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Assay of Molybdenum Sulfide ex Ammonium Tetrathiomolybdate

INTRODUCTION

Valyon and Hall have very recently published a method of assaying reductively sulfided molybdena-alumina catalysts (*1*), with a view of establishing whether valence states lower than Mo(IV) exist in such preparations. Valyon and Hall started with a molybdenum oxide-alumina catalyst, prepared by impregnation of alumina with aqueous ammonium heptamolybdate, followed by drying and precalcination. Treatment with H_2S/H_2 leads to reduction and replacement of O by S, the extent of both depending on reaction conditions. The assay in their work depends on measurement of the consumption of oxygen on reoxidation of the reduced catalyst. The salient finding was that valence states lower than Mo(IV) are indeed present in these reductively sulfided catalysts.

We had been interested in the same question and had also adopted an assay method based on oxygen consumption by the reduced catalyst (*2*). Our work differed from that of Valyon and Hall in several respects. First, our alumina-supported catalysts were prepared by impregnation of alumina with aqueous ammonium tetrathiomolybdate (ATTM), not the heptamolybdate salt. ATTM decomposition in He leads directly to a (nonstoichiometric) MoS_2 (*3*). This has certain advantages, in that there is no need to replace lattice O by S on sulfidation; it suffers in that the original stoichiometry of the supported sulfide is not well established. We have also studied the assay of unsupported Mo sulfide, prepared by decomposition of ATTM, by the oxygen consumption method. An interesting difference appears in the average valence state of Mo, after reduction in H_2, for the unsupported and alumina-supported sulfide. Our results, on a different material and by a methodology differing in detail, are in agreement with the conclusion of Valyon and Hall that an average valence state less than 4 exists in the reduced supported sulfide; for the unsupported sulfide, however, the stoichiometry seems to be $S/Mo = 2$ after H_2 reduction.

EXPERIMENTAL

Catalysts

Ammonium tetrathiomolybdate was prepared by bubbling hydrogen sulfide through a solution of ammonium heptamolybdate (50 g) and ammonium hydroxide (500 ml conc. soln.) in water (150 ml) for 30 min. The solution was cooled in an ice bath, and the deep red crystals of ATTM were separated by filtration, dried under vacuum at room temperature, and stored in a desiccator. Davison alumina (235 m^2/g, pore volume 0.735 ml/g, average pore diameter 126 Å) was used as support. Impregnation was done at room temperature: 5 g of ATTM was dissolved in 15 ml water and 50 ml conc. ammonium hydroxide in a beaker; 25 g of alumina was then introduced into the beaker and allowed to equilibrate under a nitrogen blanket for 20 hr, in order to obtain as high and as uniform a loading of ATTM as possible. The color of the solution and of the supported ATTM was deep red throughout. The ATTM/alumina was dried under vacuum and stored in a vacuum desiccator until use in a reduction experiment. The color remained red during storage unless the catalyst was deliberately exposed to air for prolonged periods (more than 2 days), in which case the catalyst turned black. Determination of the Mo content of the ATTM/alumina catalyst was made by a standard wet chemical method: the Mo in

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TABLE 1

Hydrogen Reduction of Ammonium Tetrathiomolybdate (ATTM)

Catalyst	Weight (g)	Hydrogen consumption [ml(STP)]	
		Theoretical	Experimental
Unsupported ATTM	0.265	22.8	22.0
ATTM/alumina (0.079 g ATTM/g)	1	6.8	17.8

the catalyst was first oxidized by air calcination at 500°C; then the ASTM method D-3943 was used to determine total Mo by dissolving the catalyst in sulfuric acid, reducing the Mo with amalgamated zinc (Jones reductor), adding excess ferric ammonium sulfate, and titrating with ceric sulfate the ferrous ion produced. The loading was determined to be 0.079 g ATTM/g catalyst.

