Journal of Thermal Analysis, Vol. 31 (1986) 835–843

CHARACTERIZATION OF Fe AND Ni-PROMOTED UNSUPPORTED MoS_2 CATALYSTS AND THEIR PRECURSORS VIA THERMAL EFFECTS IN TEMPERATURE-PROGRAMMED REACTIONS

Q Wu[1], *S. Gőbölös*[2], *D. S. Thakur*[3], *F. Delannay*[3] and *B. Delmon*[4]

GROUPE DE PHYSICO-CHIMIE MINÉRALE ET DE CATALYSE,
UNIVERSITÉ CATHOLIQUE DE LOUVAIN, PLACE CROIX DU SUD,
1 B–1348 LOUVAIN-LA-NEUVE, BELGIUM.

(Received September 20, 1985)

Precursors of unsupported NiMo and FeMo sulfide hydrodesulfurization catalysts with concentration ratios r = Ni(Fe)/(Ni(Fe)+Mo) ranging from 0.1 to 0.3 were prepared by three methods: homogeneous sulfide precipitation (HSP), inverse HSP and coprecipitation. Differential thermal analysis was used to study the decomposition under argon, and the reduction/sulfidation under 15% H_2S—H_2 of the precursors and the subsequent oxidation under air of the samples obtained after these reactions. The reactivity of the solids varies as a function of the preparation method, the nature of the promoter and the concentration ratio. The degree of sulfidation of the precursor and the presence of either NH_4NO_3 or NH_4Cl formed from group VIII metal salts and $(NH_4)_2S$ may affect the thermal behaviour of samples during DTA.

Unsupported MoS_2-based catalysts promoted by group VIII metals are extensively used as model catalysts for the investigation of hydrodesulfurization (HDS) catalysis. Industrially, nickel and iron are used less than cobalt. Nevertheless, they have important specific uses, and exploration of the similarities and differences between them and cobalt in HDS is important, both practically and scientifically.

We have shown in a previous work [1] that differential thermal analysis (DTA) under a controlled atmosphere is a convenient tool for detection of the various solid–state reactions involved in the preparation of unsupported CoMo sulfide

---

[1] On leave from the Beijing Municipal Chemical Industry Research Institute, Cheng Fu, Haidian, Beijing P. B. 2653, People's Republic of China.

[2] On leave from the Central Research Institute for Chemistry, Hungarian Academy of Sciences, 1025 Budapest, Pusztaszeri út 59–67, Hungary.

[3] Research Center Internorth, 4840 F Street, Omaha, Nebraska 68117, U.S.A.

[4] To whom all correspondence should be addressed.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

catalysts. This method provided fingerprints for characterizing the degree of interaction of cobalt and molybdenum in the precursor and sulfided state of the catalysts. This interaction has been shown to be extremely critical with respect to catalytic activity.

Using the same approach as in our previous work [1,2], we investigated the influence of the details of the preparation conditions (promoter salt used, concentration of solutions and excess of $(NH_4)_2S$) on the reactivity of unsupported NiMo and FeMo sulfide catalysts and their precursors. Indeed, both the structural properties and the HDS activity of unsupported NiMo and FeMo catalysts were found to be affected by changes in the preparation conditions [3].

Experimental

Preparation of catalyst precursors

The starting solids investigated in this study are "catalyst precursors" obtained by drying "precursor slurries" made by mixing, by different procedures, chosen proportions of compounds of molybdenum and nickel or iron in a solution of $(NH_4)_2S$ (or ammonium thiomolybdate). The details of the preparations of the precursor slurries are listed in Table 1. The concentrations of ammonium heptamolybdate (AHM) and $(NH_4)_2S$ (which are not given in Table 1) can be calculated from the indicated concentration of group VIII metal (M = Ni or Fe), the predetermined atomic composition ratios $r = M/(M+Mo)$, and the $S/(4Mo+M)$ values.

