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Measurement of Acid Site Density on Molybdenum Sulfide

In the study of the catalytic properties, the specific activity, as expressed, e.g., in the rate of conversion of reactant per unit surface area of catalyst, provides a unique measure of catalytic reactivity. However, in the case of molybdenum sulfide, the surface-area measurements by N_2 physisorption (BET method) have been found to correlate poorly with experimentally determined hydrodesulfurization (HDS) reaction rates (*1*). On the other hand oxygen chemisorption by the molybdenum sulfide sample appears to offer some correlation with catalytic activity. Recently considerable debate has ensued concerning the interpretation of the oxygen data in terms of edge-site or basal-plane adsorption (*2–4*). We do not wish to speculate on this problem of oxygen adsorption but provide an alternative procedure for measurement of the active-surface-site density of molybdenum sulfide. It involves the room-temperature chemisorption of a base, such as ammonia, on the surface of molybdenum sulfide in the absence of any support material.

For these measurements the catalyst sample was exposed at 300 K to pulses of ammonia (1 to 10 vol% in He) in a microreactor system connected to a thermal conductivity cell. Pulsing was continued until no further pickup of NH_3 by the sample was detectable. The amount of NH_3 adsorbed was determined from the difference between the NH_3 concentration in the inlet and outlet of the reactor, as monitored by thermal conductivity measurement. Also the amount adsorbed could be determined by means of a temperature-programmed desorption (TPD) experiment. In this procedure the catalyst after saturation exposure to NH_3 was heated at a linear rate (0.3 K s^1) in a flowing stream of inert carrier gas (He), and the NH_3 concentration in the effluent was monitored as a function of time by means of a thermal conductivity cell. By integration of the area under the curve, the total mass of NH_3 adsorbed could be evaluated.

The acidity measurements were conducted with a sample of molybdenum sulfide (catalyst A) prepared from ammonium thiomolybdate in accordance with the procedure given in Ref. (*5*). This material exhibits initially a ratio S/Mo ~ 3. But on exposure at elevated temperatures to H_2S/H_2 or H_2 significant changes in stoichiometry occur as a result of the dynamic equilibrium between the sulfur activity in the gas and solid phases. The results of the surface-area measurements (BET/N_2) and the ammonia saturation coverage, identified as "acid site equivalent," are listed in Table 1. It is quite apparent that the surface-area variation resulting from various pretreatments at elevated temperatures is relatively small when compared to changes in the number of acid sites.

Similar results were obtained with a commercial catalyst of molybdenum sulfide (catalyst B, Harshaw M0-0401-T). Again the various pretreatments produced a small change in surface area (BET/N_2) relative to the variation in acid site equivalent (Table 1).

Finally, we determined the change in acid function of a molybdenum sulfide catalyst prepared from ammonium molybdate by exposure to H_2S/H_2 gas mixtures. In these measurements the thermodynamic activity of sulfur in the gas phase, as given by the partial pressure ratio of H_2S to H_2, was fixed at different levels in the gas phase and the acidity function of the sample de-

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TABLE 1

Surface Area and Surface Acidity of Molybdenum Sulfide Catalysts

Catalyst[a]	Pretreatment			Surface area ($m^2 \cdot g^{-1}$)	Acid site equivalent ($mol \cdot g^{-1}$) $\times 10^6$	Acid site surface density (cm^{-2}) $\times 10^{14}$
	Gas[b]	Temp. (K)	Time (min)			
A	He	823	150	114	274	1.45
	2500 ppm H_2S in H_2	823	960	85	99	0.70
	H_2	823	960	67	28	0.25
B	He	800	960	80	194	1.46
	3100 ppm H_2S in H_2	800	960	75	120	0.97
	H_2	800	960	52	48	0.56

[a] See text for description of catalysts.

[b] Total gas pressure = 1 atm.

termined. The results (Table 2) demonstrate the marked increase in acid site equivalent (ASE) with growing sulfur activity in the gas phase. At each of the sulfur activities employed the catalyst had been converted from MoO_3 to MoS_2, as determined by X-ray diffraction analysis and X-ray photoelectron spectroscopy. However, the increase in ASE is indicative of progressive incorporation of sulfur into the MoS_2 lattice and growth in the ratio S/Mo. This conclusion is based on the wide range of solubilities for sulfur which this chalcogenide compound exhibits and the associated variation in electronic properites (*6, 7*).

TABLE 2

Surface Acidity of Sulfided Molybdenum Oxide at Different Sulfur Activities in the Gas Phase[a]

Exposure		Acid site equivalent
(ppm)	(min)	($mol \cdot g^{-1} \times 10^6$
500	960	56
2500	960	78
5000	960	132

[a] Catalyst prepared by reductive sulfidation of MoO_3 at 800 K.

