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A New Class of Models to Explain the Role of Promoters in Hydrodesulfurization Catalysts[1]

R. W. PHILLIPS AND A. A. FOTE

The Aerospace Corporation, El Segundo, California 90245

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Two models have been developed that qualitatively explain the reactivity curves for hydrodesulfurization catalysts promoted by various amounts of transition metals (e.g., MoO_3–CoO). Both models, the surface complex model and the boundary model, make use of the concept of surface segregation. The ideas presented are applicable to other systems as well in that the models also explain the oxidation and isomerization activity of the MoO_3–P_2O_5 catalyst, the dehydrogenation activity of the MoO_3–Bi_2O_3–P_2O_5 catalyst, and the hydrogenation activity of the Ni–W–S catalyst as a function of bulk composition.

INTRODUCTION

A large amount of research has been directed toward elucidating the catalytic nature of promoter-molybdenum-type catalysts. However, no adequate explanation has been given for the promoting effect of the added component. Studies described in the open literature show that maximum hydrodesulfurization occurs at a specific bulk ratio of promoter metal P to molybdenum (*1*, *2*). Explanations of the most effective promoter metal as well as the optimum bulk atomic ratios have been subject to controversy. For example, for cobalt-molybdenum on an alumina support, the optimum cobalt to molybdenum atomic ratio reported has ranged from 0.2 to 5.0 (*3*). It has also been observed that the optimum ratio depended on the surface area of the catalyst (*2*). At the optimum ratio, different promoter metals exhibited large differences in catalytic activity (Figs. 1a and b).

Attempts to correlate catalytic activity with detailed chemical and physical characteristics have generally been unsuccessful. From magnetic susceptibility measurements, Richardson concluded that an unknown Co–Mo complex is responsible for hydrodesulfurization (*4*). From ir and reflection spectra, however, Lipsch and Schuit believe that octahedral MoO_3 is the main catalytic species (*5*). The cobalt was found to be distributed through the bulk as $CoAl_2O_4$, whereas the MoO_3 was spread over 20% of the alumina surface as a monomolecular layer. If this were to be the case, the role played by cobalt would indeed be obscure since it has been shown that both $CoAl_2O_4$ and Al_2O_3 are catalytically inactive (*4*, *5*). Alternative explanations have proved equally inconsistent. A model of tetrahedral surface site occupation by the promoter metal has also been advanced (*1*). As the authors point out, this model suffers from the fact that one would expect all the maxima to fall at the same P/Mo ratio. Other cobalt compounds, such as $Co_{1-x}Mo_2S_4$, Co_9S_8, $CoMoO_4$, CoO,

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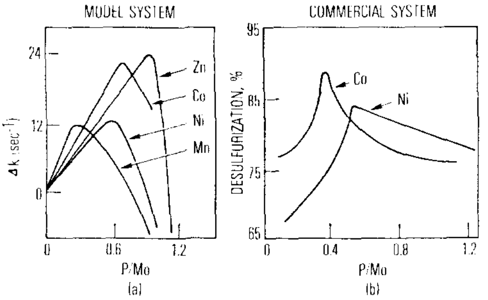

FIG. 1. Effect of promoter P on catalytic activity. (a) Plot of Δk, the difference between the reaction rate constant for the PO–MoO_3–Al_2O_3 and the MoO_3–Al_2O_3 catalysts, vs the P/Mo atomic ratio for thiophene desulfurization [Ref. (*1*)]; (b) Plot of percentage desulfurization vs the P/Mo atomic ratio for a light catalytic gas oil [Ref. (*2*)].

Co_3O_4, and $Co_2Mo_3O_8$, have also been ruled out as being the primary catalytic species (*6–9*).

The only hypothesis given so far to explain promotional effects has been for cobalt in crystalline MoS_2 samples (*10*). It was suggested that the activity of pure MoS_2 domains is enhanced in some undefined way by the presence of adjacent separate domains of cobalt sulfide. As for amorphous or supported catalysts, no clue or reasonable explanation has been postulated for the observed enhancement.

A significant problem in correlating the catalytic activity of these systems to their composition is the fact that catalysis is a surface phenomenon whereas the compositions generally reported are bulk compositions. Bulk and surface compositions are not necessarily equal. Preferential concentration of one component at an interface is well known in polymers, alloys, and oxides (*11–13*). Even minor amounts of MgO and NiO will segregate at grain boundaries in alumina (*14*). Surface enrichments can be up to 10^4 to 10^5 times those of the bulk concentrations even when the components are completely miscible (*15*). Mechanisms for this phenomenon include surface tension, solute-vacancy flow, and immiscibility (*16, 17*).