Unsupported NiMo sulfide catalyst precursors were prepared with $r = 0.1$ and 0.3, by the homogenous sulfide precipitation (HSP) [4] and inverse HSP (IHSP) [5] methods.

In the HSP method, a mixed solution of AHM and nickel nitrate was added to a vigoruously stirred solution of $(NH_4)_2S$. In the IHSP method, a solution of $(NH_4)_2S$ was added to a mixed solution of AHM and nickel nitrate. The slurries formed were then evaporated to dryness. All steps of the preparation procedures were carried out either under argon at 343 K, or in air at 353 K, for the HSP and IHSP methods, respectively.

Unsupported FeMo sulfide catalyst precursors were prepared with atomic ratios $r = 0.15$ and 0.3 by the HSP and the coprecipitation (CP) [6] methods.

In the HSP method, $FeCl_2, 4H_2O$ and AHM were used as starting materials. The details of the preparation procedure were identical to those used to prepare the NiMo catalyst precursors by the same method.

In the CP method, a mixture of FeS and MoS_3 (or mixed sulfides) was

Table 1 Preparation of the precursor slurries

Sample[a]		Solution $(NH_4)_2S$	Mixed Solution AHM + Group VIII metal salt			S^b
		Volume, cm^3	Volume, cm^3	Group VIII metal salt		(4 Mo + M) M = Ni or Fe
				Nature	Concentration, 10^{-3} *M*	
NiMo-HSP(1.5)–0.1	0.1	600	1500	$Ni(NO_3)_2 \cdot H_2O$	4.8	1.5
NiMo-HSP(1.5)–0.3	0.3	600	1500	$Ni(NO_3)_2 \cdot H_2O$	14.4	1.5
NiMo-IHSP(0.93)–0.1[c]	0.1	100	145	$Ni(NO_3)_2 \cdot H_2O$	59	0.93
NiMo-IHSP(1.66)–0.1[c]	0.3	100	110	$Ni(NO_3)_2 \cdot H_2O$	158	1.66
FeMo-HSP(1.5)–0.15	0.15	600	1500	$FeCl_2 \cdot 4H_2O$	7.2	1.5
FeMo-HSP(1.5)–0.3	0.3	600	1500	$FeCl_2 \cdot 4H_2O$	14.4	1.5
		Solution ATM	Solution Fe Salt			
		Volume cm^3	Volume cm^3	Nature	Concentration, 10^{-3} *M*	
FeMo-CP(1.03)–0.15	0.15	1000	500	$Fe(NO_3)_3 \cdot 9H_2O$	22	1.03
FeMo-CP(1.03)–0.3	0.3	1000	500	$Fe(NO_3)_2 \cdot 9H_2O$	44	1.03
FeMo-CP(1.5)–0.3	0.3	1000	500	$Fe(NO_3)_2 \cdot 9H_2O$	44	1.5

a) In the symbol characterizing the samples, the metals present are followed by the indication of preparation method, the excess of sulfur (b) and r.

b) S/(4Mo + M) = 1 would correspond to the complete sulfuration of the metals into MoS_4^{2-} and MS.

c) The weight concentrations of the $(NH_4)_2S$ and mixed solutions were fixed to 20 and 10%, respectively.

precipitated by adding a solution of iron(III) nitrate to a previously prepared and vigorously stirred solution of ammonium thiomolybdate (ATM).

The precipitation and the subsequent evaporation of the slurries were carried out under argon at 343 K.

DTA Under controlled atmosphere

Temperature-programmed reactions (TPR) of the dry precursors and sulfide catalysts were studied in a purpose-built, atmospheric-pressure, all-glass DTA apparatus. A 300 mg sample was heated at a rate of 11 deg $\min^{-1}$ from 373 K to 703–723 K.

