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Characterization by temperature-programmed reduction of non-conventional catalysts for hydrotreatment

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A temperature-programmed reduction (TPR) study of three series of biphasic hydrotreating (HDT) catalysts – PtS/γ-Al_2O_3/(PtS/γ-$Al_2O_3 + MoS_2$); Rh_2S_3/γ-AlOOH/(Rh_2S_3/γ-AlOOH + WS_2) and PdS/γ-Al_2O_3/(PdS/γ-$Al_2O_3 + WS_2$) – is presented. In all cases, the quantity of H_2S produced is larger than that which would correspond to the arithmetic addition of the quantities produced by each of the sulfide phases alone. This fact suggests that the noble metal sulfide dissociates the hydrogen molecule to spillover hydrogen (H_{SO}), the latter producing a deeper reduction of molybdenum sulfide or tungsten sulfide. The similitude of catalytic effect in hydrogenation (HYD) and hydrodesulfurization (HDS) observed with the same mechanical mixture strongly suggests that H_{SO} also plays a role in the synergy between MoS_2 or WS_2 and the noble metal sulfides.

Keywords: hydrotreatment, TPR, noble metals, spillover hydrogen, Mo–Pt, W–Rh, W–Pd, mechanical mixtures

1. Introduction

In order to comply with the drastic restrictions imposed worldwide upon oil refinement products to protect the environment (e.g., diminution of the minimum sulfur content by a factor of ten and decrease of the amount of aromatics and polyaromatics for diesel hydrotreating catalysts) [1], studies are expanding. It is widely known that noble metals have hydrodesulfurizing properties and excellent hydrogenating properties [2–4]. The existing literature allows us to forecast that these materials will be an important component of future catalysts for HDT, especially for dearomatization of diesel carburants. Fundamental studies aiming at determining the origin of the catalytic synergy phenomena between the different active phases will no doubt help to acquire the necessary knowledge for the development of more efficient catalysts.

This article presents a study of TPR of three series of non-conventional catalysts for HDT: Mo–Pt (PtS/γ-Al_2O_3/(PtS/γ-$Al_2O_3 + MoS_2$)); W–Rh (Rh_2S_3/γ-AlOOH/(Rh_2S_3/γ-AlOOH + WS_2)) and W–Pd (PdS/γ-Al_2O_3/(PdS/γ-$Al_2O_3 + WS_2$)). This technique is widely used for the characterization of solid catalysts [5]. In the case of sulfided catalysts, TPR allows an evaluation of reducibility of the catalysts, i.e., the chemical reaction with hydrogen, which in principle, may be closely linked to the catalytic activity [6,7], specifically to the synergy effect observed in biphasic solids [8].

2. Experimental

2.1. Preparation of catalysts

Three series of catalysts were synthesized: Mo–Pt, W–Rh and W–Pd. They were prepared through mechanical mixtures of noble metal sulfide supported on alumina (PtS/γ-Al_2O_3, Rh_2S_3/γ-AlOOH or PdS/γ-Al_2O_3) and unsupported (bulk) molybdenum sulfide or tungsten sulfide (MoS_2 or WS_2). Each series consists of catalysts with different compositions, characterized by the weight fractions of the noble metal sulfide supported (Rm). These catalysts were prepared following the procedure described in a previous article [8]. The catalytic activity in thiophene hydrodesulfurization and cyclohexene hydrogenation is described elsewhere [9].

Bulk molybdenum or tungsten sulfides have been prepared through the homogeneous sulfide precipitation method (HSP) [10] by acidic precipitation of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $(NH_4)_{10}H_{12}(W_2O_7)_6$ salts, under inert atmosphere. Noble metals supported on alumina – Pt(0.3 wt%)/γ-Al_2O_3, Pd(0.3 wt%)/γ-Al_2O_3 (Engelhard) and Rh(5 wt%)/γ-AlOOH (Johnson Matthey) – were commercial catalysts. The supported metal catalysts as well as the bulk MoS_x and WS_x, were ground and sieved to a particle size of less than 40 μm. These powders (5 g) were sulfided by the following procedure: drying with a flow of argon (1.66 ml s^{-1}) at 423 K for 1 h. The argon was then replaced by a mixture of H_2S (15 vol%)/H_2 (1.66 ml s^{-1}) and the temperature was raised to 673 K at a rate of 0.166 K s^{-1}. After maintaining these conditions for 4 h, the samples were cooled down to room temperature and flushed with argon. The

