JOURNAL OF CATALYSIS **137**, 232–242 (1992)

Hydrodesulfurization Catalysts Prepared by Two Methods Analyzed by Transmission Electron Microscopy

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Received August 12, 1991; revised January 28, 1992

Samples of molybdenum sulfide, cobalt sulfide and mixtures in atomic ratios r = Co/(Co + Mo) of 0.0, 0.3, 0.5, 0.7, and 1.0 were prepared by two different methods, homogeneous sulfide precipitation (HSP) and impregnated thiosalt decomposition (ITD). Samples were observed by high-resolution electron microscopy using imaging and diffraction modes. Both preparation methods present the "rag structure" typical of MoS_2–2H with some structural differences between them. The average number of layers (n) in molybdenum disulfide crystals is about the same in both preparation methods, while the average length (L) of the molybdenum disulfide crystallites obtained by HSP is larger than that of those obtained by ITD. The particle size is smaller for ITD samples. The presence of cobalt does not greatly modify the number of layers of the MoS_2–2H stacks in mixed samples. An increase in the intracrystallite disorder is observed. © 1992 Academic Press, Inc.

INTRODUCTION

The role of the promoter in hydrotreating sulfide catalysts has been the subject of study for several years. In order to explain the beneficial promoting effects that cobalt or nickel atoms have on the catalytic properties of molybdenum-disulfide-based catalysts, two approaches are currently being used: (a) The electronic model (*1*), which proposes that an electron transfer from cobalt or nickel to molybdenum generates a bimetallic sulfided complex, which is responsible for the improved catalytic activity. (b) The geometric model (*2, 3*), which suggests that a specific cobalt phase observed under particular conditions and existing only in combination with molybdenum disulfide leads to a synergy in the catalytic properties.

Although theoretical calculations have confirmed that electron donation occurs from the promoter to molybdenum atoms in mixed sulfide phases (*1*), clear evidence for the interaction of cobalt on specific positions of MoS_2–2H has only been given for single crystals (*4*). Evidence of the position occupied by the promoter atoms in the disordered structure of MoS_2–2H has not yet been fully demonstrated. Most concern in this subject comes from a lack of understanding of the microstructure of molybdenum disulfide catalysts. A clear picture of the sites, and therefore the role of promoter atoms, will be achieved only through a better understanding of the MoS_2–2H "poorly crystalline" structure.

In this work we study, by high-resolution electron microscopy (HREM), two sets of samples obtained by homogeneous sulfide precipitation (HSP) (*5*) and impregnated thiosalt decomposition (ITD) (*6*). We characterize the changes induced in the stacking of (002)–MoS_2–2H planes when the cobalt concentration is increased from 0.0 (pure MoS_2) to 1.0 (pure cobalt sulfide), and compare the differences between both preparation methods.

EXPERIMENTAL PROCEDURE

Samples of molybdenum sulfide, cobalt sulfide and mixtures in atomic ratios r =

0021-9517/92 $5.00

Co/(Co + Mo) of 0.0, 0.3, 0.5, 0.7, and 1.0 were prepared according to the HSP method as follows: (a) an aqueous solution of $(NH_4)_2S$ is poured into an aqueous solution of a mixture of salts of metals, (b) the resulting solution is continuously stirred for 36 hr at 343 K, and (c) it is then filtered in vacuum and dried.

Similar pure and mixed sulfide samples were prepared by the recently developed ITD method (*6*) that makes use of the concept of impregnation, commonly practiced in the preparation of supported metals. The intermediate is $(NH_4)_2MoS_4$ (ATM), 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 added dropwise to the (NH_4) MoS_4 crystals suspended in the solvent. The mixture is stirred at 313 K for 5 hr, adding solvent until the treatment is complete.

In both methods, the precursors are subsequently sulfided in a mixture of H_2S for 4 hr at 673 K. All the catalysts used in this work were bulk (unsupported) catalysts.

The sulfide samples were ground with a mullite mortar and pestle and were ultrasonically dispersed in heptane. A drop of the suspension was air-dried on a carbon-coated electron microscope grid for examination in a Jeol 4000 EX electron microscope (0.18-nm point-to-point resolution).

RESULTS

In Fig. 1 we present electron diffraction patterns (EDP) of samples prepared by HSP with r values of (a) 0.0, (b) 0.3, (c) 0.5, (d) 0.7, and (e) 1.0 [r = Co/(Co + Mo)]. Figure 1a shows an EDP from a pure molybdenum sulfide sample. According to data from the X-ray Powder Data File, card No. 37-1492, rings can be indexed as corresponding to the MoS_2–2H phase. Reflections (002), (100), (103), (110), and (008) are clearly identified, and other reflections are diffuse. Most rings are broad, which suggests the presence of poorly crystallized or very small crystals of the MoS_2–2H phase. This and the rest of Fig. 1 shows that the most intense reflections of MoS_2–2H are present for r values up to 0.5 and they tend to disappear for larger r values. We can also note the presence of ill-defined halos from the carbon support used for the TEM observation.

