

Methanation and HDS Catalysts Based on Sulfided, Bimetallic Clusters

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INTRODUCTION

Environmental concerns have led to an increased interest in hydrotreating catalysts, i.e. catalysts for hydrodesulfurization (HDS) or hydrodenitrogenation (HDN) (1-3). Although HDS may be catalyzed by bulk or supported MoS_2 and related sulfides, the most effective catalysts are those derived from "sulfided cobalt molybdate" supported on Al_2O_3 . These catalysts are prepared conventionally by impregnating the alumina support with solutions of molybdate ions and cobaltous ions. The impregnated support is then calcined to convert the adsorbed species to their respective oxides. The supported metal oxides are then converted to sulfides ("sulfided") with a mixture of H_2 and H_2S (or the feed stream itself) at temperatures in the range 300-400°C. Alternate promoters, e.g. Ni and Fe, may be used in the place of Co, but the resulting catalysts usually show a lower activity.

Despite intensive study, the exact nature of the active "CoMoS" phase is still uncertain, and hence the role of the Co promoter and the exact mechanism of HDS remain obscure. XPS and Mössbauer Emission Spectroscopy has been used to show that a "CoMoS" phase, distinct from Co_9S_8 or MoS_2 , is present and that the activity of the catalyst parallels the amount of this CoMoS phase present (4).

More recently, EXAFS has been used to study these cobalt molybdate catalysts in both the oxidized and sulfided states (5-11). The most popular model has Co-atoms coordinated to sulfur at the edges of basal planes of small (10-30Å) crystallites of MoS_2 (see Figure 1). The EXAFS results also are best fit by assuming the MoS_2 rafts are essentially two dimensional.

The promoter metal, Co or Ni, is intimately involved in the active site. The activities of the promoted MoS_2 can be 10^2 that of unpromoted MoS_2 , usually with the Co/Mo ratio ≈ 1.0 (12). It is therefore surprising that Co-Mo vectors have never been identified in the EXAFS studies of these catalysts. Therefore, the location of the Co relative to the Mo in these CoMoS catalysts is still uncertain. New approaches are necessary to probe the nature of the active site of these sulfided catalysts.

MOLECULAR MODELS OF PROMOTED MoS_2 PHASES

We have prepared discrete, molecular clusters which may serve as models for the active sites in promoted molybdenum sulfide catalysts (13-15). These clusters are composed of one metal each from the sets, {Mo,W} and {Fe,Co,Ni}; they contain sulfur in the cluster framework and organic ligands, e.g. carbonyls, cyclopentadienyls (Cp), etc. on the periphery of the cluster. The structures of representative clusters are shown in Figure 2.

These clusters have been deposited on oxide supports by dissolving the molecular cluster in an appropriate solvent, e.g. CH_2Cl_2 , and then adding the calcined support. With the low loadings (1% total

metal) employed in this study, the clusters are quantitatively adsorbed onto the support from solution. The solvent is then removed and the solid dried under vacuum. The supported clusters are then subjected to temperature-programmed decomposition (TPDE) in a stream of H₂ or He. The exit gas stream is analyzed for CO, CO₂, hydrocarbons, etc. by GC and GC/MS. Figure 3 shows a typical TPDE curve for the MoFeS cluster, 1, (Figure 2).

In the TPDE of cluster 1 on γ -Al₂O₃, ca. 5 CO per cluster are lost at 100°C, and heating to 400°C causes gradual loss of one additional CO/cluster. In addition, small quantities of Me₂S, CH₄, and CO₂ are lost between 150°C and 400°C. The average composition of the remaining surface species is found to be C₅Mo₂Fe₂S_{1.8}O_xH_y (the oxygen and hydrogen are uncertain since surface OH groups may contribute to the formation of CO₂, CH₄, etc.). Similar results are obtained for all the clusters investigated. The high carbon retention observed even with TPDE in flowing H₂ is attributed to carbide formation.

The facile loss of CO by the supported cluster stands in contrast to the thermal stability of the pure compound which is stable to >250°C. Therefore, there must be a strong support-cluster interaction which facilitates loss of CO from the adsorbed cluster.

