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Sulfiding of Tungsten Oxide Supported on Silica–Alumina

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Tungsten trioxide supported on silica–alumina was sulfided with mixtures of hydrogen sulfide and hydrogen at temperatures between 500 and 1100°F and hydrogen sulfide partial pressure of 0.1–5 atm. Kinetic data were correlated with a logarithmic-type growth law, which accounts for the rather flat percentage sulfur versus time profiles. Rates were proportional to the square root of the hydrogen sulfide partial pressure. The apparent activation energy for sulfidation was 36 kcal/mole of W. Studies of partially reacted samples showed the sulfided species to be WS_2 and the unconverted oxide to be $W_{20}O_{58}$, suggesting that partial reduction precedes sulfidation. Evidence is advanced to support a pore-blocking model for the sulfidation. Differences in reactivity of bulk compared to supported tungsten trioxide are discussed.

INTRODUCTION

Many catalysts employed in industry are presulfided prior to use. The patent literature is prolific in the number and variety of uses of catalysts employing sulfided tungsten, either singly or in conjunction with other metals. Yet, no systematic study of the kinetics of sulfidation has been reported. Indeed, a definitive study of the sulfidation of even bulk tungsten trioxide appears not to have been undertaken. A recent study reported on the sulfidation of tungsten metal in pure hydrogen sulfide (*1*).

Since tungsten catalysts are usually sulfided in a hydrogen-rich atmosphere to avoid deposition of sulfur from decomposition of hydrogen sulfide, complications might arise between reduction of the oxide phase and direct sulfidation. Hence, the course of the reaction and the kinetics could be affected by the relative rates of reduction versus sulfidation which may vary with reaction conditions. In fact, direct reduction of tungsten trioxide has been shown to proceed through several intermediate, stable oxides (*2, 3*).

The objectives of the present study were to establish the mechanism of the sulfidation of supported tungsten trioxide with hydrogen sulfide–hydrogen mixtures and to correlate the rate of sulfidation as a function of time, temperature, and pressure. The study involved two approaches. In the first, utilizing a flow, microbalance apparatus, the chemical properties of bulk and supported tungsten trioxide were characterized, as well as the products of sulfidation. In the second, using a fixed-bed reactor, the kinetics of sulfidation of the supported tungsten trioxide were determined.

THEORY

The overall reaction for the sulfidation of tungsten trioxide by H_2S/H_2 mixtures is given by:

$$WO_3(s) + 2H_2S(g) + H_2(g) \rightarrow WS_2(s) + 3H_2O(g). \tag{1}$$

In gas–solid reactions of this type, the following general steps must be considered: initial reaction on the surface, adsorption of the gases on the product formed, transport of reactant gases to the unreacted solid, chemical reaction at the interface, and counter transport of product gas.

Usually, mass transport or diffusion is the rate-limiting step in the process.

For porous materials, Evans (*4*) discusses a number of kinetic rate expressions based on transport through pores.* One of the models assumes that the reaction products in a given pore set up compressional stresses in the solid causing blockage of neighboring pores. The number of pores blocked is proportional to the density of pores, so that

$$-dN = k_2 N \, d\alpha, \tag{2}$$

and the rate of sulfidation is determined by the number of pores still remaining open,

$$d\alpha/dt = k_1 N, \tag{3}$$

where α is the degree of sulfidation (conversion) in going from WO_3 to WS_2, N is the number of pores remaining open per unit weight of oxide, t is time and k_1 and k_2 are constants. Solution of these two equations with the boundary condition at $t = 0$, $\alpha = 0$ and $N = N_0$, where N_0 is the initial number of pores per unit weight of original oxide, yields the basic logarithmic expression,

$$\alpha = (1/k_2) \ln (1 + k_2 k_3 t), \tag{4}$$

where

$$k_3 = k_1 N_0. \tag{5}$$

Conversion may be expressed in terms of weight percentage of sulfur in the sample, S, since,

$$\alpha = \frac{S}{S_f} \tag{6}$$

where S_f is the percentage sulfur equivalent to complete sulfiding to WS_2 for the given sample. Then the logarithmic equation takes the form

$$S = (1/k'_2) \ln (1 + k'_2 k'_3 t), \tag{7}$$

where $k'_2 = k_2/S_f$, (8)

$$k'_3 = k_3 S_f. \tag{9}$$

The two fundamental constants indigenous to the logarithmic law are k_1, a reaction rate constant per pore, and k_2, a proportionality constant between the number of pores and degree of conversion. The latter constant depends only on the basic pore structure and should be independent of temperature and pressure. On the other hand, the former constant, related to the chemical process, should be influenced by temperature and pressure. Since the experimentally derived rate constant k_3 is equal to $k_1 N_0$ and N_0 is related only to material properties, k_3 should be a function of reaction conditions.