Figures 1b through 1d show spots, besides the rings assigned to MoS_2–2H. These spots match cobalt sulfide phases, the most frequently identified was Co_9S_8, although $CoS_{1.035}$, and $CoS_{1.097}$ can not be disregarded. In Table 1 we present, for r = 0.3, experimentally measured interplanar spacings as compared to the theoretical spacings for the various phases considered for both preparation methods. Other diffraction patterns show comparable trends, and therefore only one is listed as an example.

Figure 2 shows EDP similar to those shown in Fig. 1 for samples prepared by ITD with r values of (a) 0.0, (b) 0.3, (c) 0.5, and (d) 0.7. In Fig. 2a, for pure molybdenum sulfide, rings can be indexed as corresponding to the MoS_2–2H phase. Reflections (002), (100), (103), (110), and (008) are identified. Also, most rings are broad. Similar to Fig. 1, we observe the presence of the most intense reflections of MoS_2–2H in all the samples with molybdenum, although it is interesting to note that in this case they are present up to an r value of 0.7. There are also some weak halos due to the amorphous carbon support, as explained above. Also, akin to the results for the HSP method, shown in Fig. 1, we observe a collection of spots due to the formation of cobalt sulfide phases, which within our accuracy cannot be unequivocally assigned. As an example, Table 1 also gives a list of possible crystalline phases for the different interplanar spacings (larger than 0.4 nm), observed for the case of r = 0.3.

In Fig. 3 we present HREM images of samples generated using the HSP method for r values of (a) 0.0, (b) 0.3, (c) 0.5, (d) 0.7, and (e) 1.0. Figure 4 shows similar HREM images of samples prepared by the ITD method for r values of (a) 0.0, (b) 0.3, (c) 0.5, and (d) 0.7. In both figures we can note the presence of typical "rag" structure of

