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Synergism in alumina-supported noble metals and molybdenum stacked-bed catalysts via spillover hydrogen in gas–oil hydrodesulphurization

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ABSTRACT

A study is made of Ru/γ-Al_2O_3//Mo/γ-Al_2O_3, Rh/γ-Al_2O_3//Mo/γ-Al_2O_3, Pd/γ-Al_2O_3//Mo/γ-Al_2O_3, and Pt/γ-Al_2O_3//Mo/γ-Al_2O_3 stacked beds, separated by SiO_2, in the gas–oil hydrodesulphurization reaction. Synergism between these beds is clearly detected. This synergism occurs in the absence of mixed phases. The results show that the presence of hydrogen spillover must be considered to explain the promotion effects in all HDS the reactors in which sulphides of Ru, Rh, Pd or Pt, and Mo are present.

1. Introduction

At present it has become necessary to exploit deeper layers of oil fields which contain a higher amount of refractory sulphur compounds resistant to hydrotreating. Furthermore, over the last years environmental regulations have become increasingly stringent, especially with respect to the maximum allowable sulphur content in fuels [1]. Therefore, it becomes necessary to develop new systems that offer better catalytic activity, selectivity and sulphur tolerance than conventional Co–Mo/γ-Al_2O_3, Ni–Mo/γ-Al_2O_3, and Ni–W/γ-Al_2O_3 catalysts [2]. To develop new catalysts it is essential to understand the origin of the synergism in the conventional catalysts, because although this synergism was reported for the first time more than 70 years ago [3], its origin is still controversial. As is well known, many theories have been proposed to explain the origin of the synergism, but now only two remain in effect: the theory of contact synergy or remote control model [4] and the CoMoS theory [5].

Since 2003 [6] in our laboratory we have been working under operating conditions that do not allow the formation of mixed phases, because we use three stacked beds: Co/γ-Al_2O_3, a separator, and Mo/γ-Al_2O_3. Therefore, the origin of the Co–Mo synergism observed in these systems can only be explained by the remote control model, via Hso. The good news is therefore that in real catalysts Co–Mo synergism can occur via the Co–Mo–S phase and via Hso simultaneously. We have seen that synergism via Hso depends on the nature of the Hso donor (initially Co and Ni) and the donor content (Co or Ni sulphides) [7]. In subsequent studies [8] it was verified that the synergy factor grows by (a) decreasing the reaction temperature; (b) decreasing the distance between Co and Ni sulphides; (c) decreasing the isoelectric point of the solid used as separator; (d) having a continuous surface—like a monolith impregnated with donor (D) and acceptor (A)—along which the migrating Hso moves, instead of "jumping" between particles; and (e) using alumina phosphate as separator between the D and A beds [9]. It was also found that no synergism is detected if SiC is used as a separator, suggesting that superficial –OH groups are necessary for the migration of the Hso from donor to acceptor. Recently, it has been shown that Mn, Fe, Cu, and Zn sulphides, in addition to Co and Ni, are able to generate Hso and to promote the Mo [10] in stacked beds like Mn//Mo, Fe//Mo, Co//Mo, Ni//Mo, Cu//Mo, and Zn//Mo. In all these cases the synergism has been attributed to the ability of metal sulphides (Mn, Fe, Co, Ni, Cu, and Zn) to generate Hso. Similarly, the Ru–Mo, Rh–Mo, Pd–Mo, and Pt–Mo pairs have also been studied as potential new catalysts [11–22] (see Table 1).

Table 1 shows clearly that the synergism results are controversial. In the Ru–Mo pair the synergic effect has been reported as negative [11], nil [12], and positive [11,14–18]; however, the Ru–Mo pair has been described mostly as positive. In the Pd–Mo pair the synergic effect has been described as negative [13–15], nil [12], and positive [16,18], while in the Pd–Mo pair it has been mostly described as negative. In the Pt–Mo pair the effect has been described only as nil [12] and positive [14,16–20]; nevertheless, the Pt–Mo pair has been reported mostly as positive. In the Rh–Mo pair the synergic effect has been described in two papers [16,21] and it was qualified as positive. In those studies in which the

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Table 1
Summary of synergic effect in N_M–Mo pairs (N_M = Ru, Rh, Pd, Pt).

