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Symmetrical synergism and the role of carbon in transition metal sulfide catalytic materials

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Abstract

Considerable progress has been made in understanding the basis for the activity and the selectivity of molybdenum and tungsten based hydrotreating catalysts [R.R. Chianelli, M. Dagge, M.J. Ledoux, Adv. Catal. 40 (1994) 177]. Despite this progress, a number of fundamental questions persist: How does the catalyst function at the surface in the presence of a reacting molecule? What is the stable phase presenting the active sites to the reacting hydrocarbons? What is the function of Co and Ni promoters, and how do they operate?

In this paper, we report on recent progress in understanding these and other questions and emphasize two aspects that have been neglected in attempting to answer these questions. The first aspect is the concept of ‘symmetrical synergy’. This concept recognizes that Co_9S_8 can be promoted by Mo in an analogous manner to the well-recognized promotion of MoS_2 by Co.

The second aspect is the role of carbon in promoted and unpromoted transition metal sulfide (TMS) catalytic materials. Evidence is presented that the active surface in stabilized, catalytically active TMS catalysts is carbided. Thus, the active TMS catalysts should be viewed as sulfide supported transition metal carbides (SSTMC). On the basis of upon this understanding the active phase in the Co and Ni promoted TMS should be viewed as CoMoC and NiMoC phases supported on their respective sulfide bulk phases. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: MoS_2; $MoS_{2-x}C_x$; $RuS_{2-x}C_x$; CoMoC; NiMoC; Hydrodesulfurization

1. Introduction

Since Weisser and Landa wrote their classic book [2], ‘*Sulfide Catalysts: Their Properties and Applications*’ more than 20 years ago, considerable progress has been made in understanding the basis for the activity and selectivity of molybdenum and tungsten based hydrotreating catalysts. Despite this progress, a number of fundamental questions persist.

The first published reference to a catalyst based on molybdenum and cobalt sulfides capable of desulfurizing coal oils in the presence of hydrogen was a patent from I. G. Farben Industrie dated May 24, 1928 [3]. It was in 1933 that Pease and Keithon at the University of Princeton published the first results showing the activity of a mixture of cobalt and molybdenum oxides and sulfides for the hydrodesulfurization of a mixture of benzene and thiophene [4]. Irreproducibility of these early results marked the beginning of a long controversy regarding the nature of the active phase in these catalysts that continues today.

Following these early results, it is only through rare publications from the closed world of petroleum company’s research laboratories that it is possible to follow the evolution of the cobalt-molybdenum system applied to hydrodesulfurization (HDS) of petroleum feeds and to observe the birth of the ‘concept of syn-

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ergy'. In 1959, H. Beuther et al., 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 [5]. 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. This was the first of many published promotion curves, showing the activity of NiMo/Al_2O_3 catalysts as a function of the value of the atomic ratio Ni/Mo or Co/Mo.

In the 1970's, probably linked to the first oil crisis, many publications appeared providing the first models for the promotion effect. The first research group to propose a description of the structure of CoMo catalysts was led by Schuit and Gates [6]. This group introduced the so called 'monolayer' model involving a special role for the alumina support in the promotion of Mo or W by Co or Ni. We now know that the promotion effect occurs without the alumina support thereby nullifying the monolayer model.

J.T. Richardson first proposed the existence of a special Co/Mo entity [7]. Voorhoeve and Stuiver [8,9], and Farragher and Cossee [10] from Shell proposed a new model derived from the structure of intercalated sulfides. In these types of compounds, the first row transition metal sulfides (Fe, Co, Ni) can penetrate the van der Waals layers of the layered WS_2 to occupy octahedral holes. Complete filling of the layer only occurs at elevated temperatures (>700°C), well above temperature typical of catalytic preparation (<400°C). At temperatures of catalytic preparation the first row metal only penetrates near the edge of the crystallite.

They called this model the 'pseudointercalation' model to incorporate the idea that promotion occurred via intercalation of the Ni promoter in to the van der Waals gap near the edges of WS_2 catalysts. Voorhoeve et al. did not study HDS directly but rather the hydrogenation of benzene and cyclohexene in the presence of CS_2 on WS_2. It was found that Ni strongly promoted the hydrogenation of benzene but only weakly the hydrogenation of cyclohexene. From electron spin resonance (ESR) and kinetic evidence, they concluded that the active sites for benzene hydrogenation sites were unsaturated W^{+3} and that the active sites for cyclohexene hydrogenation were unsaturated W^{+4} sites. The later they called 'edge sites' (doubly unsaturated binding cyclohexene) and the former 'corner sites' (triply unsaturated binding benzene). They also concluded on the basis of ESR evidence that the W^{+3} sites were increased by the pseudointercalation of Ni through charge transfer from Ni to W. This was the first and still the most geometrically specific model for promotion.

