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THE INFLUENCE OF PHOSPHORUS ON THE STRUCTURE AND HYDRODESULFURIZATION ACTIVITY OF SULFIDED Fe AND Fe-Mo CATALYSTS SUPPORTED ON CARBON AND ALUMINA

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Phosphorus-containing Fe and Fe-Mo sulfide catalysts supported on γ-Al_2O_3 and activated carbon were evaluated for their thiophene HDS activities at atmospheric pressure. The thiophene HDS activity of the carbon-supported catalysts decreased considerably in the presence of phosphorus, while the activity of the alumina-supported catalysts was not affected. It was shown by Mössbauer spectroscopy that in both the oxidic carbon- and alumina-supported catalyst precursors the presence of phosphorus resulted in an improved dispersion of the Fe phase. In the sulfided carbon-supported Fe and Fe-Mo catalysts, the presence of phosphorus resulted in the formation of an "Fe(II)-phosphate" phase, which was held responsible for the decrease in HDS activity. With regard to the sulfided alumina-supported catalysts, it was found that phosphorus did not influence the structure of the metal sulfide species.

1. INTRODUCTION

Hydrotreating catalysts such as alumina-supported molybdenum sulfide promoted by Co or Ni sulfide are widely used in the oil-processing industry. Hydrotreating includes several processes like hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodemetallization (HDMe). In commercial alumina-supported Co-Mo and Ni-Mo catalysts the catalytic activity is often improved by additives. One of the most effective modifiers is phosphorus, present as phosphate in the oxidic catalysts. Phosphoric acid is widely used in the catalyst preparation stage since it increases the solubility of the precursor metal salts in the impregnation solutions as a result of which high loaded catalysts can be prepared with a single impregnation step [1-5]. In addition, the phosphate additive is also reported to act as a promoter for HDN [1-3,6-12], HDS [1-10,13,14] and HDMe [13,15] reactions and to increase the strength and heat stability of the alumina support [16,17]. The promotion effect of phosphorus on the catalytic activity is sometimes explained in terms of an improved dispersion of the precursor metal salts on the support [1-5].

However, the promotion effect of phosphorus is not universal. For instance, it was reported that large amounts of phosphate (larger than 12 wt%) adversely affect the HDS and HDN activity of the catalyst [3]. In case of carbon as support material for molybdenum sulfide catalysts, it was even shown that phosphorus acts as a severe poison since it drastically reduces the thiophene HDS activity of these catalysts already at very low phosphate contents [18-20]. In an attempt to clarify this contradictory effect we examined by in-situ Mössbauer spectroscopy and thiophene HDS activity at atmospheric pressure the properties of phosphate containing Fe and Fe-Mo catalysts supported on alumina and activated carbon. In the following sections phosphorus and phosphate will be abreviated by P.

2. EXPERIMENTAL

2.1. Catalyst preparation

P-containing catalysts, supported on alumina (Ketjen Grade B; surface area 270 $m^2.g^{-1}$, pore volume 1.9 $cm^3.g^{-1}$) were prepared by a stepwise pore volume impregnation method using aqueous solutions of H_3PO_4, $(NH_4)_6Mo_7O_{24}.4H_2O$ and

$Fe(NO_3)_3.9H_2O$ (all Merck p.a.). P was always added first, whereas Fe was added last. After each metal impregnation step, the catalysts were dried in air, starting at 293 K and gradually increasing the temperature up to 383 K in 3 h where they were kept overnight. Finally, the alumina-supported catalysts were subjected to a calcination treatment at 823 K for 2 h in air.

For the P-containing catalysts, supported on an activated carbon (Norit RX3-Extra; surface area 1190 $m^2.g^{-1}$, pore volume 1.0 $cm^3.g^{-1}$), H_3PO_4 was added by the pore volume impregnation method (aqueous solution) to oxidic carbon-supported Fe and Fe-Mo (Mo introduced first) catalysts. After each impregnation, the catalysts were dried in air, starting at 293 K and increasing the temperature up to 383 K in 3 h, where they were kept overnight.

Catalysts will be denoted Fe(w)/Y+P(z) and Fe(w)-Mo(x)/Y+P(z), in which Y stand for the type of carrier (Al for alumina and C for carbon) and P stands for phosphorus and phosphate. The values w and x in parentheses represent the weight percentages of Fe and Mo, respectively and z represents the molar PO_4-to-Fe ratio.

