Sulphidation of an oxidic CoMo/Al_2O_3 catalyst under practical conditions: different kinds of sulphur species

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The sulphidation of a CoMo/Al_2O_3 hydrotreating catalyst was studied under pressure and flow conditions close to industrial practice. The sulphiding mixture contained equal amounts of H_2S and CH_4 diluted in hydrogen under 3.9 MPa total pressure. The oxidic precursor was flushed by the reagent gas at 40 °C for 10 h, then the temperature was raised to 400 °C within 2 h. Mass variation was continuously recorded by means of a suspension magnetic balance, and the gas phase was analysed by mass spectrometry. Sulphur contents were also determined at intermediate temperatures by chemical analyses. Thus, mass variations due to the presence of adsorbed species or to the formation of CoMo sulphides could be distinguished. The rapid gain in mass noted at 40 °C was mostly due to adsorption of H_2S over the oxidic solid, since it increased with H_2S partial pressure. At this stage, however, a small amount of the reactive oxygen was already exchanged for sulphur. Upon raising the temperature, the mass decreased due to a combination of desorption and sulphiding steps. Above 140 °C, H_2S consumption was evidenced, together with water production, and the rate of sulphiding increased with the H_2S partial pressure. At 300 °C, the mass variation was close to that expected for complete transformation into Co_9S_8 and MoS_2. Above 350 °C, the mass further increased due to the replacement of adsorbed water by H_2S. At 400 °C, an important excess mass was observed at all H_2S partial pressures. Thus, the adsorption sites on the metal sulphides are essentially saturated by H_2S species under practical conditions.

KEY WORDS: hydrotreating catalyst; CoMo/Al_2O_3; solid reactivity; sulphidation; H_2S adsorption; gravimetric analysis under pressure and flow conditions

1. Introduction

The increasing severity of environmental regulations is a strong incentive to improve the catalytic elimination of sulphur and nitrogen pollutants from oil feedstocks [1]. Due to the low reactivity of dibenzothiophenic compounds, hydrotreating catalysts such as Co–Mo supported on γ-alumina are operated under a stream of hydrogen at high temperature (320–380 °C) and pressure (3–4 MPa) [2]. Under such conditions, Co and Mo oxides are converted into stable Co_9S_8 and MoS_2 sulphides, or mixed Co–Mo–S particles where Co atoms decorate the edges of MoS_2 slabs [3].

Presulphidation of the oxidic catalyst is very critical because it determines the future catalytic performance [4,5]. This step is generally performed by running a feedstock free from olefins and spiked with dimethyldisulphide [6], which is readily converted to H_2S [5,7]. Then, the oil processing occurs at a higher temperature [8]. The transformation of supported oxides into sulphides combines reduction of the metal cations with sulphidation by H_2S. Both processes yield water, e.g.,

$$CoO,MoO_3 + H_2 + H_2S \rightarrow Co_9S_8,MoS_2 + H_2O \quad (1)$$

This may affect the nature and the dispersion of the sulphides on the alumina support.

Presulphidation has been extensively studied in the last 20 years [3,9].The final solids have been characterised by XPS and TEM [4,10–12]. However, such measurements are carried out in vacuum with catalysts that have been sulphided *ex situ*, so that results might not be representative of the real catalysts in a sulphur environment. A better characterisation of the metal-containing phase is provided by *in situ* spectroscopies such as Raman (LRS) [13,14], Mössbauer (MES) [15], and EXAFS [16–19]. The consumption or evolution of gases during temperature-programmed sulphidation (TPS) have been recorded [20–23]. Several factors have been investigated such as temperature, H_2S partial pressure and reaction time by decreasing order of importance [24], and various mechanisms have been proposed for the solid-state transformation. Interestingly, results obtained on commercial catalysts, with 2–4 wt% CoO and 12–16 wt% MoO_3, were strikingly similar to those obtained on laboratory-made CoMo/γ-Al_2O_3 catalysts [16,18,22,25,26].

The aforementioned studies may be summarised as follows:

(i) H_2S adsorbs readily at room temperature, and sulphidation occurs already at this stage [20,27]. Then, little H_2S is desorbed upon raising the temperature up to 100 °C [20].

(ii) At moderate temperatures, i.e., below 200 °C, H_2S is consumed while water is released, indicating some reduction of the Mo ions [19,20]. However, in this temperature range, the exchange of reactive oxide ions for sulphur predominates over reduction [24]. EXAFS data

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showed that Mo–S bonds are formed on catalysts sulphided at 90–100 °C [16,17]. Using LRS, Schrader and Cheng [13] detected molybdenum oxysulphides. Moreover, Payen et al. [14] claimed the formation of sulphido compounds and MoS_3 intermediates.

