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Hydrotreating catalysts, an old story with new challenges

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Abstract

Environmental constraints and energy saving concerns are strong driving forces for improving the quality of fuels. In particular, deep hydrodesulphurization and dearomatization of diesels are mandatory. Preparation or modification of optimized hydrotreating catalysts are related to scientific bases and precise knowledge of the real active sites during operating conditions. This paper will review the updated results on the most promising model attempting to explain the catalytic synergy in hydrodesulphurization and the recent evolution of the formulation of such catalysts.

Keywords: Review; Hydrosulfurization (HDS); Hydrosulfurization, deep; Diesel

1. Introduction

Hydrotreatment is an important group of processes in the petroleum refining industry and has been used for more than 40 years. Several reviews have been devoted to this subject during the last decades [1–37]. Additional specific references have been presented in the different European workshops on hydrotreating [38–42].

The treatments which are usually applied to oil feedstocks in order to make them suitable for utilisation in later processes can be divided in two main groups.

The first one is hydropurification corresponding to the removal of heteroatoms such as S, N, O, V, Ni, etc. from the organic molecules that contain them. It is the case of, respectively, hydrodesulphurisation (HDS) for sulphur, hydrodenitrogenation (HDN) for nitrogen, hydrodeoxygenation (HDO) for oxygen and hydrodemetallisation (HDM) for nickel, vanadium, arsenic, etc.

The second one is hydroconversion, which enables to change the molecular weight and structure of organic molecules. It is the case of hydrogenation (HYD), hydrodearomatisation (HDA), isomerisation (ISM) and hydrocracking (HCG).

Generally, several types of reactions occur during the treatment and, depending on the feedstocks and the aim, emphasis is laid on one or several directions.

The purification by hydrogen treatment is applied to all the fractions that come from the distillation except for the light ends. The elimination of these impurities is required for:

1. The protection of the catalysts used in latter stages of the refining process.
2. The abatement of NO_x and SO_2 emissions that could arise from the combustion of organic molecules.
3. The improvement of the properties of the final products issued from the refining (colour, smell, stability, ...).

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Table 1
Specifications for diesel fuels

	Present			Future		
	Sulphur (ppm)	Aromatics (wt%)	Cetane	Sulphur (ppm)	Aromatics (wt%)	Cetane
European Union	2000	no limit	47	500 (from 1996)	25	47
Sweden						
Class 1	10	5	50			
Class 2	50	20	47			
Finland	50	20	47–49			
USA	500	35	40			
California	500	10	48			
Japan	2000	no limit	40	500 (from 1997)	—	45

4. The valorisation of heavy feedstocks.
5. The possible future utilisation of biomass through the upgrading of pyrolytic bio-oil.

It appears that, in the very near future, environmental problems will be one of the driving forces of research and development of hydrotreating catalysts, in particular for diesel and gas oils. This is based on legal regulations already existing in some places, such as California, Sweden and Finland, or to be issued, such as in the European Union (EU) or Japan. As an example, Table 1 illustrates some of the proposed new specifications as compared to the present ones.

Another strong motivation to study and develop new performing hydrotreating catalysts, and which is far from industrial applications, deals with the development of renewable, non-fossil-fuel. An important fundamental programme has been supported by the EU since 1980. Among the different routes, gasification and pyrolysis of biomass are also proposed. As liquid fuels should give more promising development for potential use, pyrolysis was undertaken. The main problem, even when using flash pyrolysis, is that the quality of the final product is quite unsatisfactory. The main characteristics are illustrated in Table 2.

From this table, it is evident that the improvement of this pyrolytic bio-oil goes through the elimination of oxygen-containing molecules and the improvement of the H/C ratio in order to decrease the viscosity and increase the calorific content of the final product. HDO is then the adequate process which presents a great similarity with conventional HDS or HDN processes [43–50].

Table 2
Physico-chemical characteristics of pyrolysis oil [47]

Density		
	1.20	
Viscosity (25°C) Pa s	as such	dried
	0.110	15
Water content (%)	27	
Char content (%)	0.6	
HHV (MJ kg^{-1})	17	
Oxygen content	as such	dried
	48	37

All these reasons explain the increasing interest in hydrotreating catalysts and processes in the last years, and the appearance of new commercial catalysts which are claimed to offer an increased activity, selectivity and sulphur tolerance as compared with those of the last generation.

In spite of the intensive work devoted to the topic and the strong industrial interest for improved catalysts, a full understanding of the structure, the nature of the catalytic sites and how they work has not yet been reached so far.

It is clear that the identification of the active phase through different physico-chemical techniques, the proposal of a model aiming at correlating all the experimental data and in some cases to predict some new and unexpected behaviours, and a better understanding of the dynamics of the modification of transformation of the catalysts on-stream are some key parameters to improve the catalyst. We will underline the remote control model, its practical consequences and the recent advances in hydrotreating.

2. Identification of the active phase

2.1. Origin of the synergy and proposed models

All the industrial hydrotreating catalysts contain at least two elements from the Groups VI and VIII of the periodic table. The amount of active phase is roughly the same and a maximum activity, or catalytic synergy, is observed for a Co(Ni)/[Co(Ni) + Mo(W)] ratio at approx. 0.3, whatever the catalytic active phase and nature of the main reaction. This proportion always remains the same, even if some modification of reactivity is observed [7], as illustrated in Table 3.

Important progress has been made concerning the preparation and the characterisation of sulphided catalysts. However, the origin of the catalytic synergy between the two main elements of the active phase is the main problem for the scientific as well as the industrial development of hydrotreating catalysts. More than 17 theories or proposals have been made in order to explain this synergy. Table 4 summarises some of them.

It can be said that the main debate rests on two proposals: the structural association called 'CoMoS' (CoMoS phase) or 'NiMoS' and 'FeMoS' and the remote control theory, which is based on cooperation between two separate and well-identified single sulphided phases. We shall outline the main facts supporting both of them, underlining that the remote control model is not only demonstrated by numerous scientific experiments, but is able to predict, a priori, specific behaviours of the catalysts as a function of the experimental conditions of the reaction.

