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Hydrodesulfurization Activity and Defect Structure of Co–Mo Sulfide Catalyst

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To elucidate the effect of cobalt on the hydrodesulfurization (HDS) activity of molybdenum-sulfide catalysts, experimental studies have been made with a single crystal of MoS_2 doped with Co^{2+}. From electrical conductance and Hall coefficient measurements it was determined that the addition of Co^{2+} (<0.1 mole%) caused a change from n-type to p-type conductivity on the MoS_2. Without the foreign cation additive, the MoS_2 catalyst exhibited a range of catalytic properties for the HDS of butyl mercaptan which varied with the density of S^{2-} anion vacancies. But the Co^{2+}-doped catalyst was found to be (1) stable to sulfiding or reduction on exposure to reactants, (2) catalytically active for the production of butane and hydrogen sulfide, and (3) relatively constant for reactant conversion and product distribution. Kinetic analysis showed that the HDS activity is proportional to hole carrier density.

INTRODUCTION

The demand for low-sulfur fuels has placed renewed emphasis on the development of efficient hydrodesulfurization (HDS) catalysts for industrial applications. Of special importance are the alumina-supported catalysts containing molybdenum or tungsten compounds with cobalt and nickel as additives. In the interpretation of the role played by the additives, several solid-state models are currently under discussion. One involves the formation of Mo^{3+} and W^{3+} cations in the sulfide crystallite adjacent to vacancies located at crystal edges and promoted by intercalation of the additive ions (*1*). The other model is based on the observation that Co^{2+} tends to form a cobalt aluminate surface spinel and tends to stabilize the Mo^{4+} sites octahedrally coordinated in a layer on the surface of the support (*2*). Also the intercalation of Co^{2+} in the molybdenum sulfide layer structure has been suggested in an interpretation of the promoting effect of cobalt (*3*). To examine in greater detail the role played by cobalt addition to MoS_2 we have used the experimental approach previously described in which a single crystal of molybdenite is employed as the catalyst (*4*) for HDS of a sulfur-containing compound, such as butyl mercaptan. Powdered molybdenum sulfide has been shown to exhibit HDS properties similar to those of sulfided molybdenum-oxide catalyst (*5*). However, the use of a single crystal allows simultaneous measurement of electronic and chemical properties of the catalyst during reaction.

In the case of MoS_2, measurement of electronic properties is of particular interest since this compound semiconductor can exhibit both excess and defect conductivity (n and p type), and deviations from stoichiometric composition ($Mo^{4+}/S^{2-} \lesssim \frac{1}{2}$) can be established from electrical properties. Similarly "controlled conductivity,"

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as suggested by Verwey (*6*), can result from the incorporation of foreign ions. Thus the introduction of Co^{2+} or S^{2-} into MoS_2 will favor the formation of cation vacancies and hole carriers (p-type conductivity). On the other hand, the removal of S^{2-} anions from MoS_2 will lead to electron injection (n-type conductivity) and the formation of anion vacancies. Thus the electrical conductivity and the type of electronic majority carrier in MoS_2 can be controlled by the addition or removal of "impurity" ions. The objective of this research is to relate the defect structure of MoS_2 to its catalytic properties as manifested in the HDS of butylmercaptan.

EXPERIMENTAL DETAILS

Catalyst

A small single crystal (typical dimensions, $1 \times 1 \times 0.06$ cm) was cut from a large crystal of the naturally occurring mineral molybdenite[1] (hexagonal crystal structure C7). It was mounted in a quartz reactor provided with four glass-coated platinum leadthroughs for electrical contact with the crystal and electrical conductivity measurements by the four-probe technique (*7*). Hall coefficient determinations (*8*) at room temperature demonstrated n-type conductivity for the freshly cleaved crystal of molybdenite. The introduction of Co^{2+} was achieved by dipping the crystal in an aqueous solution of $Co(NO_3)_2$ (0.1 *M*) followed by evaporation of the solvent in a vacuum oven at 325 K. Subsequently, the crystal was placed in the quartz reactor and heated in a helium stream to 900 K before exposure to a hydrogen stream at 880 K. Incorporation of Co^{2+} into the crystal was facilitated by heating the doped crystal in He for various time intervals. The doping process was monitored by electrical conductivity and Hall coefficient studies (Table 1). Based on the electrical conductivity data we estimate a doping level of 10 to 100 ppm.

