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Transition Metal Sulfide Catalysis: Relation of the Synergic Systems to the Periodic Trends in Hydrodesulfurization

The hydrodesulfurization (HDS) of dibenzothiophene (DBT) is catalyzed by binary[1] transition metal sulfides (TMS). Rates of the catalyzed reaction vary across the periodic table by over 3 orders of magnitude (*1*). The binary sulfides of the first transition series are relatively inactive but the binary sulfides of the second and third transition series yield "volcano" curves with maxima occurring near Ru and Rh in the second row, and near Os and Ir in the third row. The curves for the most active catalysts are shown in Fig. 1.

It is well known that the presence of a second metal can in some cases lead to catalysts which have activities greater than the simple sum of the activities of catalysts based on binary sulfides. Such "promotion" of MoS_2 or WS_2 by Co and Ni occurs in either supported or unsupported catalysts. Although the subject of promotion has been well studied no consensus exists as to the origin of this effect. In this note we suggest a relation between the activity of the well-known Co- and Ni-promoted MoS_2 and WS_2 catalysts, and the periodic trends for the binary sulfides.

Studies of promotion have led to the idea of "contact synergy" for sulfided catalysts containing Co or Ni together with Mo or W (*2*). Although this specific idea appears to be incorrect, Ni/Mo, Co/Mo, Co/W, and Ni/W can be said to behave as "synergic pairs" which retains the idea that the members of these pairs "work together or cooperate." Although the bulk binary phases for these elements Ni_3S_2, Co_9S_8, MoS_2, and WS_2 are present in the unsupported catalysts, recent work by Topsoe et al. (*3*) has shown the presence in both supported and unsupported CoMo catalysts of a unique form of sulfided Co (the "CoMoS" phase) which correlates with activity. Moreover, although Co_9S_8 or Ni_3S_2 phases have been described as "promoters" of MoS_2 or WS_2, it has been shown that these phases themselves have activities which are of the same order as MoS_2 (*4*). The synergic pairs of active sulfides give enhancements of activity far greater than would be expected by the simultaneous presence of noninteracting phases. Is there a relation between the activity of these synergic pairs and the periodic trends for the binary sulfides? Such a relation is suggested if we examine the *average* heats of formation of the sulfides of the synergic pairs.

The heats of formation of the most active binary sulfides fall into an "optimum" range as shown in Fig. 2. The maximum in activity for the second transition series occurs near RuS_2 (where $\Delta H_f = 49.2$ kcal/mol) and in the third transition series near Os (where $\Delta H_f = 35.3$ kcal/mol). Although, there is some uncertainty in the position of the exact maxima due to incomplete correlation of HDS activity to BET surface area (*1*) this does not affect the arguments in this paper. The most active catalysts have heats of formation in the range of 30–50 kcal/mol. Recent work shows that heats of formation of the sulfides are linearly correlated with heats of adsorption of sulfur on transition metal surfaces (*5*). We believe that the correlation of ΔH_{ads}, ΔH_f, and activity reflects the optimum metal–sulfur bond strength on

[1] The term binary transition metal sulfide is used in the metallurgical or mineralogical sense meaning consisting of two elements, i.e., the transition metal and sulfur.

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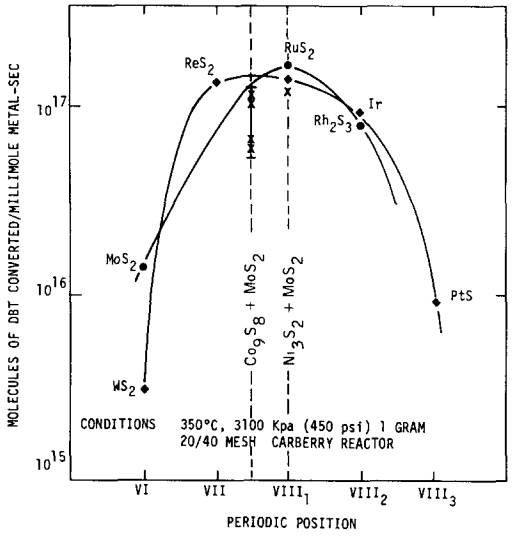