2.1.1. The 'CoMoS' theory

The success of the 'CoMoS' theory stands on the discovery of a special signal in Mössbauer Emission Spectroscopy [59,68–74], which was not ascribed to any of the cobalt phases known at that time, namely cobalt sulphide or cobalt aluminate. Topsøe et al. attributed it to a mixed 'CoMoS' phase, on which cobalt is located on the edges of the MoS_2 layered crystallites and presents a specific coordination. These signals, obtained on sulphided unsupported and sup-

Table 3

Hydrodesulphurisation [7]	Co—Mo > Ni—Mo > Ni—W > Co—W
Hydrodenitrogenation [7]	Ni—Mo = Ni—W > Co—Mo > Co—W
Hydrodeoxygenation [8]	Ni—Mo > Co—Mo > Ni—W > Co—W
Aromatic or olefin hydrogenation [1,12]	Ni—W > Ni—Mo > Co—Mo > Co—W

Table 4

Authors	Proposal	Reference
Lipsch and Schuit	Monolayer of oxide	[51]
Delmon	Contact synergy	[52,60–62,90,91]
Schuits and Gates	Oxysulfide monolayer	[53]
Voorhoeve and Stuiver	Intercalation of Co	[54]
Farragher and Cossee	Pseudo-intercalation	[55]
Aoshima and Wise	Structural defect	[56]
Jacquin	Mixed sulphide	[7]
Okamoto et al.	Metallic cobalt	[57]
Harris and Chianelli	Electronic effect	[58]
Topsøe	'CoMoS' phase	[17,59,68,70–74,77]
Delmon	Remote control	[60–62]
Chianelli and Daage	Rim/edge contribution	[35]
Ledoux	Specific configuration of Co	[63]
Prins, de Beer, Clausen and others	Support effect	[64–68]

ported catalysts, activated prior to reaction, were correlated to HDS catalyst activity. The authors illustrated that both the decrease of the Mössbauer signal and the appearance of the Co_9S_8 signal were correlated to the decrease of the catalytic activity. Further characterisation by extended X-ray absorption fine structure (EXAFS), analytic electron microscopy (AEM), electron paramagnetic resonance (EPR), X-ray photo-electron spectroscopy (XPS) and infrared (IR) studies of adsorbed NO probe molecules indicated that the architecture of the catalyst was identical to that of sulphided Mo/Al_2O_3, i.e., the active phase consisting of slabs of hexagonal MoS_2 layers having approx. 30 Å diameter and 5–10 slabs in each crystallite. The cobalt was detected as in the case of Co in alumina subsurface pseudo-aluminate form, and bulk Co_9S_8 – depending on the composition and preparation conditions of the 'CoMoS' phase.

However, some important drawbacks have been observed. The most important fact is that the 'CoMoS' phase decomposes during the catalytic reaction [75–79]. This suggests that the so-called 'CoMoS' phase present in fresh activated sulphided catalysts is the precursor of the real active phase. This may explain the difficulties of a well-defined characterisation, since it means that it would be necessary to investigate the physico-chemical characteristics of the catalysts after stabilisation of the active phase under high pressure reaction, obviously avoiding any further transformation or reoxydation by contacting the catalyst with air. The second point is that the Mössbauer spectroscopy signal attributed to the 'CoMoS' phase should be interpreted with much care, since it has been demonstrated that the same signal appears in catalysts without Mo [79–81]. This is especially the case for Co supported on carbon catalysts, which present an important HDS activity. This may be explained by a very high dispersion of the cobalt in the precursor state. A structural promoting effect was also recently proposed [67], for explaining the increase of activity of non-supported CoMo catalysts containing high bulk concentration of the Co_9S_8 phase.

The third experimental evidence suggesting that the 'CoMoS' phase might not be the stable active species is obtained by a careful study of mechanical mixtures of solids of the 'CoMoS', 'NiMoS' or 'FeMoS' phase with bulk Co_9S_8 and supported noble metals [78,82–85] demonstrating that the hydrogen activating phase promotes the 'CoMoS' phase. In addition, the synergy is obtained for both HDS and HYD and the synergy may be tuned by proper adjustment of the mechanical mixture composition.

2.1.2. *The remote control mechanism*

The second proposal seems more realistic today for explaining the formation of the active sites, the modification or the tuning of these sites during the catalytic reaction. It is also able to predict some unexpected behaviour of the catalysts. It has been proposed and developed by Delmon [28,30,32,60–62,86]. Let us mention that this mechanism has also been successfully developed in selective catalytic oxidation [87–91].

It is based on the proposal that the activity and selectivity of the optimised solid are related to the presence of two distinct phases, and that a contact synergy between these two separate phases occurs during the catalytic reaction. A remote control of the active phase located on the hexagonal MoS_2 (or WS_2) crystallite is exerted by the second phase which is able to activate hydrogen. The activating hydrogen solid, called donor phase, produces hydrogen 'H_{so}', which 'spills over' onto the acceptor. The main role of this activated hydrogen is not to participate directly to the hydrogenolysis or HYD reaction, but to create or modify the catalytic active site. We have shown [92] that, in the same way as noble metals, Co_9S_8 may activate hydrogen. The spilled over hydrogen then partially reduces the molybdenum sulphide phase. XPS of non-supported Co–Mo catalysts shows that the maximum of the catalytic activity corresponds to the decrease of the oxidation state of the Mo species [93]. The binding energy of the Mo corresponds to a lower value of the Mo^{4+} cation. Two additional proofs of the formation of activated hydrogen and modification of the surface of MoS_2 have recently been demonstrated [94,95]. Chu and Schmidt [95] have observed, using STM–AFM in quite severe conditions, that the molybdenum sulphide surface, in particular the edges of the hexagonal crystallites, is partially destroyed by hydrogen and that sulphur is removed. This effect is strongly enhanced when a hydrogen activating metal, i.e., Co or Ni, is present.

The phenomena of reduction of the surface of Mo may be illustrated in the following way (Fig. 1).

The remote control theory assumes that, depending on the reduction state of the molybdenum (or tung-

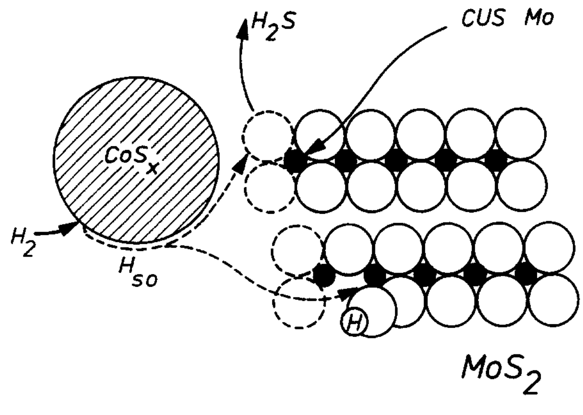

Fig. 1. Schematic representation of the remote control model: formation of HYD centres (CUS Mo) and of hydrogenolysis carbon-heteroatom bands (MoSH neighbouring a CUS Mo) by action of hydrogen spillover (H_{so} on the edges of MoS_2) [28].