Supported on	Reactant/reaction	Referred to Hso	Synergic effect attributed to	Synergic effect			Ref.
				Negative	Nil	Positive	
γ-Al_2O_3	Thiophene/HDS	No	Formation of mixed phase	Ru–Mo	–	Ru–Mo	[11]
Al_2O_3	Thiophene/HDS	No	Formation of mixed phase	–	Pt–Mo Pd–Mo Ru–Mo	–	[12]
HY zeolite	Dibenzothiophene/HDS	No	Formation of HxMoS_2 and S[PdH^+] hydride-like species in PdMo zeolites	Pd–Mo	–	–	[13]
γ-Al_2O_3	Dibenzothiophene /HDS	Yes	(a) Electron transfer, (b) generally might be Hso	Pd–Mo	–	Pt–Mo Ru–Mo	[14]
ASA	Dibenzothiophene/HDS Gas–oil/HDS	No	(a) Poorer dispersion and low surface exposure, (b) enhances molybdenum surface exposure in binary samples	Pd–Mo[a]	–	Ru–Mo	[15]
Al_2O_3	Thiophene/HDS, pyridine/HDN	Yes	(a) Experimental data do not argue in favor of or against the existence of such a mixed phase, (b) better dispersion	–	–	Pt–Mo Pd–Mo Rh–Mo Ru–Mo	[16]
γ-Al_2O_3	Thiophene/HDS	Yes	Hso, argue that the relatively low content of noble metal decreases the probability of formation of some kind of mixed phase	–	–	Pt–Mo Ru–Mo	[17]
γ-Al_2O_3	Dibenzothiophene/HDS	Yes	(a) Production of more reduced sites on the surface, (b) Dispersion	–	–	Pt–Mo Pd–Mo Ru–Mo	[18]
γ-Al_2O_3	Dibenzothiophene/HDS	Yes	(a) Formation of mixed phase, (b) Hso and (c) Dispersion	–	–	Pt–Mo	[19]
MSA	Thiophene/HDS	No	Positive effect of Pt on reducibility of the MoS_2 phase	–	–	Pt–Mo	[20]
γ-Al_2O_3	Dibenzothiophene/HDS	No	Interaction between Rh and Mo. It can be speculated that the phase containing Rh acts independently and promotes the active sites on Mo			Rh–Mo	[21]
γ-Al_2O_3	Dibenzothiophene/HDS	Yes	(a) Dispersion, (b) Hso	Pd-CoMo	Pd–NiMo	Ru–CoMo Ru–NiMo	[22]

[a] Only for HDS of DBT.

authors report a positive synergic effect, it has been attributed to (a) the formation of a mixed phase, (b) dispersion changes, and (c) the presence of Hso as summarized in Table 1.

Thus, the aim of this study is to know if there is synergism, via Hso, in the Ru–Mo, Rh–Mo, Pd–Mo, and Pt–Mo pairs in the absence of mixed phases. To prevent the formation of mixed phases, stacked beds Ru//Mo, Rh//Mo, Pd//Mo, and Pt//Mo are used.

2. Experimental

2.1. Sample preparation

Commercial noble metal catalysts (N_M) were used (ALDRICH). The N_M used were Ru (0.48%)/γ-Al_2O_3, Rh (0.47%)/γ-Al_2O_3, Pd (0.48%)/γ-Al_2O_3, and Pt (0.50%)/γ-Al_2O_3.

The support of the four commercial catalysts was the same, γ-Al_2O_3 from the same supplier. In all cases the metal was present in the metal form and not in the oxide form and the surface area of the catalysts was ~90 $m^2\ g^{-1}$.

