Behavior of Iron–Vanadium Sulfide Catalysts for Hydrotreating Reactions

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Fe–V pure and mixed sulfides have been prepared from solutions containing iron nitrate and/or ammonium tetrathiovanadate and precipitation with ammonium sulfide. After treatment with H_2S (15%)–H_2 at 673 K, they exhibit quite high surface area from 57 to 5 $m^2 \cdot g^{-1}$. X-ray diffraction and Mössbauer spectroscopy show the existence of a continuum from the pyrrhotite phase ($Fe_{0.85}S$) to a V_3S_4-like phase ($V_{0.74}S$). The structure of the solids is not modified by the catalytic tests which consist in hydrodesulfurization (HDS) of thiophene, hydrogenation (HYD) of toluene, and hydrodeporphyrinization (HDP) of vanadyl octaethyl porphyrine. X-ray photoelectron spectroscopy characterizations indicate a surface Fe–V homogeneity in the mixed sulfides corresponding to the bulk composition and show an effective surface oxidation of the prepared or tested samples occuring during air exposure. Surface compounds like $VOSO_4$, V_2O_5, Fe_2O_3, xH_2O, and FeOOH have been identified. Concerning the catalytic behaviors, it is worth mentioning that bulk $Fe_{0.85}S$ is only active for HDP whereas bulk $V_{0.74}S$ has a high potential activity in HDS, HYD, and HDP by comparison with bulk MoS_2. Moreover, a synergy effect is detected for about 30 atomic% in Fe which origin could be assigned to an optimal dispersion of the V active sites. © 1997 Academic Press

INTRODUCTION

For a better protection of the atmospheric environment, there is little doubt that catalytic hydroprocessing will become increasingly important in the years to come. As a matter of fact, recent and future legislations, some of which are already applied in the United States, will impose reductions in emissions of pollutants like SO_2, carcinogenic hydrocarbons, or soots. Therefore, the refiners must be prepared to significantly reduce sulfur and aromatic levels in fuels. Diminishing the metal content in heavy fractions may be also desirable as poisoning of catalysts is in part provoked by metal deposits. A possible strategy to overcome these difficult problems is to develop new catalyst formulations which have to be more active and selective. Replacement of the classical Promotor–MoS_2-γ Al_2O_3 catalysts (which have already been improved by some additives like phosphorus) by other transition metal sulfides TMS, namely those of Re, Ru, Os, Rh, Ir, Pd, or Pt is promising (1–3) for specific reactions (i.e., hydrodesulfurization (HDS) of dibenzothiophene) but the cost of these metals has a detrimental effect on possible industrial development.

Our strategy was therefore to concentrate on the use of TMS of the first row of the periodic table. Former studies have shown the beneficial effect, probably catalytic, of iron containing compounds, among which pyrite is the most notable, in coal–gas reactions (4). Indeed, presence of pyrite FeS_2 in coal enhances production of liquid products with lower viscosity and is efficient to catalyze hydrogenolysis of benzothiophene (5). However, numerous studies involving Mössbauer characterizations have shown that in the presence of H_2 under the conditions of coal liquefaction, pyrite is easily transformed into nonstoichiometric iron sulfides $Fe_{1-x}S$ which are identified as pyrrhotite ($0 \leq x \leq 0.125$) (6–9). More recently, it has been shown that when clays are used in the hydrodemetallation (HDM) of heavy oils, the active phase is a pyrrhotite-type sulfide formed during the process (10). Pyrrhotite is also a catalyst for hydrogenation of diphenyl ether in presence of H_2S (11). As a consequence, the iron sulfide $Fe_{1-x}S$ appears as a good candidate to be incorporated in new catalytic formulations. Indeed, recent publications (12–16) indicate that mixed Fe–Mo sulfides exhibit interesting properties such as high catalytic activity in HDS of thiophene (13) or, on the contrary, high hydrodenitrogenation HDN and low HDS activity (14). Methods of preparation of the sulfides may have a considerable influence on their properties. In particular, it has been found by high-resolution electron microscopy (HREM) that single layers of MoS_2 are supported on the pyrrhotite phase (17), whereas Danot et al. (18) showed that iron in Fe(II) and Fe(III) oxidation states is intercalated between the MoS_2 layers. Mixed Fe–Ru and Fe–Pt systems supported on carbon have also been tested in HDN of pyridine (19).

