

The Influence of Phosphorus on the Structure and Hydrodesulfurization Activity of Sulfided Co and Co-Mo Catalysts Supported on Carbon and Alumina

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The thiophene HDS activities of phosphorus-containing Co and Co-Mo sulfide catalysts supported on γ -Al₂O₃ and activated carbon were measured at atmospheric pressure. Phosphorus decreased the thiophene HDS activity of the carbon-supported catalysts considerably but did not affect the activity of the alumina-supported catalysts. From XPS it was inferred that phosphorus improves the dispersion of the cobalt phase in the oxidic precursor state of both the carbon- and alumina-supported catalysts. In the sulfided state the interaction between phosphorus and the metal sulfide phase appeared to depend on the support. In the sulfided carbon-supported catalysts, phosphorus formed a Co-phosphate phase, which is responsible for the decrease in HDS activity, while on alumina phosphorus did not influence the structure of the metal sulfide phase. © 1991

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INTRODUCTION

In the oil processing industry alumina-supported molybdenum sulfide promoted by Co or Ni sulfide is extensively used to catalyze hydrotreating processes such as hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodemetallization (HDM). Phosphorus, present as phosphate in the oxidic catalysts, is frequently applied as a secondary promoter. It is reported to improve the catalyst performance for HDS (1-18), HDN (3-10, 19-21), and HDM (11, 22) reactions and to have a beneficial effect on the strength and heat stability of the alumina support (23, 24). Furthermore, addition of phosphoric acid during the catalyst preparation reduces the number of impreg-

nation steps required (5-7, 12-15, 25, 26). 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. Because of the high solubility of the metal salts in the phosphoric acid-containing impregnation solution, the deposition of large crystalline aggregates on the support surface is minimized (5-7, 12-15). In contrast with the above, phosphorus was also reported to cause negative effects. For example, it was found that at concentrations above 12 wt% phosphate adversely affects the HDS and HDN activity of the catalyst (7) and that in the case of carbon-supported molybdenum sulfide catalysts, phosphate drastically reduces the thiophene HDS activity, even when present in very small amounts (27,28). Recently, we studied this contradictory behaviour of phosphorus by evaluating the properties of phosphate-containing activated carbon- and alumina-supported mo-

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lybdenum sulfide catalysts (29). The phosphorus poisoning of the carbon-supported catalysts could not be related to a decrease in active phase dispersion, nor to incomplete sulfidation of the oxidic precursor catalyst. Therefore, it was suggested that the deactivation is related to phosphine (PH_3) created by reduction of phosphate, which adsorbs on the active sites of the catalysts, in this way deactivating these sites. The fact that alumina-supported catalysts were not poisoned by phosphorus was explained by the strong interaction of phosphate with the alumina support, as a result of which phosphate could not be reduced to phosphine. Since the latter study only concerned molybdenum sulfide as the active phase, it is of interest to investigate if other transition metal sulfides are subject to the same phosphorus poisoning mechanism. Therefore, phosphate-containing Co and Co–Mo catalysts, supported on alumina and activated carbon, were characterized by means of a thiophene HDS activity test, X-ray photoelectron spectroscopy (XPS), and dynamic CO chemisorption. The results will be discussed in the perspective of those obtained from a Mössbauer and thiophene HDS study (30) of comparable Fe and Fe–Mo catalysts.

EXPERIMENTAL

Catalyst Preparation

Alumina-supported phosphate-containing catalysts were prepared by a stepwise pore volume impregnation of the alumina (Ketjen Grade B; BET surface area, $270 \text{ m}^2 \text{ g}^{-1}$; pore volume, $0.9 \text{ cm}^3 \text{ g}^{-1}$) with aqueous solutions of H_3PO_4 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (all Merck, p.a. grade). The sequence of addition was P, Mo, Co. After each impregnation, the catalysts were dried in air, starting at 293 K and gradually increasing the temperature to 383 K (3 h) where they were kept overnight. The catalysts were subjected to a final calcination for 2 h in air at 823 K. Series of catalysts were prepared containing a nearly constant amount of metal(s) and varying amounts of phosphate.