As in previous studies [6–10], the Mo/γ-Al_2O_3 monometallic samples were prepared using $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Merck pa) as precursor, γ-Al_2O_3 BASF D10-10 (N_2 BET 212 $m^2\ g^{-1}$ and pore volume 0.500 $cm^3\ g^{-1}$) was used as support, and SiO_2 BASF D11-10 (BET 154 $m^2\ g^{-1}$ and pore volume 0.270 $cm^3\ g^{-1}$) was used for diluting the Mo/γ-Al_2O_3 bed and as bed separator in stacked beds. The Mo/γ-Al_2O_3 catalyst was prepared by wet impregnation in excess solvent using a rotary evaporator, dried for 12 h at 373 K, and calcined at 823 K for 4.5 h. The nominal metal content was close to 14%.

2.2. Reaction conditions

Determination of the catalytic activity in HDS was carried out in a stainless steel continuous-flow micro-reactor, under operating conditions similar to industrial ones: total H_2 pressure was 3 MPa, LHSV = 30 h^{-1}, GHSV = 3600 h^{-1}, reaction temperatures were 598, 623, 648 K, and a gas–oil (0.38% S) was used as sulphur in the liquid feed.

As shown in Fig. 1 the stacked bed was made as follows: the top bed consisted of N_M/Al_2O_3 (as Hso donor, D), the third bed was 1 g of Mo/γ-Al_2O_3 or N_M/Al_2O_3 catalysts (as Hso acceptor, A) diluted 1:1 by volume with SiO_2. To prevent the formation of a mixed

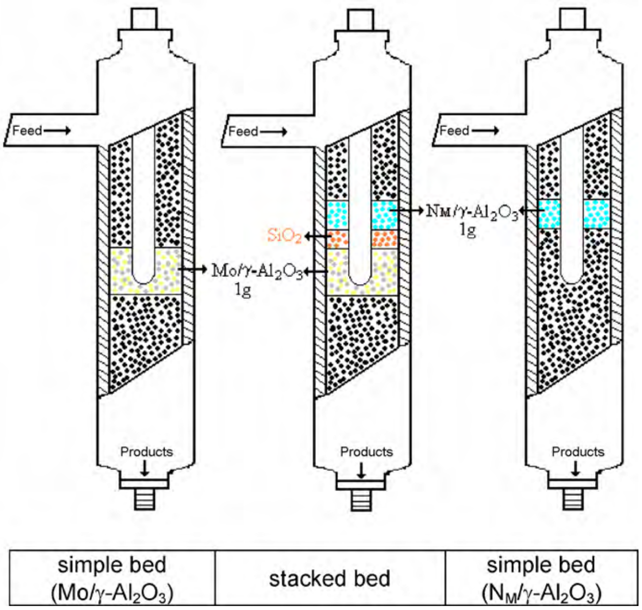

Fig. 1. Scheme with different ways to load the reactor.

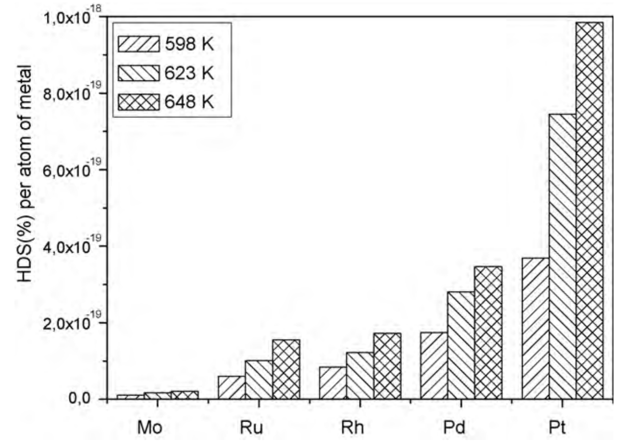

Fig. 2. Catalytic activity in HDS of M/γ-Al_2O_3 systems (simple beds) where M = Mo, Ru, Rh, Pd, or Pt, at three reaction temperatures.

Table 2
Catalytic activity and synergism factor in Ru//Mo stacked-bed system at different distances and with different separators.

