

# M<sub>D</sub>//Mo and M<sub>D</sub>//W [M<sub>D</sub> = Mn, Fe, Co, Ni, Cu and Zn] promotion via spillover hydrogen in hydrodesulfurization

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## A B S T R A C T

The promotion effect of Mn, Fe, Co, Ni, Cu and Zn sulfides on the hydrodesulfurization (HDS) activity of Mo and W sulfides, under experimental conditions like industrial ones, using staked beds, was studied. Synergism between staked beds in all the studied pairs, with a magnitude that leads a volcano curve with a maximum in Co and Ni sulfides was detected. Promotion was well explained by the formation of spillover hydrogen (H<sub>so</sub>) in the first bed (in which Mn, Fe, Co, Ni, Cu or Zn sulfides supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were located) that migrate to the second bed (in which Mo or W sulfides supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were located), 5 mm below.

### Keywords:

Spillover hydrogen  
Hydrotreating  
Promotion effect  
Volcano curves

## 1. Introduction

The literature concerning industrial hydrotreating processes, especially removal of sulfur (hydrodesulfurization, or HDS), is continuously announcing improvements. This concerns in particular activity and selectivity between HDS and hydrogenation (HYD). Hydrogenation of unsaturated bonds is a reaction that often plays a useful role in the HDS mechanism of certain molecules, but is not desired in general, because it leads to a decrease of the octane number. The influence of most of the parameters that controls the efficiency of industrial hydrotreatment concerning both the preparation and use of catalysts has been explored in detail. Molybdenum and sometimes tungsten sulfides have been identified as the efficient components of most catalysts. The crucial role of promoters for practical use has been recognized, especially that of cobalt or nickel. An enormous amount of knowledge has been accumulated in the course of the 90 years during which the processes has developed since the initial developments that have described in reference [1] was published. However, in spite of that, the fundamental reasons of the positive effect of these promoters are not fully understood. Essentially, this concerns two narrowly

linked aspects, namely the structure of the active sites at the atomic scale and the mechanism of the promoted reaction that crucially depends of the knowledge of this structure. The activation of hydrogen is certainly crucial, as indicated in particular by the fact that hydrotreating reactions must be conducted under moderate to high pressures (3–8 MPa).

The difficulty for determining the structure of the active site is encountered both in surface science and in theoretical chemistry studies. For models to be representative, the edge planes of the hexagonal sheets of pure MoS<sub>2</sub> should contain at least three underlying layers of the S–Mo–S 'sandwich' and extend along the edge at least over five Mo atoms, each linked to up to six sulfur atoms in total or partial distorted coordination. The clusters mentioned in literature do not meet these demands either with respect to underlying layers (other supports or different Mo–S arrangements) or with respect to size. Under the working conditions, the presence of adsorbed hydrogen and the removal of part of the surface sulfur atoms lead to an unsaturated coordination of Mo atoms. Theoretical chemistry studies indicate that the number of S atoms and the number of electrons available (partial degree of reduction of the surface) strongly influences structure and reactivity [2,3]. Adding doping atoms to these hypothetical structures just adds additional arbitrary choices with respect to their possible position. It seems that surface science or theoretical chemistry does not yet offer promising approaches.

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The remaining possibility would be to rely on direct measurements concerning the structure of real promoted catalysts. Only Mössbauer spectroscopy, and perhaps EXAFS-related techniques, are able to detect structural connections between Mo and Co or Ni. This has led to the “Co–Mo–S” concept developed by Topsoe et al. [4–8]. They explain the synergism between Co and Mo by the formation of Co–Mo–S like structures [8]. “In this model cobalt is atomically dispersed on the MoS<sub>2</sub> edges. Strictly speaking Co–Mo–S is not a phase from the physical point of view but rather a collection of different states of Co local structure” [9]. On the basis of *ab initio* calculations, Chianelli et al. [10] concludes that the strength of the Mo–S bond would be reduced by a Co substitution for Mo at the edges of MoS<sub>2</sub> labs, leading to coordinative unsaturated site (CUS) formation. A majority of authors say that their results and advances in hydrotreating catalysis are explained by the Co–Mo–S model [11]. In 1984 [12], some of the present authors added information concerning the association of Co and Mo in sulfided catalysts using electrophoretic measurements. When a mixture of Co<sub>9</sub>S<sub>8</sub> and MoS<sub>2</sub> is prepared by a homogeneous simultaneous precipitation procedure, a single species with specific characteristics is detected, indicating an association between Co and Mo in sulfided form. However, if an ordinary co-precipitation procedure is used, two phases (probably Co<sub>9</sub>S<sub>8</sub> and MoS<sub>2</sub>) are formed [12].

