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Understanding the trends in the hydrodesulfurization activity of the transition metal sulfides

J.K. Nørskov *, B.S. Clausen and H. Topsøe

Haldor Topsøe Research Laboratories, DK 2800 Lyngby, Denmark

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It is shown that the trends in the hydrodesulfurization activity of the transition metal sulfides can be understood from the variation in the binding energy of sulfur to the transition metals. A model based on the ab initio calculations of Gelatt, Moruzzi, and Williams is used to describe the binding energy trends and to single out the important parameters determining them. One important aspect of the model is, that it predicts that the trends in the catalytic activity are given to a large extend by the coupling between the sulfur chemisorption energy and the sulfur-induced distortions of the metal lattice. The simple model also appears to describe promotional effects.

Keywords: Hydrodesulfurization; transition metal sulfides; trends across the periodic table; model calculations

The purpose of the present letter is twofold. First, we will show how the trends in the activity of the transition metal sulfides as hydrodesulfurization (HDS) catalysts can be described in terms of a simple model for the strength of the metal-sulfur bonds at the surface. The second purpose is to point out that if this model is correct, the implication is that we have an example of a catalytic reaction where the coupling between adsorption and distorsions in the surface structure is of vital importance for the activity of the catalyst.

The trends in the HDS activity from one transition metal sulfide to the next have been studied in great detail by Pecoraro and Chianelli and others [1–6]. As shown in fig. 1 the activity has a characteristic *volcano* dependence on the number of d electrons of the transition metal for the 4d and 5d series, whereas the shape is more complex for the 3d series.

Several models have been proposed to explain this. Based on electronic structure calculations for model transition metal sulfide clusters, the activity has

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[1] Present address: Laboratory of Applied Physics, Technical University of Denmark, DK 2800 Lyngby.

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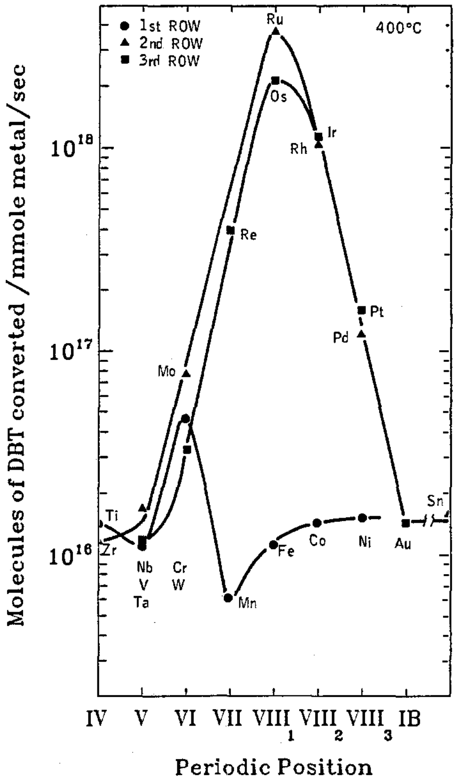

Fig. 1. The measured variation in the activity of various transition metal sulfides for hydrodesulfurization along the transition metal series. From ref. [1].

been correlated with various aspects of the electronic structure such as the covalent contribution to the metal-sulfur bond and the d-electron density of the metal [3]. In spite of a strong correlation between the measured HDS activities and certain linear combinations of the calculated parameters characterizing aspects of the electronic structure of the sulfide, it is not yet clear *why* these linear combinations should determine the activity.

More recently Burdett and Chung have discussed the HDS trends in terms of the strength of the sulfur-sulfur interactions of the sulfide [7]. The contention is that the HDS activity correlates with the metal-sulfide bond energy. Since this is extremely difficult to calculate they concentrate on the S–S interaction, which they believe will describe the trend in the binding energy from one transition metal to the next.

The approach we take is a more direct one. We also assume that the trends in the activity are given by the trends in the metal-sulfur bond energies, but we employ a set of ab initio band structure calculations of the bond strengths in the 4d transition metal sulfides [8] to construct a model that allows us to study the trends in the sulfur binding energies of *all* the transition metal sulfides directly.

The model also allows us to point out the important factors determining the trends and thus gives us a tool for understanding even more complex phenomena, such as the role of Co and Ni atoms as promoters for MoS_2 and the role of the CoMoS-type structures in the active HDS catalysts [9].