Thermal decomposition (TPD) or reduction/sulfidation (TPRS) was conducted under argon and under a 15% H_2S–H_2 mixture, respectively. After completion of either of these reactions, a subsequent temperature-programmed oxidation (TPO) of the resulting sample was performed using air as reacting atmosphere. The details of these experiments are described elsewhere [1,2].

Results and discussion

DTA curves recorded during the temperature-programmed reactions of NiMo and FeMo-containing samples are shown in Fig. 1 and Fig. 2, respectively.

We shall first recall the general characteristics of the DTA curves of the CoMo system as discussed in the previous paper [1]. Thereafter, we discuss the new information provided by this study.

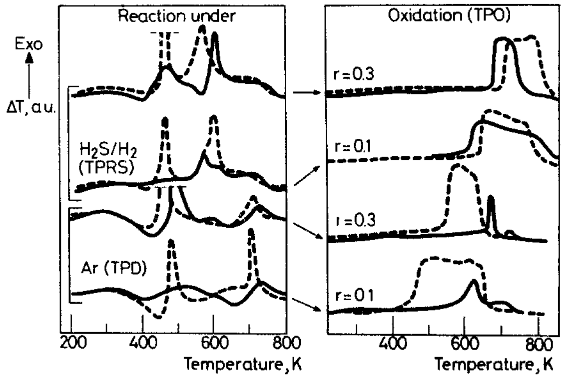

Fig. 1 DTA curves of decomposition and reduction/sulfidation of unsupported NiMo catalyst precursors and subsequent air oxidation of the catalysts prepared by the HSP and IHSP methods. NiMo... HSP, ———IHSP

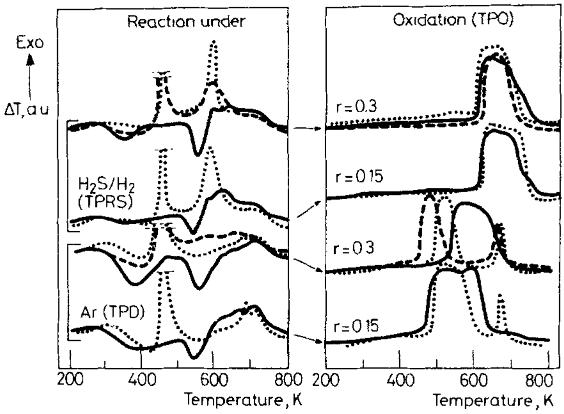

Fig. 2 DTA curves of decomposition and reduction/sulfidation of unsupported FeMo catalyst precursors and subsequent air oxidation of the catalysts prepared by the HSP and CP methods. FeMo: ——— HSP, ... CP (1.03) - - - CP (1.5)

General characteristics of DTA curves obtained with unsupported CoMo catalysts

1 The endothermic effect observed below 450 K in both the TPD and the TPRS of the precursors is due to the decomposition of $(NH_4)_2MoS_4$ and $(NH_4)_2MoO_2S_2$ (present in the precursor slurry) to form MoS_3 or a mixture of $MoOS_2$ and MoS_3. This occurs with release of ammonia and H_2S [7].

2 The highly exothermic peak appearing between 450 and 550 K in the DTA spectra of the catalyst precursors during the TPD and TPRS is attributed to the decomposition of NH_4NO_3 formed in the precursor slurries when nitrates are used as starting materials [1, 2, 8].

3 The exothermic effects observed between 500 and 700 K in both the TPD and the TPRS of the catalyst precursors are due to the decomposition of MoS_3 and $MoOS_2$ to MoS_2, accompanied by the release of elemental sulfur and the crystallization of MoS_2 [9].

The reduction of MoS_3 to MoS_2 under H_2S–H_2 occurs at lower temperatures than its decomposition under argon.

