Catalysis Today 147 (2009) 275–286

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Unsupported transition metal sulfide catalysts: 100 years of science and application

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ARTICLE INFO

Article history:
Available online 9 December 2008

This article is dedicated to the 60th anniversary of Marc Ledoux, innovator, scientist, colleague and friend.

Keywords:
Transition metal sulfides
Anisotropy
Hydrodesulfurization
MoS_2

ABSTRACT

For more than 100 years the transition metal sulfides (TMS) have been mainstays of hydro-processing fuels and upgrading bitumen and coal. Every refinery in the world uses them everyday to remove sulfur and other pollutants from transportation liquid fuels. As environmental regulations increase the need for improved active and selective TMS will continue to grow. This need can only be met through increased understanding and research on the next generation of TMS catalysts. In this report we outline the growth in fundamental studies of structure/function in the TMS and suggest are where improved understanding is needed. An understanding of the fundamental properties that lead to both the activity of the simple binary sulfides and the mechanism by which two metals (Co + Mo) acted together to enhance activity (promotion) has been developed. Initial efforts focused on supported commercial catalysts with limited success. In the early 1980s the periodic trends of TMS catalysts on unsupported catalysts were discovered and these results formed the foundation for further basic understanding of the key properties that led to catalytic activity. These results have been extended over the years to include supported catalysts and many petroleum based substrates. Progress has been made by combining synthetic, experimental and theoretical techniques. Theoretical studies support the fact that the d electrons in the frontier orbitals of the catalysts were key in determining catalysis at the surface. The triumph of this approach was that it unified the promoted TMS systems with the binary TMS and provided a common rational for the activity of both. Constant progress since then has been achieved through the application of density functional theory (DFT) narrowing the gap between instinct and a formal description of catalyst structure/function made by combining synthetic, experimental and theoretical techniques. Theoretical studies support the fact that the d electrons in the frontier orbitals of the catalysts were key in determining catalysis at the surface. The triumph of this approach was that it unified the promoted TMS systems with the binary TMS and provided a common rational for the activity of both. Constant progress since then has been achieved through the application of DFT narrowing the gap between instinct and a formal description of catalyst structure/function.

It is crucial to remember that for real understanding to develop we must study the catalytically stabilized materials and not materials that are changing under catalytic conditions. In the case of the TMS this means that we must study materials like $MoS_{2-x}C_x$ and $RuS_{2-x}C_x$. It has been demonstrated that "surface carbides" are the catalytically stabilized state under hydro-treating conditions. The original relation between the d electrons and later DFT calculations all point to the importance of these electrons in the catalytic reaction. However, more work is needed to define the relation between these electrons and the stabilized carbide surfaces before detailed active site structures can be developed with confidence. In addition the presence of Co metal in active hydro-processing catalysts stabilized for four years in a commercial reactor, calls in to question current theories of the structure of promoted catalysts.

1. Introduction

The field of TMS (transition metal sulfide) catalysis arose in earnest after the end of WWI. WWI initiated the large-scale industrial use of catalysts to produce nitrates because of the fact that Germany was cutoff by blockage from the guano sources that

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doi:10.1016/j.cattod.2008.09.041

were used to produce nitrates for explosives. The introduction of the catalytic Haber process to fix nitrogen is a well-known story [1]. Technological advances leading to air and tank warfare at the end of WWI led to a race to produce liquid fuels with local coal resources to reduce dependence on imported petroleum with vulnerable supply lines. Following the lead of the Haber process researchers investigated the hydrogenation of coal with metal catalysts. After processing the metal had been converted to TMS catalytic materials. This was the beginning of the field of catalysis by TMS. This story and the technical details behind are beautifully described up to 1973 by Weisser and Landa [2].

The race to provide liquid fuel supplies produced intensive research efforts particularly in Germany. Research efforts were lead by I.G. Farbenindustrie (IGF) and Badische Anilin u, Sodafabrick (BASF) in Germany and between 1920 and 1930 these companies tested over 6000 catalysts. Scientists such as Paul Sabatier, Friedrich Bergius and M. Pier were leaders in investigating the TMS for fuel and chemical production. Paul Sabatier is considered the "Father of Modern Catalysis" for his early work in TMS catalysis that led to a Nobel Prize in 1912. Bergius won the Nobel Prize in 1931 for his work on coal hydrogenation. Much of the work in this period was secret and appeared only in the patent literature. The field of petroleum processing also arose in this period and the records become obscure during WWII reemerging primarily in the U.S. and European petroleum industry after the war [3]. Since that time TMS catalysis for fuel upgrading has played a major role in petroleum catalysis particularly in removing pollutants such as sulfur and nitrogen from liquid fuels. TMS catalysts will continue to play an increasingly important role in fuel processing as emphasis switches to cleaner and sustainable fuel supplies. In addition, the TMS catalyze many other reactions that have not been thoroughly explored. The major reactions catalyzed by TMS are: hydrogenation of olefins, ketones, and aromatics; hydrodesulfurization (HDS); hydrodenitrogenation (HDN); hydrodemetallation (HDM); hydrocracking; dealkylation; and ring opening of aromatics. But the TMS catalysts have many other uses as well, including: reforming, isomerization of paraffins, dehydrogenation of alcohols, Fischer–Tropsch and alcohol synthesis, hydration of olefins, amination, mercaptan and thiophene synthesis, and direct coal liquefaction. More esoteric applications can also be found in polymer and in inorganic syntheses (silanes and metal hydrides). A comprehensive list of the TM catalyzed reactions is found in Ref. [4]. In this article we present the fundamental principles of the TMS catalytic materials that govern their activity and selectivity. Furthermore we outline research that will lead to increasing improvements in the usefulness of these versatile catalytic materials.

2. The modern TMS catalytic material

The first description of a synergetic effect due to a mixed cobalt-molybdenum catalyst (oxides and sulfides) appeared in 1933 by the catalysis group of Princeton University [5]. The catalytic system studied was active for the HDS of a mixture of benzene and thiophene. Much of the work performed in Germany, the United States and other countries submerges during WWII and there is a story yet to written regarding the transfer of technology from Germany to the United States and other countries following the end of the war. The birth of the concept of cobalt-molybdenum synergy appears only in few publications from the research laboratories of major petroleum companies. In 1943 for example, Byrns et al. [6] of Union Oil of California published the first study showing under semi-industrial conditions the relative activities of MoO_3 and CoO and the mechanical mixture of these two oxides, which they compared to $CoMoO_4$ supported on bentonite6. These authors demonstrated that a mixture of molybdenum and cobalt in their oxidic state should be chemically associated in order to be very active, while the simple mechanical mixture only showed the additive activities of the individual oxides. In 1959, Beuther et al. [7] of Gulf Oil Company published the first systematic study of the HDS activity of CoMo and NiMo supported on alumina as a function of the atomic ratio Co(Ni)/Mo. As a result, they showed what they called a "promoter effect" of the cobalt (or nickel) on the molybdenum for atomic ratios Co/Mo = 0.3 and Ni/Mo = 0.6.

TMS catalysts, used in refineries, are generally molybdenum or tungsten sulfides supported on alumina and promoted by Group VIIIB elements (Co or Ni) with a promoter atomic ratio: Co(Ni)/[Co(Ni) + Mo(W)] between 0.2 and 0.4. $CoMo/Al_2O_3$ catalysts are very efficient in the HDS process but are less active for HDN or aromatic hydrogenation. Conversely, NiMo phases are better HDN and hydrogenation catalysts and are preferred in order to treat feedstock with a high concentration of unsaturated compounds. Phosphorus is sometimes added to the alumina support improving the selectivity toward hydrogenolysis versus hydrogenation. NiW catalysts are highly effective for aromatic hydrogenation reactions but their higher cost has limited their uses. The hydrotreating process needs a large amount of hydrogen to treat crude oils. Pressure varies from 10–20 atm for naphtha to 25–40 atm for gas oil. Temperature conditions are generally 320–340 °C. However, for some hydrocracking residues, pressure and temperature conditions can reach 100–150 atm and 400–440 °C.

What is the role of the alumina? Traditionally it has been thought that the role of the alumina support is primarily to disperse and stabilize the MoS_2 based hydrotreating catalyst. This support effect is caused by a strong interaction between MoS_2 and Al_2O_3. The alumina also serves the function of making the catalyst less expensive by diluting the metal. Many papers have been written in an attempt to understand the effect of the support. In this paper we present results that describe the role of alumina as secondary. The fundamental activity and selectivity resides in the sulfide phase. Because of the strong sulfide/support interaction the total activity of the catalyst is actually reduced per metal atom as a result. Thus, it appears that historically the alumina supported catalyst arose because of reduced cost and stability of the un-sulfided catalyst precursor which makes the material easier to transport, store and load in reactors.