Figure 4 shows the IR spectrum of pure cluster 1 and spectra of the cluster adsorbed on γ -Al₂O₃. The bridging CO band at 1795 cm⁻¹ is most strongly perturbed, suggesting that the cluster is bound to a Lewis acid site (e.g. Al⁺³) on the surface through the bridging CO, normally the most basic CO on the cluster (16). As the adsorbed cluster is heated to 110°C, the intensities of the CO bands diminish and finally disappear as the CO is lost. No new CO peaks are observed during the TPDE and no new CO bands appear if the decarbonylated cluster is placed in an atm. of CO at 25°C. Since the TPDE shows the loss of only 5 of the 8 CO-groups under these conditions, the remaining 3 CO's must be either dissociatively adsorbed or must be bonded in a multi-hapto manner with very low frequency CO-stretching vibrations.

The Mössbauer parameters (Table 1) suggest that the Fe in the cluster is oxidized during TPDE from Fe⁰ to Fe⁺³.

Table 1. Mössbauer Spectral Parameters (mms⁻¹)

	<u>Pure 1</u>	<u>MoFeSA-01</u> *	<u>Used Cat.</u>
I.S.	-0.01	0.38	0.43
ΔE_Q	0.78	0.84	0.84

* 1% loading of cluster 1 on γ -Al₂O₃

METHANATION CATALYSIS

Clusters 1 and 3 (1% total metal loading) on γ -Al₂O₃ were pre-treated in flowing H₂ (1 atm.) at 400°C for 6-12 hr. The resulting catalysts are labelled MoFeSA-01 and MoCoSA-01. The methanation activity of these catalysts was determined in the temperature range 250°-500°C with total pressures from 30 psi to 300 psi. The feed stream composition was 3:1 or 1:1 H₂:CO. A differential flow reactor

with GHSV \approx 2500 hr⁻¹ and CO conversions \leq 2% was employed for kinetic measurements.

A break-in period of several hours was observed during which time the methanation activity was nearly zero. Methane then appears and the activity goes through a peak and then reaches steady state behavior which remains constant for days if the temperature is \geq 300°C. At lower temperatures, a very gradual decrease in activity, presumably due to coking, was observed.

Arrhenius plots of the formal turnover frequency, N_f , vs. $1/T$ are shown in Figure 5 (N_f is defined as moles of CH₄/mole of cluster precursor/sec). Apparent activation energies are approximately 22 kcal/mol for MoCoSA-01 and 26 kcal/mol for MoFeSA-01.

The methanation reaction over MoFeSA-01 seems to follow Langmuir-Hinshelwood kinetics with the rate expression (T = 300°C, P in psi):

$$N_f (\text{s}^{-1}) = \frac{(4.0 \times 10^{-6}) P_{\text{H}_2} P_{\text{CO}}}{\{1 + (0.018 P_{\text{H}_2})^{1/2} + 0.143 P_{\text{CO}}\}^2}$$

This rate law is consistent with a CO dissociative mechanism in which CH(ads.) + H(ads.) \rightarrow CH₂(ads.) is the rate limiting step and all previous steps are in steady-state equilibrium.

The product distributions are plotted in Figure 6 for MoFeSA-01 and MoCoSA-01 under typical conditions. Selectivity for methane ranges from 90-98% depending on the temperature and pressure. Higher temperatures and lower pressures favor methane formation. Small amounts of C₂ and C₃ alkanes and olefins are formed, the latter are in greater abundance with the MoCoSA-01 catalyst. At higher pressures, dimethyl ether constitutes 2-4 mole % of the product stream, but methanol has never been detected.

It should be pointed out that the selectivities of MoFeSA-01 and MoCoSA-01 differ from Mo/Al₂O₃, MoS₂, Fe/Al₂O₃ or Co/Al₂O₃ which all produce less CH₄ and more C₂-C₅ hydrocarbons in a Schultz-Flory distribution. This result suggests that the clusters are not fragmenting and re-aggregating into larger metal (or metal sulfide) crystallites. After reaction, SEM and STEM also failed to reveal any particles $>10\text{\AA}$, the resolving power of the microscope under the conditions used. The Fe I.S. (Table 1) increases somewhat after time on stream, possibly indicating that Fe(III) is being reduced somewhat.