FIG 1 Activity of the second and third row transition metal sulfides and the relation of the "synergic pairs" Co_9S_8/MoS_2 and Ni_3S_2/MoS_2 to the binary sulfides

the surface of the catalyst Under catalytic conditions this quantity is related both to the ease of formation of sulfur vacancies and to the strength of binding of S-containing reactants to the surface The elements to the left of the periodic table have high heats of formation, bind sulfur or sulfur-bearing molecules too strongly, and are in a sense "poisoned" by sulfur Sulfides of elements to the right of the periodic table have low heats of formation and sulfur-bearing molecules are likely bound too weakly for reaction to occur Those sulfides which have intermediate heats of formations bind sulfur-bearing molecules neither too strongly nor too weakly and are effective catalysts The preceding argument is well known in other areas of catalysis (*6*)

We have noticed that if we take the *average* heat of formation of the individual sul-

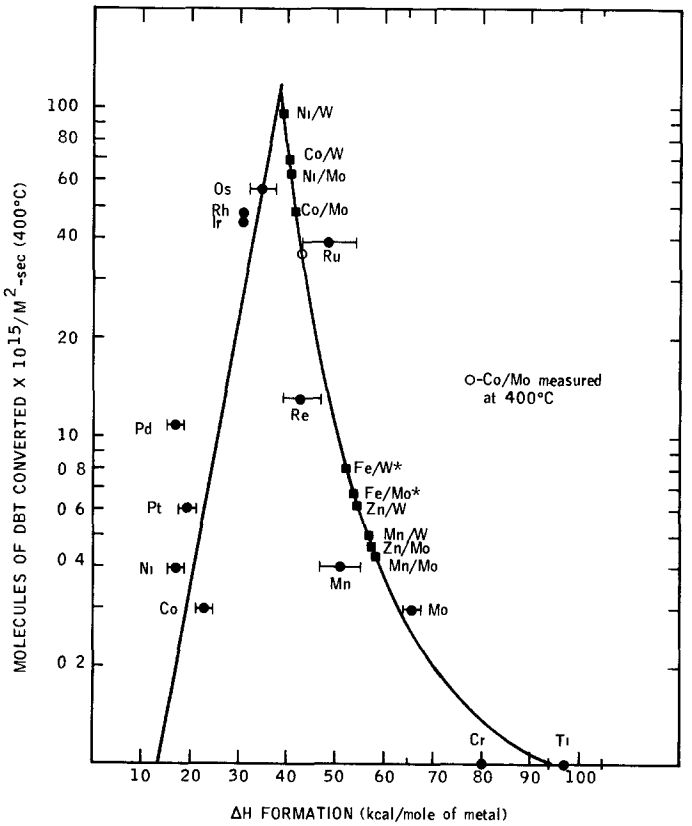

FIG 2 HDS activity of the transition metal sulfides vs heat of formation of sulfides (circles are the binary sulfides, squares are the average heat of formation of the pairs of binary sulfides taken from Table 1) Open circle is a measured activity for Co/Mo catalyst

TABLE 1

Average Heats of Formation of Pairs of Transition Metal Sulfides

		MoS_2	WS_2
		65 8	62
MnS	51 1	58 5	56 6
FeS_2	42 6	54 2	52 3
FeS	24	44 9	43
Co_9S_8	19 8	42 8	40 9
Ni_3S_2	17 2	41 5	39 6
CuS	12 7	39 3	37 4
ZnS	46	57 3	54