The support used for the carbon-sup-

ported catalysts was an activated carbon (Norit RX3-Extra; BET surface area, $1190 \text{ m}^2 \text{ g}^{-1}$; pore volume, $1.0 \text{ cm}^3 \text{ g}^{-1}$). Phosphate was introduced by immersing the support in an aqueous solution of H_3PO_4 . After refluxing for 1 h, in which most of the phosphate was chemisorbed by the carbon, the samples were filtered off and dried overnight in air at 383 K. Catalysts were prepared on the phosphate-containing carbon support by pore volume impregnation using aqueous solutions of the same metal salt components as mentioned before. Promoted catalysts were prepared by introducing the Mo phase first. Series of catalysts containing a nearly constant amount of active metal components and various amounts of phosphate were prepared. One carbon-supported cobalt catalyst was prepared by using $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Merck p.a.) as metal salt. After each impregnation, the catalysts were dried in air, starting at 293 K and increasing the temperature to 383 K over 3 h, where they were kept overnight. The carbon-supported samples were not subjected to a calcination step because this is detrimental to the dispersion of the active phase.

The metal and phosphate content of the precursor catalysts were determined by means of atomic absorption spectroscopy (Perkin–Elmer 3030 AAS spectrometer) and a standard analysis procedure (31), respectively. Catalysts will be denoted as: $\text{Co}(w)/\text{Y} + \text{P}(z)$ and $\text{Co}(w)\text{–Mo}(x)/\text{Y} + \text{P}(z)$, in which Y denotes the type of carrier (Al for alumina and C for carbon) and P stands for phosphate. The values w , x , and z in parentheses represent the weight percentages of Co, Mo, and phosphate/Co molar ratio, respectively. In Table 1 all Co and Co–Mo catalysts are listed together with Fe and Fe–Mo catalysts used in a comparable study of the phosphorus effect (30).

Catalyst Activity

A microflow reactor operating at 673 K was applied for testing of the thiophene HDS activity at atmospheric pressure. Catalyst samples (0.2 g) were sulfided *in situ* with a mixture of 10 mol% H_2S in H_2 (60 std cm^3

TABLE 1
Schematic List of Catalysts

Support material	Type of catalyst ^a
Alumina	Co(2.4)/Al + P(z) $z = 0, 0.1, 0.4, 0.5$
	Co(2.8)-Mo(6.9)/Al + P(z) $z = 0, 0.1, 0.3, 0.4$
	Fe(5.4)/Al + P(z) $z = 0, 0.4, 1.3$
	Fe(3.1)-Mo(7.7)/Al + P(z) $z = 0, 0.5, 2.0$
Carbon	Co(4.3)/C + P(z) $z = 0, 0.02, 0.05, 0.08, 0.1, 0.2, 0.3, 0.5$
	Co(2.6)-Mo(6.1)/C + P(z) $z = 0, 0.03, 0.05, 0.08, 0.1, 0.2, 0.6, 0.8$
	Co(2.6)-Mo(7.6)/C + P(z) $z = 0.8$
	Fe(4.3)/C + P(z) $z = 0, 0.2, 1.5$
	Fe(3.1)-Mo(8.0)/C + P(z) $z = 0, 0.3, 2.0$
	Co ₃ (PO ₄) ₂ /C (4.7 wt% Co) $z = 0.7$

^a The weight percentages of Co, Fe, and Mo are represented in parentheses, while z denotes the PO₄-over-Co(Fe) molar ratio. The Fe and Fe-Mo catalysts are the same as those used in a comparable study on the phosphorus effect (30).

min⁻¹, 6 K min⁻¹ from 293 to 673 K, 2h at 673 K). After sulfidation at 673 K a mixture of 6.2 mol% thiophene in H₂ was led through the reactor (50 std cm³ min⁻¹). The reaction products were analyzed by on-line chromatography. First-order rate constants for the HDS reaction were calculated using the activity data measured after a 2h run (32). The intrinsic catalytic activity is expressed as a quasi turnover frequency (QTOF: moles thiophene converted per mole Co per s).