Delmon and co-workers found that the unsupported catalysts they prepared had the phases MoS_2 and Co_9S_8 present acting together by being in close contact, 'synergy by contact'. This description defines well the promotion phenomenon from the macroscopic point of view by identifying the important bulk phases present and by noting the absence of a ternary promoted phase. However, this idea does not specifically give insight into the mechanism of how the phases interact to cause the promotion effect.

Topsøe and his group presented the first physical proof of a specific Co environment. The introduction of very small amounts of ^{57}Co into bulk MoS_2 allowed this group to observe a specific emission Mössbauer spectroscopy (EMS) signal from a new Co site different from the usual signal characteristic of Co_9S_8 called the 'CoMoS' phase [11]. In addition, using XAFS analysis, this group showed that the local atomic structure of MoS_2 was preserved in the sulfided catalyst [12]. High resolution transmission electron microscopy (HRTEM) on MoS_2 crystallites, containing a small amount of Co, provides evidence that the Co atoms were located on the edges of the MoS_2 platelets, leading to a model very close to the pseudo-intercalation model with similar limitations [13]. The interaction of the Co or Ni with edges is now well established [14].

However, most of the measurements and thus the models described were made on fresh catalysts. Fundamental properties of need to be established on catalysts that are stabilized in a catalytic environment. This is necessary to show conclusively that the CoMoS phase measured by Mössbauer is directly related to the promotion site and not a precursor that leads to the active site [15]. Because of this, the origin of the promoted state is still in question. In this paper, we report on recent progress in understanding the origin of the promotion effect and emphasize two aspects that have been neglected in attempting to understand promotion.

The first aspect is the concept of 'symmetrical synergy'. It is now well known that a Co promoted state can be established at the edges of MoS_2 (Co promoted

MoS_2). What is less well recognized and less studied is that a promoted state can also be established on the surface of Co_9S_8 by addition of small amounts of Mo (Mo promoted Co_9S_8). This is called 'symmetrical synergy' and all theoretical promoted catalyst systems (Co_9S_8/MoS_2 synergy by contact, Co promoted MoS_2 edges, etc.) are located by referring to a binary immiscible phase diagram appropriate for the system.

The second aspect is the role of carbon in promoted and unpromoted transition metal sulfide (TMS) catalytic materials. Evidence is presented that the active surface in stabilized, catalytically active TMS is carbided. Catalysts based on Ru or Mo take the form $RuS_{2-x}C_x$ and $MoS_{2-x}C_x$ with the value of x dependent on the surface area of the catalyst. Thus, the active TMS catalysts should be viewed as sulfide supported transition metal carbides (SSTMC). It has been the lack of recognition of this fact that has led to much of the confusion regarding the specifics of problem like the 'promotion' problem in TMS catalytic materials. Based upon this understanding the active phase in the Co and Ni promoted TMS should be viewed as CoMoC and NiMoC phases supported on their respective sulfide bulk phases.

2. Experimental

A common synthesis of group VIB sulfides exists for the preparation of thiosalts such as $(NH_4)_2MoS_4$ and $(NH_4)_2WS_4$. The salts were obtained by bubbling hydrogen sulfide in a solution of ammonium molybdate or tungstate in ammonium hydroxide at room temperature. Co or Ni catalysts were prepared either by precipitating the thiomolybdate salt with Co or Ni acetate or by impregnating previously prepared MoS_2 or WS_2 catalysts with Co or Ni acetate and then pretreating as described below. Similarly, alkylammonium Mo and W thiosalts were synthesized and converted to sulfides with high surface areas. The preparation of RuS_2 from $(NH_4)_2RuCl_6$ has been previously reported [16].

Precursors were either decomposed at 400°C in H_2/H_2S (15%) or decomposed directly in the catalytic reactor as previously described [17]. The former catalysts are termed 'ex-situ' catalysts and the latter are termed 'in-situ' catalysts. Catalyst composition with respect to sulfur and carbon were obtained by combustion in oxygen at 1600°C followed by analysis of the resulting SO_2 and CO_2 by infrared spectroscopy and thermal conductivity measurement techniques. X-ray diffraction and BET surface area analyses were performed using standard methods [18].

