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A unified theory of periodic and promotion effects in transition metal sulphide hydrodesulphurization catalysts

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The dependence of the hydrodesulphurization (HDS) activity of monometallic transition metal sulphides for thiophenic species is an electronic effect: the quality of the active site determines the rate of the rate-limiting step in the HDS process. It is shown that the strength of the interaction between the metal d electrons and sulphur 3p electrons, *I*, correlates well with catalytic activity. *I* depends strongly on the oxidation state of the transition metal. The synergistic promotion effect in Co–Mo–S and Ni–Mo–S is explained in terms of electron transfer from Co(Ni) to Mo. This corresponds to the removal of σ metal–sulphur antibonding electrons from Co(Ni), greatly increasing their intrinsic catalytic activity. It follows that Co and Ni are the active elements in these mixed sulphides.

Keywords: hydrodesulphurization; transition metal sulphides

1. Introduction

The purpose of this Letter is threefold: (1) to review two competing theories for the dependence of hydrodesulphurization (HDS) activity of monometallic transition metal sulphides (TMS) on the position of the transition metal in the periodic table, (2) to present a new theory based on the strength of the interaction between metal d and sulphur 3p electrons, and (3) to demonstrate how this theory explains promotion effects in mixed sulphides, particularly Co–Mo–S and Ni–Mo–S.

2. The periodic variation of HDS activity in monometallic sulphides: a critical review of two competing theories

A systematic investigation of the dependence of HDS activity of monometallic TMS on the position of the transition metal in the periodic table was first carried out by Pecoraro and Chianelli [1]. Previously, it had been observed that HDS activities do not, in general, correlate to BET surface area [2]. Normalised on a per mole metal basis, it is seen that the first row TMS are generally less active than second and third row TMS, fig. 1. A distinct minimum occurs for MnS. Maxima in HDS activity occur for Ru and Os for second and third row TMS respectively. Similar trends were later observed by Vissers et al. for carbon-supported TMS [3], and by Ledoux et al., also for carbon-supported TMS [4].

It is generally agreed that the catalytic activity takes place at anion vacancies on the surface/edges of the catalyst, where exposed metal atoms can interact with the thiophenic species [5]. It follows that the *number* of vacancies directly relates to the activity of the catalyst. The rate of the rate-limiting step in the overall HDS process may, however, be determined by the *quality* of the active site. As yet there is no general agreement whether the activity differences between different TMS are due to differences in the number of active sites, or alternatively due to the quality of such sites (or both).

When the HDS activity is plotted against the heat of formation of the TMS (on a per mole metal basis), ΔH_f, a Balandin or volcano curve appears [6], typical for many catalytic processes. According to Sabatier's principle [7], the metal–sulphur

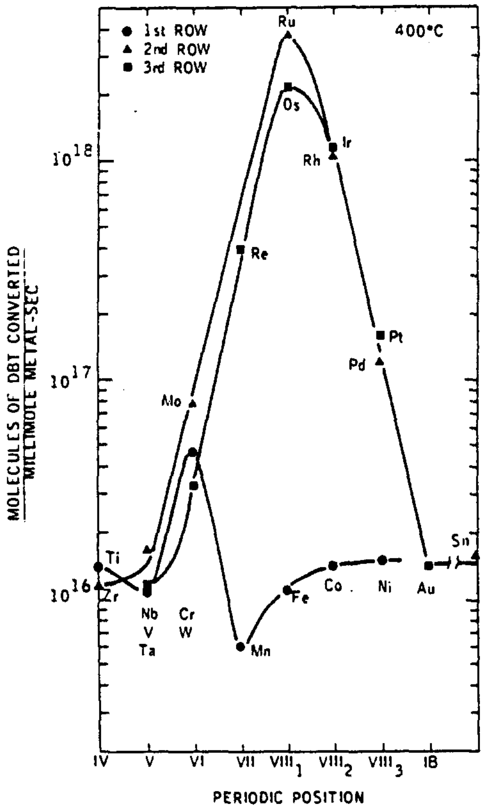

Fig. 1. The activity of binary TMS for DBT desulphurization (ref. [1]).