In the 1970s, the first oil crisis caused an attempt to understand and improve the nature of the cobalt-molybdenum promotion effect. Moreover, during this period, refinement of the heavy crude fractions, especially desulfurization, became imperative to make up the deficit in light fractions used in transportation and the petrochemical industry. Consequently, the necessity to synthesize more efficient catalysts emphasized fundamental research on CoMo catalysts. Finally, the new environmental regulations concerning the sulfur content of vehicle transportation fuels bring new challenges in order to remove very refractive sulfur organic compounds such as alkyldibenzothiophenes [8].

The first research group to propose a description of the structure of CoMo catalysts was led by Schuit and Gates [9]. This group introduced the so-called "monolayer" model in which each sulfur atom of an upper layer is bonded to a molybdenum atom located into a second layer below the first one. These molybdenum atoms are bonded to two oxygen atoms also located in this second layer. The active sites are then created when a sulfur atom was removed from the surface by reduction of molybdenum atoms (from Mo^{5+} to Mo^{3+}). The promotion effect would be due to the presence of cobalt incorporated into underlying layers of the alumina support that pushed up to the second layer aluminum ions in tetrahedral sites. Each atom of sulfur from the first layer is then being bonded to two molybdenum atoms. Therefore, a sulfur vacancy now liberated two molybdenum atoms instead of one for the adsorption site. The higher activity would be then related to an increase of the number of active sites rather than to an improvement of their quality. However, this model was rapidly discarded by Schuit's team itself, which observed that the sulfur stoichiometry of the molybdenum and cobalt which observed that the sulfur stoichiometry of the molybdenum and cobalt compound corresponded to a mixture of MoS_2 and Co_9S_8 instead of the MoS_{1-x} stoichiometry required by the monolayer model [10].

At the same time, Voorhoeve and Stuiver and Farragher and Cossee from Shell proposed a new model derived from the structure of sulfides called intercalated solids [11,12]. Compounds such as $Ni_{0.5}MoS_2$ and $Co_{0.5}MoS_2$ are produced by high temperature solid-state synthetic techniques and Voorhoeve and Stuiver proposed that promotion was related to the change in Mo or W oxidation state as occurs in these materials. In this type of intercalated compound, the Group VIII transition metals of the first row of the periodic table (Fe, Co, Ni) penetrate the Van der Waals layers of the lamellar tungsten sulfide to occupy the octahedral symmetrical voids and the Mo^{4+} and W^{4+} are reduced to Mo^{3+} and W^{3+}. However, evidence for the formation of these phases was not found in working HDS catalysts. Therefore, these authors modified this previous "intercalation" model by assuming that only the sites located on the edges of the MoS_2 crystallites were occupied by the Co^{2+} and Ni^{2+} ions under catalytic conditions. They called this model the "pseudointercalation" model to incorporate this idea. In their study of the hydrogenation of benzene and cyclohexene in presence of CS_2, the authors ascribed the active sites to W^{3+} with different degrees of unsaturation for binding of benzene and cyclohexene. They called these edge sites (doubly unsaturated binding cyclohexene) and corner sites (triply unsaturated binding benzene). The promotion effect would result from a charge transfer from pseudo-intercalated Ni promoting atoms to W unsaturated binding benzene). The promotion effect would result from a charge transfer from pseudo-intercalated Ni promoting atoms to W^{3+} sites. According to their model, the active sites do not change in nature after Ni promotion, only their number increases via indirect electron transfer to the layers. Elements of this theory remain in today's explanation of promotion theory.

At about the same time, Delmon and co-workers proposed a simple model, coherent with their experimental observations. This model was based on the interaction of MoS_2 and Co_9S_8 phases [13]. The Delmon's group proposed that the molybdenum and cobalt sulfides acted together by being in close contact, from which came the term "contact synergy". The HDS reaction took place at the interface between the two sulfides with each phase "helping". The authors also proposed a reaction mechanism, which they called "remote control mechanism", where the sulfided organic molecule was adsorbed on MoS_2 to be desulfurized by dissociated migrating hydrogen atoms coming from Co_9S_8 active sites. However, the promotion effect does not seem to require the presence of Co_9S_8 as shown by Wivel et al. using emission Mössbauer spectroscopy (EMS) [14]. Nevertheless, in any case, this model was very helpful in understanding metal sulfides activity and has clearly showed that the alumina support does not play any role in the promotion effect and that promotion resides uniquely at the interface of the two MoS_2 and Co_9S_8 phases. This work also developed the use of the idea of synergy (cooperation between two phases) as opposed to the idea of promotion (increase of activity induced by the presence of a second metal). It is useful for the reader to remember the distinction between these two terms for later reference.

The first physical proof of a specific Co environment in the mixed cobalt-molybdenum catalytic system was presented by Topsøe and his group. A systematic study of CoMo catalysts with Emission Mössbauer spectroscopy (EMS) showed the existence of three different Co compounds in the catalyst: cobalt contained in alumina support as aluminate (type 1), cobalt contained in Co_9S_8 (type 2), and a third cobalt species (type 3) associated in small amounts with the MoS_2 phase. Topsøe et al. located the cobalt inside or on the edges of MoS_2 crystallites and called the type 3 Co the CoMoS phase [15]. In addition, using EXAFS analysis, this group showed that the local atomic structure of MoS_2 was preserved in the sulfided catalyst [16]. Many other experimental techniques were used to confirm these results but, due to the disorder of these catalytic systems, only TEM on MoS_2 crystallites, containing a small amount of Co, showed that the Co atoms were located on the edges of the MoS_2 platelets: this model is also called edge decoration model [17]. By using EMS, Topsøe's group was able to evaluate the amount of the new CoMoS phase contained in different catalysts with increasing loading of Co, identifying the type 3 Co that correlates linearly to the HDS activity of these catalysts [18]. These results were the first to provide strong evidence in favor of the existence of a specific active phase involving Co and Mo. Also, Topsøe et al. could differentiate two kinds of CoMoS sites: a type I found on monolayer slabs and a type II that occurs on multilayered slabs [19]. They also observed that these two sites exhibited different HDS activities due to either electronic or geometric factors induced by the support. Consequently, the Type I site appeared less active than the Type II sites.

The edge decoration model is strikingly illustrated by the beautiful image of a single layer MoS_2 catalyst precursor created under vacuum and then sulfided can be found in the work of Topsøe and co-workers [20]. The STM (scanning tunneling microscopy) image of a single triangular layer of MoS_2 may be seen in Fig. 1. The single layer crystallite is approximately 3 nm wide and was prepared on an Au (1 1 1) substrate by depositing the metal in an atmosphere of H_2S (1×10^{-6} mbar at 400 K) and then annealing (673 K for 15 min). Sulfur vacancies were also imaged after treatment with hydrogen by treating the catalyst with atomic hydrogen. The edge chemistry of these materials is complex and flexible as expected for a catalyst, but the basic morphology of the MoS_2 illustrated in Fig. 1 best describes a model for subsequent fundamental studies of the catalytic chemistry of the SLTMS. However, one should consider that operating SLTMS are generally highly disordered, thus introducing another level of complexity.

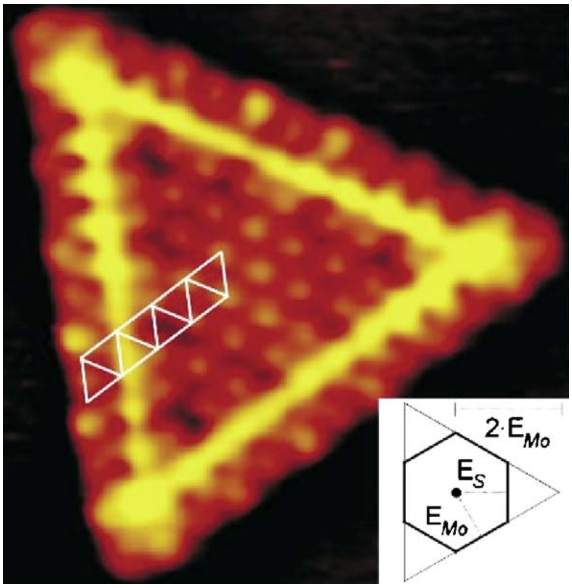

Fig. 1. STM picture of single layer MoS_2 on gold substrate (from Ref. [20]).