Catalytic measurements were performed in a Carberry type reactor with flowing H_2 (35 atm) continuously flushing the reactor. The hydrodesulfurization (HDS) of dibenzothiophene (DBT) was used as probe of the catalytic effectiveness. Catalysts were run at 350°C for approximately 8 h with samples for GC analysis being taken approximately every hour. The procedure has been described in detail elsewhere [18]. Characterization of activity tested catalysts by HRTEM and X-ray diffraction has been previously reported [19].

3. The stable TMS catalytic phases

Sulfide catalysts operate at high temperatures (typically 300–400°C) and under reducing conditions. In situ characterization of TMS materials is generally difficult and limited because of the conditions under which they are used (high-temperature, high-pressure, and liquid-phase reactions). Therefore, it is necessary to characterize the catalyst that has stabilized under catalytic conditions as well as the fresh catalyst. The phases that are stable under catalytic conditions are the 'stable states', and it is from these that information regarding the relation between the electronic/geometric structure and the catalytic activity/selectivity can be obtained. Many papers on the TMS ignore this point, leading to confusion regarding the origins of fundamental properties of the active catalyst.

After HDS at 400°C and 35 atm H_2, the catalytically stable phases, as identified by X-ray diffraction and elemental analysis, of the binary TMS are: TiS_2, VS_x, Cr_2S_3, MnS, FeS_{1-x}, Co_9S_8, Ni_2S_3, NbS_2, MoS_2, RuS_2, TcS_2, Rh_2S_3, PdS_x TaS_2, WS_2 ReS_2, OsS_x IrS_x, PtS [20]. The stable phases described are identified as unsupported catalysts because of the difficulty of making this identification on supported phases. However, the catalytic results on supported catalysts are generally the same [1].

When two or more metals are 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 ($Co_9S_8 + MoS_2$). The X-ray diffraction pattern of the bulk material is characteristic of a mixture of the two corresponding binary phases with no evidence of a mixed phase.

When both components belong to the isotropic class, solid solutions, crystallizing in a cubic pyrite structure, may be obtained as observed for $Co_{1-x}Ru_xS_2$, $Co_{1-x}Rh_xS_2$, and $Rh_{1-x}Ru_xS_2$ [21]. However, under HDS conditions, these ternary compounds also separate into their binary component phases (for example, Co_9S_8 and RuS_2). These are the immiscible, phase separated stable states of common sulfide catalysts with more than one component.

The concept of the stable catalytic phases and of immiscible, phase separated stable states is one of the most fundamental concepts in sulfide catalytic materials. As stated above ternary phases may be prepared at higher temperatures usually above about 900°C. Often they are too crystalline with low surface areas for useful catalytic measurements. Preparation under conditions suitable to produce catalysts of useful surface areas almost always results in phase separated systems.

It must also be emphasized that the stable phases refer to the bulk crystalline solids as determined by X-ray diffraction after catalytic operation. This does not refer to the stable surface states that become more important as the catalyst particles become smaller. It is the identification of the catalytically stable surface phases which becomes the next important frontier in understanding sulfide catalytic materials.

4. Symmetrical synergy

In a little known paper Phillips and Fote reported that the promoted systems should be viewed as mixtures of two immiscible phases (Co_9S_8 and MoS_2) that interact by forming surface phases or surface complexes [22]. This is illustrated in Fig. 1 by a hypothetical phase diagram of Co/Mo/S catalytic materials existing below about 550°C. Below this temperature no ternary phases have been prepared in the Co/Mo/S system. All current catalyst preparation techniques that produce stable sulfide catalysts with sufficient surface area for catalytic activity produce materials in the phase region indicated.

The left-hand portion of the phase diagram is the region most commonly accessed by conventional catalyst preparations. In this region as Co is added to the system, the promotion effect increases until a maximum is reached. This maximum occurs typically between Co/Mo ratios of 0.10–0.30. 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 available. Thus, higher edge area catalysts will require more Co to reach the activity maximum, which will be higher and further toward the Co rich side of the diagram. Such is the case for supported catalysts. Lower edge area catalysts will require a lower amount of Co to reach a lower maximum. We can equate the Co/Mo/S surface phase with the CoMoS phase or with the pseudo-intercalation phase described above.

As more Co is added, Co_9S_8 will begin to phase separate, and we enter a region where both phases coexist. In the idealized model presented, phase separation of Co_9S_8 occurs at the promotion maximum. This region can be described as the 'synergy by contact' region dominated by the two immiscible phases.

