Thermochimica Acta, 133 (1988) 143–148
Elsevier Science Publishers B.V., Amsterdam

TEMPERATURE-PROGRAMMED REACTION AND DESORPTION STUDIES OF UNSUPPORTED MoS_2-BASED HYDROTREATING CATALYSTS

S. GÖBÖLÖS[1], Q. WU[2], O. ANDRÉ[3] and P. GRANGE[3]

1 Central Research Institute for Chemistry of the Hungarian Academy of Sciences, 1025 Budapest, Pusztaszeri ut 59-67 (Hungary)
2 Beijing Municipal Chemical Industry Research Institute, Cheng Fu, Haidian, Beijing, P.B. 2653 (People's Republic of China)
3 Groupe de Physico-Chimie Minérale et de Catalyse, Université Catholique de Louvain, Place Croix du Sud 1, B-1348 Louvain-la-Neuve (Belgium)

ABSTRACT

Unsupported MMo-sulfide catalysts (M = Fe,Co,Ni) and their precursors were studied by temperature-programmed reactions (decomposition, sulfuration, oxidation, reduction) and by adsorption and thermodesorption of NO. Differential thermal analysis of sulfuration of the precursors and subsequent oxidation of the sulfided samples can be used for detecting "M-Mo-S" mixed sulfide structure in the catalysts. The amount of NO adsorbed on M atoms, the onset temperature of oxidation and the reducibility of the catalysts correlated with their activity in the hydrodesulfurization of thiophene.

INTRODUCTION

In the last decade differential thermal analysis (DTA) (1) or GC-MS analysis (2) of temperature-programmed (TP) reactions (reduction, sulfuration) and desorption of chemisorbed H_2 (3) provided useful information about structural and surface properties of both unsupported and supported MoS_2-based hydrodesulfurization (HDS) catalysts. In this work TP reactions (decomposition, sulfuration, oxidation, reduction) and desorption of preadsorbed NO were used to characterize the dispersion and state of Group VIII metal atoms in unsupported CoMo-, FeMo- and NiMo-sulfide HDS catalysts. Correlations between physico-chemical properties and HDS activity of the catalysts will be also evaluated.

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

EXPERIMENTAL

CoMo-sulfide catalyst precursors with atomic ratios r=Co/(Co+Mo)= = 0, 0.1 and 0.3 were prepared by the comaceration (CM) method (4), in which MoO_3 and Co_3O_4 were added to a 20 % solution of $(NH_4)_2S$. CoMo-sulfide precursors with r = 0, 0.1, 0.3, 0.5, 0.84 and 1 were also prepared by the homogeneous sulfide precipitation (HSP) method (5), in which a mixed solution of ammonium heptamolybdate (AHM) and $Co(NO_3)_2.6H_2O$ was added to a dilute solution of $(NH_4)_2S$. A NiMo--sulfide precursor with r = 0.3 was prepared by the HSP method using $Ni(NO_3)_2.6H_2O$ and AHM as precursor compounds. A FeMo-sulfide precursor with r = 0.3 was prepared by the coprecipitation (CP) method (6), in which a solution of $Fe(NO_3)_3.9H_2O$ was added to a solution of ammonium thiomolybdate (ATM). The precipitation and subsequent evaporation of the slurries were carried out under Ar at 343 K. Details of the preparations are described elsewhere (6,7). Samples will be dubbed in terms of the metal(s) present, followed by the method of preparation and r (e.g. CoMo-CM-0.3). In addition, two samples referred as Mo/CoS-0.82 and Mo/Co_9S_8-0.82 (r=0.82) were prepared by impregnating cobalt sulfides with solutions of ATM.

TP measurements were performed at atmospheric pressure by heating samples at a rate of 0.17 $K.s^{-1}$ from 273 to 773 K. DTA of decomposition (TPDE) under Ar or reductive-sulfuration (TPS) under 15% H_2S-H_2 of the precursors and subsequent oxidation (TPO) in air of samples obtained after such treatments were studied in a glass apparatus (7). Prior to reduction (TPR), NO adsorption and HDS activity test catalyst precursors were treated in 15 % H_2S-H_2 and then in Ar at 673 K for 4 and 1 h, respectively. TPR experiments were performed in H_2, and the amount of H_2S released was measured by a thermal-conductivity detector (TCD). The adsorption and desorption (TPD) of NO were carried out in flowing He using a TCD. The uptake of NO was measured by dynamic method at 293 K using a 5% NO-He mixture. The activity of the catalysts was tested in the HDS of thiophene at 573 K (8).