In the last 10 years, progress made in terms of calculation has accelerated the development of theoretical chemistry and has allowed the application of density functional theory (DFT) methods to simulate the morphology of hydrotreating catalysts. A huge amount of work was done on this subject and only the main conclusions are presented here. Raybaud [21] has suggested that the localization of Co occurs only on the (1 0 −1 0) "Mo-edge" plane. On the contrary, nickel would be present on both (1 0 −1 0) "Mo-edge" and (−1 0 1 0) "S-edge" planes. Moreover, according to the H_2S partial pressure, the MoS_2 slabs would exhibit varying proportions of (1 0 −1 0) or (−1 0 1 0) planes leading to morphologies going from a pure triangular aspect to a perfect hexagonal shape through intermediate truncated hexagonal forms. However, these results are contradictory to those reported by Lauritsen et al. [22] combining DFT calculations and STM characterization. Indeed, these authors concluded to a Co localization on the (−1 0 1 0) "S-edge". The nickel case is even more complex with different "NiMoS" species whose the main one would correspond to Ni accommodated on the (1 0 −1 0) "Mo-edge".

3. Immiscible phases and symmetrical synergy

However, the *promotion* or *synergistic effect* is more complex and at this writing only partially understood. To describe this complexity we must revert to the older model *synergy by contact* described above [13]. The principle of a *synergy by contact* between the MoS_2 and Co_9S_8 phases was generalized by Chianelli [23]. Developing an idea of Phillips and Fote, Chianelli was able to describe mixtures of Co/Mo (Ni/Mo) in terms of "symmetrical synergy" [24]. In this hypothetical phase diagram (Fig. 2) existing below 550 °C, three different regions can be observed as Co is added to the system. Firstly, the most commonly region accessed by conventional preparations is situated at the left-hand portion of the phase diagram. In this region, the promotion effect increases until a maximum is reached. No Co_9S_8 is detected because the Co/Mo/S surface phase is being produced. The boundary of this region is determined by the MoS_2 "edge" area. At the point where the edge area is exhausted, more Co is added and the Co_9S_8 will begin to phase separate. In this idealized model, this occurs at the promotion maximum, but in real catalysts, the situation may be more complex with an equilibrium existing between the surface Co/Mo/S phase and Co_9S_8.

On the right-hand portion of the phase diagram, a Mo/Co/S surface phase exists that is exactly analogous to the Co/Mo/S phase with Mo promoting Co_9S_8 in the same way that Co promotes MoS_2. The lower activity of the promotion peak in the right-hand region is due to the difficulty in preparing Co_9S_8 of high surface area. The activity of the resulting catalyst that occurs in the region in the middle of the phase diagram will be the resultant of the mixture of the two surface-enriched phases. The conclusion from this idea is that any promotion model must be "symmetric" in the sense that the promotion site of Co on MoS_2 must be closely related to the promotion site of Mo on Co_9S_8. This phenomenon has not been widely addressed in the literature. However, the existence of this "symmetry" in the promotion behavior suggests an electronic origin of promotion.

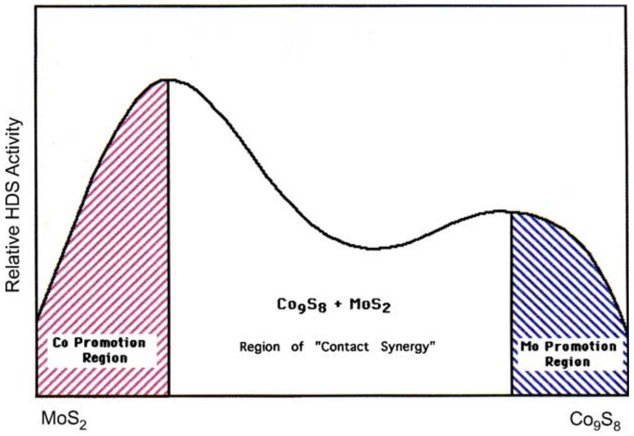

Fig. 2. Phase diagram for hypothetical Co/Mo/S catalytic material illustrating symmetrical synergy (from Ref. [23]).

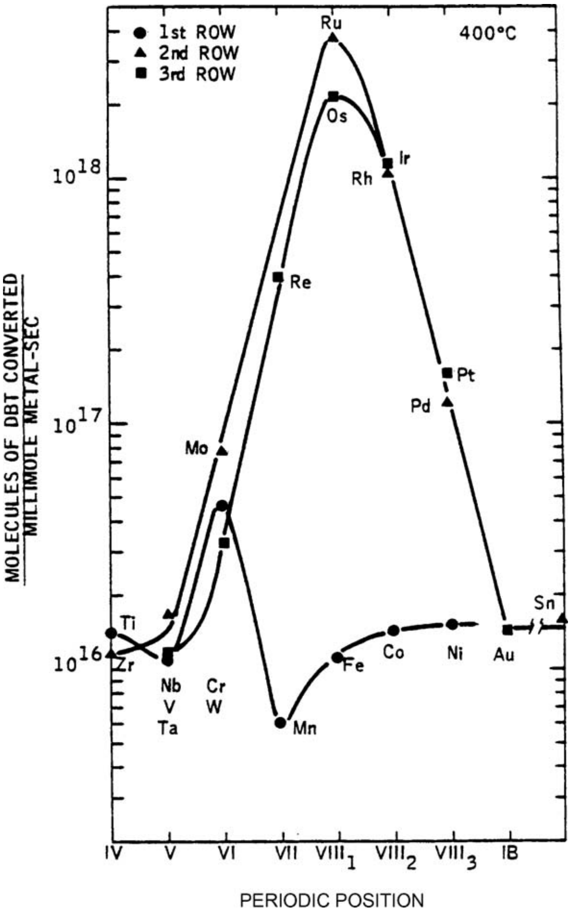

Fig. 3. Periodic trends for HDS [25].

4. Electronic structure and periodic effects

Periodic effects form the underpinning for any fundamental understanding related to the electronic structure. For example, a typical "volcano" plot between the HDS activity for dibenzothiophene and the periodic position is shown in Fig. 3 [25]. Group VIII TMS such as Ru, Rh, Os, and Ir were the most active. Similar trends were later observed for hydrogenation reactions and HDN, as well as for the hydrotreating of a heavy gas oil [26–29]. These trends are of fundamental importance because they emphasize both the importance of the 4d and 5d electrons or the metal sulfur bond strength in catalysts. Several correlations to the HDS activity have been described in several papers (metal–sulfur bond strength, optimum heat of formation of the sulfide, and Pauling percentage d-character). Bernard et al. have shown that the heat of formation of the sulfides is linearly correlated to the heat of adsorption of sulfur on the transition metals [30].

Harris and Chianelli proposed a theoretical approach in which several electronic factors are related to catalytic activity: the

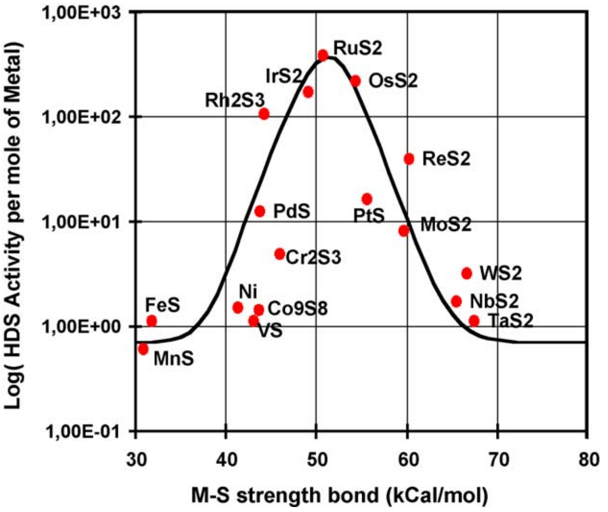

Fig. 4. HDS activity vs. bond strength [34].

orbital occupation of the HOMO (highest occupied molecular orbital), the degree of covalency of the metal–sulfur bond, and the metal–sulfur bond strength [31]. They showed that, to be a good catalyst, the sulfide should have a HOMO filled with as many electrons as possible and be of t_{2g} symmetry instead of e_g. Tan and Harris have confirmed these earlier calculations and assume that a nearly complete localization of electron density in the metal t_{2g} orbitals in RuS_2 and Rh_2S_3 may be partly responsible for their intrinsic high HDS activity [32].