In this paper, we develop two models that explain the functional dependence of catalytic activity on promoter concentration. These models make use of the surface enrichment phenomenon described above.

THEORETICAL ANALYSIS

A. *Surface Complex Model*

The following simple model provides a qualitative explanation of the data of DeBeer and others (*1*) (Fig. 1). A method of calculating reactivity curves is presented. These theoretical curves are very similar to the experimental results. The model requires only three assumptions.

First, assume the surface has a higher promoter concentration than does the bulk. Some experimental evidence for this is suggested by the ESCA studies of Brinen (*18*). Surface enrichment profiles generally take the form shown in Fig. 2 (*19*). The surface concentrations of A and P, defined as the fraction of metal sites occupied, are plotted versus the bulk concentration of P. The sum of the two curves must equal unity.

Second, two phases exist at the surface for a given bulk composition (Fig. 3). The first of these is a promoter atom–molybde-

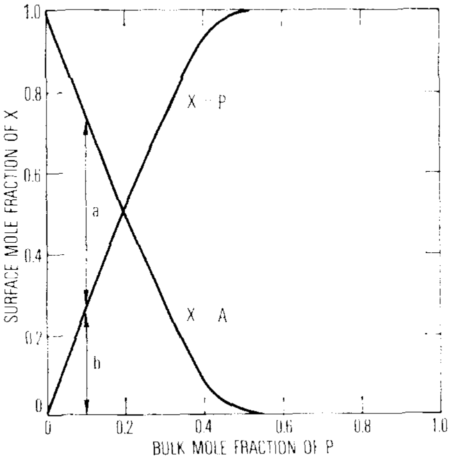

FIG. 2. Relationship of surface composition to bulk composition (surface composition not equal to bulk composition).

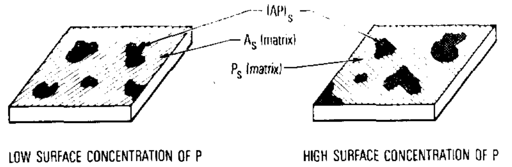

FIG. 3. Catalyst surface at different promoter concentrations using the surface complex model.

num complex, represented by $(AP)_s$. The other phase is either A_s, a compound containing no P atoms, or P_s, a compound containing no A atoms. The relative concentrations of the two phases at the surface can be determined from Fig. 2. To see how this is done, assume that $(AP)_s$ contains a 1:1 ratio of A and P atoms. For a bulk mole fraction of P of 0.1, draw the vertical line as shown in Fig. 2. The length of the line segment *b* then gives the number of AP pairs available to form the $(AP)_s$ complex. The line segment *a* gives the excess number of A atoms available to form the A_s phase. At this bulk concentration of P, there are no P_s sites at the surface. If, on the other hand, the bulk mole fraction of P in Fig. 2 were to exceed 0.2, then the situation would be reversed. In this case, only $[AP]_s$ and P_s phases would be present. At the optimum value of $P = 0.2$, only the $[AP]_s$ phase exists.

Finally, represent the specific rate constants per site for the three phases by γ_A, γ_{AP}, and γ_P. Since the promoter atom phase P_s (P = Zn, Co, Ni, or Mn) has little, if any, hydrodesulfurization activity, we take $\gamma_P = 0$(*1*, *20*). Now, the third assumption is that γ_{AP} is larger than γ_A.

It is generally assumed that desulfurization is a first-order reaction (*1*, *4*):

$$\frac{-d[S]}{dt} = k[S], \tag{1}$$

where [S] is the concentration of sulfur compound and *k* is the observed rate constant, normalized to unit area. One can further state that

$$k = \sum_i \gamma_i C_i, \tag{2}$$

where γ_i is the specific rate constant ($\sec^{-1}$) at a particular site for phase *i*, and C_i is the number of surface sites per unit surface area for phase *i*.

Values of C_i, i.e., C_A, C_P, and C_{AP}, as functions of the bulk mole fraction of P, can be derived directly from the data in Fig. 2 by taking the surface area of each phase and dividing by the effective molecular areas. The area for each phase is obtained from Fig. 2 as described earlier.