X-ray Photoelectron Spectroscopy (XPS)

XPS spectra of the oxidic samples were recorded on a Physical Electronics 550 XPS/AES spectrometer equipped with a Mg anode (1253.6 eV) and a double-pass cylindrical mirror analyzer operating at a pass energy of 50 eV. The powdered samples were pressed on double-sided adhesive tape. Spectra were recorded in steps of 0.2 eV. The pressure did not exceed 6.6×10^{-6} Pa and the temperature was approximately 293 K. XPS spectra of the sulfided samples were recorded on an AEI ES 200 spectrometer equipped with an Al anode (1486.6 eV) and a spherical analyzer operating at a pass energy of 60 eV. In order to avoid contact of the sulfided catalysts with air, a special sulfiding reactor was used (33) which al-

lowed transfer of the samples to a N₂-flushed glove box attached to the XPS apparatus without exposure to air. After sulfidation according to the procedure described above, the catalyst samples were flushed with purified He for 15 min at 673 K and subsequently cooled to room temperature. The samples were mounted on the specimen holder by means of double-sided adhesive tape. Spectra were recorded at 293 K in steps of 0.2 eV; the pressure was lower than 1.3×10^{-6} Pa. The C 1s peak (284.6 eV) was used as an internal standard for binding energy calibration and the metal-over-C photoelectron intensity ratios were used to measure the degree of dispersion of the metal (oxide or sulfide) phase on the support. Theoretical intensity ratios were calculated according to the quantitative XPS model described by Kuipers (34). Electron mean free paths were calculated according to Seah and Dench (35), electron cross sections according to Scofield (36).

Dynamic CO Chemisorption

Dynamic CO chemisorption was measured after sulfidation of the oxidic catalysts in a thiophene/H₂ (7.9 vol% thiophene) reaction mixture at 693 K. At the end of a 24 h period needed for stabilization, the sulfided

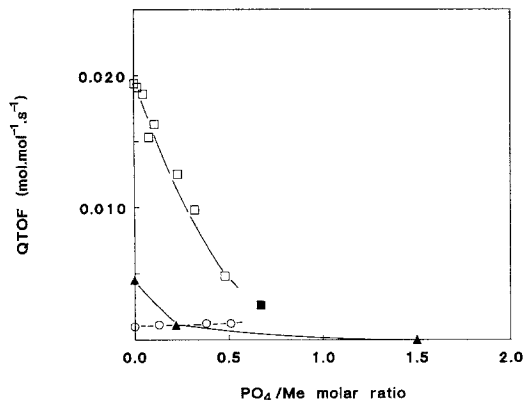


FIG. 1. QTOF values of sulfided carbon- and alumina-supported Co and Fe catalysts as a function of the PO_4 -to-Me ratio (z) ($\text{Me} = \text{Co}, \text{Fe}$) in the oxidic precursor state. The values of the Fe catalysts are taken from Ref. (30). (\square) Co/C + P; (\blacksquare) $\text{Co}_3(\text{PO}_4)_2/\text{C}$; (\blacktriangle) Fe/C + P; (\circ) Co/Al + P.

catalyst was subsequently flushed with Ar for 2 h at 693 K, then measured for its carbon monoxide chemisorption capacity in the reactor itself by a dynamic method. Successive pulses are run over the sulfided catalyst held at 273 K until the cumulative adsorption remains constant. More detailed information is given in Bachelier *et al.* (37).

RESULTS

The quasi-turnover frequencies (QTOF) as a function of the PO_4 to Co molar ratio (z) are plotted for various carbon- and alumina-supported catalysts in Figs. 1 and 2. The QTOF values calculated for comparable Fe and Fe–Mo sulfide catalysts (30) are also included in these figures. The activities of the carbon-supported catalysts decreased considerably with increasing amounts of phosphate. From Fig. 1 it is further apparent that a Co catalyst prepared by impregnation with $\text{Co}_3(\text{PO}_4)_2$ as precursor salt behaved like a common Co/C + P catalyst. In the case of the alumina-supported catalysts with similar phosphate contents to their carbon-supported counterparts, the presence of phosphate had little effect on the HDS activity and was certainly not resulting in an activity decrease.

