

## CHARACTERIZATION OF UNSUPPORTED CoMo SULFIDE CATALYSTS AND THEIR PRECURSORS BY TEMPERATURE-PROGRAMMED REACTIONS

Q. WU \*, S. GÖBÖLÖS \*\*, P. GRANGE and F. DELANNAY

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

(Received 31 May 1984)

### ABSTRACT

Precursors of unsupported CoMo sulfide catalysts with concentration ratios,  $r = \text{Co}/(\text{Co} + \text{Mo})$ , varying from 0 to 1 were prepared by four different methods: comaceration (CM); homogeneous sulfide precipitation (HSP); inverse HSP (IHSP); and coprecipitation (CP). Differential thermal analysis (DTA) was used to investigate successively the thermal decomposition (under argon) or the reduction/sulfidation (under 15%  $\text{H}_2\text{S}-\text{H}_2$  mixture) of these catalyst precursors and the air oxidation of the decomposed or sulfided samples. Various proportions of  $(\text{NH}_4)_2\text{MoS}_4$  and  $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$  were found in the precursors, depending on the preparation method. The presence of cobalt markedly affected the reaction under  $\text{H}_2\text{S}/\text{H}_2$  mixture. Upon oxidation, the CM catalysts behave like pure  $\text{MoS}_2$ , indicating the biphasic nature of these samples. In contrast, the HSP (IHSP, CP) catalysts appear more difficult to oxidize, owing to the presence of finely dispersed cobalt species. The amount of  $\alpha\text{-CoMoO}_4$  detected in the oxidized catalysts by X-ray diffraction may be used as a convenient estimation of the dispersion of cobalt in the precursor sulfides.

### INTRODUCTION

Previous studies have shown that structural and catalytic properties of unsupported CoMo sulfide hydrodesulfurization (HDS) catalysts strongly depend on the method of preparation [1–4]. Two different models have been proposed to explain the promoting effect exerted by cobalt on the activity of such catalysts. The main difference between these models lies in the assumed structure of the active phase: a mixture of pure  $\text{MoS}_2$  and  $\text{Co}_9\text{S}_8$  phases [5]; or a mixed Co–Mo–S phase [1]. The relative proportion of these phases is very much affected by the method of preparation [1,4]. Therefore, it is

\* On leave from Beijing Municipal Chemical Industry Research Institute, Cheng Fu, Haidian, Beijing P.B. 2653, China.

\*\* On leave from Central Research Institute for Chemistry, Hungarian Academy of Sciences, 1025 Budapest, Pusztaszeri ut 59–67, Hungary.

interesting to study the effects of the various preparation steps (precipitation, evaporation, decomposition/sulfidation) on the physico-chemical properties of the catalysts and, especially, on the dispersion of cobalt.

The present work aims at investigating, by means of differential thermal analysis (DTA), the various solid-state reactions involved in such preparations. We have characterized differently prepared, unsupported CoMo catalysts in their precursor and sulfided state by temperature-programmed decomposition/sulfidation and air oxidation. The reacted samples were also studied by X-ray diffraction (XRD). The objective is a critical assessment of the potentialities of such an approach for providing information on the dispersion of cobalt in the catalysts. The possible use of these methods as "fingerprints" for the detection of a mixed sulfide phase is evaluated.

## EXPERIMENTAL

### *Preparation of catalyst precursors*

Unsupported CoMo sulfide precursors were prepared by four different methods. All methods involve the mixing of chosen proportions of compounds of molybdenum and cobalt in a solution of  $(\text{NH}_4)_2\text{S}$  at 343 K. The  $\text{S}/(\text{Co} + \text{Mo})$  ratio in the mixture was more than 1.5 times that needed for the complete sulfidation of cobalt and molybdenum into  $\text{CoS}$  and  $\text{MoS}_4^{2-}$ . The details of the experimental procedure are given in ref. 6. All preparations were carried out under argon atmosphere.

In the homogeneous sulfide precipitation (HSP) method [1], a very dilute mixed solution of ammonium heptamolybdate (AHM) and cobalt nitrate is slowly added to a dilute, vigorously stirred solution of  $(\text{NH}_4)_2\text{S}$ .

In the inverse HSP (IHSP) method [2], it is the dilute solution of  $(\text{NH}_4)_2\text{S}$  that is added to the mixed solution of cobalt nitrate and AHM.

In the coprecipitation (CP) method [7] a dilute solution of cobalt nitrate is added under vigorous stirring to a previously prepared solution of ammonium thiomolybdate (ATM) and oxythiomolybdates (AOTM). Exceptionally, only a 3% excess of sulfur was used in this case instead of 50%. This method induces the formation of a precipitate which, according to ref. 8, is a mixture of  $\text{CoS}$  and  $\text{MoS}_3$ .

In the comaceration (CM) method [9], powdered  $\text{MoO}_3$  and  $\text{Co}_3\text{O}_4$  are added to a hot concentrated (20%) solution of  $(\text{NH}_4)_2\text{S}$ .

The slurries obtained by these various methods are then stirred at 343 K until all the liquid phase has evaporated. Two samples with atomic ratios ( $r = \text{Co}/(\text{Co} + \text{Mo})$ ) of 0.1 and 0.3 were prepared by the HSP, IHSP and CM methods. Only one sample with  $r = 0.3$  were prepared by the CP method.

Two samples of pure molybdenum disulfide precursors ( $r = 0$ ) were

prepared by the HSP and CM methods. A pure cobalt sulfide precursor ( $r = 1$ ) was also prepared by the HSP method.

The dry promoted catalyst precursors will be designated in this communication by the composition, followed with the method of preparation of the slurry (HSP, IHSP, CP and CM) and the concentration ration,  $r$ , e.g., CoMo-CM-0.3. The pure sulfide precursors will be designated in the same way, e.g., Mo-CM-0.0, Co-HSP-1.0.

