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Sulfur-35 Exchange between Hydrogen Sulfide and Tungsten Disulfide

JOHN FREEL, JOHN G. LARSON, AND JOHN F. ADAMS

Gulf Research and Development Company, P.O. Drawer 2038, Pittsburgh, Pennsylvania 15230

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The exchangeable sulfide ion in this system was always a small part (<1%) of the total sulfur content of the solid up to 400°C, the highest temperature investigated. Approximately 40% of the calculated surface sulfide ions in WS_2 were exchangeable below 80°C. The exhange kinetics were first order in distance from equilibrium. A second first-order reaction observed at 100°C and above involved a similar number of exchangeable sulfide ions. The combined reactions involved surface sulfide ion and could presumably be used to measure the surface area of WS_2 in supported catalysts. The surface exchange probably proceeds by place exchange between surface S–H groups and gas phase or adsorbed H_2S.

INTRODUCTION

Supported catalysts containing tungsten and molybdenum sulfides are important in petroleum refining and have been widely investigated, particularly in the case of molybdenum/alumina systems. Their structure has proved difficult to elucidate because the catalysts lack long-range order despite having relatively high metal loadings. Calcined molybdenum–alumina, for example, is thought to have a complex structure (*1*). Recent studies by Raman spectroscopy (*2*) and EXAFS (*3*), however, suggest that MoS_2 is the predominant molybdenum phase after sulfiding cobalt–molybdenum–alumina at conditions comparable with those used commercially.

If this is true, the dispersion of tungsten and molybdenum sulfides on supports may help determine catalyst performance, but there is no generally accepted method of determining this dispersion. Isotopic exchange between gas and solid offers a possible approach. Lukens *et al.* (*4*) examined the exchange of S^{35} between hydrogen sulfide and a variety of metal sulfides including tungsten and molybdenum sulfides. They suspended the metal sulfide in toluene saturated with tagged hydrogen sulfide and used liquid scintillators to follow the reaction. They observed a slow exchange at room temperature which equilibrated in several days, and showed that the number of sulfide ions exchanged could be related to BET surface area, but the exchangeable sulfide ion was rarely equal to its expected surface concentration. For tungsten disulfide, the exchange involved roughly 50% of the sulfur anticipated in a close packed sulfide ion layer.

The present study extends the work of Lukens *et al.* (*7*) by examining the exchange of S^{35} between tungsten disulfide and gas-phase hydrogen/hydrogen sulfide mixtures. The use of a gas–solid system allowed hydrogen to be included in the equilibrium and permitted studies at the temperatures where tungsten disulfide is an effective catalyst.

EXPERIMENTAL

Apparatus

The exchange reaction was studied in a mercury-free, glass circulation system. Two-stage pumping with a conventional fore-pump and a titanium ion pump gave a dynamic vacuum of about 10^{-7} Torr. Gas pressures were measured in an all-glass

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Bourdon gauge, and gas circulation was by a glass piston-type pump actuated by an external solenoid. The detector was a lithium doped, cerium activated silicate glass scintillator of the flow type. It was attached to the glassware by a low vapor pressure epoxy resin and optically coupled to a photomultiplier tube. Pulses were amplified and displayed on a digital ratemeter. Counting efficiency for the 0.167-Mev beta radiation of S^{35} was 20% at optimum peak-to-background ratio.

Materials

S^{35} as hydrogen sulfide was supplied by the Matheson Company (specific activity 0.375 millicuri/millimole). It was pumped briefly at −195° and distilled at −60°C before use, in case of air or water contamination. "Research grade" hydrogen (Matheson Company) was used as received.

Tungsten disulfide was manufactured by the Chemical and Metallurgical Division of the Sylvania Corporation and had the following specifications:

	Specifications	Typical analysis	Theoretical
Tungsten %	73.0 min	73.8	74.18
Sulfur %	27.0 max	26.2	25.82
Total impurity content %	0.5 max	0.2	—

Its BET surface area was determined in this laboratory from Krypton isotherms at −196°C. Duplicate determinations gave values of 0.92 and 0.98 m^2/g. Scanning and transmission electron micrographs showed that it was composed mainly of well defined crystals with a hexagonal platelet habit. The size range was broad, roughly 0.1–5 μm on the side. The surface area calculated from the scanning electron micrographs was about 1 m^2/g, so that the surface roughness factor must be close to one.