bond should be neither too weak nor too strong for maximum catalytic activity. Effective catalysts must easily form and regenerate surface vacancies, yet have the ability to adsorb the thiophenic species onto the vacancy. However, $\Delta H_{f,\mathrm{MnS}}$ falls in the optimum range, but the activity of MnS is extremely low. V_2S_3 also poses a problem. Scattered-wave Xα calculations [8] on octahedral MS_6^{n-} clusters (where M denotes the transition metal atom and *n* is the total charge of the cluster if all the elements are in the formal oxidation state representative of the TMS) led Harris and Chianelli [9,10] to propose that it is the ability of the metal atom to bond covalently to sulphur which determines the activity of the catalyst. The low activity of MnS and other first row TMS is explained by the ionicity of the metal–sulphur bond, which is not adequately reflected in the value of ΔH_f. A theoretical activity parameter was constructed, based on the covalency of the metal–sulphur bond and the number of electrons in the highest occupied molecular orbital (HOMO), which correlated well with the experimental HDS activities. One is thus led to believe that the quality of the active site governs the catalytic activity. Harris and Chianelli pointed out that this is not inconsistent with a one-point end-on mechanism whereby the thiophene molecule binds into a surface vacancy through its sulphur atom. We emphasize that it does not follow that adsorption must be the rate-limiting step in the overall HDS process (experiments indicate that it is not); the observed correlation merely indicates that the rate-limiting step must involve metal–sulphur bonding. We will return to the analysis of Harris and Chianelli shortly.

Topsøe and co-workers [11,12] point out that a volcano relationship is not observed if the HDS activity is plotted against the heat of formation of the TMS on a per mole *sulphur* basis. Rather, a monotonic decline in activity is observed with increasing ΔH_f, but the scatter in the data points is very large. Topsøe argues that it is easy to create sulphur surface vacancies if ΔH_f is small and concludes that most of the variations in activity between various TMS can be explained through variations in the number of surface vacancies, although the catalytic activity may also, to a limited extent, depend on the rate of the rate-limiting step. Sulphur binding energies are obtained from augmented-spherical-wave calculations on 4d TMS having the CsCl structure [13]. Values for 3d and 5d TMS are based on an approximate model. This approach has, in our opinion, several severe limitations, e.g.: (1) None of the TMS have the CsCl structure, in which each metal atom has eight sulphur nearest neighbours. Most TMS have octahedral (e.g. RuS_2) or trigonal prismatic (e.g. MoS_2) symmetry, in which there are six nearest neighbour sulphur atoms. Exceptions are PdS and PtS where the metal atom is in a square planar environment (four nearest neighbours). The important aspect of this discussion is not the detailed structure of all the TMS, but the fact that the stoichiometry, structure and symmetry of the TMS affect the oxidation state of the metal atom. This is not taken into account in the CsCl-structure calculations, nor in the approximate model based on those calculations. (2) Many catalysts, e.g. MoS_2 and WS_2, form sheets, stacked on top of each other with weak Van der Waals bonding between them. The catalytic activity takes place at the edges of these sheets, where metal atoms are exposed, not on the basal planes, where they are not. The Topsøe values for the sulphur binding energies apply to the bulk catalyst, i.e. to the basal planes!

To settle the issue whether the periodic variation in activity results from different numbers of active sites or alternatively from the difference in the quality of those sites one needs the *intrinsic* activity for a number of different catalysts. Oxygen titration experiments provide information on the number of sites, the total catalytic activity can be measured in the usual way. Thus, Carvill and Thompson [14] report that the intrinsic activity of MoS_2 is roughly 40–50 times higher than for FeS and CoS, and 3–4 times lower than for CoMoS, etc. Arnoldy et al. [15] show that Re is 2–20 times more active than Mo. This unambiguously demonstrates that the variation in activities is an electronic effect, explained by the quality of the active sites. This is not to say that the number of sites is not important for the overall activity. Obviously, more sites will mean a higher activity, regardless of the rate of the rate-limiting step. Small, finely dispersed particles are likely to have relatively many surface vacancies: the analysis of Kasztelan [16] remains valid even if the periodic variation is an electronic effect.

