

Synergy between the CoMoS Phase and Supported or Unsupported Cobalt Sulfide. Existence of a Remote Control Effect

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Unsupported Co_9S_8 , MoS_2 , and CoMoS sulfides (prepared by the HSP method) as well as supported $\text{MoS}_2/\text{Al}_2\text{O}_3$ and CoS_x/C (prepared by impregnation) were used to prepare a series of binary mechanical mixtures of various compositions. A variety of physicochemical techniques (temperature programmed decomposition and sulfidation, both followed by subsequent TPO, XRD, TPR, microelectrophoresis, XPS and AEM) were used to study the samples, verify the formation of the "CoMoS phase" in the mixed CoMo sulfide and investigate the existence of interactions between the sulfides forming the mechanical mixtures. The catalytic activity of the supported and unsupported HSP sulfides as well as that of the mechanical mixtures was tested in the hydrodesulfurization of thiophene (HDS) and the hydrogenation of cyclohexene (HYD) at 573 K and 3 MPa. The mechanical mixtures exhibit a synergy in HDS and HYD. This shows that cobalt sulfide (supported or unsupported HSP) can promote the activity not only of molybdenum sulfide, but also of the unsupported HSP "CoMoS phase". In addition, XRD and AEM (performed before and after catalytic tests) were used to study the evolution of the unsupported "CoMoS phase" during the catalytic reaction. It was found that this phase is unstable; cobalt segregates from the CoMoS association to form Co_9S_8 , even after a relatively short period in the reactor. These results provide more evidence that the remote control mechanism plays a major role in the synergetic behavior of the CoMo hydrotreating catalysts.

Although hydrodesulfurization (HDS) is an old industrial process, the origin of the activity of the catalysts is still debated. In addition to molybdenum, the most common HDS catalysts contain cobalt, which acts as a promoter. The catalysts are supported (usually on alumina) and the metals are sulfided. The origin of the catalytic synergy between Mo and Co has been the object of more than 15 interpretations, which differ essentially with respect to the role of Co in increasing the hydrodesulfurization activity of molybdenum sulfide.^{1–5)} Of these 15 interpretations or theories, only a few are still considered as relevant. The debate tends to concentrate now on two of them. One attributes the activity to some structural association of Co with MoS_2 ; for convenience, it has become usual to refer to this association as "CoMoS phase". The other focuses on the existence of separate sulfides, namely MoS_2 and cobalt sulfides (usually Co_9S_8), and supposes that a **remote control** operates, controlling the coordination of surface molybdenum atoms.

The interpretation mentioning the "CoMoS" species was proposed about ten years ago by Topsøe et al.⁶⁾ It seems quite widely accepted. The authors attribute the HDS activity to some amorphous phase which would

associate Co, Mo, and S atoms (with Co contents up to $\text{Co}/(\text{Co}+\text{Mo}) < 0.3$). But many points remain obscure. These authors have proposed that the phase was characterized by various special signals^{7–11)} in addition to the originally mentioned special signal in Mössbauer emission spectroscopy (MES).

There is no doubt that the special MES signal exists. The catalysts which, when fresh, exhibit this signal possess a high catalytic activity. But the existence of direct and unequivocal links between that signal, formation of a "CoMoS" compound and catalytic activity faces several criticisms, and alternative explanations exist.

A first series of criticisms concern the physicochemical characteristics attributed to the "CoMoS phase". Pure cobalt sulfide deposited on carbon exhibits the same MES signal (same quadruple moment Q , same chemical shift I),^{12,13)} thus weakening the argument that the signal necessarily corresponds to a ternary "CoMoS" compound. The "CoMoS" signal results from a mathematical treatment of the MES spectra which is not exempt from pitfalls.¹⁴⁾ Actually more than one signal could be contained in the spectrum.¹⁵⁾ This casts some doubt on the linear relationship found between the intensity of the "CoMoS" signal and activity. A compli-

cating factor is the existence of two types of "CoMoS" called CoMoS I and CoMoS II, corresponding to a different correlation with activity, found by the authors of the "CoMoS" theory.¹⁶⁾ A second maximum of activity is sometime found for Co contents ($\text{Co}/(\text{Co}+\text{Mo})=0.33^{17)}$ or $\text{Co}/(\text{Co}+\text{Mo})=0.44$,^{18,19)} exceeding those claimed to correspond to maximum formation of "CoMoS".

The EXAFS technique could, in principle, prove the existence of a structural relation between Co and Mo in "CoMoS". Different authors have obtained results showing that Co is in a special coordination.^{19–25)} It is, however, much more difficult to prove the existence of a well-defined CoMo bond. This is not surprising, account taken of the complication of the deconvolution technique. Recent calculations seem to unveil signals corresponding to Co–S–Mo distance.^{26–28)} Ledoux et al.,²⁹⁾ using a special NMR technique for measuring the resonance of ^{57}Co , showed that only one cobalt site, labeled "octahedral rapid", possessed a structural relation with MoS_2 via a vacant site. But this cobalt seems to play no role in catalytic activity. Its function might be to stabilize MoS_2 .

The second objection against a direct role in catalysis of the species responsible of the MES signal is its low stability, which has been mentioned by several authors^{14,15,30–33)} and confirmed by the group who had put forward the "CoMoS" explanation.³⁴⁾ An experiment conducted in the hydrodesulfurization of a vacuum gas-oil in relatively mild conditions (625 K; $P=10$ MPa), with a catalyst of composition $\text{Co}/\text{Mo}=0.5$, showed that the special MES signal disappeared almost completely after 19 h.³⁵⁾

Summarizing, one could object to the supposed role of a "CoMoS phase" by saying that the results are also compatible with the existence of a special cobalt sulfide of a special structure, separated from MoS_2 ,^{5,13)} and that this species is not very stable, thus leaving unsolved the real origin of synergy.

The second interpretation is anterior to the "CoMoS" model. It rests on the observation that the maximum synergetic effect is always observed when MoS_2 and cobalt sulfides are detected: This is the case even when MoS_2 and Co_9S_8 are well crystallized, for example after a high temperature preparation.³⁶⁾ It was proposed by Hagenbach et al. that the synergy have its origin in the contact or vicinity between MoS_2 and cobalt sulfides.³⁷⁾ Simple mechanical mixtures do indeed exhibit a synergy.^{38,39)} The effect was interpreted by a remote control. In this hypothesis, cobalt sulfides CoS_x would dissociate molecular hydrogen to spill-over hydrogen H_{so} . This spill-over species would react with the surface of MoS_2 , thus resulting in the creation of catalytic sites.⁴⁰⁾ This theory qualitatively explains the most important observations concerning the MoS_2 – CoS_x mixtures, either supported or non supported^{41–44)} and, without forgetting the structural characteristic of the catalysts (including the supposed

"CoMoS" structure), also considers the fact that reaction conditions (including the presence of spill-over hydrogen) influence the coordination of surface atoms during catalysis.

The present work is aimed at contributing with new arguments to the debate opposing, on the other hand, the view that the ternary "CoMoS" compound is the active phase and, on the other hand, the remote control theory.

As a synergy is consistently observed when CoS_x is mixed with MoS_2 , it was interesting to investigate whether cobalt sulfides, as separate phase, could also activate the "CoMoS" species. In addition, supposing, as the above results suggest, that "CoMoS" is actually not structurally associating cobalt and molybdenum in a single phase (or with atomically dispersed Co combined structurally with the surface of MoS_2), it could be legitimate to raise the hypothesis that the segregated CoS_x would not bring about optimal activation and that additional Co_9S_8 could further increase activity. The original data of Topsøe et al.⁴⁵⁾ strongly suggested this conclusion: They found maximum activity when segregated CoS_x was detected.

