Catalysis Letters 9 (1991) 387–394

MIXED IMPREGNATED THIOSALT DECOMPOSITION CATALYSTS CHARACTERIZED BY X-RAY DIFFRACTION

J. CRUZ-REYES

Facultad de Ciencias Químicas de la UABC, Apartado Postal 117-"B", Tijuana, B.C. 22100, Mexico

M. AVALOS-BORJA, M.H. FARÍAS and S. FUENTES

Instituto de Física de la UNAM, Laboratorio de Ensenada, Apartado Postal 2681, Ensenada, B.C. 22800, Mexico

Received 8 February 1991; accepted 25 April 1991

We used the impregnated thiosalt decomposition method (ITD) to prepare catalysts of molybdenum sulfide promoted with cobalt in atomic ratios ($r = \mathrm{Co}/(\mathrm{Co}+\mathrm{Mo})$) ranging from 0.0 to 1.0. Measurements obtained by X-ray diffraction (XRD) show the presence of the MoS_2-2H phase in all mixed samples, and segregation of cobalt in two phases: Co_9S_8, for $r \geq 0.3$, and $CoS_{1.035}$, for $0.3 \leq r \leq 0.5$.

Keywords: Impregnated thiosalt decomposition (ITD), Molybdenum sulfide catalyst, transition metal sulfide catalyst, X-ray diffraction

1. Introduction

Transition metal sulfides are very important in catalytic processes and they have been used for many years for processing of fuel in a variety of reactions [1–4], among them, hydrodesulfurization (HDS). There are several methods to prepare mixed-sulfide catalysts: sulfidation of coprecipitated oxides [5,6], comaceration [7,8], homogeneous sulfide precipitation (HSP) [9,10], synthesis of unsupported catalysts using a ceramic method [11], or impregnated thiosalt decomposition (ITD) [12]. These different methods have been developed because promoted sulfide catalysts are complex and their catalytic properties are very dependent on the preparation method [9].

In this work we measured by using XRD the different crystallographic phases present in mixed cobalt-molybdenum disulfide catalysts prepared by ITD for various concentrations of cobalt.

2. Experimental procedure

A set of samples of molybdenum sulfide and mixtures of molybdenum sulfide promoted with cobalt in atomic ratios $r = Co/(Co + Mo)$ of 0.0, 0.3, 0.5 and 0.7 were prepared according to the recently developed method of impregnated thiosalt decomposition (ITD) [12]. The pure cobalt sulfide sample was prepared by the homogeneous sulfide precipitation (HSP) method [9,10].

The procedure for preparing catalysts with the ITD method consists of two parts, and is summarized as follows.

(a) preparation of precursors (pure molybdenum sulfide and mixtures). The pure molybdenum sulfide precursor (ammonium tetrathiomolybdate, $(NH_4)_2MoS_4$), is prepared by flowing hydrogen sulfide gas (H_2S) for 30 minutes in an aqueous solution of ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}$, and ammonium hydroxide, after which crystallites of $(NH_4)_2MoS_4$ are formed [13]. Finally, this solution is filtered and the crystals are dried. In order to avoid oxidation, the crystals are placed in sealed flasks in an atmosphere of dry nitrogen.

The preparation of the mixed precursors involves the reaction of the intermediate $(NH_4)_2MoS_4$, which acts as the support and is slightly soluble in acetone. An acetone solution, the impregnating agent, containing the appropriate salt, $Co(NO_3)_2$, is then added dropwise to the $(NH_4)_2MoS_4$ crystals suspended in this solvent. It is stirred at 313 K for 5 hours adding solvent as necessary until the treatment is complete.

(b) decomposition of these precursors. The precursors are subsequently decomposed by sulfiding in a mixture of 15% vol H_2S in H_2 for 4 hours at 673 K.

All catalysts used in this work were bulk (unsupported) catalysts.

X-Ray Diffraction (XRD) patterns shown in fig. 1 were obtained with a Philips diffractometer (Cu Kα radiation, $\lambda = 0.154$ nm), and those shown in fig. 2, with a Siemens diffractometer (Mo Kα radiation, $\lambda = 0.071$ nm).