#### *DTA under controlled atmosphere*

Temperature-programmed reactions (TPR) of the dry precursors under controlled atmosphere were studied in a purpose-built atmospheric pressure, all glass, DTA apparatus. During the reaction, the temperature difference between a 300-mg sample (particle size  $< 0.4$  mm) and a 300-mg SiO<sub>2</sub> reference (Spherosil XOA 400, particle size 0.1–0.2 mm) was measured by Cr–Al thermocouples. A constant heating rate of 11 K min<sup>-1</sup> was used from 373 to 703–723 K. The standard deviation of the reported temperatures is  $\pm 2$  K. The gas flow was 57.7 cm<sup>3</sup> min<sup>-1</sup>.

Thermal decomposition and reduction/sulfidation were conducted under argon and a 15% H<sub>2</sub>S–H<sub>2</sub> mixture, respectively. When the maximum temperature (703–723 K) was reached, the samples were kept at 673 for 2 h under the reacting atmosphere and then allowed to cool down to room temperature under argon.

After completion of either of these reactions, temperature-programmed oxidation of the resulting sample was performed under identical conditions using air as reacting atmosphere. The details are as above.

The samples obtained after such reactions will be designated by adding the letters D (for decomposed) after treatment under argon, S (for sulfided) after treatment under a 15% H<sub>2</sub>S–H<sub>2</sub> mixture, and DO or SO after air oxidation, e.g., CoMo-HSP-0.3-DO and CoMo-CM-0.1-SO.

#### *XRD analysis*

XRD analysis was performed on a Philips PW-1010-X-ray diffractometer using CuK $\alpha$  radiation and a monochromator to suppress the fluorescence from cobalt.

## RESULTS

The differences between the final catalysts originate from the different modes of preparation of the dry precursors. In order to characterize these differences, we will first study the transformations occurring during the heat treatment of these precursors under argon or a 15% H<sub>2</sub>S–H<sub>2</sub> mixture.

Second, we will compare the behaviors of these heat-treated samples when submitted to an oxidizing treatment. Finally, we will characterize the final sulfided and oxidized samples by XRD.

*Temperature-programmed decomposition and reduction/sulfidation of the dry precursors*

Figure 1 presents the DTA curves recorded during the temperature-programmed reaction of precursors CM (—), HSP (-----) and CP (·····), under argon (a–c) and under a 15% H<sub>2</sub>S–H<sub>2</sub> mixture (d–f). The curve pairs a/d, b/e and c/f correspond to  $r = 0.0, 0.3$  and  $1.0$ , respectively. The curves for samples with  $r = 0.1$  and CoMo-IHSP-0.3 are not shown as they were very similar to those for samples with  $r = 0.3$  and CoMo-HSP-0.3, respectively.

*Mo-CM-0.0 and Mo-HSP-0.0 (curves a and d)*

When reacted under argon, samples Mo-CM-0.0 and Mo-HSP-0.0 exhibit

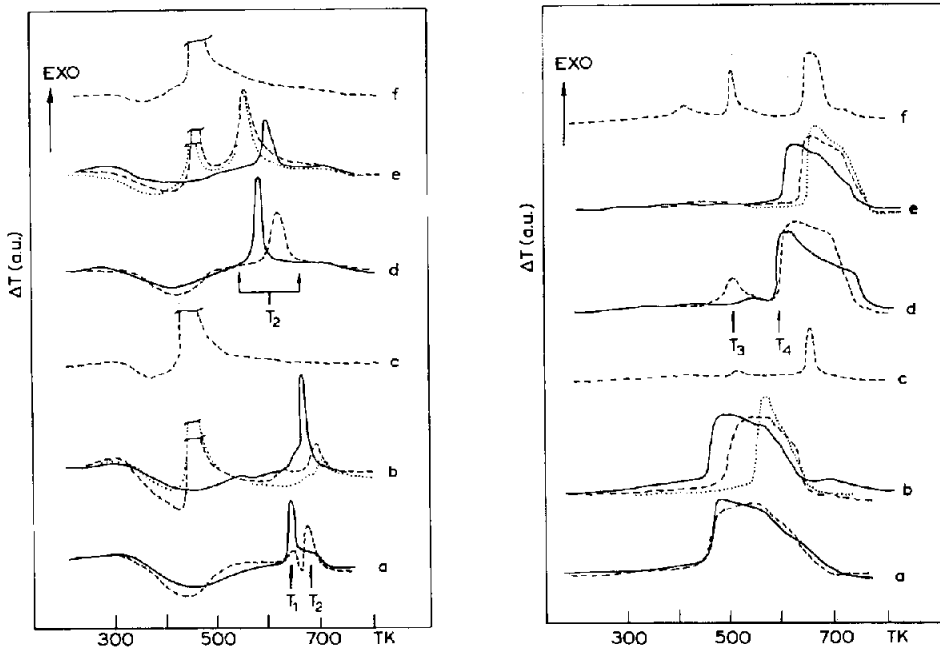


Fig. 1. DTA curves of decomposition/sulfidation of CoMo precursors prepared by the CM (—), HSP (-----) and CP (·····) methods. (a–c) Samples decomposed in Ar; (d–f) samples sulfided in a 15% H<sub>2</sub>S–H<sub>2</sub> mixture, with  $r = 0.0, 0.3$  and  $1.0$ , respectively.

Fig. 2. DTA curves of air oxidation of heat-treated CoMo samples prepared by the CM (—), HSP (-----) and CP (·····) methods. (a–c) Samples decomposed in Ar; (d–f) samples sulfided in a 15% H<sub>2</sub>S–H<sub>2</sub> mixture, with  $r = 0.0, 0.3$  and  $1.0$ , respectively.