[1] The molybdenite crystal was kindly provided by the Climax Molybdenum Company of Michigan.

TABLE 1

Properties of Co^{2+}-Doped MoS_2 Crystal

Treatment	Electrical conductivity at 300 K ($mho \cdot cm^{-1}$)	Electronic majority carrier
Before deposition of Co^{2+}	0.17	n Type[a]
After deposition of Co^{2+} and heating at 900 K for 18 hr in He	0.42	p Type[b]
After reduction in H_2 at 880 K	0.35	p Type[a]
After exposure to H_2S	0.47	p Type[b]

[a] Based on Hall coefficient measurement.

[b] Based on direction of conductivity change on exposure to butyl mercaptan or hydrogen sulfide (*4*).

Apparatus

The reactor housing the catalyst crystal was so designed to allow operation in the pulse mode or under continuous flow conditions. In the pulse mode a stream of hydrogen gas (volume flow rate = 2 ml/sec NTP) was passed continuously through the reactor (36 ml 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. Liquid butyl mercaptan was vaporized in a special device employing as a heating element a porcelain-encased wire resistor (Ohmite, 10 watt) covered with several layers of glass fiber. The liquid was displaced onto this heater from a mechanically driven syringe and vaporized into a carrier stream of hydrogen. By adjusting the liquid feed rate and the carrier gas flow rate, we were able to obtain specified concentrations of reactant. In most of the experiments 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. After passage over the catalyst it entered the gc column for product analysis. Provisions were made to bypass

the reactor for sample analysis of the inlet compositions. For chromatographic analysis of butenes, butane, hydrogen sulfide, and butyl mercaptan, a temperature programmed Poropak R column was employed.

Under continuous flow conditions the gas mixture of hydrogen and butyl mercaptan (volume ratio = 75/1) was passed through the reactor at a volumetric flow rate of 2 ml/sec (NTP). After passage over the catalyst, an aliquot of the product stream could be subjected to gc analysis. The experimental configuration permitted sampling of the reactor inlet and outlet gas mixtures.

For quantitative analysis of the reactant product distribution, the gc apparatus was calibrated for each component. Also for catalyst pretreatment, a special line was provided to admit H_2, He, or H_2S to the reactor with a bypass of the gc system.

EXPERIMENTAL RESULTS

Changes in the electrical properties of the catalyst crystal could be monitored during both the pretreatment procedure (H_2, or H_2S, or Co^{2+} doping) and the catalytic experiments. For initial activation of the catalyst for HDS the undoped molybdenum sulfide was reduced in hydrogen at 880 K. The electrical measurements demonstrated sulfur removal accompanied by an increase in conductivity due to electron (e) injection in accordance with:

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

TABLE 2

HDS of Butyl Mercaptan[a] Catalyzed by Molybdenum Sulfide at 700 K

Experiments	Electrical conductivity[b] (mho·cm^{-1}) (n type)	Total exposure (min)	Conversion (vol%)		$C_4^{2-}/\Sigma C_4$ (vol%)
			Initial	Final	
1	2.1	190	73	67	50
2	2.9	180	53	40	45
3	3.25	150	10	6	70

[a] H_2/C_4H_9SH = 77 (by volume).
[b] After various extents of reduction by H_2 at 880 K.

