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Recent studies on the preparation, activation and design of active phases and supports of hydrotreating catalysts

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Abstract

Commercial hydrotreating catalysts are usually composed of a sulfide active phase, molybdenum or tungsten sulfide promoted by cobalt or nickel, supported on alumina. Due to very stringent environmental regulations, the research effort to enhance the properties of these catalysts is still very important. The present article summarizes studies carried out recently by French scientists in three directions, the improvement of the preparation and activation methods of molybdenum or tungsten sulfide based catalysts, the search for new active phases based on solid state chemistry concept or bifunctional mechanism, and the design of new supports.

Keywords: Hydrotreating catalysts; Hydrotreatment; Sulfides catalysts; Preparation of sulfides catalysts; Activation of sulfides catalysts; Support effect

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1. Introduction

Between the oil crises in 1973 and 1979, a themed program of activity (ATP in French) on the hydrodesulfurization (HDS) of petroleum fractions started at the Institut de Recherches sur la Catalyse (IRC). This programme also involved three university laboratories in Lille, Montpellier and Toulouse. This collaboration related to hydrotreatment catalysts and reactions went on through the years within several types of contracts gathering CNRS, University and industrial laboratories (ELF, TOTAL, PROCATALYSE (AXENS), IFP, EURECAT S.A.) It extended its interest to other topics, such as hydrodenitrogenation (HDN), aromatics hydrogenation (HYD), heavy crude conversion and more recently, deep hydrodesulfurization. Depending on the objective of the contract and in order to get complementary competences, several other laboratories joined the first group, such as the laboratories of Caen and Poitiers and also occasionally some specialists from solid state chemistry, organic chemistry and chemical engineering.

Since the 1970s, very important progress has been made in the worldwide community studying hydrotreating catalysts and reactions. However, ‘‘ultra clean transportation fuels’’ is still a topic of enormous interest in petroleum and automotive industries since stricter fuel specifications demand redrawing of refinery flow sheets with the inclusion of desulfurization units at many stages of petroleum refining. The worldwide research effort in these subjects is still important, especially the search for efficient catalysts for the HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT) [1].

Besides the objective of getting a detailed fundamental understanding of industrial hydrotreating catalysts and hydrotreating reactions, an important part of the research effort in France was devoted to unconventional active phases and supports thanks to a fruitful collaboration with researchers of solid state chemistry, soft chemistry and coordination chemistry. A large number of phases were synthesized and tested at the laboratory scale using model molecules, but very few passed this first step and were tested with real feedstock [2].

The objective of this article is to present an overview of various concepts developed recently by French scientists leading to new preparation methods, activation procedures and the design of sulfide active phases and supports for hydrotreating catalysts.

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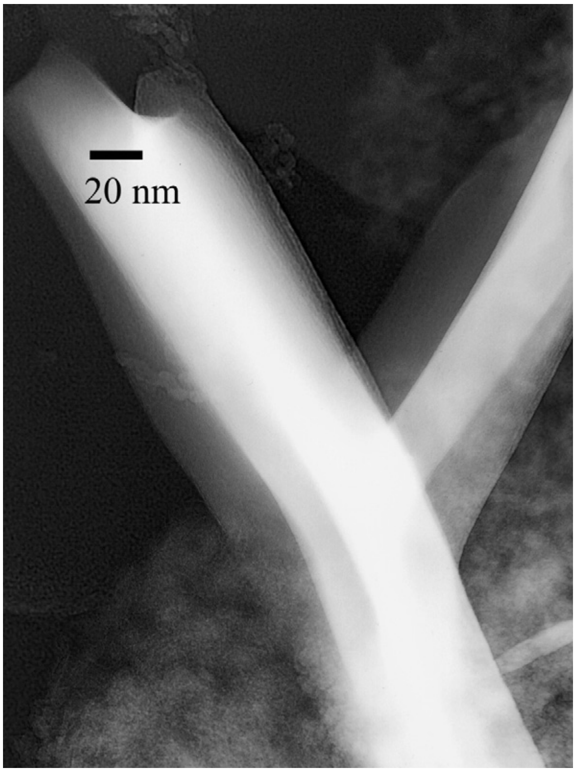

Fig. 1. TEM image of $Al(OH)_6Mo_6O_{18}$ entities deposited upon impregnation of Mo on alumina [6].

2. New methods of preparation and activation of molybdenum or tungsten sulfide based catalysts

2.1. New methods of preparation

2.1.1. Heteropolyanions

Currently, all the industrially used techniques for the preparation of hydrotreating catalysts utilize oxide precursors which are sulfided into their active form. For those catalysts, the distribution and nature of the oxidic species on the surface of the alumina support are of primary importance for their activation and performance in the active state. Early characterizations demonstrated that the presence of bulk MoO_3 or $CoMoO_4$ particles is detrimental to catalytic activity when high Mo or Co loadings are deposited on the supports. Therefore, the supported species should be deposited as isolated oxoanions. However, alumina is not an inert support toward the precursors of the active phase. Thus, a loss of Co atoms may occur with the formation of cobalt aluminate [3] and alumina can also react and form $(NH_4)_3[Al(OH)_6Mo_6O_{18}]$ like heteropolyanion (HPA) [4,5]. The presence of such HPAs was evidenced by Raman and XRD, but it can also be imaged by TEM, as illustrated in Fig. 1 [6]. The formation of HPA itself is not a major problems but its crystallisation observed at Mo loading higher than 3.5 Mo at/nm^2 may be detrimental for a high dispersion of the active phase (formation of MoO_3 crystals after calcination) [7]. Other heteroatoms such as P, Si or Co can form HPAs with Keggin, Dawson or Anderson structure with Mo. The use of this type of HPA as precursors of a promoted phase has been systematically explored at the University of Lille. Phosphomolybdates ($Co_{3/2}PMo_{12}O_{40}$, $Co_3PCoMo_{11}O_{40}$, reduced $Co_{7/2}PMo_{12}O_{40}$), silicium heteropolymolybdates ($SiMo_{12}O_{40}$) or molybdocobaltates such as $Co_{3/2}CoMo_6O_{24}H_6$ and $(NH_4)_6(Co_2Mo_{10}O_{38}H_4)$ were supported on alumina and demonstrate to have high catalytic performance [8,9]. Fig. 2 summarizes the promoting effects obtained in the conversion of thiophene by using sulfide catalysts prepared from such HPA precursors. These compounds may also be representative of oxidic species deposited on alumina when phosphorus is used during catalyst preparation. Overall, the importance of the heteropolyanion entities for the preparation of conventional catalysts was demonstrated, as well as their potential for the design of new catalysts.