(iii) Starting at 280 °C [19–23], surface MoS_2 entities are detected by EXAFS. Thus, the oxysulphides and MoS_3 intermediates are progressively reduced. Besides, Scheffer et al. reported that elemental sulphur is liberated and reduced to H_2S at this stage [20].

(iv) From 300 to 400 °C, the structure of the surface MoS_2 slabs remained unchanged [16]. Complete sulfidation into Co_9S_8 and MoS_2 under various conditions was confirmed by using H_2S labelled with ^{35}S [25,26]. The presence of Co caused no change in the EXAFS spectra of Mo [19], although MES data suggested a redispersion of Co species over the edges of the MoS_2 crystallites [15]. The precise role of the Co promoter is not fully elucidated. Indeed, Co ions increase the rate of sulphidation of Mo and the H_2S uptake [20], but, CoMo/Al_2O_3 catalysts with 1–3 wt% Co exhibited TPS patterns similar to those of Mo/Al_2O_3 [23].

In conclusion, important structural modifications occur when the temperature of sulphiding increases from 100 to 400 °C. However, the influence of reactant pressure over the course of sulfidation deserves further study. For instance, Koizumi et al. [18] have sulfided CoMo catalysts at 400 °C under an H_2S–H_2 flow. Using *in situ* EXAFS they found that the structure of the promoted MoS_2 slabs was unchanged when the pressure varied from 0.1 to 5.1 MPa. However, catalysts sulphided at high pressure featured a lower amount of vacancies associated with non-promoted Mo and Co sites, as probed by NO.

Thus, the influence of pressure might be more important for the steps occurring at moderate temperature, as both tightly or loosely bonded sulphur species are involved in sulphidation. In this sense, Parham and Merrill [16] found that a CoMo/Al_2O_3 cooled to room temperature under the sulphiding atmosphere had excess sulphur amounting to 40% of the uptake during sulphiding. This excess sulphur leaves the Mo–S coordination by EXAFS unchanged. Surprisingly, it seems that the amount of H_2S adsorbed under hydrotreating conditions has not been reported yet, although H_2S competes with organic reactants on catalytic active sites [28,29].

Our aim is, therefore, to work under pressure and flow conditions matching the industrial practice, and to determine precisely (i) the amount of H_2S adsorbed on a CoMo/Al_2O_3 catalyst, and (ii) the extent of formation of the metallic sulphide. These might be obtained from *in situ* mass measurements combined with gas-phase analyses using various H_2S partial pressures. A novel gravimetric apparatus was designed for this purpose.

2. Experimental

The CoMo/Al_2O_3 catalyst was the HR306C-1.2 from Procatalyse, with 2.4 wt% Co and 9.3 wt% Mo. The BET area was 200 $m^2\,g^{-1}$, pore volume 0.5 $cm^3\,g^{-1}$, and grain size 0.2–0.5 mm. A γ-alumina from Procatalyse (GFS-C) with similar textural characteristics was studied for comparison. The solids (3.5 g samples) introduced in the sulphidation reactor were first calcined under a stream of air at 400 °C and 0.1 MPa (mass loss about 6%) then cooled to 40 °C under dry argon.

The system was then pressurised to 3.8 MPa under dry H_2. The sulphiding mixture was then introduced. It was provided by flowing H_2 and dimethyldisulphide (DMDS) through a pre-reactor containing 100 g of sulphided CoMo/Al_2O_3 heated at 350 °C. Decomposition of DMDS yielded equal amounts of H_2S and CH_4. Thus, the partial pressure of H_2S could be varied between 0.015 and 0.3 MPa by setting the DMDS feed rate. The H_2 flow rate was fixed at 0.02 $mol\,h^{-1}$.

The experimental set-up is shown in figure 1. All lines of the flow system excepting the catalyst zone were heated at 100 °C. In the steel reactor, the mobile array consists of a permanent magnet under which an Inconel-600 basket containing the catalyst hangs suspended. The balance (Mettler Toledo, AT261) stays outside the reactor and is coupled to the mobile array by means of a magnetic device (Rubotherm), essentially an electromagnet hooked on the pan of the balance. In the normal position (figure 1), the upper part of the basket sits on the reactor internal wall, so that the sulphiding gas flows through the solid bed. The sample weight is determined by adjusting the current intensity in the electromagnet, so that the permanent magnet is lifted to a predetermined and fixed position. In this measurement position, the catalyst load is in a suspended state. After correcting for buoyancy effects, the accuracy on mass is estimated to be 0.05 mg. Mass variations Δm (in %) will refer to the mass of the dried oxidic sample.