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catalysts obtained – MoS_2, WS_2, $PtS/\gamma\text{-}Al_2O_3$, $Rh_2S_3/\gamma\text{-}AlOOH$, $PdS/\gamma\text{-}Al_2O_3$ – were used for the preparation of the mechanical mixtures. In order to improve the contact between the two separated compounds and to avoid phase modifications, the powders have been dispersed in *n*-pentane, stirred 3 min in an ultrasonic bath, mechanically stirred for 3 min (Ultra-Turrax T-50 $(5\text{–}8)\times 10^3$ rotations min^{-1}), then *n*-pentane was removed at room temperature under Ar flow. The pure bulk sulfur and the noble metal catalysts underwent the same treatment.

2.2. Equipment and measuring conditions

TPR of catalysts sulfides were carried out in a home-made, all-stainless-steel, atmospheric pressure, temperature-programmed reaction apparatus, adapted to use with sulfur-containing substances. The H_2S produced is measured through a twin set of TCD's in a Wheatstone bridge. The electric current of the filament of the detector is 150 μA and the temperature is 423 K. Between the exit from the reactor and the entrance into the detector, the gases pass through a trap at 260 K (a steel pipe submerged in a solid–liquid mixture of NaCl–saturated water) in order to condense any trace of water that might be formed during reduction. The efficiency of the trap was verified by reducing a sample of nickel oxide (NiO BDH Chemicals Ltd.); no water signal was detected during this reduction. The temperature was measured with a thermocouple (chromel–alumel) located at the catalytic bed.

The equipment used for the analyses of the TPR signal is not as sophisticated as the one described by Mangnus et al. [6,7], as it consists of a TCD detector without additional FID and UV spectrophotometer. However, the signal can be unambiguously attributed to H_2S since the cold trap condenses the water; besides, methane cannot be produced during TPR because any carbon contamination would be eliminated during the reactivation procedure of the catalysts described in section 2.3. Additional XPS analysis [11] of all catalysts did not detect contamination compounds which could give rise to a signal in the TCD.

2.3. Procedures

Two hundred milligrams of catalyst, in particles ranging from 0.315 mm to 0.500 mm were put into a U-shaped quartz reactor used for the pretreatment and TPR measurements. Since the catalyst was in contact with air during its manipulation before starting the TPR, it was subjected to a reactivation in situ according to the following procedure: (i) drying with a flow of Ar ($1.66\ cm^3\ s^{-1}$) 423 K for 1 h, (ii) reduction–sulfurization with a flow of H_2S (15 vol%)/H_2 ($1.66\ cm^3\ s^{-1}$) at 573 K and 0.1 MPa for 1 h; (iii) cooling to room temperature with a flow of H_2S (15 vol%)/H_2; (iv) cleaning with Ar. To avoid oxidation of the catalyst when in contact with air, the transfer to the TPR equipment, of the reactor loaded with the activated catalyst, is carried out under Ar atmosphere.

After stabilization of the response of the detector, the flow of Ar is replaced by a flow of ultra pure H_2 (99.9999% from "Air Liquide") and the programmed temperature reduction process was started at 303 K.

The TPR measurements were carried out within a temperature range of 303 to 1180 K. The gradual increase rate of the temperature was $0.166\ K\ s^{-1}$ and the flow of H_2 was $3\ \ell\ h^{-1}$. The response factor of the detector was determined by injection of known amounts of H_2S ($0.25\times 10^{-3}\ \ell$ at 293 K and 0.15 MPa); this factor allows us to calculate the amount of H_2S produced during TPR from the area of the obtained profiles. The areas were measured with a planimeter taking the horizontal base line from 303 to 1073 K, since after this temperature the samples start to decompose.

3. Results

Figures 1, 2, 3 show the profiles obtained during the TPR of the three series of catalysts studied and table 1 shows the amounts of experimentally produced H_2S ($(H_2S)_e$). From the $(H_2S)_e$ values corresponding to monophasic catalyst MoS_2 or WS_2 ($Rm = 0.0$) and $PtS/\gamma\text{-}Al_2O_3$, $Rh_2S_3/\gamma\text{-}AlOOH$ or $PdS/\gamma\text{-}Al_2O_3$ ($Rm = 1.0$), the theoretical or expected amount of H_2S ($(H_2S)_t$) released by each biphasic catalyst was deter-