2.2. Catalytic activity

Catalytic activity for thiophene HDS was tested in a micro flow reactor operating at 673 K and atmospheric pressure. Catalyst samples (0.2 g) were sulfided in-situ in a mixture of H_2S/H_2 (10 vol% H_2S, flow rate 60 $cm^3.min^{-1}$). The following temperature program was applied: starting at 293 K, the temperature was linearly increased at a rate of 6 $K.min^{-1}$ until 673 K, followed by extended sulfidation at 673 K for 2h. At 673 K a mixture of thiophene and H_2 (6.2 vol% thiophene) was introduced at a flow rate of 50 $cm^3.min^{-1}$. The reaction products were analyzed by on-line gas chromatography. The thiophene conversion was measured after a 2 h run.

2.3. Mössbauer spectroscopy measurements

Mössbauer spectra were recorded using a ^{57}Co in Rh source at room temperature. Doppler velocities are given relative to sodiumnitroprusside (SNP) at room temperature. The spectra were fitted by computer with calculated subspectra consisting of Lorentzian-shaped lines.

Mössbauer spectra of the oxidic catalyst precursors were recorded at 293, 77 and 4.2 K. Catalyst sulfidation took place in a stainless steel Mössbauer in-situ reactor, the design of which is described in detail elsewhere [21]. The sample was heated to 673 K (heating rate 5.5 K per minute) in a 50 $cm^3.min^{-1}$ flow of the sulfidation gas mixture (10 mol % H_2S in H_2), and then cooled to room temperature in the same gas flow. Hereafter, Mössbauer spectra were recorded in-situ at 293 K.

3.   RESULTS

3.1. Thiophene HDS activity

In Figure 1 the thiophene conversions as a function of the PO_4-to-Fe molar ratio (z) are plotted for carbon- and alumina-supported catalysts. It is clear that the activity of the carbon-supported catalysts decreases considerably with increasing z. In case of the alumina-supported Fe-Mo catalysts, containing similar P contents as their carbon-supported counterparts, no clear influence of P on the thiophene conversion can be discerned. If any, the influence of the P is to increase the thiophene conversion.

3.2. Characterization by Mössbauer spectroscopy
-    Oxidic precursors

For all the oxidic catalyst precursors the spectra recorded at 293 and 77 K only consist of a quadrupole doublet, while in the spectrum recorded at 4.2 K a superposition of a quadrupole doublet and a magnetic hyperfine sextuplet is observed. The observed temperature behaviour is typical for ultrafine iron(III)oxide particles showing superparamagnetism [22]. The appearance of the magnetic hyperfine sextuplet depends both on the temperature and the mean iron(III)oxide particle size [22]. As only in the spectra recorded at 4.2 K a spectral contribution of the magnetic hyperfine sextuplet is observed, its relative magnitude determines   the   sequence   in   the   mean   iron(III)oxide   particle

size. The spectra recorded at 4.2 K of the oxidic Fe(4.3)/C+P(z), Fe(5.4)/Al+P(z)
and Fe(2.8)-Mo(8.0)/Al+P(z) catalyst precursors are shown in Figure 2. Because in
the 4.2 K spectra of the Fe(3.1)-Mo(8.0)/C+P(z) catalysts no spectral contribution
of a magnetic hyperfine sextuplet is observed they are not included. It turns out
that the mean iron(III)oxide particle size is smaller when P is present in the
oxidic   carbon and alumina-supported catalysts. As this holds for all catalyst
systems shown in Figure 2, including Fe-Mo/Al+P(z) it may be assumed that for the
carbon supported Fe-Mo catalyst precursors the mean iron(III)oxide particle size
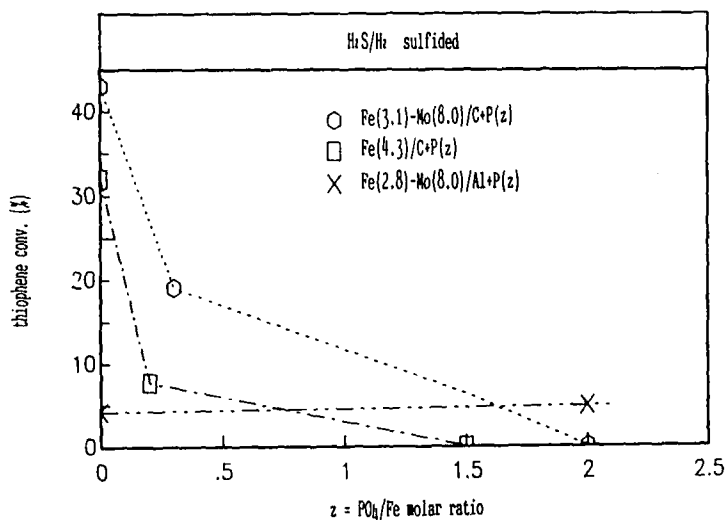is influenced in a similar way.