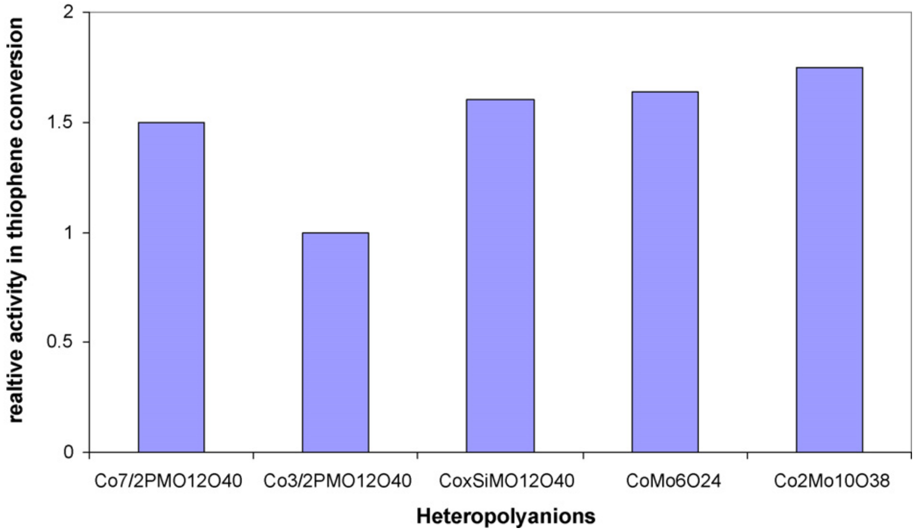

Fig. 2. Relative catalytic activities of various heteropolyanions deposited on alumina. The reference catalyst contains the same loading of active phases and P, adapted from refs. [7–9].

2.1.2. Preparations of unsupported MoS_2 based catalysts and their applications to highly loaded supported MoS_2

Recently a new family of highly loaded or bulk sulfide catalysts emerged on the market (NEBULA-type catalysts) [10]. Such systems, bearing a very high amount of active sites per unit of volume, provide much deeper HDS levels than conventional catalysts, using the same refinery equipment. Thus, the preparation of new bulk or highly loaded sulfide catalysts seems to be a promising research direction. Since such HDS catalysts all have $Mo(W)S_2$ sulfide phase as a major component, new methods of preparation of these sulfides are of key importance. Like the majority of metal sulfides, MoS_2 can be prepared by direct combination of the elements. However, for catalytic applications, methods leading to higher dispersion of the resulting materials are needed. These are usually ‘‘soft chemistry’’ methods (*chimie douce*). These types of preparations occur at much lower temperature than the corresponding solid state reactions. The existing techniques can be categorized into several groups, thermal decomposition of sulfur-containing precursors such as thiomolybdates [11,12], hydrothermal and solvo-thermal preparations, solution reactions, surfactant-assisted syntheses and many others [13,14]. Among the large variety of existing methods, we will focus our attention here on our most recent studies leading to highly active HDS systems.

The first example is aqueous solution reactions for the preparation of highly loaded supported and unsupported catalysts. MoS_2 was produced directly in aqueous solution using thiomolybdate precursor [15,16], and hydrazine, which can be easily removed from the products, as reductant. Providing that the pH and the reaction temperature were properly controlled, this method allowed high specific surface area samples (100–150 $m^2 g^{-1}$) to be obtained, which consisted of very small randomly oriented MoS_2 slabs (see Fig. 3). The catalytic tests showed very high HDS activity. The preparation method may be also conducted in the presence of an appropriate support slurry, and then highly active supported hydrotreating catalysts may be obtained. In this case, molybdenum sulfide slabs were deposited, from the solution, onto the support by mechanical adhesion. This approach overcomes the impregnation limit of conventional methods. To further promote these highly loaded MoS_2/Al_2O_3 catalysts, cobalt has to be introduced in the form of a soluble salt. Mild reflux with cobalt acetylacetonate led to exceptionally high promotion levels in HDS. As suggested by EXAFS study, cobalt species were selectively grafted onto the MoS_2 edges during the solution reflux and easily formed the CoMoS-like species. Note that optimal cobalt loadings in such systems are very low (Co/Mo ratio of 0.08–0.15) and far from those used for the impregnated systems (Co/Mo ratios of 0.4–0.5), meaning that in this latter case, a large part of Co is wasted due to interactions with the support.

Another approach which led to highly efficient hydrotreating catalysts was surfactant-assisted synthesis. Highly active hydrotreating catalysts were prepared with the addition of ionic or non-ionic surfactants [17,18]. Using the same reaction of reduction of thiomolybdate by hydrazine precursors as in ref. [15], cetyltrimethylammonium bromide (CTBA) was added to the reaction mixture [18]. As a result, MoS_2 nanoparticles with low stacking and exhibiting a high specific surface area (up to 210 $m^2 g^{-1}$) were obtained. No ordered mesophase was observed in the dried materials and we suppose that the surfactant played the role of a scaffold, either before or after thermal activation. An effective promotion by Co or Ni was obtained by using a non-ionic surfactant of the alkyl aryl-polyethylenglycol family (known as tergitols or tritons) and ethylene glycol