An important aspect of the observed surface acidity of the catalyst under study is its relationship to chemisorbed hydrogen, since it is a reactant in a number of reactions catalyzed by molybdenum sulfide compounds, such as HDS, hydrogenation, and isomerization. In these measurements catalyst sample "A" after pretreatment in H_2S/H_2 gas mixtures of specified composition at 800 K, was exposed to pulses of 10% H_2 in argon at 475 K until saturation coverage was attained, as monitored by breakthrough of the H_2 pulse. The results (Fig. 1) show that the uptake of H_2 by this catalyst is greatly affected by the sulfur activity in the condensed phase, i.e., by the ratio S/Mo, as controlled by the ratio H_2S/H_2 in the gas phase. The hydrogen sorption capacity appears to parallel the ammonia sorption capacity. In fact, a comparison of the adsorption capacities of these two gases indicates that the amount of NH_3 adsorbed per unit mass of catalyst is twice that of H_2. For example, in the case of catalyst A, the saturation coverage amounts to 1.6×10^{20} molecules NH_3/g catalyst and 0.74×10^{20} molecules of H_2/g catalyst. For dissociative

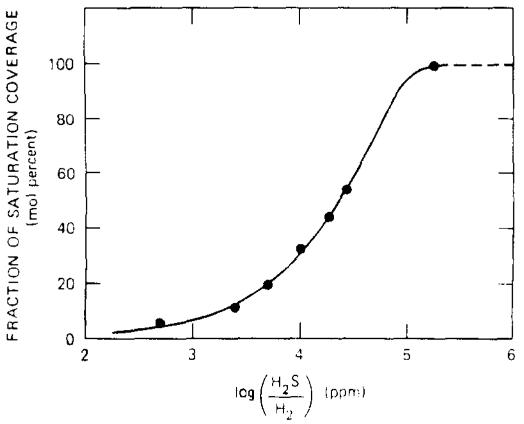

FIG. 1. Fractional surface coverage with H_2 of catalyst A at 475 K. (Saturation coverage = 123×10^{-6} mol/g catalyst at $H_2S/H_2 > 10^5$ ppm.)

hydrogen chemisorption the saturation surface coverge corresponds to 1.5×10^{20} hydrogen atoms/g catalyst, a value close to that observed for NH_3.

The temperature-programmed desorption (TPD) experiments provide not only a quantitative measure of the amount of NH_3 adsorbed but also of the binding energy. At a heating rate of 0.3 K s^{-1} two broad desorption peaks were observed with different temperature values T_p, at which the desorption rate of NH_3 passes through a maximum. The distribution of adsorbed NH_3 between the two binding states is shown in Table 3. For freshly prepared catalyst A with a high ratio of S/Mo, the TPD data indicated that most of the NH_3 is adsorbed in the α-state. As sulfur was removed from the catalyst by exposure to H_2S/H_2 of progressively lower sulfur activity, the accompanying decrease in S/Mo of the catalyst causes a shift of the NH_3 surface population to the β-state, a more strongly bound adsorption state.

TPD experiments with chemisorbed hydrogen demonstrated that at temperatures up to 775 K no hydrogen is desorbed from the sample. At higher temperatures hydrogen sulfide and hydrogen are released by the catalyst, indicative of the strong hydrogen bond formed.

The close relationship between the acidity of the catalyst and its hydrogen chemisorption capacity suggests that the ammonia titration involves acid sites on molybdenum sulfide with chemical functions comparable to those of solid acids, as found for the transition aluminas. The very strong bonding of the protonic hydrogen and the removal of –SH with the formation of H_2S during heating at high temperatures have their counterpart in the behavior of surface hydroxyl group on aluminas. The ammonia titration provides a useful procedure for determination of the acidic properties of surface sulfhydryl groups. Good correlation has been observed between the ASE and chemical reactivity for reactions involving hydrogen (*8*), when account is taken of both the ASE and the surface area

TABLE 3

Distribution of Acid Sites on Molybdenum Sulfide Catalyst[a]

Pretreatment H_2S/H_2 (ppm)	NH_3 adsorbed (%) in binding state:		Peak desorption temperature (K) for binding state:		Acid site equivalent $(mol \cdot g^{-1}) \times 10^6$
	α	β	α	β	
0 (He)	100	0	385	0	274
10,000	73	27	385	525	180
2,000	60	40	400	575	90
0 (H_2)	49	51	400	575	28

[a] Catalyst A.

[b] Sixteen hours at 800 K.

of the catalyst. This ratio, identified as the acid site surface density, is evaluated in Table 1.

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