A second reason for undertaking this work came from the objection sometimes raised against our results, namely the synergy observed when Co_9S_8 and MoS_2 are mixed together. This objection is the possible formation of a phase similar to "CoMoS", by mutual contamination of MoS_2 and CoS_x when these single phases are mixed. A contamination of MoS_2 by Co corresponding to the values announced for the synergy maximum ($\text{Co}/(\text{Co}+\text{Mo})\cong 0.2\text{--}0.5$) has never been observed in these mixtures, but it has been argued, in contradiction to the accepted views on the role of the "CoMoS" species in HDS, that a very small quantity of Co was sufficient. For that, we also performed another type of experiment, by mixing MoS_2 supported on alumina with CoS_x supported on carbon (CoS_x/C) (the choice of C as a support is dictated by the fact that CoS_x disperses easily on this support, whereas alumina either gives a poor dispersion—with conventional impregnation techniques—or reacts extensively to form cobalt pseudo-aluminates). As the majority of the metals in supported sulfides are located inside pores, contamination is practically impossible or, at least, cannot concern more than a very small proportion of the catalytic material. The existence of a synergy would give more strength to the idea of a cooperation via a mobile species. Quite logically, this mobile species would be H_{so} , which can be produced from H_2 on Co_9S_8 . The same phenomenon has been observed in the reduction of MoO_3 .⁴⁶⁾

For realizing these objectives, we used powders mixed gently as suspensions in *n*-pentane, and dried. The catalytic tests were carried out in conditions representative of the reaction in HDS, namely a pressure of 3 MPa, and temperature of 573 K. Hydrodesulfurization is always accompanied by some hydrogenation (HYD) of unsat-

urated hydrocarbons. We therefore used, as previously in the laboratory, a mixture of thiophene (for measuring the HDS activity) and cyclohexene (for HYD) in cyclohexane.

In two recent notes, we have shown that, indeed, physical mixtures of (i) "CoMoS" and Co_9S_8 ⁴⁷⁾ or (ii) $\text{MoS}_2/\text{Al}_2\text{O}_3$ and CoS_x/C ⁴⁸⁾ exhibited a synergy. The present publication presents new results and, in particular, a detailed characterization of the catalysts. By eliminating arguments directed against the conclusions of the two previous notes, it will give additional weight to the remote control interpretation. In addition, it will help discuss the surprising claim that cobalt sulfide deposited on carbon has an activity comparable to the best catalysts containing both Mo and Co.^{3,49)} As the "CoMoS phase" is a focal point of the debate, we shall use mechanical mixtures containing this phase. In the corresponding experiment, much care must be taken that the "CoMoS phase" is identical to that described by its discoverers. Much attention will be given to this demonstration and a substantial part of the work is devoted to the characterization of our CoMoS samples, without resorting to Mössbauer emission spectroscopy, which implies the use of radioactive ⁵⁷Co and makes such operations as the efficient mixing of powders (as described below) and the characterization of many properties, including catalytic activity, hazardous or very difficult.

Experimental

Preparation of Catalysts. Precursors. The precursors (oxi-sulfides) of the unsupported catalysts, namely pure sulfides of Mo and Co, and that of the "CoMoS" species (atomic ratio $r = \text{Co}/(\text{Co} + \text{Mo}) = 0.3$) have been prepared according to the so-called homogeneous sulfide precipitation method (HSP).³²⁾ The procedure has been reported previously.⁵⁰⁾ Briefly, this method consists of dissolving appropriate quantities of cobalt nitrate and ammonium heptamolybdate in distilled water; this solution is subsequently dropped slowly into a 0.54 M solution of $(\text{NH}_4)_2\text{S}$ at 343 K. The obtained slurry is then stirred for 2 h and evaporated in vacuum to dryness at 343 K. Particles of sizes between 200 and 400 μm were obtained by sieving. For convenience, we shall refer to these samples as HSP samples.

The oxidic forms of Co deposited on carbon (3 and 5% as element weight), and Mo on alumina (13% as element weight, corresponding to 20% MoS_2 by weight) were prepared by dry impregnation of carbon (RX3 EXTRA of Norit N.V, surface area 1250 $\text{m}^2 \text{g}^{-1}$) or alumina (Rhone Poulenc, 222 $\text{m}^2 \text{g}^{-1}$) with, respectively, a solution of cobalt nitrate or ammonium heptamolybdate. The preparation is described in detail elsewhere.⁴⁸⁾

Sulfides. The HSP samples (MoS_2 , Co_9S_8 , and CoMoS) and supported sulfides ($\text{MoS}_2/\text{Al}_2\text{O}_3$ and CoS_x/C) were obtained by treating 4 g of their precursors by argon (100 ml min^{-1}) at 373 K for 1 h, then switching to an $\text{H}_2\text{S}/\text{H}_2$ (15% H_2S) mixture (100 ml min^{-1}) and increasing the temperature at a rate of 3.3 K min^{-1} up to 673 K. The temperature was then maintained at this level for 4 h.

The supports used in the mechanical mixtures were treated in exactly the same way, so that their catalytic activity has the same meaning as that measured for the catalysts.

Mechanical Mixtures. Table 1 lists the mechanical mixtures (denoted by: phase 1+phase 2) and their compositions (expressed by the mass ratio $R_m = m_2/(m_1 + m_2)$), where m_1 and m_2 represent the amounts (in grams) of phase 1 and 2 respectively).

The mechanical mixtures were prepared by introducing the sulfides (2 g) in a flask containing *n*-pentane (50 ml). The flask was subjected to a moderate manual agitation for 15 min. Before their use, either for testing their catalytic activity or for characterization, *n*-pentane was removed by evaporation at atmospheric pressure and ambient temperature.

The pure catalysts were subjected to the same *n*-pentane treatment before test.

Physicochemical Characterization. Specific Surface Area. The specific surface areas of fresh and used sulfides (supported and HSP) were measured according to the B.E.T. method. The nitrogen adsorption at liquid nitrogen temperature was measured by gravimetry using a thermobalance (Setaram MTB 10-8).

Differential Thermal Analysis (DTA) under Controlled Atmosphere. Temperature programmed reactions of the dry (dried at 70 °C, 2.6 kPa, 2 h) precursors of the Mo, Co, and CoMoS sulfides were carried out in a home-made, all glass, atmospheric pressure DTA apparatus, adapted to the use of sulfur-containing substances. During the reaction, the temperature difference between the sample (400 mg, particle size 200–400 μm) and the reference (400 mg $\alpha\text{-Al}_2\text{O}_3$, Merck, particle size 200–400 μm) was measured by chromel–alumel thermocouples. Heating rate and gas flow were constant and equal to 10 K min^{-1} and 60 ml min^{-1} , respectively. The standard deviation of the reported temperature is ± 3 K.

Two experimental procedures were followed. In the first one, the thermal decomposition of the precursor was conducted under Ar. When the maximum temperature (823 K) was reached, the samples were cooled to 673 K and maintained at this temperature for 2 h. The samples were cooled down to room temperature and the temperature programmed oxidation (TPO) of the resulting solid was performed under identical conditions, using air as reacting atmosphere.

The second experimental procedure consisted of the temperature programmed sulfidation-reduction (TPS) of the precursor (reaction atmosphere: $\text{H}_2/\text{H}_2\text{S}$, 15% vol H_2S) followed by TPO, as above. All other experimental conditions were kept constant.

Temperature Programmed Reduction (TPR). The MoS_2 , Co_9S_8 , and CoMoS HSP sulfides as well as the mechanical mixture $\text{Co}_9\text{S}_8 + \text{MoS}_2$ ($R_m = 0.4$) were studied, in situ, by TPR in a home made equipment described elsewhere.⁵¹⁾ A quantity (200 mg) of the sulfided sample was reconditioned in situ by an $\text{H}_2\text{S}/\text{H}_2$ (15% vol H_2S) mixture (100 ml min^{-1}) at 673 K for 2 h. In the case of the $\text{Co}_9\text{S}_8 + \text{MoS}_2$ mechanical mixture, the reconditioning took place at 573 K for 2 h (the molybdenum and cobalt sulfides had already been sulfided separately at 673 K for 2 h, before mixing). After reconditioning, the sample was cooled down to room temperature under an Ar flow (100 ml min^{-1}).