The correlation proposed by Harris and Chianelli is supported by Ledoux et al., by studying the activity of very dispersed sulfides on activated charcoal in order to overcome the difficulty to measure really the number of accessible active sites [33]. They improved the first calculations made by Harris and Chianelli who assumed each sulfide to be in an octahedral symmetry, and preferred to take into account the stabilized form of the latter TMS that requires a coordination of 4 instead of 6. They also proposed that the electronic configuration of the HOMO was a necessary condition but not a sufficient one. The concept of metal lability to sulfur adsorption/desorption, coordination flexibility (for example, PtS(coord4)/PtS_2(coord6)) would be an additional important factor to the electronic theory. Finally, the electronic description of the catalytic activity for the TMS as described above has undergone considerable refinement since it was first hypothesized. The theory was updated in a recent article [34]. We can see in Fig. 4 the activity for HDS against bond strength yielding the classic volcano plot as presented in the first report. Clearly an intermediate bond strength is required for maximum activity.

Chianelli et al. were the first to propose a “chemical” explanation for the synergy based on the heat of formation of the sulfides [35]. The metals for which the sulfide has a high heat of formation are too strongly bonded to the sulfur and sulfur vacancies cannot form. The sulfides having low heat of formation are too weakly bonded to the sulfur and adsorption of the organic molecule rarely occurs. Only metals of which the sulfides have an intermediate heat of formation strong enough to lead to a significant adsorption of the organic molecule and weak enough to release H_2S after desulfurization, will be good catalysts (Fig. 5). This is the “Sabatier Principle” as applied to the TMS. Averaging the heat of formation of the sulfides of each of the following couples CoMo, NiMo, CoW, and NiW, generates average values between 30 and 50 kcal/mol (120–200 kJ/mol) for the sulfide pairs that exhibit promotion. This strongly suggested that promotion occurred through mimicking of noble-metal sulfide electronic structure by sharing of sulfur atoms between pairs of metals previously indicated. Thus, the *synergic pairs* behave as *pseudo-binaries* with average electronic properties.

The promotional effect of first-row transition metal on the activity of molybdenum-based catalysts was originally correlated with an activity parameter suggesting that the interaction between the Mo 4d electrons and the 3d electrons of the second metal is required [36]. This interaction occurs through an electronic transfer between the two metals at a site existing near the surface or interface of the two relevant phases. In octahedral coordination, the calculation showed that Co and Ni had the property to transfer electrons to Mo creating promoted *pseudo-binaries* with enhanced activities. Whereas, Cu has the property of removing electrons from Mo causing it to have electronic properties of Nb with less catalytic activity and is thus a poison. The other metals did not transfer or attract electrons to or from Mo. Nørskov et al., extended the theoretical investigation of the TMS using *ab initio* calculations. They emphasized the binding energy of sulfur to the transition metal as the important variable in explaining the periodic trends and the promoted systems. They also evoked the importance of the sulfur chemisorption energy and the sulfur-induced distortions of the metal lattice as described further on [37].

5. Structure and properties of TMS catalytic materials

The catalytic activity of TMS catalysts is related to surface defects in the crystal lattice. However, the properties and stability of these defects are determined by the bulk atomic and electronic structure. Thus, it is crucial to understand the *catalytically stable phases* of the TMS phases in order to understand the fundamental origins of the catalytic effects that they exhibit.

Sulfide catalysts operate at high temperatures (typically 200–400 °C) and under reducing conditions, and significant restructuring can occur under catalytic conditions. In situ characterization of TMS materials is generally difficult and limited because of the

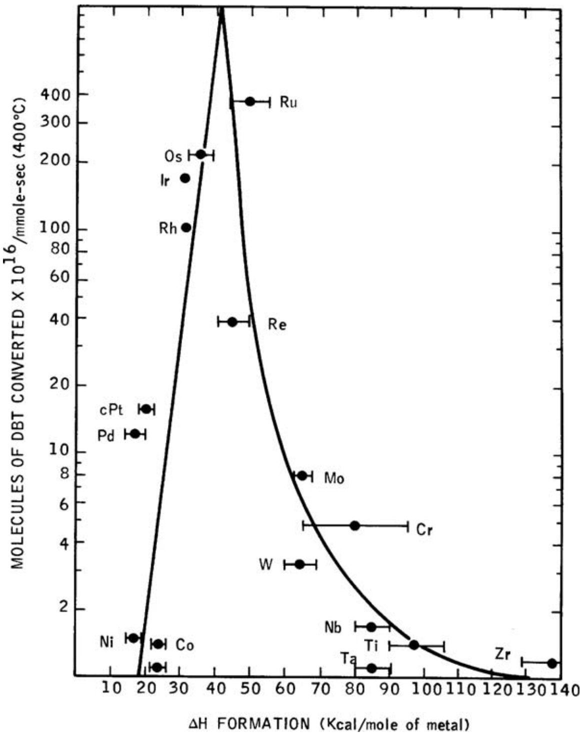

Fig. 5. Correlation HDS activity vs. heat of formation of sulfides per mole of metal [35].

conditions under which they are used (high-temperature, high-pressure, and liquid-phase reactions). Therefore, the characterization of the "stabilized" catalyst under catalytic conditions as well as of the fresh catalyst is necessary and gives information regarding the relation between the electronic/geometric structure and the catalytic activity/selectivity as previously described.

For the binary phases, there are two main classes of TMS structures. Isotropic sulfides dominate the Group VIII sulfides. Many different structures exist in this group, such as pyrite (RuS_2), pentlandites (Ni_3S_2), and others. The coordination of the metals in this group by sulfur is generally an octahedral arrangement. However, some special structures, such as Co_9S_8, can also contain mixed six- and four-fold tetrahedral coordination. Other structures, such as PdS and PtS, contain metals in distorted six-fold coordination. Layered sulfides predominate in Groups IV to VII except for MnS, which is isotropic. The main structural feature of this class is a strong chemical anisotropy that greatly affects catalytic properties. In the molybdenite structure (MoS_2), the metal is in trigonal prismatic coordination. Other layered sulfides are octahedrally coordinated or distorted octahedrally coordinated (ReS_2) with the metal surrounded by six sulfur atoms. It should also be noted that some TMS sulfides have structures that fall in between isotropic and layered sulfides. Rh_2S_3 is an example and others are completely amorphous, such as IrS_x and OsS_x.

When a second or third metal is present, the identification of the phases becomes more complex. In general, poorly crystalline mixed-metal materials, such as Co/Mo/S, are not stable as intercalated bulk phases under catalytic conditions and are phase separated ($Co_9S_8 + MoS_2$). When both components belong to the isotropic class, solid solutions, crystallizing in a cubic pyrite structure, are obtained as observed for $Co_{1-x}Ru_xS_2$, $Co_{1-x}Rh_xS_2$ and $Rh_{1-x}Ru_xS_2$ [38]. However, under HDS conditions, these ternary compounds also separate into their binary component phases (for example, Co_9S_8 and RuS_2).

Chevrel phases have also been studied for HDS. The family of Chevrel phases is based on a Mo_6S_8 cluster unit with a general formula $M_xMo_6S_8$ with M representing more than 40 different metallic elements. Until recently, their high-temperature synthesis prevents from preparing active catalysts for useful application. However, low-temperature synthesis route for molybdenum sulfides have been found and developed [39]. Chevrel phases are the only known ternary phases that appear to exhibit high activity and remain stable without undergoing phase separation.

6. Anisotropic materials and the difficulty to measure dispersion

The morphology, particle size, and surface area of these materials are obtained by conventional methods such as HRTEM, X-ray diffraction line broadening, and nitrogen BET (Brunauer–Emmett–Teller) measurements. The characterization of the isotropic class of TMS compounds presents no major difficulties and the materials are well behaved. However, characterizing TMS materials particularly for MoS_2 is complicated due to their anisotropic structures. The basal plane surface corresponds to a close-packed surface of sulfur atoms bounded to three metal atoms. This stable environment of the sulfur results in weak Van der Waals interaction between the layers. Therefore, the basal plane exhibits a low reactivity and leads to the ability of MoS_2 to act as a very effective lubricant. In contrast, the edge planes are highly reactive. The ratio edge area/basal area is of primary importance for developing catalytic structure/function relationships in anisotropic systems. Moreover, catalytically active MoS_2 is in a poorly crystalline and highly disordered state best described as the "rag structure". Electron micrographs are however difficult to interpret in order to estimate the particle size of such a material [40]. Calais et al. have shown that particle sizes determined by using temperature-programmed reduction (TPR) techniques are in good agreement with electron microscopy data whereas EXAFS results are strongly affected by a strong structural disorder of the periphery of the MoS_2 particles and thus, the technique cannot predict particle sizes for the anisotropic materials [41–44].

