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New technical challenges and recent advances in hydrotreatment catalysis. A critical updating review

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The petroleum industry gets confronted with more stringent requirements with respect to transportation fuels: diminution by a factor of 10, or more, of the sulphur content, and a drastic diminution of the aromatic content. Besides, the quality of the crude oil supply keeps diminishing on an average. For this, the hydrotreating processes (HDS, HDN, HDM, hydrogenation, hydrocracking) will occupy a still increasing place in the refining processes. In a first part, we shall select some of the most important results published recently: use of new modifiers and supports (TiO_2, ZrO_2, mixed oxides), of metals not yet used in hydrotreating (Ru, Rh, Pd, Pt, possibly Nb, associations RuU, PdU, VU etc.), confirmation of the existence of distinct catalytic sites (hydrogenation and hydrogenolysis of the heteroatom–carbon bonds). Other new results should contribute to clarify the controversies and uncertainties concerning the origin of synergy between different elements and the changes of selectivity as a function of the experimental conditions. For this last topic, reference shall be made to the CoMoS model and the remote control theory. In a second part, we shall summarise the new constraints that the hydrotreating processes will face. It will be necessary to save still more energy. It will also be necessary to achieve a better balance of the various reactions taking place in a given process. The overall selectivity of catalysts and processes will have to be improved. In the third part, we shall try to emphasize directions of research which could help reach the objectives. We shall shortly outline the future contributions of chemical engineering. We shall examine with more details the problems concerning the genesis of adequate catalytic sites (underlining the enormous influence of the activation steps) and the modification of activity by means of the composition of the reacting medium. As the problem of synergy remains crucial for the future developments, we shall also present results with new synergetic systems (WS_2 + supported Rh or Pd; MoS_2 + supported Pt). The new results give hope that the mechanisms of synergy could get clarified in the near future.

Keywords: Hydrodesulfurization; hydrodenitrogenation; hydrodemetallation; hydrogenation; hydrocracking

1. Introduction

Twenty years ago, the hydrotreating processes (HDS, HDN, hydrocracking) were considered as relatively primitive. The catalysts they used were not very elaborate. This was wrong in the sense that the formulation is still essentially unchanged, but has been strongly justified by the tremendous progresses achieved, for dispersion of the active species and porosity design in particular. As a whole, hydrotreating did not seem to deserve much attention. In the last four years, it has become clear that the corresponding processes actually are the key to the production of the fuels that we shall need for buses, trucks and cars in the near future. New regulations have been adopted in Sweden and various states of the USA. The corresponding specifications cannot be met presently, and it is not yet clear how it will be possible to comply with these regulations. The European Community is preparing similar recommendations or directives.

As an example, table 1 presents some of the new or future specifications for diesel fuels, compared to the present ones. The reduction of the sulphur content could be by a factor as high as 300, and the major part, or all, of the aromatics will have to be eliminated. It should be emphasized that the cetane number, as essential characteristic for combustion, will practically not be allowed to change.

At the beginning of the seventies, it was usual to say more than half-seriously that the choice of a hydrodesulfurization catalyst was made with price as the sole criterion. More precisely, the criterion was the price per cubic meter. The catalyst was used to fill up the internal volume of the reactor! It was expected that the improvements should come from a better heat balance and improved plant design. In the near future, in contrast, it is essentially catalytic science which will have to show its innovative ability. It will be necessary to discover new catalysts, to analyse precisely the reaction mechanism (with emphasis on selectivity), to develop new, more adequate kinetic models and, probably, to design new reactors and imagine new operating conditions. There is absolutely no doubt that a large part of the necessary innovations will have their origin in catalysts quite different from those traditionally used in hydrotreating.

We shall first discuss the most conspicuous advances mentioned in the last years. The present paper constitutes a sort of continuation or up-dating of the review published three years ago [1]. Fortunately, fundamental research recently led to new results which hopefully will facilitate the industrial developments of improved processes. Nevertheless, many important problems have not yet found

Table 1
Specifications for diesel fuels

	Swedish tax categories (Jan. 1991)		Proposals (European Community)	Present
	Class 1	Class 2		
sulphur (ppm)	10	50	500	3000
aromatics, total (% vol.)	0	20	25	no limit
polyaromatics (% vol.)	0	0.1	1	no limit
cetane number	50	47	47	45

satisfactory solutions. These problems concern, for a part, catalyst characterisation and the identification of the different types of catalytic sites, and, for another part, the main reaction mechanisms at the level of the catalytic sites. We shall mention in some detail some of them.

In a second section of this paper, we shall discuss the demands the future hydrotreatment processes will be faced with.

The third part will constitute an attempt to analyse the problems set by the fabrication of products corresponding to the new specifications. We shall try to identify the bottlenecks and to formulate the basic questions related to the catalysts as well as to the reaction mechanisms or, in a less detailed way, some chemical engineering aspects. In that part, an attempt will be made to set up a list of objectives for future studies. Some suggestions concerning possible ways to reach these objectives will be made.

2. Most conspicuous recent results

Fundamental investigation in the field of hydrotreating took much time before it became sizeable and developed. It was clear only in the last six years that the number of investigators expert in the field had significantly increased. Simultaneously, research benefited from a new impulse.

This paper does not constitute a systematic review, but rather a selection of particularly important new results, correlations or theories. In spite of the intention of the author to discern the most conspicuous advances, it is difficult to avoid that the selection be somewhat incomplete or arguable. This work is based on important articles in the general scientific literature, two topical issues of Catalysis Today [2,3], the proceedings of the IVth Workshop on Hydrotreatment (Louvain-la-Neuve, 21–22 November 1991) [4] and those of the 1st Japan-European Community Joint Workshop JECAT '91 (Tokyo, 2–4 December 1991) [5]. It also takes into account recent results from the laboratories of the author and colleagues with whom he cooperates.

2.1. CATALYST TEXTURE

New catalyst textures, with large pores, bimodal porosity, etc., continue to be developed with some success. Unfortunately, the corresponding investigations do not take into account explicitly the fact that the sites which correspond to the various types of catalytic activity are located at different places inside the porosity. It seems likely that a large proportion of acid sites are located in small pores [6,7]. On the other hand, a large part of the activity for hydrogenolysis of the carbon–metal bond, and, possibly, hydrogenation, would be located in larger pores or outside the pores. One could logically speculate that a more detailed analysis of the corresponding effects would permit a finer control of selectivity. This could also help control deactivation by coke deposits or formation of nickel, vanadium or other metal sulphides. It is easy to demonstrate that coke deposition can reduce proportionally more the hydrogenation than hydrodesulfurization activity [8]. It is not sure that all the results recalled above have been accounted for in the extensive work using modifications of the pore structure done in the hope of increasing selectivity or life of catalysts.

2.2. MODIFIERS

The research on modifiers of supports for CoMo and NiMo catalysts is continuing. Previously, the emphasis was either on elements which were supposed (probably in an erroneous way in certain cases) to inhibit the reaction of cobalt or nickel with alumina (e.g. boron) on phosphorus, in order to study its influence on NiMo catalysts. The line of research concerning modifiers of acidity, such as fluorine [9–11], did not develop much. The modifiers most often used in recent studies are titanium and zirconium. Such studies demonstrate that these additives, as oxides, simultaneously modify the interaction between the impregnation solution and the support, the dispersion of the active phase [12–15] and the strength with which the crystallites of the active phase are attached to the supports.

2.3. NEW CARRIERS

A large number of results concerning new supports have accumulated in the last years (table 2). These add to a list which essentially contained the traditional carriers (γ-Al_2O_3, silica–alumina, and zeolites – if the latter are considered as real supports) and natural minerals. Carbon might play a special role: it permits a very high dispersion of the active sulphides, and makes that cobalt sulphide adopts, even when alone, a structure identical to that attributed to cobalt in the CoMoS phase [16]. Another advantage of carbon as a support is that the recycling of the active metals is made easier. It suffices to calcine used catalysts (more precisely to achieve a complete roasting of spent catalysts) to obtain oxides of molybdenum, cobalt and nickel, which can be easily transformed to salts of commercial grade. Other interesting supports contain titania or zirconia as main components [17,18].

Table 2
Supports for hydrotreating catalysts (sulphides of metals of group VI–group VIII) [12,13,19–25]

γ-Al_2O_3	ZrO_2–Y_2O_3
silica–alumina	TiO_2–ZrO_2·V_2O_5
zeolites	clays
SiO_2	bauxite
carbon	sepiolite
TiO_2	actapulgite
TiO_2–MeO_x (Me = Zr, Ce, Mn, Mg, Zn)	

A review on supports, their uses and advantages, has been presented by Luck in 1991 [19]. Important contributions can be found in refs. [12,13,20–25], in particular in relation to the textural modifications produced by non-conventional supports [24–26].

2.4. NEW ACTIVE ELEMENTS

Another very important development in the field of hydrotreatment is the systematic study of metals different from cobalt, nickel, iron, molybdenum and tungsten [12,27–33]. Ruthenium and platinum seem to attract particular attention. Platinum is used at a small scale for certain advanced hydrodesulfurization processes. New bimetallic catalysts are also studied: Ru–U, Pd–U, V–U [28] or Co–Ru, Ni–Ru, Fe–Ru, Ru–Mo [32,33]. An interesting feature of these new metals is related to hydrogenation and hydrogenolysis of the heteroatom–carbon bonds: selectivity, namely the ratio of the rates of these reactions, is different, compared with the usual metals, as noted by Zdrazil (fig. 1) [27]. This figure indicates that ruthenium and platinum are much more selective for hydrogenation. This could be a useful property, for reducing the aromatic content of transportation fuels.

Nevertheless, these data need a word of caution. Selectivity, or, more precisely, the ratio of the rate of hydrogenation to that of hydrodesulfurization, HYD/HDS (or, more generally, to those of other hydrogenolysis reactions), undergoes very

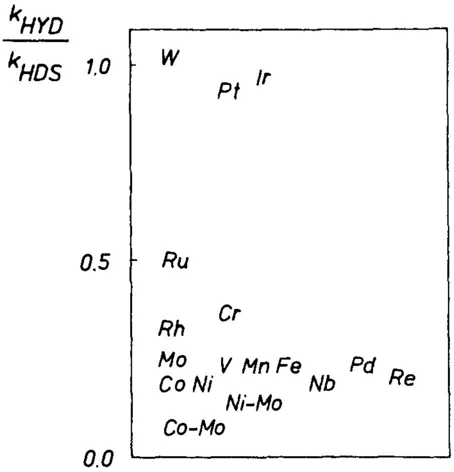

Fig. 1. Hydrogenation/hydrodesulfurization selectivity scale. The results are based on pseudo first order values in parallel reactions of hydrogenation of naphthalene (measured at 350°C) and hydrodesulfurization of benzothiophene (measured at 300°C). Pressure 1.7 MPa. The position of the chemical symbols in the horizontal direction has no special meaning. For other details see publication [27] from which the figure is adapted.

large changes as a function of the H_2S/H_2 ratio in the reacting medium. When the effect of the partial H_2S pressure is studied (fig. 2), certain tendencies are observed with Co–Mo and Ni–Mo catalysts [27], see also ref. [34]. It could be expected that H_2S will also modify selectivities in the case of other metals, possibly in a different way, as demonstrated by recent investigations [30,31].

In spite of these results it has not yet been possible to understand perfectly the influence of this parameter. It remains to determine the experimental conditions which would allow these new metals to acquire really useful properties. In addition, it will be necessary to identify the most adequate supports for these metals or associations of metals.