The tungsten disulfide was also examined after sulfidation at 400°C, the pretreatment used before exchange experiments. This did not change the BET surface area.

Surface sulfide ion concentrations were calculated from the BET data based on the cross-sectional area of sulfide ion and also by a calculation based on the crystallography of tungsten disulfide. The two were in reasonable agreement; the value obtained by the simpler calculation was 0.89×10^{19} surface sulfide ions/g WS_2.

Procedure

In preliminary work, tungsten disulfide was outgassed at 450°C prior to exchange. Exchange experiments were not repeatable, and mass balances showed that hydrogen sulfide was always lost from the gas phase. A standard presulfidation was therefore adopted and was carried out in the circulation system prior to each exchange experiment. After outgassing, a 10/1 hydrogen/hydrogen sulfide mix was passed over the tungsten disulfide at 400°C until hydrogen sulfide was no longer lost from the gas phase. Small amounts of water formed during the pretreatment were frozen out at −60°C and hydrogen sulfide made up if necessary.

Even with this pretreatment, some hydrogen sulfide was lost from the gas phase if its partial pressure in the exchange experiment was higher than in the presulfidation and vice versa. The amount was small, however, and reproducible equilibrium data were obtained in exchange experiments.

Two types of exchange experiments were carried out. "Load" exchange was the exchange of S^{35} between tagged hydrogen sulfide and the inactive solid. "Strip" exchange was that between inactive hydrogen sulfide and the previously tagged metal sulfide. In most cases, each experiment included load and strip exchanges in sequence.

In a typical experiment, the metal sulfide was presulfided at 400°C, evacuated, cooled to the desired exchange temperature, and closed off. 0.2–0.4 × 10^{19} molecules of tagged hydrogen sulfide (pressure–volume measurements) and 10 times this amount of hydrogen, which had been mixed in a bypass circulating loop, were directed over the metal sulfide to begin the exchange experiment. On completion of the load exchange, the furnace was cooled, hydrogen sulfide frozen in a U-trap, and hydrogen pumped off. The hydrogen sulfide was transferred to the Bourdon gauge by freezing and its final pressure measured. The strip exchange was carried out in a similar way except that the volume of hydrogen/hydrogen sulfide used was about 10 times greater to improve sensitivity.

RESULTS

Isotopic exchange occurred at a conveniently measurable rate between 70 and 400°C, the maximum temperature employed. At these temperatures, the exchangeable sulfide ion was always much less than the total sulfur content of the solid (4.86×10^{21} sulfide ions/g WS_2), but reaction was not always confined to the surface. In one experiment, exchange was commenced at 150°C, continued at 250°C when the reaction at 150°C became very slow, and the temperature raised twice more to 350 and 400°C under similar circumstances. Approximately 3×10^{19} sulfide ions/g were exchanged; substantially higher than the expected surface concentration of 0.89×10^{19} sulfide ions/g. In a second experiment, the exchange reaction at 150°C was allowed to continue for 160 hr. Approximately 2×10^{19} sulfide ions/g were exchanged. The reaction was comprised of a rapid exchange, followed by a very slow exchange which was zero order with time (Fig. 1). Extrapolation of the slow reaction to zero time showed that 0.76×10^{19} sulfide ions/g were exchanged in the fast reaction, in fair agreement with the calculated surface sulfide ion.

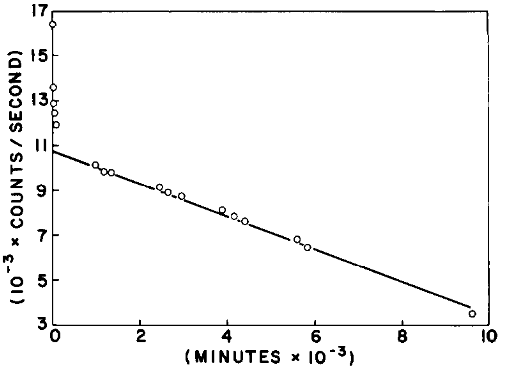

FIG. 1. Continuing slow exchange between H_2S and WS_2 at 150°C.