Table 1. List of the Mechanical Mixtures Used, Their Composition (Expressed by the Mass Ratio R_m) and the Values of the Maximum Synergy Intensity ($I_{\text{syn}}\text{max}$) Observed in the HDS and HYD Reactions

Mechanical mixture	Mass ratio : R_m	$(I_{\text{syn}})_{\text{max}}^{\text{a)}$	
		HDS	HYD
CoMoS+Co ₉ S ₈	0.0, 0.25, 0.5, 0.75, 1.0	35.4 (0.5)	0.0 (—)
CoMoS+Co(3%)S _x /C	0.0, 0.25, 0.5, 0.80, 1.0	33.4 (0.5)	21.6 (0.25)
MoS ₂ +Co ₉ S ₈	0.0, 0.2, 0.4, 0.5, 0.75, 1.0	24.8 (0.4)	26.7 (0.25)
MoS ₂ /Al ₂ O ₃ +Co(3%)S _x /C	0.0, 0.25, 0.5, 0.75, 1.0	26.0 (0.5)	22.0 (0.25)
MoS ₂ /Al ₂ O ₃ +C	0.0, 0.5, 1.0	0.0 (—)	0.0 (—)
MoS ₂ +CoMoS	0.0, 0.25, 0.5, 0.75, 1.0	0.0 (—)	0.0 (—)

a) The number in parentheses indicates the composition R_m of the mixture for which the maximum synergy was obtained.

Then, the Ar stream was replaced by a flow (40 ml min⁻¹) of H₂ (ultra pure 99.9999%, Air Liquide) and the TPR measurement was performed in the temperature range 303–783 K. The heating rate was kept constant (10 K min⁻¹) and the temperature was measured with a chrome-thermocouple placed in a well in the catalyst bed. A TCD detector (Intersmat, IGC 120 ML) was used to obtain the TPR patterns.

Electrophoretic Migration Measurements. The MoS₂, Co₉S₈, and “CoMoS” HSP sulfides as well as the Co₉S₈+MoS₂ ($R_m=0.5$) mechanical mixture were studied by microelectrophoresis. Their isoelectric points (IEP), as defined by Parks,⁵²⁾ were obtained by measuring the electrophoretic migration rate in a Laser-Zee Meter model 500 (Pen-Kem-In). The construction of the measurement cell permitted the exclusion of air, thus avoiding the presence of oxygen during the measurements. All experiments were carried out at ambient temperature using suspensions containing 20 mg of the sulfided samples. The particles (25 μm; obtained by sieving) were dispersed ultrasonically (10 min) in 500 ml of a 10⁻³ M KCl solution. The pH values were adjusted with a 10⁻¹ M HCl solution. The IEP of the samples were determined from the electrophoretic migration curves with an accuracy of 0.1 pH units.

Analytical Electron Microscopy (AEM). Measurements were performed on a JEOL Temscan 100 CX electron microscope fitted with a KEVEX 5100 C energy dispersive spectrometer. The accelerating voltage was 100 kV. Samples were studied by both conventional (CTEM) and scanning electron microscopy (STEM). The KEVEX instrument was used with the microscope operating in the STEM mode for electron stimulated X-ray emission spectroscopy. The finely focused electron beam in STEM allowed the analysis of the elemental composition of local points on samples (with a resolution of about 20 nm).

Three samples were studied: the Co₉S₈ and CoMoS HSP sulfides, and “CoMoS” used in HDS reaction (573 K, 3 MPa, 12 h). Before the introduction into the microscope, all samples were stored in *n*-pentane to avoid exposure to air. Particles were ultrasonically dispersed in *n*-pentane, and a drop of the suspension was deposited on standard copper grids covered by a carbon film.

X-Ray Diffraction (XRD). The XRD spectra were obtained with a Kristalloflex 805 diffractometer (Siemens) equipment with a highly sensitive detector (Siemens D-500), using Cu *Kα*. Before XRD analysis, the catalysts, fresh or

used in HDS reaction (573 K, 3 MPa, 12 h), were stored in *n*-pentane.

X-Ray Photoelectron Spectroscopy (XPS). The XPS analysis was performed at room temperature with an SSX-100 model 206 Surface Science Instruments (SSI) photoelectron spectrometer, interfaced to a Hewlett Packard 9000/310 computer. The residual pressure in the spectrometer was in the range 1.3 to 6.5×10⁻⁷ Pa. An Al anode (energy of the Al *Kα* monochromatic line 1486.6 eV), powered at 10 keV and 20 mA, was used for the X-ray production. The binding energy scale of the spectrometer was calibrated with the Au4f_{7/2} line (binding energy 83.98 eV). The analyzer energy and spot size were, respectively, 50 eV and 1.4 mm². These conditions give an FWHM on Au4f_{7/2} of 1 eV. The positive charge developed on the samples (insulators), due to the photoejection process, was compensated by a charge neutralizer (a flood gun) whose energy was adjusted at 6 eV (50 μA). The binding energies were calculated with respect to the C1s peak (C–C, C–H) set at 284.6 eV. The intensities were estimated by calculating the integral of each peak after “S-shaped” background subtraction.⁵³⁾ Atomic concentration ratios were calculated by correcting the intensity ratios with the theoretical sensitivity factors based on Scofield⁵⁴⁾ cross sections (the transmission function of the spectrometer was assumed to be independent of kinetic energy (E_k); the electron mean free paths (IMFP) were taken to vary as (E_k)^{0.7}). Decomposition of peaks was done with the best fitting routine of the SSI instrument.

We used XPS to study the Co₉S₈ sulfide, the Co(5%)/C catalyst (in both precursor, oxidic, and sulfided forms) and the carbon support sulfided under the same conditions as the unsupported and supported cobalt sulfide.

The precursor of Co(5%)/C was introduced into the spectrometer without any special precautions. The other samples were sulfided (673 K for 4 h) in a special reactor which could be isolated from the sulfidation panel and transferred into a glove box connected to the spectrometer. There, under a dry N₂ atmosphere, the reactor was opened and the sample was mounted on the specimen holder, by means of double-sided adhesive tape, and transferred into the spectrometer. This procedure prevents the contact of the sulfides with air, thus avoiding surface oxidation.

Catalytic Activity Measurements. The activity measurements were performed in a stainless steel automatic high pressure “Catatest” apparatus (Géomécanique), work-

ing in the continuous flow regime. The reactant was a mixture of cyclohexane (70%wt) and cyclohexene (29.5%wt) to which 5000 ppm of thiophene was added. The H_2 (gas N.T.P)/hydrocarbon (liquid) ratio was 600. For all catalysts and mechanical mixtures, the catalytic activity of 2 g of catalyst was measured at 573 K under a pressure of 3 MPa. The sulfided samples were transferred into the reactor where they were resulfided in situ at 573 °C and 1.5 MPa for 1 h by a mixture of H_2S (15%vol)/ H_2 (20 $dm^3 h^{-1}$). The liquid hourly space velocities (LHSV) were 34 h^{-1} for MoS_2 , Co_9S_8 , and $CoMoS$, and 20 h^{-1} for CoS_x/C and MoS_2/Al_2O_3 . For the mechanical mixtures ($CoMoS+CoS_x/C$) and (MoS_2/Al_2O_3+C), the liquid hourly space velocities were kept equal to 30 h^{-1} by adding glass balls if necessary (for compensation for a slight change of apparent density). For the present measurements, where the objective was to qualitatively detect cooperation effects, it suffices to take the percent conversion of thiophene (HDS) and percent hydrogenation of cyclohexene (HYD) as approximate measures of the catalytic activity. This corresponds to assuming, as a first approximation, that the reactions are zero order. Conversions were measured at the steady-state conditions after 10–12 hours of reactions.

The synergy intensity (I_{syn}) observed for catalyst of mass ratio R_m , is expressed by:

$$I_{syn} = X_{12} - (X_1 + X_2)$$

$$X_{12} = \% \text{ conversion of the mechanical mixture } (R_m)$$

$$X_1 + X_2 = \text{addition of theoretical conversion due to the quantities of phase 1 and phase 2 contained in the mixture } R_m, \text{ assuming zero order kinetics.}$$

Results

Specific Surface Areas. BET surface areas of fresh and used catalysts are given in Table 2. Surface areas always decrease during catalytic testing, especially in the case of the MoS_2 .

