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Hydrodesulfurization Activity and Electronic Properties of Molybdenum Sulfide Catalyst*

A. AOSHIMA AND H. WISE

Solid-State Catalysis Laboratory, Stanford Research Institute,
Menlo Park, California 94025

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The relationship between the defect structure of molybdenum sulfide and its hydrodesulfurization (HDS) activity is examined. The S^{2-} ion vacancy concentration of the catalyst is adjusted by pretreatment in H_2 or H_2S and monitored by electrical conductivity measurements. Exposure of the catalyst to pulses of butyl mercaptan and hydrogen allows determination of the conversion rate and product distribution as a function of the electronic defect structures of the catalyst. The results demonstrate the existence of a "window" in catalyst composition for optimum HDS performance. During catalytic reaction, interface charge transfer is observed with gradual modification of the electronic properties of the catalyst and changes of its catalytic activity for HDS. The results indicate a close relationship between the density of S^{2-} ion vacancies and catalyst performance. The mechanism of catalytic HDS is examined in terms of the defect structure of the solid.

INTRODUCTION

Hydrodesulfurization catalysts of industrial importance, containing molybdenum or tungsten compounds as the active phase on an alumina support, exhibit gradual decline in performance generally associated with changes in surface area, pore structure, and the deposition of carbon- and metal-containing compounds. To elucidate those properties of a hydrodesulfurization (HDS) catalyst that provide sustained activity and high specificity, we have initiated our studies with molybdenum sulfide. This compound has been shown to exhibit similar HDS properties to that of sulfided molybdenum oxide catalysts (*1*), and is present in a number of catalyst formulations employed industrially for sulfur removal from crude oil by catalytic hydrotreating (*2*, *3*).

The existence of electronic charge transfer at the catalyst/reactant interface was demonstrable in experiments in which under continuous flow conditions prolonged exposure of the catalyst crystal to the reactants (hydrogen and organo-sulfur compound) caused a progressive decay in catalytic conversion accompanied by pronounced changes in the electrical conductivity of the crystal. To study these phenomena in more detail, a pulsed-flow reactor was employed which allowed the introduction of single pulses of reactant pulses and examination of the gradual changes in catalytic and electronic properties.

EXPERIMENTAL DETAILS

Catalyst

The source material was a large crystal of the naturally occurring mineral molybdenite (kindly provided by the Climax Molybdenum Co. of Michigan; hexagonal crystal structure C7). A small single crystal of this material was cut to typical dimensions of about $1 \times 1 \times 0.06$ cm^3 and mounted in a cylindrical reactor made of quartz. For the electrical conductivity measurements by the four-probe technique (*4*), contacts were made with the crystal

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by means of tungsten clips attached to glass-coated tungsten leadthroughs in a graded seal. Also by this means mechanical support was provided for the crystal. The room temperature resistivity of the individual crystals used in the catalytic studies was found to lie between 8 and 10 Ω cm, a value comparable to that reported for molybdenum sulfide (*5*). Analysis of the crystal by emission spectroscopy indicated the presence of several impurities as shown in Table 1.

Apparatus

The pulse reactor was of conventional design. A stream of hydrogen gas (vol flow rate = 2 cc/sec NTP) was passed continuously through the reactor (36 cc in volume) housing the catalyst crystal and surrounded by a furnace maintained at a specified temperature. Into this stream of hydrogen, pulses of gaseous reactant (C_4H_9SH) could be injected at the desired time intervals. A special device was assembled to vaporize the butyl mercaptan into the feed stream. By adjusting the liquid feed rate and the carrier gas flow rate, metered through flowmeters, we were able to obtain specified concentrations of reactant. In most of the experiments reported below, the volumetric ratio of H_2/C_4H_9SH ranged from 70 to 80.