3. Results

In fig. 1 we present the XRD patterns of (a) the $(NH_4)_2MoS_4$ precursor, and (b) the pure molybdenum sulfide catalyst ($r = 0.0$). Curve (a) shows an X-ray diffractogram with sharp peaks, and the reflections (011), (111), (200), (020) and (022) of the $(NH_4)_2MoS_4$ phase (orthorhombic system, space group *Pnma*, $a = 0.957$ nm, $b = 0.699$ nm, $c = 1.221$ nm) are identified in this sample [14]. In contrast, curve (b) shows broad peaks, and the reflections (002), (101), (103) and (110) corresponding to the MoS_2-2H phase are identified. The broad peaks in curve (b) indicate either poor crystallinity or very small crystallite size.

Fig. 2 a–d shows, the XRD patterns for $r = 0.3$, 0.5, 0.7, and 1.0, respectively. Curves (a), (b) and (c) show (similarly to fig. 1(b)), the reflections (002), (101),

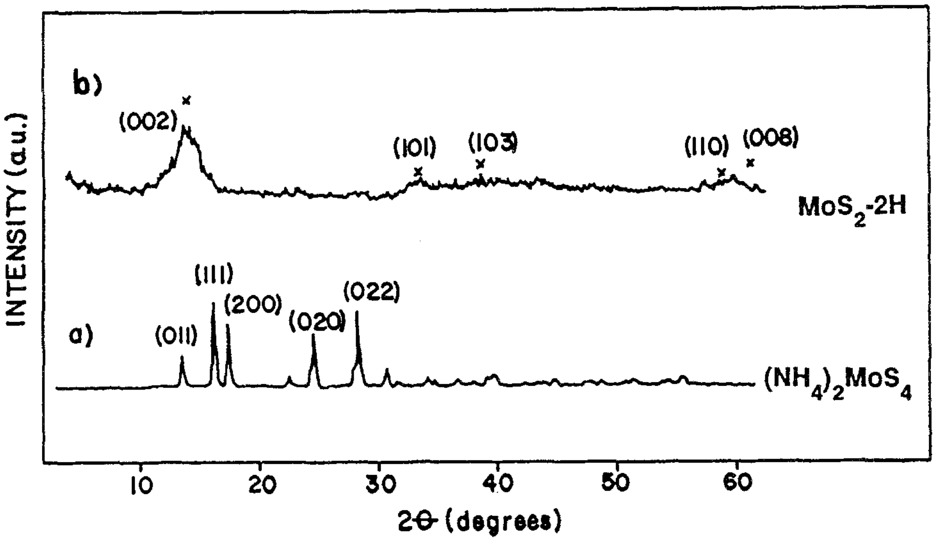

Fig. 1. XRD patterns (Cu Kα, $\lambda = 0.154$ nm) of (a) the $(NH_4)_2MoS_4$ precursor, and (b) the pure molybdenum sulfide catalyst.