DTA Experiments. The DTA patterns obtained during the thermal decomposition under Ar and the subsequent TPO of the precursors of the Mo, Co, and $CoMoS$ sulfides, as well as those obtained during TPS of these precursors (and the subsequent TPO) were all similar to those reported in literature for MoS_2 , Co_9S_8 , and “ $CoMoS$ species”.^{33,55–66}

TPR. The TPR diagrams of MoS_2 , Co_9S_8 , and $CoMoS$, as well as that of the $Co_9S_8+MoS_2$ ($R_m=0.4$) mechanical mixture, are presented in Fig. 1. In agreement

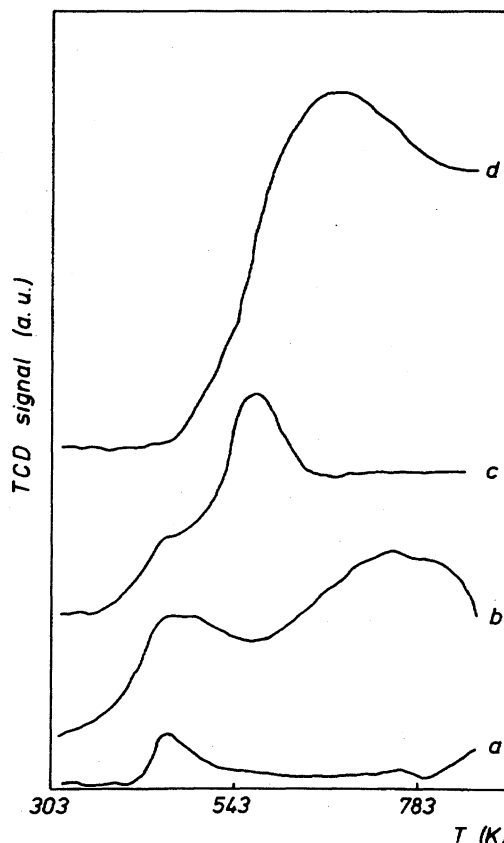


Fig. 1. TPR diagrams of ; a: Co_9S_8 , b: MoS_2 , c: $Co_9S_8+MoS_2$ mechanical mixture ($R_m=0.4$), and d: $CoMoS$ sulfide.

with literature, Co_9S_8 presents only one peak at 450 K, assigned to weakly bound sulfur species adsorbed on the catalyst.^{66–69} The increase of the signal observed at about 730 K correspond to the release of H_2S due to the decomposition of Co_9S_8 .⁷⁰

The TPR curve of MoS_2 shows, in addition to the first peak (assigned to weakly bound sulfur species), a second broad peak in the region above 550 K. This peak corresponds to the partial reduction of MoS_2 crystallites.¹⁷

The TPR diagram of $CoMoS$ exhibits a broad, very intense, peak starting at about 423 K with a maximum situated in the range 643–683 K. Compared to the unpromoted sample, $CoMoS$ releases a much higher quantity of sulfur in the temperature range above 500 K and the maximum is situated at lower temperature. This behavior has also been reported by Breyse et al.⁶⁶

The TPR pattern of the $Co_9S_8+MoS_2$ mechanical mixture ($R_m=0.4$) is composed of a peak at 573 K with a shoulder at 453 K. The former is due to the reduction of MoS_2 crystallites, whereas the latter corresponds to the weakly bound sulfur species. Compared to the TPR diagram of the unpromoted MoS_2 sulfide, the reduction of the molybdenum sulfide in the mixture occurs at a significantly lower temperature than pure MoS_2 . Thus, the presence of the promoter in the mixture results in an

Table 2. BET Surface Areas of Fresh (S_0) and Used (S_1) Catalysts

Catalyst	S_0	S_1
MoS_2	51.8	29.0
$CoMoS$	22.1	17.2
Co_9S_8	23.4	21.4
MoS_2/Al_2O_3	202.6	181.5
$Co(3\%)S_x/C$	1119.0	972.9
$Co(5\%)S_x/C$	994.2	769.0

increase of the MoS_2 reactivity towards hydrogen. The explanation of this effect lays very likely in the action of spill-over hydrogen species. As proposed by Delmon et al.,⁴⁰⁾ these species created on Co_9S_8 are transferred by surface diffusion on the MoS_2 surface and facilitate the reduction on this phase.

Electrophoretic Migration Measurements.

The electrophoretic migration velocity curves of the MoS_2 , Co_9S_8 , and CoMoS sulfides are presented in Fig. 2a. The IEP (more precisely: pH value where the electrophoretic migration velocity is zero) of the MoS_2 , Co_9S_8 , and CoMoS were found to be 3.0, 2.0, and 1.5, respectively. These values are in good agreement with those reported in the literature for similar preparations.^{50,71)}

The electrophoretic migration velocity curve of the $\text{MoS}_2 + \text{Co}_9\text{S}_8$ mechanical mixture ($R_m=0.5$) is shown

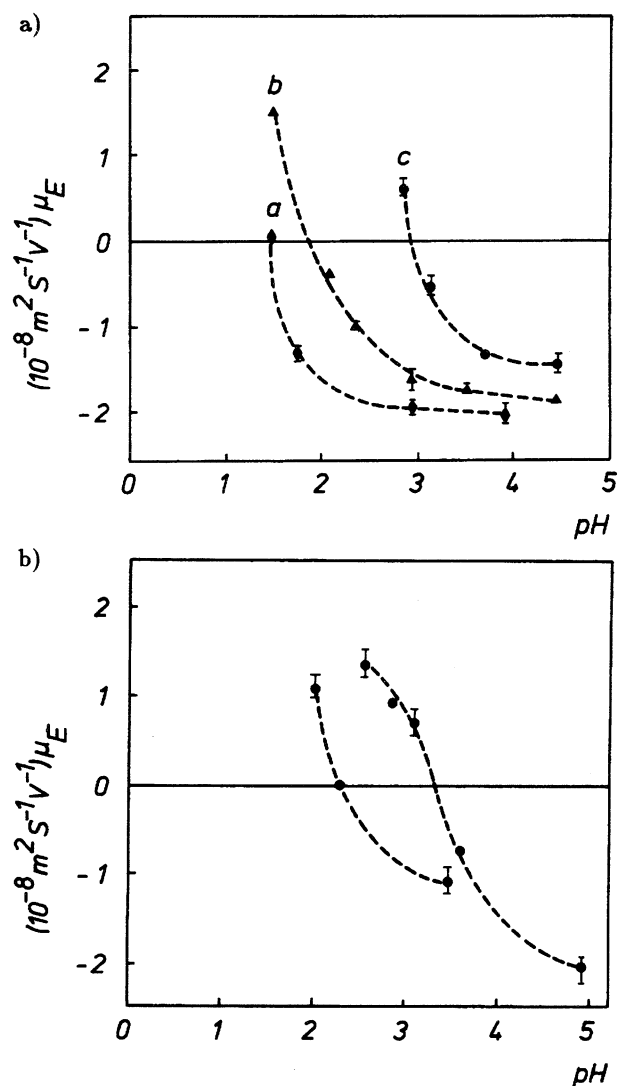


Fig. 2. Electrophoretic migration rate (μ_E) vs. pH curves of a) a: CoMoS, b: Co_9S_8 , and c: MoS_2 sulfides and b) of the mechanical mixture $\text{Co}_9\text{S}_8 + \text{MoS}_2$ ($R_m=0.5$).

in Fig. 2b. Contrary to the CoMoS sulfide, where only one family of particles was observed, two families of particles are now detected, with IEP values of 3.3 and 2.2, close to those assigned to the separate MoS_2 and Co_9S_8 phases forming the mixture.