In a typical pulse experiment an aliquot of the prevaporized gas mixture was injected into the reactor. A typical electrical response of the catalyst to the reactant pulse is shown in Fig. 1. After passage over the catalyst the gas mixture entered the gc column for product analysis. Provisions were made in the experimental configuration to sample the inlet and outlet compositions. For chromatographic analysis of butene, butane, hydrogen sulfide, and butyl mercaptan, a Porapak R column was found suitable (6 ft × 0.25 in.). The various components could be separated by temperature programming of the gc column in the range from 358 to 483 K. For the purpose of catalyst pretreatment, a special gas line was provided to admit hydrogen, helium, or hydrogen sulfide to the reactor with a bypass of the gc system.

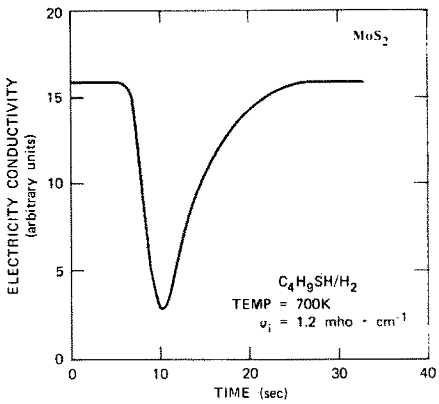

FIG. 1. Electrical response of MoS_2-crystal to passage of reactant pulse ($H_2/C_4H_9SH = 77$).

TABLE 1
IMPURITY CONTENT OF MOLYBDENUM SULFIDE CRYSTAL BY EMISSION SPECTROSCOPIC ANALYSIS

Element	Concn[a] (wt%)
Si	0.15
Al	0.02
Ca	0.015
Pb	0.04
Mg	0.015
Ni	0.003
Cu	0.001
Ag	0.002

[a] Reported as oxides of element.

EXPERIMENTAL RESULTS

Changes in the electrical properties of the catalyst crystal could be monitored during both the pretreatment procedure and the catalytic experiments. For initial activation of the catalyst for HDS the molybdenum sulfide was exposed to hydrogen. The electrical measurements demonstrated that temperatures in excess of 900 K were required to attain a measurable rate of sulfur removal from the crystal, accompanied by an increase in conductivity due to electron injection, such as:

$$S^{2-} + H_2 \rightarrow H_2S + 2e + V_a \qquad (1)$$

or

$$S^{2-} + H \rightarrow SH^- + e + V_a,$$

where e represents an electron and V_a an anion vacancy.†

From the change in conductivity with exposure to 1 atm of hydrogen and the known carrier mobility (*5*), the electron injection rate into the crystal was calculated to be of the order of 10^{14} electrons/cm^3 sec at 980 K. Just the opposite electrical effect was brought about by treatment of the catalyst in a H_2S environment. Under these conditions a decrease in electron density was observed due to electron capture by a reaction such as

$$H_2S + 2e + V_a \rightarrow H_2 + S^{2-}. \qquad (2)$$

This sulfidization of the catalyst was observed to take place at much lower temperatures, generally between 700 and 750 K. The reaction proceeds at a much higher rate than reduction by hydrogen, especially on a catalyst that exhibited a high density of S^{2-} ion vacancies introduced into the crystal by previous reduction in hydrogen. In a typical H_2S-pretreatment experiment at 700 K, the measured electron capture rate amounted to 2×10^{15} to 10^{16} electrons/cm^3 sec.

By these pretreatment procedures the defect structure of the catalyst could be adjusted and its effect on catalytic activity could be examined. The extent of exposure of the catalyst to H_2 or H_2S had a pronounced effect on catalytic activity as shown by the results presented in Fig. 2 in which we correlate the degree of conversion of butyl mercaptan with reactor temperature and electrical conductivity of the catalyst.