Mo sulfide, alumina-supported or unsupported, was prepared by *in situ* decomposition of the ATTM in hydrogen at 450°C. An all-glass gas-volumetric system was used for this study, similar to that described by Parekh and Weller (*4*), except that pressures were monitored by a digital pressure gauge (MKS Baratron) rather than a mercury manometer. The system permits operation in either a continuous flow mode, or in a closed loop mode with in-line cold trap and internal recycle of gas by an electromagnetic circulating pump.

Reduction Procedure

The decomposition of ATTM was carried out by introducing a known volume of hydrogen into the system and circulating the gas through the sample. A liquid nitrogen bath was placed around the in-line trap to condense hydrogen sulfide and ammonium sulfide formed during the decomposition. The sample was heated to 450°C at a rate of 20°C/min and kept at 450°C until no further change in pressure was observed. Manifold volumes were determined with He. Pressures were monitored throughout, care being taken that the level of liquid nitrogen was kept constant. The total hydrogen sulfide evolution was measured, after the reduction was complete (and the catalyst still at 450°C), by replacing the liquid nitrogen bath with an ice bath and flowing nitrogen gas through the system. The effluent was passed through zinc acetate solution in a flask to absorb H_2S; zinc sulfide was determined by iodometric titration.

Reoxidation

After evacuation at 450°C, a known quantity of oxygen was introduced in a similar fashion, but the in-line trap in this case was immersed in an acetone-slush bath (prepared by adding liquid nitrogen to acetone) at −95.5°C, the freezing point of acetone. This served to condense SO_2. The reoxidation was continued until no further change in pressure was observed.

RESULTS

Hydrogen Consumption in a Closed, Circulating System

Table 1 contains results for hydrogen consumption, on reduction in a closed system, for both unsupported and alumina-supported ATTM. A comparison is made in the table between the observed values of hydrogen consumption and those predicted for conversion to stoichiometric MoS_2.

The experiments on unsupported ATTM indicated that agreement between observed and theoretical values was good: for a 265-mg sample of ATTM, the two values were 22.8 (theoretical) vs 23.0 (observed). Reduction was complete (as evidenced by pressure measurements) within 1 hr at 450°C. The implication is that the final valence state of the Mo is 4 in the case of unsupported ATTM.

The situation is very different for alumina-supported ATTM. The average hydrogen consumption experimentally observed in 10 replicate determinations was 17.3 ml(STP)/g catalyst. This is 2.5 times greater than the theoretical amount (6.8

ml(STP)/g) for reduction to stoichiometric MoS_2.

Evolution of Hydrogen Sulfide on Reduction

Owens and Amberg (*5*) reported that hydrogen sulfide is strongly adsorbed on a sulfided catalyst, and Massoth (*6*) showed that at least 1 hr of purging is needed to remove it. Hydrogen sulfide evolution was determined in our experiments in two ways, one direct, the other indirect. In the direct method, nitrogen was flowed through the system, after the catalyst had been reduced and was still at 450°C, into zinc acetate solution. During this nitrogen purge an ice bath was placed around the in-line trap to permit condensation of ammonium sulfide. The amount of hydrogen sulfide evolved was found, by this direct method, to be 5.3 ml(STP)/g of sample.

In two cases the hydrogen sulfide evolution was measured indirectly. A known weight of ATTM/alumina was reduced in circulating hydrogen at 450°C; the in-line trap was cooled with water-ice during the reduction in order to condense the product ammonium sulfide but not hydrogen sulfide. After reduction was complete, the in-line trap was cooled with liquid nitrogen while the internal circulation of hydrogen was still continued; now hydrogen sulfide was also condensed. The change in manifold pressure when the bath was changed permitted indirect calculation of the hydrogen sulfide evolved during reduction of the sample. The apparent manifold volumes were measured with He with the appropriate (water-ice or liquid nitrogen) bath around the trap. The hydrogen sulfide evolution calculated in this indirect way was found to be 4.7 ml(STP)/g sample. This is close to the value of 5.3 ml(STP)/g measured directly (see above).