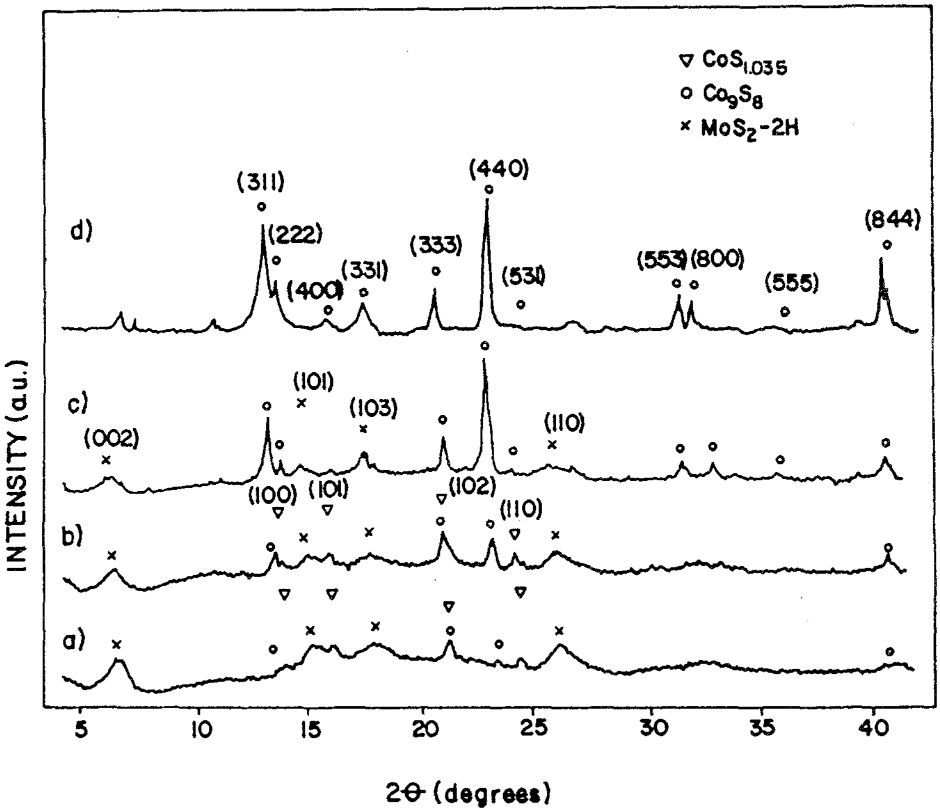

Fig. 2. XRD patterns (Mo Kα, $\lambda = 0.071$ nm) of the different samples for r values [$r = Co/(Co + Mo)$] of (a) 0.3, (b) 0.5, (c) 0.7 and (d) 1.0.

Table 1
X-ray reflections and the corresponding phases for the various ITD catalyst samples.

Fig.	Curve	$r = \mathrm{Co}/(\mathrm{Co}+\mathrm{Mo})$	Phase	Main reflections observed
1	a	0.0	$(NH_4)_2MoS_4$	(011), (111), (200), (020), (022)
1	b	0.0	MoS_2-2H	(002), (101), (103), (110)
2	a	0.3	MoS_2-2H	(002), (101), (103), (110)
			Co_9S_8	(311), (333), (440), (844)
			$CoS_{1.035}$	(100), (101), (102), (110)
2	b	0.5	MoS_2-2H	(002), (101), (103), (110)
			Co_9S_8	(311), (333), (440), (844)
			$CoS_{1.035}$	(100), (101), (102), (110)
2	c	0.7	MoS_2-2H	(002), (101), (103), (110)
			Co_9S_8	(311), (222), (331), (333), (440), (553), (844)
2	d	1.0	Co_9S_8	(311), (222), (400), (331), (333), (440), (553), (800), (844)

(103) and (110) that correspond to the MoS_2-2H phase, indicating that this phase is present in these catalysts for r values up to 0.7. Curve (d) shows the reflections (311), (222), (400), (331), (333), (440), (553), (800) and (844) corresponding to the Co_9S_8 phase [14]. The peaks are sharp indicating good crystallinity of the cobalt sulfide ($r = 1$) catalyst. Curves (b) and (c) exhibit also some of these reflections of the Co_9S_8 phase. Finally, curves (a) and (b) show also some weak reflections that could be associated to the $CoS_{1.035}$ phase (hexagonal system, space group $P6_3/mmc$, $a = 0.3384$ nm, $c = 0.5196$ nm [14]), these are (100), (101), (102), and (110). This indicates the presence of this phase for r values between 0.3 and 0.5.

In table 1, a list of the reflections and the corresponding phases for all samples is presented.

4. Discussion

It is known that the catalytic activities of CoMo sulfided catalysts are strongly dependent on the method of preparation [15]. In a previous work, it was reported that the intrinsic activities of mixed sulfide catalysts obtained by the ITD method are higher than those measured on catalysts prepared by precipitation [12]. The characterization of both types of catalysts using electron microscopy, X-ray diffraction and Auger spectroscopy revealed marked differences in morphology, crystallinity and cobalt concentration at the surface [16]. From these results, the better catalytic properties of ITD samples were explained through an increased dispersion of cobalt onto the surface of MoS_2 catalysts, whereas the lower activity of HSP samples was explained by the segregation of cobalt to form Co_9S_8.

Taking into account these results, it is clear that the two preparation methods lead to different precursors and catalysts for all the atomic ratios studied.

Therefore, it is interesting to make a comparison of the crystalline structure involved in both types of catalysts.