RESULTS AND DISCUSSION

In the DTA curves of catalyst precursors the endothermic effect around 400 K is due to the decomposition of ATM and ammonium oxothiomolybdates (AOTM), formed in the precursor slurries, to $MoOS_2$ and MoS_3 (9) (Fig. 1.a.). The large exothermic peak around 445 K is due to the decomposition of NH_4NO_3 originated from Group VIII metal nitrate (7). The exothermic effects observed above 500 K, appearing at lower temperature for ATM than for AOTM (9), are due to the transformation of Mo-containing species to MoS_2 (7, 9). The position and intensities of these peaks, in both TPDE and TPS, for precursors with $r = 0$ indicate that less ATM is formed in the HSP than in the CM preparation. In TPS, i.e. in the presence of H_2 the high temperature exothermic peak of DTA curves shifted towards lower temperatures. The position of this peak is the same for both CM precursors, indicating that Co do not affect the reduction of Mo species is sample CoMo-CM-0.3. This is due to the biphasic nature of bimetallic CM catalysts. Indeed, separate Co_9S_8 and MoS_2 were also detected by X-ray diffraction in the sulfided catalysts (8). In TPS of HPS and CP precursors the high temperature exothermic peak shifted towards lower temperatures by 50-70 K for samples with

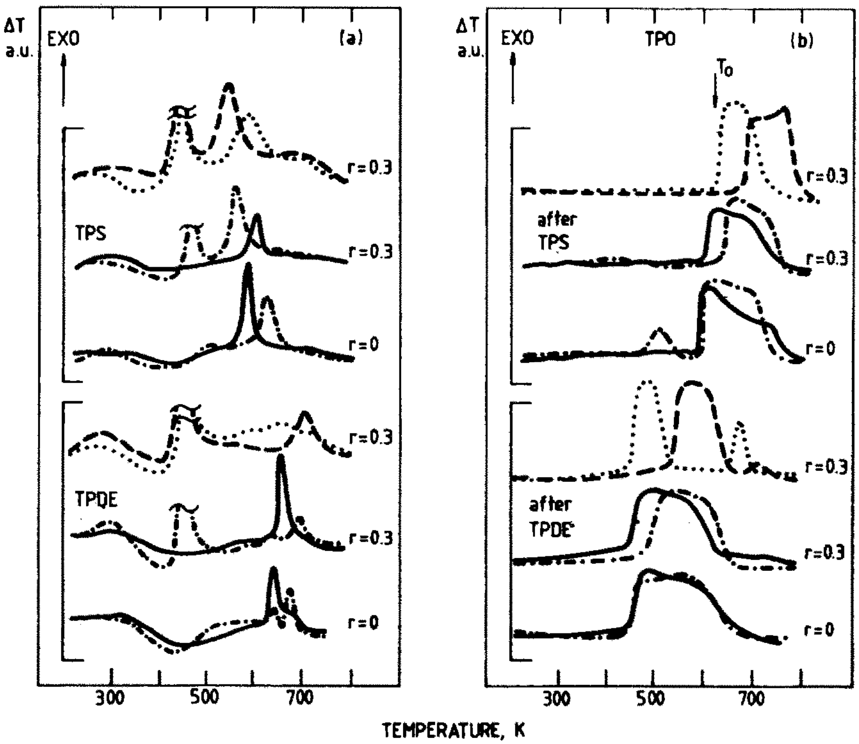
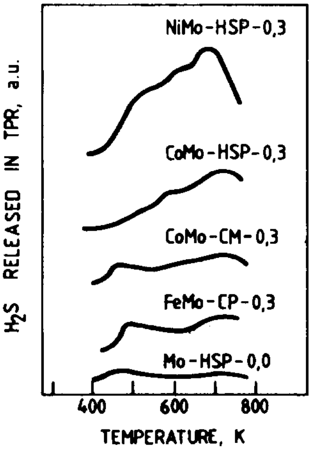


Fig. 1. DTA curves of TPDE and TPS of catalysts precursors (a), and subsequent TPO of heat treated samples (b): CoMo-CM: ——— , CoMo-HSP: —·—·—·, FeMo-CP: ········· , NiMo-HSP: – – – – .

r=0.3. This indicates that in these precursors the transformation of Mo-containing species to MoS_2 is made easier by highly dispersed promoter atoms. This can be attributed to the formation of easily reducible precursor compounds of a mixed sulfide phase in the HSP and CP preparations (7).