XPS measurements were carried out on the following catalysts: Co(4.3)/C, Co(4.3)/C + P(0.3), $\text{Co}_3(\text{PO}_4)_2/\text{C}$ (6.7 wt% Co), and Co(2.6)–Mo(7.6)/C + P(0.8), in both the oxidic and the sulfided state. The Co $2p_{3/2}$ spectra are shown in Fig. 3. From Fig. 3(a,b) it can be seen that the Co $2p_{3/2}$ spectrum of the oxidic Co/C catalyst shows a pronounced shake-up structure, which decreased strongly after sulfidation. The phosphate-containing catalysts all show a very strong shake-up structure in their oxidic state which, remarkably, did not decrease much after sulfidation (except for the promoted catalyst). This finding points to a different sulfidic structure in Co(4.3)/C + P(0.3) and $\text{Co}_3(\text{PO}_4)_2/\text{C}$ than in the phosphate-free cobalt catalyst. In fact, the clear presence of a shake-up structure in the sulfidic state of these catalysts indicates that cobalt in an oxidic surrounding is still present. The shake-up structure of the sulfided Co(2.6)–Mo(7.6)/C + P(0.8) catalyst, although small, is slightly more pronounced than that in the sulfided phosphate-free Co/C catalyst. Moreover, the Co $2p_{3/2}$ binding energy of the former catalyst shifted to a somewhat higher value than that of the sulfided Co/C catalyst, suggesting that the sul-

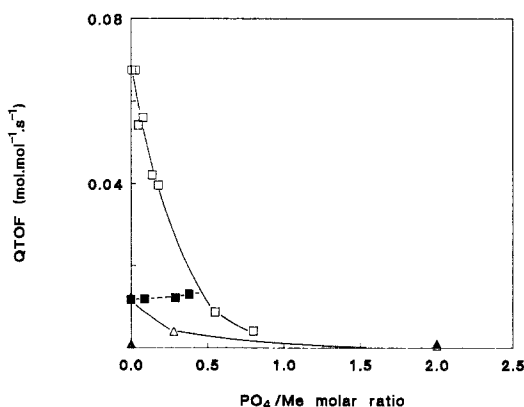


FIG. 2. QTOF values of sulfided carbon- and alumina-supported Co–Mo and Fe–Mo catalysts as a function of the PO_4 -to-Me ratio (z) ($\text{Me} = \text{Co}, \text{Fe}$) in the oxidic precursor state. The values of the Fe–Mo catalysts are taken from Ref. (30). (\square) Co–Mo/C + P; (\triangle) Fe–Mo/C + P; (\blacksquare) Co–Mo/Al + P; (\blacktriangle) Fe–Mo/Al + P.