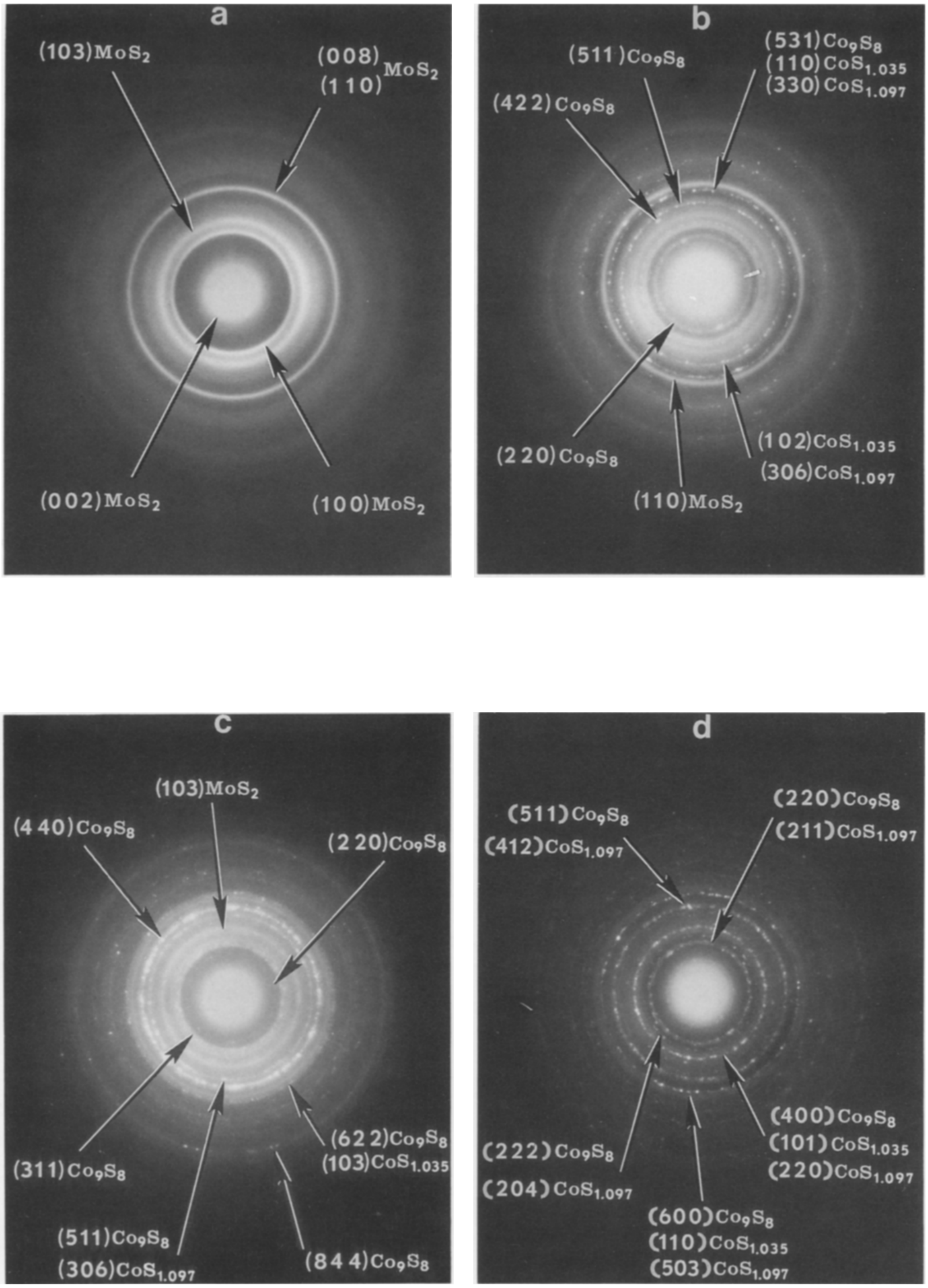


FIG. 1. Electron diffraction patterns from samples prepared by HSP for r values [r = Co/(Co + Mo)] of: (a) 0.0, (b) 0.3, (c) 0.5, (d) 0.7, and (e) 1.0.

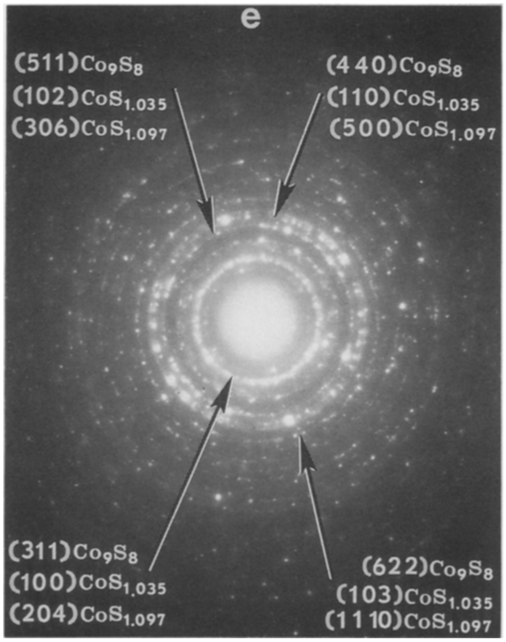


FIG. 1—*Continued*

(002) MoS_2–2H planes with spacing of 0.62 nm (except in Fig. 3e, where no molybdenum sulfide is present). There are some amorphous-like regions in all samples, which appear to be larger in samples prepared by the HSP method.

On the other hand, planes (111) of Co_9S_8 with interplanar distance of 0.57 nm are identified in Fig. 3e, where $r = 1$ and there is no molybdenum sulfide. These planes are formed by well defined straight lines and the crystal shown is larger than any of the molybdenum sulfide crystals. The same cobalt sulfide planes are also present for images with r values of 0.5 and 0.7 by the HSP method (Figs. 3c and 3d), and for r values of 0.3, 0.5, and 0.7 by the ITD method (Figs. 4b, 4c, and 4d).

Statistics on the number and length of MoS_2–2H layers were performed on enlarged micrographs taken from several samples. Since weakly bound crystals, like MoS_2, can easily turn out of diffraction conditions and thus "disappear" from the field of view, our measurements do not necessarily yield the absolute or "true" values of these parameters. Rather, since this orientation phenomenon affects all samples in a random way, mesurements over each sample will likewise be affected. Therefore, comparisons dealing with trends, likenesses, or differences between the two preparation methods remain valid, regardless of the orientation effect.