We return to the analysis of Harris and Chianelli. Prins et al. [17] have noted that it remains unclear why the product of the particular electronic parameters identified (number of electrons in the HOMO of an octahedral MS_6^{n-} cluster, n, and the covalency of the metal–sulphur bond) would correlate so well to HDS activity. Furthermore, the analysis contains several unsatisfying features: (1) Spinned calculations were carried out for the first row TMS, but not for second and third row TMS. As a result, the maximum value of n, hence also of the activity, is twice as low for first row TMS as it is for second and third row TMS. While the effect of spin is without question significant for first row TMS, n as such does not have any physical/chemical meaning. We will show that one should instead focus on the absolute and relative numbers of π and σ metal d–sulphur 3p antibonding electrons. (2) The HOMO is a π metal d–sulphur 3p antibonding orbital for all the second and third row TMS, except for Pd and Pt, where it is a σ antibonding orbital. The occupation of this orbital is forced by the total d-electron count. Again, n does not have any physical/chemical meaning, for it does not take into account the character of the orbital to which it applies. While we agree with Harris and Chianelli that the dependence of activity on the position of the metal atom in the periodic table is an electronic effect, and that it is the ability of the metal atom to bond covalently to sulphur which determines the activity of the catalyst, the above issues must be addressed. In the following we will provide a chemical basis/understanding for the observed correlation between theory and experiment. Our analysis fundamentally differs from that of Harris and Chianelli in that it takes into account the absolute and relative numbers of σ and π electrons and the character of those orbitals. This leads to a completely different interpretation of the promotion effect in mixed TMS.

3. An alternative explanation of the periodic variation of HDS activities based on the metal d–sulphur 3p interaction strength

Recently, we reported calculations on thiophene–catalyst complexes which indicate that interactions between the sulphur atom in thiophene and the sulphur atoms in the catalyst dominate the adsorption process [18–20]. Metal–sulphur interactions are weak at this stage in the HDS process. In contrast, dihydrothiophene–catalyst complexes display significant interactions between the sulphur "lone pairs" in the thiophene molecule and the metal d orbitals. This suggests that adsorption is not the rate-limiting step in the overall HDS process and that hydrogenation must take place before, or in conjunction with, desulphurization. Furthermore, the strength of the metal d–sulphur 3p interaction is a function of the transition metal: weak for Zr but strong for Ru. This suggests that the rate of the rate-limiting step is determined by the quality of the site and prompts a new look at the octahedral TMS clusters examined by Harris and Chianelli. A schematic representation of a molecular orbital diagram is given in fig. 2 for the non-magnetic second and third row TMS, starting from metal d–sulphur 3p σ and π bonding orbitals. Going up in energy, one first finds a manifold of states dominated by sulphur 3p contributions (with some metal s character mixed in). A non-bonding sul-

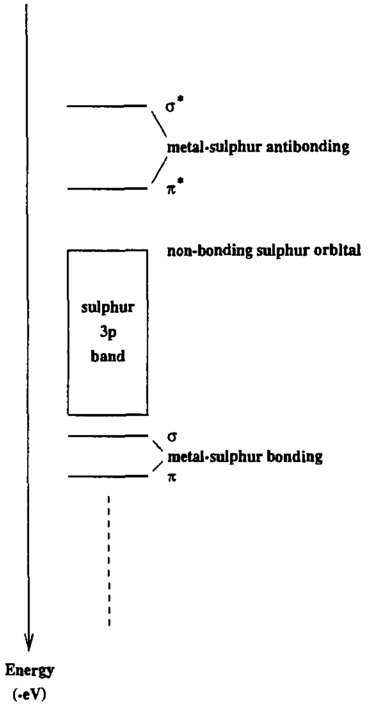

Fig. 2. A schematic representation of the electronic structure of an octahedral TMS MS_6^{n-} cluster. See text for details.