The gas phase was permanently analysed by means of a gas chromatograph (Girdel SE30) using a six-way valve injection port, and a mass spectrometer (Pfeiffer, QMA 200) connected to the reactor by a capillary leak. The concen-

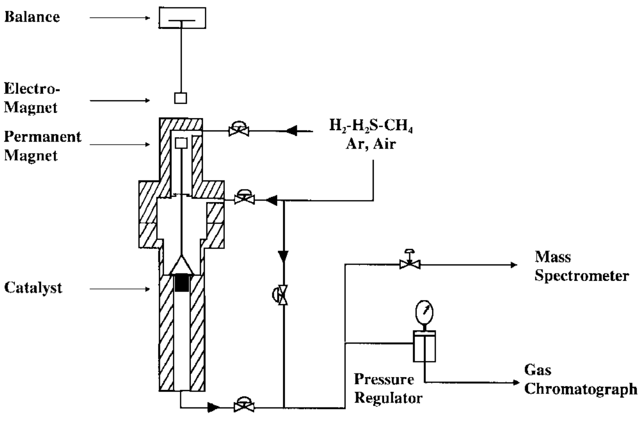

Figure 1. Schematic view of the experimental set-up and flow diagram.

trations of H_2S and CH_4 were continuously monitored from the peaks at $m/z = 34$ (H_2S^+) and 15 (CH_3^+), respectively. Hydrogen could not be determined by MS owing to its large excess.

Catalysts sulphided at some key temperatures (130, 300, or 400 °C) were cooled and removed from the reactor under an Ar atmosphere, then purged under He flow at 200 °C for 2 h. Chemical analysis (CNRS, Vernaison, France) yielded an S content (wt%) that will be referred to as "metallic sulphur".

3. Catalyst mass and evolution of gas products during presulphidation

3.1. Initial adsorption of the sulphiding gas at 40 °C

In a typical experiment, the oxidic catalyst previously dried at 400 °C was initially flushed by pure hydrogen at 40 °C and 0.1 MPa. When the pressure was raised to 3.8 MPa, the mass of the solid did not vary (figure 2). Keeping the temperature at 40 °C, the sulphiding gas (H_2S partial pressure 0.03 MPa) was then introduced. The mass increased rapidly at first, but, it took 8 h before it stabilised at a level $\Delta m_0 = 5.6\%$ above the initial value. This mass increase was mostly due to adsorption of H_2S, since the mass of adsorbed of hydrogen or methane was found to be negligible. Indeed, the mass of the oxidic catalyst did not noticeably change during the pressurisation step. On the other hand, the CH_4 concentration measured at the reactor exit immediately after introducing the sulphiding gas was slightly below that of the entering gas, but, equal values were found after 20 min-on-stream. This effect was likely due to a transient dilution of the new mixture replacing H_2 in the reactor, rather than to adsorption of methane.

By contrast, the deficit in H_2S was more pronounced and its concentration reached a stable value only after 8 h. The preferential adsorption of H_2S over that of CH_4 was established in other binary adsorption studies. Dreisbach et al. reported that methane was much less adsorbed than H_2S on carbon at 25 °C [30], and Talu and Zwiebel reported a similar finding with propane at 10–90 °C over an acidic HM zeolite [31]. Furthermore, if the phase adsorbed at 40 °C is treated as a bulk liquid in equilibrium with the gas, flash calculations [32] indicate that H_2S accounts for 96% of the mass in the binary liquid H_2S–CH_4. Therefore, the 5.6% mass gain finally recorded at 40 °C corresponds essentially to H_2S adsorbed on the supported Co and Mo oxides, as well as on alumina. This is not far from the 7.4 wt% sulphur content expected if complete sulphidation to Co_9S_8 and MoS_2 had occurred (equation (1)). Therefore, enough sulphur was already available on the solid at 40 °C.