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. That Co_9S_8 can be promoted just like MoS_2 has been overlooked in the literature. This effect can be seen from the work of the Delmon group 10. The activity of the promotion peak in the right-hand region is usually lower because it is difficult to prepare Co_9S_8 of high surface area. The surface dependence of the MoS_2/Co_9S_8 interaction has not yet been determined.

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. This can be quite complicated because each phase affects nucleation and surface area of the other phase during preparation. We term this behavior 'symmetrical synergy', and similar arguments apply to the other promoted systems.

The Co/Mo/S surface-phase structures have been described elsewhere [23]. But the Mo/Co/S surface phase structure has not been described previously. The existence of this 'symmetry' in the promotion behavior must be taken into consideration in any model and strongly suggests an electronic origin of promotion since any structural model proposed cannot be too

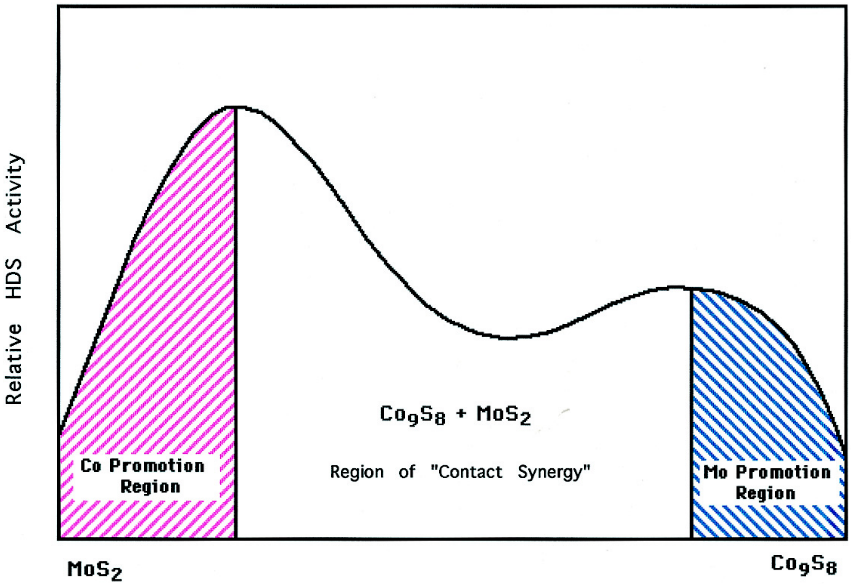

Fig. 1. Hypothetical phase diagram demonstrating ‘symmetrical synergism.’

specific to one of the participating bulk structures for example Co promoted MoS_2. Thus, the CoMoS phase or the pseudo-intercalate phase can only be part of the story and fundamental conclusions regarding promotion are incomplete.

At this writing the origins of symmetrical synergy need further study. However, it appears that the origin of this phenomenon rests in the immiscibility of the phases Co_9S_8 (Ni_3S_2) and MoS_2 (WS_2) in the region in which catalysts are prepared for commercial use. Because of the immiscibility, surface phases exist in which the bulk crystal phase is surface enriched with the other metal present and the magnitude of the enrichment will depend on the surface area of the crystalline phase present. The existence of the surface phase permits the charge transfer responsible for promotion to occur. Thus charge transfer from Co (Ni) to Mo (W) can occur regardless of the bulk crystalline phase present. That Co/Mo is the dominant commercial catalyst is only a result of the difficulty of dispersing Co effectively.

5. Role of carbon

Recently, the entire 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 [24]. They found that a RuS_2 catalyst that had been stabilized in a catalytic environment had a composition, $RuS_{2-x}C_x$. An example of a catalytic stabilized sulfide supported carbide is shown schematically in Fig. 2. The sulfur rich RuS_{2+x} precursor phase is converted into the $RuS_{2-x}C_x$ stable catalytic phase during the desulfurization of dibenzothiophene in a decalin carrier at 350°C and 35 atm of H_2. The stable catalytic phase is obtained after 8 h under catalytic conditions in the modified Carberry reactor. The catalyst was also shown to be stable for more than 1000 h in a flow reactor with catalytic conversion of the dibenzothiophene constant at approximately 90% conversion during the run under the same temperature and pressure conditions as those in the Carberry reactor.