The starting point for our analysis of the trends in the HDS activity of the transition metal suphides is the experimental studies of the state of the active CoMo and NiMo catalysts [9]. In combination with mechanistic and kinetic modelling of the HDS reactions these studies strongly indicate that the sulfur containing molecules adsorb at sulfur vacancies on the surface of the catalyst. The rest of the molecule is then 'hydrogenated' away, leaving a sulfur atom on the surface. The catalysis thus takes place at metal sites that are not covered with sulfur, as was originally proposed by Lipsch and Schuit [10]. Thus, irrespective of the exact mechanism or the nature of the rate limiting step in the HDS reaction, the rate will be proportional to the concentration of sulfur vacancies in the surface, which in turn will depend on the composition of the reaction mixture and the strength of the metal-sulfur bonds. The weaker the bonds the more sulfur vacancies and the higher the catalytic activity will be. Obviously, the catalytic activity will also depend on the rate constant of the rate limiting step, and in a detailed theory of the trends in the HDS activity, the variations in the rate constants must also be included. We will, however, show in the following that most of the variations from one metal to the next can be accounted for by the variations in the sulfur binding energies [11].

Gelatt, Williams, and Moruzzi [8,12] have made an extensive set of ab initio total energy calculations for compounds between transition metals and non-transition metal atoms. On the basis of the results they have proposed a simple model to describe the stability of the compounds. The compound formation is imagined to take place in two steps. First, the transition metal is expanded to make room for the non-transition metal atoms. The non-transition metal atoms are then introduced and the hybridization between the transition metal and non-transition metal states is included. The binding energy of the non-transition metal atom is then

$$\Delta E = E_{\text{expand}} + E_{\text{hyb}}. \tag{1}$$

The energy involved in the expansion of the metal lattice will be proportional to the bulk modulus B of the metal, $E_{\text{expand}} = c_1 B$.

The hybridization energy E_{hyb} will in the case of the non-transition metal being sulfur have two contributions, a term, E_{pd}, describing the hybridization of the sulfur valence states with the transition metal d states, and a term involving the hybridization of the sulfur states with the metal s states. The latter term is approximately independent of the transition metal because they all have the same number of s states. E_{pd}, on the other hand, will vary approximately linearly with the number of d-electrons of the transition metal before the interaction is included. This is very simple to understand. The large sulfur electronegativity means that the sulfur (3p) valence states are below the transition metal d states and are completely filled (so as to make the sulpur atoms approximately S^{2-}). This happens to a large extend due to interactions with the transition metal s states (even non-transition metals without d states will give rise to the same picture). Because the sulfur p and transition metal d states are so well separated in energy, the interaction between them can be treated using second order perturbation theory. If the transition metal d bands are centered at ϵ_d, the filled sulfur p states at ϵ_p and they couple by the matrix element V_{pd} the interaction is [13]

$$\Delta E_{pd} = -2(1 - f_d)\frac{|V_{pd}|^2}{\epsilon_d - \epsilon_p}. \tag{2}$$

Here f_d is the degree of filling of the d band ($f_d = N_d/10$, where N_d is the number of d electrons).

The first term on the right hand side of eq. (2) involving the 1 in the parenthesis stems from the down-shift of the two electrons in the sulfur p level due to the interaction with the d states, and the f_d term comes from the corresponding up-shift of the d states. Since only the fraction f_d of the d states are filled the up-shift only involves f_d of the spin state that interacts with the adsorbate state. The fact of two in front of the parenthesis comes from spin.

Combing the different terms, the total sulfur binding energy can be written

$$\Delta E_S = c_1 B + c_2(1 - f_d) + c_3. \tag{3}$$

Here c_1 is related to the volume taken up by the sulfur atoms, c_2 is related via eq. (2) to the matrix element that couples the sulfur p and metal d states, and c_3 measures in particular the hybridization between the sulfur valence states and the transition metal s states. The coupling matrix elements entering both c_2 and c_3 will vary from one transition metal to the next, but not nearly as strongly as B and f_d. We shall therefore in the following take c_1, c_2, and c_3 to be constants, approximately independent of the metal. The quality of this choice is illustrated in fig. 2 where we compare the result of an analysis based on eq. (3) with the results of an ab initio calculation within the local density approximation [12] of the heat of formation of the 4d transition metal sulfides in the CsCl structure.