2.5. EXISTENCE OF DIFFERENT TYPES OF CATALYTIC SITES IN HYDROTREATING CATALYSTS

Contrary to many others, certain authors of scientific publications have been for a long time of the opinion that hydrogenation and hydrogenolysis of heteroatom–carbon bonds corresponded to the same sites. But, the opinion of the engineers in charge of industrial processes was definitely that, in addition to the acidic sites, at least two other types of sites were involved in the reaction of hydrogen. The confusion was due to the complexity of the reaction mechanisms. The majority of the heteroatom-containing molecules (with S, N or O) in commercial feeds are complex. A partial hydrogenation facilitates the rupture of the heteroatom–carbon bonds.This rupture can involve the participation of hydrogen (hydrogenolysis as such) or take place thanks to pure heterolytic reactions, or some other mechanism, possibly catalysed by acidic centres. Zdrazil, for example, demonstrated that a

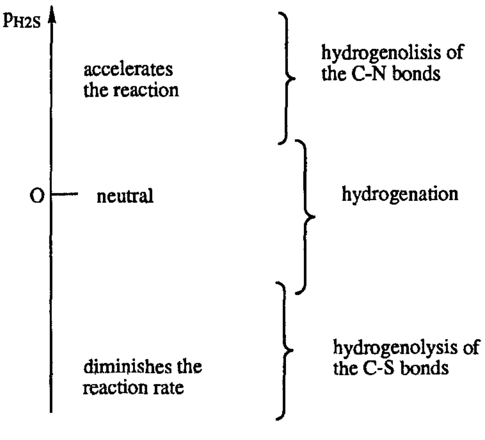

Fig. 2. Influence of H_2S partial pressure on the rate of various reactions or reaction steps during hydrotreating on Co–Mo or Ni–Mo catalysts (after [27]).

β-elimination is quite probable in many cases [35]. Other mechanistic considerations have been presented by other authors [36,37].

Kinetic studies made under strict conditions [27,38] demonstrate that hydrogen is necessary for breaking certain bonds and this, independently of acidity. Other more qualitative measurements using a large number of compounds lead to the same conclusion [39,40].

Various new arguments and data proving the existence of two types of catalytic sites (hydrogenation and hydrogenolysis of the heteroatom–carbon bond) have been presented (e.g., articles [41–43], review papers [1,44]; see also ref. [45]). A chemical engineering laboratory having a long expertise in precise kinetic measurements also reached the conclusion that two types of sites are necessary [46–49].

Recently, studies on the reactions of nitrogen-containing molecules also permitted to conclude that two different types of sites are present. It had been discovered in industry that the reactions of various molecules did not change in a parallel way when the properties of the catalysts were changed. In an empirical way, the nitrogen-containing molecules were classified into basic, neutral, and, paradoxically, acid, as a function of the way they behaved when the global acidity of the catalysts was modified. A reason for these differences is that, in the five-membered ring heterocycles (pyrrole and homologues) the density of electrons in the nitrogen atom is low, compared to the nitrogen atoms present in six-membered rings (pyridine) or in amines (e.g., aniline). In a sense, the nitrogen could indeed be considered as "acidic".

On the basis of these results, we have suggested that a particular site on the surface of MoS_2 could serve for the hydrogenolysis of the heteroatom–carbon bonds in five-membered rings (thiophene, pyrrole, furan and their homologues) [1,50]. Simultaneously, we proposed a mechanism which would be common to the breaking of S–C, HN–C and O–C bonds. The catalytic site which would permit this breaking would be constituted of a threefold coordinatively unsaturated Mo atom and an adjacent –SH group.

It is almost certain that, in the hydrotreating catalysts, hydrogen could participate in the reaction through two types of catalytic centres. The first ones would catalyse direct hydrogenolysis; they would be those described above. The second category would catalyse hydrogenation. In agreement with the new well-accepted proposal of the research group in Lille, these would correspond to molybdenum atoms possessing three unsaturated co-ordination positions [51,52]. If one accepts our proposal [50], it would suffice to add an –SH group in a vicinal position to transform these hydrogenation sites into hydrogenolysis sites. It seems very likely that, in addition, acidic sites are necessary for breaking certain heteroatom–carbon bonds. These would constitute a third type of sites in hydrotreating catalysts. They would be particularly useful in hydrodenitrogenation.

Results are accumulating which demonstrate that an interconversion of the hydrogenation and hydrogenolysis sites is possible. More precisely, H_2S partial pressure can influence the ratio between the number of hydrogenating sites and sites responsible for the hydrogenolysis of heteroatom–carbon bonds [47,48]. Moreover, these sites get poisoned or inhibited in a different way [53]. The results presented in fig. 3 correspond to competitive reactions between aniline, pyridine or naphthalene, on the one hand, and indole (a five-membered ring) on the other hand. The presence of indole strongly inhibits the reactions of aniline and naphthalene. Pyrrole, another five-membered ring, has the same inhibitory action as indole [53]. But neither aniline nor naphthalene exerts any influence on the hydrodenitrogenation of the five-membered rings of indole or pyrrole. Pyridine and naphthalene compete with each other.

It is known that the rate-determining step, in the hydrodenitrogenation of pyridine, is hydrogenation. The strong inhibition suffered by aniline and naphthalene shows that indole or pyrrole strongly inhibit the hydrogenation function. This phenomenon has great practical importance, because hydrodenitrogenation and hydrodeoxygenation, in the majority of cases, require that the aromatic rings be first hydrogenated, namely demand a strong hydrogenating activity (see Böhringer and Schulz [54]).

2.6. THEORIES

Approximately 17 theories have been proposed for explaining the synergy between group VI (Mo, W) and group VIII metals (Co, Ni, Fe) [1,55,56]. Let us recall that the first ones, the most famous example of which is the "monolayer theory" [57–59], actually dealt with the *precursor* of the sulfide catalysts, namely the more of less spontaneously spread layer of MoO_3 on $CoAl_2O_4$ [57] or Al_2O_3 or the more sophisticate bi-layer constituted by a sort of bidimensional cobalt or nickel molybdate adhering on Al_2O_3 ([60–63], see also a review of these results in ref. [1]). A second group of theories assumed some doping of the group VI sulfides (MoS_2 or WS_2) by Co, Ni (or Fe): these were essentially the "pseudo-intercalation theory" where cobalt or nickel were supposed to decorate the edges of the layered group VI sulfides [64–68], the hypothesis of a bulk doping with minute amounts of group VIII metals (much less than actually present in catalysts) [69,70] or hypothetical formation of a never detected bulk bimetallic sulfide [71]. Other hypotheses were based on correct observations, essentially the strong activity of cobalt when alone, if deposited on carbon [72–74], but they seem insufficient for explaining the activity of real catalysts where cobalt alone deactivates rapidly; it has also been shown recently that this Co/carbon benefits from a contact with MoS_2 or MoS_2/Al_2O_3 [75,76], thus excluding that the whole activity of practical catalysts be due only to cobalt.

Finally, only two of these theories survive. One of them is in the line of the pseudo-intercalation theory [64–68]. It attributes the catalytic activity to a structural association called "CoMoS" (or "CoMoS phase") or "NiMoS" or "FeMoS". The other one is the remote control theory, which supposes a co-operation between distinct phases, e.g., $MoS_2 + Co_9S_8$. Neither of them has succeeded

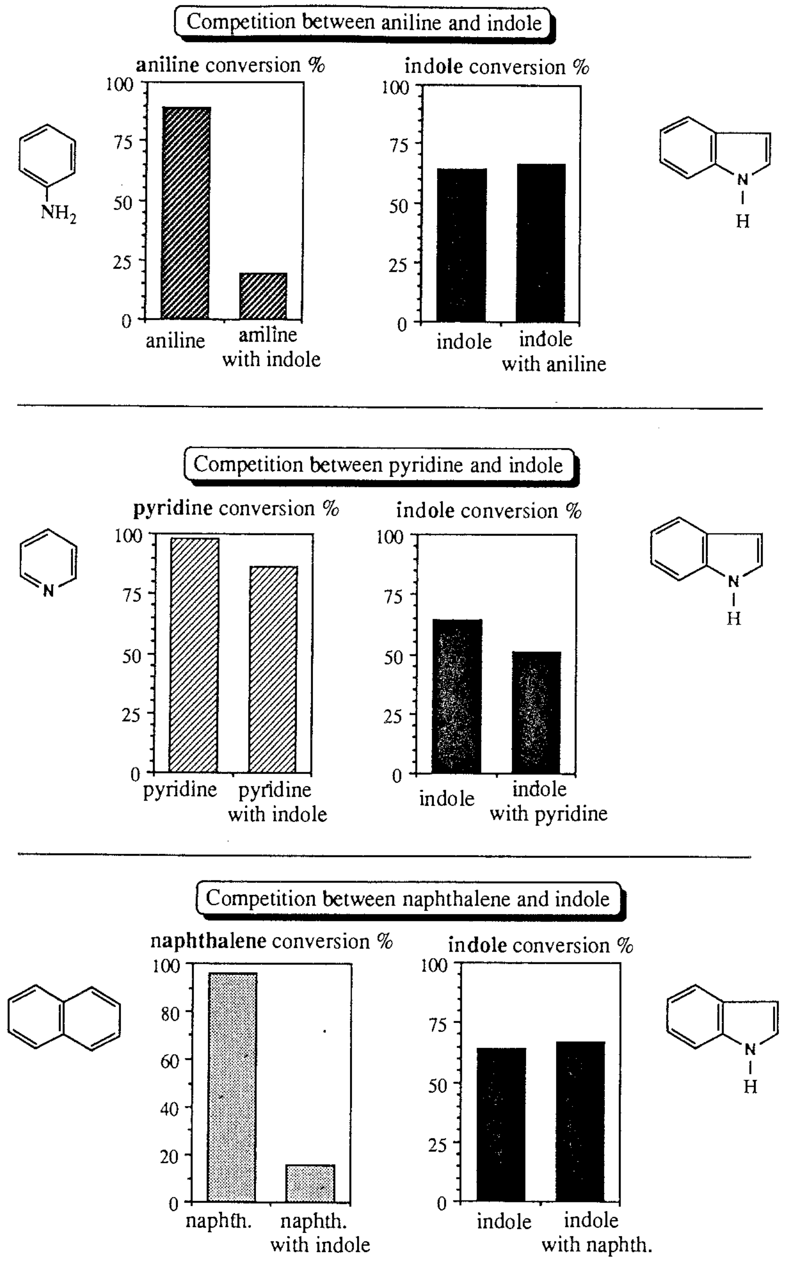

Fig. 3. Competitive reactions (573 K; total pressure 5 MPa; NiMo/γ-Al_2O_3 catalyst: 0.89 g; H_2 flow rate: 30 $\ell\ h^{-1}$; liquid feed; 30 $cm^3\ h^{-1}$; carbon disulphide: 2.37 wt%, in the liquid feed; carbon sulphide is used for maintaining the catalyst in the sulphided state; the solvent was heptane; concentrations of reactants were (molar concentrations): aniline: 0.0246; indole: 0.0504; pyridine: 0.0246; naphthalene: 0.2000. The figure compares the conversions of the various compounds either pure or mixed with other compounds [53].

in convincing the scientific community up to now. This still constitutes a hot topic.

The present author is at the origin of the remote control theory. Because of that, he may not be able to analyse in a totally unbiased way the arguments in favour or against each theory. Nevertheless, important results have been presented in the last years. They provide strong arguments for deciding on the validity of these theories. We shall summarise these arguments in what follows.

The authors of the CoMoS hypothesis [77–85] themselves demonstrated that the largest part of this "phase" decomposed during the catalytic reaction when the catalyst had a composition (Co/Mo = 0.5) in the normal range. This decomposition took place in a short time (19 h) in mild reaction conditions (352°C) [86]. Numerous other experiments, in our and other laboratories, have shown the instability of "phases" associating, in the sulfided state, cobalt or nickel with metals of the first line of group VIII [1,75,87–95].