A previous study of HSP samples [17] showed the presence of the crystalline phases MoS_2-2H, Co_9S_8 and $CoS_{1.035}$. The $CoS_{1.035}$ appeared in the composition range of $0.3 \Leftarrow r \Leftarrow 0.5$ and was the only phase detected in the sample showing the highest catalytic activity.

In this work, for all the samples for which $r \leq 0.7$ the XRD results show the characteristic reflections of MoS_2-2H, as broad bands. Other measurements by Chianelli [18] for $r = 0.0$ on HSP catalysts show similar "peaks". These broad reflections are indicative of poor crystallinity [23]. In our samples, the MoS_2-2H phase is present at higher values of r, as compared to the usual HSP method, where the reflections of the MoS_2-2H phase disappear at much lower values of r [9,17]. This is most likely due to the fact that the core of the crystals prepared by ITD remains as MoS_2 even for high concentrations of Co.

We can also observe that Co_9S_8 reflections start to show up for $r \geq 0.5$. This phase was found by Phillips and Fote [19], and has been detected by other workers [2,17,21,22]. Thermodynamic calculations show that the stable phase in the conditions of the HDS reaction is Co_9S_8, which has a cubic structure, whereas the hexagonal phase, CoS_{1+x}, is formed at higher temperature under high H_2S/H_2 ratio [2].

The reflections of the $CoS_{1.035}$ phase appear for intermediate values of r. The peaks are noticeable and appear for $0.3 \leq r \leq 0.5$. The phase $CoS_{1.097}$ (hexagonal system, space group $P6_3/mmc$ $a = 1.01$ nm, $c = 1.548$ nm [14]) has reflections very close to the $CoS_{1.035}$ ones, and it is very difficult to distinguish between them. Although we might have contributions from both phases, the relative intensities of the diffraction peaks favor the $CoS_{1.035}$ phase. If the phase was $CoS_{1.097}$ we would expect a relatively large peak (606) at 32.3 degrees. On the other hand, the expected peak at that position for the $CoS_{1.035}$ (202) should be much smaller, which seems to agree more with the experimental data in fig. 2.

This intermediate phase has been detected in other more traditional methods of preparation. The first ones were Hagenbach et al. [7] who found the phase $CoS_{1.035}$ for $r > 0.2$ on crystallized samples prepared by comaceration, that consists of co-digesting MoO_3 and Co_3O_4 in ammonium sulfide, treating in a mixture of H_2S and Ar, evacuating, and finally heat treating under Ar at 1000°C for 4 hours. Also, on supported and unsupported catalysts prepared by HSP, Topsøe et al. [20] using Mössbauer spectroscopy identified this and other cobalt sulfide phases. More recently, Göbölös et al. [21] identified by Mössbauer spectroscopy several phases of cobalt sulfide: Co_9S_8, CoS_{1+x}, Co-Mo-S and two unidentified phases, where the relative concentrations depended on the preparation conditions.

In fig. 2 we can observe that the 002 peak is visible up to $r = 0.7$. On the other hand, the same peak dissappears at about $r = 0.3$ when the catalysts are prepared by the HSP method [24]. This indicates that the MoS_2 crystals are smaller and/or

Table 2
Crystallographic phases and r values [$r = \mathrm{Co}/(\mathrm{Co}+\mathrm{Mo})$] for ITD and HSP catalyst samples.

	MoS_2-2H	Co_9S_8	$CoS_{1.035}$
ITD (this work)	$r \leq 0.7$	$r \geq 0.5$	$0.3 \leq r \leq 0.5$
HSP [22]	$r \leq 0.3$	$r \geq 0.3$	$0.2 \leq r \leq 0.7$

more amorphous in the latter case. Also the ITD method produces crystals with a longer lasting MoS_2 core, since the impregnation method involves diffusion of Co from the surface towards the center of the crystal, as mentioned above.

The comparison of both types of catalysts, for the entire range of composition, is shown in table 2. This table clearly shows that three crystalline phases are involved in mixed CoMo sulfided catalysts, MoS_2-2H, Co_9S_8 and $CoS_{1.035}$. However, the relative amounts of these phases indicated by the intensity of the diffracted peaks varies with the method of preparation. In general, ITD catalysts appear more "poorly crystalline" than HSP catalysts.