phur level delineates this sulphur "band" for all the TMS clusters and has been used as a reference state in the calculations reported here. Next there are π and σ metal d–sulphur 3p antibonding levels, in that order. Different transition metals will have different numbers of d-electrons. This, in conjunction with the oxidation state of the transition metal, *directly* affects the occupation number of the antibonding orbitals. However, many aspects of the electronic structure are *indirectly* affected. E.g., the metal contribution to the bonding orbitals (generally increasing when going from left to right in the periodic table), the sulphur contribution to the antibonding orbitals (also increasing from left to right), the orbital energies of the antibonding levels (decreasing), the energies of the bonding levels (decreasing), the width of the sulphur band (increasing), all depend on the position of the transition metal in the periodic table. Our goal is to define a parameter, I, which takes into account all these manifestations of the character of the transition metal *and* accurately represents the strength of the metal d–sulphur 3p interaction. This can be achieved by multiplying the orbital occupation numbers by the energy of that orbital relative to the non-bonding sulphur reference state, and summing over all the orbitals depicted in fig. 2. E.g., if the σ orbital, occupied by four electrons, lies 2.5 eV below the reference state, it contributes 10 units to this parameter. Similarly, antibonding orbitals, lying above the reference state, lower the value of I.

It follows that the σ antibonding level, if occupied, has a much larger effect on I than the π antibonding orbitals, for this orbital lies relatively high in energy. When the topologies of these orbitals are considered, fig. 3, it is immediately clear that this indeed should be the case. A σ antibonding electron strongly contributes to the repulsion between one sulphur atom and the remainder of the cluster, MS_5^{n-}, for it is unambiguously antibonding between the metal and the sulphur atom, fig. 3a. A π antibonding level on the other hand is antibonding between the metal and sulphur atoms, but bonding between the sulphur atoms, fig. 3b. Furthermore, the π levels with the largest sulphur contents (strongest sulphur–sulphur attraction), e.g. RuS_2, lie lowest in energy. This is consistent with the definition of I. Turning to the experimental activity curve, it is striking that a significant decrease in activity is observed precisely when the σ antibonding level is first occupied. For first row TMS, this occurs at MnS, due to the importance of spin. For the non-magnetic second and third TMS, the σ antibonding level is first occupied for Pd and Pt. This goes to show that I takes into account both the number of d electrons and the absolute and relative number of σ and π electrons, as well as the character of these orbitals.

Scattered-wave density-functional calculations on octahedral TMS clusters have been carried out on all the first, second and third row TMS for which Pecoraro and Chianelli report experimental HDS activities. The exchange-correlation potential of Hedin and Lundqvist [21] was used for the second and third row TMS. Spin was included for the first row TMS, for which Ceperley and Alder's [22] exchange-correlation potential was used. Note that there is no inconsistency here since *all* d electrons are incorporated in I. I does not depend on the number of elec-