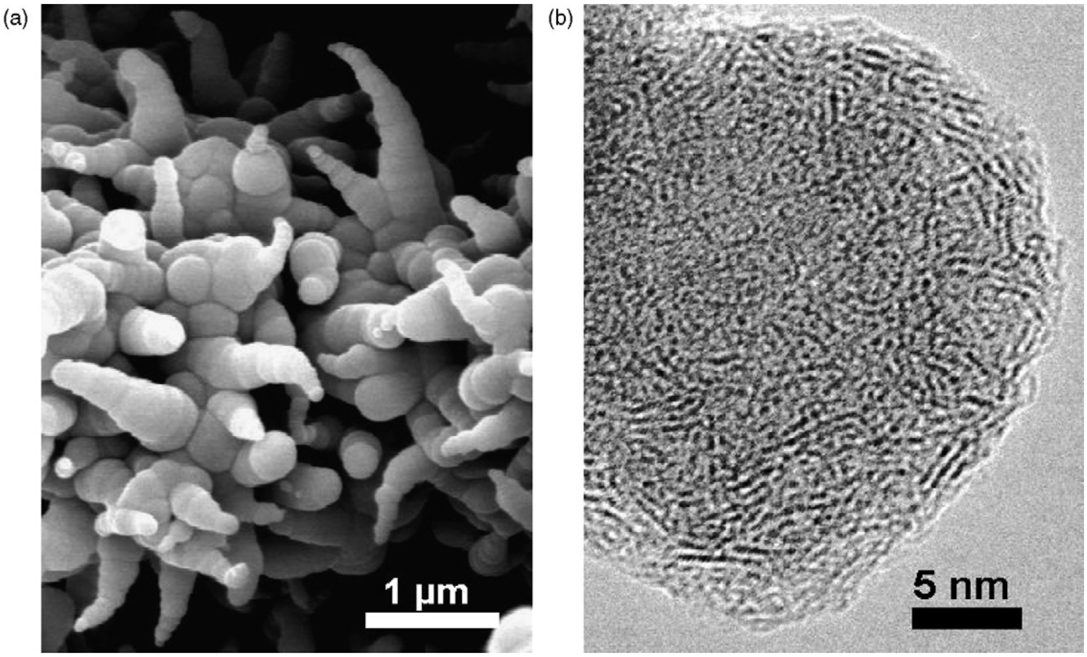

Fig. 3. SEM morphology of MoS2 obtained in aqueous solution at 90 °C from the ATM reduction by hydrazine: (a) TEM image of reduction of one spherical agglomerate in the sample dried in nitrogen at room temperature (b).

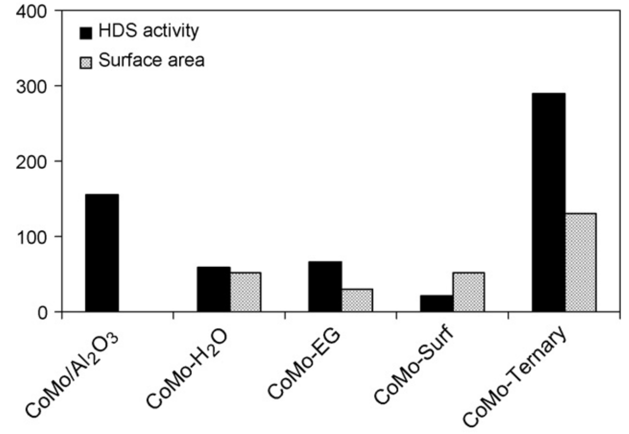

Fig. 4. Thiophene HDS activity (10^{-8} mol/g s at 573 K) and specific surface areas (m^2/g) of the CoMo sulfide catalysts prepared from the precipitation in aqueous solution (CoMo–H_2O); in water ethylene glycol (CoMo–EG), water–surfactant (CoMo–Surf) and water ethyleneglycol–surfactant ternary solvent (CoMo–ternary).

(EG) [19]. Fig. 4 summarizes the catalytic activity in thiophene conversion of these various preparations and compares them to an industrial CoMo catalyst. An increase in the catalytic activity of a factor two is observed. These catalysts demonstrated exceptionally high HDS activity in the conversion of 4,6-DMDBT, five times higher than that of a commercial reference catalyst [18].

2.2. New methods of activation, understanding industrial activation

The activation stage of an oxide catalyst into the active sulfide form is a crucial step for the performance in an HDT unit. Several procedures and sulfiding agents are proposed by catalyst manufacturers. Safer and faster activation methods are always required. The conventional procedure uses dimethyl disulfide (DMDS) as a spiking agent together with straight run gas oil. Industrially, a step-wise activation procedure is used and the role of relatively low temperature dwells was demonstrated to be of primary importance [20]. At the laboratory scale, a mixture of H_2/H_2S is usually used to proceed to this activation stage and kinetic studies were performed either under atmospheric pressure [21] or under high pressure (4 MPa) [22]. Alternative industrial sulfidation methods were proposed. For instance, Eurecat SA developed a process called TOTSUCAT® based on fundamental research performed at the IRC. The activation of the catalyst is done ex situ using H_2S as sulfiding agent on catalysts previously impregnated with gas oil or rapeseed oil. The resulting performances of these catalysts are similar or higher than those measured after in situ sulfidation [23]. Such a process provides an alternative and safe method for the loading of an HDT reactor. Recently, we demonstrated that it is possible to optimize the activation procedure with straight run gas oil spiked with DMDS by monitoring the H_2S produced during the HDS reaction [24].

3. Contribution of solid state chemistry for the design of new active phases

3.1. Binary transition metal sulfides

The pioneering paper of Pecoraro and Chianelli describing the "volcano" curve activities of the transition metal sulfides (TMS) was the starting point in the quest of new active phases [25]. Several TMS appeared as good new candidates for active phases presenting either very high activities or specific selectivities (for instance, isomerisation) [26]. The specific study of each of these systems greatly widened the knowledge relative to nanoparticles of TMS (Table 1). Several concepts were developed which can be further applied to conventional phases.

The most recent studies have been devoted to Ru sulfide on zeolites and Re sulfide on alumina.

Zeolite-supported RuS_2 exhibits unique properties which might be partly attributed to the presence of nanodomains of metallic Ru [39]. This hypothesis has been recently confirmed by in situ XAS studies of RuS_x/HYd catalysts which showed that these metallic domains were chemisorption sites for aromatic molecules (toluene) [40].

Rhenium sulfide appears highly active in the volcano curve of Pecoraro and Chianelli [25], but only a few studies were devoted to the role of the activation of ReS_2 catalysts and its impact on the catalytic activity [41,42]. Escalona et al. [43] recently focused their attention on the activity of $Re/\gamma Al_2O_3$ catalysts for the HDS of thiophene. These authors showed that whereas the HDS activity was not significantly modified by calcination, it was significantly improved by sulfidation with H_2S/N_2 instead of H_2S/H_2. Such an effect was confirmed for different Re loadings and lead to highly active catalysts (the activity of a catalyst with a loading in Re of 3.3 at/nm^2 was 1.6-fold higher than that of a $NiMo/Al_2O_3$ industrial reference catalyst).