Figure 5 shows the frequency of appear-

TABLE 1

Experimental Interplanar Spacings for Both Preparation Methods (Same Composition of $r = 0.3$) as Compared to the Closest Theoretical Plane from the MoS_2–2H, Co_9S_8, $CoS_{1.035}$, or $CoS_{1.097}$ Phases

HSP	ITD	Theoretical planes	
3.42		3.49	(220) Co_9S_8
3.20		3.20	(211) $CoS_{1.097}$
2.94	2.96	2.98	(311) Co_9S_8
		2.93	(100) $CoS_{1.035}$
		2.89	(204) $CoS_{1.097}$
2.70		2.73	(100) MoS_2–2H
	2.67	2.67	(101) MoS_2–2H
2.51		2.54	(101) $CoS_{1.035}$
		2.52	(220) $CoS_{1.097}$
		2.48	(400) Co_9S_8
2.37	2.25	2.28	(331) Co_9S_8
		2.27	(103) MoS_2–2H
		2.25	(215) $CoS_{1.097}$
		2.22	(420) Co_9S_8
2.04		2.02	(422) Co_9S_8
1.93		1.94	(102) $CoS_{1.035}$
		1.93	(306) $CoS_{1.097}$
		1.91	(511) Co_9S_8
	1.72	1.75	(440) Co_9S_8
		1.74	(500) $CoS_{1.097}$
		1.69	(110) $CoS_{1.035}$
1.68		1.69	(110) $CoS_{1.035}$
		1.67	(330) $CoS_{1.097}$
		1.67	(531) Co_9S_8
1.58	1.55	1.58	(110) MoS_2–2H
		1.53	(008) MoS_2–2H
	1.49	1.49	(622) Co_9S_8
		1.49	(103) $CoS_{1.035}$
		1.47	(1,1,10) $CoS_{1.097}$
	1.22	1.21	(733) Co_9S_8
		1.21	(621) $CoS_{1.097}$
		1.19	(104) $CoS_{1.035}$
	0.99	1.01	(212) $CoS_{1.035}$
		0.99	(933) Co_9S_8
		0.99	(814) $CoS_{1.097}$