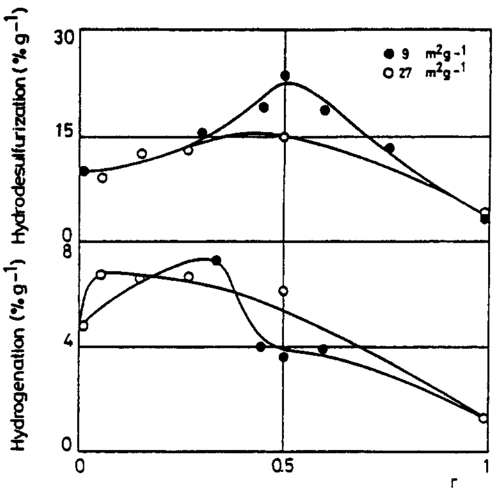

Fig. 2. Catalytic activities in (a) HDS and (b) HYD of samples prepared by mechanical mixtures of one MoS_2 batch with cobalt sulphides of two different specific surface areas [96].

sten) cation, two kinds of activated species are promoted by fine tuning of the coordination state of the acceptor phase. If sulphur atoms are removed, a triple unsaturated coordination site (CUS) is created which is a HYD centre. Upon more severe reduction, a MoSH group neighbouring the triple unsaturated atom is created. This centre could be responsible for the HDS activity [30].

A very large number of experiments have been done in order to verify this mechanism, both on industrial and model catalysts. The most convincing deal with unsupported sulphided solids, in particular with mechanical mixtures. In this case, care has been taken in order to avoid any side effect due to contamination or formation of mixed-phases during the preparation. For that, the single-phases were dropped into *n*-pentane, the suspension was then stirred and the solvent evaporated. Mechanical grinding was not used. Proofs of the remote control mechanism have been demonstrated with different mixed sulphides and for different hydrotreating reactions (HDS, HDN, HDO, HCG) always involving both hydrogenolysis and HYD reactions.

We shall illustrate that a catalytic synergy is present when (1) Group VI and Group VIII sulphides are mechanically mixed and (2) even that the so-called 'CoMoS', 'NiMoS' or 'FeMoS' phases can be promoted by an additional activating phase. Furthermore, we shall also highlight that the same behaviour is obtained with other activating hydrogen agents, such as (3) noble metals, and (4) that the number of contacts increased the synergy. Finally, we shall also show that (5) the maximum of the synergy can be changed as a result of the interconversion of the hydrogenolysis-HYD sites, and (6) we shall also give some new proofs of the spill-over hydrogen.

The cooperation between two different sulphide phases prepared by mild mixing has been demonstrated with cobalt, nickel and iron sulphides.

Fig. 2 illustrates the HDS and HYD activities of mechanically mixed MoS_2+Co_9S_8 [96]. The two series have been obtained with two Co_9S_8 samples prepared in such a way that they have different surface areas. In this way, it may be hoped that the number of contacts between the two sulphided phases will be different. It can be noted that the remote control model predicts such a behaviour. Fig. 3 illustrates the theoretical shift in the position of the synergy for the two reactions as a function of the number of contacts between the two separate phases of the biphasic catalyst.

In mechanical mixtures, the highest synergy does not correspond to the Co/Co+Mo ratio of 0.3, which is used in industrial. This is simply explained by the fact that (1) the dispersion of the sulphides are not the same in bulk sulphides than in alumina supported catalysts, and (2) the number of contacts between the two different phases is not optimal. In addition, assuming

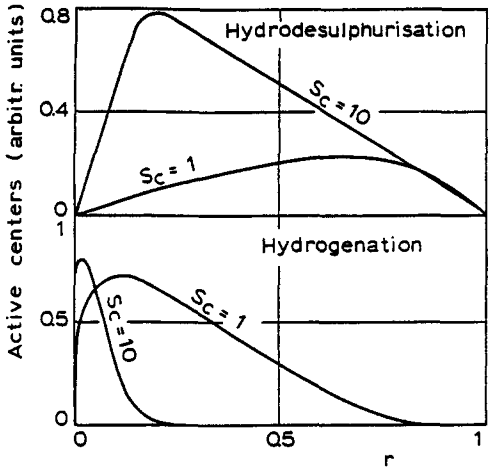

Fig. 3. Theoretical influence of the surface area of Co_9S_8 (Sc) on the catalytic activities of mechanical mixtures of Co_9S_8 and MoS_2 predicted by the remote control theory. The curves give the number of active sites for a series of catalysts prepared with a Co_9S_8 of surface 1 and for a series prepared with a Co_9S_8 of surface 10 [60].

the interconversion of HDS–HYD sites, the relative concentration of both sites should depend on the efficiency of the spill-over hydrogen and thus on the Co/Mo ratio. However, when the Co_9S_8 concentration increases too much, it tends to reduce or to be self-reduced, decreasing its ability to produce H_{so}. On the other hand, under these conditions, the amount of acceptor MoS_2 phases diminishes, leading to a very drastic decrease of the potential activated centres.

Using sophisticated physico-chemical characterisation techniques, it was never possible to observe, in mechanical mixtures, the formation of new mixed phases. However, one criticism was related to the potential contamination of MoS_2 with traces of Co (Ni or Fe) leading to the formation of the mixed 'CoMoS' phase. In order to avoid this phenomenon, or at least to decrease it drastically, mechanical mixtures of Co_9S_8 supported on carbon and MoS_2 supported on alumina were obtained using the same experimental protocol. An important synergy both in the HDS of thiophene and HYD of cyclohexene at 573 K and a total pressure of 3 MPa was observed [97] (Fig. 4).

In the same way, in order to prevent any contact or contamination of the MoS_2 by the promoting Co (or Ni) phase, mechanical mixtures of Co- or Ni-exchanged Y zeolites with MoS_2 were also prepared.

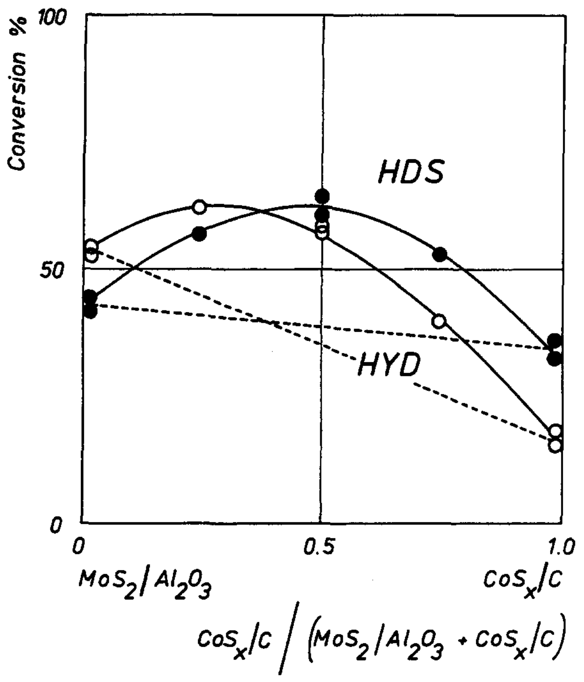

Fig. 4. Synergy between mechanical mixtures of CoS_x/C and MoS_2-γAl_2O_3 at 573 K and 3 MPa total pressure.

