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Overview of support effects in hydrotreating catalysts

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Abstract

The commercial hydrotreating catalysts are usually composed of a sulfide active phase supported on alumina. It has been known for more than 15 years that other supports might lead to enhanced catalytic properties. The present article summarizes the progress which have been made in this area, often related to new methods of preparation of supports, active phases deposition or activation procedures. The properties of active phases supported on oxides, pure or mixed, basic and acidic supports, zeolites, mesoporous materials, carbon and clays are examined.

Keywords: Hydrotreating catalysts; Hydrotreatment; Support effect; Sulfides catalysts

1. Introduction

Industrial hydrotreating (HDT) catalysts are composed of a molybdenum sulfide (or tungsten sulfide) phase promoted by cobalt or nickel and usually supported on alumina. The origin of the almost exclusive use of alumina as support has to be ascribed to its outstanding textural and mechanical properties and its relatively low cost [1]. One important factor is also the ability to regenerate catalytic activities after intensive use under hydrotreating conditions. Nevertheless, it was recognized in the very first studies related to CoMo or NiMo/Al_2O_3 catalysts that alumina is not an inert carrier and that the promoter ions, Co and Ni, can react with the support and occupy octahedral or tetrahedral sites in the external layers or even form $CoAl_2O_4$ ($NiAl_2O_4$) depending on the conditions of preparation [2]. More recently, it has been shown by Carrier et al. [3] that when heptamolybdate was deposited on γ-Al_2O_3 by the equilibrium adsorption method, the Anderson-type heteropolymolybdate $[Al(OH)_6Mo_6O_{18}]$ formed and was then deposited on the surface providing a very strong metal–support interaction from the very first step of catalyst preparation. Also very early, it was assumed by Candia et al. [4] that, upon increasing the sulfiding temperature, the nature of the CoMoS structure changes from a low temperature form CoMoS I, with Mo–O–Al anchors, to a high temperature CoMoS II without such Mo–O–Al anchor. The pure CoMoS II phase presented a much higher activity than the CoMoS I phase. This evidence of interactions between the active phase and alumina has urged numerous researches devoted to other supports. Using carbon, titania, zirconia, for example, it was claimed that higher activities than those of the alumina counterpart were obtained. Two review articles, published at the beginning of the nineties summarized the role of the support in hydrotreating catalysts [5,6] and gave data concerning the properties of sulfide phases

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supported on carbon, simple oxides (TiO_2, ZrO_2), binary oxides, silica–alumina, zeolites and clays. The different interpretations of the support effect, i.e. modification of the morphology of the sulfide active phase, existence of chemical bonds with the carrier, role of the supports acid sites were also examined.

Since these first reviews, the researches concerning the development of new supports for hydrotreatment catalysts have been very active urged by the stringent regulations concerning the maximal amount of sulfur admitted in fuels. Some results have been summarized in general reviews or books concerning hydrotreatment catalyst and deep hydrodesulfurization [7–9]. Nevertheless, due to the great importance of this subject from the applied and fundamental view points it appears necessary to address this question in depth once again and examine what progresses have been done within the last 10 years. The articles within this issue give detailed information on the properties of the sulfide phases supported on various supports. The objective of this overview is to highlight some particular aspects of this problem showing the progress which have been made and the difficulties which are not yet solved.

2. Improvement of the textural properties of the supports

As already reported [5,6], TiO_2 and ZrO_2 supported MoS_2 catalysts present, respectively, three to five times higher hydrodesulfurization and hydrogenation activities than alumina-supported ones with an equivalent Mo loading per nm^2. However, before 1991, the specific surface area of such oxides remained below $100\,m^2/g$ (after calcination at 773 K) restricting the interest of such supports. The porosity was also not adapted for hydrotreating applications. Within the last decade, many improvements in the preparation of these oxides were achieved and supports with higher specific surface area and larger pore diameters were obtained (see Fig. 1). Molten salt TiO_2 preparation provided good textural properties with specific surface areas as high as $120\,m^2/g$ but with the drawback of the presence of sulfates (originating from the precursor salt) [10]. While, Chiyoda Corporation successfully developed a novel method for preparing mesoporous TiO_2 ($120\,m^2/g$) based on an aqueous precipitation method called "pH-swing" previously applied to alumina [11]. In previous studies, the Mo loading was