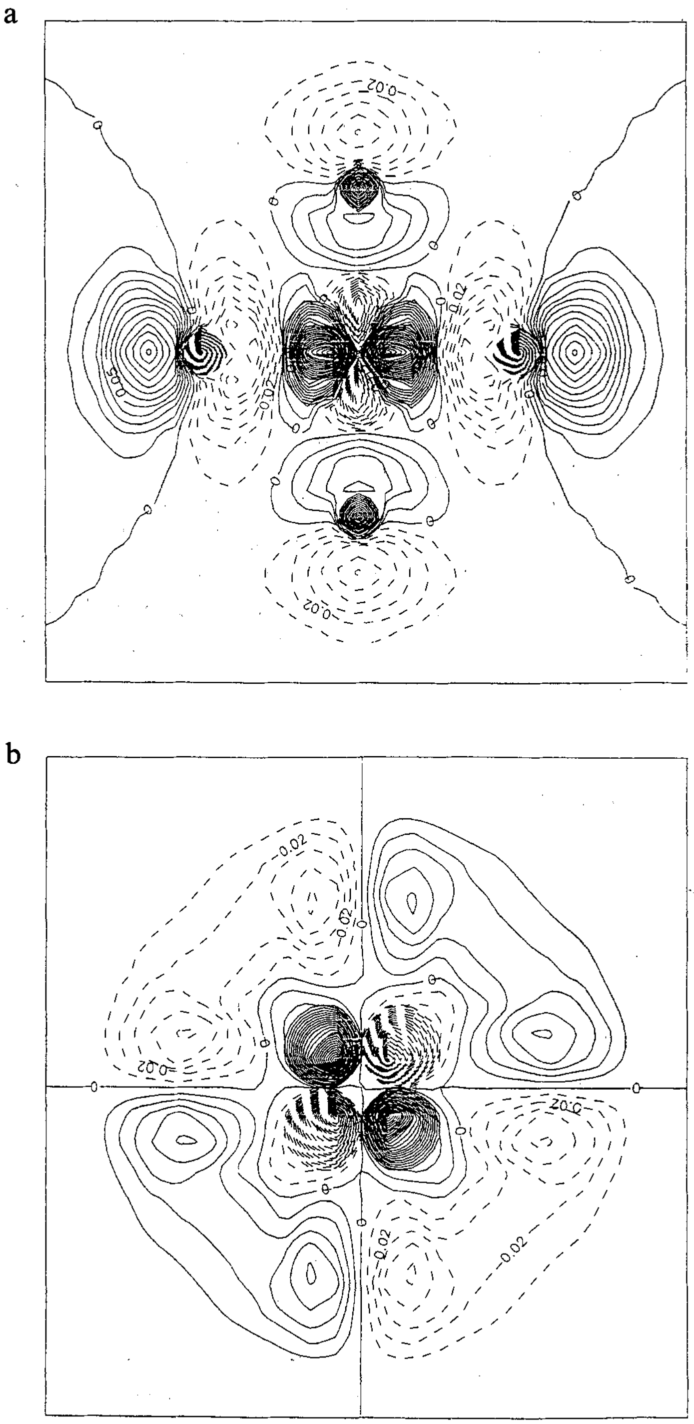

Fig. 3. The metal–sulphur σ* (a) and π* (b) antibonding orbital for an octahedral RhS_6^{9-} cluster.

trons in any specific orbital. Further details of the calculations are provided in ref. [20]. Fig. 4 demonstrates that *I* correlates well with the experimental HDS activities.

Two factors in the present analysis critically affect the value of *I*: (1) the oxidation state of the transition metal, affecting the number of electrons that contribute to *I* (hence our objection to the CsCl-structure calculations of Topsøe and coworkers), and (2) the metal–sulphur bond length, affecting the energy of the levels that contribute to *I*. We have chosen the oxidation state based on the stoichiometry of the TMS, see table 1 (except for Ir: if Ir(IV) is used, the value of *I* is substantially higher). The metal–sulphur bond length, table 1, corresponds to the observed bond length in the TMS, except for PdS and PtS. Only for the latter two compounds is the metal atom in a fourfold sulphur environment. Hence for these sulphides the bond length has been estimated from the Shannon ionic radii [23].