The broad exothermic peaks in DTA curves of TPO indicate that the oxidation of samples obtained after TPDE or TPS proceeds through several steps (Fig.1.b). The exothermic effect starting around 450 K may be assigned to the oxidation of elemental S into SO_2, which reaction can "catalyze" the oxidation of MoS_2 in the Ar-treated samples (7). The small exothermic peak around 670 K in TPO of Ar-treated FeMo-CP-0.3 sample is due to oxidation of separate FeS_x. The onset temperature of oxidation (T_o) of Ar-treated samples is lower by 140--160 K than that of H_2S-H_2 treated ones. Both samples with r=0 start to oxidize at 455 and 600 K, respectively, after TPDE and TPS. Due to biphasic nature of CM type catalysts, Co atoms in sample CoMo--CM-0.3 do not affect the oxidation of MoS_2. In contrast, after reaction of bimetallic HSP and CP precursors in H_2S-H_2, the T_o of MoS_2 shifted towards higher temperatures. The largest effect was obtained with Ni the lowest with Fe. Since the oxidation of MoS_2 proceeds from the edges of slabs, the increase in T_o can be explained by the presence of M atoms in the "M-Mo-S" structure (5) on the edges of MoS_2 salbs (7, 8). Co atoms in the "Co-Mo-S" structure



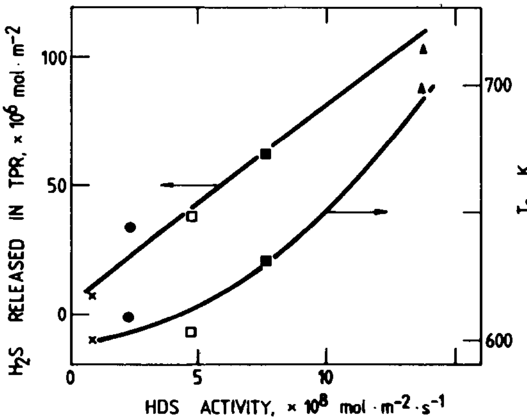


Fig. 2. TPR curves of unsupported MoS_2-based HDS catalysts.

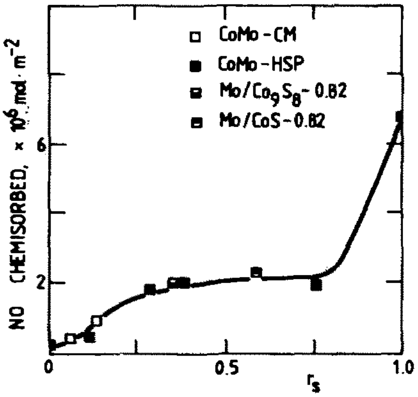
Fig. 3. Correlation between HDS activity of the catalysts and the amount of H_2S released in TPR, or T_o: x Mo-HSP-0.0, ● FeMo-CP-0,3. ▫ CoMo-CM-0.3, ■ CoMo-HSP-0.3, ▲ NiMo-HSP-0.3.

were also detected by Mössbauer spectroscopy in catalyst CoMo-HSP-0.3 (8).

The main characteristics of TPR curves, shown in Fig.2., are twofold: a small peak appears between 450-550 K for MoS_2 and biphasic catalysts (FeMo-CP-0.3, CoMo-CM-0.3), and a large one appears with a maximum around 700 K for catalysts CoMo-HSP-0.3 and NiMO-HSP-0.3, containing promoter atoms in the "M-Mo-S" structure. This indicates that the reduction of MoS_2 is facilitated by promoter atoms dispersed on the edges of slabs. The amount of H_2S released in TPR increased in the following order: Mo-HSP-0.0 < FeMo-CP-0.3 ≈ CoMo-CM-0.3 < CoMo-HSP-0.3 < NiMoHSP-0.3 (Fig. 3.).

Curves in Fig. 3. show that the higher the amount of H_2S released in TPR, the higher are T_o and the HDS activity of the catalysts. This means that both HDS activity and T_o correlate with the reducibility of catalysts, i.e. with the ease of formation of sulfur anion vacancies (8).