3.2. Ternary and quaternary systems

In order to modify the electronic properties of the solids, a systematic approach based on solid state chemistry was used to identify potential ternary systems which could provide synergetic effect. These systems could be either solid solutions or new ternary compounds. In order to facilitate the

Table 1
Summary of the specific studies dedicated to supported TMS

Supported TMS	Findings	references
RuS_2	Heterolytic adsorption of H_2	[27,28]
	Sensitivity to sulfidation	[29]
	High performance Ru/zeolite	[30,31]
NbS_3, NbS_2	Support effect with respect to sulfidation	[32]
	H_2S insensitive, acidic properties	[33]
V_2S_3	Contribution to catalytic activity respect to HDM	[34,35]
Cr_2S_3	Promoting effect of H_2S, acidic properties	[36,37]
ReS_2	Highly active, activation procedure	[38]

Table 2
Mixed sulfides selected from solid state chemistry used for HDT

Ternary phases	Findings		References
$Ni_{1-x}Ru_xS_2$	Synergetic effect in hydrogenation	Unsupported	[44]
		Alumina supported	[45]
MCr_2S_4	Synergetic effect with Ni	Unsupported	[46]
$Nb_{1-x}Mo_xS_2$	Evidence of mixed lamellar supported nanoparticles, no inhibition by P_{H2S}	Alumina	[47]
$NiMo_6S_8$	Chevrel phases prepared in the supported state	Alumina	[48]
$NiRh_2S_4$	Synergetic effect	Unsupported	[49]
$W_{1-x}Mo_xS_2$	Synergetic effect with Ni, activity higher than NiMo catalyst	Unsupported	[50]
		Alumina	[51]

determination of their intrinsic catalytic activities, they were synthesized under relatively soft conditions in order to obtain moderate or high specific surface areas. Then, these mixed systems were deposited on various supports. Characterizations demonstrated that the ternary phases were maintained in the supported states. Table 2 illustrates this concept of transposition of solid state chemistry to the supported state.

With the strong improvement of theoretical methods, one can, like in the case of binary systems, relate the catalytic activity to a theoretical descriptor such as $E_{M\text{-}S}$ bond energy. Thus, using a solid solution like $Mo_{1-x}W_xS_2$, we were able to modulate continuously the bond strength energy. Promotion by Ni on such $Mo_{1-x}W_xS_2$ active phases can provide catalysts more active than NiMoS or NiWS ones [52]. This example illustrates how the combination of solid state chemistry and theoretical calculation can lead to a predictive approach for the design of HDT catalysts.

4. Doped conventional sulfides catalysts

4.1. Bifunctional approach, Ru and Pt addition

It is well admitted that the conversion of DBT and its derivatives, as well as the conversion of nitrogen containing molecules, involves hydrogenation steps which might be rate determining [53,54]. Consequently, increasing the hydrogenating function of conventional industrial catalysts by mixing them with more strongly hydrogenating, phases such as Pt or RuS_2, is a promising route.

Pt can be introduced as a dopant [55,56] or as a catalyst mixture [57]. Some of the studies previously published in the literature pointed out the importance of introducing Pt on an already sulfided conventional catalyst or by means of S-containing precursors [58].

In agreement with this, we observed, in a recent study, an enhancement of the catalytic properties of conventional HDT catalysts in DBT HDS, tetralin hydrogenation and the conversion of an hydrotreated straight run gas oil when Pt was impregnated onto sulfided CoMo, NiMo or NiW catalysts [59]. In that case, the catalytic properties corresponded to the addition of the properties of each component, i.e. PtS and conventional sulfides. The HRTEM pictures confirmed this biphasic character of the catalysts with well dispersed slabs of the lamellar sulfide and tiny particles of Pt with an average size of 0.8 nm (Fig. 5). Inversely, when Pt was impregnated on the oxidic form of the catalyst a sharp decrease of the activity of the conventional catalysts was observed. In this last case, the strong interaction between Pt and polytungstates and polymolybdates [60] could prevent the formation of the highly active CoMoS or NiWS entities at the oxidic precursor state.

Catalyst blends of supported RuS_2 and industrial catalysts were utilized by Isoda et al. [61,62] for the HDS of 4,6-DMDBT and by Zotin et al. [63] for the conversion of nitrogen-containing molecules. Both works pointed out that the hydrogenation properties of the conventional catalysts were enhanced by addition of ruthenium sulfide either supported on alumina (Isoda's work) or zeolite (Zotin's work). Thus ruthenium sulfide catalysts provide a means to increase the formation of the hydrogenated intermediates which are then easily transformed by conventional industrial catalysts. As in the Pt case, i.e. both catalysts work independently and this kind of synergy corresponds to a bifunctional mechanism.

As a dopant alone, Ru did not present any significant promoting effect for MoS_2, no ternary phase could be formed but, as suggested in an earlier work, a RuMoS phase might exist [64]. By contrast, increases of activities were observed for DBT

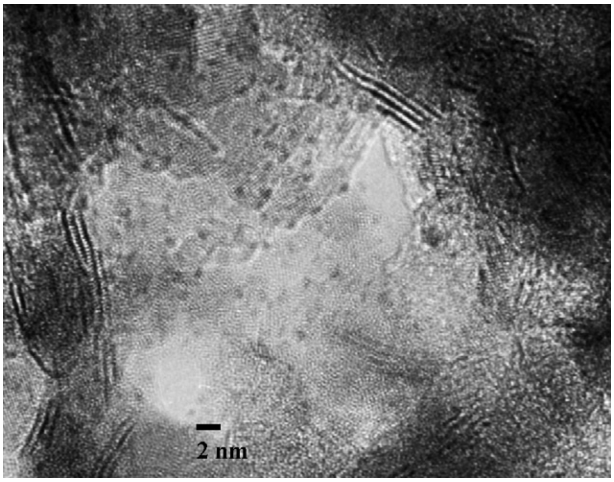

Fig. 5. HRTEM image of a Pt(0.3)NiW on alumina catalysts prepared from impregnation of Pt on the sulfided catalyst [59].

