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X-RAY DIFFRACTION STUDY OF A CoMo SULFIDE OBTAINED BY THE IMPREGNATED THIOSALT DECOMPOSITION METHOD

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X-ray powder diffractometry was used to characterize the phases produced during the preparation of MoS_2 catalysts promoted with Co, by the impregnated thiosalt method. After a crystallization process at 673 K and 1043 K the X-ray analysis seems to indicate the presence of a mixed CoMo sulfide, in addition to the MoS_2 and Co_9S_8.

Unsupported molybdenum or tungsten sulfides, promoted by cobalt or nickel can be prepared by several procedures. Different methods have been proposed: the comaceration method described by Hagenbach et al. [1], the homogeneous sulfide precipitation (HSP) developed by Candia et al. [2], the decomposition of thiobismetalato complex salts [3], and some others. All of these methods look for the formation of mixed phases in the sulfided samples.

Recently, a preparation procedure was reported called Impregnated Thiosalt Decomposition method (ITD) that selectively deposes the promoter on the surface of the MoS_2 precursor [4]. The CoMo and NiMo catalysts obtained by this technique showed an improved intrinsic catalytic activity, as compared with other catalysts prepared by conventional methods.

In this letter, we report an X-ray diffraction characterization of the different phases obtained when preparing CoMo sulfides by the impregnated thiosalt method. We focussed our attention on one CoMo catalyst, with an atomic composition $Co/Co + Mo = 0.3$, which showed the highest activity in HDS and hydrogenation reactions, among other CoMo sulfided catalysts with a large range of compositions [5].

Pure ammonium thiomolybdate crystals [$(NH_4)_2MoS_4$, ATM] were prepared by a conventional method [6]. The ATM crystals were impregnated with cobalt using an acetone solution of $Co(NO_3)_2.6H_2O$, as reported elsewhere [4].

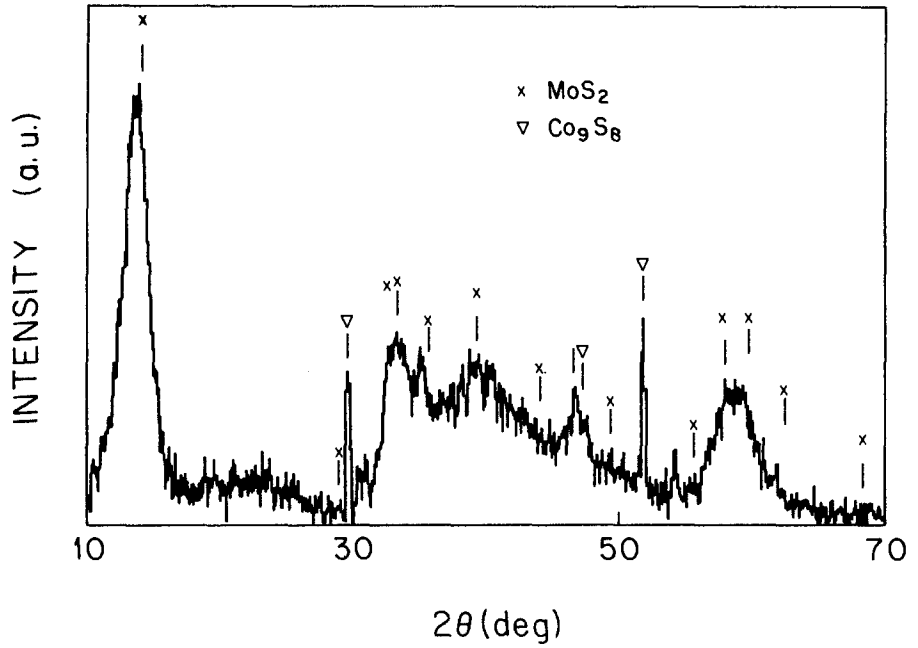

Fig. 1. X-ray powder spectrum of a crust sample sulfided at 673 K for 4 h. The position of the peaks of the Co_9S_8 and MoS_2-2H phases are indicated.

X-ray powder diffractograms were obtained from freshly prepared samples crushed on an agate mortar, by using Cu-Kα radiation. A secondary monochromator allowed us to eliminate almost all of the fluorescence radiation (mainly from Co). All the spectra were corrected for the Kα2 component on the incident beam. Peaks on the spectra were identified by comparing them with those in the 1987-JCPDS files. A clear change in the colour of the surface of the ATM crystals was observed during impregnation, indicating that some surface reaction was taking place. In order to eliminate the strong signal comming from the ATM base in the X-ray diffractogram, we have dissolved the ATM by first crushing the sample and then washing it exhaustively with distilled water.