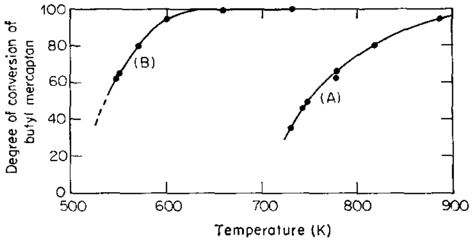

Fig. 2. HDS activity of catalyst crystal for different initial electrical conductivities. Reactant pulse: $H_2/C_4H_9SH = 77$; (A) initial conductivity = 3.6 mho cm^{-1}; (B) initial conductivity = 0.35 mho cm^{-1}, measured at 700 K.

Two curves are shown. One of them (curve A) refers to a catalyst of high electrical conductivity (3.6 mho cm^{-1}) attained by prolonged exposure to hydrogen; the other (curve B), to a catalyst of much lower electrical conductivity (0.35 mho cm^{-1}) attained by pretreatment in hydrogen sulfide. It is apparent that the latter pretreatment has resulted in a most active HDS catalyst with high conversion detected at relatively low temperatures. The results of additional catalytic measurements are shown in Fig. 3 in which we examine the temperature required for 80 vol% conversion of butyl mercaptan as a function of the electrical conductivity of the catalyst. The data indicate that a decrease in electrical conductivity, associated with a dimunition in S^{2-} ion vacancies [Eq. (2)] brings about a marked increase in HDS activity.

Also the defect structure of the catalyst markedly affected the product distribution. Under condition of high electrical conductivity butene was the major hydrocarbon product. On the other hand butane predominated at low conductivity (Fig. 4).

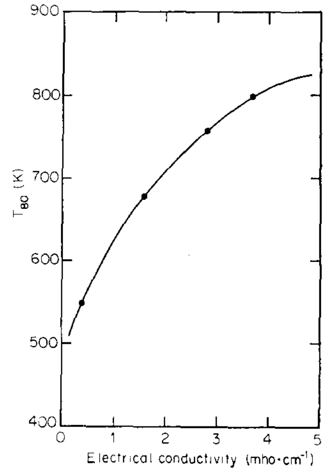

Fig. 3. Temperature for 80 vol% conversion as a function of electrical conductivity of crystal measured at 700 K. Reactant pulse $H_2/C_4H_9SH = 77$.

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† It is not certain whether molecular hydrogen or chemisorbed hydrogen atoms are involved in the reduction process. Activated chemisorption of hydrogen has been reported (*6*).

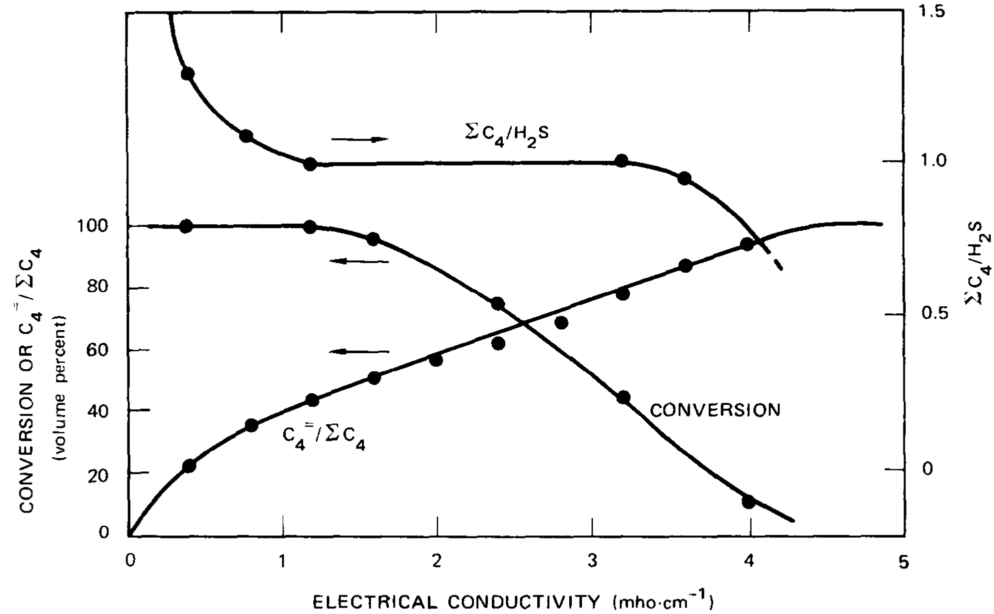

FIG. 4. Variation in HDS activity and product distribution with catalyst crystal conductivity at 700 K.