On the other hand, it has been proposed (20) that during the course of the HDM reaction, the initial pyrrhotite traps V from the feed and evolves to mixed Fe–V sulfides keeping the same structure (NiAs like structure); these mixed sulfides are active as well for the HDM reaction. Moreover, Rosa-Brussin and Moronta (21) have found that vanadium added to a clay containing iron sulfide increases its

HDM activity. Bulk vanadium sulfides on their own, particularly V_2S_3, have been shown to be efficient catalysts for HDS, HDN, and hydrogenation (HYD) of aromatic molecules (22). Vanadium deposited on a MoS_2–alumina catalyst also significantly improves HDM of the vanadyl octaethyl porphyrin (VOOEP) as well as HYD of toluene (23). By comparison with MoS_2, unsupported Mo–V sulfides present higher HYD and cracking properties (24). From all the above observations, it appears promising to investigate the catalytic properties of Fe–V mixed sulfides. In a previous paper (25), we have already shown that these mixed sulfides exhibit synergy when comparing intrinsic activities measured per surface area of catalyst in thiophene HDS at high pressure. They also present an unusual high selectivity toward formation of tetrahydrothiophene. The aim of the present paper was to explore the catalytic potentiality of these Fe–V mixed sulfides in some important reactions related to the hydrotreatment processes such as thiophene HDS, toluene HYD, and hydrodeporphyrinization HDP of VOOEP. The characteristics of the catalysts before and after tests will be also extensively examined.

EXPERIMENTAL

Catalysts Preparation

The procedure was already described in Ref. (25). It consists of a modification of the method reported by Guillard *et al.* (22) and according to a previous publication (26). It has been claimed that this method has the advantage of producing vanadium sulfides with appropriated surface areas and avoiding the existence of vanadium–oxygen bonds in the final catalysts (22). In fact, the presence of appreciable amounts of oxygen in the surface layers of the solids will be shown. For the preparation, an aqueous solution of Fe(III) nitrate nonahydrate (Merck, purity >99%) was slowly added to a solution of ammonium tetrathiovanadate (ATTV) (Strem Chemicals) and of ammonium sulfide (20% in aqueous solution, Strem Chemicals). The concentration of both solutions is worked out to have the appropriate Fe/V stoichiometry of the expected final sulfide, but taking into account that the final solution must contain at least 10^{-1} mol $\cdot$ liter^{-1} of vanadium to ensure the stability of ATTV. The solution was filtered and the solid product dried at room temperature and heated up to 673 K in a flowing mixture of 15% H_2S in H_2 and then kept for 4 h under the same conditions. Pure iron sulfide was prepared in the same way, but without any ATTV in the ammonium sulfide solution. Pure vanadium sulfide was prepared by treating solid ATTV by the same procedure as used for the dried mixed precipitates.

Two mechanical mixtures (MM) of the pure Fe and V sulphides have also been obtained by simply grinding in a mortar the desired proportions of the respective powders.

For comparison, a bulk MoS_2 sulfide has been prepared by decomposition of ammonium tetrathiomolybdate in a H_2S (15%)–H_2 mixture at 673 K.

Catalytic Tests

Hydrodeporphyrinization of vanadyl octaethylporphyrin. The reaction was carried out in a high-pressure continuous-flow (both liquid and gas) system. A solution of VOOEP (3.10^{-4} mol $\cdot$ liter^{-1}) in decahydronaphtalene (purity >98%, *cis–trans* mixture, Janssen Chimica) containing 2% of dimethyldisulfide (DMDS, purity >99%, Janssen Chimica) to maintain a sulfiding atmosphere, was used as a liquid feed. The catalysts were sulfided prior to testing. The reaction products were analyzed by UV-visible spectroscopy. The experimental details for the tests are reported in Table 1.