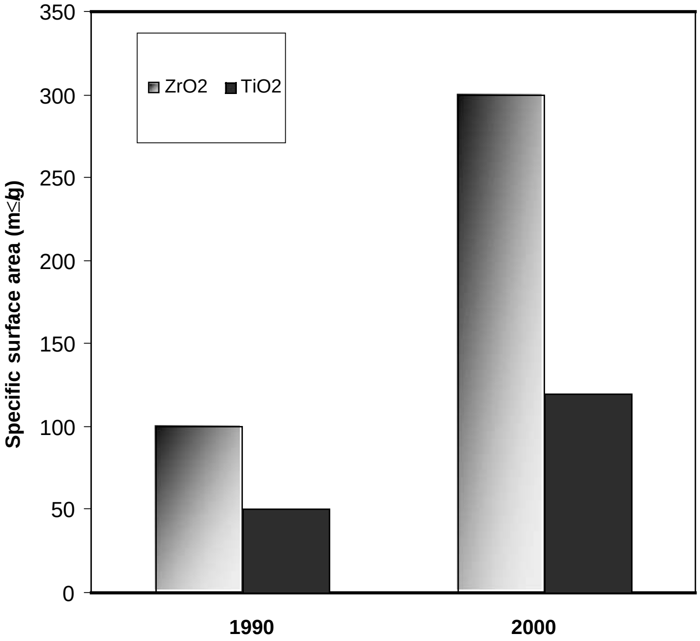


Fig. 1. Evolution of the textural properties (specific surface areas) of TiO_2 and ZrO_2 (calcined above 773 K) during the last decade.

limited to 6 wt.% because of the lower surface area of the titania supports. The Chiyoda support provides the opportunity to increase the Mo loading up to a level comparable to that of conventional alumina catalysts, i.e. 10–12 wt.% [12], keeping a good dispersion of the active components. A TiO_2 support with a specific surface area of 150 m^2/g (Norton) was also used for HDT purposes [13].

Similarly, numerous efforts have been devoted to the preparation of ZrO_2 for HDT applications [14]. In the past, the specific surface areas of the available zirconia supports were at best in the range of 100 m^2/g, i.e. more than two times lower as compared to commercial alumina. Different chemical preparation approaches were explored and various textural stabilizers were tried to improve ZrO_2 textural properties. Then, the molten salt method was applied in 1991–1996, in order to obtain pure and doped zirconias [15]. First efforts concerned either pure or yttria stabilized zirconia and surface areas up to 120 m^2/g were obtained. Later on, a one step preparation of the supported oxide catalysts (Mo/ZrO_2 and W/ZrO_2) was proposed. The surface areas of these mixed oxides dispersions (up to 250 m^2/g) were much higher than those of all previously reported pure or doped zirconia. Due to the smooth (almost spherical) shape of microparticles, the oxides obtained by this method had an increased thermal stability and they sustained calcination at 873 K without considerable loss of surface area. Moreover, the molten salt derived Mo–Zr and W–Zr oxide systems can be used directly as precursors for the hydrotreating catalysts. Subjected to further sulfidation, they lead to highly active $(Ni)MoS_2/ZrO_2$ catalysts [16,17]. The disadvantages of the molten salt method are related to its relative complexity and production of polluting gases (NO and NO_2). This production of polluting gases can be decreased by addition of alkali metal carbonates to the flux [18]. Since the improvement of textural properties is due to the decrease of particles size, the pores size decreases as well to 2–3 nm, which could be prohibitive for some applications including viscous liquid feeds. The surfactant-assisted synthesis method was applied with a relative success to the ZrO_2 based materials. Cationic [19], anionic [20] and neutral surfactants [21,22] were tried. In many cases, the presence of the surfactant leads to a scaffolding of the oxide structure and no real mesoporous ordered structures resulted from these preparations. The problems encountered are of the same kind as for the majority of non-siliceous mesoporous materials. Even if it is possible to prepare various ordered organic–inorganic phases, it is much more difficult to remove the surfactant and preserve intact the zirconia framework. However, several successful syntheses were described leading to ordered frameworks with honeycomb structure of pores and specific surface area as high as 350 m^2/g after calcination at 773 K in air [19,23]. The best compromise between specific surface area and porosity was obtained using the digestion in moderately basic medium. This allowed to Chuah et al. [24] to obtain zirconia with a specific surface area of 300 m^2/g and a high pore volume.