AEM. Three typical micrographs of CoMoS fresh,

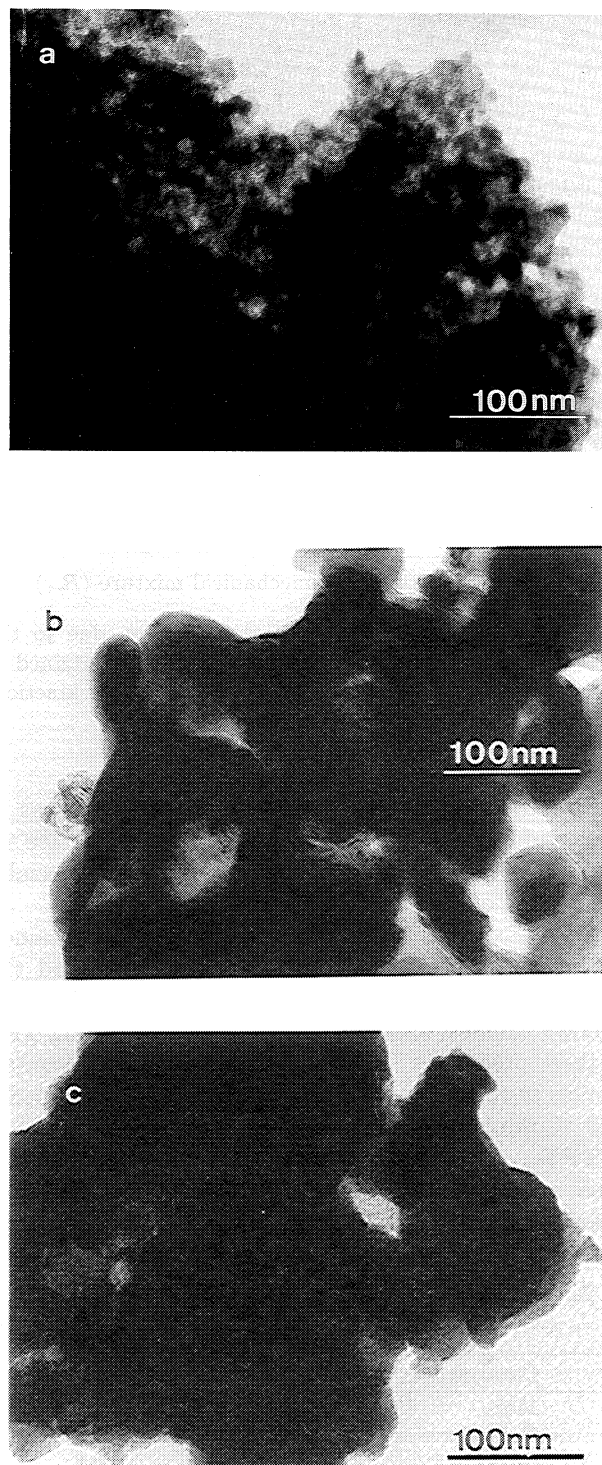


Fig. 3. Typical CTEM micrographs of; a: CoMoS fresh, b: CoMoS used in the catalytic reaction (573 K, 3MPa, 12 h) and c: Co_9S_8 .

CoMoS used, and Co_9S_8 , taken in the CTEM mode, are presented in Fig. 3. The fresh CoMoS HSP sulfide has the shredded rag appearance mentioned by Topsøe.²⁾ After catalytic test, it takes a completely different appearance, and looks very much like pure Co_9S_8 .

The X-ray emission spectra (in the STEM mode) of the fresh and used catalysts were taken. The Co/Mo ratios of the fresh CoMoS sulfide (Co/Mo=1–2), were fairly reproducible from point to point (we recall that the resolution is about 20 nm), as well as from grid to grid, indicating that Co and Mo were always present together and in the same proportion at all locations. No particle with only one element was detected. The situation concerning the **used** CoMoS was completely different. The Co/Mo intensity ratio varied considerably from point to point (Co/Mo=0.8– ∞), demonstrating the presence of particles enriched either in Mo or Co. Many particles composed only of Co were detected and their shape and appearance (CTEM) are similar to those observed in the pure Co_9S_8 sample.

XRD. The XRD patterns of the Co_9S_8 , MoS_2 , and CoMoS sulfides, as well as that of the used CoMoS, are presented in Fig. 4. The XRD pattern of Co_9S_8 (Fig. 4a) exhibits strong and narrow (111), (220), (311), (222), (400), (420), (511), (440), (523), (644) reflections, indicating a sample consisting of a well crystallized Co_9S_8 . The MoS_2 sulfide (Fig. 4b) exhibited a typical XRD pattern for a poorly crystallized MoS_2 , similar to that reported by Chianelli et al.⁷²⁾ In accordance with Candia et al.,³²⁾ the fresh CoMoS sulfide gives an XRD pattern (Fig. 4c) similar to that of the unpromoted sulfide, indicating the presence of a MoS_2 -like phase. After catalytic reaction, however, the used CoMoS sulfide (Fig. 4d) clearly exhibits (in addition to the broad reflections characteristic of the MoS_2 and MoS_2 -like phase) the reflections of Co_9S_8 (311), (222), (511), and (440)). This demonstrates that during the

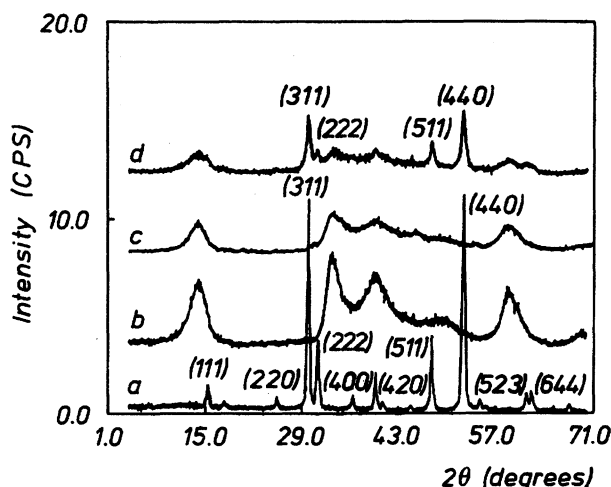


Fig. 4. XRD patterns of; a: Co_9S_8 , b: MoS_2 , c: CoMoS fresh, and d: CoMoS used in the HDS reaction (573 K, 3 MPa, 12 h).

HDS reaction (performed under industrial-like, but relatively mild conditions), Co segregates from the “CoMoS phase” and forms well crystallized Co_9S_8 sulfide.

XPS. The X-ray photoelectron spectra of the Co2p photoelectrons of the fresh unsupported CoMoS sulfide are presented in Fig. 5a. For comparison purpose the spectrum of a sulfided industrial CoMo/ γ - Al_2O_3 catalyst (Procatalyse HR306) has also been included in the same figure (Fig. 5b). Both the morphology of the spectra and the binding energies are the same for these two samples.

In the case of the oxidic Co(5%)/C precursor the spectrum (Fig. 5c) is composed of the two main lines at 781.4 and 797.1 eV, accompanied by the shake-up satellite lines shifted 6 eV towards higher binding energies. The atomic ratio Co/C was found equal to 0.05.

The $\text{Co}2p_{3/2}$ and $\text{Co}2p_{1/2}$ binding energy values of the carbon supported cobalt sulfide (Fig. 5d) were found to be equal, to 778.4 and 793.4 eV, respectively, corresponding to a spin-orbit splitting equal to 15 eV. These values are, within experimental error, identical to those found for unsupported Co_9S_8 (Fig. 5e). The Co/C atomic ratio calculated for the Co(5%) S_x /C sample was equal to 0.01.