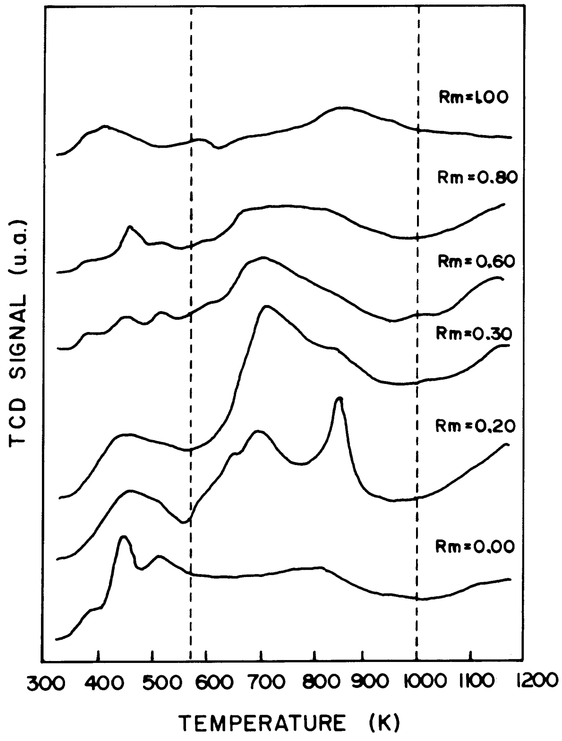

Figure 1. TPR diagrams of the Mo–Pt catalytic system.

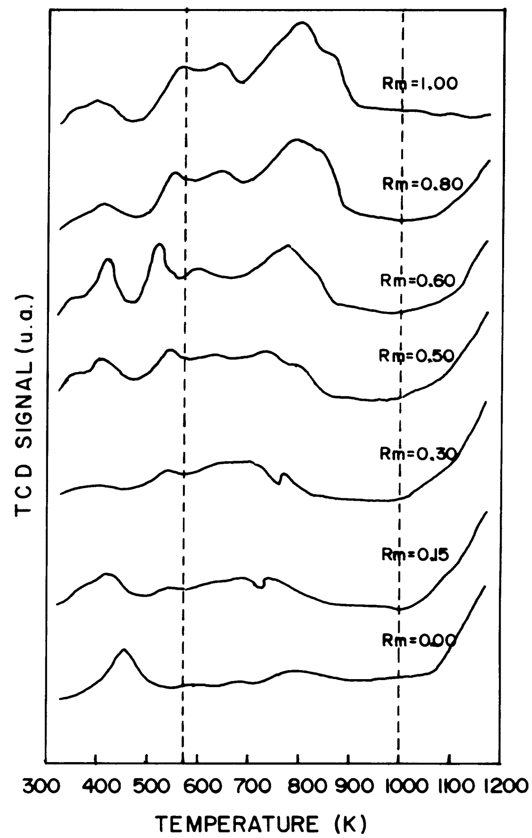

Figure 2. TPR diagrams of the W–Rh catalytic system.

mined as the arithmetic sum of the contributions of each of the phases according to the proportion in the mixture, as follows:

$$(H_2S)_t = (Rm)H_2S_{Rm=1} + (1 - Rm)H_2S_{Rm=0}\,.$$

Since the $(H_2S)_t$ was larger than $(H_2S)_e$, the additional H_2S produced was expressed as the excess percentage according the following equation:

$$\%H_2S = \frac{(H_2S)_e - (H_2S)_t}{(H_2S)_t} \times 100\,.$$

Figure 4 shows the excess of H_2S evaluated by TPR as a function of the composition of the mechanical mixtures. The maximum of H_2S is located at a different composition for each of the catalytic systems. This excess is especially noticeable in the Mo–Pt system for Rm around 0.3.

4. Discussion

4.1. Monophasic catalysts

MoS_2 (figure 1, Rm = 0.0). The first shoulder observed at 398 K can be attributed to physically adsorbed H_2S and the peak at 448 K to chemically adsorbed sulfur [12]. In the case of MoS_2, the presence of over-stoichiometric amounts of sulfur was detected by XPS [11]; this sulfur species detected on the surface does not correspond to elemental sulfur on the surface, since it would be catalytically hydrogenated during the reduction–sulfurization process. In fact, the existing literature reports that elemental sulfur is reduced at 550 K on a Mo/γ-Al_2O_3 catalyst [13]. The nature of the species of sulfur corresponding to the peak that appears at 448 K is not clear. This species is formed during the sulfurization and its amount is strongly dependent upon the composition of the mixture of H_2S/H_2 [14]. The signal above 600 K corresponds to the partial reduction of the small