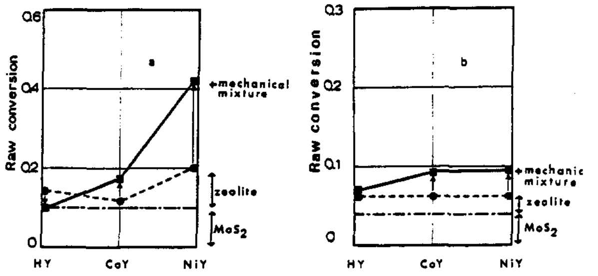

Fig. 5. (a) HDS and (b) HYD activity of mechanical mixtures (*n*) of MoS_2 and Co, Ni exchanged zeolite. The horizontal broken line represents the measured activity of a quantity of pure MoS_2, equal to that contained in the sample. The arrows correspond to the increase of activity due to the mechanical mixture.

Both the CoY+MoS_2 and NiY+MoS_2 biphasic solids also present a synergy [96] (Fig. 5).

The same phenomenon was observed in HDN reaction, but the mechanism is more complicated since it assumed [28,98–101] that three types of catalytic sites are involved – HYD, breaking of the C–N bond by reaction of hydrogen, i.e., hydrogenolysis, and rupture by acid catalysis (probably similar to

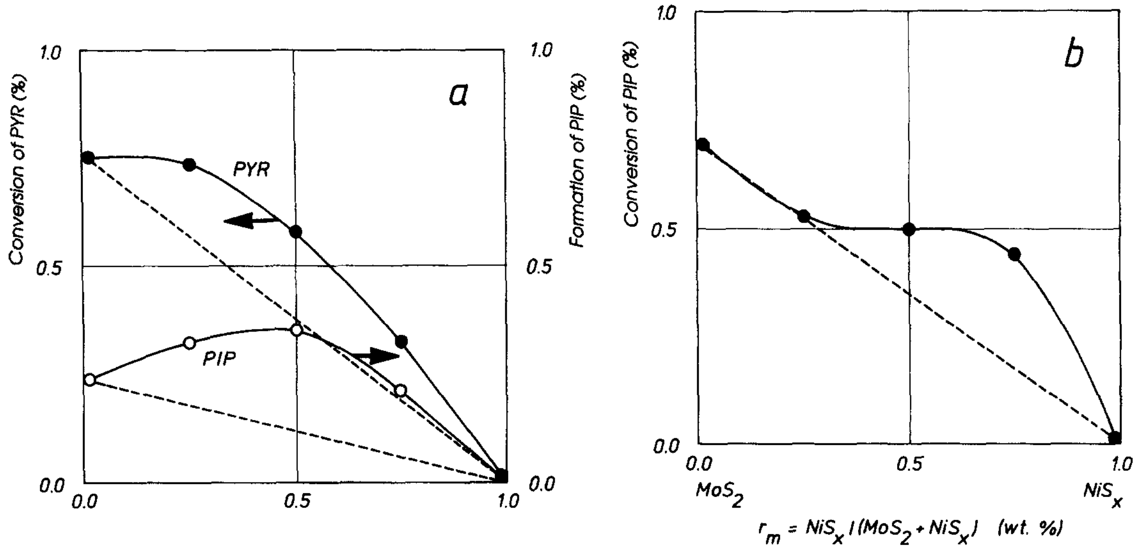

Fig. 6. Synergy due to mechanical mixture of NiS and MoS_2 in HDN reaction (T=573 K, 5 MPa): (a) conversion of pyridine and yield of piperidine; and (b) conversion of piperidine reacted alone.

β-elimination or nucleophilic substitution) which also influence the entire HDN reaction. In order to understand the HDN reaction, we simplified the catalyst using unsupported biphasic catalysts, eliminating or at least drastically decreasing their acidity. The NiS_x and MoS_2 were prepared in the same way as previously described, namely, suspended in n-pentane, agitated and dried. The reaction of pyridine and piperidine at 573 K and 5 MPa total pressure was studied in continuous dynamic flow reactor. In order to keep the catalyst in the sulphided state, dimethyl disulphide (2.2 wt%), which produces H_2S during the reaction, was added to the feed. The results are illustrated in Fig. 6 [28,101].

A synergy was observed in this case. The intensity and maxima of the synergy was different for the HYD and hydrogenolysis of the C–N bonds. Let us also remark that, when piperidine reacted alone, the position of the maximum of synergy is modified. This behaviour, not yet fully explained, could be related to differences between adsorption coefficients of the different molecules, as already suggested [98–100] in the case of aniline, indole, pyridine and the partially hydrogenated intermediate of reaction.

In spite of the care taken during the preparation of the mechanical mixtures in order to avoid any contamination of the acceptor phase by the donor phase, and a possible formation of the mixed phases, one can always suspect that a decoration of the edges of the hexagonal structure of the sulphided layer is possible. Two sets of experiments undoubtedly support the remote control mechanism due to the H_{so} spillover in biphasic catalysts. It has been shown [33,84,102] that an important synergy is observed, both in HDS of thiophene and HYD of cyclohexene, when well-prepared mixed phases 'CoMoS', 'NiMoS' or 'FeMoS', prepared by the HSP method [31] are mechanically mixed with a hydrogen activating sulphided donor phase (Fig. 7).

In addition, it seems that there are some indications that the pure Co_9S_8 phase accelerates the decomposition of the mixed '*Me*MoS' (*Me*=Co, Ni, Fe).

Another evidence of the relevance of the biphasic nature of the most active phases was recently presented by Inamura and Prins [67] (Fig. 8).

These authors prepared cobalt containing MoS_2 catalysts by impregnation of pure MoS_2 obtained by decomposition of $(NH_4)_2$ MoS_2 at 673 K with cobalt acetate in acetone. The suspension was refluxed under stirring at 325 K for 5 h under N_2 and then evaporated to dryness. The solids were then resulphided in 10% H_2S/H_2 at 393 K for 1 h, and then at 673 K for 2 h.

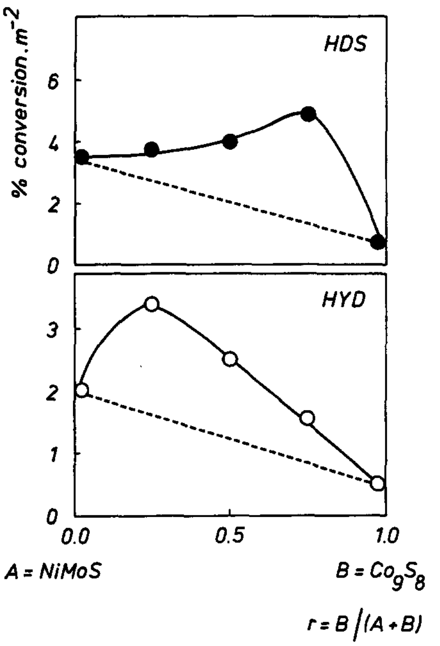

Fig. 7. Synergy between Co_9S_8 and 'NiMoS' phase (T=623 K, 3 MPa).