Fig. 2 summarizes the effect of new preparation methods on the textural properties of ZrO_2 supports as compared to the conventional precipitation method. Shaping technologies of ZrO_2 and TiO_2 were also improved and extrudates or pellets are now available opening new perspectives for these supports.

3. Mixed oxide supports

In parallel to the development of new synthesis method, another way to overcome the small specific surface area of TiO_2 or ZrO_2 is the combination of oxides. For instance, TiO_2 was combined with alumina, zirconia or SiO_2; TiO_2–Al_2O_3 composite being the most studied. Two approaches were examined, in one case, high content of TiO_2 was doped with a small amount of Al_2O_3 acting as a textural promoter (2–10%), in the other case alumina was used as a carrier of a small amount of TiO_2 (2–10%) well dispersed at the surface of the support. The combination provided much higher specific surface areas but the supports were often composed of a heterogeneous mixture of the two oxides. The positive effect of these composite supports is illustrated in Fig. 3. Then, various preparation methods were proposed to control the dispersion: co-precipitation of Ti and Al isopropoxydes [25–27] or of sodium aluminate and $TiCl_4$ [28], impregnation of Al_2O_3 with an aqueous solution of $TiCl_4$ [29,30], molten salt synthesis [31,32] or CVD deposition of $TiCl_4$ over the alumina substrate [33–35]. This combination of oxides often implied the genesis of new acid–base properties. Various correlations between surface acid sites [36] or reducibility

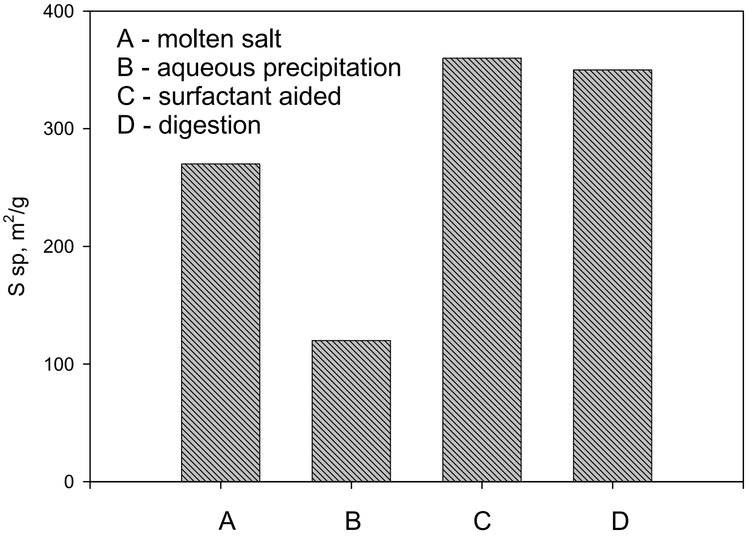


Fig. 2. Influence of the preparation method on the specific surface area of ZrO_2 (calcined above 773 K).

of the sulfide phase [31] and catalytic activity were proposed. These composite supports were found to be very efficient catalysts for the hydrogenation of aromatics [37] and the conversion of dibenzothiophene (DBT) and its alkyl-derivatives [38,39].

Other mixed oxide systems such as TiO_2–ZrO_2 [13], TiO_2–SiO_2 [40], and new composites such as La, Ce–TiO_2 [41] were investigated and present interesting features. As mentioned above the combination of ZrO_2 with TiO_2 provided high specific surface