This fast reaction observed at 150°C was studied in a series of isothermal experiments between 70 and 180°C. Experimental equilibrium was defined as that point at which no further change in gas activity could be observed in two successive intervals of 5 hr. Using this definition, the extent of exchange was reproducible at any temperature, but did increase with temperature; e.g., the exchangeable sulfide ion at 100°C was about twice that at 70°C.

This effect of temperature on the extent and rate of exchange is shown in Fig. 2, where S_t is the exchangeable sulfide ion at time t. In a load exchange, for example,

$$S_t = \frac{I_0 - I_t}{I_t} \times C_g \qquad (1)$$

where C_g is the number of hydrogen sulfide molecules in the gas phase, and I_0 and I_t are the counting rates in the gas phase initially and at time t, respectively.

The exchange reactions observed at 70 and 80°C were first order within the accuracy of the measurements (Fig. 3). Thus, the sulfide ions exchangeable at these temperatures (about 0.36×10^{19} sulfide ions/g) were equivalent.

The exchange observed at 100°C involved additional sulfide ions (Fig. 2) and was not a simple first-order process (Fig. 4). The data shown in Fig. 4 suggest the possibility of two concurrent first-order processes, one being the reaction observed at 70°C. If this is true, the linear portions of the first-order plots in Fig. 4 represent a second first-order process too slow to follow at 70 and 80°C. The equilibrium value for the fast reaction can then be obtained by extrapolating the linear part of the semilog plot to zero time. (This is a reasonable ap-

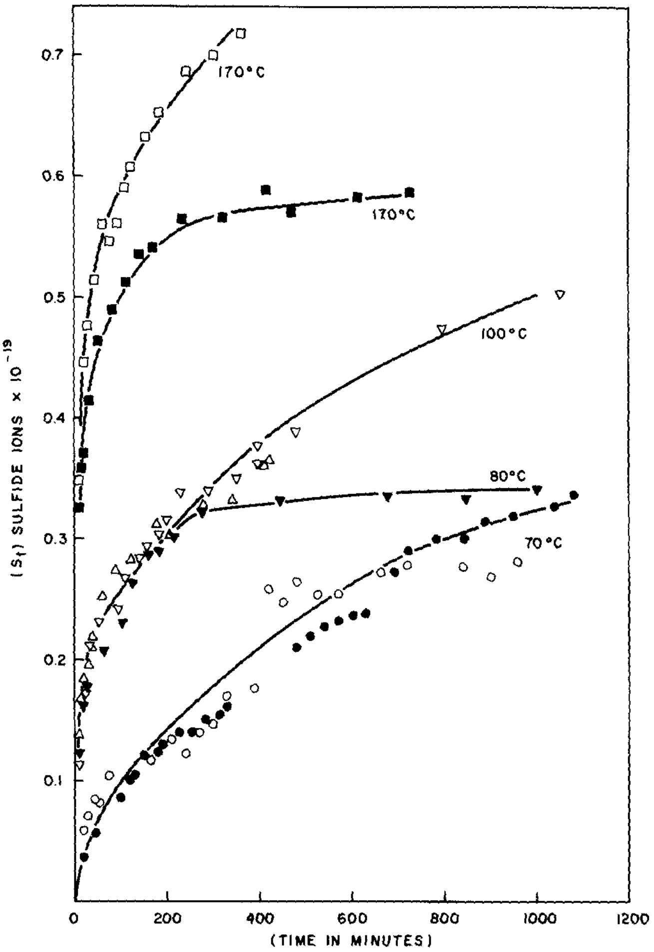

FIG. 2. S_t versus time plots for isothermal runs. S_t is the number of sulfide ions which would have to be in equilibrium with the gas phase at time t to give the observed specific activity. Open points are for load exchange runs, the exchange of tagged H_2S with an inactive solid; closed points are for strip exchange runs in which inactive H_2S was contacted with the pretagged solid. ○ = T-1a; ● = T-1b; △ = T-2a; ▼ = T-2b; ▽ = T-3a; □ = T-5a; and ■ = T-5b; all of Table 1.

proximation, provided the rates of the two reactions are very different.)