This simple model does not take into account the detailed surface structure of the catalyst, yet *I* correlates rather well with experimental activities. This analysis is aimed at identifying electronic factors relevant for the HDS process. We consider such information essential for the rational design of new catalysts. From the observed correlation it appears that the interaction between the sulphur 3p lone pairs on the thiophene molecule with the metal d orbitals (but also with the sulphur atoms in the catalyst) greatly influences the activity of the catalyst. Keeping this

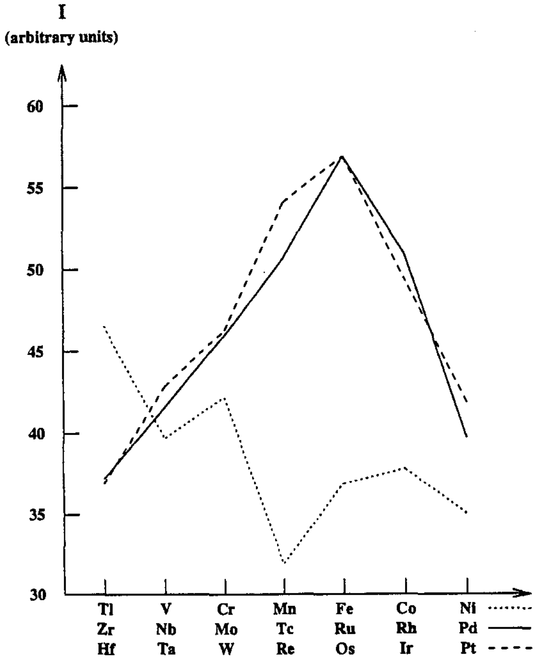

Fig. 4. The metal d–sulphur 3p interaction strength, *I*, plotted against the position of the transition metal atom in the periodic table. See text for details.

Table 1
The oxidation state of the metal atom and the metal–sulphur bond length in octahedral MS_6^{n-} clusters, which were used to calculate I (fig. 4). Also given is the number of σ^* and π^* electrons in these clusters

TMS	Metal ion oxidation state	Metal–sulphur bond length (a.u.)	Number of σ^* electrons	Number of π^* electrons
TiS_2	4+	4.57	–	0
V_2S_3	3+	4.48	–	1
Cr_2S_3	3+	4.57	–	3
MnS	2+	4.89	2	3
FeS	2+	4.27	–	6
Co_9S_8	2+	4.38	1	6
Ni_3S_2	2+	4.54	2	6
ZrS_2	4+	4.84	–	0
NbS_2	4+	4.67	–	1
MoS_2	4+	4.57	–	2
TcS_2	4+	4.50	–	3
RuS_2	4+	4.45	–	4
Rh_2S_3	3+	4.48	–	6
PdS	2+	4.76	2	6
HfS_2	4+	4.84	–	0
TaS_2	4+	4.61	–	1
WS_2	4+	4.55	–	2
ReS_2	4+	4.38	–	3
OsS_2	4+	4.42	–	4
IrS_2	3+	4.48	–	6
PtS	2+	4.53	2	6

in mind, the relatively high I-value for TiS_2 is unsatisfactory, but no cause for great concern since Ti^{4+} lacks d electrons altogether.

Before addressing promotion effects, we note an interesting observation by Carvill and Thompson [14], consistent with the theory presented. The average state of reduction of molybdenum in MoS is much higher than it is in MoS_2, but the intrinsic catalytic activity is significantly higher for MoS_2.

4. Promotion effects

Co–Mo–S and Ni–Mo–S are the most commonly used industrial HDS catalysts. The activity of these catalysts is higher than that of CoS (NiS) and MoS_2 separately. The nature of this synergistic promotion effect has not been conclusively determined. It may be electronic (meaning that Mo and Co(Ni) may act together to create especially active HDS sites) and/or structural (meaning that the dispersion of the catalyst is improved, thus increasing the number of sites). A related question is whether the promoter element is merely a promoter element, as the name suggests, or itself the active site.