Electron microscopy results have failed to give a clear picture of the CoMoS or NiMoS alumina supported phase due to interference from the alumina support and the anisotropy of MoS_2. However, this technique has been successful in order to elucidate some crucial problems. By studying unsupported WS_2 promoted by Ni, Farragher and Cossee were able to observe a structural change of the WS_2 crystal edges induced by the Ni promoter [12]. Pratt and Sanders for bulk NiMo sulfide and Vrinat and De Mourgues for bulk CoMo sulfide were the first to produce pictures from electron microscopes, showing a high dispersive effect of cobalt and nickel added to molybdenum sulfide [45,46]. With very high-resolution transmission electron microscopy, Yacamán and co-workers [47] and Topsøe and co-workers [20] were able to localize cobalt on the edge of bulk MoS_2.

7. Measurement of active sites

Because of the anisotropy of MoS_2 and WS_2 other methods have been developed to measure active sites. For example, poorly crystalline MoS_2 samples exhibit an ESR signal, attributed to defects such as Mo(III) and/or Mo(V) and this signal correlates to activity in unpromoted MoS_2. This is also true of magnetic susceptibility, but the measurements also provide evidence that ESR technique does not measure the whole number of defects but only a fraction. Both magnetic susceptibility and ESR techniques can be correlated to the HDS of dibenzothiophene (DBT) indicating that surface defects are being measured [48]. These surface defects are on the order 1×10^{19} spins for a typical catalyst, but absolute determination of the number and oxidation state of these defects has been hard to unambiguously determine. This result suggests that a complex metallic structure exists at the active edges as described by Helveg et al., and indicated in Fig. 1 [20]. These are the so-called *Brim Sites*.

8. Crystal structure and reaction selectivity

The existence of two active sites on WS_2 and MoS_2 is well established throughout much of the literature, originally in the work of Voorhoeve [11]. In this work discussed above, two sites are described: *edge sites* and *corner sites*. *Corner sites* were described as ESR active W^{3+} sites responsible for benzene hydrogenation and *edge sites* (ESR inactive) for cyclohexene hydrogenation. This was based on the ideal WS_2 crystal structure and hexagonal crystallites. In this model *edge sites* greatly outnumber *corner sites* and have different degrees of sulfur coordination.

Tanaka in an elegant experiment showed that by cutting along the *c* axis a MoS_2 single crystal into several pieces the selectivity of the reaction investigated could be modified [49]. Indeed, this operation increased the area of the edge planes while the area of the basal planes stayed constant, as shown in Fig. 6. The hydrogenation and isomerization activities of 1-butene as well as the H_2–D_2 or C_2H_4–C_2D_4 isotopic exchange activities increased consecutively to this increase of the ratio edge plane/basal plane. This result effectively established the importance of the MoS_2 *edge planes* in agreement with the previous work of Tauster et al. in which O_2 chemisorption was used to correlate to HDS activity of MoS_2 when BET surface area measurements failed to distinguish between MoS_2 catalyst of various of varying surface area [50].

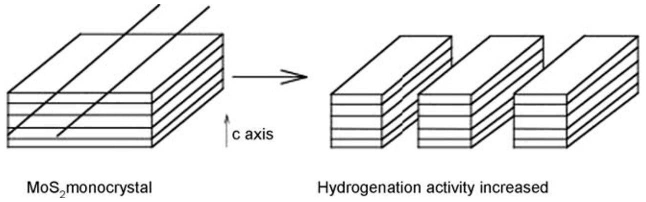

Fig. 6. The Tanaka experiment cutting a MoS_2 crystal along the *c* axis increases its hydrogenation activity (from Ref. [49]).

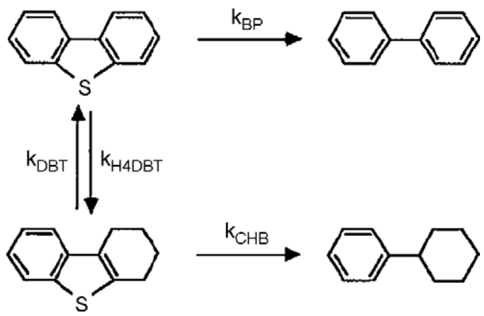

Fig. 7. Reaction pathway for the HDS of DBT [51].

Daage and Chianelli proposed a model called "rim–edge" in order to correlate the morphology of the MoS_2 particles to their relative selectivity towards hydrogenation or direct desulfurization and, therefore, to localize the different active sites [51]. Indeed, as shown in Fig. 7, the HDS of DBT exhibits two different pathways. In the first pathway, the reaction leads directly by desulfurization to biphenyl (BP). In the second pathway an intermediate product, tetrahydrodibenzothiophene (THDBT) is formed first by hydrogenation, hydrogenation followed by a desulfurization step leading to significant amounts of cyclohexylbenzene (CHB). By varying the preparation conditions of MoS_2 layers, such as the annealing temperature, Daage and Chianelli were able to modify the stacking height (h) and to observe that the ratio $S = k_{THDBT}/k_{BP}$ (S represents selectivity) is linearly correlated with the reciprocal of the stacking height (h). They developed then a two-site model for this result. The two sites are distinguished by their location on the edge. One site exists at the edge of exterior layers with adjacent basal planes exposed to the reacting environment. These are the "rim sites" on which both hydrogenation and desulfurization occur. The second site occurs on interior layers that have no exposed basal plane surfaces. These are the "edge sites" and only the desulfurization reaction occurs on this site. The relative proportion of rim and edge sites can then be calculated by using a simple physical model to describe the morphology of the MoS_2 particle as illustrated in Fig. 8. This model assumes that the catalyst particles are made of discs n layers thick with a diameter d. The ratio of rim sites to total sites is then deduced from the expression: $[r/(r + e)] = 2/n$, where r is the number of rim sites and e the number of edge sites. The ratio of sites does not depend upon the particle diameter, but only on the stacking of the layers. Consequently, according to this model, catalysts with a predominance of single unstacked layers will have a greater selectivity to hydrogenated products than those with a predominance of stacked layers.

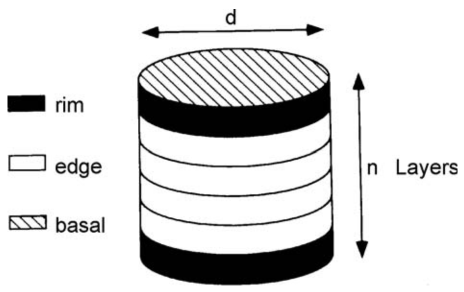

Fig. 8. The rim–edge model [51].

The rim–edge idea was confirmed in a real feed system using single layers of MoS_2 supported on small crystallites of pyrrhotite (FeS_{1-x}) [52]. Catalysts of this type were tested on aromatic distillate feeds and exhibited stable activity for over 500 h at temperatures up to 355 °C in the absence of any conventional support material. This attests to the stability of the MoS_2/FeS_{1-x} interaction. These catalysts showed unusual selectivity toward HDN in the presence of sulfur. HDS was relatively low. In fact, this surprising result was expected. Indeed, according to the rim–edge model, single layers will favor hydrogenation and therefore HDN. In this respect, recent synchrotron XRD studies have revealed that single layers represent more than 90% of the particles on incipient wetness impregnated supported catalysts leading to apparent single active site kinetic results since rim sites able to perform both hydrogenation and C–S bond rupture steps would be almost the only kind of active sites [53].