4 In TPO, the large and broad exothermic peaks appearing in the DTA curves of both samples previously reacted under Ar or H_2S–H_2 indicate that oxidation proceeds through several steps [10]. It is interesting to recall that, in the case of a sample containing only molybdenum and treated under H_2S–H_2, the oxidation of stoichiometric MoS_2 is characterized by an exothermic threshold at 600 K [1]. In comparison, the lower onset temperature of oxidation for the samples previously reacted under argon is due to the presence of excess sulfur [1, 2], resulting from the

preparation of catalyst precursors. It is less efficiently removed under argon than under the 15% H_2S–H_2 mixture. This excess sulfur starts to be oxidized at 450 K and initiates further bulk oxidation of MoS_2 [1].

5 As pure Co_9S_8 oxidizes at a higher temperature than MoS_2 [1], the presence of Co atoms on the edges of MoS_2 crystallites (as proposed for the Co-Mo-S model [11]) protects MoS_2 from oxidation in unsupported CoMo sulfide catalysts prepared by the HSP and IHSP methods. This results in a shift of the onset temperature of oxidation to above 600 K for the H_2S–H_2-treated samples.

New findings

NiMo-containing samples

1 *TPD and TPRS*

The lower intensities of the exothermic peaks (and their shifts towards higher temperatures) for the IHSP samples than for the HSP samples are undoubtedly due to the incomplete sulfidation of the NiMo–IHSP precursors. The amount of NH_4NO_3 formed in the reaction of nickel nitrate and $(NH_4)_2S$ is also lower (e. g. for NiMo–IHSP (0.93)–0.1 precursor) (Fig. 1). This incomplete sulfidation of the IHSP precursors was mostly due to the fact that the preparation was carried out under air instead of argon.

The difference in the preparation conditions may also affect the composition, structure and texture of the solids obtained after either TPD or TPRS. Indeed, XRD indicates the presence of NiS_2 in the H_2S–H_2-treated NiMo–IHSP (1.66)–0.3 catalyst (Fig. 3), whereas it is not detected in the NiMo–HSP (1.5)–0.3 catalyst after the same treatment. The higher dispersion of Ni in the HSP catalyst confirms the importance of avoiding exposure to air during preparation of the precursor.

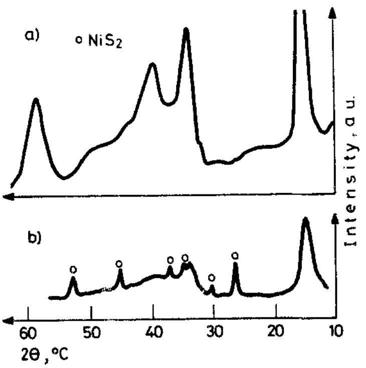

Fig. 3 X-ray diffractograms of unsupported NiMo sulfide catalysts with r = 0.3 prepared by the a) HSP and b) IHSP methods. ○ NiS_2

2 *TPO*

If we compare the TPO curves of Ar-decomposed samples of NiMo prepared by the HSP and IHSP methods, we notice the low intensities of the exothermic peaks and their shifts towards higher temperatures for NiMo–IHSP samples. This confirms that the degree of sulfidation of these samples is significantly lower than that of the samples NiMo–HSP (1.5)–0.1 and –0.3 (Fig. 1).

After reaction under H_2S–H_2, the higher threshold of oxidation for the promoted samples than for pure MoS_2 (600 K) [1] is probably due to a higher coverage by Ni of the edges of MoS_2 slabs, forming the Ni–Mo–S structure [11]. Since the oxidation of MoS_2 proceeds from the edges [12], the presence of Ni (or more probably of Ni–O complexes similar to the Co–O complexes formed on the surface of Co_9S_8 at 460 K [13]) protects MoS_2 from bulk oxidation up to temperatures higher than 600 K. The higher threshold of oxidation for NiMo–HSP samples than for the corresponding NiMo–IHSP samples suggests a lower Ni coverage on the edges of MoS_2 in the latter. Indeed, the above-mentioned XRD results (Fig. 3) seem to confirm this explanation. In correlation with the dispersion of Ni, the steady-state reaction rates for HDS of thiophene (30 bar, 573 K) are $10.9.10^8$ and $13.6.10^8$ mol $m^{-2}s^{-1}$ for sulfided NiMo–IHSP (1.66)–0.3 and NiMo–HSP (1.5)–0.3 catalysts, respectively [3].

