalyst. This means that the surface developed by Co_9S_8 becomes rapidly significant with respect to that of MoS_2.

The increase in binding energy for Mo and S observed in XPS is most simply interpreted by a slight modification of the formal oxidation state of those elements on the surface of the catalysts. We may describe the corresponding ions as carrying an extra positive charge $+\epsilon$, i.e., $Mo^{4+(+\epsilon)}$ and $S^{2-(+\epsilon)}$. This may correspond to the formation of molybdenum partially in the Mo^{5+} state and sulfur in the disulfide $(S\text{–}S)^{2-}$ form. Expressed this way, these results confirm previous findings (*25–27*).

We had expressed the hypothesis that cobalt entered the MoS_2 lattice in the low concentration range (*2*). This would explain the decrease in the *c* parameter of the lattice observed for MoS_2 with Co(*2*) and with Ni (*23*), as well as similar phenomena observed with similar unsupported hydrodesulfurization catalysts (*24*). A substitution of cobalt for molybdenum in the MoS_2 layers is possible, account being taken of the size and allowed coordination of the cobalt ion (*22*). If such a substitution takes place, it requires electronic rearrangements, with cobalt and/or molybdenum and sulfur ions acquiring higher positive charges. The presence of Co^{4+} seems to be detected with magnetic measurements (*28*). The present results give evidence of molybdenum and sulfur ions carrying an extra positive charge. All compensation processes thus seem to take place.

The intricate catalytic behavior of the catalysts in the low concentration range could thus be related to the presence of the abnormal surface ions.

Synergetic Concentration Range

We shall now discuss the phenomena observed for cobalt concentration in the range $0.15 < r < 0.50$, which corresponds to that where the synergetic effect of cobalt and molybdenum is observed and is the range used in all practical catalysts.

All previous results by ourselves and other authors (*1–6, 21, 22, 29*) indicate that unsupported systems in the synergetic range are mainly (if not exclusively) composed of two distinct sulfided phases, MoS_2 and Co_9S_8.

An increase in the specific surface area of the catalyst has been observed in unsupported cobalt–molybdenum catalysts prepared by a different method (*21*). Electron microscopic observations indeed indicate a loss of crystallinity and a higher dispersion, in comparison with the cobalt low concentration range (*24*). Similar microscopic examinations have been reported on different hydrodesulfurization catalysts (*22*). XPS relative intensity measurements, which indicate a tendency toward an increase in the relative partial surface occupied by Mo, in the synergetic range (compare the slope of the curve, very small, with the slope which would correspond to a dilution of identical particles by another compound, which would correspond to a straight line pointing to the point $r = 1.0$, intensity $= 0$, in Fig. 5), also corroborate this finding.

Catalytic activities in the hydrogenolysis of thiophene (hydrodesulfurization) and isomerization exhibit a strong maximum, when expressed per unit surface area. The maximum is still more important when activity per unit weight is considered because of the higher surface area. In addition, the activity in hydrogenation, expressed per unit weight of catalyst, also exhibits a maximum in the synergetic range (Fig. 12), which was not the case if intrinsic activity, rather than activity per unit weight, was used.

Our results thus confirm that the maximum of activity in the synergetic range has

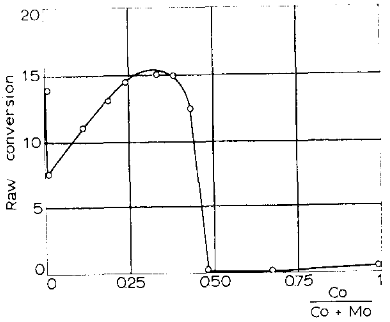

FIG. 12. Hydrogenation of cyclohexene.

a complex origin, partly as a consequence of higher activity per unit surface area and partly as a consequence of a higher development of the specific surface area. Our results also indicate that activities in hydrogenolysis and hydrogenation (and isomerization) do not vary in a parallel way, thus confirming and even giving more weight to the observation previously reported.

Our XPS findings are one of the very few clues which are presently available for identifying the surface species responsible for catalysis. The binding energy of Mo decreases in the synergetic range, whereas the binding energy of Co remains substantially unchanged. This suggests that the particular changes undergone by the surface during catalysis in the synergetic range do not involve Co_9S_8 but only MoS_2. Actually, this conclusion might seem too strong, as the S signal comes both from Co_9S_8 and MoS_2. However, the behavior of the apparent binding energy of S is easily explained. For $r < 0.4$, the majority of the sulfur ions (more than 75%) are bound to Mo, and hence the binding energy reflects the properties of MoS_2. Conversely, for large values of r, the behavior of S corresponds to that of cobalt sulfide. For the intermediate range of composition, one could only expect a very modest increase in the width of the S line (~0.2 eV) as a consequence of two S species, and it is not surprising that the experimental data cannot prove nor disprove this prediction.