Test	Catalyst	HDS (%)			Synergism factor		
		598 K	623 K	648 K	598 K	623 K	648 K
1	Mo	6.3	10.0	12.2	–	–	–
2	Ru	1.8	3.0	4.6	–	–	–
3	Ru + Mo	8.1	13.0	16.8	–	–	–
4	Ru//3-mm SiO$_2$//Mo	9.0	15.8	21.3	1.11	1.22	1.27
5	Ru//6-mm SiO$_2$//Mo	8.2	13.2	17.6	1.01	1.02	1.05
6	Ru//3 mm SiC//Mo	8.5	13.5	17.6	1.05	1.04	1.05

phase these beds were separated by 3 mm of SiO_2. The remaining space in the reactor was filled with SiC particles. Particle size in all the beds as well as that of SiC was between 0.84 and 1.19 mm.

Before the reaction, each system was submitted to an in situ sulphidation treatment during 4 h, at 623 K and 3 MPa, using a 7% solution of CS_2 in gas–oil.

The total sulphur liquid feed and effluents were determined using a LECO S-144DR analyzer with infrared detector. Catalytic activity was expressed as HDS (%) = $[(S_o - S)/S_o] \times 100$, where S_o and S correspond to the initial sulphur content and that after the reaction, respectively. To represent the stacked bed synergism we defined the synergism factor as $\%HDS_{(stacked\ bed)}/\%HDS_{(acceptor)}$, where $\%HDS_{(stacked\ bed)}$ is the activity of the stacked bed donor// acceptor and $\%HDS_{(acceptor)}$ is the activity of the Hso acceptor. Factors greater than 1 determined a synergistic effect between donor and acceptor.

The experimental conditions used in this study were proved [23] that the reactor works as trickled bed, without diffusion limitation.

3. Results and discussion

Fig. 2 shows that the HDS activity of Mo/γ-Al_2O_3, Ru/γ-Al_2O_3, Rh/γ-Al_2O_3, Pd/γ-Al_2O_3, and Pt/γ-Al_2O_3 single beds per atom of metal at three reaction temperatures follows the trend Mo $\ll$ Ru $\ll$ Rh < Pd < Pt. This trend is in close agreements with the results of Mangnus et al. [24] for Mo, Rh, and Pt metal supported on Al_2O_3, and those of Pawelec et al. [15] for Mo, Ru, and Pd supported on ASA. However, using other supports the trends are different; for example, supporting on carbon the trend is Pt < Mo < Pd < Ru $\ll$ Rh [25]; and in the case of the unsupported samples the trend is Mo < Pd < Pt < Rh $\ll$ Ru [26]. In brief, the trend of HDS activity of Mo, Pd, Pt, Rh and Ru depends clearly on the support used [27]. However, this trend may also depend on the feed used as well as on the activation method [27]. The HDS of refractory molecules such as 4,6-dimethyldibenzothiophene (4,6-DMDBT) will be favored in active phases that have more hydrogenation sites, which will be formed more easily in active phases that present high affinity for the adsorption of hydrogen. On the contrary, the HDS of molecules such as dibenzothiophene is favored in active phases that have more hydrogenolysis sites. This must be studied further.

Table 2 shows, first, that both Mo/γ-Al_2O_3 and Ru/γ-Al_2O_3 beds are active in HDS under the experimental conditions used in this study. From this standpoint, Ru//Mo stacked beds were different from previous ones in which the upper beds of M_D/γ-Al_2O_3 (M_D = Mn, Fe, Co, Ni, Cu, and Zn) are not active under the experimental conditions used [10]. For this reason in the present study the synergic effect will occur if the activity of the N_M//Mo stacked beds is higher than that of the sum of the activities of N_M + Mo single beds.