In the theory presented in the previous section, the oxidation state of the metal atom plays a very significant role. Harris and Chianelli have shown that only Co and Ni, and possibly Fe, have the ability to donate electrons to Mo in the mixed sulphides, thus altering the d-electron density on these atoms [24]. These are precisely the elements for which promotion effects have been observed [14]. Magnetic susceptibility measurements by Topsøe and co-workers indicate that extensive electron delocalization occurs in Co–Mo–S and Ni–Mo–S [25]. XPS data of Shepelin et al. [26] show that partial transfer of electron density from nickel to tungsten (molybdenum) occurs through the formation of mixed surface sulphides: the oxidation state of Ni is higher in the mixed sulphide than it is in the monometallic sulphide [26,27]. In the interpretation of Harris and Chianelli [24], the increase in catalytic activity in Co(Ni)–Mo–S (compared to MoS_2) is due to the increased d-electron density on the Mo atoms. However, the value of I is lower for an $Mo(II)S_6^{10-}$ cluster than it is for $Mo(IV)_6^{8-}$ since two π antibonding electrons have been added to the cluster. On the other hand, the reduction of Mo corresponds to the removal of σ antibonding electrons from Co(Ni). This significantly increases the value of I. If I indeed represents the intrinsic HDS activity accurately, then this crude first-order analysis (no change in the metal–sulphur bond length has been incorporated) shows that the activity of the Mo atoms has gone down, but also that the activity of the Co(Ni) atoms has increased sharply! In other words, the theory predicts that Co and Ni are in fact the active sites in Co–Mo–S and Ni–Mo–S. Although there is still no consensus on the exact structure of the Co–Mo–S and Ni–Mo–S phase, there are many reports that Co and Ni decorate the edges of MoS_2 sheets, covering the Mo atoms. This essentially means that MoS_2 acts as a support for highly active Co(Ni) atoms [27,28]. This offers interesting possibilities for designing new catalysts. Doping the support with appropriate elements may alter the d-electron density on the catalytically active sites. If this does not sacrifice the dispersion of the catalyst on the support, a significant increase in catalytic activity may thus be achieved.

The role of the support has received much interest over the years. E.g., Arnoldy et al. [15] found that the activity of rhenium sulphides depends slightly on the support used (in the order $SiO_2 < Al_2O_3 <$ carbon), but the effect on MoS_2 is much more pronounced. Ramirez et al. [29] observed a higher intrinsic activity for TiO_2- than for Al_2O_3-supported Mo–S and Co–Mo–S catalysts. Since they do not observe a significant shift in XPS binding energies, an electronic basis for this phenomenon is ruled out. However, it must be noted that the presence of some Mo^{6+} was detected for the sulphided catalysts supported on TiO_2, but not if Al_2O_3 was used as a support. This is consistent with the theory presented, for the removal of two π antibonding electrons from the MoS_2 cluster leads to an increase in the value of I. Similarly, doping of a TiO_2 support with fluorine (a very electronegative element) has a strong promoting effect, as shown by Ramirez et al. [30].

Experimental verification of the theory presented (or any other theory of promotion effects for that matter) is a challenging task, since electronic and structural promotion effects often occur simultaneously. Further research in this area of HDS catalysis is clearly needed.

5. Conclusions

(1) The dependence of the HDS activity of monometallic TMS on the position of the metal atom in the periodic table is above all an electronic effect. The quality of the active site determines the rate of the rate-limiting step.

(2) The strength of the interaction between the sulphur 3p and metal d electrons, I, correlates well with the experimental HDS activities. The main factors determining the value of I are the oxidation state of the transition metal atom and the metal–sulphur bond length.

(3) In Co(Ni)–Mo–S, cobalt and nickel donate electrons to molybdenum. The removal of σ antibonding electrons greatly enhances the intrinsic activity of these elements. It follows that MoS_2 acts as a support for highly active Co(Ni).

(4) The catalytic support not only influences the dispersion of the catalyst, but may also interact electronically with the active phase by influencing the d-electron density on the transition metal atom.