Only S^{2-} ions (BE $\text{S}2p=162.4$ eV) were formed in the Co_9S_8 sample. Although cobalt sulfides are very

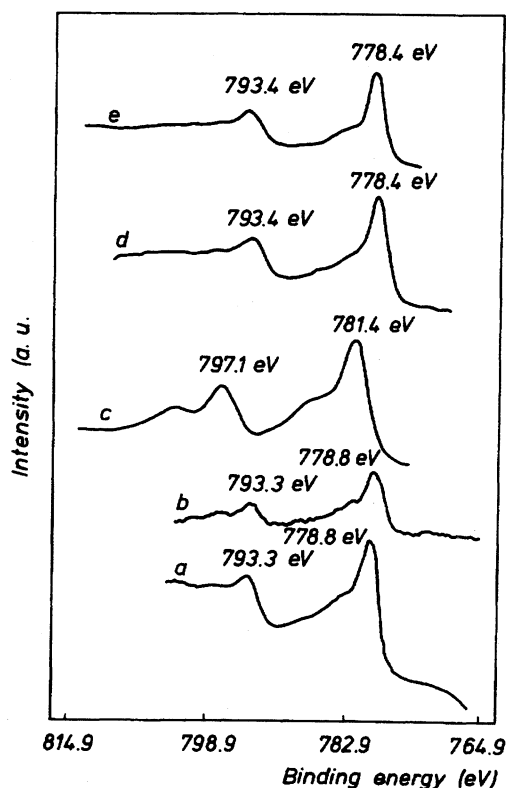


Fig. 5. XPS spectra of the Co2p photoelectrons; a: fresh CoMoS sulfide, b: sulfided CoMo/ γ - Al_2O_3 , c: Co(5%)/C precursor, d: sulfided Co(5%) S_x /C, and e: Co_9S_8 .

reactive towards oxygen, the absence of any XPS detectable quantity of sulfate in the case of the Co_9S_8 sample demonstrate the efficiency of the procedure followed for protecting the samples from exposure to atmospheric oxygen during their introduction into the spectrometer. This implies that sulfur species at a high oxidation state (detected in both carbon support and carbon supported cobalt sulfide) are really present on the carbon surface. This also justifies our choice to use only the S2p peak assigned to S^{2-} to calculate the S/Co atomic ratio. In the case of the carbon supported cobalt sulfide, in addition to S^{2-} ions (BE S2p=162.7 eV), elemental sulfur S^0 (BE S2p=165.2 eV) and sulfur species in a higher oxidation state, probably S^{6+} , (BE S2p=167.8 eV) were also detected. Only elemental sulfur and the higher oxidation sulfur species were found in the sulfided carbon support. The atomic ratios S/Co were found to be equal to 1.09 and 1.3, respectively, for the unsupported and carbon supported cobalt sulfides.

The presence of elemental sulfur (produced during sulfidation) on the carbon and the carbon supported cobalt sulfide is not surprising. In fact, it is known that microporous materials, and especially microporous carbons, can efficiently catalyze the oxidation of H_2S into elemental sulfur.^{73,74} In addition, carbons can retain important amounts of the elemental sulfur produced in the adsorbed state. Steinjns et al.⁷⁴ have reported that 1 g of an activated charcoal, having a micropore volume of $0.45 \text{ cm}^3 \text{ g}^{-1}$, can adsorb as much as 0.25 g of sulfur even at 623 K (our carbon support has a micropore volume of $0.5 \text{ cm}^3 \text{ g}^{-1}$).

Catalytic Activity Measurements. The HDS activities (expressed as $10^{-6} \text{ mol g}^{-1} \text{ s}^{-1}$) measured for the $\text{MoS}_2/\text{Al}_2\text{O}_3$, $\text{Co}(3\%)\text{S}_x/\text{C}$, and $\text{Co}(5\%)\text{S}_x/\text{C}$ catalysts were found equal to 1.64, 1.32, and 2.2, respectively.

The results of the catalytic activity measurements of the mechanical mixtures $\text{MoS}_2 + \text{Co}_9\text{S}_8$, $\text{MoS}_2/\text{Al}_2\text{O}_3 + \text{Co}(3\%)\text{S}_x/\text{C}$, $\text{CoMoS} + \text{Co}_9\text{S}_8$, and $\text{CoMoS} + \text{Co}(3\%)\text{S}_x/\text{C}$, are reported in Figs. 6, 7, 8, and 9, respectively. These mechanical mixtures exhibited a synergy in both HDS and HYD reactions, with the exception of the $\text{CoMoS} + \text{Co}_9\text{S}_8$ mechanical mixture where no significant synergy was observed for the HYD reaction.

The values of the maximum synergy intensity $(I_{\text{syn}})_{\text{max}}$ observed for each mechanical mixture in HDS and HYD reactions are summarized in Table 1. The maximum promoting effect for the HDS reaction was observed in the mechanical mixtures consisting of CoMoS and Co_9S_8 (either unsupported or carbon supported). Indeed $(I_{\text{syn}})_{\text{max}}$ values of these mixtures are 1.5 time higher than those obtained with the mechanical mixtures of MoS_2 and Co_9S_8 (supported or unsupported).

In addition, control measurements were performed with the $\text{CoMoS} + \text{MoS}_2$ and $\text{MoS}_2/\text{Al}_2\text{O}_3 + \text{C}$ mechanical mixtures to investigate whether there was, respec-

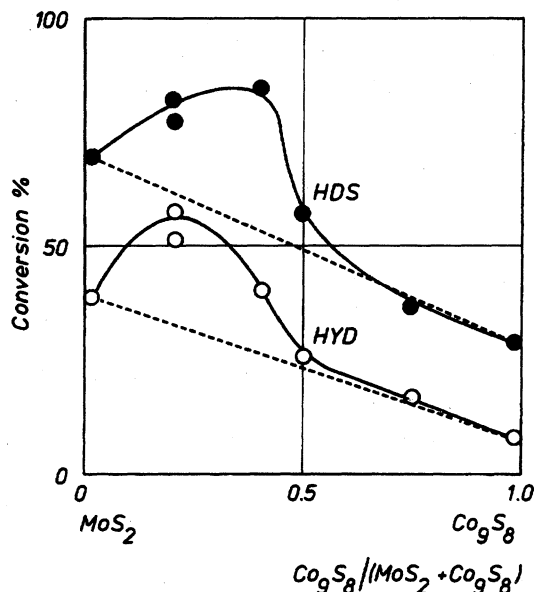


Fig. 6. Activity of the $\text{Co}_9\text{S}_8 + \text{MoS}_2$ mechanical mixtures in HDS and HYD reactions.

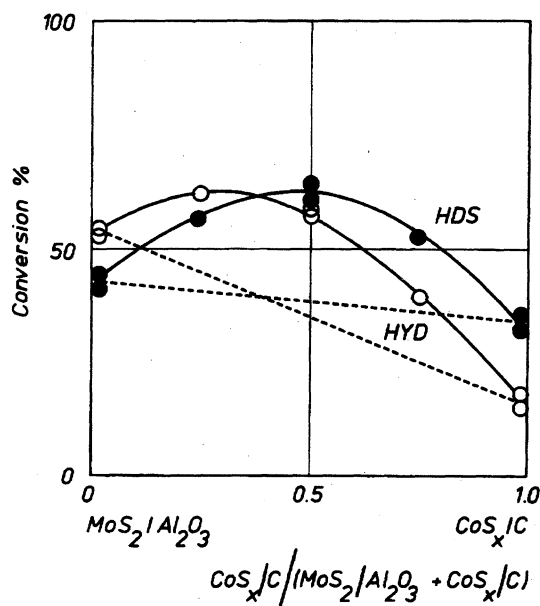


Fig. 7. Activity of the $\text{Co}(3\%)\text{S}_x/\text{C} + \text{MoS}_2/\text{Al}_2\text{O}_3$ mechanical mixtures in HDS and HYD reactions.

tively, an influence of the carbon support or a promoting effect of the CoMoS phase on the MoS_2 sulfide. In both cases, no synergy was observed in the HDS or in the HYD reactions.

Discussion

Three main topics will be discussed. First, we will present the arguments, based on the information provided by the various characterization techniques, proving that our mixed CoMo sulfides consist of the "CoMoS species" as described in literature. In addition, the physicochemical characteristics of the other catalysts studied will also be discussed. The second part of

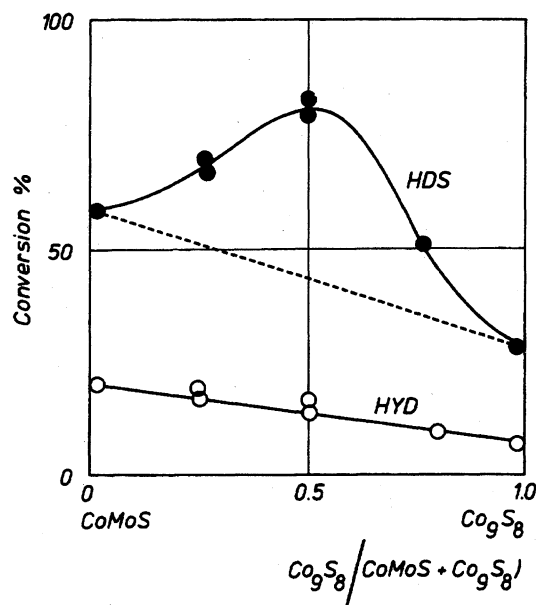


Fig. 8. Activity of the CoMoS + Co₉S₈ mechanical mixtures in HDS and HYD reactions.