The present article corresponds to another approach to the origin of synergism, exclusively based on activity and selectivity measurements made under conditions corresponding to industrial operations using feedstocks employed in industry. The promoter and the active phases are separated by distances of more than 1 mm. This is considerable compared to atomic dimensions. Our approach is based on previous investigations that highlighted the special role of hydrogen. More precisely, the results considered the documented mobility of hydrogen and the special reactivity of spillover hydrogen (H<sub>so</sub>) when it interacts in different ways with surfaces. The synergism is explained by the remote control (RC) model developed by Delmon and co-workers [13–19] working with unsupported mechanical mixtures of MoS<sub>2</sub> and CoS<sub>x</sub> sulfides. The remote control model supposed that the spillover hydrogen (H<sub>so</sub>) that was formed on the promoter, called donor phase D (D = CoS<sub>x</sub>), migrated to the acceptor or catalytically active component A (A = MoS<sub>2</sub>), and modified the latter. In essence, the hypothesis was that H<sub>so</sub> created coordinative unsaturated sites on MoS<sub>2</sub>, able to catalyze either HDS or hydrogenation (HYD) reactions, according to the degree of coordination unsaturation. Models based on these hypotheses were verified by measurements of HDS and HYD activity, and other reactions, under moderate pressures with model compounds [20,21], where the proportions D/A were modified. This led to a change of the HYD/HDS selectivity. Concerning other reaction parameters, another quantitative model also accounted for data obtained in a rigorous way in a laboratory specialized in chemical engineering [22].

It is remarkable that even if there are two models to explain the origin of the synergism between cobalt and molybdenum in HDS and hydrotreating catalysts, both agree on the role of coordinative unsaturated sites present on the edges of the MoS<sub>2</sub> structure. The good news is, however, that CUS in conventional catalyst can be formed by two simultaneous mechanisms; (i) Co substitution for Mo at the edges of MoS<sub>2</sub> labs besides; and, (ii) by superficial removal of specific atoms on the edges of the MoS<sub>2</sub> crystallites.

In order to separate completely the partners in the synergism, we used successive staked beds of different composition in a continuous-flow reactor. In 2003, a conspicuous synergism between two separated staked beds of Co/SiO<sub>2</sub> and Mo/SiO<sub>2</sub> catalysts in the hydrodesulfurization of a gas oil at 325, 350 and 375 °C under classical operating conditions, was reported [23]. In

that study, Co/SiO<sub>2</sub> and Mo/SiO<sub>2</sub> single beds were separated by an intercalated bed (noted I later) of SiO<sub>2</sub> of 5 mm thickness. The formation of a new mixed phase must be excluded in that case. The remote control (RC) model was thus proven to explain the synergism. The effect could therefore be named “long distance remote control” (LDRC).

The same effect was detected using an intercalated bed of 5 mm of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> instead of SiO<sub>2</sub> between Co (or Ni)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> monometallic catalysts [24]. The Co//Mo and Ni//Mo synergism in staked beds increased if (a) the reaction temperature decreased; (b) the distance between both beds decreased; (c) the isoelectric point of the separator material decreased; and (d) a continuous surface, as that of a monolith, permitted the migration of H<sub>so</sub>, instead of jumping from particle to particle, as occurs in the case of beds made of powders [25]. As the location of the promoters in our experiments is different from the ones where the promoters are located on the same support as MoS<sub>2</sub>, it is necessary to examine whether the magnitude of the synergetic effects is compatible with our explanations. Based on the experiments using monoliths [25], an estimation of the effect of distance promotion on the overall promotion effect indicates that the relative contribution in commercial catalysts [24] of the promotion via H<sub>so</sub> is larger than 60%.