References

[1] T.A. Pecoraro and R.R. Chianelli, J. Catal. 67 (1981) 430.
[2] S.J. Tauster, T.A. Pecoraro and R.R. Chianelli, J. Catal. 63 (1980) 515.
[3] J.P.R. Vissers, C.K. Groot, E.M. van Oers, V.H.J. de Beer and R. Prins, Bull. Soc. Chim. Belg. 93 (1984) 813.
[4] M.J. Ledoux, O. Michaux and G. Agostini, J. Catal. 102 (1986) 275.
[5] M. Salmeron, G.A. Somorjai, A. World, R.R. Chianelli and K.S. Liang, Chem. Phys. Lett. 90 (1982) 105.
[6] R.R. Chianelli, T.A. Pecoraro, T.R. Halbert, W.H. Pan and E.I. Stiefel, J. Catal. 86 (1984) 226.
[7] P. Sabatier, Ber. Deutsche Chem. Ges. 44 (1911) 2001.
[8] K.H. Johnson, Advan. Quantum. Chem. 7 (1973) 143.
[9] S. Harris and R.R. Chianelli, J. Catal. 86 (1984) 400.
[10] S. Harris and R.R. Chianelli, Chem. Phys. Lett. 101 (1983) 603.
[11] H. Topsøe, N.Y. Topsøe, S. Sørensen, R. Candia, B.S. Clausen, S. Kallesøe, E. Pedersen and R. Nevald, *Solid State Chemistry in Catalysis*, Washington, August 1983 (Division of Petroleum Chemistry, Am. Chem. Soc., Washington, 1985) p. 235.
[12] J.K. Nørskov, B.S. Clausen and H. Topsøe, Catal. Lett. 13 (1992) 1.
[13] C.D. Gelatt Jr., A.R. Williams and V.L. Moruzzi, Phys. Rev. B 27 (1983) 2005.
[14] B.T. Carvill and L.T. Thompson, Appl. Catal. 75 (1991) 249.
[15] P. Arnoldy, E.M. van Oers, V.H.J. de Beer, J.A. Moulijn and R. Prins, Appl. Catal. 48 (1989) 241.
[16] S. Kasztelan, H. Toulhoat, J. Grimblot and J.P. Bonnelle, Appl. Catal. 13 (1984) 127.

[17] R. Prins, V.H.J. de Beer and G.A. Somorjai, Catal. Rev.-Sci. Eng. 31 (1989) 1.
[18] T.S. Smit and K.H. Johnson, Chem. Phys. Lett. 212 (1993) 525.
[19] T.S. Smit and K.H. Johnson, J. Mol. Catal., submitted.
[20] T.S. Smit and K.H. Johnson, in preparation.
[21] L. Hedin and B.I. Lundqvist, J. Phys. C 4 (1971) 2064.
[22] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. 45 (1980) 566.
[23] R.D. Shannon, Acta Cryst. A 32 (1976) 751.
[24] S. Harris and R.R. Chianelli, J. Catal. 98 (1986) 17.
[25] H. Topsøe, B.S. Clausen, N.Y. Topsøe, J. Hyldtoft and J.K. Nørskov, *Symp. on The Mechanism of HDS/HDN Reactions*, Chicago, August 1993 (Division of Petroleum Chemistry, Am. Chem. Soc.) p. 683.
[26] A.P. Shepelin, P.H. Zhdan, V.A. Burmistrov, A.N. Startsev and Yu I. Yermakov, Appl. Catal. 11 (1984) 29.
[27] A.N. Startsev, in: *New Frontiers in Catalysis*, Proc. 10th Int. Congr. on Catalysis, Budapest, July 1992, Studies in Surface Science and Catalysis, Vol. 75C, eds. L. Guczi, F. Solymosi and P. Tétényi (Elsevier, Amsterdam, 1993) p. 1911.
[28] S.M.A.M. Bouwens, D.C. Koningsberger, V.H.J. de Beer, S.P.A. Louwers and R. Prins, Catal. Lett. 5 (1990) 273.
[29] J. Ramirez, S. Fuentes Díaz, M. Vrinat, M. Breysse and M. Lacroix, Appl. Catal. 52 (1989) 211.
[30] J. Ramirez, R. Cuevas, L. Gasque, M. Vrinat and M. Breysse, Appl. Catal. 71 (1991) 351.