HDS and tetralin hydrogenation when 0.25–0.5% of Ru was added to a NiMoS catalyst [65]. As mentioned above for Ru catalysts the activation method plays a crucial role and sulfidation in the absence of hydrogen lead to the highest activities. The synergetic effects were ascribed to the formation of dual decoration sites of the MoS_2 slabs by Ru and Ni. This concept of dual decoration is new and will probably open new perspectives in the preparation of doped catalysts.

4.2. Gallium as additive to alumina

It is well known that alumina is not an inert carrier (see above). The promoter ions can react with the support and occupy octahedral or tetrahedral sites in external layers, or even form some aluminate such as $CoAl_2O_4$ ($NiAl_2O_4$) [66]. In any case part of the promotor is lost and not involved in the formation of the active CoMoS (NiMoS) phase. Gallium has in rare occasions been used as an additive of HDT catalysts, although some papers dealing with the characterization of Ga added to alumina indicated a high affinity of Ga^{3+} to the tetrahedral sites of the support [67,68]. Such an effect led to a modification of the ratio of tetrahedral/octahedral species of Ni ($Ni^{2+}_{tet}/Ni^{2+}_{oct}$) in the Ni/Al_2O_3 solid. A similar effect was observed when Ga was added to the $CoMo/Al_2O_3$ catalyst and these authors observed that the $Co^{2+}_{tet}/Co^{2+}_{oct}$ ratio changed as a function of the metal loading (Ga, Co and Mo) and of the impregnation sequence. Moreover, a positive effect of gallium was also reported for the HDN of pyridine over a $NiMo/Al_2O_3$ catalyst [69].

Such observations have led Altamirano et al. [70] to re-examine the modification of alumina with Ga and the effect on the catalytic activity of NiMo/Ga-Al_2O_3 catalysts (Ga content ranging from 0 to 5.9 wt.%). Fig. 6 shows the beneficial effect of Ga at low content, which corresponds to an increase of circa 30% of the activity in 4,6–DMDBT conversion. Characterizations demonstrated that the ratio tetrahedral to octahedral Ga species Ga^{3+}_{t}/Ga^{3+}_{o}, decreased as the Ga content increased, with a parallelism to catalytic activity. Thus, the presence of Ga in tetrahedral coordination enhances the sulfidability of the oxidic Mo species and decreases the formation of $NiAl_2O_4$.

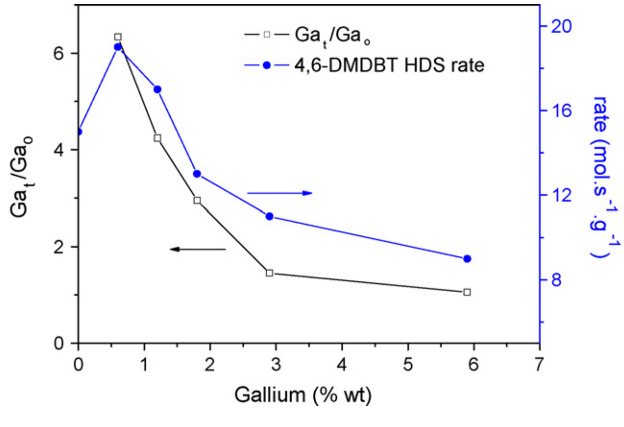

Fig. 6. Evolution of the rate of transformation of 4,6-DMDBT as a function of the gallium species. Ga_t, Tetrahedrally coordinated; Ga_o, gallium octahedrally coordinated.

5. New support materials

During more than 50 years, γ-Al_20_3 has been used as the support for HDT catalyst. Improvements in the preparation of this oxide as well as the use of additives such as fluorine and phosphate led to the last generation of commercialized hydrotreating catalysts. However, other supports, such as oxides, carbon and zeolites have been also used, at least at the laboratory scale, as supports for conventional CoMoS, NiMoS or NiWS active phases. In many cases, enhancements of the catalytic properties were observed which generated a great interest in the scientific community. It was shown that the general term "support effect" includes many different aspects, i.e. modification of the electronic properties or the morphology of the active phase, bifunctional reaction with acid sites. All these effects, as well as developments in the synthesis of new supports were summarized in a special issue of Catalysis Today in 2003 [71]. Since this date, progress has been made in several directions: modeling of the sulfide–support interaction, synthesis and functionalization of acidic supports, etc. Some of the recent results obtained in these areas are presented in the following.

5.1. Titania and zirconia

It was recognized very early that titania and zirconia when used as supports could impart four to five times higher activities in Mo and W catalysts by comparison to alumina [72,73]. Recently, new methods of preparation have appeared and diminished the difficulties coming from the unsuitable textural properties (low surface areas, small pore diameters) of these oxides, especially anatase-TiO_2, for future industrial application [74,75]. However, while providing very active non-promoted MoS_2 catalysts, these supports systematically lose their advantages over alumina for the promoted catalysts. This could be ascribed to the preparation methods used for depositing the active phases and in particular to the difficulties encountered with the commonly used method of co-impregnation followed by calcination and sulfidation. The co-impregnated-promoted catalyst in its oxidic state is a complex system consisting of several different oxide species with sometimes strong interaction between them (see above, Pt addition). In such a case, the observed promoting effect will depend on the evolution of the oxide precursor.

In a recent study [76] a series of titania, zirconia and alumina-supported catalysts was prepared in a highly uniform way, choosing ZrO_2, TiO_2 and Al_2O_3 supports with similar textural properties and using for all preparations strictly the same reactants and treatment conditions. Promoters were introduced onto the pre-sulfided non-promoted Mo or W sulfides. Due to this technique we sorted out the eventual preparation-dependent issues which would hinder the observation of the intrinsic support effect.