Fig.1. Thiophene conversion of sulfided Fe and Fe-Mo catalysts as a function of
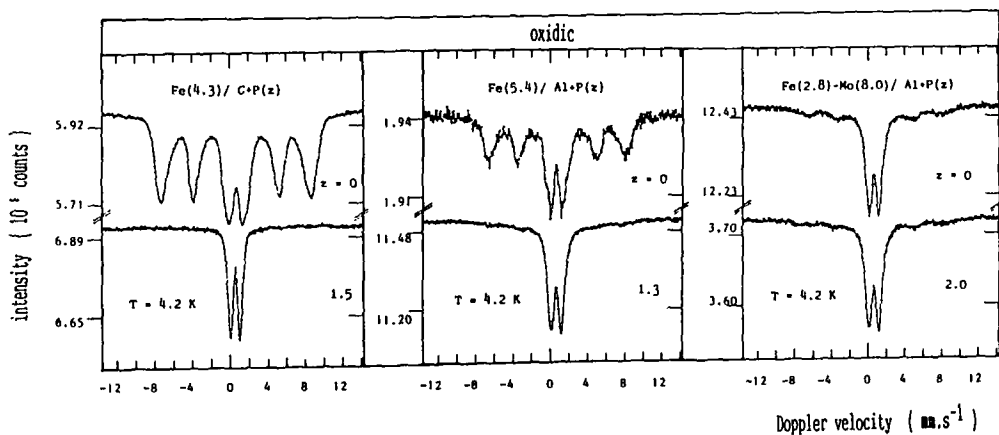the PO_4-to-Fe ratio in the oxidic precursor state.

Fig.2. Mössbauer spectra recorded at 4.2 K of the oxidic catalyst precursors:
(a) Fe(4.3)/C+P(z); (b) Fe(5.4)/Al+P(z); (c) Fe(2.8)-Mo(8.0)/Al+P(z).

Sulfided catalysts

Mössbauer spectra of the freshly sulfided catalysts are presented in Figure 3 (carbon-supported) and Figure 4 (alumina-supported). The results of the computer analyses are given in Table 1. From comparison of the results presented in this Table and those obtained earlier for sulfided Fe and Fe-Mo catalysts on carbon [23-26] and alumina [24,27] supports it follows that the spectral contributions with the smaller quadrupole splittings (indicated by a full bar-diagram in the Figures 3 and 4) are due to sulfided iron species, assigned to "$Fe_{1-x}S$", "Fe-S" and "Fe-Mo-S".

For the carbon-supported catalysts the presence of P influences the composition of the sulfided catalysts. Besides the sulfidic iron species, a high-spin Fe^{2+}-species appears in the spectra which spectral contribution increases with increasing P content. From the results presented in Table 1 it follows that the type of high-spin Fe^{2+}-species does not depend on the amount of P in the catalyst. Furthermore, the presence of molybdenum does also not change the type of high-spin Fe^{2+}-species.

The question arises whether P influences the type of sulfidic iron species. By comparing the results given in Table 1 of the Fe(4.3)/C+P(z) and Fe(3.1)-Mo(8.0)/C+P(z) catalysts, no major differences in the parameters of the sulfidic iron species present in these catalysts is observed. (Due to the small spectral contribution of "$Fe_{1-x}S$" in the Fe(4.3)/C+P(1.5) catalyst the computer fitting procedure for this contribution will be inaccurate). Hence, it is concluded that P does not influence the nature of the sulfidic iron species in the Fe(4.3)/C+P(z) and Fe(3.1)-Mo(8.0)/C+P(z) catalysts. The most dominant effect of P is that the spectral components ascribed to the different sulfidic iron species decrease strongly or even disappear completely in the P-containing catalysts.