Hydrogenation of toluene and hydrodesulphurization of thiophene. These two reactions were carried out in a high-pressure system with an on-line gas chromatography (Intersmat IGC 131) equipped with a capillary column (WCOT fused silica, CP Sil-5 CB from Chrompack) to which the products were injected by an automatic injection valve Valco. All tubings were coated and heated to avoid condensation of reactants and products.

HYD of toluene (purity >99.5%, Fluka) and HDS of thiophene (purity >98%, Fluka) were carried out

TABLE 1

Experimental Conditions for Hydrodeporphyrinization (HDP), Hydrogenation (HYD), and hydrodesulfurization (HDS)

Reaction		Feed[a]	Experimental conditions[b]
HDP	Presulfidation	Decaline, 66.6 vol% DMDS, 33.3 vol%	Hf = 6 liters $\cdot$ h^{-1} HCf = 1.2 cc $\cdot$ h^{-1} P = 1 bar T = 623 K
	Test	Decaline, 98 vol% DMDS, 2 vol% VOOEP, 5.10^{-4} M	Hf = 15 liters $\cdot$ h^{-1} HCf = 30 cc $\cdot$ h^{-1} P = 80 bar T = 573 K
HYD, HDS	Presulfidation	Heptane, 66.6 vol% DMDS, 33.3 vol%	Hf = 4.4 liters $\cdot$ h^{-1} HCf = 3 cc $\cdot$ h^{-1} P = 1 bar T = 623 K
	HYD	Heptane, 68 vol% DMDS, 2 vol% Toluene, 30 vol%	Hf = 6 liters $\cdot$ h^{-1} HCf = 1.2 cc $\cdot$ h^{-1} P = 60 bar T = 623 K
	HDS	Heptane, 90 vol% Thiophene, 10 vol%	Hf = 6 liters $\cdot$ h^{-1} HCf = 2 cc $\cdot$ h^{-1} P = 33 bar T = 573 K

[a] DMDS, dimethyldisulphide; VOOEP, vanadyloctaethylporphyrin.
[b] Hf, hydrogen flow rate; HCf, hydrocarbon flow rate; P, pressure; T, temperature.

consecutively on the sulfided catalysts according to the conditions reported in Table 1. Only steady-state activity results, including HDP of VOOEP, are reported.

Analyses and Characterizations

Chemical analysis. After the final sulfidation step, the samples were analyzed by The Service Central d'Analyse du CNRS (Vernaison, France) for determining the Fe, V, and S contents.

Nitrogen adsorption. Surface area determinations by nitrogen adsorption using BET theory were carried out in a Quantasorb Instrument on the air exposed solids.

X-ray diffraction. X-ray diffraction patterns were obtained with a Siemens D5000 diffractometer equipped with a Cu anode and a monochromator. Working voltage was set at 50 kV with an intensity of 35 mA.

X-ray photoelectron spectroscopy (XPS). XPS measurements were carried out in an AEI ES 200B spectrometer equipped with an Al anode working at 300W. Binding energies BE were calculated against the C1s level at 285 eV coming from *in situ* contamination. The atomic compositions of the examined samples, before and after tests, were determined from the integrated V3p, Fe3p, O1s, and S2p levels with a background linearly subtracted. Details for calculations are given in Ref. (25).

Mössbauer Spectroscopy (MS). ^{57}Fe Mössbauer spectra were recorded at room temperature in a triangular symmetric mode spectrometer. The data were computer fitted with lorentzian line shape. The adjusted parameters were the isomer shift (IS), the quadrupole splitting (QS), the hyperfine magnetic field (Hf) and the full width at half maximum (FWHM) of the lines. The results were expressed by the proportion of the areas of the different components contributing to the complete spectrum.