Over a range of catalyst compositions ($1.2 < \sigma < 3$ mho cm^{-1}) the product analysis indicated a satisfactory mass balance in terms of carbon and sulfur species. Thus as shown in Fig. 4 the ratio of total C_4-compounds to H_2S formed was found to be near unity ($\Sigma C_4/H_2S = 1.00 \pm 0.05$), indicative of the prevailing reaction stoichiometries

$$C_4H_9SH \rightarrow C_4H_8 + H_2S,$$
$$C_4H_9SH + H_2 \rightarrow C_4H_{10} + H_2S.$$

However for a catalyst crystal reduced in hydrogen sufficiently to exhibit a high electrical conductivity ($\sigma > 3$ mho cm^{-1}), due to a large excess of S^{2-} vacancies, the product distribution indicated a deficiency in C_4-compounds formed relative to butyl mercaptan consumed. Under these conditions the ratio $\Sigma C_4/H_2S < 1$ (Fig. 4). Conversely for a catalyst sulfided by prolonged exposure to hydrogen sulfide and exhibiting low electrical conductivity ($\sigma < 1$ mho cm^{-1}, Fig. 4), the ratio $\Sigma C_4/H_2S$ tended to be greater than unity due to a deficiency of H_2S in the product gas (Fig. 4). Under certain conditions the complete absence of H_2S was reported in HDS studies on an alumina-supported catalyst containing the sulfided mixed oxides of molybdenum and cobalt (*7*). In addition, we noted at temperatures in excess of 750 K, hydrocarbon cracking products in admixture with butene (Fig. 5). These by-products were composed predominantly of methane, ethylene, propane, and propylene. On the basis of the results presented it becomes apparent that the defect structure of the catalyst controls HDS activity in terms of (1) total conversion, (2) hydrocarbon product distribution, (butene vs butane) and (3) hydrocarbon-to-hydrogen sulfide ratio, i.e., surface accumulation of carbon and sulfur species.

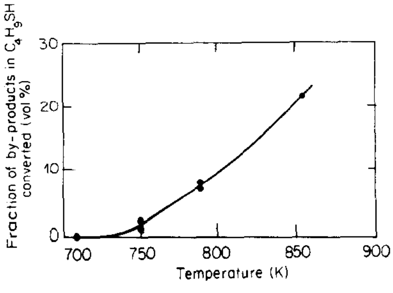

FIG. 5. By-product formation during HDS of C_4H_9SH.

DISCUSSION

The important role played by the electronic properties of molybdenum sulfide during catalytic HDS of butyl mercaptan is amply demonstrated by the experimental measurements just presented. In particular the results point to a "window" in the composition range of the solid, corresponding to electrical conductivities of $1 < \sigma < 3$ mho cm^{-1}, in which the properties of the catalyst are most favorable in terms of activity, specificity, and stability.‡ With reference to Fig. 4, it can be seen that the Mo/S can be adjusted by suitable pretreatment to yield a catalyst exhibiting high conversion as well as butane and H_2S formation. But composition regions exist at which under reaction conditions the catalyst tends to "poison" by accumulating on its surface some of the sulfur involved in the HDS of butyl mercaptan, as manifested by the fact that $\Sigma C_4/H_2S > 1$ due to a deficiency of H_2S in the product stream.