Other results concern the only signal usable for unequivocal characterisation of "CoMoS" or "FeMoS", i.e., respectively that of cobalt, in emission, or iron, in absorption, in Mössbauer spectroscopy. Thanks to extremely careful measurements, signals absolutely identical to those attributed to the CoMoS association have been detected in catalysts *containing no molybdenum* [96], confirming data obtained a few years before [97,98]. Account taken of the absence of irrefutable proofs of any structural connection between cobalt and molybdenum (see ref. [1]), these results suggest that the signal of the group VIII metal actually corresponds to a sulphide of this metal of special structure. In view of the results recalled above, this phase must be independent from molybdenum or molybdenum sulphide, but it is not excluded that it could be at a short distance from molybdenum sulphide MoS_2, or Mo-containing compounds, if molybdenum happens to be present in the catalysts. Whatever its nature or location, this special group VIII sulphide phase or association of this phase with molybdenum sulphide is not stable in the conditions in which the hydrotreatments take place.

These results confirmed the presence of separate sulphide phases (of the group VI, on the one hand, and of the group VIII, on the other hand) in active catalysts and indicated that there was a synergy due to a more or less direct contact between phases: "contact synergy model" [99,100]. But they do not demonstrate that a remote control takes place. The remote control postulates that a small fraction of hydrogen gets dissociated to spillover hydrogen on the group VIII metal sulphide. This spillover hydrogen migrates onto the surface of the group VI metal sulphide, where it creates the co-ordination unsaturation adequate for making surface ions catalytically active. If there is a change in the experimental conditions, this spillover hydrogen would be produced in different quantities and concentrations, and this could permit the conversion of hydrogenation sites to hydrogenolysis sites, or, conversely, let the reverse conversion take place [1]. The difficulty with this mechanism is to measure the number of active sites of each category and their interconversion. The proofs are indirect. As could be supposed, many of these proofs rest on kinetic measurements [46–49,101].

Several investigators still question the remote control mechanism. Nevertheless, the accumulation of results showing a synergetic co-operation between two different sulphide phases in mixtures [1,75] demands an adequate explanation. The remote control provides such an explanation. At least three series of independent experiments showed that a mixture of cobalt sulphide Co_9S_8 and molybdenum sulphide prepared separately possess catalytic activities in hydrogenation and hydrodesulfurization higher than the sum of activities of the pure sulphides [42,44,102,103]. These mixtures could be prepared according to different methods, but the most convenient one is to add the two powders to *n*-pentane, in order to make a suspension, to agitate and to dry. This very mild mixing method avoids any cross-contamination or damage to the small particles of the powders. No physico-chemical technique could detect any mixed sulphide in such mixtures. The same synergetic effect is observed when cobalt sulphide supported on carbon is mixed, using the same method, with molybdenum sulphide supported on alumina (fig. 4) [76]. In this mixture, the formation of mixed phase (such as "CoMoS") is made

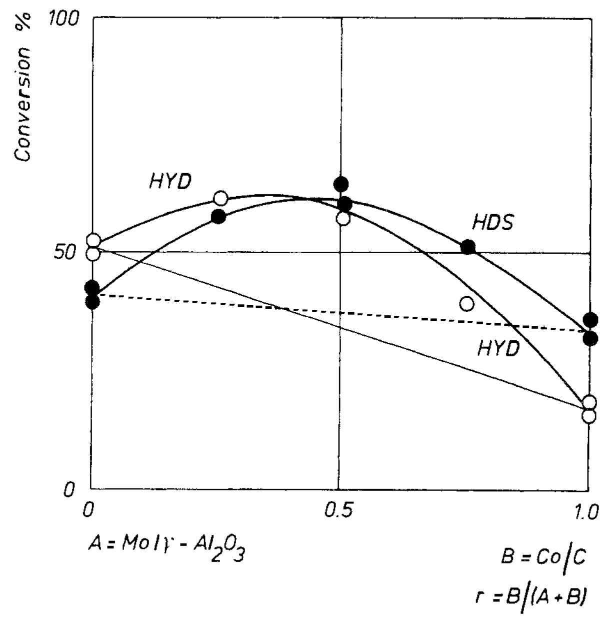

Fig. 4. Synergy between CoS_x/C and $MoS_2/\gamma\text{-}Al_2O_3$ ($T = 573$ K; 3 MPa total pressure; mass flow rates: 48 g h^{-1} (liquid), 88 g h^{-1} (H_2)). The hydrodesulfurization (HDS) and hydrogenation (HYD) activities corresponded to the conversion of thiophene and cyclohexene contained, in a proportion of, respectively, 0.5 and 29.5%, in cyclohexane (70%) [76].

impossible by the fact that cobalt and molybdenum are completely separated, each of them on a different support.

Most conspicuous, in these experiments with mechanical mixtures, is the existence of synergies between cobalt sulphide and the "CoMoS" species [103], the "FeMoS" species [75] or the sulfided association of nickel with molybdenum prepared according to the same method as "CoMoS" or "FeMoS", namely homogeneous sulphide precipitation, HSP [75]. There is no direct way to characterise the "NiMoS phase", supposing that it exists, but it is believed that the HSP method maximizes its formation. This is the reason why we used this HSP preparation for the experiments mentioned above. Fig. 5 illustrates the synergy obtained in this last case. Let us emphasize that, as said above, the mixing procedure (suspension in *n*-pentane), which protects the crystallites, and the fact that the samples of pure "MeMoS" and Co_9S_8 used for comparison have undergone the same *n*-pentane treatment, rule out an explanation based on textural changes. It seems

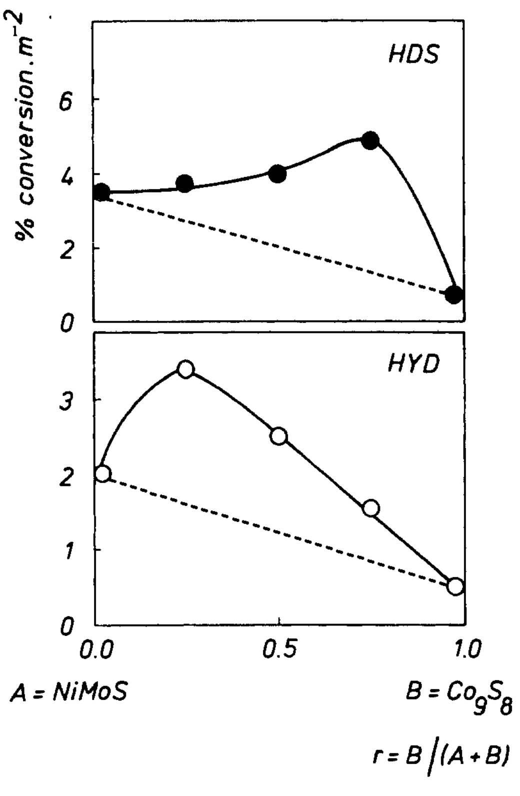

Fig. 5. Synergy between C_9S_8 and NiMoS ($T = 623$ K; 3 MPa total pressure; liquid mass flow rate 100 g h^{-1}; all other conditions are those of the caption of fig. 4). The activity is expressed as the ratio of the conversion (%) to the surface area of the catalysts [75].

that, when the "MeMoS phases" (Me = Fe, Co or Ni) are mixed with Co_9S_8, they get decomposed more rapidly during the catalytic hydrotreating reaction than when pure [75]. Admitting that there is a migration of spillover hydrogen from cobalt sulphide to the other phase of the mixture, this observation would suggest that this mobile hydrogen stimulates the segregation of the "MeMoS phases" into simple sulphides.

These are conspicuous results. It was thought that the three "MeMoS" phases were the key to catalytic activity, and their formation the explanation of synergy, but it turns out that they acquire more activity when they are mixed with Co_9S_8. This is a new result which demands an explanation. The remote control theory offers such an explanation. Spillover hydrogen imposes to the surface molybdenum atoms the coordination adequate for obtaining maximum catalytic activities. The experiments show that catalytic activity is maintained, or even increased, when the "MeMoS" phase gets decomposed. This suggests that catalytic activity is due to segregated molybdenum sulphide. This segregated molybdenum sulphide benefits from the action of spillover hydrogen the same way as molybdenum sulphide mixed with cobalt sulphide in the mechanical mixtures does. These results and the important catalytic activity of the "MeMoS phases" mentioned in many publications are perfectly consistent. In these publications, the "MeMoS phase" was indeed present in the fresh catalysts, but the authors did not check whether it remained undecomposed during the catalytic test. It very likely decomposed extensively to group VIII metal sulphides and molybdenum sulphide, with the synergy operating in this mixture. In fact, the unstable "MeMoS" association seems to constitute a good precursor of the two-phase system $MeS_x + MoS_2$. This is probably due to the fact that these two phases, namely MeS_x and MoS_2, when produced by solid-state decomposition of "MeMoS", are highly dispersed and situated in close proximity to each other. The higher activity of the "CoMoS" + Co_9S_8, "FeMoS" + Co_9S_8, and "NiMoS" + Co_9S_8 mixtures are in agreement with many other data showing that the best catalysts contain concentrations of Co, Fe or Ni higher than those that permit the MeMoS association to remain metastable.

3. Challenges in the future development of catalytic hydrotreatment

In the introduction, allusion was made to the new problems the hydrotreating processes are faced with. These problems are mainly linked to the necessity to reduce drastically the sulphur and aromatic contents of transportation fuels. This looks an easy task when considering only the chemical aspects. But it should be remembered that specifications do not allow the combustion characteristics (in particular the octane or cetane numbers) to change. In this context, the task appears as extremely difficult.

On order to understand completely the future role of hydrotreatments, one should also take into account other more general constraints, namely of environmental and economical nature. Diminishing the aromatic content and simultaneously maintaining the octane number is possible, using ethers (MTBE, TAME, ETBE), but at an elevated cost, from both the points of view of energy and economics. This requires molecules more expensive than those directly derived from petroleum, and necessitates one or two additional chemical processes for manufacturing the ethers. The synthetic additives are used in relatively large proportions, in general between 5 and 20%. This implies that the price of the additives strongly influences the price of gasoline as formulated at the refinery. With respect to diesel fuels, a diminution of the aromatic content will necessitate a higher hydrogen consumption, and hydrogen is costly. In this context, hydrotreatments must become still more efficient.

The new refining schemes will imply a higher energy consumption in all cases. This will come in addition to the consumption resulting from the diminution of the share of light crudes in the total feed of oil refineries. This evolution takes place at the moment where social and political forces demand that the emission of "greenhouse gases" are diminished; this, ultimately, implies that energy consumption be diminished. It follows from these considerations that it is unfortunately unavoidable that dangerous contradictions are detected between the various demands of environmental protection.

These contradictions have not yet been the object of a clear debate. The consumer, ecologically minded or not, will very likely react to the increase in price. There is little doubt that the otherwise contradictory demands will only converge to the necessity to spare raw materials and energy. This is the reason of the exceptional importance of catalysis. All the refining processes will have to be still more efficient. There is a general agreement that this will increase the importance of hydrotreatments compared to the other refining processes. This trend will become still more dramatic in the next years.

Account taken of all these new, more difficult objectives, the hydrotreating processes will have to change quite substantially. It will be necessary to modify or readjust all the characteristics of catalysts and operation parameters. As an example of the extensive changes which will be necessary, let us cite that sentence: "A Co–Mo/TiO_2–ZrO_2 catalyst required approximately 27% less hydrogen than a [conventional] Co–Mo to desulphurize a Kuwait residuum oil" (R.J. Mikowski, A.J. Silvestri, US Pat. 4,220,557, to Union Oil of California; cited by F. Luck ref. [19]). Simply that aspect, namely the support, constitutes a considerable change for the hydrotreating technology and nobody can tell now whether the Co–Mo/TiO_2–ZrO_2 catalysts will be practically usable.