RESULTS

Texture, Bulk Composition, and Structure of the Sulfides

Table 2 reports the surface areas measured before catalytic tests and the atomic composition of the pure mixed sulfides. The specific surface areas vary between 5 and 57 $m^2 \cdot g^{-1}$, the larger being that of pure V sulfide. There is no appreciable variation in the mixed system (13 to 15 $m^2 \cdot g^{-1}$) and the values are very close to that of MoS_2 (18.4 $m^2 \cdot g^{-1}$) which has been prepared and tested for comparison. The correlation between the bulk chemical composition and the X-ray diffraction patterns has been extensively described and discussed previously (25). Here, we only report the main observations. The atomic composition of sample FeVS-0 which is not well crystallized is $V_{0.74}S$ and could correspond to the V_2S_3 or V_3S_4 structures, the latter being more probable considering the synthesis conditions. The pure iron sulfide FeVS-1.0 has the pyrrhotite structure and corresponds to the $Fe_{1-x}S$ class of samples with here $x = 0.15$. For the mixed Fe–V sulfides, there is a continuous evolution; in the iron-rich samples, some V ions replace Fe in the pyrrhotite structure, whereas in the V-rich samples, some Fe ions replace V in the V_3S_4 lattice. The two mechanical mixtures have both $Fe_{1-x}S$ and V_3S_4 phases.

Catalytic Performances

The catalytic performances are reported in Table 2. For thiophene HDS, obviously the pure V sulfide sample is about twice more active than pure MoS_2 when comparison deals with specific activity, i.e., in moles of thiophene converted per gram of catalyst per second. On the other hand, pure Fe sulfide is not active at all. The two mechanical mixtures (MM) have intermediate activity which values are proportional to the relative amount of V sulfide but

TABLE 2

Atomic Composition, Surface Area, and Catalytic Performances of the Fe–V Sulfides

Catalyst	%Fe (atomic)	Surface area ($m^2 \cdot g^{-1}$)	Bulk composition (atomic)	Thiophene HDS		Toluene HYD		Porphyrin HDP	
				(a)	(b)	(c)	(d)	(e)	(f)
FeVS-0	0	57.1	$V_{0.74}S$	12.54	2.39	9.16	1.60	2.30	4.02
FeVS-0.3	27	15.5	$Fe_{0.19}V_{0.51}S$	5.68	3.67	2.32	1.50	2.51	16.19
FeVS-0.6	63	14.5	$Fe_{0.46}V_{0.27}S$	1.04	0.72	0.14	0.10	—	—
FeVS-0.8	81	13.2	$Fe_{0.65}V_{0.15}S$	0.00	0.00	0.00	0.00	1.36	10.30
FeVS-1.0	100	5.0	$Fe_{0.85}S$	0.00	0.00	0.00	0.00	0.96	19.20
MM-0.2	24	—	—	9.71	—	4.90	—	—	—
MM-0.7	67	—	—	4.57	—	1.82	—	—	—
MoS_2	—	18.4	—	5.87	3.20	2.02	1.10	—	—

Note. (a) Thiophene HDS specific activity in $mol \cdot g^{-1} \cdot s^{-1} \times 10^7$. (b) Thiophene HDS intrinsic activity in $mol \cdot m^{-2} \cdot s^{-1} \times 10^8$. (c) Toluene HYD specific activity in $mol \cdot g^{-1} \cdot s^{-1} \times 10^7$. (d) Toluene HYD intrinsic activity in $mol \cdot m^{-2} \cdot s^{-1} \times 10^8$. (e) Vanadyl octaethyl porphyrin HDP specific activity in $mol \cdot g^{-1} \cdot s^{-1} \times 10^9$. (f) Vanadyl octaethyl porphyrin HDP intrinsic activity in $mol \cdot m^{-2} \cdot s^{-1} \times 10^{11}$.

all the mixed Fe–V sulfides are less active. However, when comparing intrinsic activities determined by the amount of converted thiophene per square meter of catalyst per second, a synergy is found for a Fe/(Fe + V) ratio of about 0.3.