3.2. Presulphidation from 40 to 140 °C

When raising the temperature, the mass decreased considerably from 40 to 375 °C, then increased from 375 to 400 °C and also during the final stage at 400 °C (figures 2 and 3(A)). The derivative curve (figure 3(B)) shows that the mass decreased in two steps. In region I, from 40 to 140 °C, the rate of mass loss ($-\mathrm{d}\Delta m/\mathrm{d}t$) was maximum at 70 °C then went to zero at 140 °C. In region II, the mass further decreased until reaching a minimum at 375 °C. In this region, a maximum in rate of mass loss occurs at 220 °C. Finally, above 375 °C, the mass slightly increased (region III).

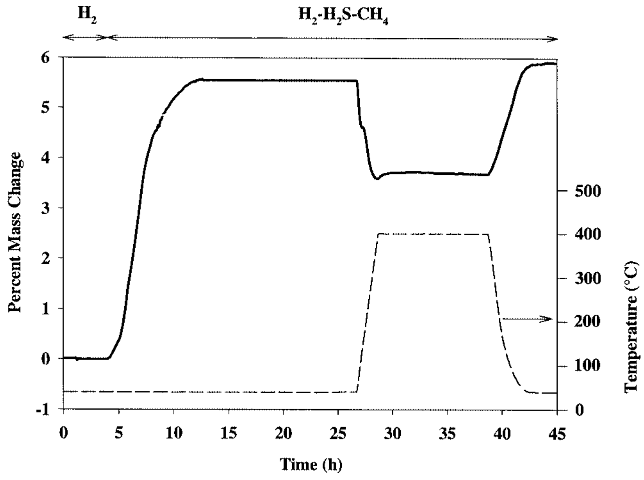

Figure 2. Percent mass variation during a complete experiment including (i) introduction of the sulphiding gas at 40 °C under flow and 3.9 MPa total pressure, (ii) sulphidation from 40 to 400 °C (180 °C h^{-1}) using 0.03 MPa H_2S partial pressure, and (iii) cooling to 40 °C under sulphiding gas flow. Temperature profile (- - -) on the right scale.

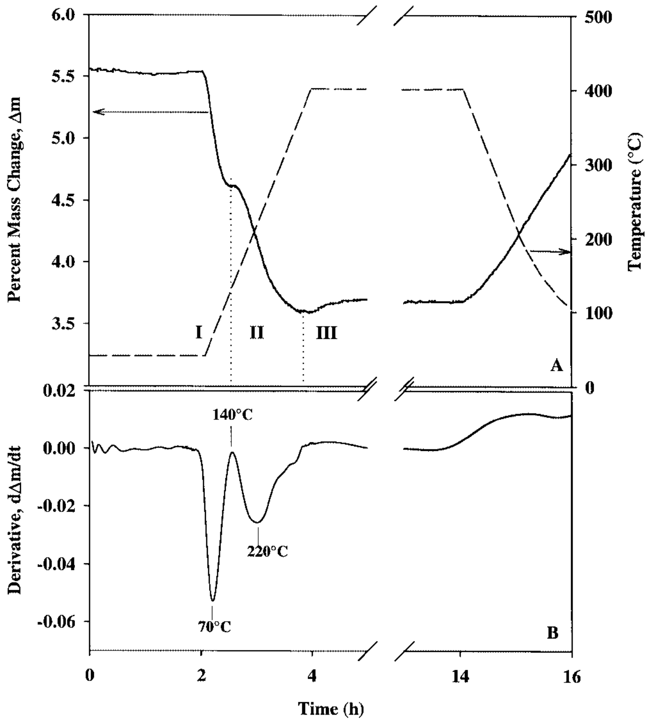

Figure 3. Sulphidation of a CoMo/Al_2O_3 catalyst: (A) percent change in mass with time-on-stream, (B) derivative of the change in mass. Conditions: $P_{H_2} = 3.8$ MPa, $P_{H_2S} = P_{CH_4} = 0.03$ MPa. Temperature profile (- - -) on the right scale.

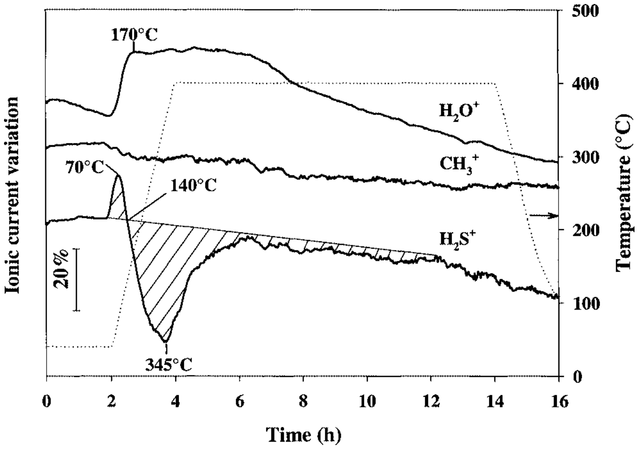

Figure 4. Variations in gas phase composition during sulphidation, as revealed by mass spectrometry, CH_4 ($m/z = 15$), H_2O ($m/z = 18$), and H_2S ($m/z = 34$). Hatched areas indicate H_2S desorption and consumption peaks.