If it were possible to reduce, by a percentage comparable to that claimed in the patent, the consumption in all the hydrotreating units, the hydrogen spared would be sufficient to feed all the ammonia plants in the world.

Nevertheless, one shall not elude the necessity to use four tons of hydrogen for each 32 tons of sulphur to remove (two out of these four tons are recoverable as hydrogen), and still more for each 14 tons of nitrogen. And a minimum of 1 ton of hydrogen will be needed to eliminate every 13 tons of aromatic rings. In this context, a good exercise would be to calculate the quantity of hydrogen necessary for diminishing by 50% the aromatic content of gasoline and diesel fuels. The world production is about *900 million* tons/year (350 million m^3 in the USA in 1988) [104]. An approximate calculation could be based on the assumption that the present aromatic content in transportation fuels is 30%. The quantity of hydrogen necessary for a giant ammonia plant is *200 thousand* tons/year.

Hydrogen consumption already constitutes, and will constitute in the next future, the major problem in the new refining flow-sheets presently under elaboration. It will be necessary to control all the individual chemical transformations in the processes in such a way that hydrogen be used selectively in the essential reactions and not wasted in unnecessary ones (such as saturation of C=C double bonds or hydrogenolysis to gases).

The results presented in the first section highlighted various parameters which will be used for a better control of the hydrotreating reactions.

The citation pointed to the role of new supports. New metals (noble metals in general) will also be used for reaching the goals. They have stronger hydrogenating properties. They are the key to advanced processes, still in development, for dearomatization of diesel fuels.

Until now, we have emphasised two types of reactions of hydrogen, namely hydrogenation, and the hydrogenolysis of carbon–heteroatom bonds. It is clear that, in the future, the catalysts and the corresponding processes will have to perform selectively either one or the other reaction, or well defined proportions of each. But this will not be sufficient. It will also be necessary to improve hydrocracking. In hydrocracking, the useful reactions are those which bring about scission at a certain distance from the ends of the hydrocarbon chains. If not, light gases are formed. As another example, let us consider a high molecular weight molecule. Hydrodesulfurization and hydrodenitrogenation give a hydrocarbon molecule that still has too high a molecular weight. This is the reason why hydrocracking is usually associated with hydrodesulfurization and hydrodenitrogenation of residues. The control of this first group of reactions is crucial for making easier the control of subsequent refining steps. This is another reason why hydrocracking processes will take, among the hydrotreatments, a still increasing importance in the future.

If we attempt to describe the future situation of hydrotreatments, we come to the conclusion that it will be characterised by a more precise control of all the selectivities: selectivity between hydrogenation and hydrogenolysis of the carbon–heteroatom bonds, between hydrogenation and hydrocracking, selectivity with respect to the position where the C–C bonds will get broken. This strongly suggests that other acidic supports, and other zeolites, will be used in the future. But a large part of the necessary basic information is still lacking presently. What is mainly at stake is a correct understanding of the interaction between the acidic functions of the catalysts and the activities in hydrogenation and hydrogenolysis of the carbon–heteroatom bonds.

Another important problem is deactivation. Almost nothing is known concerning the behaviour of hydrotreating catalysts containing non-conventional metals with respect to ageing and deactivation. An extremely rapid deactivation has been mentioned in the case of Ru/alumina and Ru/Y-zeolite [29]. We urgently need studies aimed at clarifying the mechanisms of deactivation in catalysts of non-conventional formulation.

4. Prospects for scientific advances in hydrotreating

In this last section we shall try to identify important directions for future investigations aimed at improving hydrotreating processes. In all that follows, it will be necessary to remember how important it is that engineers and scientists cooperate tightly if they wish to reach rapidly the objectives suggested in the previous section.

A first part will enumerate some of the problems that chemical engineering will be faced with. But, in order to keep this paper close to the preferred topics of this Journal, we shall mainly discuss questions related to catalysts and the understanding of catalytic reactions. An important problem concerns the nature of the catalytic sites, their formation, and the origin of the synergetic interaction between sulphides of different metals. The supports will not be the object of further discussions: we already mentioned the main effects they produce, at least in so far as their action has been analysed.

4.1. FUTURE ROLE OF CHEMICAL ENGINEERING

In this section, the objective is only to enumerate particularly important tasks that chemical engineering will have to carry out.

The overall design of the refinery and of each plant in the refinery will continue to undergo an evolution aimed at optimising the combination of the various steps. The criteria will mainly be an efficient use of hydrogen and economy of energy. But, in addition, other more specific studies are necessary. This is the case, in particular, of fundamental investigations aimed at understanding heat and mass transfers between the three phases (catalysts, liquid feed and gas) present in most hydrotreating reactors. The design and operation of the corresponding reactors (slurry, ebullating bed, trickle bed) have still to be considerably improved.

A major, although not yet common, task of chemical engineering will be to incorporate in models the results of kinetic analyses of the complicated network of reactions which is usually involved. Reasonable simplifications will be necessary. This can be done, for example, thanks to a "lumping" procedure, namely grouping together in a single ideal reaction all the reactions which are chemically similar.

Examples of such groups could be hydrogenation of aromatic rings, hydrogenation of unsaturated rings containing heteroatoms, bond breaking (similar to β-elimination, between aliphatic carbon and heteroatom), bond breaking catalysed by acidic sites, hydrogenolysis of carbon–carbon bonds, hydrogenolysis (namely with direct reaction with hydrogen) of carbon–heteroatom bonds, etc.

A new problem for chemical engineering will be to take into account the interconversion of catalytic sites. It is very likely that this line of work will lead to a more sophisticated control of the H_2S/H_2 ratio at different levels of the catalytic bed in the industrial reactor.

It seems unlikely that new studies on the effect of texture would lead to spectacular results if they are based only on classical concepts. This control of texture has been the main topic in the last 15 or 20 years. The modelling has probably become so elaborate that no substantial improvement can be anticipated if the work is pursued along the same lines. Serious contradictions exist between the experimental results presented by various authors who tried to change systematically the porous texture. It seems that calculations based on the diffusivity of molecules are not sufficient to make correct predictions. New factors or parameters must be taken into account. One such parameter, for example, could be the more or less hydrophilic or hydrophobic nature of pore walls. Another factor is related to a comment made previously, namely the fact that the different types of catalytic centres are not situated at the same depth in pores (or, at least, the systems behave as if they were situated at different depths). Still other phenomena to take into account might be the polymerisation of some molecules contained in the feed, leading to pore obstruction, effects due to surface migration, or catalytic activity due to deposits (such as nickel or vanadium [6]). With respect to this last point, it should be recalled that vanadium sulphides possess substantial catalytic activity of their own [105].

In the future, hydrotreating catalysts will certainly have a more sophisticated structure. The design of new structural details will need a close co-operation between specialists of chemical engineering and scientists expert in the nature of catalytic sites and catalytic reactions. Such a development could have its origin in the possibilities one begins to discern thanks to recent investigations. For example, the balance of the various functions (hydrogenation/hydrogenolysis) of hydrotreating catalysts changes when the active phase composition changes (e.g. ratio: group VIII metal/group VI metal) and when the partial pressure of hydrogen sulphide is modified. Following a line initiated a few years ago [101,106–108], one could control selectivity in hydrodesulfurization by designing catalysts with different distributions of each metal inside the pellets. In such a way, selectivity at each point will be optimised account taken of the diffusion processes.

4.2. GENESIS OF CATALYTIC SITES

It is well established now that the catalytic sites for the various reactions involving hydrogen in hydrotreating catalysts are situated on the edge planes of MoS_2 or

WS_2 (the edges of the layers). The work of the Group in Lille cited above [51,52] emphasizes the essential role of molybdenum (or tungsten) atoms with three unsaturated co-ordination positions in hydrogenation reaction. A consequence is that, in addition to the specific surface area (or dispersion), the *form* of the sulphide crystallites is important. It seems that one of the principal roles of new supports would be to control simultaneously both parameters, namely dispersion and form [24,26], as suggested by a comparison between Al_2O_3 and TiO_2 [24]. One of the principal effects of zirconia would correspond to this sort of action [109]. A systematic investigation of the influence of supports on the morphology of the supported phases should take place if it is wished to take advantage of this kind of phenomena.

The conditions of activation, namely catalyst sulfidation (or reduction–sulfidation) constitute important parameters for the genesis of centres for hydrogenation and hydrogenolysis of carbon–heteroatom bonds. This has been shown a few years ago in a detailed study, in the case of a commercial CoMo catalyst [43,110–112]. Recent results obtained with Ru/Al_2O_3 also mention conspicuous changes in the hydrogenation and HDS activities as a function of sulfidation temperature [32,113] (fig. 6). This sensitivity to the sulfidation conditions seems to be a general feature of all hydrotreating catalysts. A detailed study of this influence should be made with all new catalysts, either monometallic or bimetallic, using or not supports. It is

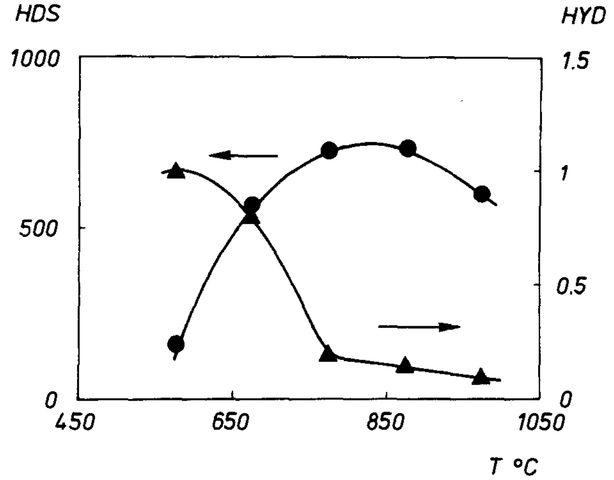

Fig. 6. Variation of the activities, measured as 10^8 mol/s per g catalyst, in the hydrogenation of biphenyl (HYD) and hydrodesulfurization of thiophene (HDS) measured separately, on a $Ru(7\%)/Al_2O_3$ catalyst, as a function of catalyst sulfidation temperature (15% H_2S/H_2, heating rate 0.16 K s^{-1}, 4 h) [32]. Although the experimental conditions are not mentioned in that article, they are likely to be those used in other articles [29,30], namely: (i) HYD: 530 K; total pressure: 25 bar; biphenyl pressure: 6 Torr; (ii) HDS: 623 K; total pressure: 1 bar; thiophene pressure: 17.9 Torr.

very important that the reduction–sulfidation procedure and pretreatment of catalysts be described in a detailed way in future publications. This is absolutely necessary to permit other authors to reproduce the results.