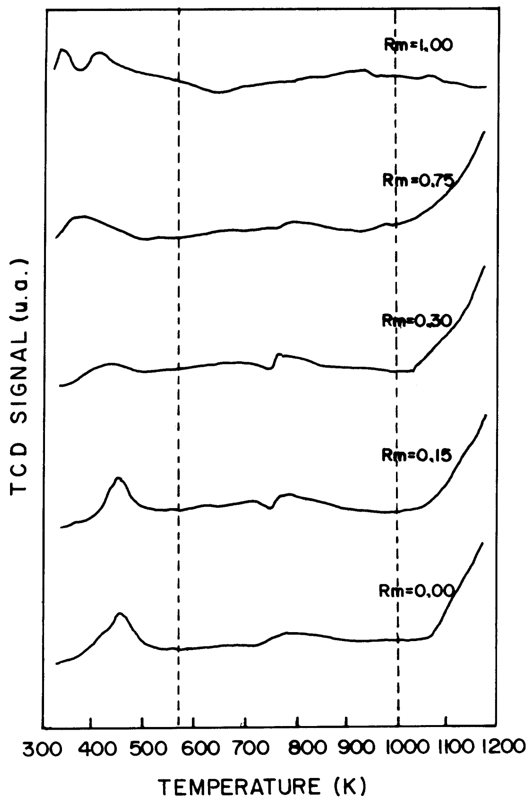

Figure 3. TPR diagrams of the W–Pd catalytic system.

Table 1
Total H_2S produced for each catalyst during the TPR for the three catalytic systems

Composition (Rm)	$(H_2S)_e$ [a] (μmol/mg of catalyst)		
	Mo–Pt	W–Rh	W–Pd
0.00	1.21	0.72	0.72
0.15	n.m.	0.80	0.72
0.20	1.85	n.m.	n.m.
0.30	2.57	0.90	0.65
0.50	n.m.	1.02	n.m.
0.60	1.14	1.18	n.m.
0.75	n.m.	n.m.	0.68
0.80	1.03	1.04	n.m.
1.00	0.56	0.97	0.41

[a] n.m.: not measured.

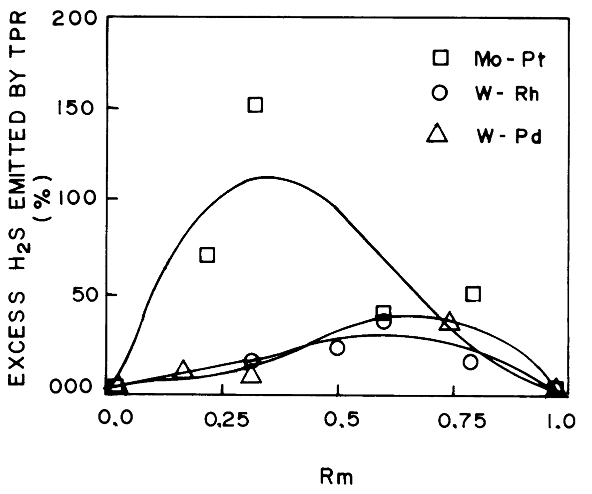

Figure 4. Excess H_2S emitted by TPR vs. catalyst composition, for the three series of mechanical mixtures.

MoS_2 crystals [12,15]. The profile of this curve is similar to others presented in literature [15]. The behavior of this catalyst during TPR was proposed by Li et al. [14]:

$$[MoS_2]_x\text{–}S \xrightarrow[<450\ K]{H_2} [MoS_2]_x + H_2S \qquad \text{(surface)}$$

$$[MoS_2]_x \xrightarrow[<673\ K]{H_2} [MoS_2]_x\text{–}H \qquad \text{(surface)}$$

$$[MoS_2]_x\text{–}H \xrightarrow[>573\ K]{H_2} [Mo_xS_{2x-1}]\square + H_2S \qquad \text{(surface)}$$

$$MoS_2 \xrightarrow[>600\ K]{H_2} MoS\square + H_2S \qquad \text{(mass)}$$

In these expressions, $[MoS_2]_x$ represents MoS_2 on the surface and □ represents an anionic vacancy.

WS_2 (figure 2, Rm = 0.0). The peak observed at 443 K can be attributed to a very reactive sulfur species, which is analogous to the species observed in MoS_2 at 448 K. Hydrogenation of a similar species has been observed in Ni, Fe and W sulfides [16–18]. The shoulder that starts at 1043 K can be attributed to the reduction of the bulk.