In other experiments, we investigated the consequences of the phenomenon in dibenzothiophene (DBT) hydrotreating, using Co//Mo and Ni//Mo staked beds [26]. The ratio cyclohexylbenzene (CHB)/biphenyl (BP) of the reaction products, or selectivity, was higher when using staked beds than with a single bed of Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The increase of HDS activity in comparison with the hydrogenation route corresponds to the predictions of the remote control explanation of synergism. Changes in the selectivity correspond to the fact that the H<sub>so</sub> formed on CoS<sub>x</sub> or NiS<sub>x</sub> in the first bed tends to increase the coordination unsaturation of the MoS<sub>2</sub> sulfide in the second bed, a conclusion reached in previous publications concerning changes of selectivity in hydrotreating [13–22].

The present article considers the possible role of other metal sulfides for producing spillover hydrogen and promoting HDS. Literature is relatively rich in data concerning promoting or, conversely, antagonistic effects due to the first and second or third series of transition metals in the periodic table [27–39] (some authors also call promoting and antagonistic effects “positive and negative synergism”). Authors agree about the positive synergetic effect in the Co–Mo and Ni–Mo pairs [27–29,31,34,37–39]. Other pairs containing Mo have shown positive synergetic effect in the hydrodesulfurization of model molecules (as thiophene and dibenzothiophene): Zn–Mo [31], Mn–Mo [31] Ho–Mo [32], Pb–Mo [32], In–Mo [32] Fe–Mo [34] and Ru–Mo [30] pairs; no effect was detected in Pt–Mo [27], Pd–Mo [27], Cr–Mo [27,28], V–Mo [27], W–Mo [27], Zn–Mo [27,28], Al–Mo [27], Ti–Mo [27], Bi–Mo [27] and Fe–Mo [32] pairs. The Cu–Mo [27,28], Ag–Mo [27], Pb–Mo [27], Sn–Mo [27] and Fe–Mo [27,32] pairs correspond to an antagonistic effect. Concerning HDS of industrial feedstocks, the positive synergetic effect in Ni–Mo and Co–Mo pairs [38,39] is the basis of innumerable applications, but no synergetic effect has been reported for the Cr–Mo [38], Mn–Mo [39], V–Mo [39], Fe–Mo [39] and Zn–Mo [39] pairs. A negative effect in the Cu–Mo [37] pair has been reported. In some cases, results disagree, according to the nature of reactants or reaction conditions. For example, in the case of the Fe–Mo pair, positive [27,34], none [34,38] and negative [34] effects have been reported. Similarly, for the Zn–Mo pair, a positive effect [31] or the absence of effect have been reported [27]. For the Cu–Mo pair, there is total agreement between different authors about the fact that the ‘synergetic’ effect is negative [27,37].

The objective of the present study is thus to evaluate possible promotion effects of elements  $M_D$  using  $M_D//Mo$  and  $M_D//W$  stacked beds [with  $M_D$  being Mn, Fe, Co, Ni, Cu or Zn sulfides].

## 2. Experimental

### 2.1. Catalyst preparation

As in previous studies [23–26],  $M/\gamma-Al_2O_3$  [ $M = Mo$  and  $W$ , as well as Mn, Fe, Co, Ni, Cu and Zn.] monometallic samples were prepared by wet impregnation, dried overnight at 100 °C and calcined at 550 °C for 4.5 h. As precursors, Mn, Fe, Co, Ni, Cu and Zn nitrates (Merck p.a) and ammonium heptamolybdate (Merck p.a) or ammonium tungstate (BDH p.a) were used. The support was  $\gamma-Al_2O_3$  BASF D1010 ( $N_2$  BET 213  $m^2 g^{-1}$  and pore volume 0.500  $cm^3 g^{-1}$ ) and, as “separator” I between beds,  $SiO_2$  from BASF D11-10 (BET 154  $m^2 g^{-1}$  and pore volume 0.270  $cm^3 g^{-1}$ ). The nominal and real metallic contents were near to 2.5 atoms  $nm^{-2}$  for Mn, Fe, Co, Ni, Cu and Zn, and 2.9 atoms  $nm^{-2}$  for Mo and W, respectively.

### 2.2. Reaction condition

The reactions with a single bed or a stack of three beds were carried out as in previous works in a continuous-flow micro-reactor build in stainless steel operated in the down-flow mode described formerly [23–26,40,41]. The 3-bed arrangement was made as follows: on top, the first bed contained 2 g of promoter (Mn, Fe, Co, Ni, Cu or Zn supported on  $\gamma-Al_2O_3$ ); the third bed (below the separator I) contained 1.0 g of active material (Mo or W supported on  $\gamma-Al_2O_3$ ). These active components were diluted 1:1 with  $SiO_2$ . The beds were separated by an intercalated bed I of 5 mm of  $SiO_2$ . The remaining space in the reactor was filled with SiC particles. The particle size in all beds as well as for SiC was between 0.84–1.19 mm. The stacked beds like  $Co/\gamma-Al_2O_3//SiO_2//Mo/\gamma-Al_2O_3$  will be indicated simply as  $Co//Mo$  staked beds.