In the following we will first show how the calculated sulfur binding energies reproduce the trends in the HDS activities of the transition metal sulfides, and then go on to discuss what it is that determines these trends.

Fig. 3 shows the binding energy of sulfur atoms in all the transition metals according to eq. (3). The three constants c_1, c_2, and c_3 are kept equal to the values determined in fig. 2. Clearly, the trend in the activities in fig. 1 closely follows the trend in the sulfur binding energies.

Note that the model implicitly gives the binding energy per sulfur atom for a fixed structure. The actual variation of the structure of the transition metal

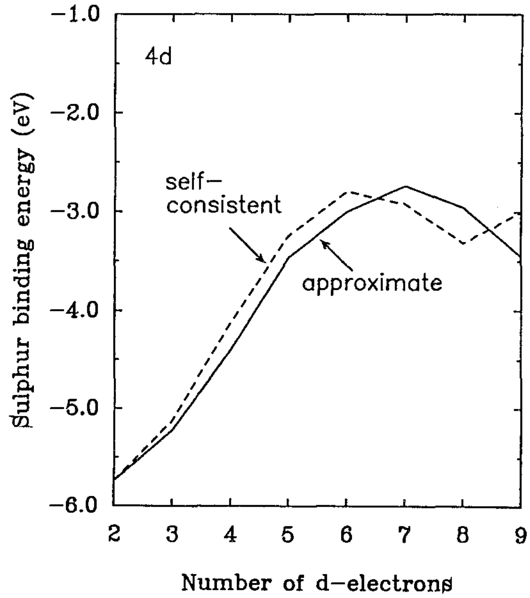

Fig. 2. Comparison of the ab initio results of ref. [12] to the results of eq. (3) for the sulfur binding energy in the 4d transition metal sulfides in the CsCl structure. The constants in eq. (3) are chosen to be $c_1 = 0.75$ eV M bar^{-1}, $c_2 = -1.72$ eV, and $c_3 = -4.64$ eV.

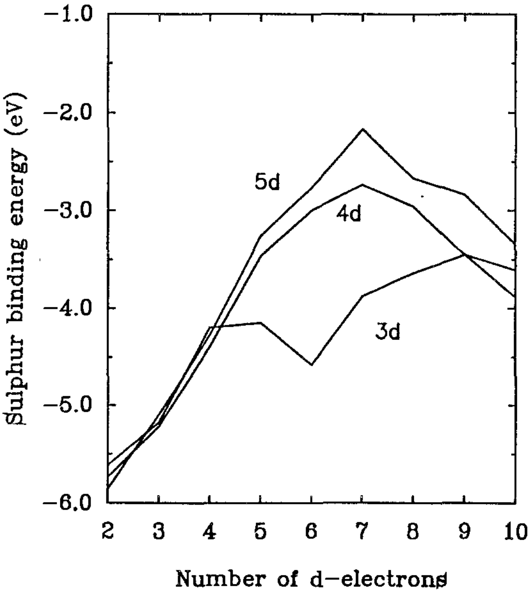

Fig. 3. The calculated variation in the sulfur binding energy in various transition metal sulfides. The trends in the sulfur binding energies follow the trends in the hydrodesulfurization activity of the sulfide catalysts.

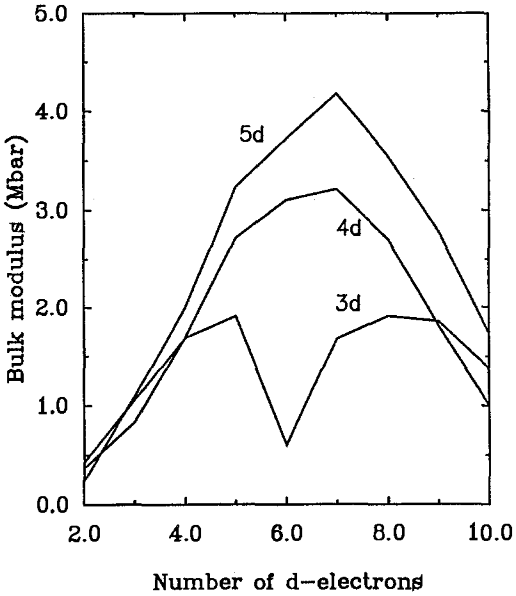

Fig. 4. The bulk moduli of the transition metals. (From [14,15].)

sulfides is not included. This means that the results in fig. 3 will give the overall trends in the sulfur binding energies of the transition metal sulfides, but not the details. The sulfur binding energy of interest for the trends in the HDS activities is, however, not the bulk values, but the value at the surface. It is not unlikely that the assumption of approximately constant local structure may be even better for the active sites at the surface than in the bulk.