PtS/γ-Al_2O_3 (figure 1, Rm = 1.0). The shoulder with a peak at 420 K corresponds to physically adsorbed sulfur. The H_2S produced at higher temperature corresponds to the partial reduction of platinum sulfide; the literature states that it is decomposed in hydrogen atmosphere at 1073 K [19].

Rh_2S_3/γ-AlOOH (figure 2, Rm = 1.0). The H_2S produced during the TPR of this catalyst must correspond to physically adsorbed hydrogen sulfide (400 K), to chemically adsorbed hydrogen sulfide (573 K) and to the reduction of superficial species (800 K) successively, as the decomposition temperature of Rh_2S_3 in hydrogen atmosphere is 2173 K [19] and this temperature is not within the range of these experiments.

PdS/γ-Al_2O_3 (figure 3, Rm = 1.0). In the first region this catalyst presents two peaks of H_2S production (350 and 426 K). The first one can be attributed to hydrogen sulfide physically adsorbed during the reactivation. The second one can be attributed to a very reactive sulfur species, similar to the species observed in the other catalysts. The H_2S produced above 900 K corresponds to the decomposition of palladium sulfide, which starts at 873 K in hydrogen atmosphere [19].

4.2. Mechanical mixtures

In every mechanical mixture the experimentally measured total amount of sulfur (table 1) turned out to be higher than the $(H_2S)_t$ calculated by considering the contribution of each monophasic catalyst, which means that the superficial reduction is more intense in the biphasic catalyst than in the monophasic catalyst (Rm = 0.0 or 1.0). This observation is more evident in the mechanical mixtures with mass fractions 0.2 and 0.3 of the catalytic system Mo–Pt (figure 1). The increase in the superficial reduction implies the appearance of more anionic vacancies which are directly related to the sites of hydrogenolysis C–S and hydrogenation [20,21].

The presence of the excess H_2S percentage (figure 4) confirms the action of the noble metal (Pt, Rh or Pd) upon the increase of reactivity of molybdenum or tungsten sulfide in the presence of hydrogen.

In the literature there is no experimental evidence concerning the activation of hydrogen by noble metal sulfides and only the work dealing with hydrogen spillover (H_{SO} on Pt/MoS_2 catalysts [22]. However, it can be observed that the amount of synergy obtained with these mechanical mixtures [8,9] varies in parallel with the activation capacity of hydrogen on metallic Pt, Pd, or Rh as follows: Pt > Pd > Rh [21]. The results of the excess of H_2S evolved during TPR reported here show the same tendency.

It is also known that activated hydrogen (H_{SO}) considerably accelerates reduction of oxides [24,25]. In studies with mechanical mixtures of MoS_2 and Co_9S_8 or NiS or FeMoS, MoS_2/γ-Al_2O_3 and CoS_x/C, a similar acceleration is observed in the reduction of MoS_2 [26–30], therefore, TPR measurements support the interpretation about the important role that H_{SO} plays in these reductions [31].

These results show that one of the phases in the mechanical mixtures presents a stronger reduction compared to its reduction when alone. The studied systems deal with MoS_2 or WS_2, the only sulfides present in appreciable amounts (the weight content of PtS or Rh_2S_3 or PdS in the monophasic catalysts is lower than 0.2%, 5.0% and 0.2% respectively and their contribution to the formation of H_2S would be at the most 0.2–5.0% of the observed values). Göbölös et al. [16] carried out comparable TPR studies with conventional catalysts (Co–Mo, Ni–Mo, Fe–Mo) and found similar behavior.

Although not direct proof to exclude the formation of bimetallic sulfide due to the mechanical mixing procedure, fine analytical electron microscopy observation (TEM-EXAFX) never evidenced the presence of bimetallic sulfides. In addition, the low noble metal content of the oxide support as well as the large surface area of the alumina, tend to indicate that a large part of the noble metal should be located within the pores of the support avoiding any direct contact between the sulfides. On the other hand, the mixing of the two different components has been done in such a way (without mechanical grinding, just making a stirred suspension in a solvent) that it should avoid any contamination of one phase by the other.

5. Conclusions

– Noble metal sulfides increase the reduction of molybdenum sulfide or tungsten sulfide, apparently due to the action of activated hydrogen: H_{SO}.

– There is a close relationship between the reducibility of MoS_2 or WS_2 and the synergy observed in the catalytic reaction [8,9].

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