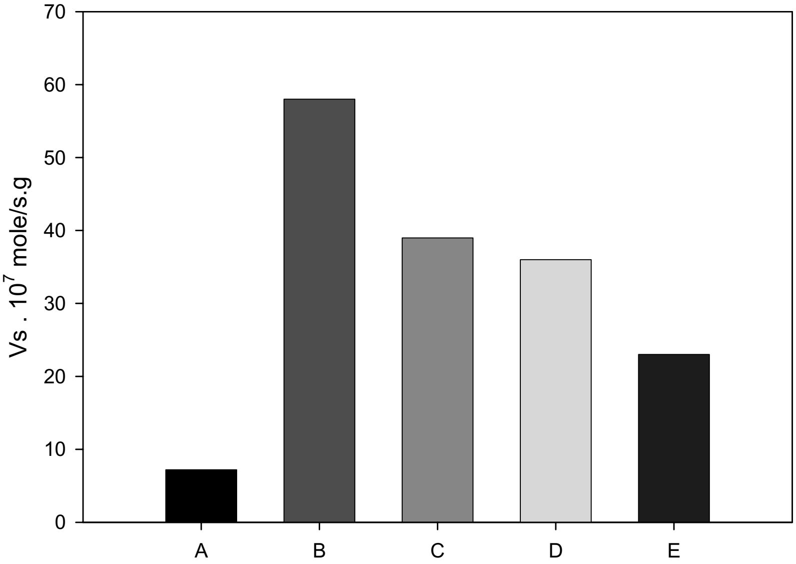


Fig. 3. Influence of Al_2O_3 content in TiO_2–Al_2O_3 on the conversion of tetralin in the presence of H_2S: (A) NiMo/TiO_2; (B) NiMo/TiO_2–Al_2O_3 (5 mol% Al_2O_3); (C) NiMo/TiO_2–Al_2O_3 (10 mol% Al_2O_3); (D) NiMo/TiO_2–Al_2O_3 (15 mol% Al_2O_3); (E) NiMo/Al_2O_3 [37].

area (>200 m^2/g). Other composites such as stabilized zirconia ZrO_2–Y_2O_3 [42], ZrO_2–Cr_2O_3 [43], SiO_2–ZrO_2 [44], ZrO_2–Al_2O_3 [45] were also studied. Similarly to titania or zirconia alone, it is often noticed that hydrogenating properties are favored on this kind of supports, a property which might be important for the deep desulfurization process.

4. Basic and acidic supports

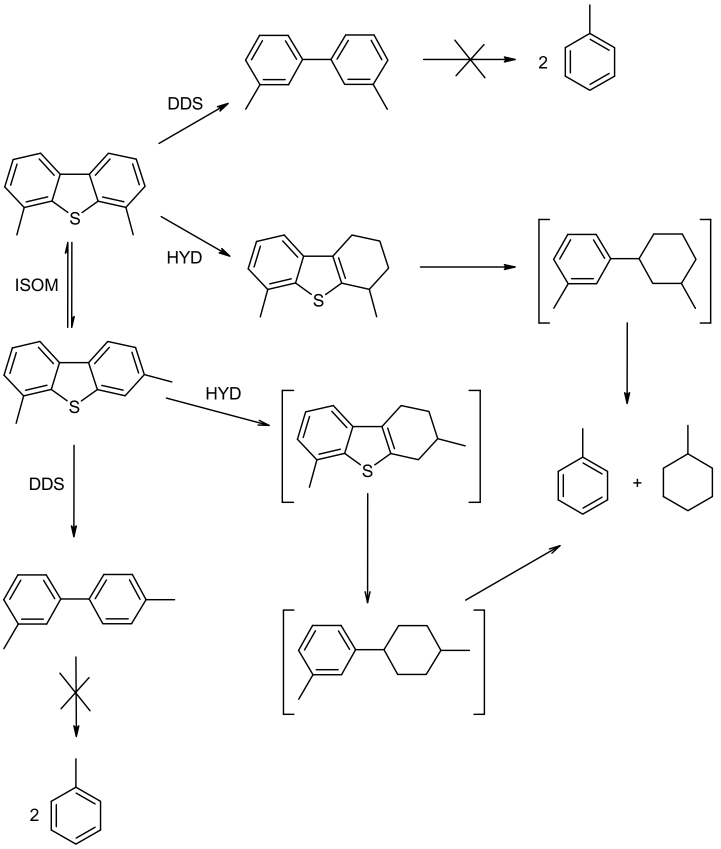
4.1. Basic supports

Basic supports are interesting for two main reasons as stated by Klicpera and Zdrazil [46]. First the acid–base interaction between acidic MoO_3 and a basic support in the oxidic precursor of sulfide catalysts should promote a high and stable dispersion of the Mo species. Second the basic character of the support should inhibit coking which is rather intensive over conventional Al_2O_3 catalysts. If we consider only the literature from 1991, two teams only have been interested in the preparation of sulfide phase supported on MgO [46,47]. An important progress has been made by Klicpera and Zdrazil [48] with a new method of preparation of MoO_3/MgO by non-aqueous impregnation which prevents the damage to the texture of the support due to the interaction with water. CoMo and NiMo catalysts were prepared from MoO_3/MgO by impregnation with methanol solution of Co nitrate and Ni nitrate. A strong synergistic effect in activity between the promoted and non-promoted catalysts (circa 20) was observed. The most active Co(Ni)Mo/MgO catalysts were 1.5–2.3 times more active than their Al_2O_3-supported counterparts for the hydrodesulfurization of thiophene. For the authors, the preparation can still be improved.