The amount of NO adsorbed on the catalysts increases in the sequence: Mo-HSP ≪CoMo-sulfides≪ Co-HSP-1.0 .(Fig. 4.). Neither the method of preparation, nor the surface composition ratio, in the range $r_s = 0.25-0.75$ (measured by X-ray photoelectron spectroscopy (8)), affect the amount of NO adsorbed on different CoMo-sulfide catalysts. This may indicate that the distribution of Co atoms among different phases (Co-Mo-S, CoS, Co_9S_8) and/or their acces-



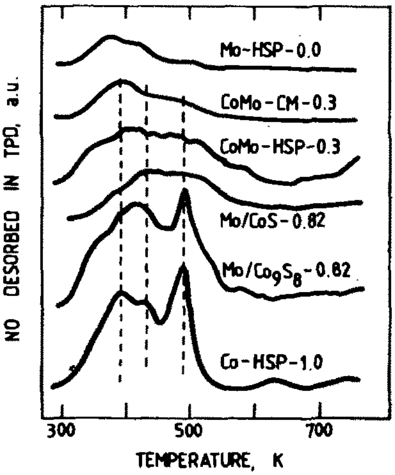


Fig. 4. The amount of NO adsorbed on CoMo-sulfide catalysts in the function of the surface composition ratio.

Fig. 5. TPD curves of NO preadsorbed on different sulfide catalysts.

sibility in the topmost layer changes with r value of catalysts.

It is noteworthy, that the following correlation between the amount of NO adsorbed on Co (NO_{Co}) (calculated from data in Fig. 4.) and the HDS activity (A) of CoMo sulfide catalysts has been found: $A(10^{-8}\ mol.m^{-2}.s^{-1}) = 0.8 + 1.0\ NO_{Co}\ (10^{-6}\ mol.m^{-2})\ (r \leq 0.5)$.

The unresolved TPD curves of NO are due to the poor crystallinity of samples (8) (Fig. 5.). Characteristic spectrum of sample Co-HSP-1.0 enables us to detect Co atoms in Co_9S_8 on the surface of catalysts. Comparison between spectra suggests that separate Co_9S_8 phase of catalyst CoMo-CM-0.3 is mostly covered by MoS_2, and the state of surface Co atoms in sample CoMo-HSP-0.3 and Mo/CoS-0.82 is similar. Adsorption and TPD results suggest, that the strength of NO adsorption increases as follows: Mo-HSP-0.0 < Co-HSP-1.0 < Mo/Co_9S_8-0.82 < CoMo-CM-0.3 ≈ CoMo-HSP-0.3 < Mo/CoS-0.82.

CONCLUSIONS

DTA of TPS of precursors and subsequent TPO of unsupported MMo-sulfide (M=Fe,Co,Ni) HDS catalysts is a suitable test for detecting "M-Mo-S" structure. TPD of NO characterize the state of M atoms in the catalysts. The onset temperature of oxidation and the reducibility of the catalysts correlate with their HDS activity.

REFERENCES

1 M. Breysse, R. Frety and M. Vrinat, Appl. Catal., 12 (1984) 165.
2 B. Scheffer, J.C.M. de Jonge, P. Arnoldy and J.A. Moulijn, Bull. Soc. Chim. Belg., 93 (1984) 751.
3 R.C. Hoodless, R.B. Moyes and P.B. Wells, Bull. Soc. Chim. Belg., 93 (1984) 673.
4 G. Hagenbach, Ph. Courty and B. Delmon, J. Catal., 23 (1971) 295.
5 R. Candia, B.S. Clausen and H. Topsoe, Bull. Soc. Chim. Belg., 90 (1981) 1225.
6 S. Göbölös, Q. Wu and B. Delmon, Appl. Catal., 13 (1984) 89.
7 Q. Wu, S. Göbölös, P. Grange and F. Delannay, Thermochimica Acta, 81 (1984) 281.
8 S. Göbölös, Q, Wu, J. Ladrière, F. Delannay and B. Delmon, Bull. Soc. Chim. Belg., 93 (1984) 687.
9 T.P. Prasad, E. Diemann and A. Müller, J. Inorg. Nucl. Chem., 35 (1973) 1895.