Figure 4 shows the variation in gas composition during the heating period, as revealed by mass spectrometry. Methane remained almost constant throughout, confirming that it was hardly involved in the process. The curves indicated that H_2S desorbed in region I; its concentration in the gas was maximum at 70 °C (figure 4), which coincides with the maximum in rate of mass loss (figure 3(B)). Therefore, the 5.6% gain in mass finally recorded at 40 °C was mainly due to physisorbed H_2S. Evolution of H_2S ceased at 140 °C, where $\mathrm{d}\Delta m/\mathrm{d}t$ was almost nil, then H_2S was consumed in region I. H_2O appeared simultaneously in the gas phase. At 140 °C, the mass had increased by $\Delta m_1 = 4.6\%$, beyond the 2.1% level expected if full sulphidation into Co_9S_8 and MoS_2 had occurred, with complete removal of water. This Δm_1 is largely due to H_2S but also to H_2O that are not fully desorbed at 140 °C. Indeed, the rate of water desorption was maximum at 170 °C (figure 4). Such formation of water attests that sulphidation undoubtedly started at low temperature. Indeed, the oxidic Co–Mo/Al_2O_3 turned black upon contact with H_2S already at 40 °C, suggesting that superficial oxygen atoms were partly exchanged by sulphur atoms, as previously pointed out by several authors [14,20–23]. In conclusion, the mass loss in region I likely arose from combined desorption of H_2S and sulphiding.

Analysis of the solid sulphided at 130 °C, then swept with He at 200 °C, indicated a 4.6 wt% sulphur content, well below the 7.4 wt% expected at full sulphidation. Thus, surface MoS_2 entities were not yet formed at 130 °C, but rather some sulphur exchanged with the more reactive oxygen to form sulphidic intermediates according to previous authors [13,14]. This 4.6 wt% sulphur content compares well with those reported by Kabe et al. for analogous CoMo/Al_2O_3 sulphided at 100 °C by $H_2{}^{35}S$–H_2 pulses [25,26]. However, Glasson et al. [27] reported higher values at the same temperature when using an H_2S–H_2 flow (15–85 mol%) at atmospheric pressure. These differences in S content are probably pertaining to the mode of sulphiding. In the work of Glasson et al. [27], the progressive heating probably avoided an over-reduction of the oxidic Co–Mo phases, which is detrimental to the sulphur uptake [4]. Thus, lower sulphur contents are to be expected when sulphiding is performed directly at high temperature [25,26].

In our case, the amount of H_2S carried by the feed gas did not exceed 0.007 g per g of solid, while the temperature rose from 40 to 130 °C. This amount is well under the 4.6 wt% metallic sulphur content found at 130 °C, so that most of the sulphur species that reacted with Co and Mo ions in this temperature range were not provided by the gas phase, but rather were present on the solid. The stabilisation period, at least 8 h at 40 °C, is therefore critical. This parameter is rarely taken into account by researchers, although it may explain some inconsistencies found in the literature.

3.3. Presulphidation from 140 to 400 °C

From 140 to 375 °C, the mass further decreased (region II, figure 3(A)), as extensive sulphidation of the Co–Mo and desorption of H_2S and H_2O lead to opposite effects. Consumption of H_2S is proved by the minimum in H_2S concentration found at 345 °C (figure 4). Between 130 and 300 °C, the mass gain over the oxidic sample had decreased from 4.6 to 3.8%, whereas the “metallic sulphur” had increased up to 7.7 wt%. Again, some of the H_2S species adsorbed at temperature lower than 140 °C participated to sulphiding, as only 1.3 wt% S could possibly come from the gas phase, whereas the S content had increased by 3.1 wt%. However, the contribution of gaseous H_2S became more important above 130 °C, as suggested by the large area of the H_2S consumption peak (figure 4).