fide components of the synergic pairs, these averages fall into the optimum range for the binary sulfides A list of the average heats of formation of the first transition series sulfides and MoS_2 or WS_2 is shown in Table 1 The known synergic pairs all lie near the center of the range for the optimum value of the heat of formation (~40 kcal/mol) This relation suggests that the synergic pairs behave catalytically as second or third row *pseudobinary* sulfides and implies a fundamental relation between the periodic trends for the binary sulfides and the activity of the synergic pairs The sulfides of the synergic pairs may have surface properties which reflect the average surface properties and therefore the average bulk properties of their individual components Thus, the sulfided Co/Mo or Ni/Mo catalysts behave at the surface as sulfides of hypothetical elements of periodic position between those of the members of the pair, hence, the term pseudobinary sulfide The average value of the heat of formation of the synergic-pair sulfides and other pairs of sulfides which are not promoters are shown in Table 1 While the average heat of formation of the synergic pairs falls in the range 35–50 kcal/mol that for pairs (with the exception of the closest metals to Co and Ni namely Fe and Co) which are not known as promoters fall outside this range The solid curve in Fig 2 illustrates a qualitative trend in relative activity which occurs for the sulfide pairs and further measurements may more accurately determine the optimum heat of formation for maximum activity In the case of iron there is ambiguity because the Fe/S phase present under reaction temperature is not unequivocally known due to the complexity of the Fe/S phase diagram (*7*) If we chose the heat of FeS_2 the Fe/Mo average heat of formation falls outside the optimum range As iron sulfide does not promote molybdenum sulfide catalysts (*8*), this choice is consistent with the literature, and with our own measurements discussed below A similar argument can be made for Cu which is also not known as a promoter

To compare directly the activities of the synergic pairs with the binary sulfides several "synergic pair" ternary sulfide catalysts were prepared and their activities for the HDS of dibenzothiophene were measured in the manner previously described for the binary sulfides (*1*) The Co/Mo catalyst was prepared as previously (*1*) by precipitation for nonaqueous solution (ethyl acetate) of appropriate mixtures of $CoCl_2$ and $MoCl_4$ with Li_2S

$$x\mathrm{CoCl_2} + y\mathrm{MoCl_4} + (x + 2y\mathrm{Li_2S}) \xrightarrow[\text{acetate } 25°\mathrm{C}]{\text{ethyl}} x\mathrm{CoS} + y\mathrm{MoS_2} + 2(x + 2y)\mathrm{LiCl}$$

The resulting mixture of amorphous sulfides and LiCl was heat-treated in 15% H_2S/H_2 at 400°C for 2 h The black solid was washed with 12% acetic acid to remove the remaining LiCl and again heat-treated in 15% H_2S/H_2 at 400°C for 2 h The resulting Co/Mo catalyst contained both Co_9S_8 and MoS_2 phases as determined by X-ray powder diffraction The Ni/Mo catalyst made in an analogous fashion contained both Ni_3S_2 and MoS_2 The measured activities normalized in several ways because of a general noncorrelation to surface area for layered sulfides are reported in Table 2 The activities normalized per gram of MoS_2 fall on the periodic trends plot (i e , activity vs ΔH_f) as indicated in Fig 1 for measurements at 350°C

TABLE 2

Activity of Pseudobinary Systems

M	M / (M + Mo)	T°C	Molecules of DBT Converted			BET (m^2/g spent)
			× 10^{16} /(g-cat s)	× 10^{16} /(g MoS_2 s)	× 10^{15} /(mmol Mo s)	
Co	0 25	350	39 5	44 5	79 5	—
Co	0 25	350	55	62 0	110 7	—
Co	0 25	350	39	44 0	78 6	19 2
Co	0 25	400	68	76 7	137 0	21 4[a]
Co	0 50	350	64	83 0	173 0	—
Ni	0 50	350	51	68 0	144 7	—

[a] Activity = 36 × 10^{15} molecules of DBT converted/m^2 s This point appears in Fig 2

The activity of the synergic-pair Co/Mo system approximates that of a hypothetical pseudobinary having the average properties of Co_9S_8 and MoS_2 The same can be seen for the Ni/Mo synergic pair vis-á-vis Ni_3S_2 and MoS_2 That some of the synergic catalysts fall below the trend curve can be attributed to differences in physical properties of the catalysts Because of the difficulty in correlating BET surface area to HDS activity previously noted (*9*) we must await turnover number information for more precise quantitation of the suggested relation This is particularly troublesome in the case of the synergic pairs and catalysts of the same nominal composition and surface area have substantially different activities However, we note that in general the surface areas of the synergic pairs are lower than those of the pure phases The synergic pairs reported in Table 2 prepared as described above had surface areas usually in the range of 15–25 m^2/g whereas MoS_2 prepared in a similar manner had surface areas in range of 50 m^2/g (*1*) This suggests that in the synergic pairs the number of active sites is not increasing but rather that the quality of the active site may be enhanced In fact, if we normalize the data point for Co/Mo at 400°C (Table 2) to surface area we see that the measured value falls quite close to the point (Fig 2) for the average value of the heat of formation of the synergic pair Co/Mo This idea is supported by a recent paper on the role of Co in unsupported MoS_2 catalysts which shows that the surface area for a series of catalysts where $0 \leq M/M + Mo \leq 1$ is equal to or lower than unpromoted MoS_2 Furthermore in the same paper the activation energy for the same series of catalysts was measured for dibenzothiophene conversion and found to be constant (20 7 ± 0 7 kcal/mol) for the entire series (*10*)