Thus, the difference in the observed first-order rate constants for desulfurization between promoted and unpromoted molybdena catalysts is given by

$$\begin{aligned} \Delta k &= [\sum_i \gamma_i C_i] - [\gamma_A C_A]^0 \\ &= [\gamma_A C_A] + [\gamma_{AP} C_{AP}] - [\gamma_A C_A]^0, \end{aligned} \tag{3}$$

where $[\gamma_A C_A]^0$ refers to the unpromoted catalyst. Therefore, from Fig. 2 and Eq. (3), the total catalytic activity can be determined for any given bulk concentration of P. For example, if $\gamma_{AP} = 4\gamma_A$ and the relative values of C_A and C_{AP} are derived from the data in Fig. 2, the curves of Fig. 4 are obtained from Eq. (3). The effective molecular areas of the A_s and P_s sites were taken to be equal, whereas the $(AP)_s$ sites were assumed to be twice as large as the A_s sites.

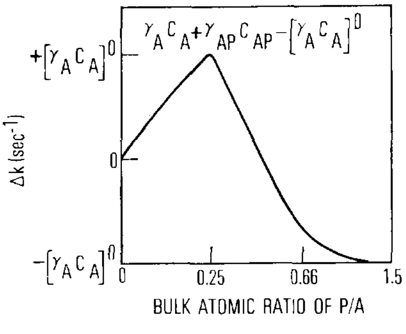

FIG. 4. Change in catalytic activity, Δk, relative to pure A_s phase.

The resultant curve is remarkably similar to the curves given by DeBeer *et al.* compare (Fig. 4 and Fig. 1a). Not only is the general shape of the curve correct, but in addition it shows that, at high P/A ratios, catalytic activity is even lower than that for unpromoted molybdenum. Furthermore, the relative positions of the peak catalytic activity for different promoters can be readily attributed to differences in promoter affinity for the surface.

Rather than requiring a 1:1 complex, an A_xP_y complex with $x \neq y$ (possibly sulfided as in $A_xP_yS_z$) may be the active surface species. For this general case, the procedures described above can still be used. However, the resultant catalytic curve would differ in the position and magnitude of the maximum from the 1:1 example. The resultant peak would be skewed to the right or left depending on whether the x/y ratio was >1 or <1, respectively. Peak positions for all of the promoters would, however, be displaced equally since Co, Ni, Zn, and Mn would be expected to form a complex with the same x/y ratio in view of the similarity of their chemical properties. For this particular model, then, peak positions would be governed solely by differences in surface segregation properties. Relative differences in catalytic activity must therefore be associated with differences in the catalytic activities of the $(AP)_s$ complexes. It is tempting to relate γ_{AP} to the electron-accepting ability of A modified by P. A more detailed analysis of this interaction is, however, beyond the scope of this paper.

B. Boundary Model

As previously stated, the above model for the effect of promoter concentration on catalytic activity is based upon three assumptions. A second model, also requiring three assumptions, can also account for the observed catalytic activity. Both models appear to be equally plausible.

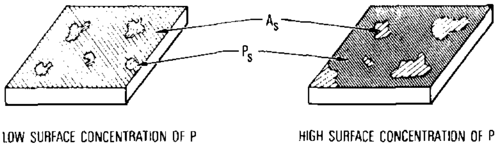

Fig. 5. Catalyst surface at different promoter concentrations using the boundary model.

For the second model, the assumptions are:

1. The surface is richer in the promoter atom than is the bulk. (This assumption is identical in both models.)
2. Only two phases exist at the surface: a phase A_s and a phase P_s (Fig. 5).
3. The specific catalytic rate constant per site at the A_sP_s grain boundaries, γ_G, is very high (γ_P is again zero). The rate constant, then, is

$$k = \gamma_A C_A + \gamma_G L_{AP},$$

where L_{AP} is the number of sites on the grain boundary per unit area. L_{AP} can be determined only by microscopic examination of the surface. As in the first model, the total catalytic activity is the sum of two terms, one of which decreases as the bulk concentration of P increases, while the other shows a maximum for some ratio of A to P. The analysis thus proceeds essentially as before with the same qualitative results.

CONCLUSIONS

A new class of models has been presented that can explain many features of promoted molybdena catalysts. In contrast to previous models, all of the following features can be taken into account: namely, (a) why catalytic activity peaks at a particular concentration of promoter, (b) why the optimum promoter concentration is different for different metals, and (c) why catalytic activity falls below the catalytic activity of unpromoted material at high promoter concentrations.

These models appear equally plausible

for other multicomponent catalytic systems as well. Bell-shaped curves have also been observed for the oxidation and isomerization of various hydrocarbons over MoO_3–P_2O_5 catalysts (*21*). Here, the activity peaked when the phosphorous to molybdenum atomic ratio was about 0.1. The dehydration activity of the MoO_3–Bi_2O_3–P_2O_5 system follows similarly (*22*). The rate constant for hydrogenation of cyclohexene as a function of the Ni/(Ni + W) atomic ratio behaves in an almost identical manner (*23*).

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