where V_a represents an anion vacancy. Just the opposite electrical effect was brought about by treatment of a sulfur-deficient catalyst ($Mo^{4+}/S^{2-} > \frac{1}{2}$) in a H_2S/H_2 environment at 880 K, i.e., establishment of a specified sulfur vapor pressure. Under these conditions a decrease in electron density was observed due to the reverse of reaction (1). However, once the stoichiometric composition was reached, further introduction of sulfur ions led to a conductivity increase caused by electronic hole carriers, in accordance with:

$$\tfrac{1}{2}S_2(MoS_2) \rightleftarrows S^{2-} + 2p + V_c. \qquad (2)$$

By these pretreatment procedures the defect structure of the catalyst could be adjusted and its effect on catalytic activity examined, since the layer structure of hexagonal MoS_2 favors rapid transport of ionic species within the lattice and equilibrium of bulk and surface properties. The extent of preexposure of the catalyst to H_2 (progressive extent of S^{2-} removal) had a pronounced effect on catalytic activity, as shown by the results presented in Table 2 in which we list the degree of conversion, the product distribution, and the electrical conductivity of the catalyst. The conversion data indicate that a catalyst of relatively low conductivity, representative of few S^{2-} ion vacancies, exhibits high and prolonged activity for HDS of C_4H_9SH over several hours of operation at 700 K. However, an increase in S^{2-} ion vacancies, brought about by pretreatment of the catalyst in H_2 at 920 K, resulted in a marked decrease in conversion rate accompanied by a higher proportion of butene in the product stream (Table 2). In addition, a gradual decay in catalyst activity with exposure time was observed, particularly for the catalyst highly deficient in S^{2-} anions (high n-type conductivity).

Variations of the hydrogen concentration in the feed stream demonstrated a marked influence of the H_2/C_4H_9SH ratio on conversion rate, product distribution, and

TABLE 3

Effect of Hydrogen on HDS of Butyl Mercaptan Catalyzed by Molybdenum Sulfide[a] at 700 K

H_2/C_4H_9SH (by vol)	Total exposure (min)	Conversion (vol%)		$C_4^{2-}/\sum C_4$ (vol%)	$\sum C_4/H_2S$ (by vol)
		Initial	Final		
77	190	73	67	50	1.0
15	210	20	13	62	1.45
3	205	5	2	70	1.6
0	90	0.7	0.1	—	—

[a] Initial electrical conductivity = 2.1 mho·cm^{-1} (n type).

activity decay (Table 3). Of interest is the relative growth of olefinic C_4 compounds (C_4^{2-}) relative to butane (C_4) with lowering of the H_2/C_4H_9SH ratio. This change in distribution of the hydrogen products was accompanied by retention of sulfur on the catalyst surface, as evidenced by the increase in the $\sum C_4/H_2S$ ratio (Table 3).

For the Co^{2+}-doped catalyst the fractional conversion of butyl mercaptan over a range of temperatures is summarized in Fig. 1. Contrary to the undoped catalyst, pretreatment in H_2S/H_2 mixtures (σ_{700} = 0.44 mho·cm^{-1}) and pretreatment in H_2(σ_{700} = 0.38 mho·cm^{-1}), under conditions similar to those employed for the undoped catalyst, causes only small changes in electronic and catalytic properties (Table 4). In addition, the HDS of C_4H_9SH yields only butane as a hydrocarbon product and the ratio of C_4H_{10}/H_2S remains close to unity. These observations are in marked contrast to the n-type material, where the introduction of S^{2-} ion vacancies into MoS_2 (high n-type conductivity) causes a marked decrease in total conversion and the formation of butene as the predominant product (Table 2).