It should be mentioned that the logarithmic equation is mathematically equivalent to the Elovich equation, usually employed in correlating adsorption rate data (*5*). However, the theoretical basis is entirely different: the Elovich law assumes surface heterogeneity, with variation of reaction activation energies with surface coverage. Applied to gas–solid reactions, this would require phase heterogeneity to account for varying activation energies with bulk conversion. We prefer the interpretation of the logarithmic law on the basis of a pore-blocking model as developed below.

EXPERIMENTAL METHODS

Materials

Pure tungsten trioxide was obtained from two sources: submicron microspheres (MS) from Vitro Labs and pure powdered tungstic acid (TA) from North Metal Chemical. The latter material was converted to the trioxide by heating in air at 1000°F for 16 hr (*6*). Both samples analyzed less than 0.1% metal impurities by emission spectroscopy. Surface areas, determined by the standard BET method, were: MS, 18.5; and TA, 6.6 m^2/g. Supported tungsten trioxide (S) was prepared by impregnating American Cyanamid Triple A silica–alumina (75% by weight SiO_2) (*7*) with a solution of ammonium metatungstate and ammonium fluoride.*

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* The term pores used in this context refers to crystalline defects in the solid oxide, whether supported or not, rather than the larger pores associated with catalyst supports.

* Fluoride was added as a promoter for later catalytic testing (not included here).

The insipient-wetted material was oven-dried and calcined in air at 1000°F for 10 hr. The 10–20-mesh calcined catalyst contained 19.0% W and 1.7% F by weight and had a BET surface area of 182 m^2/g.

Prepurified cylinder hydrogen was purged of oxygen by passing through a Deoxo unit and dried by passing through Type 5A molecular sieves. Hydrogen sulfide was used directly from cylinders without further purification.

Apparatus and Procedure

Microbalance studies. The course of the sulfiding reaction was studied in a flow, quartz spring reactor, which has been previously described (*7*). The same apparatus was used to follow the rates of reduction of bulk WO_3 in hydrogen as well as the effects accompanying gaseous HCl treatments. Spring sensitivity was 1.00 mg/mm. Weight changes attending sulfidation at various temperatures were followed using a 10-cm Gaertner cathetometer, which permitted readings to be made to ±0.02 mg for sample weights in the order of 100 mg. All runs in the microbalance reactor were carried out in a flowing stream at atmospheric pressure. Gas mixtures were prepared by using calibrated rotameters. At the end of a specified time period, reaction was terminated by switching to nitrogen. The samples were then analyzed for sulfur content by a high-temperature, oxygen combustion method. Several samples were also analyzed by X-ray diffraction. By knowing the final weight change and sulfur content, the values of X and Y in the empirical formula WS_XO_Y could be determined by the following material balances:

$$X = \frac{M_{WO_3}S}{M_S}\left[\frac{\Delta W}{W_0} + 1\right], \tag{10}$$

$$Y = \frac{M_{WO_3}(1 - S)}{M_O}\left[\frac{\Delta W}{W_0} + 1 - \frac{M_W}{M_O}\right], \tag{11}$$

where: ΔW is the change in sample weight, W_0 is the initial weight of WO_3, S is the weight fraction sulfur, and M represents the molecular weights of the indicated species. Since X-ray analysis indicated WS_2 to be the only sulfided species present, the oxygen-to-tungsten ratio, Z, in the oxide residue can be calculated according to