Similar evolutions can be detected when examining the toluene HYD activity results. Here, pure V sulfide appears about four times more active than MoS_2 on the catalyst weight basis. The performance of pure Fe sulfide appears again very weak. The linear relationship between the two pure sulfides and the corresponding MM appears less correlated than the case of thiophene HDS; this could be indicative of some inhomogeneity in the mixtures. Nevertheless, the mixed sulfides have specific activity values far below the corresponding mechanical mixtures. However, on the catalyst surface area basis, there is a small synergy effect for toluene HYD at about 30% in Fe (atomic composition) by respect to the interpolated value (1.2×10^{-8} mol · m^{-2} · s^{-1}) between the pure sulfides.

Contrary to the above results, pure Fe sulfide exhibits a detectable activity for HDP of VOOEP: the specific activity (0.96×10^{-9} mol of converted VOOEP per gram of catalyst per second) is about the half of the one obtained with pure $V_{0.74}S$ (2.30×10^{-9} mol of converted VOOEP per gram of catalyst per second). For this reaction, a small synergy is already detected for 30% of Fe in the mixed Fe–V sulfides on the catalyst weight basis, whereas intrinsic activity evolution is much more complex as pure iron sulfide is the most active on the catalyst surface area basis.

Mössbauer Spectroscopy Characterization

The Mössbauer spectra of all the prepared samples have been recorded at room temperature before and after their use in HDS of thiophene. The spectra were computer fitted with magnetic contributions due to hyperfine field distributions combined with nonmagnetic subspectra. The results are shown in Figs. 1a and 1b. The left part of the figures shows the experimental (dots) and the fitted (continuous line) spectra. In the middle, the histograms represent the proportion (%) in terms of relative areas of the nonmagnetic features in the spectra, with the isomer shift (IS) on the x-axis and the corresponding quadrupole splitting reported above each vertical bar. On the right part, the histograms represent the distribution in terms of relative areas (%) of the subspectra corresponding to the different hyperfine magnetic fields (Hf) whose values are noted on the abscissa axis.

The main aspects to consider for comparing the spectra of Fig. 1 concern (i) the characteristic features of the samples before and after HDS tests and (ii) the effect of incorporating V into the sulfide structure. The fact that the Mössbauer spectra are very similar before and after the HDS reaction seems to indicate that the pure and

mixed sulfides do not evolve during the course of this reaction contrary to what has been observed during HDP of VOOEP without any sulfur compound added in the reaction mixture (27). In that case, the sulfides evolved to phases with less cationic vacancies or less sulfur in the NiAs structure. The noticeable difference in the spectra of Fig. 1a versus those of Fig. 1b concerns the middle histogram of sample FeVS-0.6 where there is a contribution which disappears after the HDS reaction. This contribution in the catalyst before test is most probably due to partial oxidation of the sulfide during handling the sample from the sulfidation reactor. As the samples are resulfided before tests and also because the tests are conducted under a sulfiding atmosphere (see Table 1), this oxide component has been eliminated. The second point to notice is the increase of the nonmagnetic contributions (nonmagnetically ordered) when the vanadium content increases (Fig. 2) at the expense of the magnetically ordered ones. At the same time, the latter presents an evolution of the hyperfine field distribution which indicates that the cationic environment of iron species is changing. For pure Fe sulfide, the Hf distribution is centered around approximately 300, 260, and 230 kG (Fig. 1a, top histogram), which corresponds to pyrrhotite. These three fields indicate presence of zero, one, or two cationic vacancies in the near environment of the iron ions. The increase of the Hf contribution at about 260 kG when the amount of V increases indicates that the proportion of one-vacancy sites increases unless vanadium is progressively occupying the vacancies. This information is in complete agreement with the X-ray diffraction results which have indicated that there are not two distinct phases when V is progressively incorporated to the Fe sulfide.

Surface Characterization

XPS has been used to characterize the catalysts freshly sulfided before use and after HYD–HDS tests. It shows that all the samples are very sensitive to oxidation during exposure to open air. Therefore, the results could be not absolutely informative about the catalysts under working conditions. In a previous paper (25), we have already shown that the iron surface proportion relative to the total metal content Fe + V as determined by the V3p and Fe3p peak intensities increases quite linearly with the bulk composition. This linear relationship is not modified within the limit of uncertainty when the samples have been tested in HYD–HDS reactions. The examined samples appear to have a Fe–V homogeneous repartition, even in the surface layers, in accordance with the other characterizations (XRD, MS) and the catalytic tests do not influence the metallic homogeneity.