Such a gradual modification of the catalyst properties during HDS is also demonstrated by changes in the electrical response of the catalyst resulting from intermittent exposure to pulses of C_4H_9SH. With a catalyst having initially a moderately high electrical conductivity ($\sigma = 2$ mho cm^{-1}), the HDS reaction is accompanied first by a conductivity decrease followed by a recovery to its original value—a process that is reproducible over several pulse injections. But a catalyst of lower initial electrical conductivity ($\sigma = 0.35$ mho cm^{-1}) exhibits an entirely different electrical response during passage of several pulses over the catalyst crystal. As shown in Fig. 6 the magnitude of the electrical response decreases with successive pulses. In addition the electrical conductivity does not return to its initial value after passage of the pulse and subsequent exposure to hydrogen for periods of time relatively long compared to the pulse duration. With each subsequent pulse the electron density of the catalyst remains at a level somewhat lower than its original value. It is apparent therefore that, with each pulse coming in contact with the catalyst, a gradual modification of its electronic properties occurs. This effect appears to be entirely due to the accumulation of a charged, nonreactive, sulfur-bearing intermediate species on the catalyst surface, most likely S^{2-} ions which may become part of the crystal lattice. Analysis of the gaseous products reveals that the ratio of $\Sigma C_4/H_2S$ (Table 2) is greater than unity in each of the pulses, indicative of a sulfur-deficient product distribution since the mass balance for the C_4-species is well within the experimental error. Thus the incompleteness in sulfur removal from the surface is exhibited both by the electrical measurements which show that the electron density does not return to its original level following the passage of a reactant pulse, and the chemical product composition, which indicates

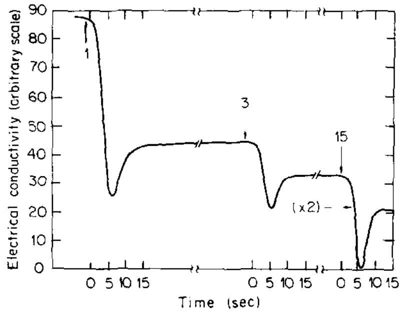

FIG. 6. Conductivity change of molybdenum sulfide crystal at 530 K during passage of reactant pulse.

TABLE 2

ELECTRICAL AND CATALYTIC PROPERTIES OF MOLYBDENUM SULFIDE CRYSTAL CATALYST DURING PULSED EXPOSURE TO BUTYL MERCAPTAN/HYDROGEN MIXTURE[a] AT 530 K

Pulse no.	Initial electron transfer rate (cm^3 sec)$^{-1}$ × 10^{-15}	Product distribution (vol basis) ($\Sigma C_4/H_2S$)
1	1.6	2.9
3	0.81	1.6
15	0.71	1.3

[a] $H_2/C_4H_9SH = 77$.

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‡ In terms of electron densities n_e(cm^{-3}) these conductivities correspond to $5.6 \times 10^{17} < n_e < 1.7 \times 10^{18}$ at 700 K.

a deficiency in H_2S relative to the total amount of butene and butane formed (or butyl mercaptan converted). Thus gradual "poisoning" of the catalyst may occur due to the retention of a sulfur species on the surface of a catalyst whose Mo/S is not carefully adjusted.

At the opposite end of electronic defect structure, namely at high electrical conductivity ($\sigma > 3.2$ mho cm^{-1}), the results indicate that the product distribution exhibits a H_2S excess ($\Sigma C_4/H_2S < 1$). This phenomenon is undoubtedly associated with deposition of a carbonaceous residue during HDS. In line with this conclusion it was found that reactivation of such a "carbon-poisoned" catalyst required pretreatment with H_2 at $T > 1000$ K followed by exposure to H_2S. Presumably the hydrogen pretreatment removed the carbonaceous residue. But at these high temperatures it caused removal of S^{2-} ions from the catalyst thereby making it more *n*-type in electronic behavior and low in activity (Fig. 4). Subsequent exposure to H_2S lowered the Mo/S ratio sufficiently to bring the catalyst into a more desirable operating mode.**