One does not know yet the location of the active sites nor the co-ordination of metal atoms determining activity in the case of non-conventional catalysts. However, there are indications that a similitude in many respects exists between these "new" metal sulphides and molybdenum disulphide (or tungsten disulphide). Just as an example, it is striking to compare a non-supported CoMo (fig. 7) and a RuMo catalyst (fig. 8) [32,115]. The experiments are not identical, as indicated in the legends. Nevertheless, it is easy to notice that, in both cases, the conditions of activation exert a crucial influence. In both cases, the hydrogenating activity (HYD) and the activity in the hydrogenolysis of the C–S bond (HDS) change in opposite directions (namely, the HYD/HDS ratio changes considerably). In both cases, HDS is favoured after sulfidation in the more severe conditions (action of pure hydrogen in the first and higher temperature in the second example). It is also inter-

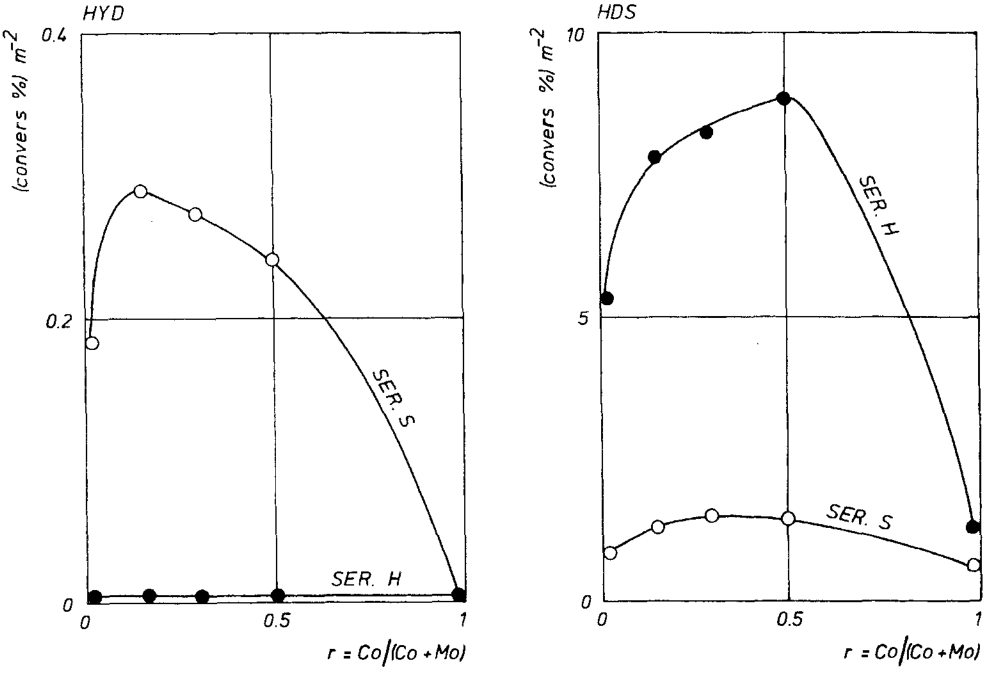

Fig. 7. Comparison of catalytic activities in simultaneous hydrogenation of cyclohexene (HYD) and hydrogenolysis of the C–S bond of thiophene (HDS) ($T = 578$ K; 3 MPa; other conditions as in fig. 4) of sulfided, non-supported CoMo catalysts pre-treated by hydrogen (series H) and an argon–hydrogen sulphide mixture (series S) at 673 K for 4 h [44,114].

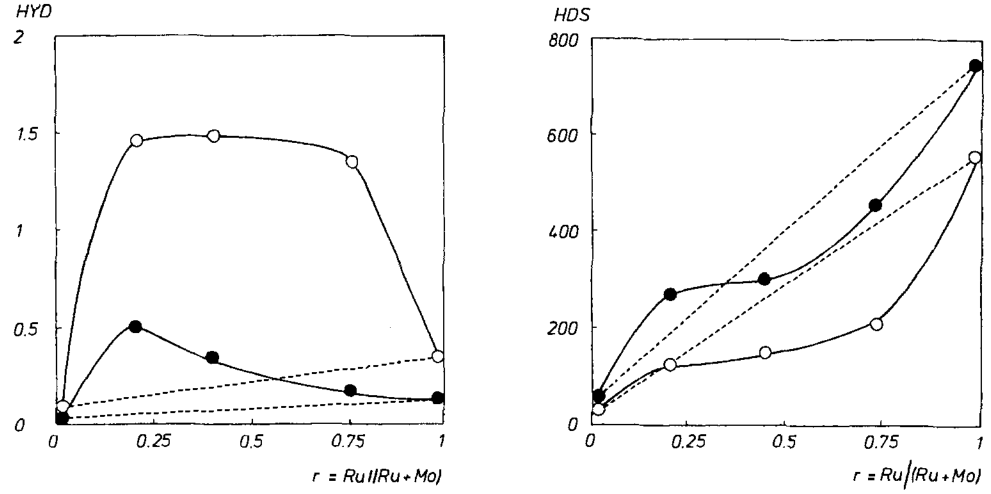

Fig. 8. Comparison of the catalytic activities in the hydrogenation of biphenyl (HYD) (a) and hydrodesulfurization of thiophene (HDS) (b) measured separately on sulfided RuMo catalysts, after activation (sulfidation at atmospheric pressure with 15% H_2S in H_2 at 673 K (○) or 873 K (●) during heating at 0.16 K s^{-1}, and further maintaining at the selected temperature for 4 h). The activities are expressed as 10^8 molec. s^{-1} g^{-1} [115]. The conditions for the tests were:

Reaction	Reactant	Temp.	Total pressure	Reactant pressure	H_2S
HYD	biphenyl	530 K	2.3 MPa	0.8 kPa	43.5 kPa
HDS	thiophene	623 K	0.1 MPa	2.4 kPa	0

esting to indicate another set of results for the RuMo catalyst: compared to fig. 8b, the variation of the HDS activity versus composition takes a different form if sulfidation is made in a H_2–H_2S mixture [115]. This observation strengthens the conclusion that the conditions of sulfidation have a very strong influence on the catalytic properties. This justifies our recommendation to give more attention to a precise control of these conditions.

A different problem is the genesis of acidic centres. This point deserves much more attention than actually received until now. In spite of the scarcity of systematic investigations, the general wisdom extracted from practical experience is that the major part of acidity is due to the support and promoters with the conventional HDS and HDN catalysts. But non-conventional metals may themselves contribute to acidity by bringing very useful strongly acidic groups, as suggested by results obtained with niobium sulphide [116]. These sites possess an appreciable activity for breaking certain C–N bonds. The acidic properties that metal sulphides bring to hydrotreating catalysts constitute an important topic for investigation to conduct in the future.

The results mentioned in this section can serve to stimulate new investigations. It is however necessary to verify that the changes of selectivity observed are not altered too rapidly as a function of time, as a consequence of ageing processes; otherwise these investigations would be useless.

4.3. INFLUENCE OF THE COMPOSITION OF THE REACTING MIXTURE

The influence of the hydrogen sulphide content on the catalytic properties of classical HDS and HDN catalysts has been shown to be considerable. A similar effect is observed with non-conventional metals. Fig. 9 [30] shows that the variations are not proportional for the sulphides of niobium, molybdenum and ruthenium.

Recent studies confirm the known conclusion that hydrogen sulphide has a different influence on HDS and HDN. It is very interesting to notice that in the HDN of 1,2,3,4-tetrahydroquinoline, the synergy between nickel and molybdenum is very weak in the absence of, but quite important in the presence of, hydrogen sulphide: it has been mentioned in literature [36] that the activity of a catalyst of composition $Ni/(Ni + Mo) = 0.30$ in the presence of hydrogen sulphide is 11 times larger than that of catalysts containing only molybdenum or only nickel in the same conditions.

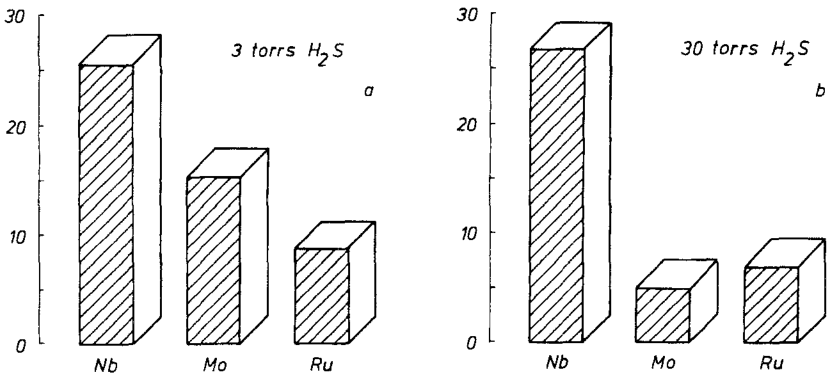

Fig. 9. Influence of the partial pressure of hydrogen sulphide on the conversion of *n*-pentylamine on sulphides of niobium, molybdenum and ruthenium. The reactivity scale is expressed in 10^{-8} molec. s^{-1} m^{-2} [30]. The conditions for the test were: temperature: 548 K; total pressure: 0.1 MPa: pentylamine pressure: 136 Pa; H_2S pressure: 395 Pa (3 Torr) or 3.95 kPa (30 Torr).

It has also been verified that the HDS and HDN reactions are not affected in the same way by a modification of the hydrogen pressure [117].

It is not yet possible to evaluate the part of these effects which is due to the interconversion between hydrogenation and hydrogenolysis sites (as mentioned in a former section), on the one hand, and the competition for active sites between hydrogen sulphide and the other reactants, on the other hand. This problem has stimulated fruitful investigations in chemical engineering laboratories [47,48]. Various models have been used [46,101,106–108], several of them based on the remote control theory. It is mandatory to pursue and refine this sort of investigations for gathering the data necessary in view of an efficient control of the industrial processes.

4.4. CATALYSTS CONTAINING TWO ACTIVE ELEMENTS

Synergy phenomena are well known in catalysts containing elements of group VI (Mo or W) and elements of group VIII (Co, Ni or Fe) in the sulfided state. Synergy is observed both in hydrogenation and hydrogenolysis of carbon–heteroatom bonds. The origin has been discussed in the first section.

Recently, the occurrence of synergies with other elements has also been discovered.

The effect observed with mixtures of CoMo/Al_2O_3 and NiMo/Al_2O_3 catalysts [118] corresponds to special interpretations. In this case, the synergy can be explained in a simple way by the fact that the mixture presents a more favourable balance of hydrogenation and hydrogenolysis activities. Another possible explanation is a bifunctional mechanism, namely that some molecules undergo a first reaction on one of the catalysts, and a subsequent reaction on the other. The existence of acidic sites in the NiMo/Al_2O_3 catalyst in the work cited (a classical commercial HDN catalyst) suggests that one of the catalytic functions involved is acidity. This effect is probably similar, mechanistically, to the co-operation between catalytic sulphides and zeolites in hydrocracking catalysts (or to the effects observed in the system: Mo-zeolite already mentioned) [29,119]. There are indications that this type of co-operation could permit to spare hydrogen [120].

But other new results correspond to synergies which seem quite similar to those observed between molybdenum or tungsten, on the one hand, and cobalt, nickel or iron, on the other hand.

Various authors mentioned a synergy between ruthenium and molybdenum (both sulfided) [32,75,121–123]. This was illustrated in fig. 8a. These catalysts had been prepared by successive impregnation of alumina by molybdenum and ruthenium. With such a preparation technique, the size of the metal sulphide crystallites (or dispersion) as well as their shape may change when the proportion of metal varies, and isolating synergetic from textural effects is difficult. For this reason, it is preferable, in experiments aimed at fundamental studies, to use catalysts in which these parameters do not change. This is what we had done in the experiments of fig. 4 ($CoS_x/C + MoS_2/\gamma\text{-}Al_2O_3$) and fig. 5 ($Co_9S_8$ + NiMoS). Each component of the mechanical mixture had an identical structure and texture in each experiment. Recently, we made similar experiments with different catalytic systems [42,75,76,103]. We started also from sulphides prepared separately. We mixed molybdenum or tungsten sulphide with supported group VIII metals (of periods 5 and 6), duly sulfided. The mixing procedure consisted in suspending the powders in *n*-pentane agitating, and drying [124,125]. Figs. 10, 11 and 12 ($WS_2 + RhS_x/Al_2O_3$; $WS_2 + PdS_x/Al_2O_3$; $MoS_2 + PtS_x/Al_2O_3$, respectively) indicate conspicuous synergies. It should be emphasised that, in these experiments, the group VIII metals are located in the pores of the support; mutual contamination of the sulphides of group VI and group VIII metals is therefore quite unlikely.