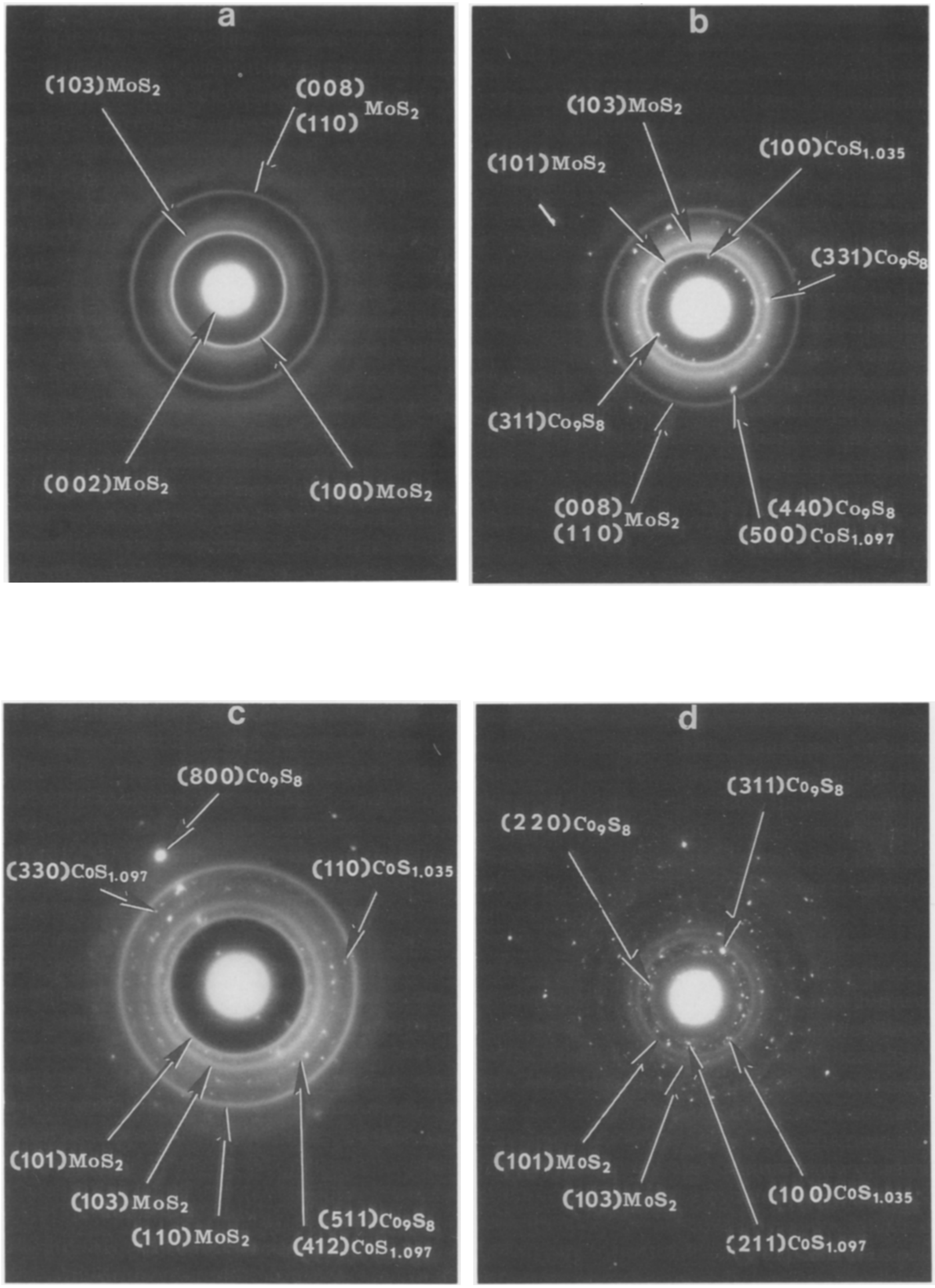
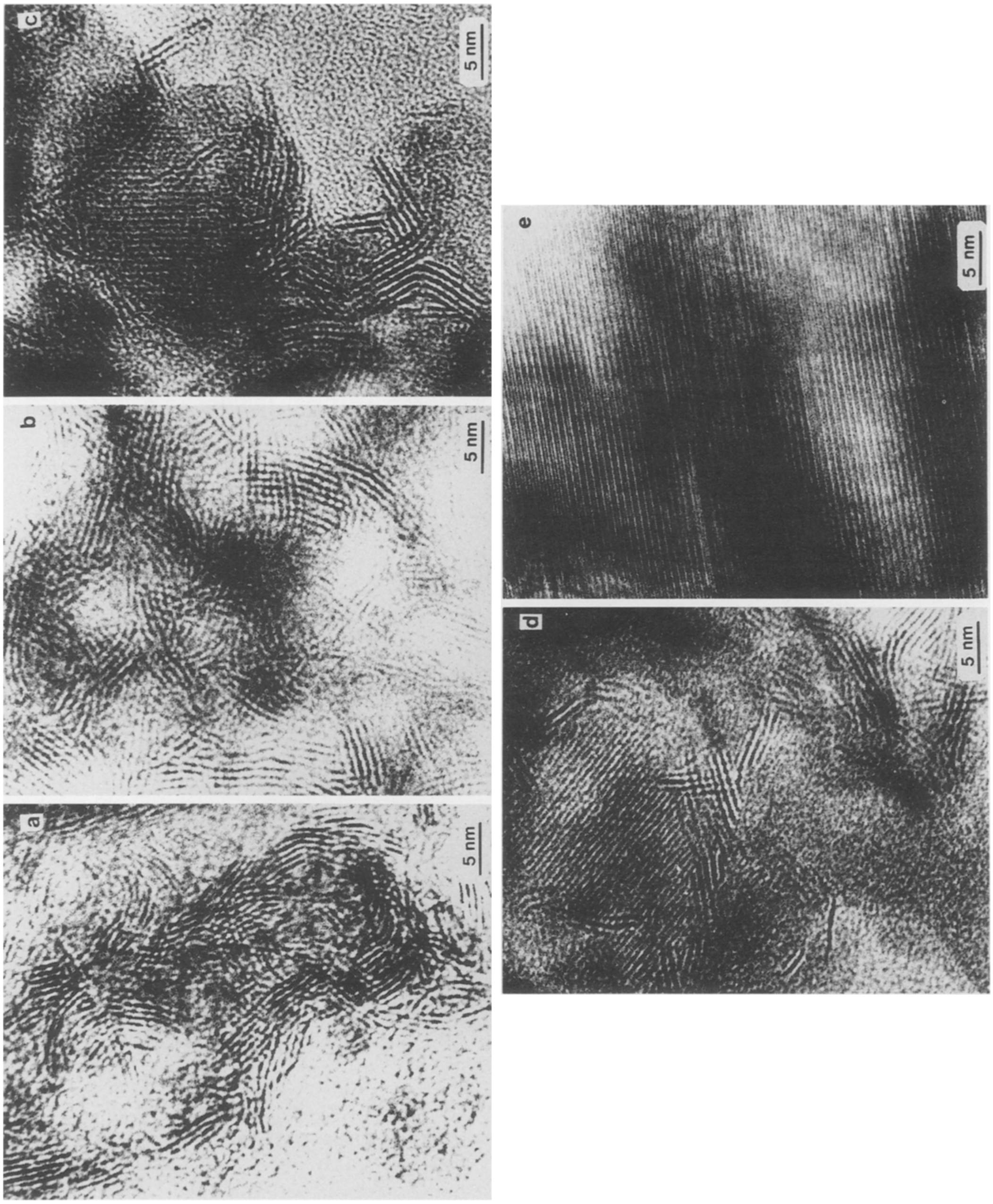