4.2. Acidic supports

Since 1991, acidic supports have been the object of numerous studies in relation with the development of deep hydrodesulfurization. Attempts were made to increase the conversion of 4,6-dimethyldibenzothiophene (4,6-DMDBT) by transforming it into a more reactive compound, either through demethylation [49] or isomerization [50,51]. These reactions are acid-catalyzed, and consequently were carried out on bifunctional catalysts, such as mechanical mixtures of the alumina-supported sulfide catalyst with an acidic component, silica–alumina or zeolite, or by associating a hydrotreating catalyst such as CoMo/alumina to a Ni/HY catalyst [52]. On such mixed catalyst, the conversion of the 4,6-DMDBT was significantly increased but a rapid deactivation of the acidic function was observed during the first hours of the reaction [17], which was not the case with sulfide catalysts, deposited on alumina–zeolite mixtures [53,54]. As it is well known that the activity and the stability of bifunctional hydrogenating-acid catalysts depend on the balance between both functions [55,56] the properties of molybdenum sulfide catalysts, promoted by cobalt or nickel, dispersed in acidic dealuminated HY zeolite were examined [57]. For the conversion of 4,6-DMDBT, the zeolite supported CoMo catalyst was much more efficient than its alumina counterpart, but additional reactions were observed, transalkylation and formation of methyl-dibenzothiophenes besides the direct desulfurization and hydrogenation routes involved in the conversion scheme of DBT and 4,6-DMDBT (Scheme 1). For the same reasons, the non-promoted Mo supported on zeolite was more active than Mo/Al_2O_3 for 4,6-DMDBT. Surprisingly, Mo/zeolite was also much more active when dispersed in zeolites by comparison to alumina (Fig. 4) for the conversion of DBT and this cannot be related to the formation of a more reactive isomer. This might be ascribed to a better dispersion of the molybdenum sulfide on the zeolite support than on alumina or to an enhancement of the catalytic properties of the sulfide phase when it is in close vicinity to acid sites, as was observed for ruthenium sulfide dispersed in zeolites, and related to the electron deficient character of the sulfide particles in an acidic environment [58]. Such a positive effect of the acidic properties of the zeolites on the catalytic properties of the sulfide phase was also mentioned by Vissenberg et al. [59]. For these authors, such an effect cannot be explained only by an improvement of dispersion. Possibly, the protons themselves play an active role in the HDS reaction or act as a promoter by increasing the electron deficient character of the metal sulfide.

In order to better understand the role of the acidity of the support on the hydrogenation properties of a molybdenum sulfide phase, a series of β zeolites with various acidities were utilized as supports



Scheme 1. Transformation of 4,6DMDBT on zeolite-supported sulfide catalysts. Isomerization (ISOM); direct desulfurization pathway (DDS); hydrogenation pathway (HYD) [57].

[60]. The electronic properties of the molybdenum sulfide phase were examined by means of IR spectroscopy of CO adsorption. As for ruthenium sulfide, the stronger is the acidity of the zeolite, the higher is the ν(CO) frequency characterizing adsorption on the sulfide phase. In parallel, the hydrogenation properties vary in a wide range, i.e. 40 times between the activity of MoS_2 dispersed in the non-acidic and most acidic samples. These data evidence that the Brönsted acidity of the zeolite has a marked influence on the catalytic and electronic properties of the sulfide phase as was observed previously for metals [61]. This finding might have important practical consequences on the design of more active catalysts for various hydrotreating reactions if it would be possible to tune the acidity for limiting undesirable side reactions.