The 7.7 wt% sulphur content found on the catalyst reacted at 300 °C shows that sulphidation was complete at this temperature, in agreement with earlier studies on progressive sulphiding [27]. With this procedure, the various metallic intermediates are reduced into surface MoS_2 particles under 300 °C [15,16,20,22]. Much lower S contents were reported after isothermal sulphiding [25,26], notably by Prada Silvy et al. for catalysts which had been pre-reduced at 300 °C [4]. This proves again the importance of the mode of sulphiding. Moreover, the sharp release of H_2S noted at 175–280 °C in TPS patterns [20–23] that was attributed to a transformation of the surface phases, was not observed in our work. This may be explained by the high hydrogen pressure used here, preventing accumulation of elemental sulphur as claimed in the TPS experiments at atmospheric pressure. Despite this difference, the final extent of sulphidation was the same as upon atmospheric sulphidation [16,27,33], suggesting that the structure of surface MoS_2 was not affected by pressure, as reported by Koizumi et al. [18].

After the final heating at 400 °C, the S content was the same as at 300 °C (7.7 wt%) in agreement with Glasson et al. [27], but the final mass increase was down to 3.6%, still higher than expected for complete sulphidation with elimination of the volatile products. Thus, some of the water produced remained adsorbed during this final stage, as confirmed by the MS signal of H_2O, which appeared constant beyond 170 °C (figure 4). Clearly, water plays an important role in the formation of the sulphided phases, as Payen et al. found that water hindered the formation of MoS_3 intermediates [14].

During the isothermal stage at 400 °C, the mass again slightly increased (figure 3(A), region III). Yet, sulphiding was complete according to chemical analyses. Some consumption of H_2S was noted (figure 4). It may be ascribed to breaking of the residual Mo–O–Al linkages [34], or to the redispersion and sulphidation of Co species [15], notably Co ions extracted from the alumina sublayers [4]. However, gas analyses suggest another possibility, namely that the mass gain is simply due to replacement of adsorbed water by H_2S. This process appeared to be slow since it took more than 8 h before water was completely eliminated from the system (figure 4). The final mass increase at 400 °C established at $\Delta m_2 = 3.7\%$, still above the 2.1% expected at complete sulphidation. Since no carbon was found in the solids sulphided at 400 °C, the 1.6% excess between actual and theoretical masses proves that H_2S species, molecular or dissociated, are still adsorbed on the surface at 400 °C.

4. Influence of H_2S partial pressure

4.1. Adsorption capacity at 40 °C

The influence of H_2S partial pressure upon sulphidation of the oxidic CoMo/Al_2O_3 was first examined at the stage of isothermal treatment with H_2–H_2S–CH_4 at 40 °C. For a constant hydrogen pressure (3.8 MPa), the H_2S partial pressure varied from 0.015 to 0.3 MPa. The gain Δm_0 measured after 8 h increased from 4.7 to 8.8% (figure 5, curve (a)). As little water is likely to be formed, the Δm_0 values were first compared with those expected if the entire surface was covered by a monolayer of H_2S. The molecular surface area (SSA) of H_2S was evaluated by assuming that the molecules were arranged in a hexagonal close-packing phase with the same mutual distances as in the bulk liquid [35]. Thus,

$$\mathrm{SSA} = 1.091\left(\frac{m}{d}\right)^{2/3},$$

where m is the mass of the H_2S molecule and d the density of liquid H_2S at 40 °C ($d = 0.727\ \mathrm{g\,cm^{-3}}$). In this way, the SSA was estimated to be 0.199 $\mathrm{nm^2}$ per molecule at 40 °C, in line with a previous report of 0.165 $\mathrm{nm^2}$ at −79 °C [36]. Then, from the BET area, it turns out that the mass should increase by 5.7% at complete H_2S monolayer. Such a value is close to the Δm_0 found at the lowest H_2S pressures (0.015–0.03 MPa) but much lower than those obtained at higher pressure (figure 5). Therefore, the catalyst surface should be essentially saturated at low H_2S pressure, with multilayer adsorption occurring above 0.05 MPa. However, H_2S is known to interact more weakly with alumina than with the CoMo oxides, since oxysulphide intermediates are formed [13,14]. Thus, the trend in Δm_0 should be interpreted as adsorption occurring over two types of sites [37].