FeMo-containing samples

1 *TPD and TPRS*

In Fig. 2, the strong endothermic effect between 500 and 600 K, with maximum at about 550 K, observed during the heat-treatment of precursors FeMo–HSP (1.5)–0.15 and –0.3, is due to the evolution and decomposition of NH_4Cl.

The absence of the strongly exothermic effect between 450 and 500 K in both the TPD and the TPRS of FeMo–HSP precursors prepared using iron(II) chloride instead of iron(III) nitrate as starting material confirms that this exothermic effect is due to the decomposition of NH_4NO_3. This result should lead to a reinterpretation of results in the literature [14, 15], which had attributed the exothermic effect to the decomposition of the precursor of a mixed Fe–Mo–S phase.

The low exothermicity of the reaction of Mo species in FeMo–HSP precursors under H_2S–H_2 is probably due to a partial compensation by the endothermic evolution of NH_4Cl in the range 500–600 K.

2 *TPO*

A comparison of the DTA curves of the TPO for FeMo- and NiMo–HSP samples, after reaction under argon, indicates that the nature of the promoter does not affect the oxidation of the samples previously reacted under argon, using otherwise identical conditions to prepare the precursors.

The exothermic peaks observed above 650 K in the TPO of FeMo–CP samples previously reacted under argon are probably due to the oxidation of a separate iron sulfide phase, which, however, could not be detected by XRD [3].

The low threshold temperature of oxidation (450 K) for the sample FeMo–CP(1.5)–0.3, after reaction under argon, indicates the presence of a large amount of elemental sulfur in this sample, originating from the sulfur excess used in the preparation.

In contrast with the oxidation of CoMo- [1] and NiMo-containing samples, the reactivity of MoS_2 towards O_2 in FeMo-containing samples reacted under H_2S–H_2 depends only slightly on the amount of promoter and the method of preparation of the precursor.

Conclusions

(1) The DTA of both the TPD or TPRS and the subsequent TPO of NiMo sulfide samples demonstrates the importance of the degree of sulfidation of the precursor and of the absence of air during the preparation of unsupported HDS catalyst precursors.

(2) The DTA of both the TPD and the TPRS of FeMo sulfide catalyst precursors confirmed that the highly exothermic effect detected between 450 and 550 K is due to the decomposition of NH_4NO_3.

(3) The degree of sulfidation of FeMo sulfide catalyst precursors affects the thermal behavior of Ar-decomposed samples in the subsequent TPO.

(4) In contrast with Co and Ni, Fe has only a slight influence on the onset temperature of oxidation of MoS_2 in H_2S/H_2-treated samples.

(5) The DTA of temperature-programmed reactions appears to be a sensitive tool for the detection of differences in the method and conditions (nature of promoter salt used, concentration of promoter, excess of $(NH_4)_2S$, atmosphere) of preparation of unsupported MoS_2-based HDS catalysts.

* * *

We thank (QW) the Beijing Municipal Chemical Industry Research Institute, Cheng Fu, and (SG) the Central Research Institute for Chemistry of the Hungarian Academy of Sciences for leave of absence which permitted the accomplishment of the present work.

Q. Wu thanks the Chinese Ministry of National Education for a Fellowship. The financial support of the Services de Programmation de la Politique Scientifique (Belgium) is gratefully acknowledged.

References

1 Q. Wu, S. Gőbölős, P. Grange, and F. Delannay, Thermochim. Acta, 81 (1984) 281.

2 Q. Wu, S. Gőbölős, F. Delannay and B. Delmon, Proceedings of the Tenth Int. Symp. on the Reactivity of Solids, (P. Barret and C. C. Dufour Eds), Elsevier, Amsterdam 1985, p. 1067–1071.