9. The role of carbon

Recently, the entire surface picture of the active sites regarding the role of sulfur vacancies has been called into question. This has come about because evidence is building that carbon plays an important role in the surface properties of active sulfided catalysts. Early evidence for this can be found in the patents of Chianelli and Pecoraro [54]. They found that a RuS_2 catalyst that had been stabilized in a catalytic environment had a composition, $RuS_{2-x}C_x$. This composition corresponded to the 100 Å catalyst particle having its surface sulfur stripped and replaced with carbon (Fig. 9). This behavior was also exhibited by the layered TMS. Seiver and Chianelli provided evidence for the formation of a carbidic catalyst surface by thermal decomposition of a $(NR_4)_2MoS_4$ precursor [55]. The Mo single-crystal work of Bussell and Somorjai is also particularly noteworthy in this respect. They studied thiophene desulfurization on Mo(1 0 0) and observed that, an initially clean

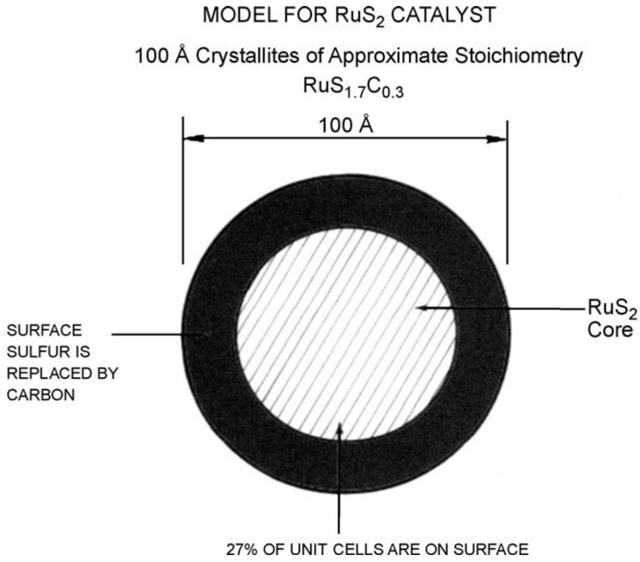

Fig. 9. Carbon stripping and replacing sulfur on the surface of a RuS_2 particle stabilized in a catalytic environment [54,55].

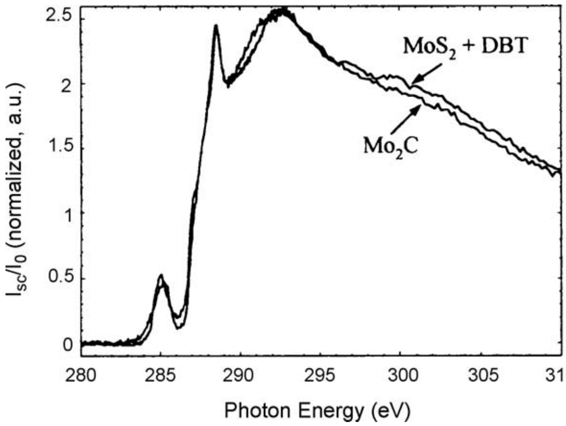

Fig. 10. NEXAFS spectra at the C K-edge of an unsupported MoS_2 sample treated under dibenzothiophene HDS conditions and a β-Mo_2C reference [57].

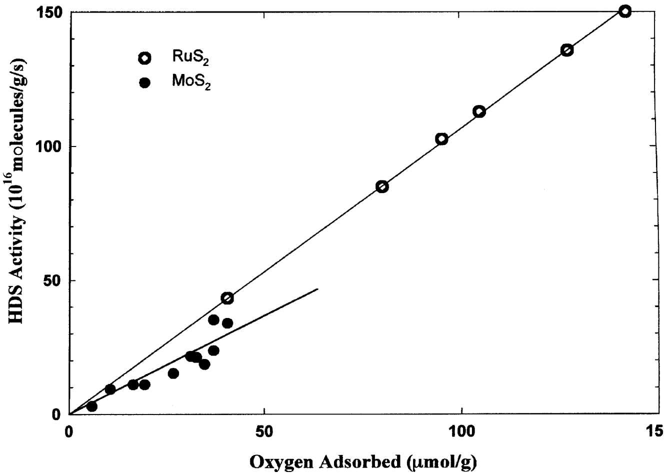

Fig. 11. O_2 chemisorption on RuS_2/MoS_2 vs. HDS activity.

Mo surface changed into a carbided surface with carbon atoms in four-fold hollow sites without blocking the active sites for thiophene HDS [56].

These results strongly suggest that a surface model for the HDS reaction on sulfided catalysts had to be developed and that all preceding models require at least some modification to include the role of carbon. This carbon effect emphasizes the necessity to characterize the real nature of the "stabilized" phase under HDS conditions. In this respect, recent progress has been made in evaluating the role of carbon on bulk TMS catalysts. Unpromoted or Co-promoted MoS_2 catalysts either treated by organosulfides compounds or directly submitted to HDS conditions have been characterized using a combination of bulk and surface-sensitive techniques. On unpromoted MoS_2, results revealed that the carburization process occurring under HDS steady-state conditions is intrinsically a surface phenomenon in which surface sulfur atoms on the edges of MoS_2 slabs are replaced by carbide-like carbon atoms. Indeed, while synchrotron XRD patterns essentially revealed a MoS_2 bulk structure, EELS (electron energy loss spectroscopy) and NEXAFS (near-edge X-ray absorption fine structure) at the C K-edge showed unambiguously the presence of a carbide-like surface phase (Fig. 10) [57]. On Co-promoted catalysts, a similar phenomenon occurred but with an even more advanced carburization [58]. Moreover, the disappearance of ν(S–S) IR vibrations after carburization suggests the formation of C=C groups on the edges of the MoS_2 layers [59]. This point was confirmed by Wen et al. through DFT calculations of the carburization of MoS_2 clusters [60]. This replacement of sulfur by carbon on the edges of MoS_2 layers had also morphological consequences. Indeed, the surface carburization results in a bending of the slabs and to an exfoliating process stabilizing single layers. It should be underlined that the interaction between S and C was also studied but starting from transition metal carbides contacted with S-containing molecules. Schwartz et al. have demonstrated the existence of a similar sulfocarbide surface composition between carbides and sulfides under HDS conditions [61]. Rodriguez and co-workers were able to observe the formation of MoS_xC_y compounds when contacting different molybdenum carbides compounds with sulfur-containing molecules and they concluded that C participates directly in desulfurization reactions instead of being a simple spectator [62,63].

10. Chemisorption properties

The chemisorption of oxygen gives valuable information for measuring the active surface of $MoS_{2-x}C_x$ and $RuS_{2-x}C_x$ in their catalytically stabilized state. However, at room temperature, 15 oxygen atoms are consumed per active site and do not allow calculating precisely a density of active sites. Nevertheless, a good correlation exists between the site density and the oxygen chemisorption due to the topotactic nature of the oxidation process. While retaining the approximate morphology of the crystallites, the corrosive nature of the oxygen chemisorption involves a deep replacement into the active sites of sulfur atoms with oxygen atoms [50]. Therefore, oxygen chemisorption is proportional to the edge area but does not directly measure the actual number of sites at the edge. A similar relationship can be observed with promoted MoS_2 (Fig. 11). However, family of catalysts cannot be compared to each other directly because of the corrosivity problem and, consequently, limits the interest of O_2 chemisorption techniques.

Chemisorption of hydrogen in combination with neutron scattering studies has been particularly useful in generating new insight into the nature of catalytic MoS_2. Wright et al., reports the high-temperature (300 °C) adsorption of hydrogen on MoS_2 and the study of this adsorbed hydrogen by neutron scattering techniques [64]. Their results indicate that hydrogen penetrates deeply into bulk MoS_2 under catalytic conditions due to intercalation phenomena of the type H_xMoS_2. Hydrogen would be bound to sulfur atoms in the Van der Waals gap. Furthermore, neutron scattering studies directly observed the chemisorbed hydrogen through the appearance of a single new peak at 640 cm^{-1} due to the formation of SH groups. They concluded that hydrogen is dissociatively chemisorbed on the MoS_2 surface [65]. However, neutron scattering techniques were unable to detect Mo–H hydride species resulting from a heterolytic chemisorption. This study raises several interesting questions described below but appears to establish unambiguously that intercalation of hydrogen is important under catalytic conditions.