Reversible Hydrogen Adsorption

Experiments were conducted to determine the extent to which hydrogen adsorption at 450°C was reversible. These measurements were made by evacuating the freshly reduced catalyst at 450°C for 1 hr and reintroducing hydrogen. The reversible adsorption was only 0.8 ml(STP)/g sample, which is a small fraction of the total hydrogen uptake of 17.3 ml(STP)/g.

TABLE 2

Reoxidation of Reduced ATTM/Alumina

Catalyst	Weight (g)[a]	Oxygen consumption [ml(STP)]	
		Theoretical	Experimental
ATTM/alumina after H_2, 450°C	1	23.8	31.2

[a] Based on original ATTM/alumina before reduction.

Oxidation of the Reduced Catalyst

If the final state of the reduced sulfide is MoS_2, then the theoretical amount of oxygen required for oxidation to MoO_3, and SO_2 is 23.8 ml(STP)/g sample. (Valyon and Hall determined, by mass spectrometry, that no SO_3 was evolved on oxidation of the reduced catalyst. They did find a small amount of sulfate on the alumina and counted this in their determination of *e*/Mo.) The average oxygen consumption in our experiments, shown in Table 2, was 31.2 ml(STP)/g sample. This is substantially greater than the theoretical amount. The oxidation at 450°C was fast; it was complete in less than 30 min.

Chemisorption of Hydrogen and Hydrogen Sulfide on Alumina

We considered the possibility that the excess consumption of oxygen on reoxidation might be due to oxidation of chemisorbed H_2 or H_2S on the support. Experiments were made to measure the amounts chemisorbed on the alumina. Hydrogen chemisorption at 450°C was essentially nil. The total amount of H_2S adsorbed at 450°C was 4.2 ml(STP)/g, of which 2.3 ml(STP)/g was reversibly adsorbed.

DISCUSSION

The hydrogen consumption for reduction of ATTM supported on alumina was much greater than the theoretical amount required for reduction to MoS_2. The experimental data for hydrogen consumption on reduction, and for oxygen consumption on reoxidation of the reduced catalyst, can be rationalized on the basis of a postulated model in which the reduction proceeds to a Mo valence state lower than Mo(IV)—in particular, to the stoichiometry $MoS_{1.5}$. Some irreversible adsorption of both H_2 and H_2S are also postulated to occur on the reduced catalyst. The detailed calculations based on this model are outlined as follows:

(1) Theoretical H_2 requirement for reduction of supported ATTM (7.9% loading) to $MoS_{1.5}$ = 10.2 ml(STP)/g;

(2) Difference between experimental and theoretical amount = 17.3 − 10.2 = 7.1 ml(STP)/g;

(3) H_2 adsorbed irreversibly = 7.1(total) − 0.8(reversible = 6.3 ml(STP)/g;

(4) H_2S adsorbed irreversibly = 10.2 (total) − 5.3(iodometric titration) = 4.9 ml(STP)/g;

(5) Theoretical O_2 for oxidation of $MoS_{1.5}$ to MoO_3 and SO_2 = 20.4 ml(STP)/g;

(6) Theoretical O_2 for oxidation of 6.3 ml(STP)/g adsorbed H_2 = 3.15 ml(STP)/g;

(7) Theoretical O_2 for oxidation of 4.9 ml(STP)/g adsorbed H_2S = 7.35 ml(STP)/g;

(8) Total theoretical O_2 consumption = 20.4 + 3.15 + 7.35 = 30.9 ml(STP)/g;

(9) Total experimental O_2 consumption = 31.2 ml(STP)/g.

This calculation cannot be considered precise, although the agreement between 30.9 and 31.2 ml(STP)/g may be gratifying. However, the major conclusion, that the supported sulfide is reduced to a valence state less than Mo(IV), appears both to be the simplest interpretation of the data ("Occam's razor") and to be consistent with the major conclusion of Valyon and Hall for a sample prepared quite differently. It remains remarkable that the reduction of unsupported ATTM seems to proceed only to the Mo(IV) stage.

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