The origin of the variations in the sulfur stability comes from a combination of the increase in p-d hybridization energy with decreasing number of d electrons seen in eq. (2) and the variation of the bulk modulus from one metal to the next. The trend in the latter is shown in fig. 4. For the 4d and 5d series it shows a maximum around the middle of the transition metal series. This is a consequence of the fact that here the d bands are half filled, which means that all the bonding states are filled and all the anti-bonding states are empty. The transition metals around the middle of the series are thus the most stable, they have the smallest lattice constants, and this also leads to the largest bulk moduli (the largest cost in energy when the volume is changed). For the 3d metals this trend is blurred by the well known anomaly related to the magnetism in some of the 3d metals [15].

The trends in the HDS activity of the transition metals thus stem from a competition between the energy gain due to the hybridization between the transition metal and sulfur valence states, and the energy cost associated with the weakening the metal-metal bonds when the sulfur atoms are incorporated into the surface. The most active transition metals are those where the metal-

metal bond strength (as measured for instance by the bulk modulus of the pure metal) is largest, because this leads to the least stable sulfur atoms on the surface.

The present explanation is quite different from that of Chianelli et al. [1,3], who suggest that for the transition metal sulfides considered here there is an *optimum* stability of the metal sulfide whereas we suggest a monotonic relation between the sulfur bond strength and the catalytic activity for the same sulfides. Chianelli et al. based their considerations on the observation that there is a maximum in the activity of the sulfide as a function of the heat of formation of the sulfide. However, the heat of formation was calculated per metal atom, and if the experimental heats of sulfide formation are normalized *per sulfur atom* there is, in fact, no maximum, but only a monotonic correlation as suggested by the present theory. Obviously, if the S-metal bond becomes too weak and the adsorption of the S-containing molecule becomes rate limiting, the activity may start decreasing with decreasing bond strength. The indication is that we have not reached this point within the transition metals series.

The activity of MoS_2 is known to increase when Co or Ni is added to the catalyst. The effect of these promoters may be to increase the rate of the rate limiting step in the reaction, but it might also be to decrease the sulfur binding energy. Persuing this line of thought, it is interesting first to note that the bulk modulus B in eq. (3) mainly depends on the d-band filling like the other important term in this equation. This means that when we consider the stability of a sulfur atom bound to a transition metal alloy then the binding energy should be given roughly by the average d-band filling. For non-magnetic alloys the 4d and 5d curves that are very similar in fig. 3 give the expected dependence of the sulfur binding energies of the number of d electrons. The sulfur atoms bound to both Co or Ni and Mo in the active CoMoS structure in these promoted catalysts (which are not magnetic) [9] are thus expected to have a binding energy corresponding to roughly 6.5–7 d-electrons, right at the maximum of the curves. By this simple argument Co and Ni should be the best promoters for a Mo based catalyst, in good agreement with observations [9]. Comparing the specific activity of MoS_2 to the value at the maximum of the 4d and 5d series in fig. 1 the activity of the Co promoted sites of MoS_2 should be one to two orders of magnitude more active than the Mo sites, which is again in good qualitative agreement with experimental observations [9]. A more detailed analysis of the promotional effects is presently being performed.

The HDS reaction may thus be a good example of a catalytic reaction where the coupling between the reaction and the structure of the substrate is important. This is a theme that Somorjai and Van Hove [16], in particular, have stressed recently. Indeed, the recent advances in studying both ordered and disordered adsorbate structures using scanning tunneling microscopy clearly indicate that adsorbate-induced restructuring of the surface may be the rule rather than the exception [17]. This clearly points to models of adsorption and catalysis that includes the coupling to the substrate distorsion as a prerequisite for even a qualitative understanding of trends in catalytic activities.

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