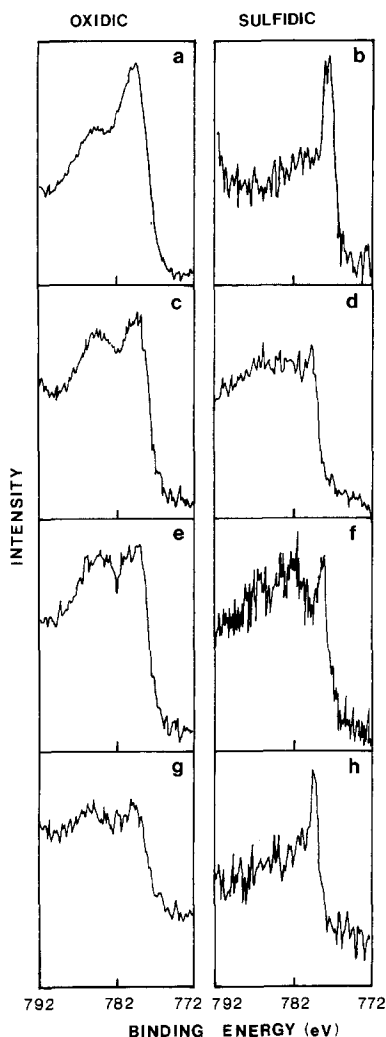


FIG. 3. XPS $\text{Co } 2p_{3/2}$ spectra of various cobalt-containing catalysts: (a) $\text{Co}(4.3)/\text{C}$, oxidic; (b) $\text{Co}(4.3)/\text{C}$, sulfidic; (c) $\text{Co}(4.3)/\text{C} + \text{P}(0.3)$, oxidic; (d) $\text{Co}(4.3)/\text{C} + \text{P}(0.3)$, sulfidic; (e) $\text{Co}_3(\text{PO}_4)_2/\text{C}$, oxidic; (f) $\text{Co}_3(\text{PO}_4)_2/\text{C}$, sulfidic; (g) $\text{Co}(2.6)\text{-Mo}(7.6)/\text{C} + \text{P}(0.8)$, oxidic; (h) $\text{Co}(2.6)\text{-Mo}(7.6)/\text{C} + \text{P}(0.8)$, sulfidic.

fided $\text{Co}(2.6)\text{-Mo}(7.6)/\text{C} + \text{P}(0.8)$ catalyst still contains a small fraction of oxidic cobalt atoms. The P $2p$ binding energy in the catalysts did not change significantly after sulfidation, its value being about 133.8 eV. The quantitative XPS results are collected in Table 2. A striking observation in this table is the low Co-to-C intensity ratio of the phosphate-containing catalysts in their oxidic as well as sulfided state compared to $\text{Co}(4.3)/$

C. According to Vissers *et al.* (38), Co/C catalysts prepared from an aqueous $\text{Co}(\text{NO}_3)_2$ solution have an inhomogeneous dispersion, with the cobalt particles concentrated on the outside of the support grains. Apparently, in the phosphate-containing cobalt catalysts the dispersion is more homogeneous. The atomic S-to-Co ratio of the sulfided $\text{Co}(4.3)/\text{C} + \text{P}(0.3)$ catalyst (0.8) is lower than that of sulfided phosphate-free Co/C catalyst (1.3–1.5 according to Vissers *et al.* (38)), whereas in the sulfided $\text{Co}_3(\text{PO}_4)_2/\text{C}$ catalyst this value is very low (0.3). Obviously, the presence of phosphate hampers a complete sulfidation of the cobalt phase. As regards the sulfided $\text{Co}(2.6)\text{-Mo}(7.6)/\text{C} + \text{P}(0.8)$ catalyst, the Mo $3d_{5/2,3/2}$ XPS binding energies are exactly equal to those of a sulfided phosphate-free Mo/C catalyst (29, 39), indicating that the Mo phase in the phosphate-containing catalyst is essentially sulfidic. Furthermore, the quantitative XPS results reveal a Mo-to-C intensity ratio of 0.07, which is comparable to a sulfided phosphate-free Mo/C catalyst (29). Hence, the Mo sulfide phase dispersion in the phosphate-containing Co-Mo catalyst is about the same as that in the Mo/C catalyst.

CO chemisorption experiments were performed on the phosphate-containing $\text{Co}(4.3)/\text{C} + \text{P}(0.3)$ and $\text{Co}(2.6)\text{-Mo}(6.1)/\text{C} + \text{P}(0.6)$ catalysts and also on the phosphate-free $\text{Co}(4.3)/\text{C}$ and $\text{Co}(2.6)\text{-Mo}(6.1)/\text{C}$ catalysts. The molar ratio CO/Co amounted to 0.25 for both phosphate-free catalysts, while its value was 0.15 for $\text{Co}(4.3)/\text{C} + \text{P}(0.3)$ and 0.16 for $\text{Co}(2.6)\text{-Mo}(6.1)/\text{C} + \text{P}(0.6)$. The decrease in CO chemisorption (40%) observed for the Co catalyst is in agreement with the decrease in thiophene HDS activity, 50%. The correlation between CO chemisorption and thiophene HDS activity is less good for the Co-Mo catalyst.

