identified rhenium fragment. We propose that formation of methylcyclopropane occurs by the mechanism outlined in Scheme I. Loss of CO or $\eta^5 \rightleftharpoons \eta^3$ isomerization of the cyclopentadienyl ring first generates a coordinatively unsaturated rhenium center. Next β-elimination gives rhenium butenyl hydride **9**, which may then reinsert the olefinic fragment in either of two ways: to regenerate the five-membered metallacycle **7** or to give rhenacyclobutane **10**. The rhenacyclobutane then rapidly reductively eliminates methylcyclopropane.[12] This is the first known example of a metallacyclopentane to metallacyclobutane ring contraction that leads to cyclopropane. It is interesting to contrast this reaction with one reported by Schrock et al.[13] in the tantalum series, where a similar ring contraction leads to olefins via β-elimination followed by reductive elimination.

Further studies involving attempts to isolate the rhenacyclobutane intermediates, characterize the second organometallic thermolysis product, and prepare larger ring systems are in progress.

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Registry No. **1**, 78809-05-9; **2**, 80926-01-8; **3**, 87145-47-9; K^+**3**, 87145-51-5; Et_4N^+**3**, 87145-52-6; **4**, 55839-81-1; **5**, 87145-48-0; **6**, 87145-49-1; **7**, 87145-50-4; $CpRe(CO)_3$, 12079-73-1; methylcyclopropane, 594-11-6.

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Correlation between Thiophene Hydrodesulfurization Activity and the Number of First Sulfur Neighbors As Determined by EXAFS in Sulfided CoMo/γ-Al_2O_3 Samples

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Several attempts have been made to correlate the hydrodesulfurization (HDS) activity with chemical or physical parameters in CoMo HDS catalysts. For example, both O_2 chemisorption[1,2] and ESR signal intensity[3] have been found to correlate with the HDS activity in MoS_2 and sulfided Mo/γ-Al_2O_3. Similarly, for a given CoMo/γ-Al_2O_3 sample that was of modified activity following its use, Tauster and Riley[4] found that O_2 chemisorption correlated with HDS activity. On the other hand, Chung and Massoth[5] and Lôpez Agudo et al.[6] found that adding Co to Mo/γ-Al_2O_3 only slightly increases O_2 chemisorption, while the HDS activity increases at least by one order of magnitude. Similar results were obtained in our laboratory for the CoMo/γ-Al_2O_3 samples described below.[7] Thus O_2 chemisorption does not generally correlate with activity.

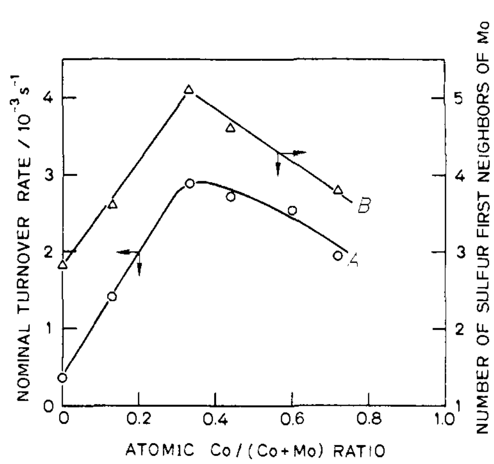

Figure 1. Dependence of NTR (curve A) and N_S (curve B) on the atomic Co/(Co + Mo) ratio of CoMo/γ-Al_2O_3 samples prepared by incipient wetness impregnation.

Here we present a correlation between the thiophene HDS activity and a structural parameter determined by X-ray absorption spectroscopy (XAS). To our knowledge, this is the first time this correlation has been noted.

Two series of samples were prepared. The first series involved incipient wetness impregnation of γ-Al_2O_3 powder with ammonium heptamolybdate solution, resulting in 7.7% Mo loading when dried and heated in air at 773 K for 2 h. Subsequent impregnations with $Co(NO_3)_2$ solutions of different concentrations produced a series with varying Co but approximately constant Mo loading. The second series was prepared by bulk impregnation of γ-Al_2O_3 pellets, using the same order of impregnation as above. The samples were reduced 0.5 h at 503 K in H_2 and then sulfided in 2% H_2S/H_2 for 0.5 h at 503 K, 0.5 h at 553 K, and 1.5 h at 613 K.

After sulfidation, the catalysts were tested for thiophene HDS in a fixed bed reactor at 573 K and atmospheric pressure. A nominal turnover rate (NTR, number of molecules of thiophene reacting per second per Mo atom) at 5% conversion of thiophene was used to compare the HDS activity of these samples. Curve A in Figure 1 shows the value of NTR vs. the atomic ratio α = Co/(Co + Mo). The nominal turnover rate increased with Co addition up to $\alpha = 0.33$, and further Co addition decreased the thiophene HDS activity. This "volcano" curve has been widely reported in the literature[8,9] for unsupported and supported CoMo HDS catalysts.

The XAS measurements of the sulfided CoMo/γ-Al_2O_3 samples were carried out in a controlled-atmosphere cell at room temperature. After sulfidation, the samples were cooled to room temperature in the gas mixture used in the sulfidation and were kept under this mixture. Spectra were taken near the K edges of Co and Mo.

The radial distribution function (RDF) of the Co EXAFS in the samples up to $\alpha = 0.44$ showed that no discrete Co phase was present. Only one single main peak at approximately 175 pm was observed in these samples. The sample with $\alpha = 0.72$ showed both RDF of the Co EXAFS and near-edge structure very similar to Co_9S_8.