Before the reaction, the catalysts were submitted to *in situ* sulfidation during 4 h, at 350 °C, using 7%  $CS_2$  dissolved in the gas-oil. The HDS reaction temperature was 325 °C, 350 °C and 375 °C; the total pressure was 3 MPa. A gas-oil containing 2700 ppm in S was used as reactant. Identical reaction conditions were used for single and staked beds. Under each reaction conditions, three samples of the reaction product were collected at intervals of 30 min. Consequently, the time to complete each experiment at the three temperatures was higher than 8 h. No significant drift in the analyses was detected, in conformity with previous experiments [42].

The total sulfur content in the liquid feed ( $S_0$ ) and effluents ( $S$ ) were determined using a LECO S-144 DR analyzer. The conversions were expressed as  $HDS (\%) = [(S_0 - S)/S_0] \times 100$ . For the synergism quantification, what we call the spillover efficiency factor or simply, a spillover factor ( $F_{so}$ ) was used:  $F_{so} = [\%HDS \text{ stacked bed} / \%HDS \text{ single bed}]$ .

## 3. Results

In conformity with other results, the  $Mo/\gamma-Al_2O_3$  catalyst is more active than  $W/\gamma-Al_2O_3$ , with  $HDS_{325^\circ C}$  values of 2.5% and 0.8% respectively [43]. Table 1 also confirms the general indications of literature recalled above. It shows that, in our experimental conditions, the  $M_D/\gamma-Al_2O_3$  catalysts are not active in HDS [24,25]. The most conspicuous result is that the HDS conversions for all stacked beds are higher than the HDS activity of the single beds. The experimental set-up being identical to that adopted previously, the discussion of the previous articles remains valid

**Table 1**

Effect on HDS of promoters (or donors) [ $M_D/\gamma-Al_2O_3$  ( $M_D = Mn, Fe, Co, Ni, Cu, Zn$ )] associated with active elements (or acceptors of Hso) [ $Mo$  (or  $W$ )/ $\gamma-Al_2O_3$ ] in staked beds  $M_D//A$

Beds	HDS (%), 325 °C		Fso, 325 °C	
	$M_A = Mo$	$M_A = W$	$M_A = Mo$	$M_A = W$
$M_D/\gamma-Al_2O_3$	0.0	–	–	–
$M_A/\gamma-Al_2O_3 = A$	2.5	0.8	–	–
$Mn/\gamma-Al_2O_3//SiO_2//A$	4.0	1.1	1.6	1.4
$Fe/\gamma-Al_2O_3//SiO_2//A$	6.2	2.6	2.5	3.3
$Co/\gamma-Al_2O_3//SiO_2//A$	7.1	3.3	2.8	4.1
$Ni/\gamma-Al_2O_3//SiO_2//A$	7.0	3.1	2.8	3.9
$Cu/\gamma-Al_2O_3//SiO_2//A$	6.2	2.4	2.5	3.0
$Zn/\gamma-Al_2O_3//SiO_2//A$	4.9	1.8	2.0	2.3

[24,25]. The synergism expressed by  $F_{so_{325^\circ C}}$  must be attributed to the action of spillover hydrogen generated by the single beds containing promoters. The promoting action of metal sulfides ( $M_D$ ) in HDS catalysts containing sulfides of Mo or W is not restricted to Ni and Co. These sulfides can also act as donors of Hso.

These results prove that Mn, Fe, Co, Ni, Cu and Zn sulfides can dissociate molecular  $H_2$  to form Hso. The promoting action can be explained in the same way as that of Co or Ni. Hso migrates to the surface of the  $MoS_2$  or  $WS_2$  sulfides, where it probably removes one or several S atoms located near the surface of  $MoS_2$  or  $WS_2$  slabs, leading to the creation of coordinative unsaturated sites.