TABLE 1

Characteristic temperatures of temperature-programmed reactions of unsupported CoMo catalysts and their precursors and XRD results on oxidized samples

<i>r</i>	Gas	Cat.	Decomposition		Oxidation		XRD
			$T_1$ (K)	$T_2$ (K)	$T_3$ (K)	$T_4$ (K)	
0	Ar	CM	635	665		458	MoO <sub>3</sub> + traces of MoO <sub>2</sub>
		HSP	633	668		453	MoO <sub>3</sub>
0.1	H <sub>2</sub> S-H <sub>2</sub>	CM		543	508	598	MoO <sub>3</sub> + traces of MoO <sub>2</sub>
		HSP		591	475	600	MoO <sub>3</sub>
0.1	Ar	CM	653	675		453	MoO <sub>3</sub> , <i>a</i> -CoMoO <sub>4</sub> , traces of MoO <sub>2</sub> + Co <sub>3</sub> O <sub>4</sub>
		HSP	624	673		448	MoO <sub>3</sub> , <i>a</i> -CoMoO <sub>4</sub>
		IHSP	620	679		435	MoO <sub>3</sub> , <i>a</i> -CoMoO <sub>4</sub>
		CM		577		598	MoO <sub>3</sub> , <i>a</i> -CoMoO <sub>4</sub> , traces of MoO <sub>2</sub> + Co <sub>3</sub> O <sub>4</sub>
0.1	H <sub>2</sub> S-H <sub>2</sub>	HSP		518		618	MoO <sub>3</sub> , <i>a</i> -CoMoO <sub>4</sub>
		IHSP		515		625	MoO <sub>3</sub> , <i>a</i> -CoMoO <sub>4</sub>
		CM	650	673		458	MoO <sub>3</sub> , <i>a</i> -CoMoO <sub>4</sub> , traces of MoO <sub>2</sub> + Co <sub>3</sub> O <sub>4</sub>
0.3	Ar	HSP	613	673		498	MoO <sub>3</sub> , <i>a</i> -CoMoO <sub>4</sub>
		IHSP	613	673		503	MoO <sub>3</sub> , <i>a</i> -CoMoO <sub>4</sub>
		CP	653	680		558	MoO <sub>3</sub> , <i>a</i> -CoMoO <sub>4</sub>
		CM		571		603	MoO <sub>3</sub> , <i>a</i> -CoMoO <sub>4</sub> , traces of MoO <sub>2</sub> + Co <sub>3</sub> O <sub>4</sub>
1.0	H <sub>2</sub> S-H <sub>2</sub>	HSP		503		630	MoO <sub>3</sub> , <i>a</i> -CoMoO <sub>4</sub>
		IHSP		511		625	MoO <sub>3</sub> , <i>a</i> -CoMoO <sub>4</sub>
		CP		513		643	MoO <sub>3</sub> , <i>a</i> -CoMoO <sub>4</sub>
		HSP			505	647	Co <sub>3</sub> O <sub>4</sub> , $\beta$ -CoSO <sub>4</sub>
				500	643	Co <sub>3</sub> O <sub>4</sub> , $\beta$ -CoSO <sub>4</sub>	

a broad endothermic peak with a maximum at 453–458 K and two exothermic peaks ( $T_1$  and  $T_2$ ) in the range 633–703 K. The starting temperatures of peaks  $T_1$  and  $T_2$  are listed in Table 1. It is worthy of note that on curve a of Fig. 1, the position of the exothermic peaks is the same for samples Mo-CM-0.0 and Mo-HSP-0.0, but that their relative intensity is completely different.

Reaction of the same samples under  $H_2S-H_2$  (Fig. 1d) produces the same broad endothermic peak. Only one exothermic peak (referred to as  $T_2$ ) is observed at a lower temperature than before. There is a 50 K difference in the position of this peak for the two samples. The total exothermic effect is significantly higher for Mo-CM-0.0.

#### *Co-HSP-1.0 (curves c and f)*

Sample Co-HSP-1.0, containing cobalt alone, shows a highly exothermic peak at  $445 \pm 5$  K both under argon and  $H_2S-H_2$  (Fig. 1c, f). Above this temperature, no thermal effect is observed, which agrees well with the work of Breyse et al. [2,4].

#### *CoMo precursors (curves b and e)*

The same high exothermic effect at  $445 \pm 5$  K, as above, is also observed when reacting samples CoMo-HSP-0.3 and CoMo-CP-0.3 under argon or  $H_2S-H_2$ . As for Mo-CM-0.0 and Mo-HSP-0.0, reaction of samples CoMo-CM-0.3 and CoMo-HSP-0.3 in argon produces two exothermic peaks,  $T_1$  and  $T_2$ , in the range 613–713 K. For CoMo-HSP-0.3, these peaks are spread over a large temperature range ( $\sim 600$ –730 K; compare curves a and b). In the case of CoMo-CP-0.3, the exothermicity of these peaks markedly decreases, and the first peak,  $T_1$ , has even almost completely disappeared. Under  $H_2S-H_2$ , only one such peak is observed at a much lower temperature ( $\sim 500$ –650 K) (Fig. 1e). The curves for CoMo-HSP-0.3 and CoMo-CP-0.3 are then almost identical. Note the inversion of the positions and relative intensities of the peaks between Fig. 1d and e.

#### *Temperature-programmed oxidation of the decomposed and reduced/sulfided samples*

The DTA curves of the air oxidation of the decomposed and reduced/sulfided samples are shown in Fig. 2. The curves are presented in a similar way to Fig. 1. Curves for samples with  $r = 0.1$  and CoMo-IHSP-0.3 are again omitted because of the similarities with the corresponding curves for samples with  $r = 0.3$  and CoMo-HSP-0.3, respectively. A large exothermic peak is observed over a wide temperature range. In some cases, a smaller exothermic peak is also detected at a lower temperature. The starting temperatures,  $T_3$  and  $T_4$ , of these two peaks are also listed in Table 1.

The DTA curves of Fig. 2 show that the starting temperatures of the main

broad oxidation peaks ( $T_4$ ) of molybdenum-containing samples are significantly higher for the  $H_2S-H_2$ -treated samples than for the argon-decomposed ones. However, the overall exothermicity of the oxidation is higher in the latter case.

#### *Mo-CM-0.0 and Mo-HSP-0.0*

For Mo-CM-0.0-D and Mo-HSP-0.0-D, the starting temperatures of the rather complex main exothermic peaks ( $T_4$ ) are the same (453–458 K). After reaction in a 15%  $H_2S-H_2$  mixture, the main oxidation reaction occurs at a higher temperature, for both Mo-CM-0.0-S and Mo-HSP-0.0-S ( $\approx 600$  K). A small exothermic peak is also detected at 508 K for Mo-CM-0.0-S and a stronger one at 470 K for Mo-HSP-0.0-S.