The decrease in the binding energy of Mo and S indicates the presence of an extra negative charge $(-\epsilon)$ on these ions, i.e., $Mo^{4+(-\epsilon)}$ and $S^{2-(-\epsilon)}$. It is remarkable that the spectra do not indicate the presence of several Mo species with various charges (e.g., the simultaneous presence of Mo^{4+} *and* Mo^{3+}), but rather of only one type of Mo, as indicated by the fact that the width of the Mo lines (Fig. 3) is not increased in comparison with that observed with MoS_2. Molybdenum in the working catalyst tends toward a lower oxidation state with a charge between Mo^{4+} and Mo^{3+}. The presence of lower oxidation states of the group VIa elements in hydrotreating catalysts has already been proposed by Voorhoeve (*30*) on the basis of EPR measurements. The existence of the same species has also been proposed on hydrogen-reduced catalysts (*31*). However, for the first time, it is evidenced on the surface, in a state as close as possible to that of working catalysts. On the other hand, the increased negative charge of the sulfur ion indicates a collective behavior of the MoS_2 lattice, charges being partially transferred from cations to anions. The semiconducting behavior of MoS_2 has been investigated by Wise and co-workers (*32*, *33*). These authors supposed that sulfur vacancies can form in the reducing atmosphere prevailing during catalysis, possibly producing sulfur vacancies. The present results support these views.

XPS measurements indicate a gradual decrease in the binding energy of cobalt. This indicates that Co_9S_8 is superficially more reduced in samples with increasing cobalt content r.

The fact that the variations in the binding energy of Mo and Co are not parallel indicates that the two categories of ions are independent. This is logical, as no mixed phase associating Mo and Co were observed in sulfided catalysts and, conversely, MoS_2 and Co_9S_8 (or $CoS_{1.035}$) were constantly observed.

CONCLUSIONS

This is the first report of significant changes in the XPS spectrum of unsupported cobalt–molybdenum catalysts. Although, unfortunately, it has not been possible to subject catalysts which have operated under pressure to XPS measurements, our catalysts are certainly much more representative to the state of working catalysts than those subjected to similar physicochemical measurements to date. We thus believe that the changes in the oxidation state of the surface species observed might serve as a base for the identification of the active centers in the various reactions involved in hydrotreating.

Much speculation has developed concerning the possible active sites (*1*, *2*, *5*, *22*, *34–37*). The present results substantiate the idea that reduced Mo^{3+} ions (or sulfur vacancies) are involved in the synergetic sites. However, we believe we cannot, at the present time, develop a sufficiently complete and proved picture of the process. Indeed, changes of selectivity (principally hydrogenolysis vs hydrogenation) are too large and must be ascribed to the presence of at least two active centers. On the other hand, the first hypotheses made on the active sites were based on supported catalysts (and corresponding pictures obviously do not apply to our case) or were derived from the study of systems which cannot, at present, be placed safely in one of the cobalt concentration ranges we feel compelled to consider, i.e., low concentration and synergetic; for example, reduced species have been mentioned in systems which, according to the overall composition, had to be placed in the low concentration domain. Further analysis, and possibly reproduction, of former experiments, is mandatory.

ACKNOWLEDGMENTS

We thank the Fonds National de la Recherche Collective (FRFC) of Belgium for the grant which enabled us to acquire the high pressure test equipment.

We thank Dr. P. Canesson and Dr. C. Defosse for their help in performing and interpreting the XPS measurements.