As expected from previous works, non-promoted Mo and W sulfides were found to be more active in tetralin hydrogenation and thiophene hydrodesulfurization when supported on titania or zirconia than the same sulfides supported on alumina. For the promoted systems, zirconia and titania supports still kept some

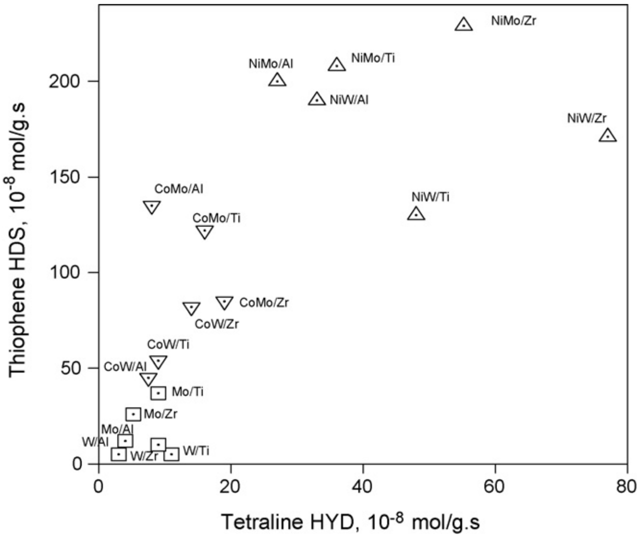

Fig. 7. Two dimensional diagram showing thiophene HDS and tetralin HYD rates at 573 K on the Ni(Co)–Mo(W) sulfides supported on alumina (Al), zirconia (Zr) and titania (Ti).

advantages in tetralin hydrogenation, but in the thiophene HDS the effect of the support was almost levelled off for nickel and became substantially lower for cobalt, as compared to the conventional alumina support (Fig. 7). This new study confirms the first observations related to the promoter effects on oxides different from alumina and shows in addition that the nature of the promoter plays a determining role for the catalytic performance.

Besides the challenging task of developing a new class of industrial supports, it is of fundamental interest to have a rational description of the support surface properties and their interaction with active sulfide phases, promoted or not. For this purpose comprehensive DFT modeling was undertaken to compare anatase-TiO_2 [77–81] and γ-Al_2O_3. Different surface orientations were considered, to take into account the influence of the morphology of the individual nanocrystallites. Under the sulfo-reductive conditions existing in HDS ($T = 600$–700 K, $P_{H_2O} \sim 10^{-2}$ bar, $P_{H_2S} \sim 1$–5 bar and P_{H_2} up to 30 bar), it was found that H_2S may partially sulfide the (0 0 1) surface of anatase-TiO_2 leading to the formation of μ_2–S species and hydroxyl groups. For γ-Al_2O_3, the formation of SH groups on the (1 1 0) surface is possible only if the water pressure is very low, leading to the formation of sulfhydryls and hydroxyls. Then, the influence of each exposed surface of the two supports on the thermodynamic stability of MoS_2 clusters was investigated. On γ-Al_2O_3 (1 1 0) and (1 0 0) surfaces, MoS_2 particles of very small sizes (<15 Å) exhibit chemical interaction as Mo–O–Al bonds for both Mo- and S-edges, whereas, for commonly observed sizes (>15 Å), H-bonds and van der Waals interactions stabilize the particles in an orientation parallel to the surface. On TiO_2 (1 0 1) and (0 0 1) surfaces, an epitaxial relationship is formed between the Mo-edge of MoS_2 particles and the support surfaces, with the formation of Mo–O–Ti–S rings. This epitaxy is not possible between the S-edge and the TiO_2 surface. Particles with sizes up to 45 Å are strongly anchored at the surface through the Mo-edge (Fig. 8). This trend was called the ‘‘chemical ligand effect’’ of anatase-TiO_2 [79]. The different nature of edge sites (higher Mo-edge/S-edge on anatase) and the stabilization of sulfur-deficient particles induced by the strong ligand effect of anatase are at the origin of the higher HDS activity observed for MoS_2 particles dispersed on this support by comparison to alumina-supported ones. The conclusion of this theoretical study is then in complete agreement with the conclusion of our first experimental study published in 1989 [73] which ascribed the role of TiO_2 to the formation of edge-up MoS_2 particles due to an interaction between the MoS_2 edge planes and some planes of TiO_2, these particles being intrinsically more active than the randomly distributed MoS_2 particles found in Al_2O_3.

The effect of the Co promoter on the active phase support interaction was examined using Mo_5CoS_n clusters [81]. The determination of adhesion energies of these clusters on the two supports shows that Co weakens the edge anchoring of the active phase. The different HDS catalytic activities for the promoted systems are explained by the distinct edge-wetting regimes inducing a significantly higher S-edge/Mo-edge ratio on γ-Al_2O_3, which is favourable for optimum Co decoration. These quantitative DFT insights give a rational interpretation to the catalytic data recalled above for Co as promoter.

To avoid the disadvantages presented by titania, especially its low surface area, the use of binary oxides, such as alumina-titania could be an attractive option. Numerous studies have been devoted to this topic (see for example, the reviews article by Saith and Segawa [82] and Murali Dhar et al. [83] published in 2003) but there are still on-going studies and developments

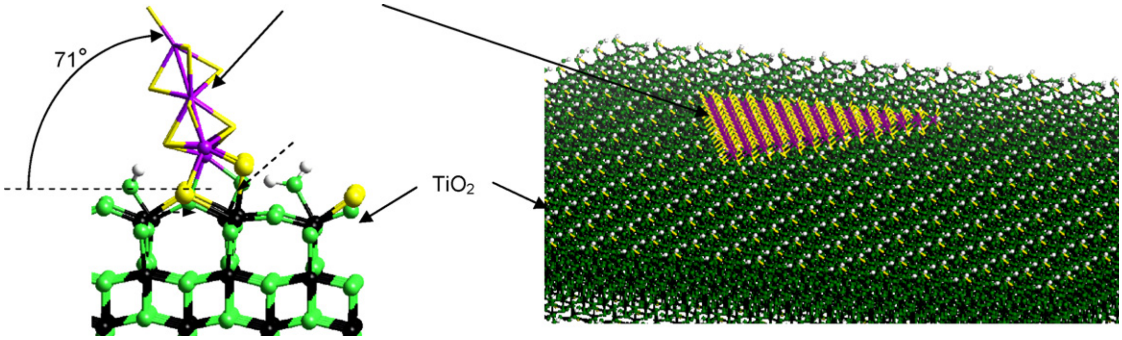

Fig. 8. Mo-edge cluster of MoS_2 on the (0 0 1) surface of anatase-TiO_2; for small sizes, MoS_2 is anchored and tilted (left side) and for bigger sizes (>45°), MoS_2 lays flat on the oxide surface (right side).

on this topic. Recently, Santes et al. [84] have shown that the catalytic properties, in several hydrotreating reactions, are related to a close contact between TiO_2 and Al_2O_3, leading to an increase of the acidity of the support.