The V2$p_{3/2}$ core level has components at 513.8, 516.6, and 517.3 eV assigned to vanadium sulfide like V_2S_3 (22), V_2O_5, and $VOSO_4$ (28) respectively. Similarly, the Fe2$p_{3/2}$ peak has
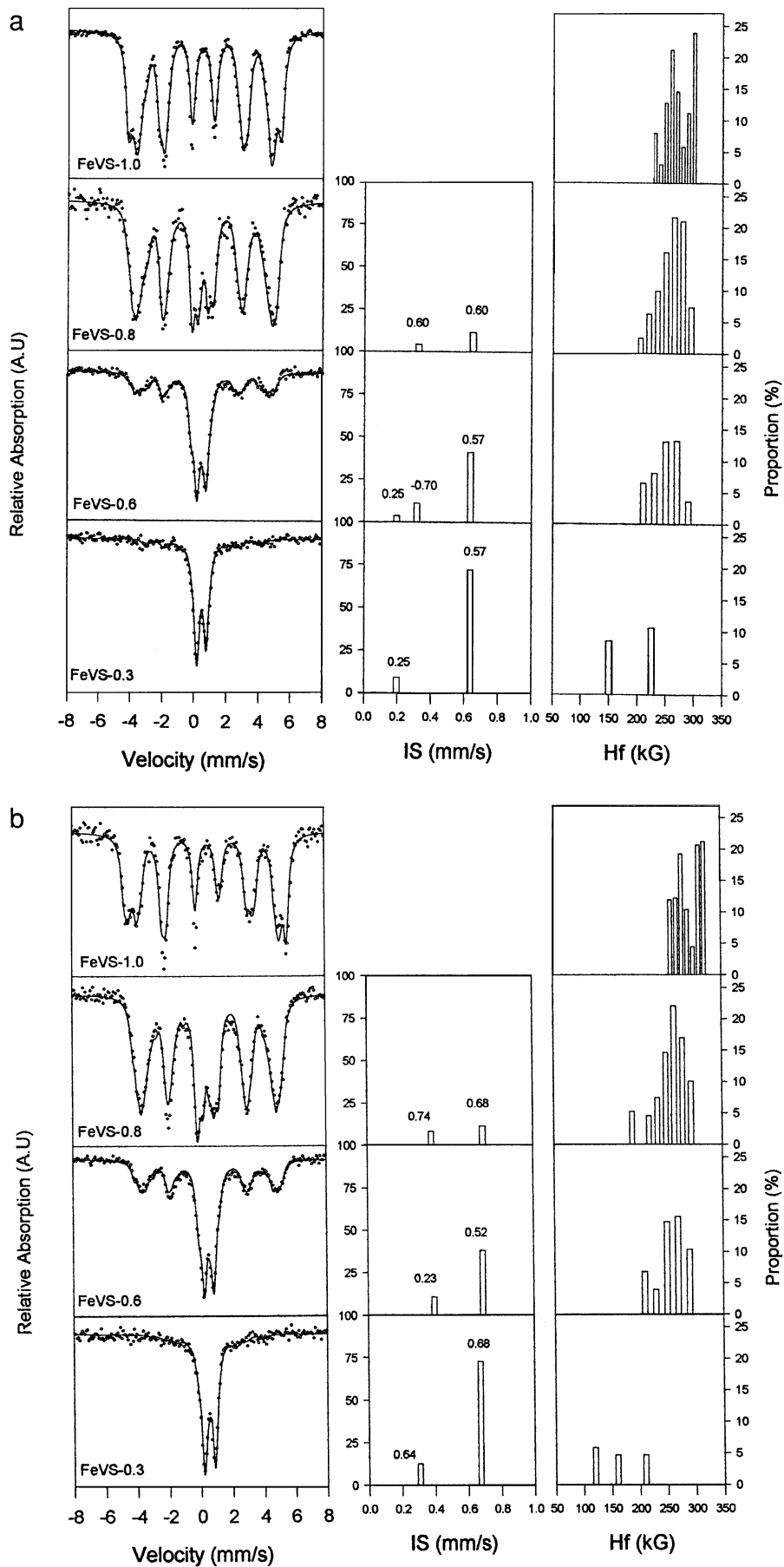
FIG. 1. (a) Mössbauer spectra and nonmagnetic, and magnetic contributions