The results presented indicate further that the formation of butene by HDS of butyl mercaptan is favored by a catalyst with a large number of S^{2-} ion vacancies, while butane formation occurs on a catalyst with fewer anion vacancies. Separate experiments on catalytic butene hydrogenation demonstrated that similar considerations apply to the olefin–alkane conversion. Only at low S^{2-} vacancies did the catalyst exhibit olefin hydrogenation activity. For interpretation of the experimental results we consider the following reaction sequence:

$$\tfrac{1}{2}\,H_2 \rightleftarrows H^{\cdot} \rightleftarrows H^+ + e, \qquad (3)$$

$$C_4H_9SH + e \rightleftarrows C_4H_9^{\cdot} + SH^-, \qquad (4)$$

$$C_4H_9^{\cdot} + H^+ \rightleftarrows C_4H_{10}^+, \qquad (5)$$

$$C_4H_{10}^+ + e \rightarrow C_4H_{10}, \qquad (6)$$

$$SH^- + H^{\cdot} \rightleftarrows H_2S + e. \qquad (7)$$

Activated chemisorption of hydrogen on molybdenum sulfide has been reported (*6*). Also scission of the C–S bond [Eq. (4)] has been observed in infrared studies of the chemisorption of alkyl mercaptans (*8*). Based on a model involving localized electronic levels at the surface (surface states), the equilibrium distribution of unoccupied (H^+) to occupied ($H^{\cdot}$) centers may be derived from Fermi–Dirac statistics (*9*). In terms of the relative location of the hydrogen surface state E_t with respect to the Fermi level at the surface E_F, the ratio of unoccupied to occupied centers is given by

$$(H^+)/(H^{\cdot}) = \exp[(E_t - E_F)/kT].$$

Thus reaction (3) would be favored by lowering of the Fermi level of the semiconductor catalyst, i.e., low electrical conductivity. From the data presented in Fig. 6, it may be concluded that reaction (7) is a slow step in the reaction sequence. Since it involves electron injection into the solid, a catalyst of low electrical conductivity would be beneficial in driving this reaction to the right side. The retention of a charged sulfur-bearing species by the catalyst under certain experimental conditions suggests additional reaction, such as

$$SH^- + e \rightarrow S^{2-} + H^{\cdot}, \qquad (8)$$

where the S^{2-} ion may become incorporated into the molybdenum sulfide lattice. As we have noted earlier, removal of lattice S^{2-} ions by reaction with hydrogen is a slow process at the experimental temperatures employed during HDS ($T < 800$ K).

For a catalyst exhibiting high electrical conductivity, electron transfer from hydrogen to the catalyst [Eq. (3)] becomes less favorable due to the relatively high Fermi energy level, and in the absence of chemisorbed hydrogen, proton addition to the butyl radical [Eq. (5)] may possibly be replaced by hydrogen abstraction:

$$C_4H_9^{\cdot} \rightarrow C_4H_8 + H^{\cdot}. \qquad (9)$$

Thus the differences in catalytic behavior at the two ends of the conductivity range are considered to be due to the availability

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** Exposure to oxygen at 800 K and resulfiding of the catalyst with H_2S/H_2 similarly restored the catalyst activity.

(or lack thereof) of surface-sorbed hydrogen, a parameter controlled by the electronic properties of the catalyst.

We may conclude therefore, that a molybdenum sulfide catalyst having a small number of *n*-type defects represents the preferred catalyst for HDS and olefin hydrogenation. One may identify the *n*-type electronic structure with the presence of Mo^{3+} impurity levels or S^{2-} vacancies in the crystal. In line with such a solid-state model one would hypothesize that the known beneficial effects resulting from the addition of Co^{2+} to MoS_2, as employed in a commercial HDS catalyst system, are due to the promotion of *p*-type conductivity, i.e., cation vacancies. Work is in progress to elucidate the role of such defect centers in the HDS activity of molybdenum sulfide.

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