REFERENCES

1. Hagenbach, G., Courty, Ph., and Delmon, B., *J. Catal.* **23**, 295 (1971).
2. Hagenbach, G., Courty, Ph., and Delmon, B., *J. Catal.* **31**, 264 (1973).
3. Zabala, J. M., Mainil, M., Grange, P., and Delmon, B., *React. Kinet. Catal. Lett.* **3**, 285 (1975).
4. Zabala, J. M., Mainil, M., Grange, P., and Delmon, B., *C. R. Acad. Sci. Paris Ser. C* **280**, 1129 (1975).
5. Canesson, P., Delmon, B., Delvaux, G., Grange, P., and Zabala, J. M., *in* "Proceedings, 6th International Congress on Catalysis" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), p. 927. Society, London, 1977.
6. Gajardo, P., Declerck-Grimee, R. I., Delvaux, G., Olodo, P., Zabala, J. M., Canesson, P., Grange, P., and Delmon, B., *in* "Proceedings, 2nd International Conference, on Chemistry and Uses of Molybdenum" (P. C. H. Mitchell and A. Seaman, Eds.), p. 151. Oxford Univ. Press, New York, 1977.
7. Delmon, B. *Prepr. Div. Petrol. Chem, Amer. Chem. Soc.* **22** (2), 503 (1977).
8. Patterson, T. A., Caver, J. C., Leyden, D. E., and Hercules, D. M., *J. Phys. Chem.* **80** (15), 1700 (1976).
9. Ng, K. T., and Hercules, D. M., *J. Phys. Chem.*, **80** (19), 2094 (1976).
10. Grimblot, J., and Bonnelle, J. P., *J. Electron Spectrosc. Relat. Phenom.* **9**, 449 (1976).
11. Ratnasamy, P., *J. Catal.* **40**, 137 (1975).
12. Armour, A. W., Mitchell, P. C. H., Folkesson, B., and Larsson, R., *J. Less Common Met.* **36**, 361 (1974).
13. Cimino, A., and De Angelis, B. A., *J. Catal.* **36**, 11 (1975).
14. Stevens, G. C., and Edmonds, T., *in* "Proceedings, 2nd International Conference on Chemistry and Uses of Molybdenum" (P. C. H. Mitchell and A. Seaman, Eds.), p. 155. Oxford Univ. Press, New York, 1976.
15. Friedman, R. M., Declerck-Grimee, R. I., and Fripiat, J. J., *J. Electron Spectrosc. Relat. Phenom.* **5**, 437 (1974).
16. Canesson, P., Defosse, C., Declerck-Grimee, R. I., and Delmon, B., *in* "Proceedings, 5th Ibero-American Symposium on Catalysis, Lisbon," 1976, in press.
17. Declerck-Grimee, R. I., Canesson, P., Friedman, R. M., and Fripiat, J. J., *J. Phys. Chem.* **82**, 889 (1978).

18. Canesson, P., and Grange, P., *C. R. Acad. Sci. Paris Ser. C* **281**, 757 (1975).
19. Lindberg, B. J. Hamrin, K., Johansson, G., Gelius, U., Fahlaman, A., Nordling, C., and Siegbahn, K., *Phys. Scripta* **1**, 286 (1970).
20. Furimsky, E., and Amberg, C. H., *Canad. J. Chem.* **53**, 2542 (1975).
21. Gajardo, P., Grange, P., and Delmon, B., to be published.
22. Farragher, A. L., and Cossee, P., *in* "Proceedings, 5th International Congress on Catalysis" (J. W. Hightower, Ed.), p. 1301. North-Holland/Elsevier, Amsterdam, 1973.
23. Thakur, D. S., Grange, P., and Delmon, B., *Bull. Soc. Chim. Belg.* **86**, 413 (1977).
24. Thakur, D. S., Grange, P., and Delmon, B., *J. Less Common Met.* in press.
25. Hagenbach, G., Menguy, P., and Delmon, B., *C. R. Acad. Sci. Paris Ser. C* **273**, 1220 (1971).
26. Galiasso, P., and Menguy, P., *Bull. Soc. Chim. Fr.* **44** (1972).
27. Hagenbach, G., Menguy, P., and Delmon, B., *Bull. Soc. Chim. Belg.* **83**, 1 (1974).
28. Perrichon, V., Vialle, J., Turlier, P., Delvaux, G., Grange, P., and Delmon, B., *C. R. Acad. Sci. Paris Ser. C* **282**, 85 (1976).
29. Delvaux, G., Leonard, A., Genet, M., Grange, P., and Delmon, B., *in* "Proceedings, 5th Ibero-American Symposium on Catalysis, Lisbon," 1976, in press.
30. Voorhoeve, R. J. H., *J. Catal.* **23**, 236 (1971).
31. Massoth, F. E., *J. Catal.* **30**, 204 (1973).
32. Aoshima, A., and Wise, H., *J. Catal.* **34**, 145 (1974).
33. Wentrceck, P. R. and Wise, H., *Prepr. Div. Petrol. Chem. Amer. Chem. Soc.* **22** (2), 525 (1977).
34. Schuit, G. C. A., and Gates, B. C., *AIChE* **19**, 417 (1973).
35. Voorhoeve, R. J. H., and Stuiver, J. C. M., *J. Catal.* **23**, 243 (1971).
36. Farragher, A. L., *Prepr. Div. Petrol. Chem. Amer. Chem. Soc.* **22** (2), 524 (1977).
37. De Beer, V. H. J., and Schuit, G. C. A., *in* "Preparation of Catalysts" (B. Delmon, P. A. Jacobs, and G. Poncelet, Eds.), p. 343. Elsevier, Amsterdam, 1976.