FIG. 2. Electron diffraction patterns from samples prepared by ITD for r values of: (a) 0.0, (b) 0.3, (c) 0.5, and (d) 0.7.



IG. 3. High-resolution transmission electron micrographs from samples prepared by HSP for *r* values of: (a) 0.0, (b) 0.3, (c) 0.5, (d) 0.7, and (e) 1.0.

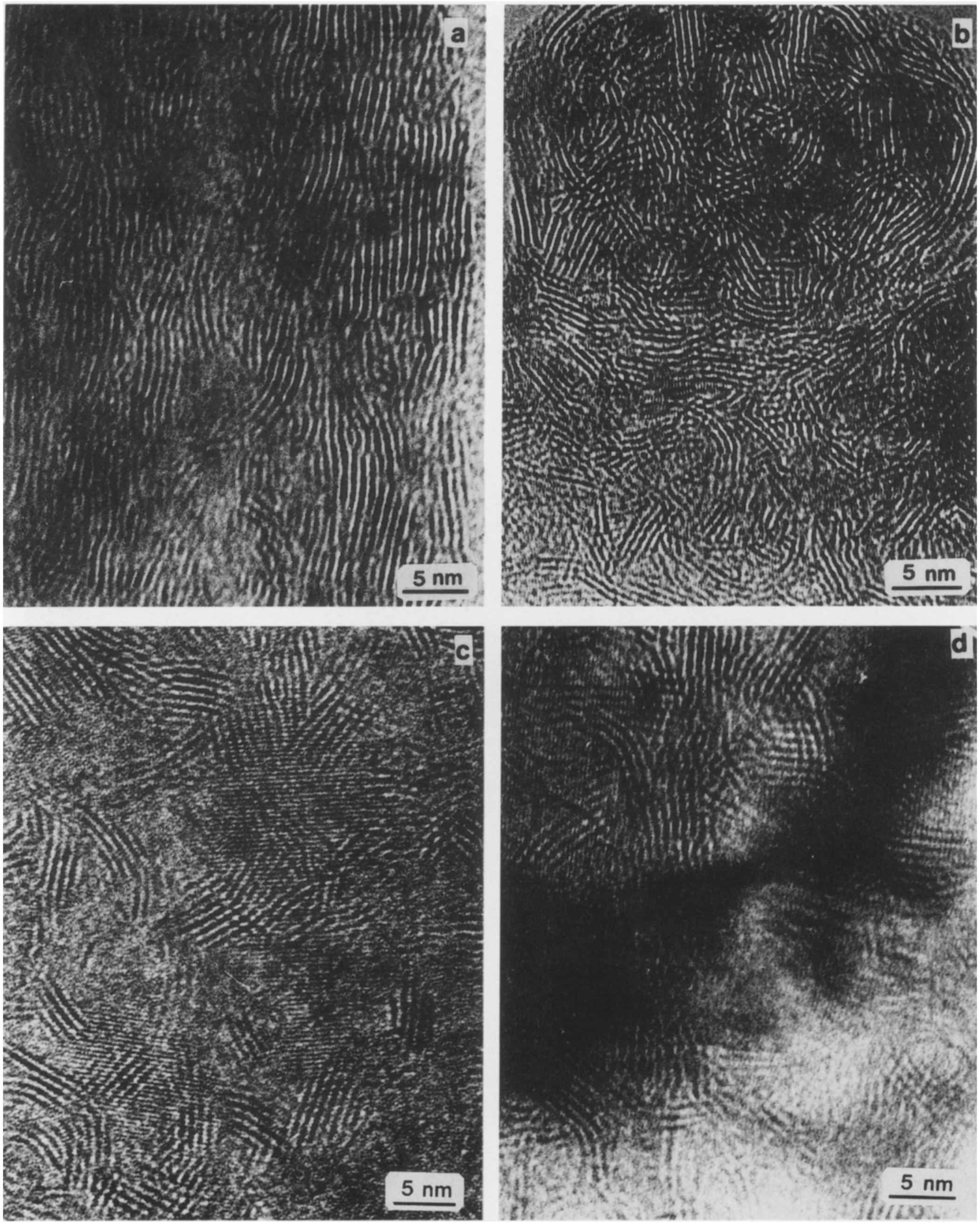


FIG. 4. High-resolution transmission electron micrographs from samples prepared by ITD for r values of: (a) 0.0, (b) 0.3, (c) 0.5, and (d) 0.7.

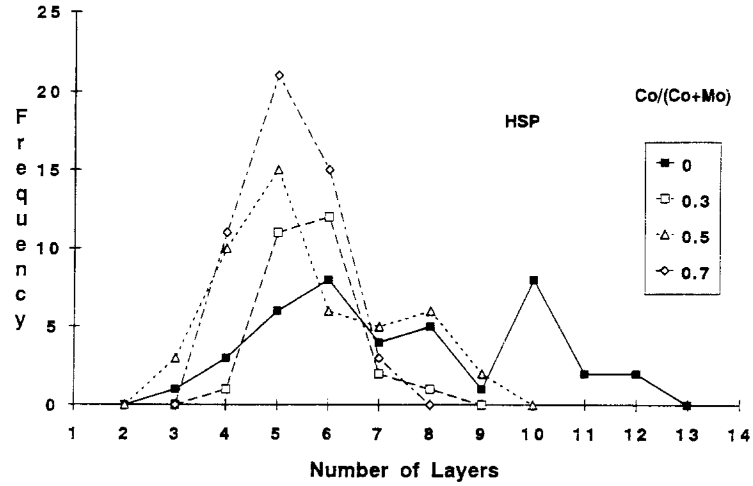


FIG. 5. Frequency of appearance of MoS_2 crystallites as a function of the number of atomic layers for different r values for HSP.

ance of MoS_2–2H crystallites, as a function of the number (n) of (002) layers for different r values (0.0, 0.3, 0.5, and 0.7) in samples prepared by HSP. The four samples present a maximum at 4–6 layers.

In Fig. 6 we give similar measurements for samples prepared by ITD and, as in the previous case, the maximum number of crystallites also occurs between four and six layers.

Figure 7 shows the frequency of appearance of MoS_2–2H crystallites, as a function of the (002) length (L), for the same samples shown in Fig. 5. Most crystals have a length between 10 and 25 nm, and no significant changes are observed with variation of r.