It has been established that as the MoS_2 edge area increases the activity of the catalyst increases [1]. However, it can also be seen from Fig. 3 that as the edge area and the activity increases the carbon content in the catalyst also increases. A careful preparation of MoS_2 catalysts from the decomposition of ammonium thiomolybdate at increasing temperatures in an atmo-

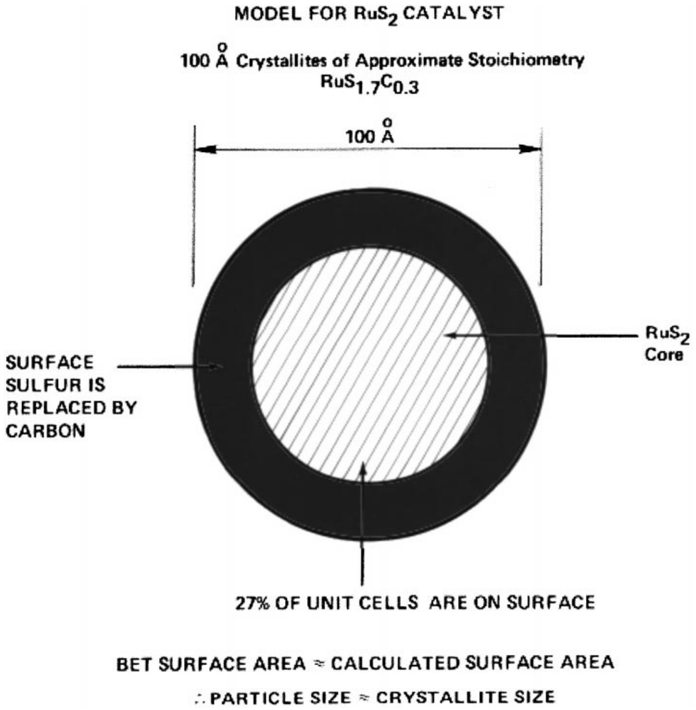

Fig. 2. Schematic representation of a catalytically stabilized Ru sulfide catalytic material.

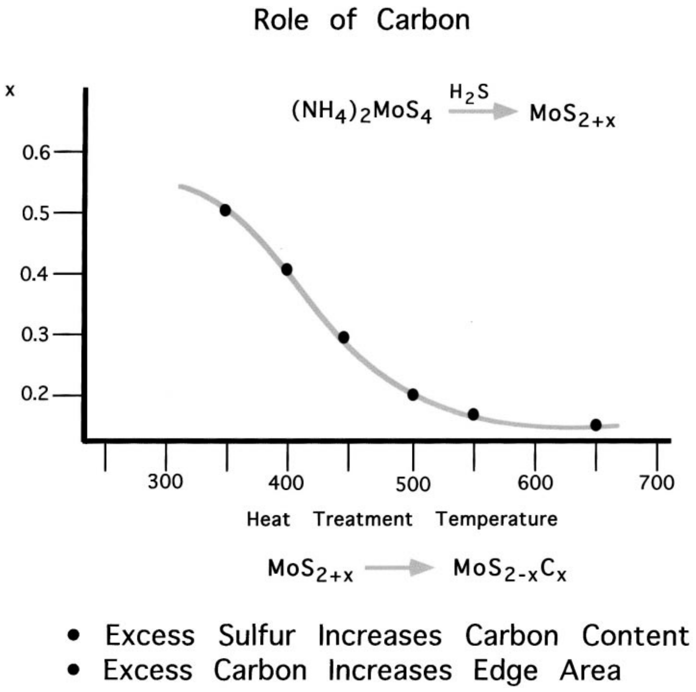

Fig. 3. Activity vs. excess sulfur in MoS_2 precursor and vs. x in $MoS_{2-x}C_x$.

sphere of H_2/H_2S, produces catalyst precursors of the form MoS_{2+x} with x representing excess sulfur in the catalyst presumably at the edges. The excess sulfur in the catalysts shown in Fig. 3 varied from 0.5 down to 0.0 as the catalyst approaches stoichiometric MoS_2 with vanishing edge area. Upon exposing these catalysts to the catalytic environment the excess sulfur as is replaced by carbon as is additional sulfur to give the stoichiometry $MoS_{2-x}C_x$. This is the stabilized catalyst composition. This catalyst can be promoted as described below.