In the sulfided alumina-supported Fe and Fe-Mo catalysts already in P-free catalysts a high-spin Fe^{2+}-species is present. From the results of the computer analyses given in Table 1, it can be learned that the Mössbauer parameters of the high-spin Fe^{2+}-species are not markedly changed by P. However, as the P content increases the spectral contribution of the high-spin Fe^{2+}-species increases. By comparing the Mössbauer parameters of the high-spin Fe^{2+}-species present in the
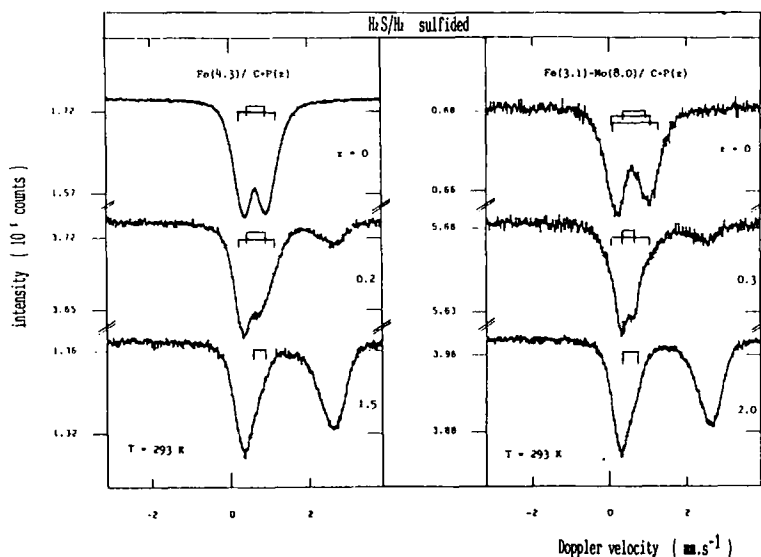

Fig.3. Mössbauer spectra of the freshly sulfided catalysts supported on carbon: (a) Fe(4.3)/C+P(z); (b) Fe(3.1)-Mo(8.0)/C+P(z).
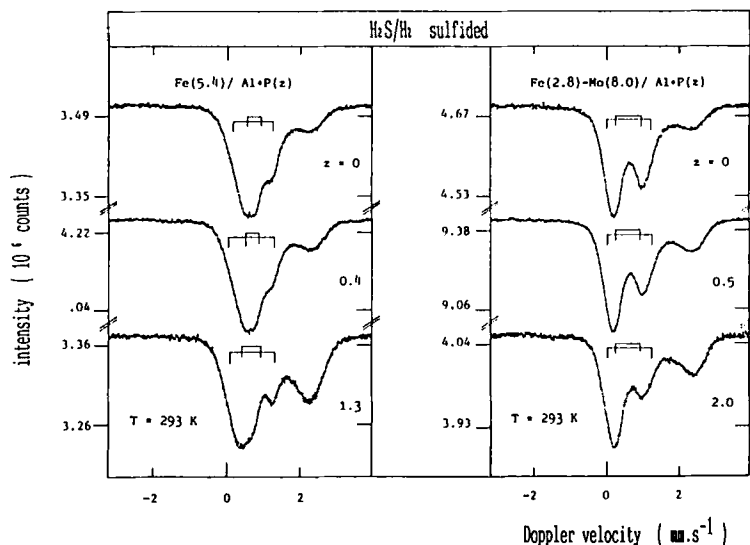
Fig.4. Mössbauer spectra of the freshly sulfided catalysts supported on alumina: (a) Fe(5.4)/Al+P(z); (b) Fe(2.8)-Mo(8.0)/Al+P(z).

carbon- and alumina-supported catalysts (see Table 1) it is found that these high-spin Fe^{2+}-species are different. Furthermore, it is concluded that P does not influence the type of sulfidic iron species, viz. "$Fe_{1-x}S$", "Fe-S" and "Fe-Mo-S", present in the sulfided catalysts.

4. DISCUSSION

4.1. Structure of the P-containing catalysts

The improved dispersion of the P-containing oxidic catalyst precursors can be related to the enhanced solubility and stability of the phosphoric-acid containing impregnation solution [1-5], as a result of which the deposition of large crystalline aggregates is minimized. An alternative explanation is that, due to a metal-phosphate interaction, transportation of the metal oxide phase towards the outer pores of the support grains and subsequent sintering of crystalline oxide aggregates during the drying procedure [23,24] is hampered.