5. Highly dispersed phase in zeolites and mesoporous materials

The interest of zeolites is not only to provide acidity but also to offer a well-defined and ordered pore structure on a molecular level. Intrinsically, high dispersions of the intra-zeolite clusters may bring about highly active catalysts. This could be also the case for mesoporous materials such as MCM-41. For these reasons, these materials have been studied as support for molybdenum and cobalt–molybdenum sulfide phase by several authors [62–68]. As a matter of fact, the high surface area of these mesoporous materials permits to achieve high CoMo loading without the restricted access of the zeolite structure to bulky molecules. Substantially more active catalysts than alumina-supported ones were obtained [64]. The

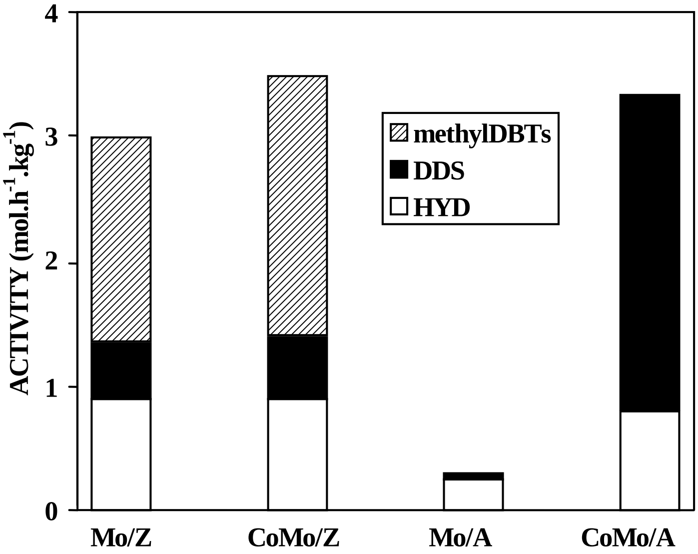


Fig. 4. Transformation of DBT on zeolite- or alumina-supported sulfided catalysts (fixed bed reactor, 603 K, 3.0 MPa H_2) [57].

interest of using mesoporous supports like MCM-41 and SBA-15 might be also to modify the selectivity in complex reaction schemes. The parallel pores of these supports might act as microreactors, in which the reactant and the intermediary products will be in the prolonged contact with the active phase [69]. However, like in zeolite, the preparation of mixed CoMoS phase inside the mesoporous structure is not an easy task (vide infra). Besides these works dealing with silica-based materials, mesoporous alumina possessing pore sizes from 3.3 to 4.5 nm and surface area between 400 and 450 m^2/g was utilized as support for a molybdenum phase. High loading can be achieved with this support which leads to enhanced catalytic properties for thiophene conversion [70].

6. Carbon and clays

Carbon support present many advantages such as minimized metal–support interaction which facilitates sulfidation and dispersion, large specific surface area and controlled pore volume [71]. Then, carbon has often been used for the elaboration of model hydrotreating catalysts but also for the development of industrial catalysts [72,73]. CoMo carbon-supported catalysts were found to be more active than alumina-supported catalysts for both DBT and 4,6-DMDBT hydrodesulfurization [74]. More details on the properties of sulfides supported on carbon will be given in this issue by Moon et al. (this issue).

This kind of support is also of great interest for supporting carbides since these active phases can be prepared by temperature-programmed reduction in flowing H_2 of an active carbon impregnated by molybdenum heptamolybdate [75]. This method of preparation avoids the use of methane as carburizing agent and allows in situ preparation of supported molybdenum carbide without any contact with air of this pyrophoric material. The properties of molybdenum carbides supported over mesoporous carbon black composites were examined by Sayag et al. [76] for indole hydrodenitrogenation.

Natural clays as well as pillared clays have also attracted attention since these supports provide high specific surface areas, thermal and mechanical resistance, acidic properties and the possibility of inserting elements such as Ti, Al, Cr, Zr inside the structure [77]. If most of the applications are related to acidic catalysis, some applications related to HDT were also reported. Thus, Co–smectite catalysts [78], montmorillonite [79–81], saponite [82] and modified raw materials were used modified for the treatment of residual oils [83]. Using the same approach, De Los

Reyes et al. [84] demonstrated the interest of NiMo catalysts prepared over zirconia pillared clays in the transformation of alkyldibenzothiophenes.