The resulting crust was insoluble in water, confirming that some compounds are formed by reaction during the impregnation process which are different from the original water soluble phases ($Co(NO_3)_2.6H_2O$ and $(NH_4)_2MoS_4$).

Following the current procedure to obtain a sulfided sample, the crust was treated at 573 K during 4 hours under a gas mixture of 15% H_2S/H_2, and then cooled at room temperature under the same atmosphere. In order to avoid undesirable reaction with oxygen in the air, the samples were analysed by X-ray diffraction after short period of time.

Fig. 1 shows a diffractogram after sulfidation of the crust sample. The two well defined peaks in fig. 1 correspond to the Co_9S_8 phase. A poorly crystalline contribution is the main feature of spectrum 1, and it is interesting to note that

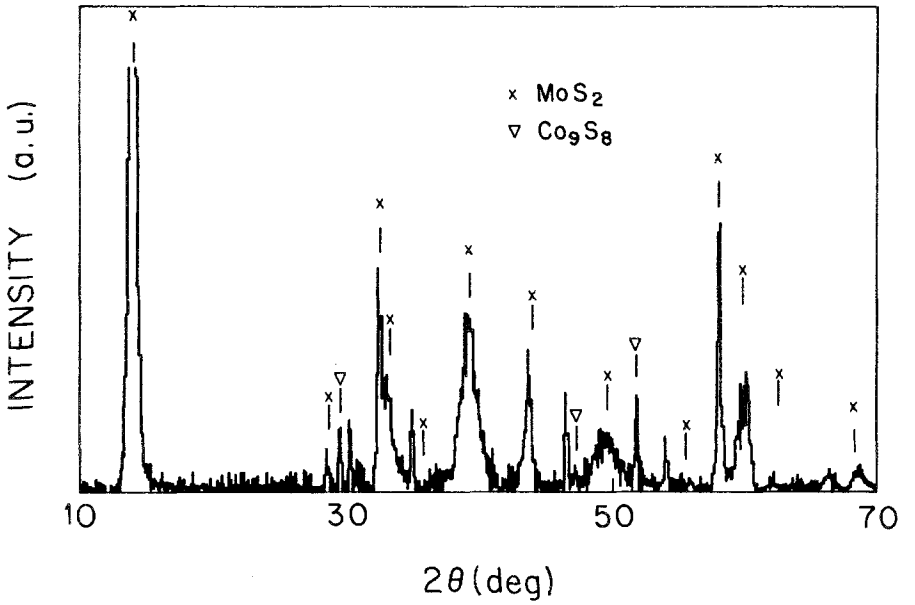

Fig. 2. Diffractogram of the sample in fig. 1 after sulfidation at 1073 K for 4 h. The degree of crystallinity of MoS_2 is now better developed.

this profile roughly agrees with the X-ray diffraction pattern of poorly crystallized MoS_2 prepared by thermal decomposition of ATM at temperatures close to those considered here, as reported by Liang et al. [7]. However, in addition to the Co_9S_8 peaks, some other contributions appear superposed to the poorly crystalline profile. In order to get a more precise identification of those extra phases, an additional heat treatment was performed to the same sample at 1073 K during 4 hours under a 15% H_2S/H_2 gas flow. The corresponding diffractogram is shown in fig. 2. Here the spectrum of molybdenite-2H (MoS_2) is better defined allowing its identification. Again this latter spectrum is in good agreement with the corresponding one reported in ref. [7].

On the other hand, other phases than the Co_9S_8 one, showed fully developed crystallinity after the treatment at 1073 K.

In order to explain the extra crystalline contributions to this spectrum, several phases were considered. Figs. 3-a, 3-b and 3-c show an enlarged region of the spectrum in fig. 2. Here the fittings with those phases which better matched the different peaks are presented.

The $CoS_{1.035}$ has its strongest line at around $2\theta = 46.78$, and fits the experimental spectrum (fig. 3-a). However, when considering the other reported lines of this compound the match is not so good. Intensity and position, and the number of lines are clearly not enough to explain all the extra peaks in the spectrum. Other closely related phases like $CoS_{1.097}$ give essentially the same result. Regarding the Co_4S_3 phase (fig. 3-b), this compound well matches several lines in both

position and intensity, but two of the strongest reported lines (at higher angles) do not appear in the experimental spectrum. Besides, it must be noted that if this phase would actually be present in the sample as a mixture with the Co_9S_8 phase (which has been already identified as present in the sample), the coinciding line for both phases at around $2\theta = 52.0$ should appear with a higher intensity than observed.