Table 2 shows that the HDS activity of Ru//Mo stacked beds (test 4) is clearly higher than the sum (test 3) of the HDS activity of Mo/γ-Al_2O_3 and Ru/γ-Al_2O_3 (tests 1 and 2): for example, at 648 K, HDS (%) is 21.3 and 16.8, respectively. Therefore these results prove that Ru–Mo synergism exists, even in the absence of mixed phase. Table 2 also shows that the HDS activity of Ru//Mo stacked bed separated by 6 mm (test 5) is only slightly higher than the sum (test 3) of the HDS activity of Mo/γ-Al_2O_3 and Ru/γ-Al_2O_3 catalysts (tests 1 and 2): for example, at 648 K, HDS (%) is 17.6 and 16.8, respectively. The experimental conditions used in test 5 and test 4 differ only in that the distance between the first and second beds is 6 mm and 3 mm, respectively. In test 5 the results suggest that no synergism is detected. These results show that conversion increases when the Ru//Mo distance decreases: for example, at 648 K, decreasing the distance from 6 mm to 3 mm the activity increases from 17.6% to 21.3%. This dependence of HDS conversion on the D–A distance proves that a sequential reaction (first on the Ru/γ-Al_2O_3 catalyst zone and then on the Mo/γ-Al_2O_3 catalyst) must be excluded because if such a mechanism occurred, the effect would not depend on the distance between the beds [8]. Finally, as expected from previous studies, test 6 in Table 2 shows that if SiC is used as separator no synergism is observed, because Hso needs terminal hydroxyl groups (silanol groups) for its displacement [7]. Thus, when the distance increases up to 6 mm or when 3 mm of SiC is used, no synergism is observed.

Table 3 summarizes the results obtained with Pt/Mo stacked beds in the same experiments shown in Table 2 for Ru//Mo. The results show that the HDS activity of stacked beds (tests 4) is clearly higher than the sum (test 3) of the activity of Mo/γ-Al_2O_3 and Pt/γ-Al_2O_3 (tests 1 and 2): for example, at 648 K, HDS (%) is

Table 3
Catalytic activity and synergism factor in Pt//Mo stacked-bed system at different distances and with different separators.

Test	Catalyst	HDS (%)			Synergism factor		
		598 K	623 K	648 K	598 K	623 K	648 K
1	Mo	6.3	10.0	12.2	–	–	–
2	Pt	5.7	11.5	15.2	–	–	–
3	Pt + Mo	12.0	21.5	27.4	–	–	–
4	Pt//3-mm SiO$_2$//Mo	14.1	24.7	33.6	1.18	1.15	1.23
5	Pt//6-mm SiO$_2$//Mo	12.4	21.5	27.9	1.03	1.00	1.02
6	Pt//SiC//Mo	12.4	19.2	27.7	1.03	–	1.01

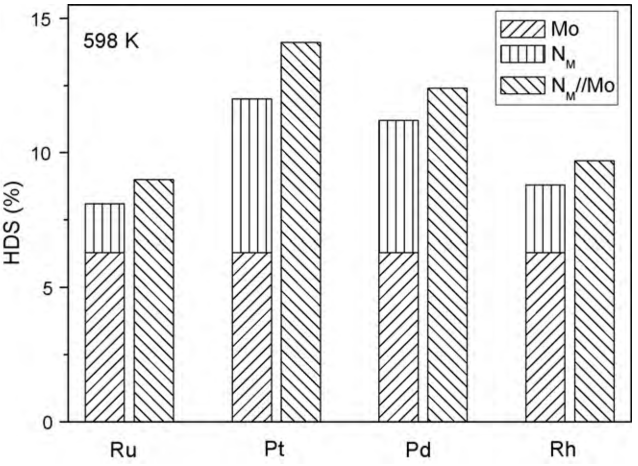

Fig. 3. Catalytic activity in $N_M/\gamma\text{-}Al_2O_3$//3-mm SiO_2//$Mo/\gamma\text{-}Al_2O_3$ (N_M = Ru, Rh, Pd, Pt) stacked-bed systems at 548 K.

Table 4
Catalytic activity and synergism factor in Pd//Mo stacked-bed system.

Test	Catalyst	HDS (%)			Synergism factor		
		598 K	623 K	648 K	598 K	623 K	648 K
1	Mo	6.3	10.0	12.2	–	–	–
2	Pd	4.9	8.0	9.8	–	–	–
3	Pd + Mo	11.2	18.0	22.0	–	–	–
4	Pd//3-mm SiO_2//Mo	12.4	19.0	26.0	1.11	1.06	1.18

Table 5
Catalytic activity and synergism factor in Rh//Mo stacked-bed system.