The RDF of the Mo EXAFS of MoS_2 and the sulfided CoMo/γ-Al_2O_3 samples were very similar. They showed two main peaks at approximately 192 and 280 pm. These peaks correspond to backscattering from sulfur and molybdenum, respectively. The number of S and Mo neighbors (N_S and N_{Mo}, respectively) of Mo in the sulfided samples was estimated from the height and position

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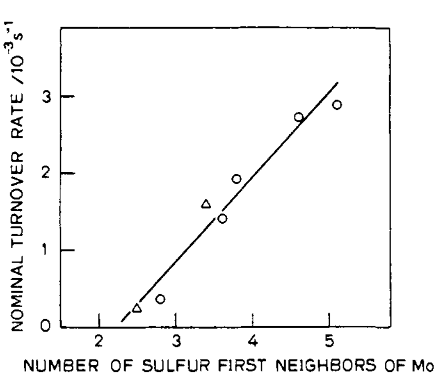

Figure 2. Correlation between NTR and N_S in CoMo/γ-Al_2O_3 samples prepared by (O) incipient wetness impregnation and (△) bulk impregnation.

of the peaks in the RDF. Effective phase shifts and amplitudes were estimated from the RDF of MoS_2.

Curve B in Figure 1 shows the dependence of N_S on the atomic Co/(Co + Mo) ratio. A "volcano" type curve similar to the NTR curve was also observed. Moreover, a linear correlation between NTR and N_S with a correlation factor of least-square fit equal to 0.98 is shown in Figure 2. This figure shows data for both series of catalysts. For example, there are two samples with $\alpha = 0.33$. The sample prepared by bulk impregnation has both lower activity and N_S values compared to the sample prepared by incipient wetness impregnation.

The number of nearest Mo neighbors of molybdenum in these samples was smaller compared to that of MoS_2 ($N_{Mo} = 6$). The value of N_{Mo} varied between 1.2 and 1.3 for both Mo/γ-Al_2O_3 samples and between 1.8 and 2.8 for the CoMo/γ-Al_2O_3 samples. This is in agreement with a very dispersed MoS_2-like phase.[8,10,11]

The dependence of N_S on Co loading can be understood in the following way: at $\alpha \leq 0.33$, Co interacts with the MoS_2-like phase, stabilizing this phase and thus increasing N_S. A "CoMoS" phase has been proposed by Topsøe et al.[12] to take into account this interaction. At large values of α, most of Co forms Co_9S_8. Thus, the stabilization role of Co is lost by the depletion of Co from the "CoMoS" phase.

A more detailed description of the structure and the effect of Co on the HDS activity of these sulfided CoMo/γ-Al_2O_3 will be published elsewhere.[13] It seems reasonable that as α increases, the sulfur binding energy of Mo increases until the maximum value of N_S is reached and then decreases as α is further increased. In their extensive work on the HDS activity of transition-metal sulfides, Pecoraro and Chianelli[14] recognize that there is a sulfur binding energy corresponding to a maximum HDS activity. Their result is expressed in a different way by the correlation between N_S and HDS activity proposed in this communication.

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Registry No. Thiophene, 110-02-1; cobalt, 7440-48-4; molybdenum, 7439-98-7; sulfur, 7704-34-9.

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Perfect Enzymes: Is the Equilibrium Constant between the Enzyme's Bound Species Unity?

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In an important study, Knowles and Albery[2,3] proposed an efficiency function to describe the effectiveness of a catalyst in accelerating a chemical reaction. The evolutionary improvement in the catalytic efficiency of enzymes can be separated into three broad stages in order of increasing difficulty: (1) "uniform binding", (2) "differential binding", and (3) "catalysis of an elementary step". The kinetics of reactions catalyzed by enzymes that have reached perfection with respect to one or more of the above three changes can be calculated by maximizing the efficiency function with respect to the same changes. One of the most interesting predictions from this calculation was that if an enzyme has reached perfection with respect to the first two changes above, the equilibrium constant between the enzyme's bound species is close to unity. This prediction has generated much interest and has been tested experimentally by Knowles and Albery[4-6] as well as by Benner.[7,8] However, the equation (eq 11 in this paper) that led to the above prediction is not general. The internal equilibrium constant can be a function of the external equilibrium constant and the intrinsic barrier of the catalytic step. The system that Knowles and Albery described is examined below.[9] Although the beginning part of the argument presented below overlaps with that given in the original study, a detailed description is given here for continuity and clarity.

The System. For the simple enzyme-catalyzed process shown

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} EP \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} E + P \tag{1}$$

the rate of the reaction, ν, is given by

$$\nu = k[E]_T \tag{2}$$

where $[E]_T$ is the total enzyme concentration and k is the overall rate constant. Assuming steady-state concentrations for E, S, ES, and EP and assuming P is consumed rapidly in a subsequent reaction, so that there is no significant back reaction, the observed rate constant, k, is given by

$$k = 1/\{1/k_1^s + 1/k_2 + 1/k_3 + 1/(K_1^s k_2) + 1/(K_2 k_3) + 1/(K_1^s K_2 k_3)\} \tag{3}$$

where $k_1^s = k_1[S]_0$, $K_1^s = K_1[S]_0$, $K_1 = k_1/k_{-1}$ and $[S]_0$ is some constant physiological concentration of the substrate.

Uniform Binding. In uniform binding, the positions of all the internal states are shifted energetically up or down by the same amount relative to the external framework. A mathematical equation that expresses the condition for optimal k attainable by uniform binding is derived below.[10]

From thermodynamic considerations:

$$K_e = K_1 K_2 K_3 \tag{4}$$

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(10) The efficiency function (E_f) is equal to k multiplied by some constant that is independent of enzyme evolution.[2] Therefore the condition for maximum k is equivalent to the condition for maximum E_f.

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