DISCUSSION

The XPS measurements revealed that the presence of phosphate in the oxidic carbon-supported cobalt catalysts leads to an im-

TABLE 2
Quantitative XPS Results

	Co(4.3)/C ^a	Co(4.3)/C + P(0.3)	Co ₃ (PO ₄) ₂ /C ^b
Oxidic state			
I_{Co}/I_C	0.59	0.17	0.19
particle thickness (nm)	^c	1.0	1.9
Sulfided state			
I_{Co}/I_C	0.31	0.12	0.19
particle thickness (nm)	^c	1.4	1.4
S/Co atomic ratio ^d	1.3–1.5	0.8	0.3

^a For the sulfided phosphate-free Co/C catalyst the XPS data of a sulfided Co(3.9)/C catalyst reported by Vissers *et al.* (38) were taken.

^b This catalyst contained 6.7 wt% Co.

^c Because the I_{Co}/I_C intensity ratio was larger than the theoretical monolayer ratio, the particle thickness could not be calculated.

^d The S/Co atomic ratio was calculated after subtraction of the sulfur uptake by the carbon support itself ($I_S/I_C = 0.003$).

proved dispersion of the cobalt phase. As regards the oxidic carbon- and alumina-supported iron catalysts, the Mössbauer results indicated the same phenomenon (30). Although the procedure of introducing phosphate into the carbon-supported Co and Fe catalysts was different (in the latter case, phosphate was introduced after the iron salt impregnation), it can be expected that this different procedure does not markedly influence the final state of the dried oxidic catalyst, since no calcination is applied. A second impregnation step, namely, will cause a redistribution of the initially present oxidic particles. The net effect will be an impregnation solution containing both phosphate and metal (Co, Fe) ions. In this way, the improved dispersion can be related to the enhanced solubility and stability of the phosphoric acid-containing impregnation solution (5–7, 12–15, 25, 26), as a result of which the deposition of large crystalline aggregates is minimized. An alternative explanation is based upon the earlier observations (38, 40–43) that, in terms of dispersion, anions (e.g., molybdate) interact more efficiently with the activated carbon surface than cations (Me^{2+}) and that the presence of anions at the carbon surface improves the

dispersion of the Me^{2+} ions because they serve an anchoring sites for these cations. In this way the presence of phosphate anions results in an increased initial Co^{2+} (Fe^{2+}) dispersion and a stabilization of this dispersion because the metal–phosphate interaction will hamper the transport of metal species toward the outer pores of the support grains and subsequent sintering during the drying procedure (44). However, the Mössbauer parameters of the oxidic iron doublets (30) did not match with those reported for iron phosphate compounds (45), implying that no typical Fe–O–P bond was formed.

With regard to the sulfided carbon-supported cobalt catalysts Co/C + P and $Co_3(PO_4)_2/C$, from the Co $2p_{3/2}$ XPS peak shapes it could be inferred that a part of the cobalt atoms have an oxidic surrounding. Furthermore, the S-over-Co atomic ratio appeared to decrease in the presence of phosphate, and the lowest sulfur content was found when cobalt and phosphate were initially present in the stoichiometric $Co_3(PO_4)_2$ phase. The XPS results, therefore, suggest that the amount of cobalt sulfide diminishes with increasing amounts of phosphate. In this respect, the lower CO chemisorption of the Co(4.3)/C + P(0.3)

catalyst compared to the Co(4.3)/C catalyst also indicates that sulfidation in the presence of phosphate results in a partly different cobalt phase. The fact that the dispersion of the cobalt is clearly changed in the presence of phosphate might indicate a close contact between the two, possibly in the form of a cobalt-phosphate phase. This suggestion is corroborated by the finding that the cobalt sulfide particle thickness in the sulfided Co(4.3)/C + P(0.3) catalyst corresponds exactly to that in the sulfided Co₃(PO₄)₂/C catalyst (1.4 nm). Concerning the chemical state of the phosphate additive, it is instructive to note that the P 2*p* XPS binding energies remained the same after sulfidation, indicating that phosphate is still present in the sulfided catalysts.