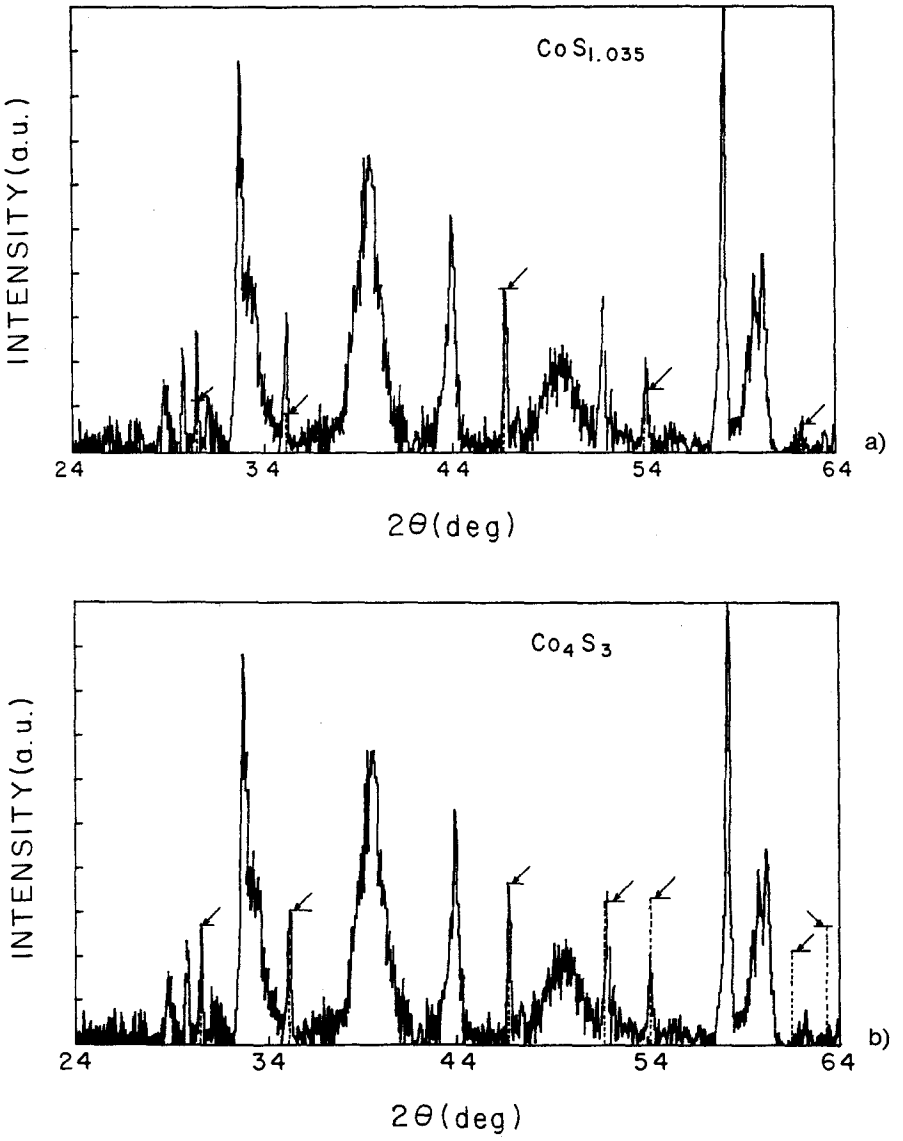

Fig. 3. Enlarged region of the spectrum in fig. 2, fitted with the reported peaks (dotted lines) of: a) $CoS_{1.035}$, b) Co_4S_3 and c) $CoMoS_{3.13}$. The arrow on each peak indicates the reported relative intensity.