Treating the data in this way, the equilibrium value calculated for the fast reaction at 100°C was equal to the experimentally determined equilibrium value at 70 and 80°C. Also, the rate of the fast reaction observed at 100°C was first order (Fig. 4), within the accuracy of the measurements.

The two reactions could also be isolated experimentally. Run 2b of Fig. 2 was a strip exchange at 80°C of a sample previously used in a load exchange at 100°C. Both reactions occurred during the load exchange at 100°C. The strip exchange at 80°C equilibrated at 0.35×10^{19} sulfide ions/g and the kinetics were first order, as shown in Fig. 3. On heating to 120°C at this point, the second first-order reaction occurred. Only 0.50×10^{19} sulfide ions/g were exchanged in the combined strip reactions, however, suggesting some migration of the tagged sulfide ion into the lattice.

Additional exchange was observed at 150 and 170°C. At these temperatures, the reactions observed at 100°C occurred quickly and were followed by fairly rapid exchange of a further $0.2–0.3 \times 10^{19}$ sulfide ions/g, then by a slow, apparently zero-order process, as described previously. Significantly, a strip exchange at 170°C (run 5b of Fig. 2) equilibrated at 0.60 × 10^{-19} sulfide ions/g, a quantity similar to that observed in the first two reactions alone and considerably lower than the exchangeable sulfide ion in the preceding load exchange at 170°C (run 5a of Fig. 2). This suggests that lattice migration of the tagged sulfide ion introduced by the two first-order exchange reactions is slow, even at 170°C, since it largely reappears in the strip exchange. This is not true of the tagged sulfide ion introduced by the incremental, zero-order reaction observed at 170°C.

Equilibrium data for these reactions are collected in Table 1, which gives the total extent of reaction at different temperatures and the equilibrium values obtained graphically for the two initial first-order reactions. Reaction rates for these two reactions, taken from the slopes of first-order plots, are given in Table 2. Both obeyed the Arrhenius rate law reasonably well. The activation energies were equal (84 ± 20 kJ/mole) within the accuracy of the measurements, but the pre-exponential factors were substantially different (3.8 × 10^6 and 2.4 × 10^5 molecules/sec/cm^2).

DISCUSSION

Lukens *et al.* (*4*) studied the exchange of S^{35} between hydrogen sulfide and metal sulfides and found that the extent of exchange was reproducible, provided the metal sulfides were preconditioned in a hydrogen/hydrogen sulfide mixture at high tempera-

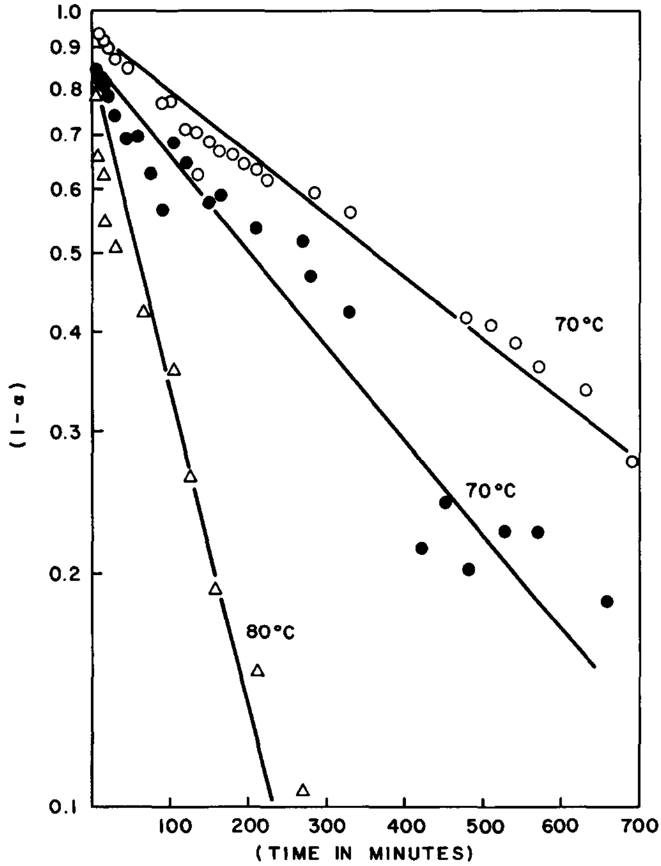

FIG. 3. First-order plots for runs T-1a (●); T-1b (○); and T-2b (△); of Table 1.