$$Z = \frac{Y}{1 - X/2} \tag{12}$$

Measurements of sample temperature change during initial sulfidation were made in separate runs by replacing the spring assembly by an auxiliary microthermocouple, which was imbedded in the sample contained in the quartz bucket. Temperature response was monitored using a millivolt recorder. At an initial temperature of 950°F, a gas flow rate of 400 ml/min, and a $\frac{1}{10}$ vol ratio mixture of H_2S/H_2, the supported tungsten sample gave the following response: (i) a very rapid temperature rise, peaking at 90°F above initial temperature in 0.5 min, (ii) an equally rapid temperature drop to about 20°F above initial temperature after 1 min, and (iii) a gradual decrease in temperature over the next 5 min with a final temperature line-out about 10°F above initial temperature. The rapid temperature peak may have been due to a rapid surface sulfiding or adsorption of H_2S. In any event, essentially constant temperature was achieved within 5 min, so that kinetic data could be treated as isothermal except for the very earliest stage of reaction.

Fixed-bed reactor studies. Sulfiding rate studies on the supported tungsten trioxide were carried out in a fixed-bed metal reactor at atmospheric and elevated pressures. Sample batches of 5 or 25 cm^3 of the supported tungsten trioxide were placed in the reactor and heated in a flow of nitrogen to the temperature and pressure of the sulfiding run. Mixtures of H_2S in H_2, which were premixed in separate high-pressure cylinders and analyzed by mass spectroscopy, were passed through the reactor directly at run pressure at a gas hourly space velocity of about 15000. After the desired reaction time, the reactor was cooled to room temperature in nitrogen. Following the run, the catalyst was analyzed for sulfur. No difference in sulfur content with bed position was detected. Based on estimated maximum initial sulfiding rates, the

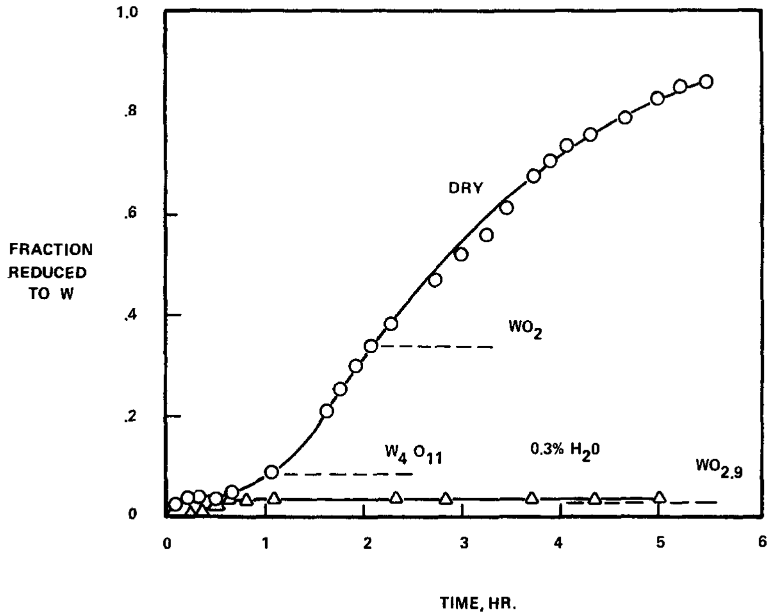

FIG. 1. Reduction of WO_3 by hydrogen: conditions: sample MS, reduced in microbalance reactor at 950°F with H_2/N_2, 1:1; ○, reduced with dry gas; △, reduced with gas containing 0.3% H_2O.

rate of H_2S supply was at least in twofold excess at the very start of the run and considerably higher for the rest of the run. Intraparticle diffusion estimated by the Weisz criterion (*8*) was negligible, except at the very earliest stage of reaction (below 0.01 hr).

RESULTS

Microbalance Studies

Reduction of tungsten trioxide. Tungsten trioxide easily reduced in hydrogen at 950°F to tungsten metal. Figure 1 shows the course of the reaction in terms of fraction converted to tungsten metal versus time, as determined by weight change measurements. An initial rapid reduction to approximately $WO_{2.9}$ occurs. This is followed by an induction period, subsequent accelatory region, and final decay region. Except for the initial reduction plateau, the sigmoid-type curve is typical of many gas–solid or solid decomposition reactions requiring a nucleation period. It is significant that once substantial reduction begins, sustained reduction at this temperature proceeds smoothly towards metallic tungsten without any breaks in the curve corresponding to other intermediate oxides. Thus, if intermediate phases are formed, they are rapidly reduced further to tungsten metal without formation of appreciable amounts of intermediates. Essentially the same results were obtained by Barret and Dufour (*9*).