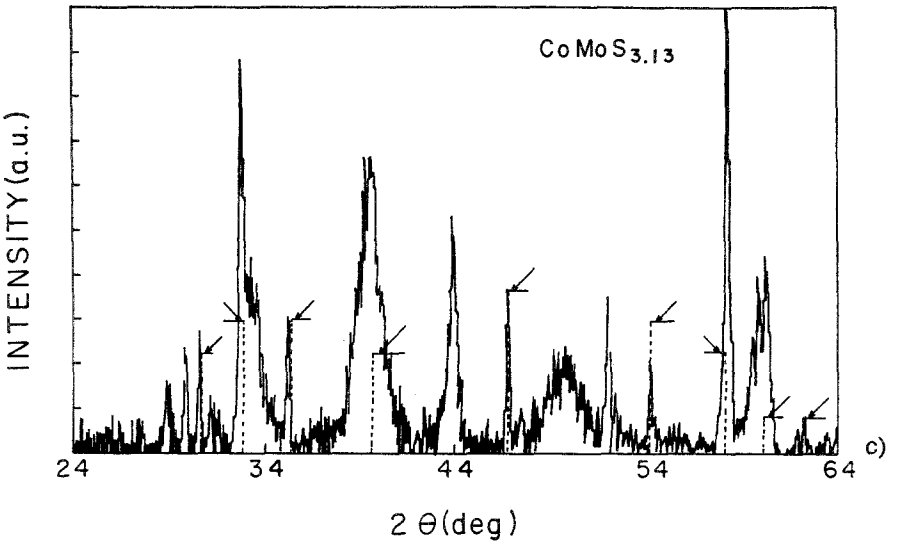

Fig. 3. (continued).

In the case of $CoMoS_{3.13}$, shown in fig. 3-c, the matching with the reported lines for this compound one is able to explain, in addition to those well-defined lines that Co_9S_8 and MoS_2 cannot explain, some particularities in the spectrum profile. This is for instance the case for the poorly crystalline peak of MoS_2 at $2\theta = 39.62$, where the shape seems to indicate that some crystalline contribution is superposed. Also, the last peak in the group of lines at higher angles where the second line in the doublet at $2\theta = 60.34$ can only be explained by introducing the $CoMoS_{3.13}$ contribution. Note that none of the other considered phases is able to explain such peculiarities.

It is worthwhile nothing that the $CoMoS_{3.13}$ compound was first identified in ref. [8] as a mixture of MoS_2 and β-CoS; nevertheless, some of the reported lines for this compound in that work do not correspond to the added diffraction patterns of those two phases. The same result is observed in fig. 3-c, where it is clear that some of the lines associated to the $CoMoS_{3.13}$ phase can not be explained by that mixture of phases. This fact could be an indication for the actual existence of this CoMo mixed sulfide, or some other closely related phase. In addition, it should be noted that the preparation method used in ref. [8] is entirely different from the one in this work. Therefore, their conclusions about the actual formation of this compound and ours are not necessarily alike. The formation of a precursor CoMo sulfide during the impregnation reaction on the ATM surface, which decomposes to the observed product during sulfidation, not necessarily occurs in other preparation methods.

From a catalytic point of view, the reactivity of these crust samples is worth interest since a very low catalytic activity of other mixed sulfides like $CoMo_2S_4$ and the Chevrel phases ($Co_{1.7}Mo_6S_8$) has been reported in the literature [9,10].

A step by step characterization of the different phases appearing during the preparation of these more efficient bulk sulfides, and the possible reaction path for them will be reported soon.

References

[1] G. Hagenbach, P. Courty and B. Delmon, J. Catal. 23 (1971) 295.
[2] R. Candia, B.S. Clausen and H. Topsoe, Bull. Soc. Chim. Belg. 90 (1981) 1225.
[3] W. Eltzner, M. Breyse, M. Lacroix and M. Vrinat, Polyhedron 5 (1986) 203.
[4] S. Fuentes, G. Díaz, F. Pedraza, H. Rojas and N. Rosas, J. Catal. 113 (1988) 535.
[5] G. Díax, N. Rosas, H. Rojas, F. Pedraza and S. Fuentes, *Proc. X Catal. Soc. Meet.* (p. 46) (1987).
[6] *Handbook of Preparative Inorganic Chemistry*, ed. G. Brauer (Academic Press, New York, 1965) vol. 2, p. 1416.
[7] K.S. Liang, R.R. Chianelli, F.Z. Chien and S.C. Moss, J. of Non-Cryst. Sol. 79 (1986) 251.
[8] P.A. Engelhard and Y. Trambouze, Bull. Soc. Chim. 195 (1959).
[9] J.M. Van den Berg, Inorg. Chim. Acta 2 (1968) 216.
[10] K.F. McCarty, J.W. Anderegg and G.L. Schrader, J. Catal. 93 (1985) 375.