The rate of thiophene HDS at atmospheric pressure at 593 K reveals two consecutive increases as the cobalt content of the catalyst increases. If the first increase at low cobalt concentration could be due to the decoration of the MoS_2 edges by the cobalt ions, this should correspond to the saturation of the edges of the molybdenum sulphide. For higher cobalt concentration, it is impossible to accommodate a larger content of the promoter, and then impossible to speculate an increase of the electronic promoting effect. The authors [67] suggest that the second increase in activity could be attributed to a support effect, i.e., a higher dispersion or accessibility of MoS_2, since the Co_9S_8, clearly detected by XRD, would act as support of some small crystallites. The remote-control mechanism can also easily explain these experimental results, through a fine tuning of the HDS sites by activated hydrogen in this biphasic system.

More evidence supports this model. The role of the donor phase, sulphided Co or Ni, being to produce activated hydrogen, any activating hydrogen compound should improve the intrinsic activity of the acceptor phase. Noble metals are well known as activating hydrogen solids. It has been shown [33,82,83,85] that Pt, Pd and Rh may act as donors in hydrotreating reactions.

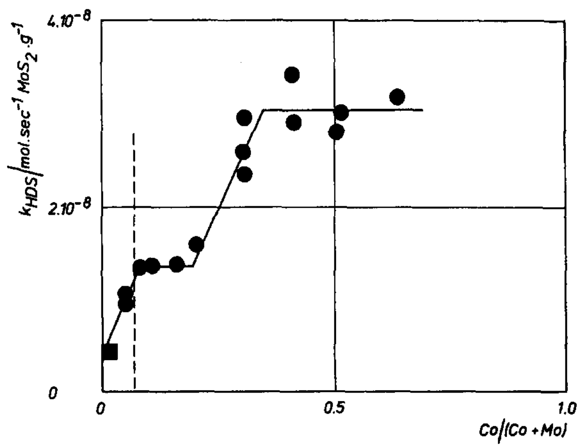

Fig. 8. Rate constant k''_{HDS} normalised to the MoS_2 content in catalysts prepared by impregnation of bulk MoS_2 solid with $Co(NO_3)_2{\cdot}6H_2O$ in acetone [67].

In the following experiments, mechanical mixtures (using the same aforementioned procedure) of pure MoS_2 or WS_2 with Pt, Pd and Rh supported on alumina have been tested in HDS and HYD reactions. The Figs. 9–11clearly show an important synergy in HDS reaction for the three systems, except for the HYD of cyclohexene, which is not affected by the presence of Pd when mixed with bulk WS_2. It is also to be underlined that the position of the maximum of

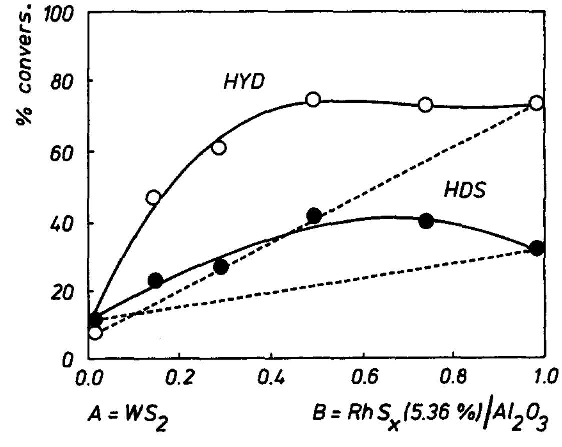

Fig. 9. Synergy between $RhS_x/\gamma\text{-}Al_2O_3$ and WS_2 (T=573 K, 3 MPa).

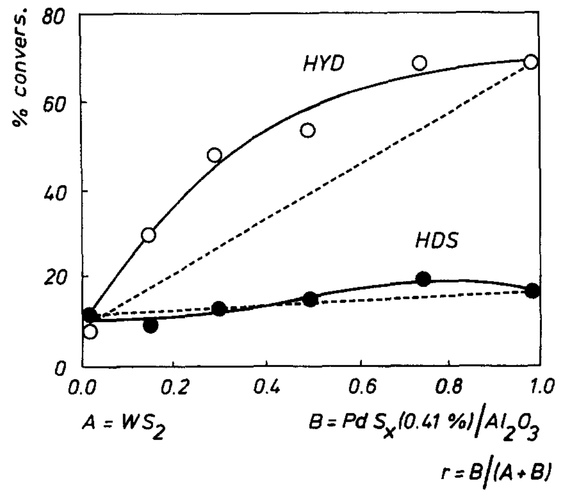

Fig. 10. Synergy between Pd/S_x-γ-Al_2O_3 and WS_2 (T=573 K, 3 MPa).

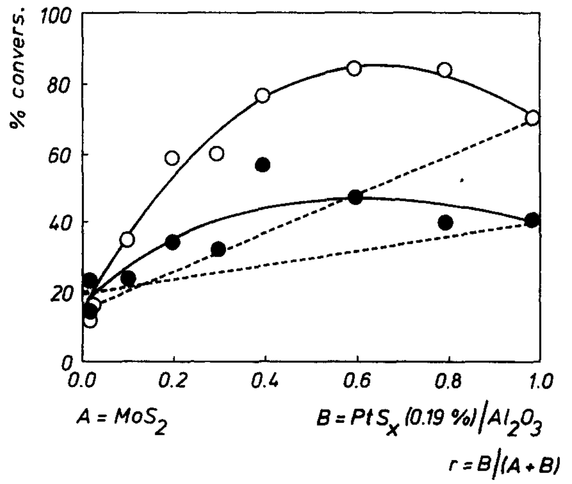

Fig. 11. Synergy between PtS_x/γ-Al_2O_3 and MoS_2 (T=573 K, 3 MPa).

activity (or the synergy) is not constant for all the studied biphasic compounds. The other observation is that the noble metals, contrary to cobalt, nickel or iron sulphides, present by themselves a high catalytic conversion. This latter point should be taken into account for the development of the new generation of catalysts with improved activity in order to fit the demand for cleaner fuels.

As it has been shown that the remote-control model is strongly established, one would guess that, if a reservoir of hydrogen is present, the efficiency or the intensity of the synergy should increase by increasing the contacts between the two separate phases. Obviously, in the experiments described, we do not try to improve this parameter. On the contrary, we try to avoid any strong contact in order to decrease any potential solid state formation of the mixed phase. This means that the model unsupported mechanical mixtures are far from the optimal architecture of the real catalyst. However, it has been demonstrated that the catalytic activity on one MoS_2–Co_9S_8 mechanical mixture may be improved by just improving the contact between the phases. The Fig. 12 illustrates this behaviour [96]. Compacting at different pressures before running the activity measurement of a biphasic mixture at one Co/Mo ratio improves the activity. This seems to indicate that the closer the individual sulphides, the higher the conversion. This is explained by the increasing ease of migration of the activated hydrogen.