As regards the phosphate-containing Co-Mo/C catalyst, the XPS results were more indicative of a sulfidic than an oxidic surrounding of the cobalt atoms, although the presence of a small fraction of oxidic cobalt could not be excluded. On the other hand, the CO chemisorption capacity of the sulfided Co(2.6)-Mo(6.1)/C + P(0.6) catalyst decreased considerably compared to the sulfided Co(2.6)-Mo(6.1)/C catalyst. In fact this decrease was remarkably similar to that of the sulfide Co/C + P catalyst. CO chemisorption, therefore, reveals that the structure of the sulfided Co-Mo phase is altered in the presence of phosphate. In view of the analogy between Co-Mo/C + P and Co/C + P and the results obtained earlier with Fe-Mo/C + P and Fe/C + P (30), it seems reasonable to ascribe the influence of phosphate on the Co-Mo/C catalyst also in terms of a close contact between cobalt and phosphate, possibly in the form of a cobalt-phosphate phase. The influence of phosphate on the sulfided carbon-supported Co catalysts is irrefutable and very similar to that observed for the equivalent Fe catalysts (30). A high-spin Fe(II)-phosphate phase is formed in the presence of phosphate at the expense of the sulfidic iron species. Additional support for the presence of an Fe(II)-phosphate phase has been ob-

TABLE 3

Sulfur Uptake (in mg per 200 mg catalyst) for the Carbon-Supported Fe and Fe-Mo Catalysts Determined from γ -ray Transmission Measurements During Sulfidation at Room Temperature

Fe(4.3)/C + P(z)		Fe(3.1)-Mo(8.0)/C + P(z)	
z	S uptake (mg)	z	S uptake (mg)
0	12.2 ± 0.2	0	19.8 ± 0.2
0.2	10.0 ± 0.2	0.3	14.5 ± 0.5
1.5	8.5 ± 0.5	2.0	10.5 ± 0.2

Note. Sulfur uptake by the support was 7.0 ± 0.2 mg per 200 mg.

tained by γ -ray transmission experiments according to a procedure described elsewhere (46). Due to the replacement of oxygen by sulfur or by sulfur deposition on the catalyst during sulfidation, the effective mass for γ -ray absorption increases and, hence, the sulfur uptake per gram catalyst can be determined from the γ -ray transmission (46). The relative sulfur uptakes, calculated in this way, of the carbon-supported Fe and Fe-Mo catalysts containing varying amounts of phosphate, are presented in Table 3. It is obvious that the sulfur uptake decreases with increasing phosphate content. This indicates that the high-spin Fe²⁺ phase is not a sulfidic phase.

Besides the formation of Fe(II)-phosphate, the presence of phosphate also strongly hampered the formation of the Fe-Mo-S phase (47) in the sulfided carbon-supported Fe-Mo catalyst (30). This effect is most probably due to a weakening of the interaction between Mo and Fe. Therefore, the effect of phosphate 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 an Fe(II)-phosphate phase at the expense of the sulfidic iron species. From the Mössbauer studies of the Fe(4.3)/C + P(z) and Fe(3.1)-Mo(8.0)/C + P(z) catalysts, no in-

dications were obtained that during sulfidation the influence of phosphate on the dispersion is lost. Hence, it was assumed that also in the sulfided carbon-supported catalysts the presence of phosphate brings about an improved dispersion.