Reduction in the presence of a small amount of water vapor in the hydrogen was radically different. After reaching the reduction stage corresponding to $WO_{2.9}$, further reaction ceased. Even after 20 hr of reaction, reduction had proceeded to only about $WO_{2.7}$ (W_4O_{11}). The sample had a dark blue-purple color, which has generally been ascribed to W_4O_{11}.

Reduction of the supported WO_3 was much more difficult than bulk WO_3. In a 16-hr period, only about 20% reduction (based on conversion to W) was obtained compared to about 95% for the unsupported WO_3. Clearly, the silica–alumina support retards the reduction of the WO_3. Nevertheless, an initial plateau region, corresponding to slightly reduced WO_3, was again observed before additional reduction occurred.

TABLE 1

SULFIDED REACTION PRODUCTS[a]

	Run conditions		Results				
				WS_XO_Y		WO_Z[c]	
Sample[b]	Temp. (°F)	Time (hr)	S (wt %)	X	Y	Z	X-ray
MS	500	90	12.9	0.96	1.50	2.88	Poor pattern
	950	2	7.7	0.57	2.00	2.80	—
	950	2	10.5	0.77	1.67	2.72	WS_2, $W_{20}O_{58}$
	950	16	21.8	1.67	0.45	2.81	—
TA	950	2	2.7	0.20	2.40	2.67	WS_2, $W_{20}O_{58}$
	950	16	14.8[e]	1.09	1.30	2.86	—
	950	70	18.8	1.42	0.87	2.99	WS_2, WO_X(?)
						Av 2.82 ± 0.11	
S[d]	950	24	18.8[f]	1.43	0.76	2.67	—
S[d]	950	21	16.0[f]	1.23	1.18	3.07	—

[a] H_2/H_2S = 1:10, total press. = 1 atm.

[b] MS = commercial micropheres of WO_3; TA = WO_3 obtained from heating tungstic acid; and S = WO_3 supported on silica-alumina.

[c] Assumes only sulfided species is WS_2.

[d] Results corrected for a small loss in fluorine.

[e] Estimated from sample weight change.

[f] Sulfur values adjusted to WO_3 basis for direct comparison with values above.

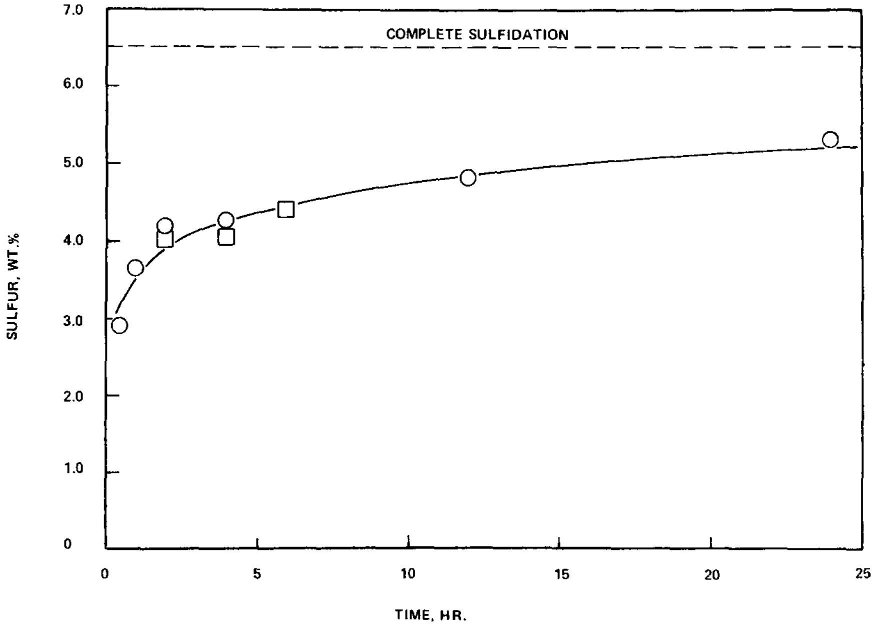

FIG. 2. Effect of time on sulfur level: conditions: sample S, sulfided in fixed-bed reactor at 950°F under H_2S partial pressure of 0.55 atm; ○, sulfided dry; □, sulfiding gas contained 0.2% H_2O; —, Eq. 16.