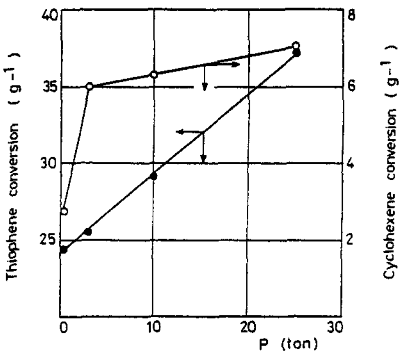

Fig. 12. HDS and HYD activities of bulk sulphided mechanical mixture of Co_9S_8 and MoS_2 as a function of the compacting pressure.

The fine tuning of the active site through hydrogen spillover and the interconversion of the HDS–HYD sites, which imply a dynamic process, is also taken into account with the remote control model. It is admitted that H_2S strongly decreases the HDS activity or accelerates the hydrogenolysis of the C–N bonds [15]. Pirotte [86], using the same model catalyst, namely the mechanical mixture of Co_9S_8 and MoS_2, activated either by hydrogen or argon–hydrogen sulphide mixture (15% H_2S) at 673 K for 4 h demonstrated that the strongly reduced molybdenum sites act as HDS sites, while the less reduced ones promote the

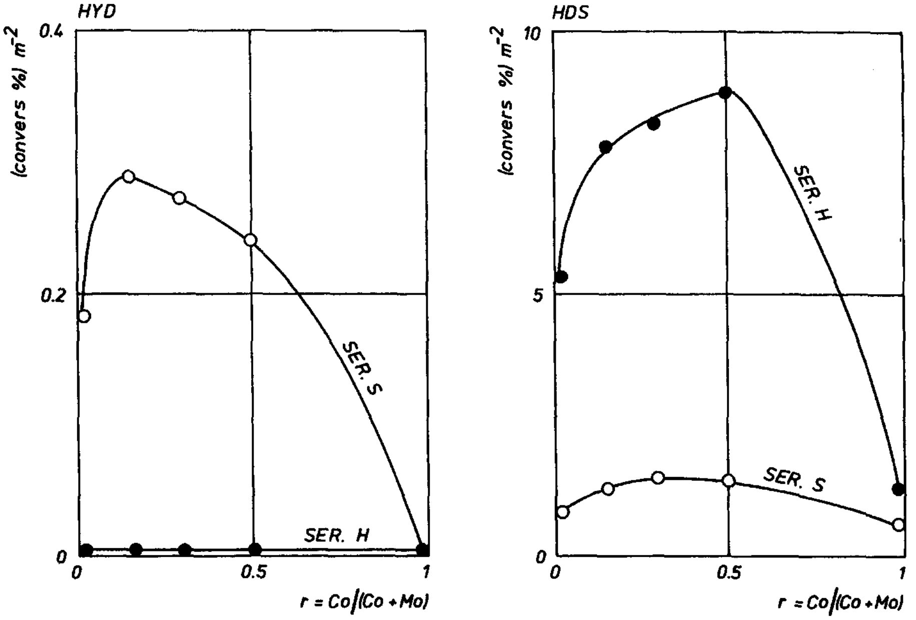

Fig. 13. Comparison of catalytic activities in simultaneous HYD of cyclohexene and HDS of thiophene (T=578 K, 3 MPa) of sulphided, non-supported CoMo catalysts pretreated by hydrogen (series H) and argon hydrogen sulphide mixture (series S) at 673 K for 4 h.

HYD activity (Fig. 13). This clearly indicates that, starting from the same precursors, depending on the activation condition, namely reduction sulphidation state of the catalysts, it is possible to adjust the HDS/HYD ratio.

An additional and recent proof of the influence of spillover phenomena on hydrotreating or, more precisely, hydrocracking catalysts have been presented [103].

If the activation of hydrogen has been shown as an important effect in hydrotreating catalysts, the question which is still pending is: how does the activated hydrogen migrate onto the surface of the donor to the acceptor phase? On oxidic catalysts promoted with noble metals, this was shown by Conner et al. [104]. It was also demonstrated that acid sites on Si-Al oxide promote the migration of hydrogen activated by Pt during the reduction of $CoCl_2$ [105]. For hydrocracking of diphenylmethane in a complex mixture (29.5 wt% diphenylmethane, 70 wt% of n-dodecane and 0.5 wt% of dibenzothiophene) we prepared biphasic catalysts consisting of mechanical mixtures of CoMo/SiO_2 with SiO_2–Al_2O_3 (500 m^2g^{-1}; 12 wt% Al_2O_3). The diphenylmethane conversion as a function of the SiO_2–Al_2O_3 content is illustrated in Fig. 14.

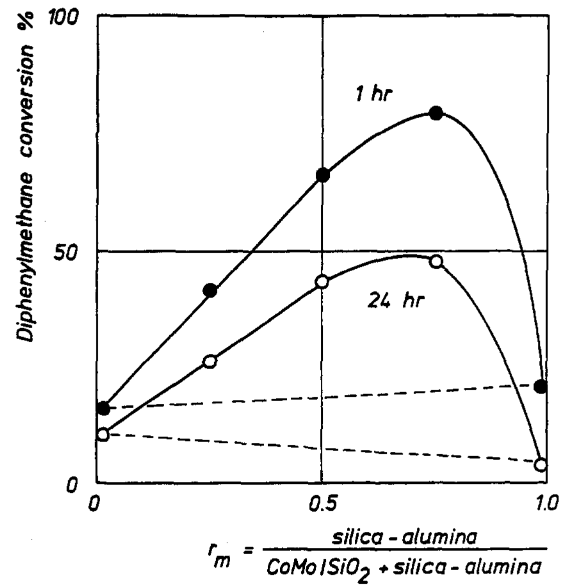

Fig. 14. Diphenylmethane conversion as a function of mechanical mixture composition: r_m (wt% SiO_2–Al_2O_3/(wt% $CoMoSiO_2$+wt% SiO_2–Al_2O_3)×100) after 1 h and at steady state 1 (T=673 K, 5 MPa).