The promoting activity likely increases with the amount of Hso emitted by the promoter. When *separated* from the active sulfides as in the present experiments, Fe and Cu come second to Co or Ni, followed by Zn and Mn. It should be emphasized that this conclusion does not infer that Fe, Cu, Zn or Mn could act as promoters in a conventional bimetallic catalyst, because these elements, during the preparation and activation of these catalysts, that intimately associate promoters with Mo or W, could undergo reactions with the latter and possibly form inactive species.

## 4. Discussion

The discussion must consider four different aspects: (i) comparison with the literature concerning potential promoters, (ii) magnitude of the synergetic effects, (iii) possible parameters influencing the promotion by spillover hydrogen and (iv) comparison with trends in HDS activity of elements in the periodic table.

### 4.1. Comparison with the literature concerning potential promoters

A remarkable result in Table 1 is the synergism of pairs  $M_D//Mo$  for which literature indicates that, according to different authors, either positive promotion or no effect at all has been detected in the corresponding bimetallic supported catalysts prepared in conventional ways. This is the case of the Mn–Mo, Fe–Mo, Zn–Mo and Cu–Mo pairs. The disagreement could be explained by the fact that, in conventional catalysts, the promoter covers the surface of the active sulfides in certain cases and not in our experiments [44,45]. A general explanation is simply that the promoter and the active elements are in close proximity and simultaneously involved in the preparation and activation. Differences in the preparation procedures could thus lead to catalysts of different surface composition and structure. In particular, the ability of the promoter to dissociate hydrogen could be suppressed. The formation or modification of the coordinative unsaturated surrounding of the active atoms could also be modified. This

cannot occur in our experiments in which promoter and active atoms are separated and the active part is always identical.

Of particular interest is the synergism detected in Co//W staked beds, because the literature agrees in indicating that cobalt does not act as a promoter in Co-W/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. There is apparently no Co-W/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> commercial catalyst. The absence of Co-W synergism has been explained by the fact that “CoS<sub>x</sub> particles tend to form Co<sub>9</sub>S<sub>8</sub> instead of Co-W-S” [46]. However, in staked beds, the formation of Co-W-S phase cannot occur, but promotion nevertheless occurs. Moreover, the intensity of the synergism (F<sub>so</sub>) in Co//W and Ni//W is similar. Still more interesting is the Cu//Mo synergism detected in staked beds, because all authors report that Cu depresses the HDS activity of Cu-Mo bimetallic catalysts. The modest Cu//Mo synergism between CuS<sub>x</sub> and MoS<sub>2</sub> sulfides, via H<sub>so</sub>, that our measurements indicate, seems to be largely compensated by another phenomenon in classical catalysts, that could perhaps be due to a coating or a sort of poisoning of the HDS sites by Cu. In summary, the disagreement between different authors concerning promotion by different elements can be explained by differences in the preparation procedures or differences in chemical properties between the potential promoters and Co or Ni.

#### 4.2. Magnitude of the synergetic effects

The magnitude of promotion factor F<sub>so325 °C</sub> in Co//Mo and Ni//Mo staked beds is modest (1–4) in comparison with effects (10–20) due to the presence of promoters in industrial catalysts or catalysts associating intimately promoters and active elements. Actually, supposing that the promotion effect is only due to spillover hydrogen emitted by the promoters, the difference should be much larger, because the distance between promoters and active phases differ considerably: several millimeters in staked beds compared to nanometers in conventional catalysts. Assuming diffusion rates to be proportional to differences in H<sub>so</sub> concentrations and inversely proportional to distances, F<sub>so325 °C</sub> should be about one million times higher in conventional catalysts than in staked beds. This could suggest that production and mobility of H<sub>so</sub> in conventional catalysts are considerably limited because of the complicated structure of materials containing two or several sulfided elements in close proximity. This could reinforce the suspicion that sulfides of different elements could contaminate each other (partially coat, poison or even make compounds) and thus alter their intrinsic properties [44,45]. This effect has been mentioned in Co-Mo catalysts [44,45]. The corresponding phenomena could deserve more investigations. In brief, it seems that the physical separation between sulfided promoters and active sulfides unveils an important effect in the activity increase of MoS<sub>2</sub> and WS<sub>2</sub>. This could suggest new approaches to the preparation of more efficient catalysts.