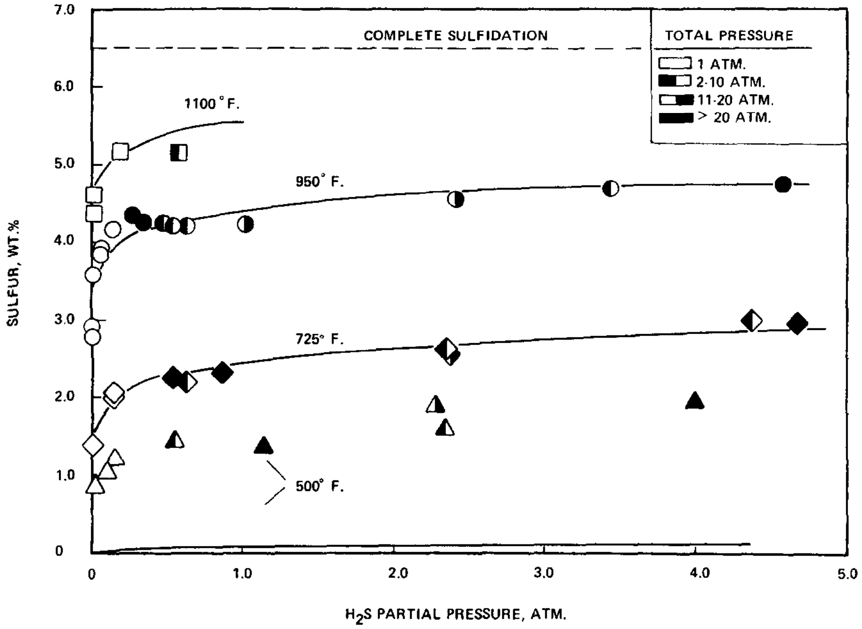

FIG. 3. Effect of H_2S partial pressure on sulfur level: conditions: sample S, sulfided in fixed-bed reactor for 4 hr; —, Eq. 16.

Reaction products of sulfidation. Several partially sulfided runs on bulk WO_3 were made to establish the overall course of the sulfidation reaction. The results are tabulated in Table 1. Total sulfiding to WS_2 corresponds to a sulfur value of 25.8 wt %. Values of X and Y corresponding to the empirical formula WS_XO_Y and Z, the oxygen-to-tungsten ratio in the oxide residue, are given in Table 1.

A regular lowering in oxide content of the sample attends in increasing sulfur content. If sulfiding proceeds directly to WS_2 without prior reduction of the WO_3, a value of Z of 3.0 should be obtained. On the other hand, if reduction to WO_2 preceeds sulfiding, Z should be 2.0. It is obvious that neither of these are the exclusive oxide phase present in the sulfided samples. The average value of Z of 2.82 could represent within experimental error either of two known intermediate oxides (*10*): $W_{20}O_{58}(WO_{2.90})$ or $W_{18}O_{49}(WO_{2.72})$.

The X-ray diffraction results on the partially sulfided samples resolved this question. The unreacted oxide pattern agreed with that for beta-tungsten oxide, $W_{20}O_{58}$ (*10*), there being no lines attributable to WO_3, $W_{18}O_{49}$, WO_2, or W. The WS_2 pattern was good for the two lower sulfided samples. The higher sulfided sample displayed some line shifts indicative of an expanded WS_2 lattice and did not give a good oxide pattern. It may be in this case that the major structure is a deformed WS_2 structure containing sulfur atoms located between the sulfur layers in the normal layer structure. In this respect, the X-ray pattern for the low-temperature run was the least well-defined, suggesting considerable disorientation of the structure at low temperature.

We conclude, therefore, that in the presence of H_2S/H_2 mixtures, WO_3 undergoes rapid reduction to $WO_{2.9}$, which then sulfides to WS_2 more slowly. This is in line with the reduction results, where a very rapid reduction of WO_3 to $WO_{2.9}$ preceded bulk reduction.

Results on the support were not as unequivocal. The tungsten phases are not observed on silica–alumina by X-ray diffraction. However, the general agreement of the microbalance results with the unsupported samples as indicated in Table 1 leads us to assume that the course of the sulfidation reaction on the support is probably identical to that for pure WO_3 with respect to intermediate oxide formation.