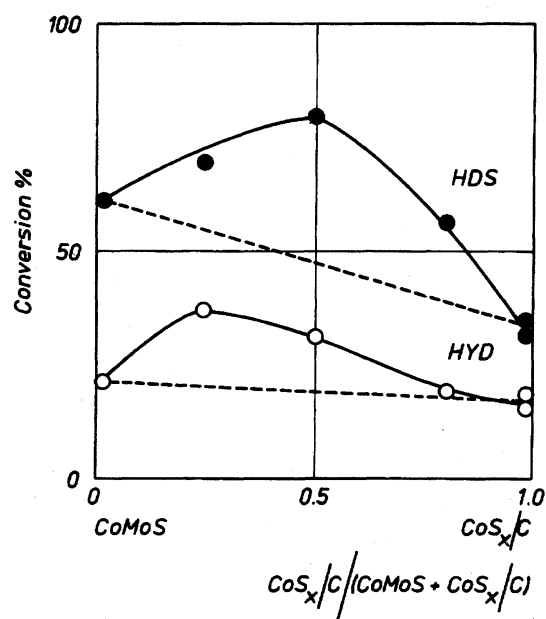


Fig. 9. Activity of the CoMoS + Co(3%)S_x/C mechanical mixtures in HDS and HYD reactions.

the discussion will be devoted to the evolution of the CoMoS phase during the catalytic reaction. Finally, the third part will deal with the catalytic activity of the various mechanical mixtures studied and with the implications that these results seem to have on the validity of the two models mentioned in the introduction which have been proposed to explain catalytic synergy in hydrotreating catalysts.

Physicochemical Characterization. HSP Sulfides. Essentially, our HSP sulfided samples possess the characteristics mentioned in literature.

DTA of the thermal decomposition under Ar and of

TPS (both followed by subsequent TPO), IEP measurements, TPR, and XRD were employed to characterize the MoS₂, Co₉S₈, and CoMoS precursors and the sulfides they produced. The DTA, TPR, and XRD patterns of the MoS₂ and Co₉S₈ sulfides, as well as their measured IEP, were similar to those reported in literature. But the main objective of the physicochemical characterization was to verify the formation of the "CoMoS species" in our HSP CoMoS sulfide.

A first evidence for the formation of "CoMoS" species in our CoMoS sulfide comes from the DTA patterns of the decomposition, TPS and TPO reactions which were identical to those reported in literature. One should also notice that for all temperature programmed reactions studied, both the precursor of CoMoS and CoMoS itself gave patterns which were quite different from those corresponding to the simple sulfides (MoS₂ and Co₉S₈). In addition, during electrophoretic migration measurements, only one family of particles was detected indicating the presence of only one type of particles. These results reflect the close interaction which exists between Mo, Co, and S in the "CoMoS species".

The IEP value of our HSP CoMoS is in excellent agreement with the result of Llambias et al.⁷¹⁾ and Göbölös et al.⁵⁰⁾ who also found a value of 1.5 for the "CoMoS species". This is the proof we wanted: Our "CoMoS species" corresponds exactly to the species described in literature.

Finally the results of other physicochemical techniques used were also compatible with the presence of the "CoMoS species". The XRD spectrum of the HSP CoMoS agreed perfectly with the one reported by Candia et al.³²⁾ for the "CoMoS species". CTEM micrographs of the fresh HSP CoMoS revealed the "shredded rag" homogeneous structure. The X-ray emission spectrum was found to be reproducible from point to point, indicating a good interdispersion of Mo and Co and no noticeable composition fluctuations of the Co/Mo composition ratio at the 20 nm scale was observed, showing the narrow association of Co and Mo described for the "CoMoS species".

MoS₂ + Co₉S₈ Mechanical Mixture. The study of this mechanical mixture by electrophoretic migration rate measurements demonstrated its biphasic character. Two families of particles were observed with IEP's equal to 2.2 and 3.0, assigned to Co₉S₈ and MoS₂ respectively. The same experiments exclude the possibility that during the preparation of the mechanical mixture a contamination of MoS₂ by the cobalt form Co₉S₈ may occur leading to the formation of some "CoMoS" association. Indeed MoS₂ particles partially covered by "CoMoS" should have an IEP value lying between the IEP values of MoS₂ and "CoMoS" (namely between 3.0 and 1.5). Instead, we found exactly the same value as for pure MoS₂ particles.

Another important feature to discuss is the behavior of this mixture during TPR. The presence of Co₉S₈ had

a dramatic influence on the reactivity of MoS₂ towards hydrogen, as evidenced by the considerable lowering of the temperature corresponding to the reduction of the MoS₂ crystallites, as compared with pure Mo₉S₈. The hydrogen spill-over species emitted from Co₉S₈ to the MoS₂ surface, as proposed by Delmon^{41–44}) can explain this behavior.

Carbon Supported Cobalt Sulfide. There is some debate concerning the nature of the cobalt sulfide supported on carbon, namely whether it corresponds to Co₉S₈ or to another sulfide with some special configuration (denoted CoS_x). Vissers et al.³) and Breysse et al.⁶⁹) found the Co2p_{3/2} binding energy values for carbon supported cobalt sulfide equal to that of pure unsupported Co₉S₈. Our XPS measurements perfectly agree with these results. Carbon rarely exhibits strong metal-support interactions. The absence of such interactions was supported by our experiments showing a strong diminution of the Co/C XPS signal ratio after sulfidation of the Co(5%)S_x/C sample. The considerable sintering observed for the supported cobalt phase indicates that carbon only has a weak stabilizing effect on CoS_x.

The possibility that a cobalt phase, different from Co₉S₈, form on the carbon supported cobalt sulfide catalysts is mainly based on the results of Bouwens et al.²⁶) and Van Der Kraan et al.¹²) These authors found that pure cobalt sulfide (without molybdenum), supported on carbon, exhibited the same MES signal (different from that of pure Co₉S₈) as the "CoMoS species". The carbon supported cobalt sulfide has an appreciable HDS activity, whereas unsupported Co₉S₈ is almost inactive. We calculated that our Co(5%)S_x/C sample has a higher S/Co atomic ratio than Co₉S₈. Our Co(5%)S_x/C is richer in sulfur, which suggests that the coordination of cobalt on the CoS_x/C catalyst might be different from that of the Co₉S₈ sulfide.

Evolution of the HSP "CoMoS Species" during Catalytic Reaction. The structural evolution of the HSP "CoMoS species" after working for a relatively short period (12 h) in the HDS reaction was investigated using XRD and analytical electron microscopy (X-ray emission spectroscopy), both performed before and after catalytic tests. Contrary to the fresh "CoMoS", well crystallized Co₉S₈ was detected by XRD in the used one. In addition, the homogeneity of this sulfide observed by AEM before catalytic reaction was lost after only 12 h of catalytic work in the reactor. This technique also revealed the presence of particles composed only of cobalt in the used cobalt-molybdenum sulfide. This proves that, during the catalytic reaction, the unsupported "CoMoS species" tends to decompose and the cobalt which segregates from this phase forms Co₉S₈. This decomposition is accompanied by the sintering of the MoS₂ crystallites. This was already proposed and demonstrated by XPS and AEM measurements³¹) and additional evidence is presented

in the CTEM micrographs (Fig. 3). After catalytic reaction (Fig. 3b), there is no doubt that the HSP CoMoS catalyst decomposed and sintered. This sintering would result in decrease of the available edge surface area and, consequently, lower quantities of cobalt could be accommodated in decoration positions forming the CoMoS phase. These new results confirm the inherently low stability of the "CoMoS species" under working conditions and raise some doubts as to whether this fragile phase could be responsible for the synergy observed in real hydrotreating catalysts, especially after they have worked for a long time. They confirm several observations,^{14,15,30}) in particular those of Topsøe et al.³⁵) obtained after a "CoMoS" catalyst had worked for 19 h in industrial hydrodesulfurization conditions.