#### *Co-HSP-1.0-D and Co-HSP-1.0-S*

The DTA curve of sample Co-HSP-1.0-D exhibits a main oxidation peak ( $T_4$ ) at 674 K and a smaller one ( $T_3$ ) at 505 K (Fig. 2c, f). Comparatively, for sample Co-HSP-1.0-S, these two peaks have increased significantly in intensity, while remaining at almost the same temperature. In addition, two slightly exothermic peaks appear at 384 and 708 K.

#### *CoMo-containing samples*

The starting temperature of oxidation is usually higher for samples CoMo-HSP (IHSP and CP) than for the corresponding samples CoMo-CM. The only two exceptions are samples CoMo-HSP-0.1-D and CoMo-IHSP-0.1-D, which start to oxidize at a slightly lower temperature than sample CoMo-CM-0.1-D (see Table 1).

All samples prepared by the CM method start to oxidize at 453–458 K after reaction in argon and at about 600 K after  $H_2S-H_2$  treatment. This behavior is very similar to that of the samples containing only molybdenum.

On the contrary, the presence of cobalt increases  $T_4$  by 40–45 K for samples CoMo-HSP(IHSP)-0.3-D and by 20–25 K for samples CoMo-HSP(IHSP)-0.3-S, in comparison with those containing only molybdenum.

It is worthy of note that samples CoMo-CP-0.3-D and CoMo-CP-0.3-S show higher oxidation temperatures than the corresponding samples CoMo-HSP-0.3-D(S) (see Table 1). The starting temperature of oxidation of CoMo-CP-0.3-S (643 K) is the same as that of Co-HSP-1.0-S.

#### *XRD analysis after temperature-programmed reactions*

After thermal decomposition or reduction/sulfidation, all samples containing molybdenum showed the typical amorphous XRD pattern of  $MoS_2$ , in agreement with the results of Candia et al. [1]. Characteristic  $Co_9S_8$  lines appear only in the case of catalysts prepared by the CM method. It is worth mentioning that while only  $Co_9S_8$  is detected in sample Co-HSP-1.0-S, small

amounts of  $\text{Co}_4\text{S}_3$ ,  $\text{CoO}$  and  $\beta\text{-CoSO}_4$  are found in addition to  $\text{Co}_9\text{S}_8$  in sample Co-HSP-1.0-D.

As indicated in Table 1, the XRD patterns of oxidized samples containing only molybdenum (Mo-CM-0.0 and Mo-HSP-0.0) show the formation of  $\text{MoO}_3$ . The X-ray diffractograms of samples Mo-CM-0.0-SO and Mo-CM-0.0-DO also indicated the presence of traces of  $\text{MoO}_2$ . Only  $\text{Co}_3\text{O}_4$  and  $\beta\text{-CoSO}_4$  were detected in oxidized samples containing only cobalt.

In the XRD spectra of oxidized samples containing both Co and Mo (Fig. 3) the two major phases detected are  $\text{MoO}_3$  and  $\alpha\text{-CoMoO}_4$ . The amount of  $\alpha\text{-CoMoO}_4$  is significantly higher for samples with  $r = 0.3$  and for samples previously treated under  $\text{H}_2\text{S-H}_2$  (compare Fig. 3a/b and c/d). It is also higher for samples CoMo-HSP (IHSP and CP) than for the corresponding sample CoMo-CM (compare Fig. 3b/d and a/c). Traces of  $\text{Co}_3\text{O}_4$  and  $\text{MoO}_2$  were also detected for samples CoMo-CM.

## DISCUSSION

### *Characterization of the dry precursors by temperature-programmed decomposition and reduction / sulfidation*

#### *Mo-CM-0.0 and Mo-HSP-0.0*

In the preparation of the slurry by the CM method, the solid  $\text{MoO}_3$  dissolves in the excess  $(\text{NH}_4)_2\text{S}$  solution to give ammonium thiomolybdate or, probably, a mixture of different thio- and oxythiomolybdates [1,2]. The same compounds are also produced in the HSP, IHSP and CP methods when mixing the solutions of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{S}$ .

The decomposition of both  $(\text{NH}_4)_2\text{MoS}_4$  and  $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$  in  $\text{N}_2$  has been studied by Prasad et al. [10]. The reduction of these compounds in a 10%  $\text{H}_2\text{-Ar}$  mixture has been studied by Naumann et al. [11]. Both papers report a reaction proceeding through an endothermic peak with a maximum in the range 441–493 K followed by an exothermic effect at a higher temperature.

According to Prasad et al. [10], the endothermic effect is due to the decomposition to trisulfide (in the case of  $(\text{NH}_4)_2\text{MoS}_4$ ) or to a mixture of oxysulfide and sulfide (in the case of  $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$ ) with the release of ammonia and  $\text{H}_2\text{S}$ . The exothermic effect corresponds to the decomposition of the trisulfide into disulfide, the release of elemental sulfur and crystallization of the disulfide [12]. The final product of the decomposition was  $\text{MoS}_2$  which might be contaminated by  $\text{MoO}_2$  in the case of the decomposition of  $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$  [13].

Table 2 summarizes the positions of the peaks observed in these two studies [10,11]. It is evident that under 10%  $\text{H}_2\text{-Ar}$ , the exothermic effect occurs at a lower temperature than under  $\text{N}_2$ . This temperature difference is



much larger in the case of  $(\text{NH}_4)_2\text{MoS}_4$ . The lowering of the exothermic peak temperature is quite expected since the reduction of  $\text{MoS}_3$  is made easier by the presence of  $\text{H}_2$ .

In good agreement with these expectations, the decomposition of pure molybdenum-containing precursors occurred in the present experiment, at a lower temperature in the presence of hydrogen (85% in the mixture).

In the experiment under argon (Fig. 1a), the wide temperature range of the endothermic effect and the presence of two exothermic peaks indicate that both Mo-CM-0.0 and Mo-HSP-0.0 contain a mixture of thio- and oxythiomolybdates. From the relative intensities and positions of the exothermic peaks in Fig. 1a and d, it can be deduced, by reference to the second and fourth columns of Table 2, that sample Mo-CM-0.0 contains more  $(\text{NH}_4)_2\text{MoS}_4$ , whereas sample Mo-HSP-0.0 contains more  $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$ . This deduction is supported by the fact that sample Mo-CM-0.0 exhibits a larger exothermic effect suggesting a higher proportion of  $\text{MoS}_3$  decomposing into  $\text{MoS}_2$ .