The same effect of carbon can be seen in MoS_2 based catalysts prepared from amine thiomolybdate catalysts. The amine thiomolybdate decomposition results in MoS_2 catalysts with surface areas exceeding several hundred square meters per gram. These materials can also be supported [25]. The HDS activity increases correspondingly and unpromoted catalysts have activities approaching those of promoted systems. In addition, the catalysts prepared by this method have not only very high surface areas but also unusual pore volume distributions as can be seen from Figs. 4(a, b). The catalysts made from the ethylene diamine precursor have a surface area of $152\,m^2/g$ and a pore volume distribution with a bi-modal maximum near 100 Å. Similarly, the catalyst prepared from the tetrabutylammonium precursor has a surface area of $243\,m^2/g$ and a pore volume distribution with a maximum near 40 Å. This later catalyst has nearly the surface area per gram of a commercial catalyst. These catalysts may be thought of as ‘amorphous zeolitic sulfide catalysts’ because of their high surface areas and narrow pore volume distributions. They also contain substantial amounts of carbon after exposure to catalytic environment. Catalysts prepared using the amine thiomolybdate method prepared in-situ and containing carbon, could then be conventionally promoted with Co or Ni producing volumetric activities 2.5–3.5 higher than commercial alumina supported catalysts [26]. They are potentially very useful because of their high volumetric activity if cost considerations can be overcome.

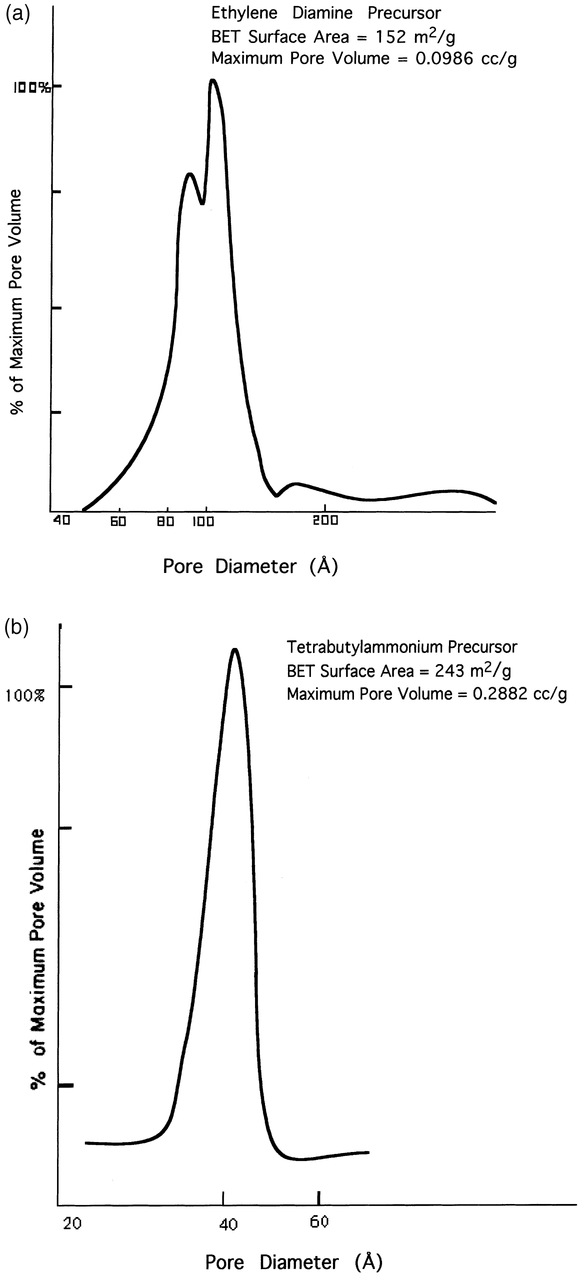

Fig. 4. Pore volume distributions of amine thiomolybdate precursors, (a) ethylene diamine precursor, (b) tetrabutylammonium thiomolybdate precursor.

Finally, the affinity of MoS_2 based catalysts for carbon can be seen in the electron microscope. When a freshly prepared unsupported catalyst powder is placed on a carbon grid, the electron beam induces a reaction with the carbon grid as seen in Fig. 5. The catalyst powder is seen to consolidate and leaves a hole in the carbon grid. Presumably the electron beam heats the catalyst in vacuum, removing labile sulfur near the edge planes. The vacancies created react with carbon forming the surface carbide. It can be seen

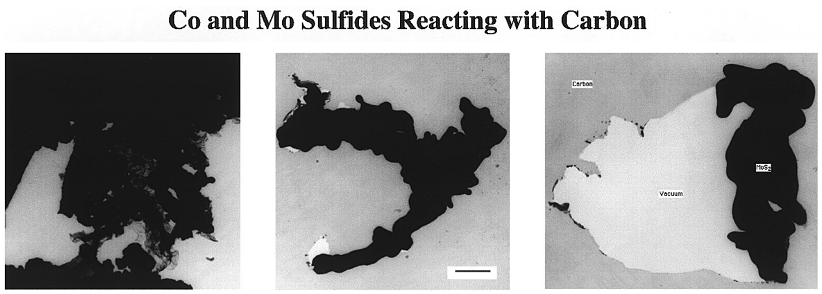

Fig. 5. Reaction of a freshly prepared unsupported Co/MoS_2 catalyst in the transmission electron microscope. The marker in the figure is approximately 20 nm.