The dashed lines represent the sum of the properly weighed individual contributions of the pure phases (CoMo/SiO_2) and silica–alumina, calculated suppos-

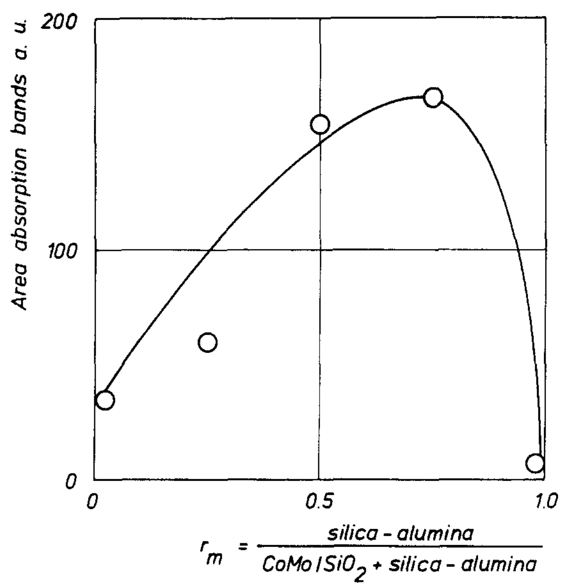

Fig. 15. FTIR analysis of the catalysts: OD band surface as a function of mechanical mixture composition r_m.

ing a zero-order reaction and the absence of interactions of any kind between these phases. A very important synergy is observed and the maximum of conversion is situated around 50 wt% of silica–alumina. Benzene and toluene are the main reaction products. No cyclohexane or cyclohexylphenylmethane was detected. It was assumed that dissociated molecular hydrogen spillover from the sulphides to the silica–alumina and create new protonic acid sites, thus increasing the hydrocracking activity. Below 50% silica–alumina, the growth reflects the increase in the number of active sites that can be generated, namely the increasing silica–alumina content. When this content is superior to 50%, the donor is not able to produce enough H_{so} to activate the acid phase. This hypothesis is strongly supported by H–D exchange followed by IR spectroscopy on the same series of catalysts activated in the same conditions as in case of catalytic activity measurement.

The intensity of the OD band as a function of the sample composition is shown in Fig. 15. The shape of the curves is absolutely similar to those of the catalytic test, suggesting that the magnitude of the synergy in catalytic activity is related to H_{so} generation in the same way as the H–D exchange. The same statement is proposed by Nakamura et al. [106–109] who studied the toluene disproportionation with mechanical mixtures of $CoMo/Al_2O_3$ and Fe–HY under high hydrogen pressure in the presence of H_2S. They proposed that H_{so}, generated on the metals in both components, migrate to the zeolites surface as a proton and promotes the acid catalysed reaction.

Another important effect was also observed by Stumbo et al. [103] and is related to the ability of H_{so} to decrease the deactivation by coke deposition. Both the rate and amount of deactivation are drastically decreased by hydrogen spillover.

3. Improvement of hydrotreating catalysts

As mentioned in Section 1, hydrotreating operations are faced with more severe constraints, due in particular to more severe environmental regulations. Deep HDS and sharp decrease of aromatic content in diesel, without decreasing or even increasing the cetane index, are mandatory.

Two possibilities have to be considered: either one-step processes, combining deep HDS, denitrogenation and aromatic saturation, or two-step processes, first HDS, HDN followed by aromatic saturation.

Limited published studies seem to indicate that a single-stage process could be efficient if operated under quite severe conditions and with a 'special' base-metal catalyst [110]. The second possible choice is the dual-stage process: the feed is here desulphurised and HYD in two different reactors.

At the present time, only one real single-stage process is operating, to our knowledge, while some two-stage processes are already at work. Descriptions of those processes are given in the Refining Handbook [111] and in Oil and Gas Journal [110].

A first process has been developed by Exxon Research and Engineering. Their 'hydrofining' process seems to be able to desulphurise down to a sulphur content of less than 0.05 wt%, but no indications about HYD are given [111]. The 'SynSat' process developed by Criterion Catalyst L.P. and ABB Lummus Crest [111–113] is a single-stage hydrotreater designed to hydrogenate diesel oils. When this unit works in the 'HDS mode', the sulphur content is lowered to less than 500 ppm and the aromatic content to 25 vol% (FIA). When working in the 'HDA mode', the remaining sulphur content is as low as 10 ppm and the aromatic content 10 vol% (FIA). This unit typically works under pressures varying from 5.2 to 6.2 MPa and in the 310–380°C range. The combination of catalysts used varies for differing applications, but generally consists of NiMo, CoMo and NiW catalysts. The 'SynSat' process can also be used to revamp hydrotreaters.

We shall not enter into chemical engineering considerations, but only review the updated improvement of the catalysts. Five main orientations can be seen:

1. Modification of the active phase with some additives.
2. Modification or change of the support.
3. Use of noble metal, but in this case it would be necessary to differentiate between pure hydrotreating catalysts and hydrodearomatization catalysts.
4. Attempt to develop novel catalysts such as molybdenum nitride.

3.1. *Influence of the additives*

Numerous modifiers have been studied and special attention given to the influence of phosphorous, mainly on NiMo catalysts. Several explanations have been proposed [110]: improvement of the dissolution of the molybdenum salt; change in Mo dispersion; modification of the hydrogenolysis step; increase of stacking of MoS_2 crystallites and change of their morphology; modification of the Mo and Co edge sites; improvement of acidity; formation of specific sites associated with the phosphate; and increase of the 'NiMoS' precursor phase [114–122]. Despite the disagreement about the exact role of phosphorous on the nature of catalytic sites, it is admitted that the sequence of impregnation procedure and the pH of the impregnation solution are the most important parameters to improve the activity [123,124]. Other additives reviewed in literature include Li, Na, K, F, B [125–128], Zn [129] as well as rare-earth metal [130].

3.2. *Influence of the support*

A review of the support effects on the activity and selectivity of hydrotreating catalysts has been recently presented by Luck [131]. The modification or the replacement of the alumina support has the following different objectives:

1. Improvement of dispersion of the active phases.
2. Modification of the reducibility of oxide precursor through change of the interaction between the active phase and support.
3. Decrease of concentration of the spinell phase, thereby increasing the useable Co(Ni) content of the catalyst.
4. Facilitate the metal recovery of spinell catalysts.
5. Reduce the deactivation via coke formation.

The properties of alternative supports for hydrotreating catalysts, as compared to conventional Al_2O_3, have been summarized by Luck [131] (Table 5).

The most widely studied carriers are TiO_2 based supports, including TiO_2–Al_2O_3 [132–137], TiO_2–ZrO_2 [138–143], which is claimed to be one of the most promising HDS catalysts due to its very high selectivity, thus drastically decreasing the hydrogen consumption. Interesting results were also observed using completely different supports, namely Al-pil-

Table 5
Properties of alternative supports as compared with Al_2O_3 for HDT catalysts (adapted from Luck [131])

Carrier	SiO_2/Al_2O_3	C	TiO_2	TiO_2MO_x	Ceramics	Clays [37]
Surface area per unit volume	>	>	<	>	≪	≪
Cost	>	=	>	>	>	<
Case of forming	=	=	<	<	≪	>
Mechanical strength	=	<	<	<	>	>
Cost of preparation	=	>	=	=	>	>
Potential HDS activity	<	>	>	>	<	<
Specific advantage	HCG HDN	HYD	HCG HYD HDN	HGC HYD HDN	?	HDM
Regenerability	=	≪	<	<	=	=

lared montmorillonite [144], magnesia [145] or silica-ceria [146] supported sulphided phases.