It can be added that the reacting mixture (thiophene and cyclohexene) is very simple. This makes unlikely or even impossible a bifunctional mechanism in which two successive steps of the reaction of a given molecule would take place respectively on the two catalysts. A bifunctional reaction cannot be imagined for the hydrogenation of cyclohexene. The instability of thiophane, theoretically a possible intermediate between thiophene and the products due to the breaking of the C–S bonds, also make quite unlikely a bifunctional mechanism in the case of thiophene. Thiophane was never observed in substantial quantities in HDS reaction. Other explanations must therefore be found.

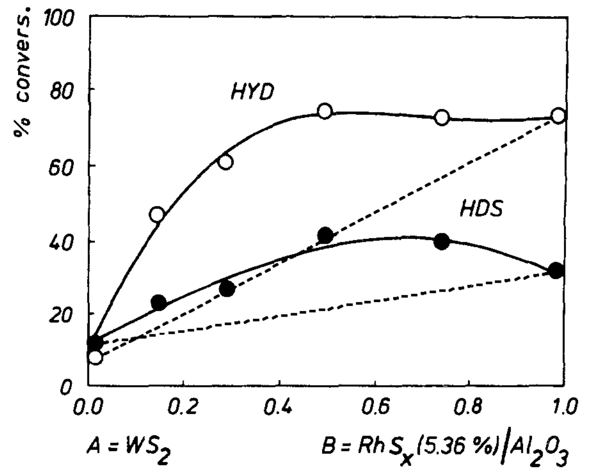

Fig. 10. Synergy between $RhS_x/\gamma\text{-}Al_2O_3$ and WS_2 ($T = 573$ K; total pressure = 3 MPa; liquid feed = 48 g h^{-1}; gaseous feed (H_2) = 3 g h^{-1}; total catalyst weight: 0.5 g, mixed with 3.0 g of quartz powder). Hydrodesulfurization (HDS) and hydrogenation (HYD) correspond to the conversion of thiophene and cyclohexene contained in 70% (weight) of cyclohexane in the proportion of 0.5% and 29.5%, respectively [124,125].

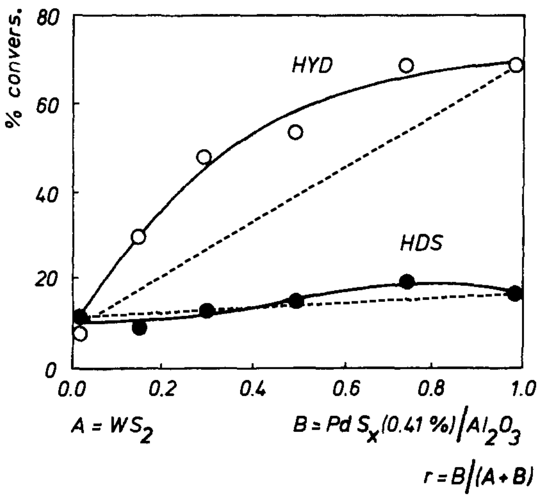

Fig. 11. Synergy between $PdS_x/\gamma\text{-}Al_2O_3$ and WS_2. The experimental conditions are the same as in fig. 10 [124,125].

It is clear that the effects illustrated in figs. 10, 11 and 12 fit perfectly in the frame of the remote control theory. But this theory, in spite of many experimental verifications, does not yet benefit from general acceptance. It is therefore not excluded that the results presented above could find an explanation or an interpretation in

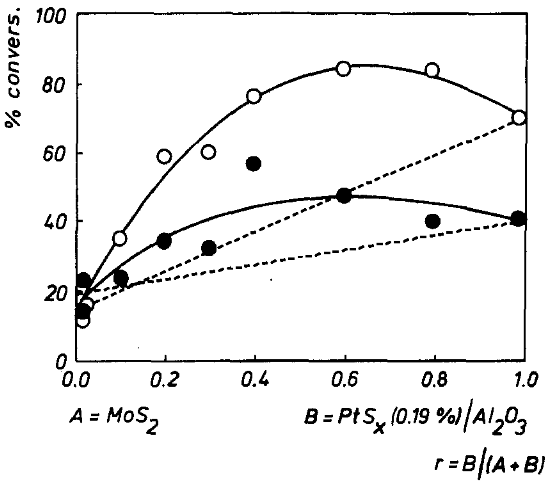

Fig. 12. Synergy between $PtS_x/\gamma\text{-}Al_2O_3$ and MoS_2. The experimental conditions are the same as in fig. 10 [124,125].

the frame of one of the 16 other theories which have been aimed at explaining the synergy between cobalt and molybdenum or nickel and tungsten, or by a new theory. It is desirable, and urgent, that such a scientific confrontation would foster advances in the understanding of synergies in all these catalytic systems.

It is interesting to consider these results with reference to the classical curves of Pecoraro and Chianelli [126] for dibenzothiophene HDS (fig. 13) or Eisbouts et al. [128] for quinoline HDN (fig. 14) or other authors [130–132]. We notice that in almost all cases where synergy has been observed, this occurs between metals situated respectively on the left-hand and on the right-hand "slope" of the volcano curves. The remote control theory supposes that the mobile oxygen species (spillover) is formed by dissociation of molecular hydrogen H_2 on the sulphide of the right-hand part. It would migrate to the other sulphide situated on the left-hand side, on the surface of which it would increase the number of active sites. If this

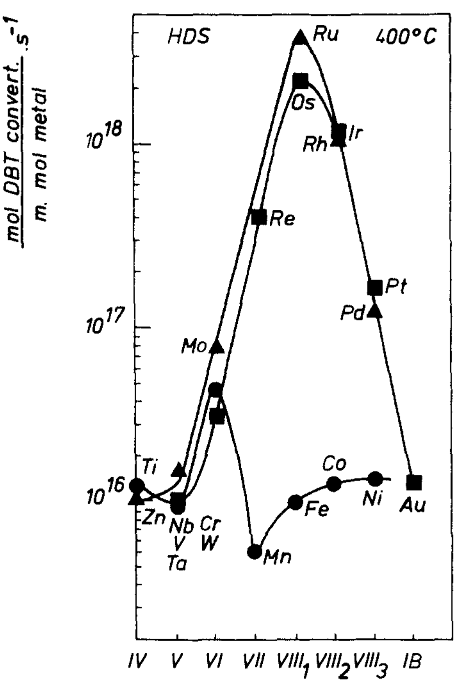

Fig. 13. Tendencies in the periodical system, for the hydrodesulfurization of dibenzothiophene (4.4 g dissolved in 100 cm^3 decaline, namely about 0.89 wt% S). Reactions in an autoclave of the Carberry type. 1 g of catalysts was presulfided in 15% H_2S in H_2 (90 min at 25–400°C). Reaction temperature was 673 K [126]. The other reaction conditions are probably those described in another paper [127], namely: total pressure: 3.1 MPa; hydrogen flow rate: 100 cm^3 min^{-1} (H_2/DBT molar ratio 700/1). Details concerning the preparation of catalysts in the above references.

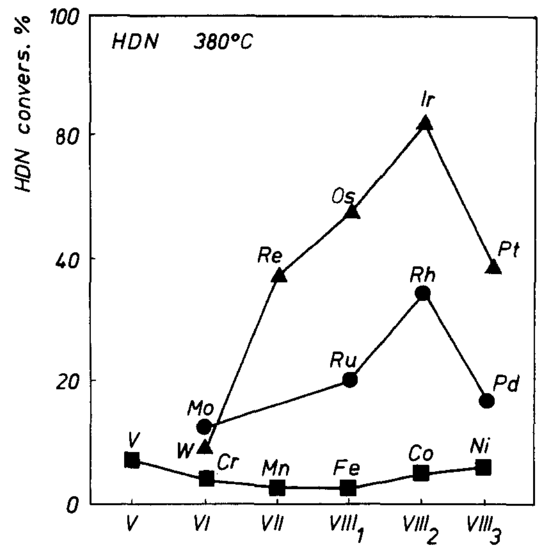

Fig. 14. Tendencies in the periodical system, for the hydrodenitrogenation of quinoline (5.9 mol% quinoline, 93.6 mol% hexadecane, 0.5 mol% carbon disulphide). Catalyst sulfided with 10% H_2S in H_2, with temperature increasing from 293 to 653 K and then maintained at 653 K for 1 h. Reactions in a stirred autoclave; 653 K; approximate pressure 5 MPa [128]. Other details, including the preparation of the catalysts, in refs. [128,129].

explanation is not accepted, another one should be proposed. The explanation of synergy effects by Harris and Chianelli [127,133] is either the formation of mixed sulphides of "pseudobinary sulphides" [134] or an electronic transfer between the sulphides [133]. Our sulphides are separated from each other in space, excluding a pseudo-binary or a mixed sulphide. They are only connected indirectly through the fluid phase and the surface of alumina and/or carbon which possess a very low conductivity. The explanations of Harris and Chianelli therefore cannot account for our results.

In order to progress in the theoretical understanding of synergy, it is necessary to investigate in-depth the modifications that a promoter brings about in the surface structure of the active phase. There are already indications that the co-ordination and/or the sulfidation state of the catalytic element could change in function of the experimental conditions. A key to the understanding of hydrotreatment catalysts would be a precise determination of the mutual influence of the different sulphides present in catalysts on the co-ordination of surface atoms. If it turns out that the majority of investigators remain reluctant to accept the remote control concept, it will nevertheless be necessary to take into account some form of superficial migration. In this case, hydrogen would be the most likely candidate for such a migration.

The lack of agreement of the scientific community with respect to the mechanism underlying synergy does not constitute an obstacle for discovering new catalytic systems with conspicuous properties. The examples presented in figs. 8a, 10, 11 and 12 indicate that the volcano curves of refs. [126–134] constitute a possible source of inspiration, even if the origin of the co-operation between elements of the left-hand "slope" of the volcano with elements of the right-hand "slope" can be explained in different ways. There is no doubt that the strength of the metal–sulphur bond changes when going from one side of the volcano to the other. The problem is to correlate the tendency of surface atoms to acquire certain co-ordination unsaturations favourable either to the hydrotreating reactions or to the dissociation of hydrogen. These might well be two distinct problems.

5. Final considerations

The number of scientific papers published on hydrotreating reactions has been increasing at an accelerated rate in the last years. Excepting the oxide coupling of methane, this is the research field that is developing most rapidly in catalysis. In addition, hydrotreatments are usually considered first when non-conventional feeds have to be refined (this includes biomass or oils obtained by pyrolysis of biomass). There is no doubt that the hydrotreatment will get still more importance in the future, from both the practical and scientific points of view.

In this contribution we insisted more on the achievements which have a direct impact than on other advances or discoveries made in the field of hydrotreating. In particular, conspicuous progresses have been made with respect to processes involved in the fabrication of catalysts. These progresses permit the manufacture of better catalysts. They also make possible the preparation of experimental catalysts with a well controlled structure in order to facilitate the interpretation of experimental results. These advances are particularly dramatic when the impregnation step is considered. Very interesting fundamental results with various supports can be obtained using equilibrium adsorption [135–141]. Thanks to a fine control of the various parameters, it was possible to make catalysts with various axial or radial profiles across pellets or beads [102,142]. Starting from results already mentioned (see, for example, refs. [9–11]), these lines of research pave the way to use promoters in a better controlled way. Other advances concern the physico-chemical techniques used for identifying the catalysts. In the last years, considerable efforts have been made for identifying catalytic sites. The methods using temperature programmed processes (TPR, TPO, temperature programmed sulphidation) and isotopic exchanges (H_2–D_2) get refined. Much effort is directed at setting up reliable methods using probe molecules: NO, CO, thiophene, and, quite logically, NH_3 or pyridine. Until now, it has not yet been possible to identify perfectly the different catalytic sites present on the sulphide phases, but there is some justified hope that we are approaching the goal.