HDS CATALYSIS

The activity of MoFeSA-01 and MoCoSA-01 toward catalysis of thiophene HDS has been determined in a differential flow reactor at GHSV \approx 3000 hr⁻¹ and thiophene conversions of 1-2% (conditions: 2.8 mol % thiophene in 1 atm. H₂ at 250°C-350°C). The catalysts were reduced in H₂ at 400°C and then presulfided with H₂S/H₂ or directly with the thiophene/H₂ feed stream. No difference in catalytic behavior due to the different pretreatments was observed. Catalytic activity was immediately established, in contrast to the methanation activity. Steady state selectivity was observed after 1 hr. on stream and no diminution of catalytic activity was observed after 3-4 days of operation.

Figure 7 is an Arrhenius plot of the formal turnover frequencies (moles converted/mole cluster/sec) for total thiophene conversion and for C₄ and C₃ products. Table 2 compares turnover frequencies and product slates of a clean Mo (100) surface, several cobalt molybdate catalysts with high metal loading, and the MoFeSA-01 and MoCoSA-01 (1% total metal loading) catalysts described above.

Table 2. Comparison of Activities and Selectivities of Various Catalysts for Thiophene HDS.

catalyst	$N_f(\text{sec}^{-1})$	T°C	BuH				
Mo(100) ^a	.02-.12	340	8	53	14	19	-
Mo14-Co4 ^{b,c}	0.05	420	-	NOT GIVEN	-	-	-
Mo8-Co3 ^d	0.03	?		"butenes"			
Mo13-Co7 ^e	0.05	290	10	-	29	62	-
MoCoSA-01	0.04	340	1	14	17	26	41
MoFeSA-01	0.01	340	2	13	18	25	41
				(11)	(19)	(27) ^f	

a) J. Catal. 1984, 88, 546. Butadiene (6%) also formed.

b) numbers refer to %Mo and %Co on $\gamma\text{-Al}_2\text{O}_3$.

c) J. Catal. 1984, 87, 292.

d) ibid. 1984, 85, 44.

e) ibid. 1984, 86, 55.

f) equilibrium ratios of butenes.

Two features are especially noteworthy. First, the activity of the MoCoSA-01 catalyst is comparable to catalysts with much higher metal loadings when compared on a per mol of Mo basis. This is unusual for HDS catalysts because the first few % of metal occupies tetrahedral holes in the Al_2O_3 lattice and is not converted to sulfides during the sulfiding step in conventional HDS catalysts.

Second, the cluster catalysts produce a large fraction of propene. Thus a carbon-carbon bond has been totally cleaved by hydrogenolysis. To our knowledge, C-C bond hydrogenolysis without C=C bond hydrogenation is unprecedented. Methane and 1-5% C₂ hydrocarbons (mostly C₂H₄) are also produced, but technical difficulties have precluded our quantifying the methane. Presumably, the amount of methane is equal to the amount of propene.

CONCLUSIONS

Sulfided bimetallic clusters of early and late transition metals have been shown to be precursors for methanation and HDS catalysts when supported on Al_2O_3 . The activities and selectivities in CO hydrogenation closely resembles other metals in very highly dispersed states on Al_2O_3 . Thus, stable metal clusters are not likely to be useful Fischer-Tropsch catalyst precursors.

However, these cluster species are exceptionally active in thiophene HDS and exhibit an unprecedented selectivity. Catalysts capable of simultaneously removing sulfur and cracking large molecules into smaller unsaturated fragments at relatively low temperatures could be especially useful for producing clean, low viscosity fluids from still bottoms and heavy coal liquids.

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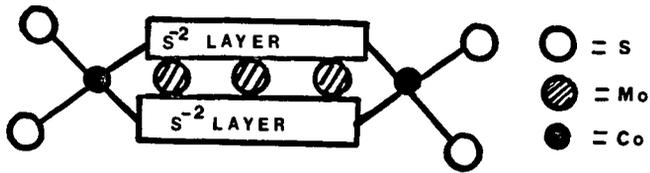


Figure 1. Proposed structure of "CoMoS" phase in promoted MoS₂ HDS catalysts.