11. Surface-sensitive techniques of characterization

Surface studies have also given further insight into the nature of the catalytic surfaces [66]. Using scanning tunneling microscopy (STM), Salmeron et al., showed that the basal plane was relatively inert by physical adsorption studies of thiophene at low pressure [67]. Spatially resolved electron energy loss spectroscopy (SREELS) has also been achieved on MoS_2 platelets showing an enhancement of surface plasmon modes at corners and edges. The surface plasmon presumably is associated with the active sites [68]. Also, the defects located on the MoS_2 edge planes have well-defined

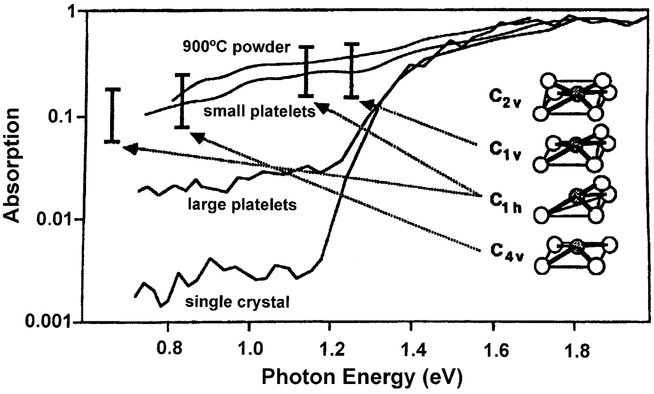

Fig. 12. Optical spectra of MoS_2 and theoretical absorption energies of defects [69].

optical characteristics and a midgap optical absorption similar to that observed for other semiconductors. The infrared optical absorption is determined by using a calorimetric technique, the photothermal deflection spectroscopy (PDS) [69]. This technique directly measures the deflection of a laser beam and is insensitive to optical scattering, and thus is ideal for powders. The defects that are catalytically active have energy levels lying between the conduction and valence bands of MoS_2 and thus absorb photons below band gap energies. As shown in Fig. 12, the different types of sulfur vacancies present optical transitions, which fall into the observed energy ranges. Sulfur vacancies appear responsible for the optical absorption measured for the edge planes.

Ledoux et al. introduced ^{59}Co metal solid NMR to this problem. By studying Co and CoMo catalysts supported on silica or carbon, they proposed that two cobalt sites exist in the CoMo structure: a distorted rapid octahedral cobalt or “trigonal prismatic” cobalt, on the edge of MoS_2, sharing four sulfur atoms with molybdenum atoms on one side, and sharing other sulfur atoms with the “tetrahedral distorted” cobalt on the other side [70,71]. These tetrahedral distorted cobalt atoms can be observed by NMR as a pure phase on carbon supports in the absence of molybdenum and are thus stable; these probably correspond to the Co sites observed by Topsøe’s group using Mössbauer spectroscopy because Crajé et al., found a similar Mössbauer doublet for both cobalt in CoMo catalysts and pure cobalt sulfide on carbon support [72]. These different structures are in full agreement with the XANES experiments performed by Ledoux [73]. In this model, the prismatic cobalt atoms bind and stabilize the unsaturated sulfur atoms at the edge of small MoS_2 crystallites; the stable distorted tetrahedral cobalt atoms terminate the construction and stabilize the octahedral cobalt atoms. The role of cobalt or nickel would be to stabilize a high dispersion MoS_2.

Topsøe and co-workers for CoMo catalysts and Prins and co-workers for NiMo catalysts performed EXAFS on the Co and Ni edges, respectively [74,75]. The two groups reached the same conclusion and localized the Co(Ni) atoms on the edge of MoS_2 crystallites in a very odd symmetry with five coordination. Each of these Co(Ni) atoms shares four sulfur atoms with molybdenum in a square plane with the fifth sulfur atom sticking out in the opposite perpendicular direction, showing that their structure would be similar to millerite.

The introduction by Ledoux et al. of ^{77}Se NMR applied to the catalysts’ study gives further insight into this difficult problem [76]. They showed that, on CoMoSe catalyst, two sorts of Se atoms clearly existed in terms of their magnetic properties: Se atoms with long relaxation time ($T_1 > 2$ s) and those with short relaxation time ($T_1 < 10$ ms) bound to highly magnetic Mo atoms. As these more magnetic atoms are located at the edge of the particles because only these atoms bear anionic vacancies, a direct correlation between short T1 selenium and dispersion was found. In addition, they directly confirmed that the addition of cobalt strongly increases the dispersion of MoS_2.

12. Amorphous zeolitic sulfides

The role of carbon as described above has led to the development of many non solid-state modes of preparation that yielded high surface area/high activity $MoS_{2-x}C_x$ and $WS_{2-x}C_x$ catalysts. These preparations involve decomposing catalyst precursors (described below) directly in a hydrocarbon feed such as DBT/tetralin under HDS conditions. Initially these preparation techniques appeared in the patent literature between 1980 and 1990. The patents appearing in this period describe various precursors that were decomposed in situ under HDS conditions yielding impressive catalytic results. A typical example can be seen in the work of Chianelli and Pecoraro [77]. Later the use of these techniques began to appear in the open literature as described below.

Typical precursors for synthesizing WS_2 are ammonium thiotungstate $(NH_4)_2WS_4$ (known as ATT) and tetraalkylammonium thiotungstates $(NR_4)_2WS_4$. For MoS_2 ammonium thiomolybdate $(NH_4)_2MoS_4$ (known as ATM) and tetraalkylammonium thiomolybdates $(NR_4)_2MoS_4$ have been used. These thiosalts were initially extensively studied by Bernard and Tridot [78] and Müller and co-workers [79]. Improvements of the synthesis techniques were achieved by McDonald et al. [80] and Pan et al. [81]. The properties of the MoS_2 or WS_2 catalysts obtained by decomposition of these thiosalts depend strongly on the processing atmosphere and heating conditions of the synthesis process as discussed below. Catalysts prepared from ammonium thiometallates precursors have been synthesized by Liang et al. [82], Wang et al. [83] and Wilkinson et al. [84]. However, the catalysts reported in these papers are low in surface area and activity. Alonso et al. reported a simple aqueous solution method producing tetraalkylammonium thiometallates as catalyst precursors [85,86]. The aqueous solution method involves a one-step substitution of NH_4^+ ions from ammonium thiomolybdate (ATM) or ammonium thiotungstate (ATT) with the respective ions of any of the salts with $(R_4N)_2Br$ formula. Precursors with several “R” groups where synthesized (R = pentyl, hexyl, heptyl and others). These authors also reported

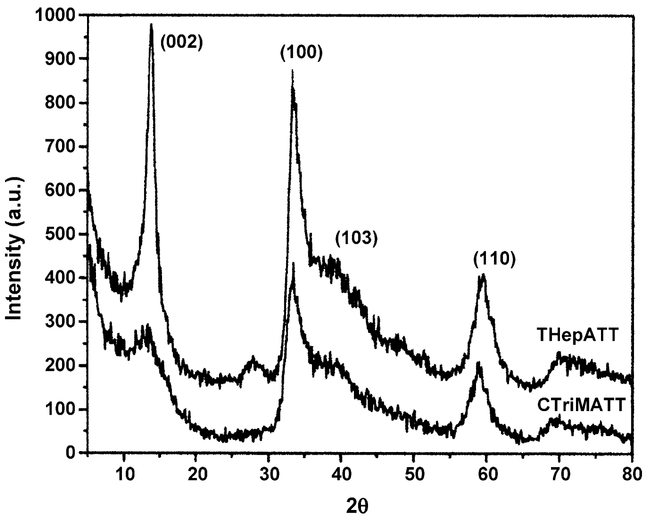

Fig. 13. XRD patterns of WS_2 catalysts formed by in situ decomposition of tetraheptylammonium thiotungstate (THepATT) and cetyltrimethylammonium thiotungstate (CTriMATT) precursors [92].

that ammonium thiometallates precursors could be decomposed in situ into high activity and high surface area MoS_2 and WS_2 catalysts [87]. A Similar approach was developed by Genuit et al. leading to highly HDS catalysts [88]. In situ decomposition of tetraalkylammonium thiomolybdate precursors led to high surface area MoS_2 catalysts presenting a narrow pore size distribution in the mesoporous domain [89]. High surface area materials were also obtained by Berntsen et al. [90]. For WS_2 catalysts, more crystalline solids were obtained through the decomposition of carbon-containing thiosalts due to a more rapid crystallization rate induced by carbon [91]. However, the use of very long alkyl chain-containing precursors like cetyltrimethylammonium thiotungstate (CTriMATT) can counterbalance this effect and produce high surface area WS_2 catalysts as analyzed by XRD as shown in Fig. 13 [92]. Another way to achieve highly active NiW catalysts was proposed by Le et al. [93] by reacting in aqueous solution $WO_2S_2{}^{2-}$ with Ni species in the presence of surfactants. The formation of mesoporous cavities of 30–40 Å inside these high surface area catalysts also led to confinement effects for (Co)/MoS_2 or WS_2 particles located inside these cavities which hinders the flat wise mode of adsorption of steric molecules like dibenzothiophene and thus limiting their aromatic hydrogenating properties [89,92,94].