Sulfided catalysts are different, in many respects, from metals and acid–base catalysts. It seems that they possess features that give them certain similitude with transition metal oxides, which, except for two exceptions, constitute the totality of the selective oxidation catalysts. Nevertheless the sulphides, generally speaking, constitute a group of their own.

There are many different members of this group, taking single sulphides and systems containing two or three different elements. It is striking that investigation in this field and the results obtained permitted new developments of catalytic science, and that these developments have consequences in other fields of catalysis. As examples of these links with other fields, one may cite the zeolites (co-operation in cracking), the poisoning of metals (thioresistance, namely the resistance to sulphur that certain associations of metals, or metals with metal compounds exhibit), the transition metal oxides (occurrence of a remote control). As the catalytic properties of sulphides get explored in more detail, their use in fine chemistry or fields reserved until now to metals (hydrogenation, Fischer–Tropsch or related reactions) which is already contemplated, might become quite important. These are probably just a few "fall-outs" of a rapidly developing field of catalytic science.

References [#1]

[1] (*Rev*) B. Delmon, in: *Catalysts in Petroleum Refining 1989*, eds. D.L. Trimm, S. Akashah, M. Absi-Halabi and A. Bishara (Elsevier, Amsterdam, 1990) pp. 1–40.
[2] P.C.H. Mitchell, ed., *Hydrodemetallisation Catalysts*, Catal. Today 7 (4) (1990).
[3] M. Breysse and S. Szabo, eds., *New Development in Hydrodenitrogenation*, Catal. Today 10 (4) (1991).
[4] P. Grange, ed., *IVth Workshop on Hydrotreatment*, 21–22 Nov. 1991, Bull. Soc. Chim. Belg. 100 (1991) 767–991.
[5] A. Nishijima et al., eds., *Proc. 1st Japan–EC Workshop on the Frontiers of Catalytic Science and Technology for Alternative Energy and Global Environmental Protection JECAT '91* (JITA and RITE, Tokyo, 1991).
[6] F. Melo Faus, P. Grange and B. Delmon, Appl. Catal. 11 (1984) 281.
[7] Ch. Kordulis, F. Melo Faus and B. Delmon, Appl. Catal. 23 (1986) 367.
[8] A. Arteaga, J.L.G. Fierro, P. Grange and B. Delmon, in: *Catalyst Deactivation*, eds. B. Delmon and G.F. Froment (Elsevier, Amsterdam, 1987) pp. 59.
[9] Ch. Papadopoulou, A. Lycourghiotis, P. Grange and B. Delmon, Appl. Catal. 38 (1988) 255.
[10] H.K. Matralis, A. Lycourghiotis, P. Grange and B. Delmon, Appl. Catal. 38 (1988) 273.
[11] J.L.G. Fierro, R. Cuevas, J. Ramírez and A. López Agudo, Bull. Soc. Chim. Belg. 100 (1991) 945.
[12] (*Rev*) M. Breysse, D. Hamon, M. Lacroix, M. Vrinat, in: *Proc. JECAT '91*, eds. A. Nishijima et al. (JITA and RITE, Tokyo, 1991) pp. 36–43.
[13] K. Segawa and D.S. Kim, in: *Proc. JECAT '91*, eds. A. Nishijima et al. (JITA and RITE, Tokyo, 1991) pp. 44–47.
[14] Zh.-B. Wei, X.-X. Guo, E.L. Sham, P. Grange and B. Delmon, Appl. Catal. 63 (1990) 305.

[#1] Articles marked (*Rev*) are reviews or can be considered as such.

[15] Zh.-B. Wei, Q. Xin, X.-X. Guo, P. Grange and B. Delmon, Appl. Catal. 75 (1991) 179.

[16] M.W.J. Crajé, V.H.J. de Beer and A.M. van der Kraan, Bull. Soc. Chim. Belg. 100 (1991) 953.

[17] J.C. Duchet, M.J. Tilliette and D. Cornet, Catal. Today 10 (4) (1991) 507.

[18] D. Hamon, M. Vrinat, M. Breysse, B. Durand, M. Jebrouni, M. Roubin, P. Magnoux and T. des Courières, Catal. Today 10 (4) (1991) 613.

[19] (*Rev*) F. Luck, Bull. Soc. Chim. Belg. 100 (1991) 781.

[20] F.P. Daly J. Catal. 116 (1989) 600.

[21] I. Wang and R.-C. Chang, J. Catal. 117 (1989) 266.

[22] C. Moreau, L. Bekara, P. Geneste, J.L. Olivé, J.C. Duchet, M.J. Tilliette and J. Grimblot, Bull. Soc. Chim. Belg. 100 (1991) 841.

[23] D. Hamon, M. Vrinat, M. Breysse, B. Durand, F. Beauchesne and T. des Courières, Bull. Soc. Chim. Belg. 100 (1991) 933.

[24] (*Rev*) M. Breysse, J.L. Portefaix and M. Vrinat, Catal. Today 10 (4) (1991) 489.

[25] J.C. Duchet, N. Gnofam, J.L. Lemberton, G. Perot, L. Bekakra, C. Moreau, J. Joffre, S. Kasztelan and J. Grimblot, Catal. Today 10 (4) (1991) 593.

[26] F. Maugé, J.C. Duchet, J.C. Lavalley, S. Houssenbay, E. Payen, J. Grimblot and S. Kasztelan, Catal. Today 10 (4) (1991) 561.

[27] (*Rev*) M. Zdrazil, Bull. Soc. Chim. Belg. 100 (1991) 769.

[28] M.J. Ledoux, C. Kippelen, G. Maire, G. Szabo, J. Goupyl and O. Krause, Bull. Soc. Chim. Belg. 100 (1991) 873.

[29] S. Göbölös, M. Lacroix, T. Decamp, M. Vrinat and M. Breysse, Bull. Soc. Chim. Belg. 100 (1991) 907.

[30] M. Breysse, J. Afonso, M. Lacroix, J.L. Portefaix and M. Vrinat, Bull. Soc. Chim. Belg. 100 (1991) 923.

[31] S. Yuan, T. Decamp, M. Lacroix, C. Mirodatos and M. Breysse, J. Catal. 132 (1991) 253.

[32] C. Geantet, J. De Los Reyes, M. Vrinat and M. Breysse, *Proc. JECAT '91*, eds. A. Nishijima et al. (JITA and RITE, Tokyo, 1991) pp. 228–231.

[33] F.-S. Xiao, Q. Xin and X.-X. Guo, React. Kinet. Catal. Lett. 46 (1992) 351.

[34] L. Vivier, P. d'Aranjo, S. Kasztelan and G. Perot, Bull. Soc. Chim. Belg. 100 (1991) 807.

[35] (*Rev*) M. Zdrazil, Appl. Catal. 4 (1982) 107.

[36] (*Rev*) G. Perot, Catal. Today 10 (4) (1991) 447.

[37] J.L. Portefaix, M. Cattenot, M. Guerriche, J. Thivolle-Cazat and M. Breysse, Catal. Today 10 (4) (1991) 473.

[38] (*Rev*) M. Zdrazil and M. Kraus, in: *Catalytic Hydrogenation*, ed. L. Cerveny (Elsevier, Amsterdam, 1986) pp. 257–276.

[39] (*Rev*) H. Schulz, M. Schon and N.M. Rahman, in: *Catalytic Hydrogenation*, ed. L. Cerveny (Elsevier, Amsterdam, 1986) pp. 201–255.

[40] (*Rev*) H. Schulz, *Proc. JECAT '91*, eds. A. Nishijima et al. (JITA and RITE, Tokyo, 1991) pp. 52–65.

[41] G. Delvaux, P. Grange and B. Delmon, J. Catal. 56 (1979) 99.

[42] D. Pirotte, P. Grange and B. Delmon, in: *Proc. 7th Int. Congr. on Catalysis*, eds. T. Seyiama and K. Tanabe (Kodansha/Elsevier, Tokyo/Amsterdam, 1981) 1422.

[43] R. Prada Silvy, J.L.G. Fierro, P. Grange and B. Delmon, in: *Preparation of Catalysts IV*, eds. B. Delmon, P. Grange, P.A. Jacobs and G. Poncelet (Elsevier, Amsterdam, 1987) pp. 605–617.

[44] (*Rev*) B. Delmon, in: *Proc. Climax 3rd Int. Conf. on Chemistry and Uses of Molybdenum*, eds. H.F. Barry and P.C.H. Mitchell (Climax Molybdenum Co., Ann Arbor, 1979) pp. 73–84.

[45] D. Pirotte, J.M. Zabala, P. Grange and B. Delmon, Bull. Soc. Chim. Belg. 90 (1981) 1239.

[46] I. Van Parijs, G.F. Froment and B. Delmon, Bull. Soc. Chim. Belg. 93 (1984) 823.

[47] C.-Y. Yu and G.F. Froment, Chem. Eng. Sci. 46 (1991) 3177.

[48] C.-Y. Yu and G.F. Froment, to be published.