5.2. Silica–alumina materials

In this section we will discuss the application of silica–alumina materials as supports for HDS active phases. Beside amorphous silica–aluminas and zeolites, less conventional materials have been proposed as supports like Al-MCM-41, Al-SBA-15 or the strongly acidic mesoporous materials obtained by organisation of zeolite seeds around surfactant micelles [85]. All these materials are promising supports for HDS as their Brønsted acidity can improve the HDS activity for refractory compounds such as 4,6-DMDBT. The positive impacts of the Brønsted acidity of the support on the HDS activities have been recently reviewed by Pérot: it can act either by improving the hydrogenation activity of the active phase (in order to take advantage of the HYD pathway, which is not hindered by the alkyl groups in 4,6-DMDBT) or by suppressing the steric hindrance brought by the alkyl groups, in order to recover the reactivity of the DBT derivatives through the direct desulfurization pathway. The first effect (improvement of the HYD activity) is due to an electronic effect of the acidity of the support on the active phase; the second (suppression of the steric hindrance) is due to the isomerisation, on the Brønsted acid sites, of the refractory derivatives in less refractory ones. As the deposition of an MoS_x phase on these supports is often a problem, we will also discuss the difficulties encountered during the preparation of the catalysts and the approaches recently proposed to overcome them.

5.2.1. Difficulties encountered during the preparation of the catalysts

5.2.1.1. Zeolites. When impregnation is used for the introduction of molybdenum on zeolite supports a poor dispersion of the deposited phase is observed and a significant part of Mo is left outside the zeolites pores. This is probably partially due to the formation of large crystals of the Anderson heteropolyanion $AlMo_6O_{24}H_6^{3-}$ (noted $AlMo_6$) by reaction with the aluminium species of the zeolite support. This phenomenon has been studied in detail by Payen and co-workers, who showed that only the extraframework Al was extracted during this process, and that, in the preparation of a Co-promoted molybdenum phase, the formation of this species could be avoided, by impregnating the zeolite with a solution containing the $CoMo_6$ Anderson polyanion [86]. The formation of the $AlMo_6$ heteropolyanion, is, however, probably not the main reason for the poor dispersion of the active phase on this type of support: the fact that the Mo species are anionic and can therefore not have ion exchange in the zeolite is also a major drawback. For this reason alternative precursors of molybdenum have been proposed like the $Mo_3S_4(H_2O)_9]^{4+}$ cation. Hédoire et al. [87] studied its insertion in the pores of beta zeolites with various Si/Al ratio (13.8, 15.1, 18.7 and >800) with pH adjustment. They observed the formation of a Mo crust on the surface of the zeolite grains, which was assigned to the precipitation of Mo oligomers. Note that, even if a high dispersion of the Mo phase was obtained, a migration of the Mo species would still be likely to occur upon sulfidation as reported in refs. [88,89]. Moreover, the size of the zeolite cavities is too small to accommodate the active phase and to ensure the access of bulky reactants like 4,6-DMDBT to it.

5.2.1.2. Silica–alumina ordered mesoporous materials. As for zeolites, the incipient wetness impregnation of heptamolybdate in silico-aluminic mesoporous supports (either AlMCM-41 or AlSBA-15 materials) leads to the formation of large crystals of $AlMo_6$ outside the pores of the support [90]. The Al species involved in the formation of this heteropolyanion, seem to be, as in zeolites, the extraframework Al and a poor dispersion of the active phase is observed after sulfidation. Moreover, co-impregnation with ammonium heptamolybdate and nickel nitrate led to the formation of large crystals of $NiMo_6$ heteropolyanions outside the pores. This effect was detrimental to the dispersion after sulfidation. In order to avoid the precipitation of $AlMo_6$ during the preparation of the catalyst, it can be proposed either to use supports that contain as little as possible of extraframework Al or to use alternative procedures like the thermal spreading of MoO_3 [91]. It is also of importance to emphasize that the formation of Anderson heteropolyanions is slower when W is used instead of Mo [92] and highly dispersed $NiWS_x$ phases have been obtained by co-impregnation on silica alumina mesoporous supports [93].

5.2.2. Acidity and catalytic properties

Using MoS_2/β-zeolite catalysts with various Si/Al ratio, Hédoire and co-workers [94] observed an increase in DBT (see Fig. 9) and tetralin conversions [95]. Although this increase

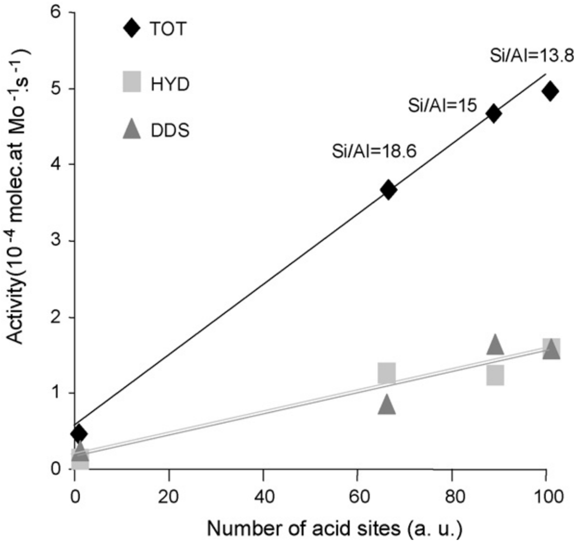

Fig. 9. Relationship between the catalytic activities of molybdenum sulfide supported on BETA zeolite, with various acidities, for the conversion of DBT and the number of Brønsted acid sites determined by IR spectroscopy. The total conversion and the conversion for each pathway (hydrogenation and direct desulfurization routes) increase simultaneously with the acidic properties (adapted from ref. [94]).

was, for both reactions, partially due to the formation of cracking products, a clear increase in the hydrogenation activities was observed (the hydrogenation activity was increased by a factor 40 for tetralin and by a factor 6 for DBT). CO adsorption experiments on the sulfided catalysts showed that the electronic properties of the active phase were modified by the acidity of the support (blue shift, from 2122 to 2158 cm^{-1}, in the position of the $\nu(CO \ldots MoS_x)$ band when the Si/Al ratio varies from >800 to 13.8). The authors concluded therefore that the increase in the hydrogenation activities of these catalysts with the acidity of the support could be assigned to an electronic effect of the acidity on the active MoS_x phase. Unfortunately, the presence of strong Brønsted sites also leads to considerable cracking of DBT and tetralin.