7. Support effect on the activation, genesis and morphology of the active phase

The activation stage which transforms the catalyst from the oxide state to the active sulfided state is of utmost importance for the performance of the catalysts and the support itself may play a significant role on this sulfidation process [7]. In fact, the support may accelerate or slow down the sulfidation process and determine the final dispersion state but sometimes also the final chemical state. For instance, niobium oxide precursors deposited on alumina can hardly be sulfided with a H_2/H_2S gas mixture [85] whereas the sulfidation of molybdenum species on alumina starts even at room temperature. Such behavior between various transition metal sulfides/oxides can be roughly estimated from the thermodynamic of the sulfidation reaction. Support interactions are weak on carbon and may be very strong with oxides like alumina or magnesia. An attempt to reduce these interactions can be obtained by deposition of a thin layer of carbon on the surface before impregnation of the active phase. The texture of the support may also greatly influence the sulfidation and the resulting species. For instance, in the case of Co/NaY or CaY zeolites, formation of large Co_9S_8 particles was related to the presence of physisorbed water in the Y-zeolite [86].

Now, if we consider the same active phase (MoS_2 based catalysts) and various supports, many references reported in this review provide information on the different length and stacking of MoS_2 nanoparticles, indicative of the support effect. However, few papers directly dealt with the activation procedure on these supports. Whatever the support, the initial state is composed of dispersed molybdate species (for instance, Mo_7O_{24} entities) grafted on the surface and the final state of larger MoS_2 particles composed of 100–200 Mo atoms. The nature of the sulfidation mechanism is still under debate, intermediate oxysulfide species have been characterized at low temperature and at medium temperature the presence of an amorphous MoS_3 like species has been proposed [7,87].The sulfidation of Co(Mo) catalysts supported on γ-Al_2O_3 or titania [88], has been studied by XAFS. For both supports, intermediate species were found to be anchored to the support via Mo–O bondings at 0.2 nm. During this activation process, the support itself may react, depending on the strength of Mo–O–X or Mo–S–X bondings and interaction with H_2S may greatly vary. Moreover, it is well admitted that carbon-supported CoMoS are more weakly bound to the support than metal oxide supports [89], this weak interaction being responsible for a higher catalytic activity. In many of these studies, the nature of the support was found to delay or accelerate the sulfidation process. Some studies have been performed on the kinetic of sulfidation of Mo or doped Mo on alumina [90,91] but none on other supports. Such detailed studies are deeply needed for the understanding of support effect.

Not only the kinetic of sulfidation but also the shape and orientation of the nanoparticles of MoS_2 may be affected. Different size and stacking of MoS_2 slabs on various supports were proposed to be responsible of the better activities on TiO_2 or ZrO_2 [92]. Several authors reported also from TEM observations raft-like structures sitting flat on the surface or flakes of MoS_2 located vertically to the surface of the support and a controversy opened on the interpretation of the images [93]. Such orientation effects were recently demonstrated on MoS_2 model catalysts prepared on γ-Al_2O_3 deposited on $MgAl_2O_4$ [94] or on TiO_2 anatase support [95,96]. However, epitaxial growth cannot be evocated in the case of amorphous supports and the number and nature of chemical bonding between the support and the catalyst remains an open question. An attempt to model the support interaction of MoS_2 with alumina or silica was performed by molecular mechanics [97]. The authors conclude from the energy of interactions that stacking is favored on silica as it is experimentally observed. Considering the development of recent and accurate DFT methods, such theoretical approach should provide new insights on the support effect.

8. Synergetic effect

8.1. Synergetic effect on non-conventional oxide supports

Non-promoted zirconia or titania supported Mo and W sulfides possess HDS and HYD activity several times higher than their alumina-supported counterparts. However, the synergy between Ni(Co) and Mo in the catalysts prepared by conventional coimpregnation technique appears to be lower than in the alumina-supported homologues. As a result, the catalysts have performances comparable or even lower than industrial references. Several explanations attempted to clarify this observation. In fact, the influence of the support was clearly illustrated by van Veen et al. [98]. These authors compared several CoMo/Al_2O_3 catalysts and CoMo/SiO_2 and concluded that a weak Mo–support interaction or acidification of the support favors the formation of $CoMoO_4$ in the calcination step which leads to Co_9S_8 poorly active species after sulfidation. Similarly, Vrinat et al. observed that in CoMo/TiO_2–Al_2O_3 (5% molar ratio $Al_2O_3/(TiO_2 + Al_2O_3)$), Co was mainly involved in the formation of $CoMoO_4$, phenomena which was correlated to the support acidity. They proposed to avoid calcination for getting more active catalysts [99]. In fact, better synergetic effect was obtained without intermediate calcination procedure [100]. Recently, it was also proposed that lower synergetic effect on NiMo on titania was due to the decoration of the MoS_2 crystallites Ti^{3+} species acting as a promoter but to a lesser extent as compared to Ni or Co [101,102].