3 Q. Wu, S. Gőbölős and D. S. Thakur, unpublished results.

4 R. Candia, B. S. Clausen and H. Topsøe, Bull. Soc. Chim. Belg., 90 (1981) 1225.

5 M. Vrinat, M. Breysse and R. Frety, Appl. Catal., 12 (1984) 151.

6 S. Gőbölős, Q. Wu and B. Delmon, Appl. Catal., 13 (1984) 89.

7 T. P. Prasad, E. Diemann and A. Müller, J. Inorg. Nucl. Chem., 35 (1973) 1895.

8 I. Hincu, E. Stefancu and D. Stefancu, Bul. Inst. Politek. Iasi, Sect. Z. Chim. Ing. Chem., 26 (1980) 33.

9 E. Ya. Rode and B. A. Lebedev, Russ. J. Inorg. Chem., 6 (1961) 608.

10 M. M. Spivak, A. S. Pashinkin, R. A. Isakova and K. S. Amosova, Zh. Prikl. Klim., (Leningrad) 51 (1978) 549.

11 N.-Y. Topsøe, J. Catal., 84 (1983) 386.

12 O. P. Bahl, E. L. Evans and J. M. Thomas, Proc. Roy. Soc. London Ser., A. 306 (1968) 53.

13 A. V. Peuski, A. R. Babenko and R. G. Kefer, Izv. Vyssh. Uchebu. Zaved. Tsvetu. Metall., 1 (1973) 37.

14 M. Breysse, R. Frety and M. Vrinat, Symp. Structure and Activity of Sulfided Hydroprocessing Catalysts, Kansas City Meet., Sept. 12–17 (1982) p. 772.

15 M. Breysse, R. Frety and M. Vrinat, Appl. Catal., 12 (1984) 165.

Zusammenfassung – Vorläufer von NiMo– und FeMo–Sulfidkatalysatoren für die Hydrosulfurierung mit Konzentrationsverhältnissen r = Ni(Fe)/[Ni(Fe) + Mo] von 0.1 bis 0.3 wurden nach 3 Methoden hergestellt: homogene Sulfidpräzipitation (HSP), inverse HSP und Kopräzipitation. Die DTA-Methode wurde zur Untersuchung der Zersetzung in Argon, der Reduktion/Sulfidierung der Precursor in einer 15% H_2S enthaltenden H_2-Atmosphäre und der darauffolgenden Oxydation der nach diesen Reaktionen erhaltenen Proben in Luft herangezogen. Die Reaktivität der festen Produkte ist von der Präzipitationsmethode sowie von der Natur und den Konzentrationsverhältnissen des Promotors abhängig. Der Grad der Sulfidierung der Precursor und die Anwesenheit von aus Salzen von Metallen der Gruppe VIII und $(NH_4)_2S$ gebildetem NH_4NO_3 oder NH_4Cl können das thermische Verhalten der Proben während der DTA beeinflussen.

Резюме — Исходные соединения для сульфидных NiMo и FeMo катализаторов без подложки с концентрационным соотношением r = Ni(Fe)/(Ni(Fe) + Mo) от 0,1 до 0,3 были получены тремя методами: гомогенным сульфидным осаждением, обратным гомогенным осаждением и соосаждением. Дифференциальный термический апализ был использован для изучения разложения исходных соединений в атмосфере аргона и в атмосфере 15% H_2S—H_2 и последующего окисления полученных при этом соединений в атмосфере воздуха. Реакционная способность твердых веществ изменялась в зависимости от метода их получения, природы промотора и концентрационного соотношения. Термическое поведение изученных образцов затрагивается степенью сульфидирования исходных веществ, а также наличием нитрата, хлорида и сульфида аммония, способных к образованию солей с металлами восьмой группы периодической системы элементов.