In Fig. 8 we present measurements similar

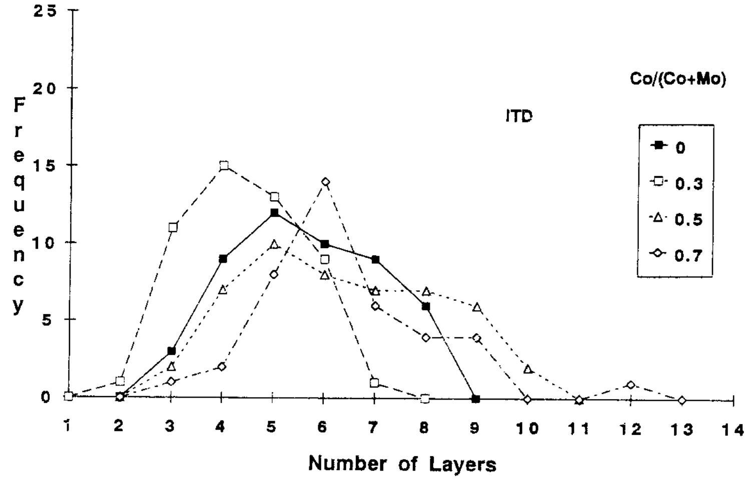


FIG. 6. Frequency of appearance of MoS_2–2H crystallites as a function of the number of atomic layers for different r values for ITD.

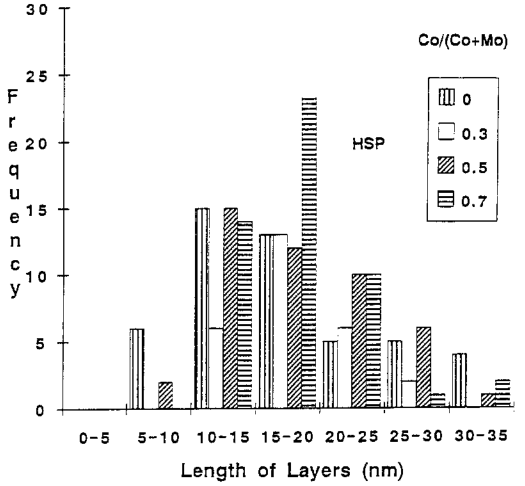


FIG. 7. Frequency of appearance of MoS_2 crystallites as a function of the length of atomic layers for different r values for HSP.

to those shown in Fig. 7, for samples prepared by ITD. In this case, most crystals have a length (L) between 0 and 15 nm.

DISCUSSION

Electron diffraction patterns of samples prepared by HSP for $r = 0.0$ show some broad rings, which suggest the presence of a poorly crystalline or very small size on the MoS_2–2H crystals. Broad bands have also been detected from results obtained with X-ray diffraction for the same preparation methods by Candia *et al.* (*5*) and Cruz-Reyes *et al.* (*7*), and for different preparation methods like low-temperature metathetical reactions, by Chianelli and Dines (*8*), and by Pecoraro and Chianelli (*9*). We also note in Figs. 3 and 4 that samples without cobalt present a slight medium-range order in the arrangements along the MoS_2 stacks (intracrystallites), forming groups of stacks in similar directions, which is more noticeable for the HSP samples. The addition of cobalt ($r > 0.0$) induces disorder in the arrangement of the MoS_2–2H stacks, and the ordering observed for $r = 0.0$ disappears. Disorder induced by cobalt in this type of catalyst (either inter- or intrastacks) and strongly dependent on the preparation method has been documented by other authors. Sørensen *et al.* (*10*) reported the observation of an increasing disorder in the packing of the MoS_2-like slabs with increasing cobalt content, but Delannay (*11*) did not confirm this observation in CoMo–HSP catalysts because it is probably highly dependent on the details of the preparation procedure. Sanders and Pratt (*12*) have shown, for NiMo catalysts, that the most active samples contain highly dispersed "books" of MoS_2.

It is interesting to note that the most intense reflections of MoS_2–2H are present for r values up to 0.5 for HSP samples, while for ITD samples they remain visible for r values up to 0.7. This is in good agreement with previous X-ray results on CoMo samples (*7, 13*). Since the precursor in the HSP method is obtained from a solution, the molybdenum sulfide crystals are probably formed without preferential order. On the other hand, in the ITD method, the MoS_2–2H phase is formed from the decomposition of the thiosalt, which was already grown, and most likely conserves some of its morphological features.