The effect of the cobalt addition as promoter is very dependent of the method of activation and on the initial presence of alkyl groups in the thiosalt precursor. Alonso and co-workers [94] have reported that ex situ activated catalysts under H_2/H_2S mixture, generates a synergetic effect due to the cobalt addition only if a thiosalt precursor without carbon is used, the cobalt promoting effect seems to be hindered strongly by carbon entities formed during the ex situ decomposition. On the other hand, for in situ prepared samples, the combined effect of the cobalt promotion and the initial presence of carbon from alkylammonium molybdates in the precursor is beneficial, leading to materials presenting high surface area compared to their homologues synthesized by ex situ activation method. These results obtained by Alonso are in agreement with those found by Nava et al., who reported the beneficial role of C when using tetraalkylammonium precursors for the in situ preparation of CoMo catalysts [95]. This beneficial role of carbon could be related to a structural effect leading to the formation of a final $MoS_{2-x}C_x$ active phase with surface carbide-like moieties and/or to a morphological effect leading to more dispersed particles if carbonaceous entities interact during the initial stages of the formation of the transition metal sulfide phase [57,58,96–98]. The structural effect would result from the interaction of C with the molybdenum disulfide phase leading to a partial replacement of surface sulfur atoms located on the edges of MoS_2 slabs by carbon leading to a “sulfocarbide” surface phase.

These preparation techniques therefore yield materials with controllable and interesting surface area and pore structures [99]. These can be seen in Table 1 and in Fig. 14. The unusual “Sponge-like” appearance of these catalysts can be seen in Fig. 15. These catalysts promise to be novel and useful catalysts for many applications in the future.

Table 1

MoS_2 catalysts from	Specific surface area (m^2/g)	Total pore volume (cm^3/g)	Element analysis	
			S/Mo	C/Mo
ATM	60	0.092	1.7	0.5
TProATM	61	0.175	2.0	3.5
TPenATM	329	0.247	2.0	2.7
THexATM	255	0.429	2.0	3.7
THepATM	267	0.472	2.0	4.0
TOctATM	278	0.546	2.0	4.5

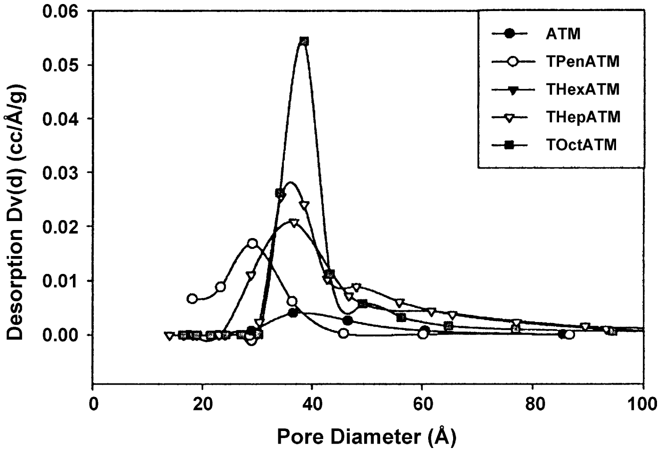

Fig. 14. Pore volume distributions for catalysts produced from Mo precursors [99].

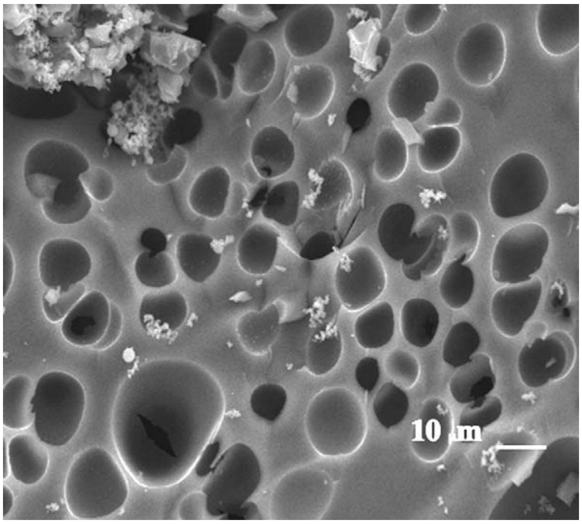

Fig. 15. “Sponge-like” SEM appearance of catalyst from Mo precursors [99].

13. Conclusions

The TMS are unique class of catalysts that are able to perform numerous hydrogenation and hydrogenolysis reactions in the presence of sulfur that is required for activity maintenance. In this report we summarize the key factors in understanding and controlling their properties. The catalytic activity and selectivity of the TMS arises from the electronic and structural properties of the sulfides themselves. Support effects are secondary, improving sulfide dispersion and reducing metal cost in commercial catalysts. Fundamental effects can only be elucidated by studying TMS catalysts in their fully sulfided and *Catalytically Stabilized States*. The study of unsupported TMS has greatly simplified the development of understanding. Furthermore, unsupported catalysts with their high volumetric activity and unusual selectivity are the “wave of the future” in many hydrotreating and chemical applications.

The TMS catalysts can generally be divided into isotropic and anisotropic sulfides from a structural point of view. However, many sulfides are highly disordered, even amorphous, and some have large nonstoichiometries that may vary under different catalytic conditions. Nevertheless, measurements of catalytic activity across the periodic table using supported and unsupported catalysts show smooth volcano plots with maxima occurring in the

Group VIII TMS for the second and third transition series. In the first transition series, the catalysts are also more active in Group VIII but significantly less active than the second and third transition series. These results establish fundamental properties of the TMS. The catalytic activity of the TMS is optimized when the maximum number of 4d and 5d electrons are present in a sulfided stable state. Theoretical studies have extended this result to understanding the importance of electronic structure in stabilizing the 4d and 5d electrons in frontier orbitals, p-bonding, metal-sulfur bond strength, and optimum heat of formation of the sulfide. Better theoretical studies are needed particularly involving bound organic intermediates.

Although many studies and models have been proposed for the structure of Co(Ni)/Mo(W) entities that share sulfurs or transfer electrons at or near the surface, the exact picture is still uncertain. This is a result of the difficulty in measuring the dispersion of the layered TMS. All models depend for their proof on this knowledge. It seems clear that pseudointercalation models and edge decoration models are beginning to describe the appropriate states but details are still lacking because of the dispersion and disorder problem inherent in the layered TMS. Lack of knowledge of the layered TMS dispersion also leads to an ambiguity in describing the electronic role of the promoter.

It is also now well established that the basal plane is inert and that reaction takes place at the edge or edge-like defects on the layered TMS. However, disorder has hindered the application of classical surface science studies to elucidating the structure and properties of these edges. It is known that maximizing the edge optimizes the activity of the catalyst and the effect of the promoter. The use of model compounds actually seems a promising way in order to progress in understanding metal sulfide properties. A prime example of this is the dependence of the selectivity of the DBT reaction on MoS_2 physical structure. The ratio of hydrogenated to desulfurized products on MoS_2 depends on the degree of stacking of the MoS_2 layers. This result gives a foretaste of future progress in this field. Future fundamental work should include:

1. Model compound studies that are calibrated with physical studies and connected to real feed studies.
2. Wider use of resonance and optical techniques that are not hindered by the presence of disorder.
3. Theoretical studies that deal with extended solids and interacting molecules.
4. Solid-state investigation of immiscible phase diagrams and the effect of surface area and carbon on them.
5. High-resolution TEM and related techniques to establish local atomic structure in disordered systems.

The role of carbon is the most neglected and potentially the most important factor. Lack of understanding regarding the role of carbon hinders the development of an accurate picture of the role of the interacting molecules. This understanding is crucial to the continued commercial success of the TMS as environmental factors surrounding the use of hydrocarbon base takes center stage.

Acknowledgements

Portions of this research were carried out at the Stanford Synchrotron Radiation Laboratory, a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences. We would like to thank Samuel Texier from the Laboratoire de Catalyse en Chimie Organique, University of Poitiers, France for performing the DBT HDS tests, Dr. Alejandra Camacho and the department of Chemical Engineering and Center for Nano and Molecular Science and Technology at the University of Texas at Austin for the HRTEM analysis. We also thank the U.S. Department of Energy Gateway Program and the Robert A. Welch Foundation for financial support.

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