Reaction with gaseous HCl. Gaseous HCl at elevated temperature reacts with tungsten trioxide quantitatively forming volatile WO_2Cl_2 (*11*) according to the equation,

$$WO_3(s) + 2HCl(g) \rightarrow WO_2Cl_2(g) + H_2O(g). \quad (13)$$

Results of tests carried out in a flowing atmosphere of HCl at 1150°F are presented in Table 2. Bulk tungsten trioxide was subjected to various pretreatments to test HCl reactivity with different states of tungsten. After the specified pretreatment conditions, the state of the tungsten was determined from weight change measurements. The pretreated samples were then subjected to the HCl treatment *in situ*.

Bulk WO_3 itself reacted completely with HCl, no residue remaining after several hours. In contrast, W metal did not react at all. A partially reduced sample of WO_3, empirically close to WO_2, reacted incompletely leaving only W metal. Weight change calculations indicated that each mole of tungsten removed by volatilization corresponded closely to the loss of 3 moles of oxygen, according to Eq. (13), implying that the reduced sample consisted of W and WO_3, in essential agreement with the reduction results presented earlier.

A completely sulfided sample, obtained via reduction to W prior to sulfiding to insure no residual oxygen, was unreactive towards HCl. However, a partly sulfided sample, containing residual oxygen, did not undergo complete removal of the oxygen with HCl. In this case, only about one-half of the oxygen was removed in a 15-hr treatment. Also, the rate of removal of tungsten was appreciably slower in this case than for the previous treatments. We feel that this result is highly significant, indicating that the presence of sulfide seriously hinders access of the HCl to the oxide phase.

Fixed-Bed Reactor Studies

The time variation in the degree of sulfiding of the supported tungsten oxide is shown in Fig. 2 where the sulfur level is plotted against time at a constant H_2S par-

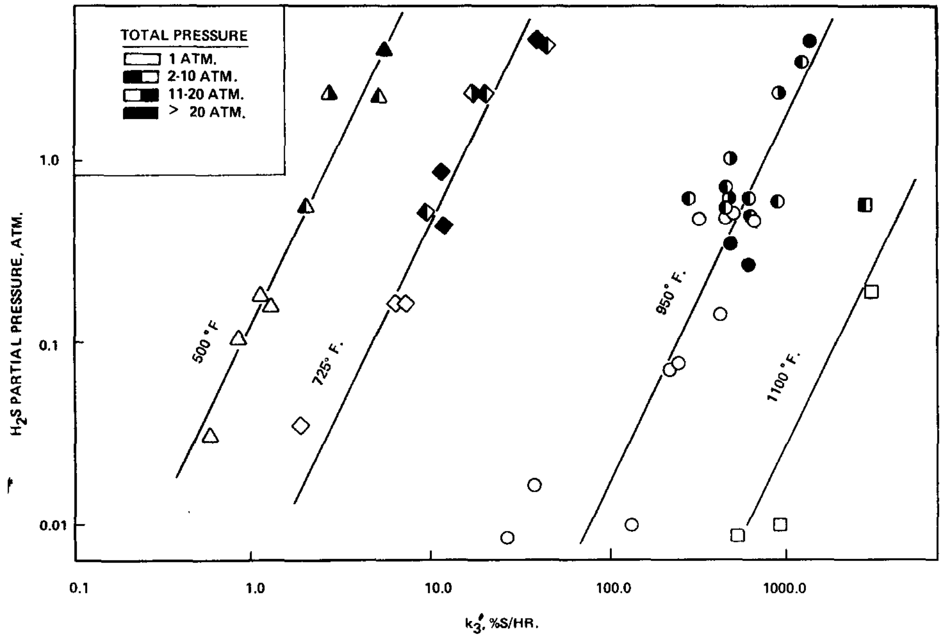

FIG. 4. Effect of total pressure and H_2S partial pressure on k'_3: conditions: sample S, sulfided in fixed-bed reactor.