From the results shown above (Figs. 1 to

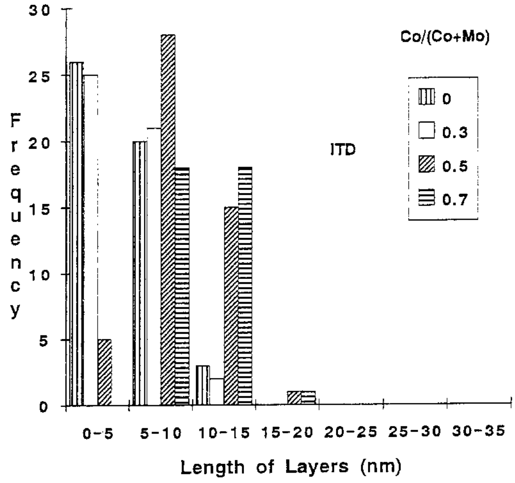


FIG. 8. Frequency of appearance of MoS_2–2H crystallites as a function of the length of atomic layers for different r values for ITD.

4 and Table 1), we observe the presence of the Co_9S_8 phase (and probably other phases like $CoS_{1.035}$ or $CoS_{1.097}$) in both preparation methods. This agrees with the finding of the phase Co_9S_8 by Phillips and Fote (*14*), and the measurements of Göbölös *et al.* on several cobalt sulfide phases (*15*).

No evidence of spots with a lattice distance between 0.4 and 0.5 nm, as those reported for CoMo catalysts supported on carbon (*16*), was found. This may be due to differences in dispersion between unsupported and carbon-supported catalysts.

G. Díaz *et al.* (*13*) have recently shown evidence, by X-ray measurements, of a mixed CoMo sulfide phase besides MoS_2–2H and Co_9S_8 in samples prepared by a slight variation of the ITD method. They assigned this mixed phase to $CoMoS_{3.13}$. Their samples were washed thoroughly with distilled water after impregnation in order to remove the excess ATM base that was not cobalt impregnated. To observe the mixed phase they annealed their samples at 800°C for 4 hr. We did not find evidence for this mixed phase, probably because we did not anneal the samples at high temperature or wash the excess ATM base. Our method could have produced a smaller concentration of this mixed phase, and therefore diffraction spots from this phase could have been masked by the ones coming from the main phases MoS_2–2H and Co_9S_8.

Some concern was raised by a reviewer about the air exposure of samples during the air-drying process of samples prior to the electron microscope experiments. It is believed that 1 min exposure to air does not greatly modify the particle's morphology as does a long exposition lasting several months (*17*). Besides, no evidence of oxidized phases was found neither in the EDP or high-resolution images.

Regarding the morphological changes induced by the promoter in MoS_2 catalysts, it has been previously suggested that in the synergetic range, cobalt could favor the formation of smaller crystals (*12, 18*). Thus, the MoS_2 crystallite size in the c direction seems to decrease with increasing Co/Mo ratio up to $r \leq 0.3$ (*5, 19*). In this work, only small differences were noticed. Our statistical measurements indicate that the number of layers (n) in the stacks of MoS_2 is about the same in both preparation methods (all samples present a maximum between four and six layers). Nevertheless, a slight variation is observed in ITD samples when the cobalt concentration goes from 0.0 to 0.5. As reported earlier (*20*), such as change suggests that cobalt affects the growth process of MoS_2 crystallites in this preparation method.

Our statistical measurements indicate that the number of layers (n) in the stacks of MoS_2–2H is about the same in both preparation methods (all samples present a maximum between four and six layers), while the length (L) of the stacks is shorter in the case of ITD (a maximum around 15 to 20 nm for HSP vs 5 to 10 nm for ITD). On the other hand, there seems to be an increase in L as a function of concentration of cobalt for the ITD method, whereas there is a less noticeable change in the case of HSP. The difference in length of layers in the ITD samples might be due to a better alignment of the MoS_2 "rag" crystallites onto the larger and more ordered Co_9S_8 crystals detected in these samples and which are more noticeable for high Co concentration. These results indicate that considering two samples with the same surface area, the ratio of edge to basal plane area in the stacks of ITD catalysts should be larger than the corresponding ones for HSP. It is commonly accepted that the most important catalytic sites reside on edge planes, therefore, this could explain the larger intrinsic rate of activity recently observed by our group (*21*), for ITD catalysts.

CONCLUSIONS

From these high-resolution electron microscopy results involving two different procedures of preparation and the entire range of promoter composition (r = 0.0, 0.3, 0.5, 0.7, and 1.0) we obtain the following conclusions. Both preparation methods, HSP and ITD, present the "poorly crystalline structure" typical of MoS_2–2H catalysts, however, some structural differences appeared between them. The average number of layers (*n*) in molybdenum disulfide crystallites is about the same in both preparation methods, although small changes were observed for ITD samples. On the other hand, the average length of the molybdenum disulfide crystallites obtained by HSP is larger than those obtained by ITD. The fact that *n* is constant in both methods, but *L* is smaller for ITD samples, indicates that the particle size is smaller for ITD samples. The presence of cobalt modifies slightly the number of layers of the MoS_2–2H stacks in mixed samples. Also, an increase in the intracrystallite disorder is observed.

ACKNOWLEDGMENTS

We are grateful to M. Del Valle for helpful comments and suggestions, and to F. Ruiz and G. Vilchis for technical assistance.

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