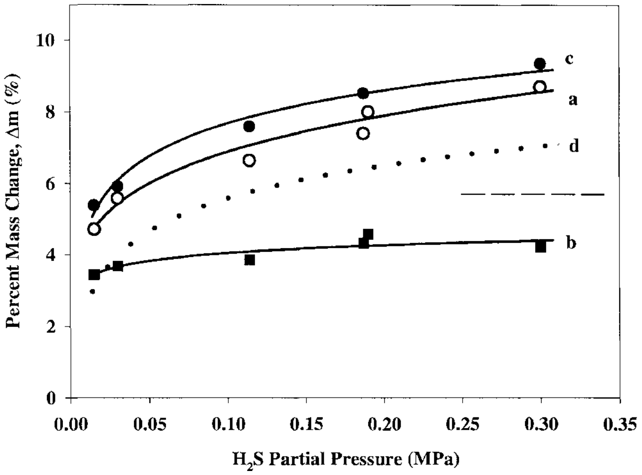

Figure 5. Influence of the H_2S partial pressure upon final mass uptake of oxidic CoMo/Al_2O_3: (a) (○) contact with $H_2S + H_2$ at 40 °C for 10 h; (b) (■) then sulphided 10 h at 400 °C; (c) (●) sulphided solid cooled to 40 °C; (d) (···) is curve (c) minus 2.1% due to sulphiding. (- - -) on the right indicates the increase in mass at the monolayer.

Inspection of figure 5 (curve (b)) shows that the final mass increases Δm_2 recorded after sulphidation at 400 °C hardly increased with H_2S pressure. At this stage, the sulphur contents of the catalysts were:

H_2S pressure (MPa)	0.015	0.03	0.12	0.16	0.17	0.20	0.30
Analytical S (wt%)	7.2	7.7	7.9	7.5	7.3	7.0	7.9

Such values nearly conform to the stoichiometric sulphidation at all investigated H_2S pressures.

The catalysts sulphided at 400 °C were then cooled to 40 °C under the H_2–H_2S flow. Their mass further increased (figure 1), due to adsorption of H_2S only, since water had been eliminated. The final level Δm_3 recorded at 40 °C established slightly above the Δm_0 on the oxidic precursor at the same H_2S pressure (figure 5, curve (c)). The adsorption capacity at 40 °C on the sulphided catalyst may be estimated by subtracting from Δm_3 a 2.1% increment due to sulphiding (figure 5, curve (d)). In the whole range of H_2S pressure, the sulphided catalyst was largely covered by H_2S species, the monolayer being completed at about 0.1 MPa. Indeed, the parallel between curves (a) and (d) in figure 5 indicates that adsorption occurred in a similar way on the alumina part of the oxidic and sulphided CoMo/Al_2O_3. Thus, the higher sorption capacity measured on the oxidic sample means that some H_2S reacted irreversibly at 40 °C with the metal oxides. This leads to a 1.4% mass increase, or 0.3 S atom per metal atom, whatever the H_2S pressure. The reactive oxygen capacity deduced in this way is probably underestimated, since Glasson et al. report a sulphur uptake of 0.75 atom per metal atom upon adsorption and O–S exchange at room temperature on an analogous CoMo/Al_2O_3 catalyst [27].

Summarising, an increase in H_2S pressure during sulphidation results in higher gain in mass mainly due to physisorbed H_2S, but O–S exchange reaction already occurred to a large extent at 40 °C.

4.2. Rate of sulphidation

The rate of the sulphiding reaction was expected to increase with H_2S partial pressure. Some mass variations recorded upon raising the temperature from 40 to 400 °C are illustrated in figure 6. Interestingly, the profiles were rather similar regardless of the H_2S partial pressure. Again, three temperature regions could be distinguished, identical to those observed at $P_{H_2S} = 0.03$ MPa.

In region I, the mass loss between 40 and 140 °C increased with H_2S pressure (figure 6), simply because more H_2S was desorbed from the solid. This was confirmed by a higher H_2S signal in the mass spectrum of the gas, while the release of water was unaffected. The rate of mass loss was maximum at the same temperature, 70 °C and nil at 140 °C (as in figure 3(B)). Thus, even a ten-fold increase in H_2S pressure had no obvious effect on the rate of sulphiding in this region, likely because most of the sulphiding species were already present on the catalyst at 40 °C whatever the H_2S pressure.