In the case of sulfided alumina-supported Fe and Fe–Mo catalysts, phosphate caused an increase in the spectral contribution of a high-spin Fe^{2+} phase, which is already present in the phosphate-free catalysts. This phase has been ascribed to iron in close contact with the alumina support (48) and is referred to as Fe(II)-aluminate. In this respect the observation that at high phosphate contents the spectral contribution of the high-spin Fe^{2+} phase increases, is in line with the finding that the dispersion of the oxidic iron phase in the precursor catalyst is improved by the presence of phosphate (30). Such an improvement of the dispersion due to phosphate addition has been also reported by Ramirez de Agudelo and Morales (49) as a result of an XPS study of sulfided Ni/Al + P catalysts. Interestingly, the sulfidic iron species present in the alumina-supported catalysts were found to be hardly influenced by phosphate (30), in clear contrast with their carbon-supported counterparts. Consequently, phosphate did not hamper (but slightly increased) the Fe–Mo–S formation in sulfided Fe–Mo/Al + P catalysts. Based on similarity considerations, it is assumed that in the case of the alumina-supported Co and Co–Mo catalysts used in the present study the effects of phosphate will be the same as those described above.

The strong decline in thiophene HDS activity with increasing PO_4/Co ratio observed for the phosphate-containing carbon-supported Co and Co–Mo catalysts (see Figs. 1 and 2) suggests a poisoning mechanism, due to the formation of a catalytically inactive cobalt–phosphate complex. In this respect it is instructive to note that a cobalt catalyst prepared from pure $\text{Co}_3(\text{PO}_4)_2$ showed the lowest HDS activity in the Co/C + P(z) series. This poisoning mechanism is in line

with the results obtained for carbon-supported Fe and Fe–Mo catalysts which showed that the decrease in HDS activity was proportional to the increase in the amount of the Fe(II) phosphate phase formed (30).

The above-described mechanism of poisoning by phosphate is not consistent with a recent study on phosphate-containing molybdenum sulfide catalysts by Bouwens *et al.* (29). In this study it was found that the structure of the molybdenum sulfide phase in the presence of phosphate remained essentially the same. Moreover, it was suggested that the poisoning is related to phosphine (PH_3) created by reduction of phosphate. The difference between phosphate-containing Co or Fe catalysts, on the one hand, and Mo catalysts, on the other hand, is probably related to the stability of the metal–phosphate compound. In case of the Mo/C + P catalysts it was shown that a molybdophosphate complex ($\text{H}_3\text{P}(\text{Mo}_3\text{O}_{10})_4$) could easily be converted into a sulfidic molybdenum phase (29), in clear contrast with the results of the present study and those reported earlier (30) which show that Co and Fe are complexed in a nonsulfidable phosphate structure. With respect to the Co–Mo/C + P and Fe–Mo/C + P catalysts, these results indicate that phosphate is primarily associated with the cobalt or iron phases. At high phosphate contents, however, it can be expected that an additional poisoning effect due to the reduction of nonbonded phosphate to phosphine may take place.

As mentioned above, it is frequently reported that addition of phosphate to alumina-supported catalysts results in an activity increase for HDS (1–18), HDN (3–10, 19, 21), and HDM (11, 22). The findings described in the present study suggest that this could be due to the positive effect of phosphate on the dispersion of promoter metal ions. Due to the strong interaction between phosphate and Al_2O_3 (23, 50), at low phosphate loading the phosphate has much less chance to interact with the metal sulfide

phase on Al_2O_3 as on carbon. However, as was observed for Fe/Al + P and Fe-Mo/Al + P catalysts (30), at high phosphate contents, a large fraction of promoter metal ions might be in close contact with phosphate, in which position they might not attribute to the catalytic activity. This effect could be the reason for the decrease in activity when large amounts of phosphate are added (7).

CONCLUSIONS

Phosphate strongly decreases the thiophene HDS activity of sulfided carbon-supported Co(Fe) and Co-Mo(Fe-Mo) catalysts, while this is not the case for their alumina-supported counterparts. XPS and Mössbauer studies of the oxidic catalyst precursor showed that irrespective of the support phosphate improves the dispersion of the metals in the oxidic phase, due to a close contact between the metal oxide phase and the phosphate. In the sulfided catalyst the interaction between the phosphate and the metal sulfide phase depends on the support material. In the alumina-supported catalysts phosphate does not influence the structure of the metal sulfide phase, while in the carbon-supported catalysts, a Me(II)-phosphate phase is formed which is responsible for the decrease in HDS activity.

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