at room temperature before HYD−HDS reactions. (b) Mössbauer spectra and nonmagnetic and magnetic contributions at room temperature after HYD−HDS reactions.
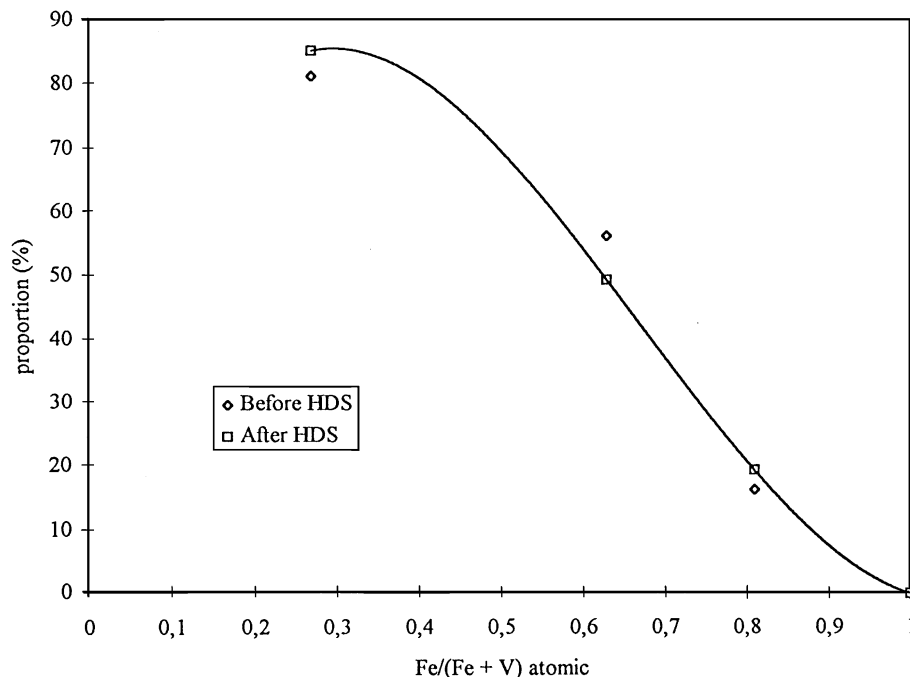
FIG. 2. Proportion (%) of nonmagnetic contribution as a function of the iron content in the mixed sulfides.