In conclusion, we can assert that, in the CM method, the  $\text{MoO}_3$  forms  $\text{MoS}_4^{2-}$  anions more easily than the HSP method forms  $\text{Mo}_7\text{O}_{24}^{6-}$  anions. This may be due to the higher concentration and pH of the solution in the CM method than in the HSP method.

Nevertheless, the presence of traces of other S-containing molybdenum compounds ( $(\text{NH}_4)_2[\text{Mo}_3\text{S}(\text{S}_2)_6]$  and  $(\text{NH}_4)_2[\text{Mo}_2(\text{S}_2)_6] \cdot 2\text{H}_2\text{O}$  type clusters [14]) cannot be excluded.

#### *Co-HSP-1.0*

When adding the solution of cobalt(II) nitrate to a solution of  $(\text{NH}_4)_2\text{S}$ ,  $\text{Co}^{2+}$  cations react immediately with  $\text{S}^{2-}$  anions to form a cobalt sulfide precipitate [15] and  $\text{NH}_4\text{NO}_3$ . The fact that cobalt is completely sulfided in precursor Co-HSP-1.0 is supported by the appearance of mostly  $\text{Co}_9\text{S}_8$  in the XRD spectrum of the sample Co-HSP-1.0-D.

The highly exothermic peak observed at  $445 \pm 5$  K when heat-treating sample Co-HSP-1.0 is due to the decomposition of  $\text{NH}_4\text{NO}_3$  [16], with the release of  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{N}_2$  and  $\text{NO}$ . Since pure cobalt sulfide precipitate has already formed in the precursor slurry, no other thermal effect is observed during the decomposition and reduction/sulfidation.

TABLE 2

Thermal effects during decomposition of  $(\text{NH}_4)_2\text{MoS}_4$  and  $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$

Compound	Under $\text{N}_2$ [9]		Under 10% $\text{H}_2$ -Ar [10]	
	Endo (K)	Exo (K)	Endo (K)	Exo (K)
$(\text{NH}_4)_2\text{MoS}_4$	493	623-673	493	523-613
$(\text{NH}_4)_2\text{MoO}_2\text{S}_2$	441	653-703	463	593-683

### *CoMo precursors*

Because of the similar behavior of precursors with atomic ratio 0.1 and 0.3, and of preparations HSP and IHSP, we will only discuss the results concerning samples CoMo-CM-0.3, CoMo-HSP-0.3 and CoMo-CP-0.3.

As pointed out by Candia et al. [1], the  $\text{Co}_3\text{O}_4$  powder used in the CM preparation method does not dissolve easily in the  $(\text{NH}_4)_2\text{S}$  solution. Consequently, sample CoMo-CM-0.3 contains a mixture of thio, oxythiomolybdates and superficially sulfided  $\text{Co}_3\text{O}_4$ . This explains the appearance of  $\text{Co}_9\text{S}_8$  lines on the XRD spectra after reaction in a 15%  $\text{H}_2\text{S}-\text{H}_2$  mixture.

The major difference between samples Mo-CM-0.0 and CoMo-CM-0.3 is the inversion of relative intensities of the two exothermic peaks observed during reaction under argon (see Fig. 1a, b). This suggests that the presence of  $\text{Co}_3\text{O}_4$  increases the degree of oxidation of the molybdenum-containing phase during the preparation procedure or during the endothermic decomposition of the mixture of thiomolybdates. The cause of this increased oxidation of molybdenum in the presence of  $\text{Co}_3\text{O}_4$  is difficult to ascertain. Another explanation of this behavior was proposed by Breysse and co-workers [3,4] who suggested that the presence of  $\text{Co}_9\text{S}_8$  or related compounds might inhibit the transformation  $\text{MoS}_3 \rightarrow \text{MoS}_2$ . Later, we will discuss this hypothesis further in the light of our other results.

The sulfidation of  $\text{Co}_3\text{O}_4$  under  $\text{H}_2\text{S}-\text{H}_2$  into  $\text{Co}_9\text{S}_8$  is only slightly exothermic ( $\Delta H_{700\text{ K}} = -90.8 \text{ kJ mol}^{-1}$ ). As discussed in more detail later, this reaction should thus be hardly detectable by DTA during heat treatment under 15%  $\text{H}_2\text{S}-\text{H}_2$  and the exothermic peak appearing on curve e (solid line) should only be ascribed to the reaction of molybdenum compounds. Reference to Table 2 indicates that the higher temperature of this peak, as compared with sample Mo-CM-0.0, is due to the higher degree of oxidation of molybdenum.

For sample CoMo-HSP-0.3, the same exothermic peak due to the decomposition of  $\text{NH}_4\text{NO}_3$  [15] is observed as for sample Co-HSP-1.0. Therefore, contrary to the explanation of Breysse et al. [2,4], this exothermic peak at 445 K cannot be attributed to the decomposition of a mixed Co-Mo-S phase. When decomposing CoMo-HSP-0.3 under Ar, a broadening of the two exothermic peaks  $T_1$  and  $T_2$  is observed, compared to sample Mo-HSP-0.0 (see Fig. 1a, b), which suggests a close interaction of cobalt with molybdenum sulfide or oxysulfide (or, at least, some sort of "dilution effect" of cobalt [2]). Compared with CoMo-CM-0.3, the lower overall exothermic effect indicates a lower degree of sulfidation of molybdenum, which might be due to a partial oxidation by reaction with the gases evolved during the decomposition of  $\text{NH}_4\text{NO}_3$  [16].

As previously mentioned, cobalt is completely sulfided in the precursors prepared by the HSP or CP methods. Compared with sample Mo-HSP-0.0, the lowering of the exothermic peak temperature observed when reacting

sample CoMo-HSP-0.3 under  $H_2S-H_2$  (curves d and e) therefore suggests that the reduction of  $MoS_3$  into  $MoS_2$  is made much easier by the presence of cobalt sulfide. This points to a possible spillover of hydrogen from cobalt sulfide. Such a spillover phenomenon has been proposed to allow the remote control of the HDS activity of  $MoS_2$  by  $Co_9S_8$  [5]. Simultaneously to this decomposition of  $MoS_3$ , these samples become completely sulfided. This justifies the larger exothermicity observed in comparison with sample CoMo-CM-0.3.