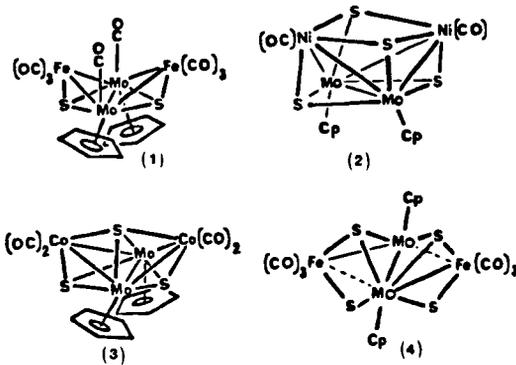


Figure 2. Structures of molecular models of promoted Mo-sulfide phases.

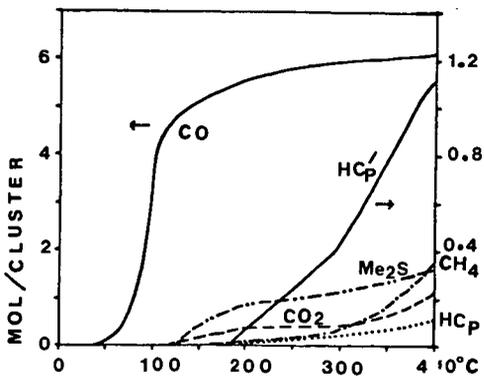


Figure 3. TPDE curves for cluster 1.

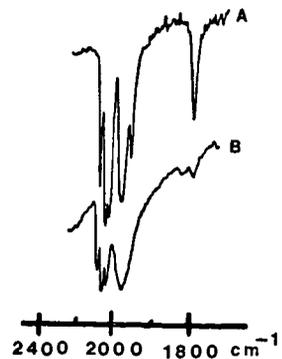


Figure 4. IR spectra of 1 in CH₂Cl₂ solution (A) and on Al₂O₃ (B).

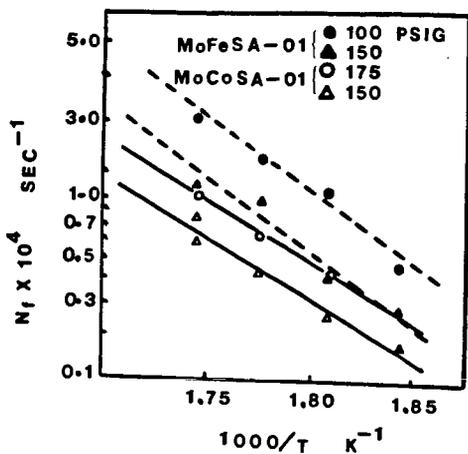


Figure 5. Arrhenius plots for CO hydrogenation with cluster catalysts.

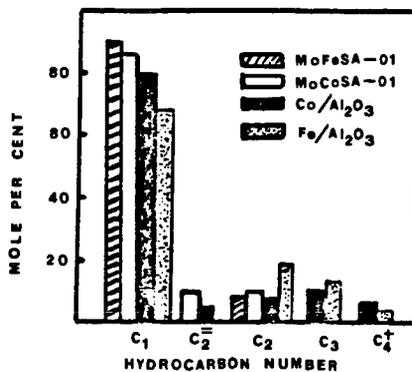


Figure 6. Product distribution in CO hydrogenation with various catalysts.

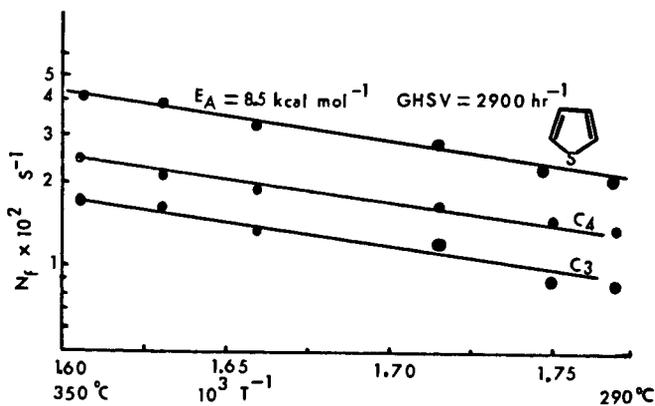


Figure 7. Arrhenius plots for thiophene HDS catalyzed by MoCoSA-01.