Catalytic Activity. MoS₂ Containing Mixtures. Both mechanical mixtures, namely MoS₂ + Co₉S₈ and MoS₂/Al₂O₃ + Co(3%)S_x/C, exhibited synergy in both HDS and HYD reactions. No synergy was observed for either reaction in the case of the MoS₂/Al₂O₃ + C mixture: the promoting effect is thus due to CoS_x. The physicochemical characterization of the first mechanical mixture (composed of unsupported sulfides), reported in the first part of this discussion, demonstrated the absence of any structural connection between the two separate sulfides: we are dealing with separate phases. In the second mechanical mixture, made with supported sulfides, the majority of the active species (MoS₂ or Co₉S₈) lies inside the pores. The portion of the MoS₂ particles coming in direct contact with CoS_x particles is very low, if not negligible. This rules out any significant mutual contamination. This confirms that the explanation of synergy must be found in a cooperation between distinct phases.

The implication of these results is that cobalt sulfide (in the HSP form or carbon supported) can exert a promotional effect on the MoS₂ (supported or not) in spite of the fact that the first sulfide has no structural connection with the latter. This also implies the existence of some long range interaction between the physically separated sulfides. This conclusion is strengthened by the effects observed with the supported sulfides, where negligible direct contact exists. Such an interaction can exist if some mobile species, either as a reaction intermediate (indicating bifunctional catalysis) or as a spill-over species, is transferred from one phase to the other. Although bifunctional catalysis cannot be formally excluded in the case of the HDS reaction, it cannot be accepted for the hydrogenation of cyclohexene. It seems more natural to consider that the mobile species is spill over hydrogen. The promotional effect is explained by the operation of remote control, via hydrogen spill-over acting as a messenger across the surface of carbon and alumina. We have mentioned the evidence that cobalt sulfide is capable to produce spill-over hydrogen.⁴⁶) Let us recall that the behavior of the MoS₂ + Co₉S₈ mechanical mixture during TPR also strongly suggests that

spill-over hydrogen is emitted by Co_9S_8 .

A further argument in favor of remote control and, consequently, of the hydrogen spill-over in both HDS and HYD reactions comes from the fact that, as predicted by the remote control theory,^{42–44} both mixtures exhibited the maximum HYD synergy at lower $r = \text{Co}/(\text{Co} + \text{Mo})$ ratios than those where the maximum HDS activity was observed.

Recently it has been suggested that CoS_x might be the real active phase in hydrodesulfurization catalysts, and that the role of molybdenum sulfide could be to act as a very efficient support for the cobalt sulfide, thus allowing an important dispersion of the latter.^{3,12,26} This suggestion was mainly based on results showing that cobalt sulfide supported on carbon is more active than molybdenum sulfide supported on alumina or carbon for the HDS reaction (performed at atmospheric pressure). In accordance with these results, we found indeed that the $\text{Co}(5\%)\text{S}_x/\text{C}$ sample was more active than the $\text{MoS}_2/\text{Al}_2\text{O}_3$, even when the reaction was performed at relatively high pressure. However, we detect another effect, namely a synergy in the case of the $\text{MoS}_2/\text{Al}_2\text{O}_3 + \text{Co}(3\%)\text{S}_x/\text{C}$ mixture. This proves that something else occurs. CoS_x and MoS_2 , being attached to different supports, are identical when the reaction starts, whether they are alone or together in the reactor. It is natural to attribute the observed cooperation to the changes occurring during the catalytic reaction through the action of spill over hydrogen, as proposed by the remote control mechanism.

"CoMoS" Containing Mechanical Mixtures.

Three mechanical mixtures containing "CoMoS" were studied; namely the "CoMoS" + Co_9S_8 , "CoMoS" + $\text{Co}(3\%)\text{S}_x/\text{C}$ and "CoMoS" + MoS_2 . Let us consider first the HDS activity. It was found that both HSP unsupported Co_9S_8 and the carbon supported cobalt sulfide $\text{Co}(3\%)\text{S}_x/\text{C}$ can greatly enhance the HDS activity of the "CoMoS phase" (Figs. 8 and 9). In principle, such an effect may be due either to remote control or to a contamination of "CoMoS" by cobalt (assuming that the "CoMoS" association in the HSP samples would not be saturated with 30 at.% Co). The second hypothesis is highly unlikely in the case of the mechanical mixture "CoMoS" + $\text{Co}(3\%)\text{S}_x/\text{C}$ where the majority of the carbon supported cobalt sulfide is deposited inside the pores of the support. Thus the portion of cobalt sulfide in direct contact with the "CoMoS species" is very small, if not negligible. On the other hand, if we consider the "CoMoS" + Co_9S_8 mixture, contamination of "CoMoS" by cobalt is in contradiction with the fact that, being contaminated by cobalt from the beginning, the CoMoS phase expels cobalt rather than combining with it: X-Ray diffraction and AEM measurements show that, during reaction, cobalt segregates from this phase to form Co_9S_8 . The hypothesis of contamination is thus excluded and the only possible conclusion is that the observed synergy is due to a cooperation via a mo-

bile species. This corresponds to the remote control mechanism.

For the HYD activity, the same reasoning stands for the promoting effect of the $\text{Co}(3\%)\text{S}_x/\text{C}$ on "CoMoS". However, in the case of the "CoMoS" + Co_9S_8 mechanical mixture, synergy in HYD is weak or non-existent. According to the remote control mechanism applied to the case of hydrotreating, the synergy for HYD reactions requires much less of the donor phase (cobalt sulfide) than for HDS. During reaction, the "CoMoS species" is decomposed to Co_9S_8 and a species poorer in cobalt. This remaining species finds itself in contact with the expelled Co_9S_8 . This expelled Co_9S_8 is probably sufficient to produce enough spill-over hydrogen for maximizing the HYD centers.

According to the remote control mechanism, the maximum hydrogenation, activity would be observed for $r = \text{Co}/(\text{Co} + \text{Mo})$ ratios, lower than those needed to observe the maximum HDS activity. Indeed, in the case of the "CoMoS" + $\text{Co}(3\%)\text{S}_x/\text{C}$ mechanical mixture (where synergy was observed in both reactions) the maximum promoting effect in HYD reaction was observed for a mixture poorer in $\text{Co}(3\%)\text{S}_x/\text{C}$ than the one which exhibited the maximum HDS activity.

The absence of synergy between the "CoMoS species" and MoS_2 shows that the "CoMoS species", as a whole, does not donate much spill-over oxygen to MoS_2 . The Co_9S_8 which is expelled from the "CoMoS species" during the catalytic reaction probably produces just enough spill-over hydrogen to keep the Co-depleted "CoMoS species" active and no (or little) additional spill-over hydrogen could flow onto MoS_2 to activate it.

Compared to the very fine dispersion and statistical distribution in space of MoS_2 and CoS_x in industrial catalysts, that of our mechanical mixtures is poor (the aggregates of each phase or the particle size of the supports have dimensions of the order of 10 to 100 μm). In spite of that, a very apparent synergy is detected. The effect would presumably be much important in industrial catalysts, and we can speculate that our conclusions are still more relevant to the way these catalysts work.

Conclusions

The present work leads to the following main conclusions.

— We confirm the existence of a synergy between Mo_2S_2 and Co_9S_8 in hydrogenation and hydrodesulfurization. The synergy is observed even if the sulfides are supported on distinct support particles.

— A synergy exists, in the hydrodesulfurization reaction, between the "CoMoS species" and cobalt sulfide (supported or prepared by the HSP method). In the hydrogenation reaction synergy was observed only in the case of supported cobalt sulfide.

— The HSP "CoMoS species" is unstable under reaction conditions similar to those of an industrial reactor.

Cobalt segregates out from this phase to form well crystallized Co_9S_8 .

—These two results imply that the existence of the “CoMoS species” alone cannot be the only explanation for synergetic behavior of the CoMo hydrotreating catalysts.

—An explanation for the observed results is that a remote control operates: spill-over hydrogen formed on Co_9S_8 creates HYD and HDS centers on MoS_2 , or possibly, on MoS_2 formed only partial or extensive decomposition of “CoMoS” to MoS_2 and Co_2S_8 .

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