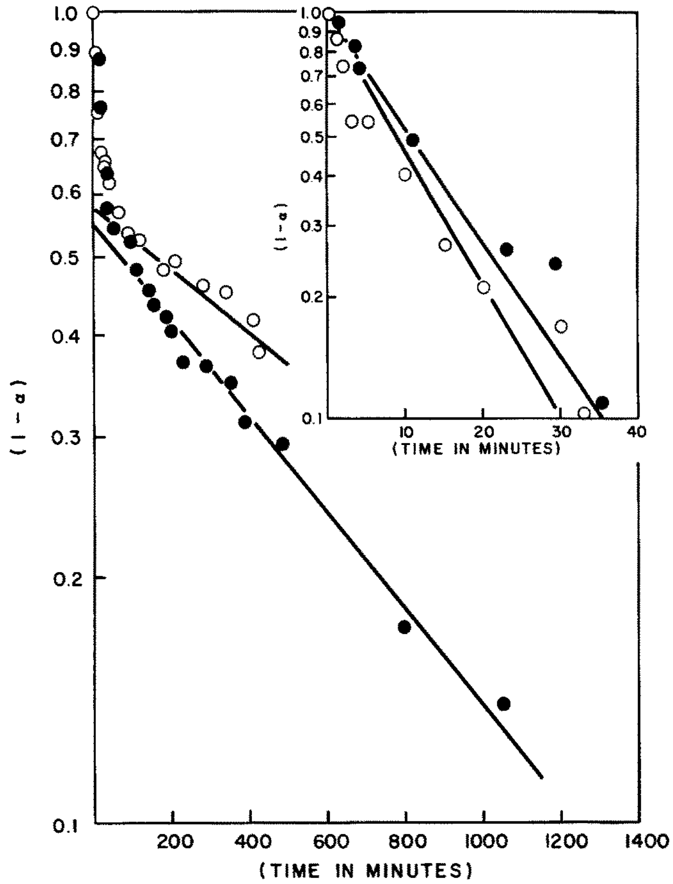

FIG. 4. First-order plots for runs T-2a (●) and T-3a (○) of Table 1, both at 100°C. The main plot suggests the duality of the overall reaction; the insert shows the initial reactions based on equilibria from zero time extrapolation of the slower exchange.

TABLE 1

WS_2 Equilibria: Comparison of Experimental Equilibria at Low Temperature with Extrapolated Values Obtained in Higher Temperature Runs

Run	Run Temp. (°C)	H_2S in gas phase (molecules $\times 10^{-19}$)	Exptl. $S^{\infty a}$ (ions $\times 10^{-19}$)	Time to reach exptl. value (min)	$S^{\infty b}$ by extrapolation (ions $\times 10^{-19}$)
T-1a	70	0.36	0.36	1900	—
T-1b	70	3.10	0.36	1640	—
T-2a	100	0.80	0.62	6000	0.28
T-2b	80	8.00	0.35	1640	0.32
	120	8.00	0.50	—	—
T-3a	100	0.80	0.70	7000	0.29
T-4a	150	0.80	2.20	6000	0.78
T-4b	150	7.85	0.82	1800	0.60
T-5a	170	0.80	0.92	1380	0.62
T-5b	170	8.00	0.60	1440	

[a] The number of sulfide ions per gram of WS_2 required for the observed equilibrium condition.

[b] The initial reaction defined by extrapolating the final slow process to zero time. At 100°, the final slow process was first order and defined an initial first-order reaction. At 150 and 170°, subtraction of the final slow part left the two processes observed at 100°.

TABLE 2

Rate Constants[a] for the Two Initial First-Order Reactions on WS_2

Run	Temperature (°C)	k_1[b] (min^{-1} × 10^4)	k_2[c] (min^{-1} × 10^4)
1a	70	1.03	—
1b	70	0.92	—
2b	80	4.22	—
2a	100	27.4	0.365
3a	100	27.4	0.701
5a	170	735.0	54.2
5*b*	170	888.0	64.9

[a] The true rate constants here = observed rate × $(a + b/ab)$, where a and b are the concentrations of sulfide ion in the two equilibrating phases (9). The quantity of solid sulfide ions was assumed to be 0.30×10^{19}/g in each of the two reactions.