This explanation contradicts the previously mentioned proposal of Breyse and co-workers [3,4] that  $Co_9S_8$  or related compounds might inhibit the transformation  $MoS_3 \rightarrow MoS_2$ . We believe that, in the CoMo-CM precursors, cobalt is present essentially as badly dispersed, superficially sulfided  $Co_3O_4$ , and that  $MoS_3$  will decompose before the complete sulfidation of  $Co_3O_4$  into  $Co_9S_8$ . On the contrary, in the CoMo-HSP precursors, cobalt is present in a highly dispersed, sulfided form which can produce spillover hydrogen, thus lowering the temperature of decomposition of  $MoS_3$ .

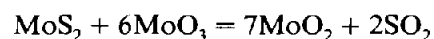
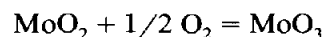
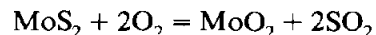
However, one cannot exclude the presence of the mixed compounds formed during the preparation procedure from complex anions of the type  $[Co(MoS_4)_2]^{2-}$  or  $[Co(MoO_2S_2)_2]^{2-}$  [17,18]. These mixed compounds may be less stable than the pure Mo-containing ones, especially in the presence of hydrogen.

The decomposition of CoMo-CP-0.3 under  $H_2S-H_2$  showed exactly the same DTA properties as CoMo-HSP-0.3, indicating a similar structure of these precursors (see Fig. 1e). The lower exothermicity and higher temperatures of decomposition under argon (Fig. 1b) indicate an even lower sulfur content due, probably, to the lower sulfur excess used in the preparation of CoMo-CP-0.3 precursor, compared to CoMo-HSP-0.3.

#### *Characterization of the decomposed and sulfided samples by temperature-programmed oxidation*

##### *Mo-CM-0.0 and Mo-HSP-0.0*

It is known that oxygen preferentially adsorbs on the edges of  $MoS_2$  crystals [19]. As the edges are much more reactive than the basal planes, the oxidation reactions [20]



will more probably proceed from the edges. It can therefore be assumed that the start of the reaction will be controlled by the formation of oxidic nuclei on the edges [21]. The formation of these nuclei might also be affected by the nature of the species present on the edges (e.g., sulfur or atoms of promoters).

Our DTA curves of the highly exothermic [22] oxidation of  $\text{MoS}_2$  showed rather complicated broad peaks with two or three shoulders, which indicate an oxidation reaction proceeding through several steps. These observations are in good agreement with the results of Spivak et al. [20], and Irisova et al. [23] reporting three main stages in the stepwise air oxidation of  $\text{MoS}_2$  through the lower oxides in the temperature range 663–823 K. This stepwise character of the  $\text{MoS}_2$  oxidation was explained by these authors as due to the presence of three types of sulfur differing in their reactivity toward oxygen.

In the case of  $\text{H}_2\text{S-H}_2$ -treated samples (Fig. 2d), we can attribute the small exothermic peak appearing at about 500 K to the oxidation of free elemental sulfur. Indeed,  $\text{MoS}_2$  obtained after sulfidation under  $\text{H}_2\text{S-H}_2$  can contain a certain amount of nonstoichiometric elemental sulfur, oxidizing easily to  $\text{SO}_2$  at about 473–503 K, or at even lower temperatures [24]. It can therefore be assumed that the exothermic threshold at 600 K for both samples Mo-HSP-0.0-S and Mo-CM-0.0-S corresponds to the oxidation of stoichiometric  $\text{MoS}_2$ . The somewhat higher oxidation temperatures reported in previous works [20,23] may be due to the higher crystallinity of these samples. Indeed, it is well expected that the nucleation of oxide nuclei on  $\text{MoS}_2$  is highly influenced by the particle size and crystallinity [25].

In comparison, the lower temperature of oxidation and larger overall exothermic effect for samples decomposed under argon (Fig. 2a) is probably due to the large excess of free sulfur contained in these decomposed samples. Indeed, the sulfur excess resulting from the decomposition of the excess  $(\text{NH}_4)_2\text{S}$  is much less efficiently removed under argon than under a hydrogen-rich atmosphere. We can speculate that the oxidation of this large amount of sulfur will “catalyse” the oxidation of  $\text{MoS}_2$  at a lower temperature than for pure  $\text{MoS}_2$ .

#### *Co-HSP-1.0*

The oxidation of  $\text{Co}_9\text{S}_8$  was studied by Penski et al. [26]. The formation of  $\text{Co}_3\text{O}_4$  and  $\text{CoSO}_4$  has been observed in the presence of  $\text{SO}_2$  + air mixture. The oxidation in pure oxygen led to the formation of complex compounds at 458 K, which were stable up to 653 K and started to oxidize above this temperature. In good agreement with these results, the main exothermic peak of Fig. 2c, f also appeared at 643–647 K.

The oxidation of  $\text{Co}_9\text{S}_8$  under  $\text{O}_2$  into  $\text{Co}_3\text{O}_4 + \text{SO}_2$  is more than five times more exothermic than the sulfidation of  $\text{Co}_3\text{O}_4$  under  $\text{H}_2\text{S-H}_2$  ( $\Delta H_{700\text{ K}} = -483.1 \text{ kJ mol}^{-1}$ ). By comparison, the exothermic peak corresponding to the sulfidation of  $\text{Co}_3\text{O}_4$  when reacting CoMo-CM-0.3 under  $\text{H}_2\text{S-H}_2$  (Fig. 1e, solid line) should be about 15 times smaller than the main exothermic peak of Fig. 2f. This justifies why the reaction  $\text{Co}_3\text{O} \rightarrow \text{Co}_9\text{S}_8$  in sample CoMo-CM-0.3 could not be detected.

The smaller exothermicity of the peak at 645 K for sample Co-HSP-1.0-D is due to the higher degree of oxidation of cobalt which results from the

partial oxidation of cobalt sulfide by the gases evolved during the decomposition of  $\text{NH}_4\text{NO}_3$ .