The influence of P on the sulfided carbon-supported catalysts is irrefutable. From the Mössbauer spectra of the carbon-supported Fe and Fe-Mo catalysts it is clear that high-spin Fe^{2+}-species are formed in the presence of P at the expense of the sulfidic iron species. Because it is possible that the high-spin Fe^{2+}-species is related to phosphate, its Mössbauer parameters were compared to those reported for Fe(II)-phosphate complexes. From this comparison it appears that one of the doublets in Table 1 (IS_2, QS_2) is the one all $Fe_3(PO_4)_2.nH_2O$ compounds have in common [28]. Therefore, it can be assumed that the high-spin Fe^{2+}-species has a similar structure. When it is supposed that all P is incorporated in the high-spin Fe^{2+}-species, the stoichiometry of this species, expressed in the PO_4-to-Fe molar ratio, can be calculated from the spectral contributions in Table 1. The values of this ratio are 1 and 0.8 for the Fe(4.3)/C+P(0.2) and Fe(3.1)-Mo(8.0)/C+P(0.3) catalysts, respectively. Due to the inaccuracies in the determination of the spectral contributions these ratios are not conflicting with the presence of a $Fe_3(PO_4)_2$-like stoichiometry (PO_4-to-Fe ratio = 0.7). Consequently, the high-spin Fe^{2+}-species will be called "Fe(II)-phosphate". However, as the Mössbauer parameters of only one doublet are

Table 1
Computer analyses of the Mössbauer spectra recorded at 293 K of carbon- and alumina-supported catalysts after sulfidation at 673 K.
(experimental uncertainties: IS: 0.05 mm/s; QS: 0.05 mm/s; A: 5%)

Fe(4.3)/C+P(z)

	sulfidic iron species						high-spin Fe^{2+}					
	"$Fe_{1-x}S$"			"Fe-S"			"Fe(II)-phosphate"					
z	IS_1	QS_1	A	IS_2	QS_2	A	IS_1	QS_1	A	IS_2	QS_2	A
	(mm/s)		(%)	(mm/s)		(%)	(mm/s)		(%)	(mm/s)		(%)
0	0.64	0.47	83	0.71	0.85	17						
0.2	0.60	0.39	55	0.66	0.90	21	1.43	1.99	12	1.50	2.50	12
1.5	0.70	0.20	7				1.43	1.98	52	1.50	2.48	41

Fe(3.1)-Mo(8.0)/C+P(z)

	sulfidic iron species									high-spin Fe^{2+}					
	"$Fe_{1-x}S$"			"Fe-Mo-S"						"Fe(II)-phosphate"					
	IS_1	QS_1	A	IS_2	QS_2	A	IS_3	QS_3	A	IS_1	QS_1	A	IS_2	QS_2	A
	(mm/s)		(%)	(mm/s)		(%)	(mm/s)		(%)	(mm/s)		(%)	(mm/s)		(%)
0	0.61	0.57	39	0.60	1.04	46	0.63	1.44	15						
0.3	0.47	0.34	54	0.60	1.04	20				1.43	1.99	17	1.50	2.50	9
2.0	0.51	0.42	13							1.43	2.00	54	1.49	2.53	32

Fe(5.4)/Al+P(z)

	sulfidic iron species						high-spin Fe^{2+}					
	"$Fe_{1-x}S$"			"Fe-S"			"Fe(II)-aluminate"					
z	IS_1	QS_1	A	IS_2	QS_2	A	IS_1	QS_1	A	IS_2	QS_2	A
	(mm/s)		(%)	(mm/s)		(%)	(mm/s)		(%)	(mm/s)		(%)
0	0.70	0.36	47	0.70	1.10	26	1.39	1.42	14	1.44	2.16	13
0.4	0.67	0.34	38	0.68	1.12	22	1.40	1.50	18	1.42	2.23	22
1.3	0.65	0.52	36	0.67	1.22	15	1.31	1.58	20	1.35	2.30	29

Fe(2.8)-Mo(8.0)/Al+P(z)

	sulfidic iron phase						high-spin Fe^{2+}					
	"$Fe_{1-x}S$"			"Fe-Mo-S"			"Fe(II)-aluminate"					
z	IS_1	QS_1	A	IS_2	QS_2	A	IS_1	QS_1	A	IS_2	QS_2	A
	(mm/s)		(%)	(mm/s)		(%)	(mm/s)		(%)	(mm/s)		(%)
0	0.60	0.71	55	0.61	1.22	17	1.16	1.62	11	1.31	2.34	17
0.5	0.59	0.70	42	0.63	1.22	22	1.21	1.66	15	1.30	2.37	21
2.0	0.60	0.66	27	0.62	1.24	26	1.17	1.64	21	1.32	2.31	26

in common with those reported for Fe(II)-phosphate complexes, the so-called "Fe(II)-phosphate" will not be a bulk Fe(II)-phosphate.