Table 1 shows that the magnitude of the spillover factor depends on the nature of the sulfide used as promoter or as active sulfide. The much higher value of F<sub>so</sub> found for M<sub>D</sub>//W than for M<sub>D</sub>//Mo in staked beds is surprising. This possibility strongly to promote the activity of WS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was not suspected. Nevertheless, this might be related with the lower bond energy for S-W than for S-Mo [47] and the corresponding facility to create CUS sites, with consequences for the adsorption of reactants and H<sub>2</sub>S desorption. The result could suggest special studies.

#### 4.3. Possible parameters influencing the promotion by spillover hydrogen

The promotion via spillover hydrogen is important in the range of temperature where moderately difficult HDS and hydrotreating

reactions are conducted industrially (up to 325–350 °C). The highest temperature at which the synergism is still observed, 375 °C, is the highest temperature where other reactions, like hydrocracking and cracking, begin to occur. Figures that will be presented later show that the magnitude of the synergism between promoter sulfides and active phases diminishes when the temperature increases. This has already been noted in promotion due to the action of spillover hydrogen and in a similar phenomenon concerning spillover oxygen in selective oxidation reactions, [15]. The explanation is that spillover is possible because the active species (here H<sub>so</sub>, or O<sub>so</sub> in oxidation) only exists in the adsorbed state. When temperature increases, its adsorption coefficient decreases, and the increase in the rate of dissociation of hydrogen, often found to be low when measured, apparently cannot compensate this increase, thus leading to an overall diminution of the effect.

Differences in the F<sub>so</sub> factor of sulfided promoters in our results could be attributed to differences in dispersion or sulfidation state of M<sub>D</sub> in M<sub>D</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples. The precautions we took, however, should limit these effects. One reason is that all the M<sub>D</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples have the same metal concentration (2.5 atoms. nm<sup>-2</sup>) and that this concentration being small, sintering is difficult. In addition, it has been reported that the transition metals used are totally sulfided when using nitrates as precursors under the experimental conditions employed in this study for sulfidation [48]. It is possible to speculate on differences in the crystallographic structures of the respective sulfides. We can notice, however, that Cr<sub>2</sub>S<sub>3</sub> and Ni<sub>3</sub>S<sub>2</sub> both have trigonal structure [49] but the promoter effect is clearly different. It is therefore logical to search for other causes for explaining differences in F<sub>so</sub> due to different promoters.

#### 4.4. Comparison with trends in HDS activity of elements in the periodic table

Figs. 1 and 2 show that the dependence between the F<sub>so</sub> of M<sub>D</sub>//Mo and M<sub>D</sub>//W pairs, respectively, and the metal position in the periodic table correspond to a volcano curve, with a maximum for metals of the VIII group, Co and Ni. A similar volcano curve was obtained by Harris and Chianelli [28] in M<sub>D</sub>-Mo unsupported bimetallic catalysts on the basis of quite different results. The promotion factor calculated by us from Harris and Chianelli activity results were included in Fig. 3. Considering that our F<sub>so</sub> values were obtained in staked beds while the curves obtained by Harris and Chianelli correspond to the activity of classical

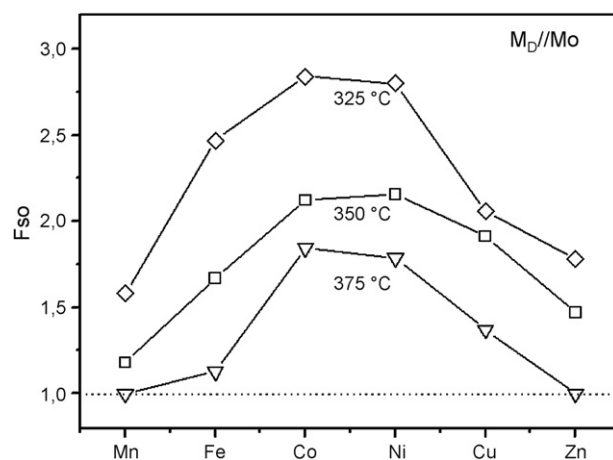


Fig. 1. Dependence of spillover factor (F<sub>so</sub>) of M<sub>D</sub>//Mo with the metal position in the periodic table.