In the case of the oxidation of Co-HSP-1.0-S, the small peak at 387 K may be attributed to the surface oxidation of cobalt. Indeed, surface oxidation of cobalt sulfide is known to occur rapidly upon exposure to air at room temperature [27]. The presence of such a protective oxide overlayer [1] may explain the relatively high temperature of oxidation of the bulk. The peak at 500 K is probably due to the oxidation of free elemental sulfur.

*Samples CoMo-CM, CoMo-HSP and CoMo-CP*

*Samples CoMo-CM-0.1 and CoMo-CM-0.3.* The threshold temperatures of the oxidation of samples CoMo-CM-0.1 and CoMo-CM-0.3 (Fig. 2b, e, solid line and Table 1) are similar to those of the corresponding pure Mo-CM-0.0 samples. This confirms the biphasic character of these samples. Indeed, badly dispersed  $\text{Co}_9\text{S}_8$  will not significantly influence the oxidation of  $\text{MoS}_2$ .

*Samples CoMo-HSP-(r)-D and CoMo-CP-(r)-D.* As compared to sample Mo-HSP-0.0-D, samples CoMo-HSP-0.3-D and CoMo-CP-0.3-D exhibit a higher threshold temperature of oxidation (Fig. 2b). This is probably due to the lower content of free sulfur resulting from the oxidation of part of this free sulfur into  $\text{SO}_2$  during the decomposition of  $\text{NH}_4\text{NO}_3$ . One can also speculate that the oxygen in these samples acts as a substitute for the most oxidizable sulfur of  $\text{MoS}_2$ , especially on the edges of the layers. Consequently, the onset of oxidation will require a higher temperature and the total exothermicity of the reaction will be lower.

The lower temperature of oxidation of sample CoMo-HSP-0.1-D (even slightly lower than sample Mo-HSP-0.0-D) suggests that the amount of  $\text{NH}_4\text{NO}_3$  in the precursor was insufficient to allow the removal of a significant part of the free sulfur.

*Samples CoMo-HSP-(r)-S and CoMo-CP-(r)-S.* It is striking that these samples start oxidizing at about the same temperature as sample Co-HSP-1.0-S (Fig. 2e, f). One can thus speculate that the higher threshold temperature, in comparison with sample Mo-HSP-0.0-S, may be due to the segregation of cobalt on the edges of the  $\text{MoS}_2$  layers. This surface cobalt would protect molybdenum to some extent, from contact with oxygen. This hypothesis is consistent with the model of the Co-Mo-S phase [28] proposed by Topsøe, who postulated that, in such a mixed phase, cobalt substitutes for molybdenum on the edges of the  $\text{MoS}_2$  layers.

If this interpretation is correct, temperature-programmed oxidation might be a suitable tool for detecting the presence of the Co-Mo-S phase. However, it cannot be ignored that this effect could be explained as well by a lower content of element sulfur, due to the spillover of hydrogen from cobalt sulfide during treatment in  $\text{H}_2\text{S}-\text{H}_2$ .

*XRD analysis of decomposed, sulfided and oxidized CoMo samples*

The presence of CoO and  $\beta$ -CoSO<sub>4</sub> in the XRD of Co-HSP-1.0-D has been explained by the absence of H<sub>2</sub>S and the oxidizing influence of the gas evolved during the decomposition of NH<sub>4</sub>NO<sub>3</sub>. In Co-HSP-0.3-D, oxygen-containing Co compounds could not be detected. The amount of such oxidic cobalt is probably lower than in Co-HSP-1.0-D, because of the release of sulfur during the decomposition of ammonium thiomolybdates.

The XRD patterns of oxidized samples (see Fig. 3) show the presence of well-crystallized compounds (especially for samples treated under H<sub>2</sub>S-H<sub>2</sub>).

The presence of MoO<sub>2</sub> in the oxidized CoMo-CM samples and  $\beta$ -CoSO<sub>4</sub> in the oxidized Co-HSP-1.0 samples indicate an incomplete air oxidation of these samples even at  $\sim 720$  K.

In the CoMo-containing, oxidized samples, the amount of  $\alpha$ -CoMoO<sub>4</sub> was higher for the CoMo-HSP (IHSP, CP) samples and for the previously H<sub>2</sub>S-H<sub>2</sub>-treated ones, than for CoMo-CM and thermally decomposed samples. This points to a more homogeneous cobalt distribution in the former samples. The detection of pure cobalt oxides is difficult because of the complexity of the diffractograms. Nevertheless, the presence of Co<sub>3</sub>O<sub>4</sub> traces in the oxidized CoMo-CM samples is established, again supporting the biphasic character of these catalysts.

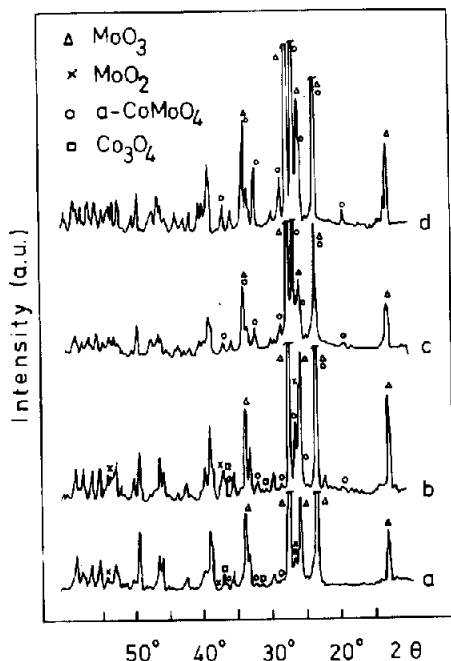


Fig. 3. XRD patterns of oxidized CoMo-containing samples with  $r = 0.3$ . (a) CM decomposed in argon; (b) CM sulfided in 15% H<sub>2</sub>S-H<sub>2</sub>; (c) HSP decomposed in argon; (d) HSP sulfided in 15% H<sub>2</sub>S-H<sub>2</sub>.

## CONCLUSIONS

The main conclusions of the present work may be summarized as follows.