Whereas in the P-free Fe(3.1)-Mo(8.0)/C+P(z) catalysts to a large extent a so-called "Fe-Mo-S" phase is formed upon sulfidation [24-26], in the P-containing catalysts nearly only "$Fe_{1-x}S$" can be discerned. This indicates that due to the presence of P the interaction between Mo and Fe is diminished to such a degree that the "Fe-Mo-S" phase can not be formed. This is in agreement with the observation that P influences already the oxidic iron phase in the catalyst precursors [24]. Consequently, the effect of P on carbon supported Fe-Mo catalysts is twofold: i) hindrance of the formation of the active "Fe-Mo-S" phase and ii) the formation of a "Fe(II)-phosphate" phase at the expense of sulfidic iron species.

The Mössbauer spectra of the sulfided carbon-supported Fe and Fe-Mo catalysts, do not show any spectral contribution of magnetically split components at room temperature. So no indications were obtained that during sulfidation the dispersion is drastically lost.

In case of the alumina-supported Fe and Fe-Mo catalysts, P causes an increase in the spectral contribution of the high-spin Fe^{2+}-species, which are already present in the P-free catalysts. These species could not be identified as belonging to a "Fe(II)-phosphate" phase, like the one present in P-containing carbon-supported catalysts. Mössbauer spectra of P-free alumina-supported catalysts show a contribution of high-spin Fe^{2+}-species and these Fe^{2+}-species can be ascribed to iron in close contact with the alumina support [24,27]. Since a comparison of the results presented in Table 1 with those obtained earlier [24,27] indicates that the Mössbauer parameters of the high-spin Fe^{2+}-species are about the same, we will confine ourselves to this attribution, a so-called "Fe(II)-aluminate". The increase in the spectral contribution of the "Fe(II)-aluminate" by an increasing P content is in line with the observed improved dispersion of the oxidic iron phase in the P-containing catalyst precursors.

The type of sulfidic iron species present in the alumina-supported catalysts are not influenced by P. From a comparison of the effect of P on the composition of the sulfided carbon- and alumina-supported Fe-Mo catalysts, it turns out that whereas in the carbon-supported catalyst P prevents the formation of "Fe-Mo-S", this phase is present in all the alumina-supported Fe-Mo catalysts studied. A remarkable effect of the addition of P to the alumina-supported Fe-Mo catalysts is that it even causes a slight rise in the spectral contribution of the "Fe-Mo-S" phase.

4.2. Relation between structure and HDS activity

In case of the carbon-supported Fe and Fe-Mo catalysts it was found that the decrease in thiophene HDS activity is correlated with the increase in the amount of the "Fe(II)-phosphate" phase. In the Fe(4.3)/C+P(1.5) catalyst almost all the iron is present in the form of this phase, and hence its HDS activity is close to zero. At low P content, a large part of the iron atoms are not complexed with P and can be sulfided into the catalytically active "$Fe_{1-x}S$" phase [23,24].

Concerning the Fe(3.1)-Mo(8.0)/C+P(z), besides the formation of a catalytically inactive "Fe(II)-phosphate" phase, the HDS activity also decreases as the highly active "Fe-Mo-S" phase is not formed in the presence of P. These results, therefore, unambiguously point to a poisoning nature of the P additive, under the experimental conditions applied here.

A general effect of P in the catalysts described in the present work is the improved iron phase dispersion in the oxidic precursor catalysts. With regard to the alumina-supported catalysts this phenomenon might partly explain why moderate amounts of P result in an increased activity of commercial catalysts. For the alumina-supported Fe-Mo catalysts an additional promotional effect might be the slight increase in the amount of highly active "Fe-Mo-S" in the presence of P. However, at high P contents a large amount of the iron phase is expected to be in close contact with the alumina support ("Fe(II)-aluminate"). Because these iron atoms not attribute to the catalytic activity, this could account for the decrease in activity observed when large amounts of P are present [3].

5. CONCLUSIONS

The thiophene HDS activity of sulfided carbon-supported Fe and Fe-Mo catalysts is strongly decreased in the presence of P, whereas their alumina-supported counterparts are not poisoned under the same reaction conditions.