[b] True rate constant for the initial first-order process.

[c] The rate constant for the second first-order process.

ture (275°C). Comparing the amount of sulfur exchanged with BET surface area on several samples of tungsten disulfide, they concluded that the extent of exchange was approximately 50% of the expected surface sulfide ion. The first-order exchange reaction observed at 70 and 80°C in the present work involved 0.36×10^{19} sulfide ions/g of tungsten disulfide, which is about 40% of the value calculated from surface area measurements. This is in reasonable agreement with the earlier work considering the different experimental approaches used.

The exchange observed at 100°C in the present study could be represented as two concurrent first-order processes, involving roughly equal numbers of exchangeable sulfide ion (Table 1). The two reactions could also be isolated fairly well by experiment, since their rates were different by an order of magnitude. 0.6–0.7 × 10^{19} sulfide ions/g were exchangeable in the combined reactions, so that both appear to involve the WS_2 surface. This suggests that two comparably sized pools of surface sulfide ions participate in the reactions observed at 100°C.

Our experiments provide no means of identifying these two pools of surface sulfide ion. Similar results have been obtained in exchange between chlorine and metal chlorides. Sensui (5), for example, observed two first-order exchange reactions between chlorine and the surface of nickel dichloride and attributed them to surface exchange with the basal plane versus higher index planes. He was able to correlate the number of chloride ions exchanged in the two reactions with the ratio of basal and higher index planes determined by electron microscopy. This explanation does not seem to be true in the present system since electron microscopy showed the WS_2 to be largely thin hexagonal platelets in which the basal plane predominates. The two first-order reactions, on the other hand, involved equal amounts of sulfide ions.

Below 400°C, the maximum temperature used in this study, exchangeable sulfide ions were always a small part (<1%) of the total sulfur content of the solid. No reaction involving true bulk diffusion would be expected below 400°C, since ionic mobility in the lattice is not anticipated below the Tamman temperature (about 600°C). Nevertheless, above 150°C there was evidence of a slow exchange reaction which continued indefinitely upon completion of the fast exchange. The kinetics were pseudo-zero order, showing great distance from equilibrium, and suggesting exchange with the interior of the tungsten disulfide crystallites. The inability to recover S^{35} which took part in this reaction during a strip exchange is consistent with this assignment. Surface and lattice exchange could always be readily distinguished, however, so that the technique has promise for measuring the WS_2 surface area in supported catalysts, if the tungsten phase is WS_2.

The mechanism of Sulfur-35 exchange between H_2S and surface sulfide ions does not appear to require H_2S dissociation at the anion vacancies found in higher index planes, which are believed to be important in hydrodesulfurization reactions. The chemisorption of H_2S at sulfide ion vacancies in tungsten disulfide is slow even at 400°C (*6*). More compelling evidence is found in the work of Katsumoto *et al.* (*7*). They studied the exchange of deuterium and hydrogen sulfide over molybdenum disulfide, which should be a reasonable analog for tungsten disulfide. They concluded that this exchange required complete dissociation of H_2S at an anion vacancy, because the initial products were D_2S and H_2, and suggested that H_2S dissociation was the slow step in the exchange. The D_2/H_2S exchange reaction was slow even at 480°C over MoS_2.

The exchange of S^{35} between hydrogen sulfide and the surface of tungsten disulfide was too fast to be controlled by this type of dissociation at anion vacancies. More likely it proceeds by place exchange between surface S–H groups, known to represent a considerable fraction of the surface (*6*), and adsorbed or gas phase H_2S. If, for example, two neighboring S–H groups expel a molecule of H_2S which is immediately replaced by dissociation of an incoming gas-phase H_2S molecule, the event is recorded using S^{35} label. It is undetected in the exchange of deuterium and hydrogen sulfide, because the label does not change position. The D_2/H_2S exchange requires hydrogen scrambling between the two gases, which is not well catalyzed by molybdenum disulfide. (*7*). Hydrogen probably does not participated in the S^{35} exchange of the present study, since our data compare fairly well with those of Lukens *et al.* (*4*), who had no hydrogen in their system.

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