In the case of ITD samples involved in this work, it is suggested that the presence of the poorly crystalline MoS_2 phase even at high cobalt concentration allows a better dispersion of atomic cobalt on the surface and therefore increases the catalytic activity. Further studies are needed in order to elucidate the relative contributions of the Co_9S_8, $CoS_{1.035}$ and/or $CoS_{1.097}$ phases to the catalytic activity.

5. Conclusions

From the results of XRD measurements we can conclude that catalysts prepared with the ITD method present the MoS_2-2H phase for $r \leq 0.7$, and the segregation of cobalt in two different phases: Co_9S_8 for $r \geq 0.3$ and $CoS_{1.035}$ for $0.3 \leq r \leq 0.5$.

Acknowledgements

We are very grateful to Drs. T.A. Early and M.B. Maple (UCSD La Jolla, CA) for providing access to their X-ray laboratory.

References

[1] R.R. Chianelli, Catal. Rev. Sci. Eng. 26 (1984) 361.
[2] O. Weisser and S. Landa, *Sulfide Catalysts: Their Properties and Applications* (Pergamon Press, Oxford, 1973).

[3] P. Grange, Catal. Rev. Sci. Eng. 21 (1980) 135.
[4] T.A. Pecoraro and R.R. Chianelli, J. Catal. 67 (1981) 430.
[5] J.V. Sanders and K.C. Pratt, J. Catal. 67 (1981) 331.
[6] K.C. Pratt, J.V. Sanders and N. Tamp, J. Catal. 23 (1971) 205.
[7] G. Hagenbach, Ph. Courty and B. Delmon, J. Catal. 23 (1971) 295.
[8] G. Hagenbach, Ph. Courty and B. Delmon, J. Catal. 31 (1973) 264.
[9] R. Candia, B.J. Clausen and H. Topsøe, Bull. Soc. Chim. Belg. 90 (1981) 1225.
[10] R. Candia, B.J. Clausen and H. Topsøe, Bull. Soc. Chim. Belg. 90 (1981) 1271.
[11] A. Bellaloui, M. Breysse, M. Lacroix, L. Mosoni, M. Roubin and M. Vrinat, Bull. Soc. Chim. Fra. 1 (1987) 16.
[12] S. Fuentes, G. Díaz, F. Pedraza, H. Rojas and N. Rosas, J. Catal. 113 (1988) 535.
[13] G. Brauer, in: *Handbook of Preparative Inorganic Chemistry*, Vol. 2 (Academic Press, New York, 1965) p. 1416.
[14] J.H. Fang and F.D. Bloss, *X-ray Diffraction Tables* (Southern Illinois University Press, 1966).
[15] R. Candia, B.S. Clausen and H. Topsøe, J. Catal. 77 (1982) 564.
[16] G. Diaz, F. Pedraza, H. Rojas, J. Cruz, M. Avalos, L. Cota and S. Fuentes, in: *Studies on Surface Science and Catalysis*, Vol. 50, Advances in Hydrotreating Catalysts, Eds. M.L. Occelli and R.G. Anthony (Elsevier Sci., 1989) p. 91.
[17] J. Cruz-Reyes, M. Avalos-Borja, M.H. Farías, G. Diaz and S. Fuentes, Mater. Lett. 8 (1989) 492.
[18] R.R. Chianelli, Intern. Rev. Phys. Chem. 2 (1982) 127.
[19] R.W. Phillips and A.A. Fote, J. Catal. 41 (1976) 168.
[20] H. Topsøe, B.S. Clausen, R. Candia, C. Wivel and S. Mørup, J. Catal. 68 (1981) 433.
[21] S. Göbölös, Q. Wu, J. Ladriere, F. Delannay and B. Delmon, Bull. Soc. Chim. Belg. 93 (1984) 687.
[22] F. Delannay, Appl. Catal. 16 (1985) 135.
[23] K.S. Liang, R.R. Chianelli, F.Z. Chien and S.C. Moss, J. Non-Cryst. Sol. 76 (1986) 251.
[24] J. Cruz-Reyes, M. Avalos-Borja and M.E. Farías, Catal. Lett. 3 (1989) 227.