two apparent positions at 711.0 and at 708.0 eV. The former one is attributed to Fe^{3+} species, whereas the second component is due to iron in a sulfide structure. The repartition of the different species appears dependent on the sample composition. Moreover, the difference $\Delta[\Delta = BE\ (Fe2p_{3/2}$ in a Fe–S structure) $- BE\ (S2p)]$ can be used to discriminate the different iron sulfides by comparison with published data (29–33) and presence of pyrrhotite is confirmed. The $S2p$ peak position varies from 162.3 eV in FeVS-0 to 161.9 eV in FeVS-1.0. This corresponds to sulfidic species in V_2S_3 (25) and $Fe_{1-x}S$ (30–32), respectively. Presence of sulfate at $\sim$169 eV is evidenced on all the mixed samples, whereas it is not detected on the two pure sulfides. The $O1s$ peaks are always very broad (FWHM from 3.0 to 3.8 eV) and sometimes assymmetric with apparent components at $\sim$531 and 532.2 eV.

DISCUSSION AND CONCLUDING REMARKS

First, we want to address the point of whether our method for preparing the Fe–V sulfides gives truly mixed compounds or a mixture of separate phases of iron and vanadium sulfides. Even though X-ray diffraction data are not totally conclusive about this point because of a rather amorphous character of the mixed sulfides (25), the main lines detected along the series are characteristic of a NiAs structure. There is a continuous homogeneity between $Fe_{1-x}S$ (pyrrhotite, with here $x = 0.15$) to V_3S_4 (here $V_{0.74}S$). Moreover, the fact that XPS shows a good agreement between surface and bulk metallic concentration, either before or

after use, is indicative of the presence of mixed sulfides. The decisive argument is provided by the catalytic measurements on the mechanical mixtures which are totally different from that of the mixed sulfides of the same composition (Table 2). Finally, the uniform evolution of the proportions of two different electronic states of iron (one magnetic with a high spin state, the other one unsensitive to magnetic order, in probably a low spin state, Figs. 1 and 2) and the change in the Hf values of the individual iron species proves also that the mixed sulfides do not exhibit two separate phases.

Oxidation at room temperature, as revealed by XPS, is very informative about reactivity of the mixed Fe–V samples. Indeed, the surface atomic ratio O/(Fe + V) varies from 0.67 to 1.89 depending on the sample composition, the most sensitive samples being FeVS-0.6 and FeVS-0.8. However, oxidation appears to mainly occur at the uppermost surface layers of the pure and mixed sulfides as neither XRD data nor the Mössbauer spectra indicate formation of bulk oxides and/or sulfates. This surface oxidation provokes formation of oxide- or hydroxide-like phases such as V_2O_5, FeOOH, or hydrated Fe_2O_3. $VOSO_4$ is likely formed when the V species are dispersed in the mixed sulfides, whereas it is not detected on the bulk $V_{0.74}S$ sulfide.

Some arguments suggested in the introduction concerning the choice of iron sulfide as being a good candidate for developing interesting hydrotreating properties is rather disappointing as the present results show no activity in either thiophene HDS or toluene HYD. The nature of

the iron phase does not seem to play an important role as it is generally admitted that pyrite in the conditions of use (presence of large amounts of H_2) is progressively transformed into pyrrhotite-like phases (6–9), what we also obtain in this study. Only HDP of VOOEP is significantly affected by the presence of the $Fe_{0.85}S$ sample. We can now advance a tentative explanation about why clays show an increase in HDM conversion when vanadium is added and why there is a maximum in activity with V addition. Iron, initially present, is converted first to pyrrhotite (10) by the sulfiding atmosphere during the HDS reaction or during presulfidation of the clay. The formed pyrrhotite is active for HDM, confirming our results on HDP, and the deposited vanadium forms mixed Fe−V sulfides (20). These mixed sulfides are more active, according to the results of Table 2, and an increase of HDM activity is observed. The decrease of activity upon continuous V deposit is probably due to pore blocking of the clay texture.

On the other hand, regarding the synergy observed in intrinsic activity, it is known that comparing activities of catalysts with different surface areas, as it is our case, may be question of debate. For vanadium sulfide, Guillard (34) has shown that there is a linear correlation between specific activity for the hydrogenation of biphenyl and surface area. Therefore, we assume that the mixed Fe−V sulfides can be compared on the intrinsic activity basis. A synergy for HDS and HYD is observed for about 30% (atomic) of iron. The methods of characterization used in this work do not give any indication which could be proposed for an interpretation of this synergy effect. A suggestion would be to assign higher activity to an optimal dispersion (V dilution in the sulfide matrix by adding iron species) of the vanadium species, assuming they are active sites. Reactivity of the surface-exposed V species, evidenced by formation of vanadium oxide or vanadyl sulfate during air exposure, is also changing as a function of the mixed sulfide composition. Further work on supported Fe−V mixed sulfides could give new information about dispersion effects and also clarify the debate about synergy when samples of very different surface areas are used. Efforts which would permit to neglect any influence of undesirable oxidation effects on the catalyst performances will be examined as well.

ACKNOWLEDGMENTS

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