However, as stated above, the difficulty in obtaining highly dispersed HDS catalysts supported on zeolites and the small size of the zeolite cavities will always impede the application of zeolites as support for HDS. These materials remain nevertheless interesting for this application, but as an additive to an alumina-supported active phase. Under these conditions a high dispersion of the active phase can be obtained together with a promotion of the DDS pathway by isomerisation of the refractory alkyl derivatives on the Brønsted acid sites of the zeolite additive (bifunctional mechanism) [96].

Similar effects of the acidity of the support have been reported with ASA. Maugé et al. [97] observed, for amorphous silica–alumina, a blue shift in the position of the $\nu(CO \ldots NiWS_x)$ band with the Brønsted acidity of the support, showing that the milder Brønsted acidity of ASA (compared to zeolites) was nevertheless strong enough to modify the electronic properties of the active phase. Michaud et al. [98] observed a 2.5-fold increase in the 4,6-DMDBT HDS when ASA was mixed with a NiMo alumina catalyst, and concluded that the isomerisation of 4,6-DMDBT to 3,6-DMDBT on the Brønsted acid sites of the ASA additive was responsible for this increase.

Using AlSBA-15 mesoporous materials as support, Blanchard et al. [106] also observed a change in the 4,6-DMDBT selectivity with the acidity of the support (again assigned to the isomerisation of this refractory compound on the Brønsted sites). However, they did not observe any modification in the DBT selectivity and attributed this to a too weak acidity of the Al-SBA-15 Brønsted sites, which would not be strong enough to modify the electronic properties of the sulfide phase. This result is, however, contradictory to the work of Turaga and Song [99] who reported an improvement of both the DDS and HYD routes for 4,6-DMDBT hydrogenation. It may be inferred that the acidity of this family of supports is a complex parameter because both the strength and the number of Brønsted acid sites may be involved.

Zeng et al. [100] examined the properties of nickel-tungsten sulfide supported on MCM-41 aluminosilicate materials assembled from β-zeolite seeds (β-MCM-41) in the conversion of 4,6-DMDBT pure or in a mixture with dimethyldisulfide, carbazole and tetralin. By carefully adjusting the synthesis conditions, the authors obtained a β-MCM-41 material which was essentially MCM-41 like, but possess a stronger Brønsted acidity than conventional AlMCM-41 materials. In order to examine the effect of the acid function of the β-MCM-41 material on the catalytic properties of the supported catalyst, the authors prepared β-MCM-41-alumina supports by mixing the two oxides (0, 15, 50 and 85% β-MCM-41). The regular increase of activity observed upon increasing the β-MCM-41 content was assigned to an increase in the hydrogenation properties of the active phase, indicating an electronic effect of the acidity on the supported phase (note that this effect was also observed in the presence of inhibitors).

6. Concluding remarks

The challenge of developing catalysts with enhanced properties for hydrotreating processes has been addressed in a multidisciplinary approach involving solid state chemistry, soft chemistry and theoretical chemistry.

- The solid state chemistry approach has allowed the identification of oxidic promoters like HPA or ternary sulfide phases of various natures, cubic, lamellar, Chevrel phases. The transposition of these bulk phases to the supported oxidic or sulfidic state has been achieved in most cases. Concerning the other ternary sulfides, due to practical problems (cost and rarity of the elements, hazardous products), it is not certain that these new phases can be utilized, apart from those involving a combination of Mo and W. Nevertheless, the synthesis of these well defined phases has lead to a much better knowledge of mixed active phases.
- The soft chemistry approach has led to new methods of preparation of unsupported catalysts and highly loaded ones.
- The theoretical chemistry approach has been particularly fruitful for predicting new mixed phases and understanding the support interaction in the TiO_2 case.

More precisely, several common features appear in the various topics presented in this paper:

The formation of heteropolyanions changes the nature of the phase deposited on the support in the oxidic state and modifies to various extents the properties of the sulfided catalyst. It can either be a drawback (formation of $AlMo_6$ by extraction of Al from the support) or an advantage (use of Ni, Co or P heteropolymolybdates for the preparation of promoted phases. The complexity of the supported mixed systems still needs a better understanding, considering also the fact that new organic additives are used.

The activation methods also play a very important role, for example for the Ru or Re based catalysts. For conventional industrial catalysts, a better understanding of the genesis of the sulfide phase has permitted the development of safer and better adapted processes.

The detrimental interaction of the promoter with the support which leads to the formation of aluminate type compounds can be avoided by addition of Ga to alumina or by using HPA as precursors. Similarly, there are some difficulties in obtaining the mixed active phases of the CoMoS, NiMoS, NiWS type due to a strong interaction with the support or

some other element, such as Pt, in the oxidic state. These difficulties can be overcome by forming first the MoS_2 phase, then adding the Co or Ni promoter.
For new developments in HDS, materials are required which would not only allow a high dispersion of the active phase but also play a role in the catalytic reaction. In this regard silica–alumina materials can be used in two different ways, either as an additive to the alumina-supported catalyst in order to enhance the DDS pathway through isomerization of the refractory compounds, or as a support in order to tune the electronic properties of the active phase. Mesoporous materials assembled from zeolite seeds could, thanks to their strong Brønsted acid properties, lead to interesting developments for this last application.

Hydrotreatment is very often considered as a mature subject since the refining industry has been able to tackle the very stringent environmental limitations. Nevertheless, due to the importance of this type of process, progress is still expected in many areas. We have shown here some of the advances related to sulfide catalysts. It should be also noted that many groups have been interested recently in carbides [101,102], nitrides [103] and phosphides [104,105], which are topics not addressed in this review restricted to sulfides.

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