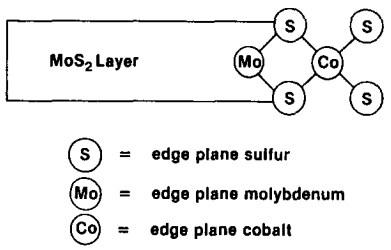

FIG 3 Schematic representation of sulfur shared between Co and Mo at MoS_2 edge Hypothetical position for Co at MoS_2 edge plane

DISCUSSION

Several microscopic theories for promotion have been presented in the literature Are any of these pictures consistent with the pseudobinary relation suggested in this report? The suggested pseudobinary relationship calls for a CoMoS unit to be

present at the surface such as is shown in Fig 3 For Co/Mo catalysts this suggestion is consistent with the Co being located somewhere at the edge of the MoS_2 crystallites For example, the Co could be located at the edge of a single MoS_2 layer as suggested by Ratnasamy and Sivasanker (*11*), or it could be located between the layers near the edge (pseudointercalation) as suggested by Voorhoeve and Stuiver (*12*) Co located at the edge of MoS_2 is also consistent with the "surface enrichment" model of Phillips and Fote (*13*) The essential point is that somewhere at the edge, sulfur atoms, which upon leaving create vacancies, are shared by Co and Mo leading to average electronic properties of the sulfur atom or the vacancy as suggested by the pseudobinary concept A sulfur attached to Co and Mo behaves in an average electronic fashion and as such is similar to sulfur atoms attached to the surfaces of noble metal sulfides such as RuS_2 Presumably, if such electronic interactions occur at the surface of promoted catalysts as experiment suggests, the strength of those metal–sulfur bonds which lead to vacancies are adjusted to intermediate values which, as the binary periodic trends suggest, are necessary for high activity Thus, in the case of Co and Ni promoters such surface states exist having sulfurs shared between the promoter and Mo which have optimum bond strength for vacancy formation as indicated in Fig 3 Further experimental and theoretical work on this concept is currently in progress

REFERENCES

1 Pecoraro, T A , and Chianelli, R R , *J Catal* **67,** 430–445 (1981)
2 Delmon, B , "Proceeding, 3rd International Conference on the Chemistry and Uses of Molybdenum, 73–85, Ann Arbor, Michigan, Aug 19–23, 1979 "
3 Topsoe, H , "Surface Properties and Catalysis by Non-Metals Oxides, Sulfides and Other Transition Metal Compounds," pp 329–360 D Reidel Publishing Co , 1983
4 De Beer, V H J , Duchet, J C , and Prins, R , *J Catal* **72,** 369–372 (1981)
5 Bernard, J , Oudar, J , BarBouth, N , Margot, E , and Berthier, Y , *Surf Sci* **88,** L35–L41 (1979)
6 Sabatier, P , *Ber Dtsch Chem Ges* **44,** 2001 (1911)
7 Chianelli, R R , *J Catal* **71**(1), 228 (1982)
8 Beuther, H , Flinn, R A , and McKinley, J B , *Ind Eng Chem* **51,** 1349 (1959)
9 Tauster, S J , Pecoraro, T A , and Chianelli, R R , *J Catal* **63,** 515–519 (1980)
10 Vrinat, M L , and DeMourgues, *Appl Catal* **5,** 43 (1983)
11 Ratnasamy, P , and Sivasanker, S , *Catal Rev Sci Eng* **22**(3), 401 (1980)
12 Voorhoeve, R J H , and Stuiver, S C M , *J Catal* **23,** 243 (1971)
13 Phillips, R W , and Fote, A A , *J Catal* **41,** 168 (1976)

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