Test	Catalyst	HDS (%)			Synergism factor		
		598 K	623 K	648 K	598 K	623 K	648 K
1	Mo	6.3	10.0	12.2	–	–	–
2	Rh	2.5	3.6	5.0	–	–	–
3	Rh + Mo	8.8	13.6	17.2	–	–	–
4	Rh//3-mm SiO_2//Mo	9.7	15.2	21.9	1.10	1.12	1.27

33.6 and 27.4, respectively. Consequently, it can be concluded that Pt–Mo synergism exists, even in the absence of mixed phases. Equally, conversion increases when the Pt//Mo distance decreases, and no synergism occurs if SiC is used as separator.

In Tables 2 and 3 it is seen that when 3 mm separates D//A the synergism factor (Fso) increases with reaction temperature for both Ru and Pt sulphides. This trend differs from that seen when $Mn/\gamma\text{-}Al_2O_3$, $Fe/\gamma\text{-}Al_2O_3$, $Co/\gamma\text{-}Al_2O_3$ $Ni/\gamma\text{-}Al_2O_3$, $Cu/\gamma\text{-}Al_2O_3$, and $Zn/\gamma\text{-}Al_2O_3$ catalysts are used as promoters of the $Mo/\gamma\text{-}Al_2O_3$ catalyst [10]. This behavior must be studied further.

Fig. 3 shows HDS activity (%) values of the N_M + Mo and N_M//Mo (N_M = Ru, Rh, Pd, or Pt) systems at 598 K. For each metal, the first bar corresponds to the sum of the activities of N_M + Mo supported on alumina, while the second bar corresponds to the activity obtained by stacked beds separated by 3 mm of SiO_2. Fig. 3 shows synergism in the Ru//Mo, Rh//Mo Pd//Mo, and Pt//Mo pairs. This synergism can be attributed to hydrogen spillover in the first bed N_M (N_M = Ru, Rh, Pd, or Pt) which migrates to the MoSx bed, increasing the concentration of coordinate unsaturated sites.

Test 4 in Tables 2–5 shows that the synergism factors of Ru, Pt, Pd, and Rh sulphides on the HDS activity of Mo sulphide are around 1.10–1.20, depending on the metal and the reaction temperature; i.e., HDS activity increases around 10–20% if stacked beds are used. A crude estimation suggests that the synergic factors of Pd are slightly lower than those of Ru, Pt, and Rh. This slight difference may be related to the well-known higher capacity of Pd for H_2 adsorption [28], particularly at higher pressures. Thus, our results suggest that if the formation of mixed phases is prevented there is synergism via Hso in all the pairs studied, including Pd//Mo, on which the literature is controversial [12–15].

4. Conclusion

$Ru/\gamma\text{-}Al_2O_3$, $Rh/\gamma\text{-}Al_2O_3$, $Pd/\gamma\text{-}Al_2O_3$, and $Pt/\gamma\text{-}Al_2O_3$ catalysts promote the catalytic activity of $Mo/\gamma\text{-}Al_2O_3$ catalyst in stacked beds of Ru//Mo, Rh//Mo, Pd//Mo, and Pt//Mo in the absence of mixed phases, under reaction conditions like those of industry and in the reaction temperature range between 598 K and 648 K. The synergism appears to be slightly lower when using Pd than the other noble metals, probably due to the higher Pd–H_2 affinity. Ru//Mo, Rh//Mo, Pd//Mo and Pt//Mo synergism occurs via Hso, in agreement with the promotional effect reported for the Mn//Mo, Fe//Mo, Co//Mo, Ni//Mo, Cu//Mo, Zn//Mo, Mn//W, Fe//W, Co//W, Ni//W, Cu//W and Zn//W pairs. Thus, the presence of hydrogen spillover may be considered in the analysis of the results obtained in all reactors in which H_2 plus Ru, Rh, Pd, Pt, Mn, Fe, Co, Ni, Cu, Zn sulphides are present.

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