DISCUSSION

The MoS_2/Co^{2+} catalyst exhibits catalytic properties that are markedly different from those observed in the absence of cobalt additive. Most striking is the ob-

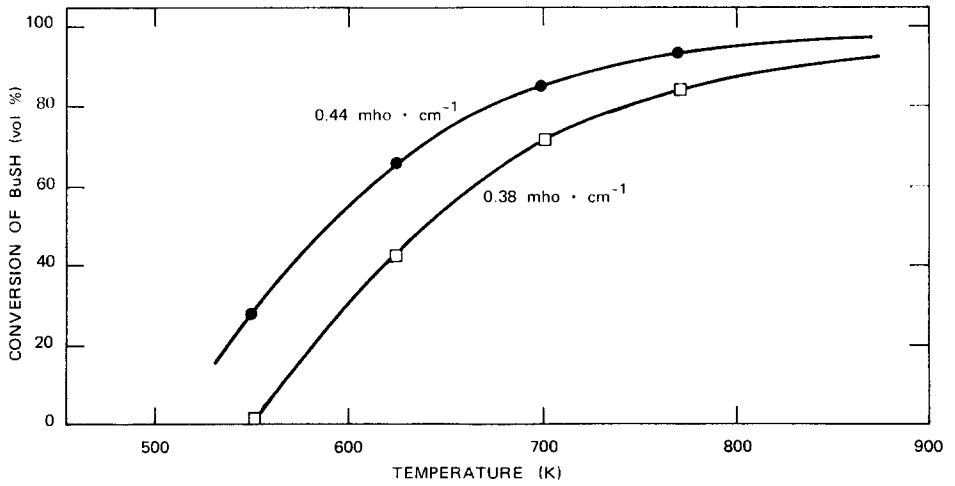

FIG. 1. HDS activity of MoS_2/Co catalyst (H_2/C_4H_9SH = 77): (●) after exposure to H_2S/H_2 mixture (cf. Table 1), and (□) after exposure to H_2 (cf. Table 1).

TABLE 4

HDS Activity and Product Distribution at 700 K[a]

Catalyst	Electrical conductivity (mho·cm^{-1})	Conversion (vol%)	Butane specificity (vol%)
MoS_2	2.1	70	50
	3.3	8	30
$MoS_2(Co^{2+})$	0.44	87	100
	0.38	68	100

[a] H_2/C_4H_9SH = 77 vol%.

servation that during prolonged exposure to reactant feed (H_2/C_4H_9SH = 77 vol%) the cobalt-promoted catalyst exhibits relatively constant activity in terms of total conversion and product distribution. Second, the products formed from the HDS reaction of butyl mercaptan are butane and H_2S, without any measurable amounts of butene. The formation of alkanes may result from rapid olefin hydrogenation (*9*), a reaction strongly catalyzed by the MoS_2/Co^{2+}. Third, the catalyst defect structure remains stable under the experimental conditions, i.e., no changes in conductivity occur during prolonged exposure to reactant gas, in contrast to our observations on an unpromoted sulfur-deficient catalyst sample.

Kinetic measurements indicate that the HDS reaction catalyzed by MoS_2/Co^{2+} is of first order with respect to C_4H_9SH in the presence of an excess of hydrogen [$40 < (H_2/C_4H_9SH) < 80$], as observed for a number of S compounds (*3*, *10–12*). Also from the variation in fractional conversion with reaction temperature, on the basis of a first-order analysis, we calculate an activation energy of 12 ± 1 kcal/mole.

To obtain a better understanding of the role of electronic carriers in HDS catalysis, we can calculate from the conductivity data the absolute electron or hole densities with the aid of published mobility data (*13*, *14*). Although the mobilities for holes are not as well established as those for electrons, the general trend of the HDS rate data as a function of carrier type and density is of interest. As shown in Fig. 2, an increase in electron carriers reduces catalyst activity, while an increase in hole carriers enhances the HDS rate. In this semilogarithmic correlation the $(BuSH)_i/(BuSH)_f$ represents the ratio of the initial to final concentrations of butyl mercaptan, whose logarithm is proportional to the first-order rate constant. Therefore the HDS reaction rate obeys a rate law of the form $-d(BuSH)/dt = k_p(BuSH)(n_p) = k_e(BuSH)/n_e$, with n_p indicating the hole density for the p-type MoS_2/Co^{2+}, n_e the electron density for the n-type MoS_2 catalyst, and k_p and k_e the appropriate rate constants.