from the micrograph that the catalyst particles appear to melt. However, the MoS_2 catalyst materials do not melt congruently. This result clearly demonstrates the reactivity of MoS_{2+x} activated catalyst precursors to react with carbon to form the stable sulfide supported catalysts. This reactivity was never seen when catalysts which were exposed to reactor conditions were observed in the microscope because they had already reacted with carbon in the reactor. In fact, it is virtually impossible to place a freshly prepared MoS_2 catalyst in any high vacuum apparatus without the catalyst reacting with carbon which is ubiquitous under these conditions. Previously reported scanning Auger spectra of MoS_2 catalytic materials clearly show the presence of carbon on both promoted and unpromoted systems 14.

6. Discussion and conclusions

This article highlights two fundamental aspects of catalysis by transition metal sulfide materials which need further study to complete the picture of how activity and selectivity arise in these catalysts. The first, symmetrical synergy has been largely ignored in developing a theory of catalyst promotion. Any theory of promotion must recognize this symmetry in the explanation. A theory such as the CoMoS phase does not recognize this symmetry and must be considered too specific by only describing the Mo rich end of the Co/Mo phase diagram. Synergy by contact recognizes the symmetry but describes only the macroscopic contact of the important phases and does not describe the microscopic details of the interaction. Enrichment of the surface of the MoS_2 or the Co_9S_8 with the other metal either Co or Mo is a better general description of the phenomenon. The charge transfer from the promoter to the Mo can operate in either case averaging the metal sulfur bonds at the surface as previously described [1].

The second aspect is the composition of the stabilized catalytic state of the transition metal sulfide catalyst. This aspect emphasizes the necessity of studying the stabilized catalyst and not a catalyst precursor. It appears that much of the confusion in the literature comes from this point. It appears that the CoMoS phase is a precursor whose presence correlates well to activity but which may not be present in an operating catalyst. This can be understood by referring to the stabilized catalyst as a Co/MoS_2 supported surface carbide or ‘CoMoC’ phase as described below.

When a RuS_2 or MoS_2 catalyst precursor is produced in an H_2/H_2S environment it becomes sulfur rich. In the case of RuS_2 the entire surface is enriched with sulfur at the surface termination. In the case of MoS_2 the enrichment only occurs at the edge planes. Upon contact with a hydrocarbon environment under catalytic conditions this excess sulfur is removed along with additional sulfur and is replaced by carbon in carbide form. This sulfide supported carbide is now the stabilized active catalyst. This is indicated schematically in Fig. 6. Similarly, a cobalt/molybdenum carbide phase supported on cobalt and molybdenum sulfide phases is also formed. This is named the CoMoC phase and is indicated schematically in Fig. 7. Finally, it is our belief that these phases will be found at the surface of all active sulfide catalysts which operate in

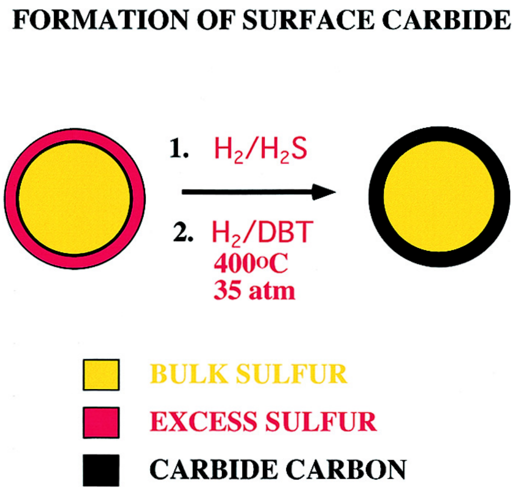

Fig. 6. Schematic representation of formation and stabilization of sulfide supported Mo carbide catalyst.