In the case of zirconia, the weaker synergy seems to be also due to the interaction between Ni species and the surfaces of ZrO_2 in the oxide precursor state and during sulfidation. On zirconia support, nickel is sulfided much easier than on alumina, leading to the early formation of the bulky crystals of NiS or Ni_2S_3, while molybdenum is not yet sulfided. To solve this problem, we can suggest the use of a chelating agent which delayed Ni sulfidation as it was proposed for NiMo/SiO_2 [103], or introduction of Ni after preliminary sulfidation of Mo.

8.2. *Formation of CoMoS phase in zeolites and mesoporous materials*

The difficult formation of the CoMoS, NiMoS, NiWS phases has been pointed out in many studies [57,104]. The origin of this phenomenon has been addressed by Plazenet et al. [105]. These authors have shown that upon co-impregnation of a HY zeolite with ammonium heptamolybdate and cobalt nitrate, the molybdenum atoms participate in the formation of the aluminomolybdate anion, from which the cobalt atoms are excluded. EXAFS results demonstrated that in this case, there is no cobalt neighbor for the molybdenum (and vice versa) and consequently there cannot be any interaction between the cobalt and molybdenum at least in the oxide form. These results may explain the lack of promotion mentioned above. The formation of $Al_2(MoO_4)_3$ was also observed by Klimova et al. [66] for mesoporous MCM-41; a deterioration of the textural characteristics and some loss in the periodicity of the pore structure was mentioned.

Different methods of preparation have been proposed to overcome the unfavorable chemistry described above. In an inorganic chemistry approach, molybdenum sulfide cluster $[MO_3S_4(H_2O)_9]^{4+}$ and nickel–molybdenum sulfide cluster $[Mo_3NiS_4Cl(H_2O)_9]^{3+}$ of the cubane-type structure have been used successfully by Taniguchi et al. [106,107] for preparing sulfide phase in various zeolites. Similarly, it was shown that mixed Anderson cobaltomolybdate anion prevents the formation of the Anderson-type entity and then would lead to a good CoMo interaction [101]. Using another approach, Okamoto et al. [108–110] reported that with metal carbonyls as precursors of Mo, Co and Co–Mo sulfide, they obtained uniform Co–Mo sulfide clusters, well defined in structure and thermally stable, encapsulated in zeolites. The formation of an intra-zeolite thiocubane structure $Co_2Mo_2S_6$ was evidenced by these authors by several techniques.

9. Conclusion

The objective of this article was to give an overview on the various support interactions encountered for hydrotreating catalysts. This review has been limited to the open literature, which means that, for example, the new patented technology of “Nebula” catalyst, based on a new carrier concept has not been addressed due to the lack of information concerning the nature of the support [111]. Detailed information are given in the present “Catalysis Today” issue concerning the interaction with various type of supports in the following articles but also the important field of alumina promoters.

The progress which have been made concerning novel catalysts based on unconventional supports are important in several areas and are very often related to new methods of preparation of supports with enhanced textural properties or to new method of deposition of the active phase. Nevertheless, the knowledge concerning these new supports is far behind that concerning alumina. In particular, it is sometimes difficult to make the extrapolation of results obtained at the laboratory scale in the gas phase to real feedstocks in trickle led reactors [112]. This might be related to the "gas–liquid phase controversy" as mentioned by Reinhoudt et al. [113] who proposed that the ionic surface of the support might play a role in the adsorption of the solvent on sites protruding from the catalyst surface. This means that more studies should be carried out with real gas oils before it can be envisaged to replace alumina by another carrier.

It has been shown in this article 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 reactions with acidic sites, absence or presence of linkage between the sulfide phase and the support. The progress in the understanding of the sulfide–support interaction is real but it is clear that a theoretical approach is still lacking. The recent and rapid development of efficient modeling technique will allow getting a better description of the surface of the support and its interaction with the active phase at the molecular level.

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