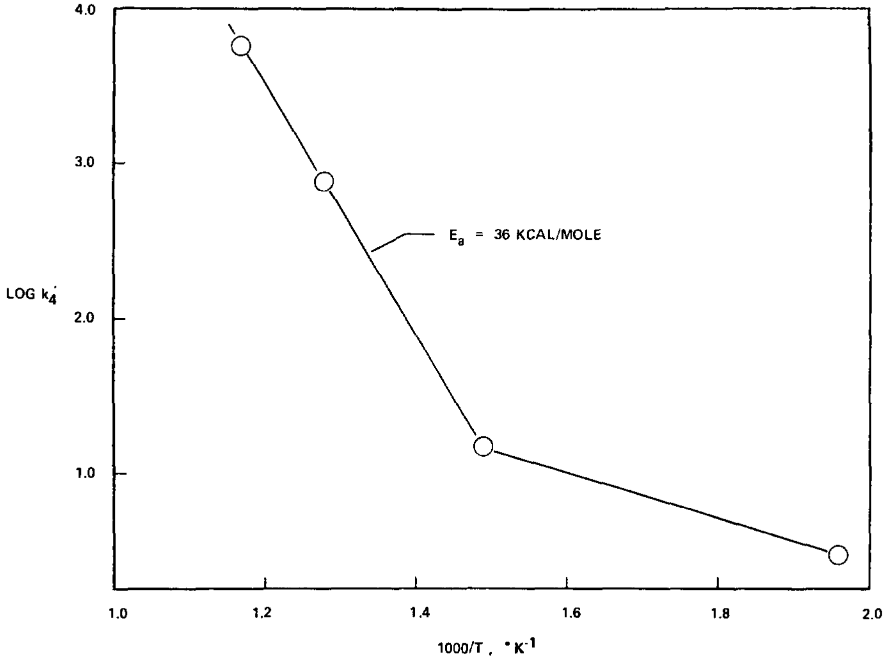

FIG. 5. Effect of temperature on k'_4: conditions: sample S, sulfided in fixed-bed reactor.

tial pressure and temperature. The rate of reaction is comparatively rapid during the early stage but then markedly drops off with time. The presence of water vapor in the sulfiding stream had no effect on the sulfidation rate. Figure 3 shows the sulfur levels obtained as a function of the H_2S partial pressure at constant reaction time and temperature. A range of total pressures from 1 to 50 atm was used. Low partial pressures have a very pronounced effect on the sulfur level; but as partial pressure is increased, the sulfur level tends to flatten out.

The time data of Fig. 2 were fitted by the logarithmic expression given by Eq. (7), with time in hours. This allowed calculation of the constant k'_2, which in turn

TABLE 2

REACTIVITY OF TUNGSTEN SAMPLES WITH GASEOUS HYDROGEN CHLORIDE[a]

WO_3 Sample	Pretreatment conditions			State	HCl results	
	Gas	Temp. (°F)	Time (Hr)		Lost	Left
TA	—	—	—	WO_3	WO_3	—
TA	H_2	1150	22	W	—	W
TA	H_2 H_2	900 1000	22 2	$WO_{1.8}$	WO_3	W
MS	H_2 H_2S/H_2[c]	1150 1150	22 22	WS_2	—	WS_2
TA[b]	H_2S/H_2[c]	950	22	$WO_{1.3}S_{1.1}$	WO_3(55%)	WS_2 + WO_3(45%)

[a] Conditions: 1150°F, 1 atm HCl, 400 ml/min; flow, 4–6 hr.

[b] HCl treatment time was 15 hr.

[c] H_2S/H_2 ratios were 1:10.

was used to calculate k'_3 for the other runs. In order to evaluate the partial pressure dependency of k'_3, it was plotted against the H_2S partial pressure, as shown in Fig. 4. The slopes of the log–log plots at the various temperatures are reasonably identical and equal to approximately 2, signifying the following relationship applies:

$$k'_3 = k'_4 p^{1/2}, \qquad (14$$

where p is the H_2S partial pressure (atm), and k'_4 is a pressure-independent rate constant. If an Arrhenius temperature dependency applies, log k'_4 should be a linear function of reciprocal temperature. The relationship is shown in Fig. 5. At the three highest sulfiding temperatures, a straight line prevails, which, however, does not fit the lowest temperature value. The activation energy in the temperature range 725–1100°F is 36 kcal/mole.