For the relative distribution of electronic carriers one finds under equilibrium conditions:

$$K_i = n_e n_p = N_c N_v e^{-E_i/kT}, \qquad (3)$$

where K_i is the equilibrium constant, n_e and n_p the electron and hole densities, N_c the number of available states in the conduction band, N_v that in the valence band, and E_i is the band-gap energy ($E_c - E_v$). In view of the fact that $n_p = K_i/n_e$, it is apparent that the functional relationship between n_e and n_p exhibited by the data in Fig. 2 is to be expected on the basis of solid-state theory.

To relate the conductivity data to the defect structure of the solid, one needs to consider the interactions at the gas–solid interface that lead to the formation of vacancies and electronic charge carriers. The vacancies perturb the local potential in the solid and give rise to localized electron energy levels located between the S^{2-} band (filled valence band, E_v) and the Mo^{4+} band (empty conduction band, E_c). Since the anion vacancy V_a can bind an electron, a localized level V_a^- will be found in the band gap. This energy level lies close to the valence band, and most likely in close proximity to the energy level associated with Co^{2+} in Co-doped molybdenum sulfide. Thus the electronic properties of n-type molybdenite are affected qualitatively in an analogous way by the addition

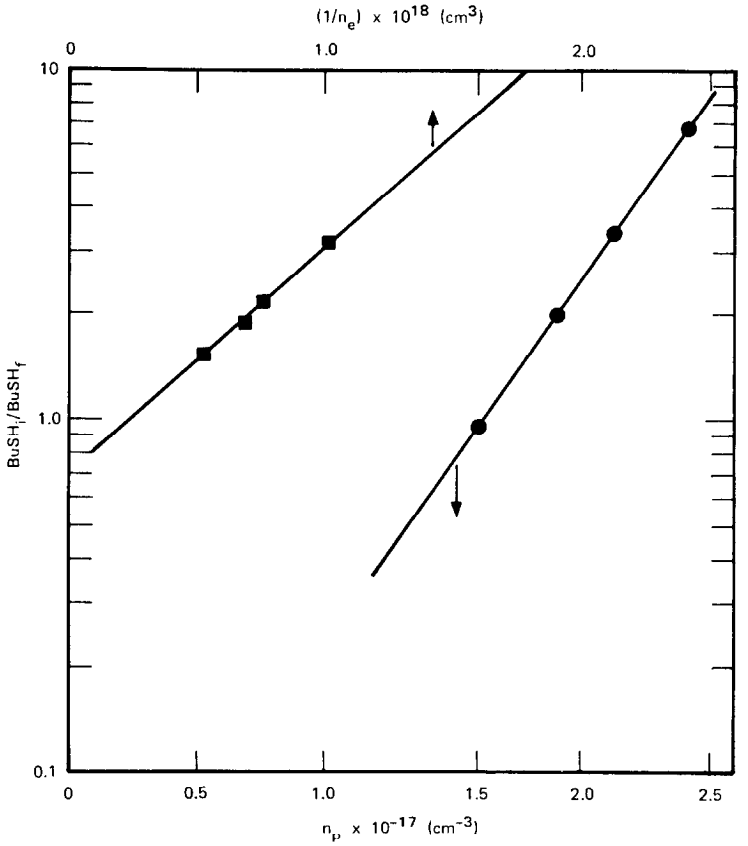

FIG. 2. HDS activity as a function of electronic carrier density.

of S^{2-} anions or Co^{2+} cations to the lattice, as observed experimentally. The advantage of Co^{2+} doping over S^{2-} addition is to be found in the stabilization of the Fermi level by Co^{2+}. The S^{2-} ions are susceptible to reaction with H_2 and their removal or introduction causes a change in the electronic structure of the solid and its catalytic properties. No such problems are encountered with the Co^{2+}-doped catalyst because the Fermi level is dominated by the foreign cation.

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