[49] C. Steurbaut, MSc Thesis, Univ. Ghent (1991);
C. Steurbaut and G.F. Froment, to be published.
[50] B. Delmon and J.-L. Dallons, Bull. Soc. Chim. Belg. 97 (1988) 473.
[51] S. Kasztelan, H. Toulhoat, J. Grimblot and J.P. Bonnelle, Appl. Catal. 13 (1984) 127.
[52] S. Kasztelan, J. Jalowiecki, A. Wambeke, J. Grimblot and J.P. Bonnelle, Bull. Soc. Chim. Belg. 96 (1987) 1003.
[53] M. Callant, P. Grange, K.A. Holder and B. Delmon, Bull. Soc. Chim. Belg. 100 (1991) 823.
[54] (*Rev*) W. Böhringer and H. Schulz, Bull. Soc. Chim. Belg. 100 (1991) 831.
[55] (*Rev*) B. Delmon, in: *Proc. Climax 3rd Int. Conf. on Chemistry and Uses of Molybdenum*, eds. H.F. Barry and P.C.H. Mitchell (Climax Molybdenum Co., Ann Arbor, 1979) pp. 73–84.
[56] (*Rev*) P. Grange, Cat. Rev.-Sci. Eng. 21 (1980) 135.
[57] J.M.J.G. Lipsch and G.C.A. Schuit, J. Catal. 15 (1969) 174.
[58] V.H.J. de Beer, T.H.M. van Sint Fiet, J.F. Engelen, A.C. van Haandel, M.V.J. Wolfs, C.H. Amberg and G.C. Schuit, J. Catal. 27 (1972) 327.
[59] J. Sonnemans and P. Mars, J. Catal. 31 (1973) 209.
[60] M.A. Apecetche and B. Delmon, React. Kinet. Catal. Lett. 12 (1979) 385.
[61] (*Rev*) F.E. Massoth and G. MuraliDhar, in: *Proc. 4th Int. Conf. on Chemistry and Uses of Molybdenum*, eds. H.F. Barry and P.C.H. Mitchell Golden, CO, 9–13 August 1982 (Climax Molybdenum Co., Ann Arbor) pp. 343–355.
[62] F.E. Massoth, G. MuraliDhar and J. Shabtai, J. Catal. 85 (1984) 53.
[63] H. Knözinger, in: *Proc. 9th Int. Congr. on Catalysis*, Vol. 5, eds. M.J. Phillips and M. Ternan (The Chemical Institute of Canada, Ottawa, 1988) pp. 20–53.
[64] R.J.H. Voorhoeve and J.C.M. Stuiver, J. Catal. 23 (1971) 228.
[65] R.J.H. Voorhoeve, J. Catal. 23 (1971) 236.
[66] R.J.H. Voorhoeve and J.C.M. Stuiver, J. Catal. 23 (1971) 243.
[67] A.L. Farragher and P. Cossee, in: *Proc. 5th Int. Cong. on Catalysis*, ed. J.W. Hightower (North-Holland, Amsterdam, 1973) pp. 1301–1318.
[68] A.L. Farragher and P. Cossee, in: *Proc. 5th Int. Congr. on Catalysis*, ed. J.W. Hightower (North-Holland, Amsterdam, 1973) pp. 1316–1317.
[69] P.R. Wentrcek and H. Wise, J. Catal. 45 (1976) 349.
[70] P.R. Wentrcek and H. Wise, J. Catal. 51 (1978) 80.
[71] Y. Jacquin, in: *Catalyse de Contact*, eds. J.F. LePage et al. (Technip Publ., Paris, 1978) pp. 495–500.
[72] S.M.A.M. Bouwens, D.C. Koningsberger, V.H.J. de Beer and R. Prins, Bull. Soc. Chim. Belg. 96 (1987) 951.
[73] A.M. van der Kraan, M.W.J. Crajé, E. Gerkema, W.L.T.M. Ramselaar and V.H.J. de Beer, Appl. Catal. 39 (1988) L7.
[74] J.P.R. Vissers, V.H.J. de Beer and R. Prins, J. Chem. Soc. Faraday Trans. I 83 (1987) 2145.
[75] M. Karroua, PhD Thesis, Univ. Catholique de Louvain, Belgium (1991).
[76] M. Karroua, A. Centeno, H.K. Matralis, P. Grange and B. Delmon, Appl. Catal. 51 (1989) L21.
[77] H. Topsøe, B.S. Clausen, R. Candia, C. Wivel, S. Mørup, Bull. Soc. Chim. Belg. 90 (1981) 1189.
[78] H. Topsøe, B.S. Clausen, R. Candia, C. Wivel and S. Mørup, J. Catal. 68 (1981) 433.
[79] C. Wivel, R. Candia, B.S. Clausen, S. Mørup and H. Topsøe, J. Catal. 68 (1981) 453.
[80] (*Rev*) H. Topsøe, in: *Surface Properties and Catalysis by Non-Metals*, eds. J.P. Bonnelle, B. Delmon and E.G. Derouane (Reidel, Dordrecht, 1983) pp. 329–360.
[81] N.-Y. Topsøe, H. Topsøe, O. Sørensen, B.S. Clausen and R. Candia, Bull. Soc. Chim. Belg. 93 (1984) 727.
[82] (*Rev*) H. Topsøe, R. Candia, N.-Y. Topsøe and B.S. Clausen, Bull. Soc. Chim. Belg. 93 (1984) 783.

[83] (*Rev*) H. Topsøe and B.S. Clausen, Catal. Rev.-Sci. Eng. 26 (1984) 395.
[84] H. Topsøe and B.S. Clausen, Appl. Catal. 25 (1986) 273.
[85] R. Candia, O. Sørensen, J. Villadsen, N.-Y. Topsøe, B.S. Clausen and H. Topsøe, Bull. Soc. Chim. Belg. 93 (1984) 763.
[86] H. Topsøe and B.S. Clausen, Appl. Catal. 25 (1986) 273.
[87] S. Göbölös, Q. Wu, F. Delannay, P. Grange, B. Delmon and J. Ladrière, Polyhedron 5 (1986) 219.
[88] S. Göbölös, Q. Wu, J. Ladrière, F. Delannay, P. Grange and B. Delmon, *2nd Czechoslovak Conf. on Preparation and Properties of Heterogeneous Catalysts*, Bechyne, Czechoslovakia, 3–7 June 1985, p. 62.
[89] M. Breysse, R. Frety, B. Benaichouba and P. Bussière, Radiochem. Radioanal. Lett. 59 (1983) 265.
[90] M. Breysse, R. Frety, M. Vrinat, P. Grange and M. Genet, Appl. Catal. 12 (1984) 164.
[91] M. Vrinat, M. Breysse and R. Frety, Appl. Catal. 12 (1984) 151.
[92] M. Lacroix, M. Vrinat and M. Breysse, Appl. Catal. 21 (1986) 73.
[93] R.A. Ware and J. Wei, J. Catal. 93 (1985) 100.
[94] R.A. Ware and J. Wei, J. Catal. 93 (1985) 122.
[95] R.A. Ware and J. Wei, J. Catal. 93 (1985) 135.
[96] M.W.J. Crajé, V.H.J. de Beer and A.M. van der Kraan, Bull. Soc. Chim. Belg. 100 (1991) 953.
[97] S.M.A.M. Bouwens, D.C. Koningsberger, V.H.J. de Beer and R. Prins, Bull. Soc. Chim. Belg. 96 (1987) 951.
[98] A.M. van der Kraan, M.W.J. Crajé, E. Gerkema, W.L.T.M. Ramselaar and V.H.J. de Beer, Appl. Catal. 39 (1988) L7.
[99] G. Hagenbach, Ph. Courty and B. Delmon, J. Catal. 23 (1971) 295.
[100] G. Hagenbach, Ph. Courty and B. Delmon, J. Catal. 31 (1973) 264.
[101] J.L.G. Fierro, J.M. Asua, P. Grange and B. Delmon, ACS Div. Petrol. Chem. Preprints 32 (1987) 271.
[102] J.M. Zabala, M. Mainil, P. Grange and B. Delmon, Compt. Rend. Acad. Sci. 280 C (1975) 1129.
[103] M. Karroua, P. Grange and B. Delmon, Appl. Catal. 50 (1989) L5.
[104] see, for example, Modern automotive retail, Shell Briefing Service, Royal Dutch Shell, February 1990.
[105] C. Guillard, M. Lacroix, M. Vrinat, M. Breysse, B. Mocaer, J. Grimblot, T. des Courières and D. Faure, Catal. Today 7 (1990) 587.
[106] J.M. Asua and B. Delmon, in: *Proc. 9th Ibero-American Symp. on Catalysis*, eds. M. Farinha Portela et al., Lisbon, 16–21 July 1984, pp. 1653–1654.
[107] J.M. Asua and B. Delmon, Appl. Catal. 12 (1984) 249.
[108] J.M. Asua and B. Delmon, Ind. Eng. Chem. Res. 26 (1987) 32.
[109] J.C. Duchet, M.J. Tilliette, D. Cornet, L. Vivier, G. Perot, L. Bekakra, C. Moreau and G. Szabo, Catal. Today 10 (4) (1991) 579.
[110] R. Prada Silvy, F. Delannay, P. Grange and B. Delmon, Polyhedron 5 (1986) 195.
[111] R. Prada Silvy, J.M. Beuken, J.L.G. Fierro, P. Bertrand and B. Delmon, Surf. Interf. Anal. 8 (1986) 167; 9 (1986) 247.
[112] R. Prada Silvy, F. Delannay and B. Delmon, Indian J. Technol. 25 (1987) 627.
[113] J.A. De Los Reyes, M. Vrinat, C. Geantet and M. Breysse, Catal. Today 10 (4) (1991) 645.
[114] D. Pirotte, PhD Thesis, Univ. Catholique de Louvain, Belgium (1983).
[115] C. Geantet, S. Göbölös, J.A. De Los Reyes, M. Cattenot, M. Vrinat and M. Breysse, Catal. Today 10 (4) (1991) 665.
[116] M. Danot, J. Afonso, J.L. Portefaix, M. Breysse and T. des Courières, Catal. Today 10 (1991) 629.
[117] (*Rev*) S. Kasztelan, T. des Courières and M. Breysse, Catal. Today 10 (4) (1991) 433.

[118] C. Moreau, L. Bekakra, R. Durand and P. Geneste, Catal. Today 10 (4) (1991) 681.

[119] T.G. Harvey and T.W. Matheson, J. Catal. 101 (1986) 253.

[120] (*Rev*) M. Sugioka, J. Japan Petrol. Inst. (Sekiyu Gakkaishi) 33 (1990) 280.

[121] P.C.H. Mitchell and C.E. Scott, Bull. Soc. Belg. 93 (1984) 619.

[122] P.C.H. Mitchell, C.E. Scott, J.P. Bonnelle and J. Grimblot, J. Catal. 107 (1987) 482.

[123] J. Shabtai, Q. Guohe, K. Balusami, N.K. Nag and F.E. Massoth, J. Catal. 113 (1988) 206.

[124] S. Giraldo, P. Grange and B. Delmon (see B. Delmon, Actas, XIII Simposio Iberoamericano de Catálisis, eds. S. Vic Bellon, F. Mendioroz Echeverria and F. MeloFaus, Segovia, 6–10 July 1992, p. 1).

[125] S. Giraldo, P. Grange, B. Delmon, in: *3rd Int. Conf. on Spillover*, eds. T. Inui et al., Kyoto, 17–20 August 1993, in press.

[126] T.A. Pecoraro and R.R. Chianelli, J. Catal. 67 (1981) 430.

[127] (*Rev*) R.R. Chianelli, in: *Surface Properties and Catalysis by Non-Metals*, eds. J.P. Bonnelle, B. Delmon and E.G. Derouane (Reidel, Dordrecht, 1983) pp. 261–378.

[128] S. Eijsbouts, V.H.J. de Beer and R. Prins, J. Catal. 109 (1988) 217.

[129] S. Eijsbouts, V.H.J. de Beer and R. Prins, J. Catal. 127 (1991) 619.

[130] M.J. Ledoux, O. Michaux, G. Agostini and P. Panissod, J. Catal. 102 (1986) 275.

[131] M. Lacroix, N. Boutarfa, C. Guillard, M. Vrinat and M. Breysse, J. Catal. 120 (1989) 473.

[132] S. Eijsbouts, C. Dudhakar, V.H.J. de Beer and R. Prins, J. Catal. 127 (1991) 605.

[133] S. Harris and R.R. Chianelli, J. Catal. 98 (1986) 17.

[134] R.R. Chianelli, T.A. Pecoraro, T.R. Halbert, W.-H. Pan and E.I. Steifel, J. Catal. 86 (1984) 226.

[135] L. Vordonis, P.G. Koutsoukos and A. Lycourghiotis, J. Catal. 98 (1986) 296.

[136] L. Vordonis, P.G. Koutsoukos and A. Lycourghiotis, Langmuir 2/3 (1986) 281.

[137] L. Vordonis, P.G. Koutsoukos and A. Lycourghiotis, J. Catal. 101 (1986) 186.

[138] K. Akratopoulou, L. Vordonis and A. Lycourghiotis, J. Catal. 109 (1988) 41.

[139] N. Spanos, L. Vordonis, Ch. Kordulis and A. Lycourghiotis, J. Catal. 124 (1990) 301.

[140] N. Spanos, L. Vordonis, Ch. Kordulis, P. Koutsoukos and T. Lycourghiotis, J. Catal. 124 (1990) 315.

[141] N. Spanos, H. Matralis, Ch. Kordulis and A. Lycourghiotis, J. Catal. 136 (1992) 432.

[142] J.L.G. Fierro, P. Grange and B. Delmon, in: *Preparation of Catalysts IV*, eds. B. Delmon, P. Grange, P.A. Jacobs and G. Poncelet (Elsevier, Amsterdam, 1987) pp. 591–601.