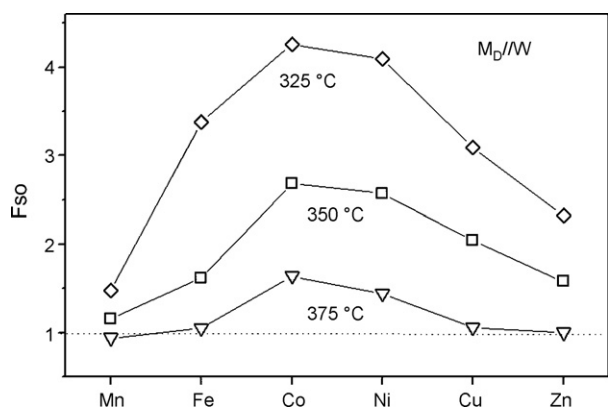


Fig. 2. Dependence of spillover factor ( $F_{so}$ ) of  $M_D//W$  with the metal position in the periodic table.

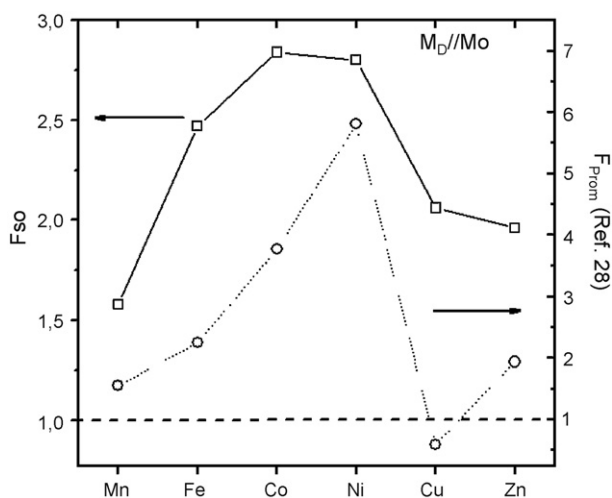


Fig. 3. Dependence of spillover factor ( $F_{so}$ ) of  $M_D//Mo$  with the metal position in the periodic table and the promotion factor calculated from results of Harris and Chianelli activity [28].

bimetallic catalyst, the similitude in trends suggests that the origin of the promotion effect in both systems is similar. Harris and Chianelli explained the trend they observed by an “electronic effect” related to the heat of formation and the %d character of the metal sulfides [50]. They reasoned that this would determine the M–S bond strength [10,51] and, consequently, the formation of sites active for the HDS reaction. Similarly, following our interpretation, the formation of Hso can also be related to “electronic effects” and the correlative modifications of the  $M_D$ –S bond strength.

The results in HDS show a striking parallelism with selective oxidations catalysis where a synergy exists between  $MoO_3$  and other oxides that were called donors (D) of spillover oxygen Oso. In that case, spillover oxygen migrates from D to  $MoO_3$ . The electronic properties of the donors have also to be considered. They dictate the dissociation of adsorbed  $O_2$  to ionic Oso adsorbed on surfaces as well as the strength of the interaction of the latter with surfaces (adsorption). These combined effects make that the intensity of the ionic character of D dictates the efficiency of the spillover process in promoting synergy [14]. This led to correlations similar to those proposed in HDS. Further studies examined other correlations and refined the interpretations [52] and led to explanations of the special reactivity of Oso in relation to the polarization of near-surface layers of donors [53].

It could be speculated that the results shown in the present article could serve for a detailed study on the genesis of Hso on sulfides and their action for generating active sites on  $MoS_2$  or  $WS_2$ .

## 5. Conclusions

A synergism occurs in HDS reaction between sulfided Mn, Fe, Co, Ni, Cu or Zn, on the one hand, and Mo or W sulfides, on the other hand, when these sulfides are physically separated from each other. The phenomenon occurs via Hso, even if the separation corresponds to millimeter distances, rather than the much smaller ones between promoter and active sulfides in ordinary catalysts. It is therefore impossible to ignore the contribution of a synergism via Hso in bimetallic HDS catalysts associating supported  $M_D$  ( $M_D = Mn, Fe, Co, Ni, Cu, Zn$ ) with Mo (or W)/ $\gamma-Al_2O_3$ . This result potentially increases the scientific impact of the ‘volcano curves’ discovered in the activity of catalysts associating  $M_D$  with Mo or W in usual supported bimetallic catalysts. The future development of new and more active and selective industrial hydrodesulfurization catalysts should certainly take advantage of the consequences of the intervention of spillover hydrogen in catalyst promotion. A new critical examination of old results and past interpretations concerning hydrotreating catalysts seems necessary.

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