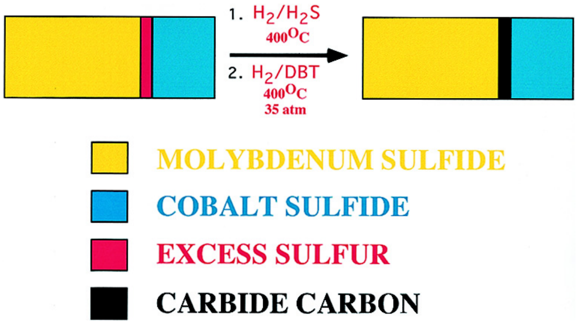

Fig. 7. Schematic representation of formation and stabilization of sulfide supported Co/Mo carbide (CoMoC) catalyst.

a sulfided environment. Thus, recent reports of transition metal carbides and nitrides hydrodesulfurization catalysts will prove to be carbide or nitride supported phases as described in this report [27].

In the near future we will present further evidence for the existence of sulfide supported CoMoC and NiMoC phases. However, by combining the concepts of symmetric synergy and sulfide supported carbide phases as the catalytically relevant phases, much of the confusion regarding the nature of the activity and selectivity in catalysis by transition metal sulfides is removed.

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References

[1] R.R. Chianelli, M. Daage, M.J. Ledoux, Fundamental studies of transition metal sulfide catalytic materials, Adv. Catal. 40 (1994) 177.
[2] O. Weisser, S. Landa, Sulfide Catalysts. Their Properties and Applications, Pergamon, New York, 1973.
[3] I.G. Farben, Br. Patent 315439 (1928).
[4] R.N. Pease, W.B. Keithon Jr., Ind. Eng. Chem. 25 (1933) 1012.
[5] H. Beuther, R.A. Flinn, J.B. McKinley, Ind. Eng. Chem. 51 (1959) 1349.
[6] G.C.A. Schuit, B.C. Gates, AIChE J. 19 (1973) 417.
[7] J.T. Richardson, Ind. Eng. Chem. Fundam. 3 (1964) 154.
[8] R.J.H. Voorhoeve, J.C.M. Stuiver, J. Catal. 23 (1971) 228, 236.
[9] R.J.H. Voorhoeve, J. Catal. 23 (1971) 243.
[10] A.L. Farragher, P. Cossee, in: J.W. Hightower (Ed.), Proc. 5th Int. Congr. on Catalysis, Palm Beach, 1972, Amsterdam, North-Holland, 1973, p. 1301.
[11] H. Topsøe, B.S. Clausen, R. Candia, C. Wivel, S. Morup, J. Catal. 68 (1981) 433.
[12] R. Candia, B.S. Clausen, J. Bartholdy, N.Y. Topsøe, B. Langeler, H. Topsøe, in: Proc. 8th Int. Congr. on Catalysis, vol. 2, Berlin, 1984, Dechema, Frankfurt-an-Main, 1984, p. 375.
[13] O. Sorensen, B.S. Clausen, R. Candia, H. Topsøe, Appl. Catal. 13 (1985) 363.
[14] R.R. Chianelli, A.F. Ruppert, S.K. Behal, B.H. Kear, A. Wold, R. Kershaw, J. Catal. 92 (1985) 56–63.
[15] R. Candia, B.S. Clausen, H. Topsøe, J. Catal. 77 (1982)564.
[16] J.D. Passaretti, R.R. Chianelli, A. Wold, K. Dwight, J. Covino, J. Solid State Chem. 64 (1986) 365–371.
[17] T.A. Pecoraro, R.R. Chianelli, US Patent, 4,508,847 (1985).

[18] S.J. Tauster, T.A. Pecoraro, R.R. Chianelli, J. Catal. 63 (1980) 515.
[19] R.R. Chianelli, E.B. Prestridge, T.A. Pecoraro, J.P. deNeufville, Science 203 (1979) 1105.
[20] T.A. Pecoraro, R.R. Chianelli, J. Catal. 67 (1981) 430.
[21] J.D. Passaretti, R.R. Chianelli, A. Wold, K. Dwight, J. Covino, J. Solid State Chem. 64 (1986) 365.
[22] R.W. Phillips, A.A. Fote, J. Catal. 41 (1976) 168.
[23] R. Prins, V.J.H. De Beer, G. Somorjai, Catal. Rev. Sci. Eng. 31 (1989) 1.
[24] R.R. Chianelli, T.A. Pecoraro, US Patent, 4288422 (1981).
[25] R.L. Seiver, R.R. Chianelli, US Patent, 4,430,443 (1984).
[26] R.R. Chianelli, T.A. Pecoraro, US Patent, 4,528,089 (1985).
[27] R. Ochoa, X.X. Bi, A.M. Rao, P.C. Eklund, in: S.T. Oyama (Ed.), The Chemistry of Transition Metal Carbides and Nitrides, Blackie Academic and Professional, London, 1996, pp. 489–510.