In region II, the mass decreased more slowly than in region I, until reaching a broad minimum, at temperature T_m. Interestingly, a constant decrease in mass (0.9%) was found between 140 °C and T_m at all H_2S pressures, suggesting that the extent of sulphidation was the same. Consumption of H_2S was observed by mass spectrometry in all cases, but there was no simple relationship between the peak area and the H_2S pressure during sulphidation. Apart from the above similarities, the temperature T_m of mass minimum was shifted to lower values with increasing pressure (arrow in figure 6). Here, the rate of sulphiding increased with H_2S pressure, confirming that H_2S species coming from the gas phase contributed more to sulphiding at intermediate temperatures.

In region III, the mass slightly increased from temperature T_m until the end of the isothermal stage at 400 °C. Analysis of the gas revealed a consumption of H_2S and a slow release of water, like when using 0.03 MPa H_2S partial pressure (figure 4). Again, this was due to completion of the sulphiding reaction, and replacement of nascent water by adsorbed H_2S. The final mass increase Δm_2 recorded at 400 °C increased but slightly with increasing H_2S partial pressure (figure 5). The excess mass over complete sulphidation ($\Delta m_2 - 2.1\%$) varied from 1.3% for the lowest pressure (0.015 MPa) to 2.1% at 0.3 MPa. Inspection of curve (c) shows that the adsorption sites were already saturated at the lowest H_2S pressure. By comparison, a γ-alumina gained only 0.9 wt% at 400 °C using a 0.2 MPa H_2S pressure. Therefore, on the sulphided Co–Mo, most of the H_2S species were adsorbed on metal sulphide sites.

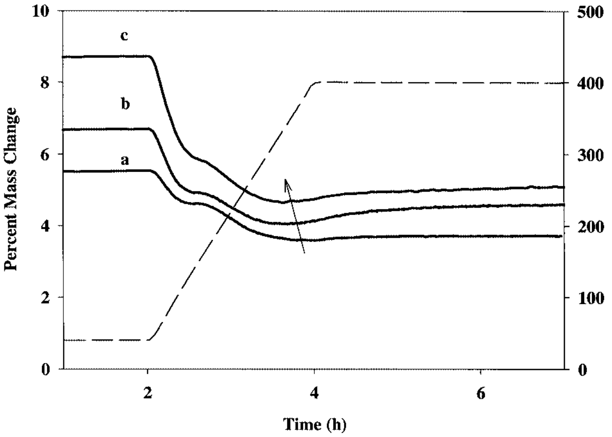

Figure 6. Effect of the H_2S partial pressure on the change in mass during temperature-programmed sulphidation. Conditions: 40 to 400 °C (180 °C h^{-1}), $P_{H_2} = 3.8$ MPa, $P_{H_2S} = P_{CH_4} = 0.03$ (a), 0.11 (b), and 0.30 MPa (c). Temperature profile (- - -) on the right scale.

The coverage of such sites in a wide range of H_2S partial pressures might be of prime importance for the optimal use of the CoMo/Al_2O_3 catalysts. H_2S and organic reactants compete on the same catalytic sites [28,29], and there are numerous examples of strong inhibition by H_2S upon model or real HDS and HDN reactions [28,29,38,39]. Consequently, the thermogravimetric technique indicates that few catalytic sites are really available under oil processing conditions, i.e., high H_2S partial pressures [40].

5. Conclusions

Upon contact with H_2S–H_2 at 40 °C, the CoMo/Al_2O_3 hydrotreating catalyst gained in mass due to adsorbed H_2S and S species strongly interacting with CoMo oxides. At least 20% of the oxygen atoms were exchanged for sulphur at this stage, regardless of the H_2S partial pressure. The surface was essentially saturated by H_2S species at very low H_2S pressure (0.015 MPa), and multilayer adsorption presumably occurred above 0.1 MPa H_2S pressure.

Three important stages were evidenced upon raising the temperature:

(i) Up to 140 °C, the supported CoMo oxides were partly sulphided; and the water formed was largely retained at the surface. Most of the sulphiding species are already present into the catalyst at 40 °C, and the stabilisation period at low temperature may be important to optimise the forthcoming sulphidation.

(ii) From 140 to 300 °C, sulphidation was completed; with partial desorption of water. The contribution of gaseous H_2S to sulphiding becomes increasingly important. The rate of sulphiding increased with H_2S pressure, but the structure of the promoted MoS_2 phases was unaffected.

(iii) From 300 to 400 °C, the metal sulphide entities presumably reorganised, and water was gradually replaced by H_2S species.

Under working conditions, the catalytic sites are essentially saturated by H_2S species. Thus, improved catalytic performance may be expected by maximising the concentration of such sites.

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