From Mössbauer experiments it follows that in the oxidic catalyst precursors (irrespective of the support) the presence of P results in a better dispersion of the oxidic phase. This improved dispersion can be related to a close contact between the metal oxide phase and the phosphate [24].

In the sulfided catalyst the support material plays a dominant role in the interaction between the P and the sulfided metal phase. In case of the alumina-supported catalysts P does not influence the type of the metal sulfide species. With regard to the P-containing carbon-supported Fe and Fe-Mo catalysts, a "Fe(II)-phosphate" phase is observed in the sulfided state, which phase may be held responsible for the decrease in thiophene HDS activity.

REFERENCES

[1]   G.A. Michelson, U.S. Patents 3,749,663, 3,749,664, 3,755,148, 3,755,150, 3,755,196 (1973).
[2]   C.W. Fitz and H.F. Rase, Ind. Eng. Chem. Prod. Res. Dev., 22(1983)44.
[3]   J.D Colgan and Y. Chonitz, U.S. Patent 3,287,280(1966).
[4]   J.N. Haresnape and J.E Morris, UK patent 701,217(1953).
[5]   D. Chadwick and D.W. Aitchison, in "Preparation of Catalysts III", eds. Poncelet, Grange and Jacobs, (Elseviers, Amsterdam, 1982) p. 323.
[6]   Jushitsuyu Taisaku Gijutsu Kenkyu Kumiai, Jpn. Patent JP 59/216,635(1984)
[7]   L.A. Pine, U.S. Patent 4,003,828(1975).
[8]   O. Togari, T. Ono and M. Nakamura, Sekiy Gakkaishi, 22(1979)336.
[9]   Y. Horita, O. Togari, T. Komoto, M. Nakamura and H. Tanji, Sekiyu Gakkaishi, 30(1987)94.
[10] Fitrol Corp., Jpn. Patent 55/165,145(1980).
[11] S.M. Brown and D.N. Wallace, U.S. Patent 3,969,273(1976).
[12] Z. Wu, S. Cao and Y. Ling, Shiyou Huagong, 15(1986)219.
[13] P.E. Eberly Jr., U.S. Patent 4,003,828(1977).
[14] G. Muraldihar, F.E. Massoth and J. Shabtai, J. Catal.·, 85(1984)44.
[15] A.L. Morales, R.E. Galiasso, M.M. Agudelo, J.A. Salazar·and A.R. Carrasquel, U.S. Patent 4,520,128(1985).
[16] K.Gishti, A. Iannibello, S. Marengo, G. Morelli and P. Titarelli, Appl. Catal., 12(1984)381.
[17] P.D. Hopkins and B.L. Meyers, Ind. Eng. Chem. Prod. Res. Dev., 22(1983)421.
[18] J.D. Voorhies, U.S. Patent 4,082,652(1978).
[19] J.P.R. Vissers, T.J. Lensing, V.H.J. de Beer and R. Prins, in "Proceedings of the 16th Biennial Conference on Carbon, San Diego, 1983", (1983) p. 607.
[20] S.M.A.M. Bouwens, J.P.R. Vissers, V.H.J. de Beer and R. Prins, J. Catal., in press.
[21] A.M. van der Kraan and J.W. Niemantsverdriet, in "Industrial Applications of the Mössbauer Effect" eds. G.J. Long and J.G. Stevens, (Plenum Publ. Corp., New York, 1986) p. 609.
[22] A.M. van der Kraan, Phys. Stat. Sol. (a), 18(1973)215.
[23] W.L.T.M. Ramselaar, R.H. Hadders, V.H.J. de Beer and A.M. van der Kraan, to be publ. in Appl. Catal.
[24] W.L.T.M. Ramselaar, Thesis, Delft University of Technology, Delft (1988).
[25] W.L.T.M. Ramselaar, M.W.J. Crajè, E. Gerkema, V.H.J. de Beer and A.M. van der Kraan, Bull. Soc. Chem. Belg., 96(1987)931.
[26] W.L.T.M. Ramselaar, M.W.J. Crajè, V.H.J. de Beer and A.M. van der Kraan, to be publ. in Appl. Catal.
[27] W.L.T.M. Ramselaar, V.H.J. de Beer and A.M. van der Kraan, to be publ.in Appl. Catal.
[28] E. Mattievich and B. Danon, J. Inorg. Nucl. Chem., 39(1977)569.