3.3. Use of noble metals

One of the most promising lines of research for reaching new regulations related to the sulphur and aromatic content of diesel is the use of new metals (noble metals or non-conventional ones) or combinations of such metals, just like it was done some years ago with the well-known Co(Ni)–Mo(W) catalysts.

Several lines of research are therefore devoted to the study of noble-metal based catalysts. These lines can be resumed either considering the process to be developed (single- or dual-stage HDS/HDA process) or by looking directly at the catalyst to be studied (supported mono- or bimetallic non-conventional catalysts, or even catalysts containing three different elements as in the case of RuCoMo/Al_2O_3 catalysts). Obviously, the choice of the process is directly related to the catalyst to be implemented, and vice versa.

The metals that could be used are more or less known; either noble metals like Pt, Pd for Ru, or 'unconventional' metals like Fe, Zn, Nb [153–160]. Even uranium was studied at least once [161].

The choice of these metals, and especially noble metals, quite often is based on the results published by Chianelli et al. who found interesting correlations between dibenzothiophene HDS activity, heat of formation of the sulphides and the position of the metals in the periodic table [153,154] (Fig. 16). The same tendency has been observed in HDN of quinoline [162,163].

Ruthenium and rhodium bulk sulphides were found to be the most active for dibenzothiophene desulphurization.

Other lines of research could be based on the work of Zdrazil [164] who classified different metals for their selectivity in HDS–HYD and HDS–HDN (Fig. 17). This is indeed an important parameter for the choice of the catalysts, as higher severity processes will require, for economical reasons, higher selectivity.

The different catalysts could be classified in three categories: mono-, bi- and trimetallic catalysts.

At the level of the industry, it seems that monometallic catalysts could only be of use for dual-stage processes. The first reactor would carry out the deep HDS on conventional CoMo/Al_2O_3 catalysts, the second one, loaded with that monometallic catalyst, would then carry on the dearomatization. For such processes, the HYD catalyst will obviously be a reduced noble-metal supported catalysts, not a sulphided one.

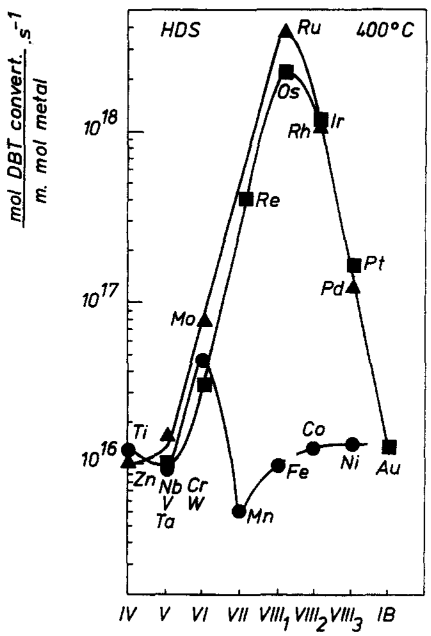

Fig. 16. Tendencies of the periodical system from the HDS of dibenzothiophene [153].

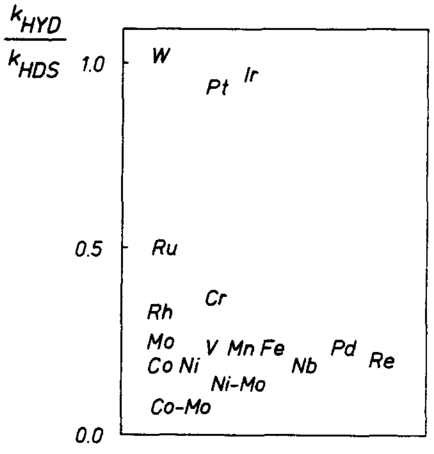

Fig. 17. Classification of selectivity: HDS/HDN and HDS/HDA [162].

More recently, bimetallic noble-metal catalysts are being investigated. Several combinations with Ru, Rh, Pt, etc. have been proposed. Iron promoted Pd, Cu, Cr supported on carbon [159] as well as RuMo [158], NiRu, CoRu, FeRu and NiRu/Al_2O_3 [165] have shown important promotion as compared with conventional solids.

The third class of catalysts consists of trimetallic solids. Most of the published works deal with promotion of conventional CoMo/Al_2O_3 catalysts by a noble metal. One interesting correlation between the increased catalytic activity and CO and NO adsorption, evaluated by FTIR, is already published [166]. This correlation is promising, since it was proposed by many authors that such infrared characterisation technique could be useful for the evaluation of the catalytic performances of sulphided catalysts. The same promotion of the catalytic activity of CoMo catalysts was recently confirmed [167].

In addition, it was suggested that this RuCoMo association was more sulphur-resistant than bulk ruthenium sulphide [168]. This could explain why, using atmospheric residual oil, ruthenium sulphide seems less active than CoMo or Ni and W promoted CoMo catalysts [169].

A possible explanation of the promoting effect of ruthenium could be made, in addition to the intrinsic activity of the noble metal, through the remote-control model in the same way as previously mentioned on mechanical mixtures.

This whole class of catalysts could furthermore lead to new proofs in favour of the remote-control mechanism. This model is indeed the only one able to explain the strong promotion exhibited by very small amounts of metals.

3.4. *Non-conventional phase*

Recent research orientation for improvement in the performances of hydrotreating catalysts includes a complete change of catalyst formulation. The objectives are not based on the discovery of catalysts presenting the same MoS_2 crystallographic structure, as for example niobium sulphide, but on the study of different families of active phases. This is the case with nitrided compounds, in particular bulk Mo_2N or Mo_2N-supported on alumina [147–152]. It has been shown that both pure and supported molybdenum nitrides are very active in HDS and HDN reactions. The drawback of this solid, in addition to the high temperature activation (up to 900°C under NH_3) is its poor stability during regeneration.

4. Conclusions

Hydrotreatment, in particular deep HDS and dearomatisation, is developing very rapidly. A review of the recent literature seems to show that a great improvement in the performances of conventional catalysts has been achieved in the last few years. The highest performance of the catalyst seems to be obtained through modification of the conventional formulation, by creation of a well-dispersed active phase and promotion by hydrogen activating species. These new developments, in addition to the experimental results obtained by the study of model catalysts, seem to strongly support the remote-control mechanism, which has been proposed to explain the synergy in these sulphided catalysts.

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