(1) In the preparation of Mo-containing precursors, a mixture of  $(\text{NH}_4)_2\text{MoS}_4$  and  $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$  is formed. The relative proportion of these compounds may be evaluated qualitatively by DTA of the decomposition of the precursors under argon.

(2) The reduction/sulfidation of the CoMo-containing precursors in an  $\text{H}_2\text{S}-\text{H}_2$  mixture is very much influenced by the nature of cobalt (oxide, sulfide). In comparison with the precursors containing only molybdenum, the significantly lower temperature of reduction/sulfidation of the CoMo-HSP (IHSP and CP) precursors suggests the presence of less stable Co-Mo-S species or/and the spillover of hydrogen from cobalt sulfide.

(3) Contrary to the explanation of Breysse et al. [2,4], the highly exothermic peak at  $\sim 450$  K, during the decomposition of CoMo-HSP (IHSP, CP) precursors is attributed to the decomposition of  $\text{NH}_4\text{NO}_3$  and not to a precursor of the Co-Mo-S phase.

(4) The larger the sulfur excess in the sample, the lower the temperature of oxidation of the catalyst.

(5) The observation of an identical temperature of oxidation for samples CoMo-CM as for sample Mo-CM-0.0 confirms the biphasic nature of the samples prepared by the CM method.

(6) The higher temperatures of oxidation of catalysts prepared by the HSP, IHSP and CP methods may indicate the segregation of cobalt atoms at the edges of  $\text{MoS}_2$ , thus supporting the model of the Co-Mo-S phase. Therefore, the oxidation of previously sulfided samples may be a suitable test for the detection of the Co-Mo-S phase.

(7) XRD measurement of the amount of  $\alpha\text{-CoMoO}_4$  in the oxidized sample may also help to characterize the dispersion of cobalt in sulfide catalysts.

## ACKNOWLEDGMENTS

We are grateful to Professor B. Delmon for many valuable discussions and to Dr. D. Pirotte for his help in the construction of the DTA apparatus. Two of us (Q.W.) and (S.G.) thank the Beijing Municipal Chemical Industry Research Institute and the Central Research Institute for Chemistry of the Hungarian Academy of Sciences, respectively, for leave of absence during which time the present work was accomplished. The financial support of the Services de Programmation de la Politique Scientifique (Belgium) is gratefully acknowledged.

## REFERENCES

- 1 R. Candia, B.S. Clausen and H. Topsøe, *Bull. Soc. Chim. Belg.*, 90 (1981) 1225.
- 2 M. Breyse, R. Frety and M. Vrinat, *Symp. Structure and Activity of Sulfided Hydro-processing Catalysts, Kansas City Meet.* 1982.
- 3 M. Vrinat, M. Breyse and R. Frety, *Appl. Catal.*, submitted.
- 4 M. Breyse, R. Frety and M. Vrinat, *Appl. Catal.*, submitted.
- 5 B. Delmon, *Bull. Soc. Chim. Belg.*, 88 (1979) 979.
- 6 S. Göbölös, Q. Wu and B. Delmon, unpublished results, 1983.
- 7 S. Göbölös, F. Delannay and B. Delmon, unpublished results, 1983.
- 8 G.M. Clark and W.P. Doyle, *J. Inorg. Nucl. Chem.*, 28 (1966) 381.
- 9 G. Hagenbach, Ph. Courty and B. Delmon, *J. Catal.*, 23 (1971) 295; 31 (1973) 264.
- 10 T.P. Prasad, E. Diemann and A. Müller, *J. Inorg. Nucl. Chem.*, 35 (1973) 1895.
- 11 A.W. Naumann, A.S. Behan and E.M. Thorstenson, 4th Int. Conf. Chemistry and Uses of Molybdenum, Golden, Colorado, 1982.
- 12 E.Ya Rode and B.A. Lebedev, *Russ. J. Inorg. Chem.*, 6 (1961) 608.
- 13 W. Romanowski, *Rocz. Chem.*, 37 (1973) 1077.
- 14 A. Müller, R.G. Bhattacharyya and B. Pfefferkorn, *Chem. Ber.*, 112 (1979) 778.
- 15 E. Dönges, *Z. Naturforsch.*, 1 (1946) 221.
- 16 I. Hincu, E. Stefancu and D. Stefancu, *Bul. Inst. Politeh. Iasi, Sect. 2. Chim. Ing. Chem.*, 26 (1980) 33.
- 17 A. Müller, E. Dieman and H.H. Heinsen, *Chem. Ber.*, 104 (1971) 975.
- 18 E. Königer-Ahlborn and A. Müller, *Angew. Chem. Int. Ed. Engl.*, 13 (1974) 672.
- 19 S.J. Tauster, T.A. Pecoraro and R.R. Chianelli, *J. Catal.*, 63 (1980) 515.
- 20 M.M. Spivak, A.S. Pashinkin, R.A. Isakova and K.S. Amosova, *Zh. Prikl. Khim. (Leningrad)*, 51 (1978) 549.
- 21 O.P. Bahl, E.L. Evans and J.M. Thomas, *Proc. R. Soc. London, Ser. A*, 306 (1968) 53.
- 22 P.R. Amman and T.A. Loose, *Metall. Trans.*, 2 (1971) 889.
- 23 K.N. Irisova, E.I. Salmanova, V.K. Smirnov and M.V. Ermolaev, *Zh. Fiz. Khim.*, 51 (1977) 1299.
- 24 K.N. Irisova, M.V. Ermolaev, V.K. Smirnov and E.I. Salmanova, *Neftepererab. Neftekhim. (Moscow)*, 8 (1978) 9.
- 25 K. Vasiliev, B.I. Kuzmanov and R. Dimitrov, *Khim. Ind. (Sofia)*, 5 (1968) 203.
- 26 A.V. Penski, A.R. Babenko and R.G. Kefer, *Izv. Vyssh. Uchebn. Zaved. Tsvetn. Metall.*, 1 (1973) 37.
- 27 E. Furimsky, *Catal. Rev. Sci. Eng.*, 22 (3) (1980) 371.
- 28 H. Topsøe, in J.P. Bonnelle, B. Delmon and E. Derouane (Eds.), *Surface Properties and Catalysis by Non Metals*, Reidel, Dordrecht, 1983, p. 329.