Since runs were made at pressures from 1 to 50 atm, the effect of pressure was separately evaluated. Combining Eqs. (7) and (14) gives,

$$k'_2 k'_4 = \frac{\exp(k'_2 S) - 1}{t p^{1/2}}. \qquad (15)$$

The right-hand side of Eq. (15) should be a constant at each temperature if total pressure is not a variable. Application of Eq. (15) to the data showed no systematic trend with total pressure. Also, Fig. 4 illustrates the independence of k'_3 on total pressure by the randomness of the experimental data scattered about the calculated lines. Hence, it can be concluded that the sulfidation rate is independent of total pressure and consequently of hydrogen partial pressure.

The overall equation which relates the sulfur level to sulfidation time, temperature, and H_2S partial pressure is,

$$S = \frac{1}{1.94} \ln \times \left[1 + 1.42 \times 10^{13} t p^{1/2} \exp\left(-\frac{36000}{RT}\right)\right]. \qquad (16)$$

The sulfur levels calculated according to Eq. (16) are plotted on Figs. 2 and 3. As can be seen, the calculated values agree well for all of the conditions except for the 500°F sulfiding temperature data, which are considerably higher than predicted.

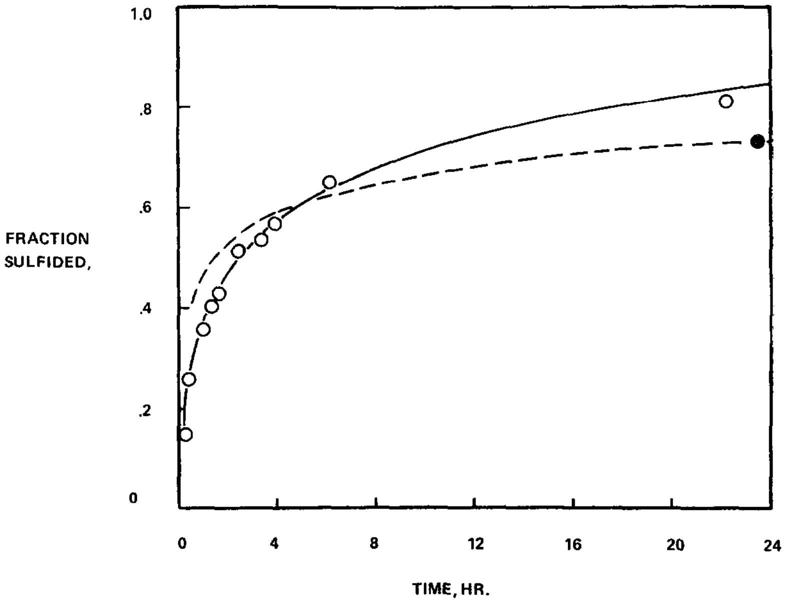

FIG. 6. Sulfidation of supported and unsupported WO_3: conditions: sulfided in microbalance reactor at 950°F with H_2S/H_2, 1:10; ○, data for sample MS; —, Eq. 4; ● , datum for sample S; —, Eq. 16.

The lack of fit of the 500°F data may be due to a change in mechanism at lower temperature. Changes of mechanism with temperature are not uncommon in the literature *(12)*; sufficient data at lower temperatures, however, were not obtained to verify this point.

Comparative Rates of Sulfidation of Bulk Versus Supported WO_3

Since our main objective was to study the sulfiding of supported tungsten oxide, only one run was made on bulk tungsten oxide to establish if the basic sulfiding mechanisms are identical. The rate of sulfidation was followed by weight change measurements in the microbalance reactor. Since we have demonstrated that only very slight reduction of the trioxide to $WO_{2.9}$ precedes sulfidation, correction of weight changes due to this fact was neglected (less than 10% error).

Figure 6 depicts data for sulfiding bulk tungsten trioxide at 950°F. The data correlate well with the logarithmic law as expressed by Eq. (4). For comparison, an equivalent curve calculated from Eq. (15) for supported tungsten trioxide under the same conditions as the microbalance run is also shown in Fig. 6 (broken line). The bulk sample reacts slower initially, but proceeds faster in the later stages of reaction compared to the supported sample. This is reflected in the values of the constants of the logarithmic equation: k_2 and k_3 for bulk WO_3 are 6.6 and 1.63 hr^{-1} versus 12.5 and 33 hr^{-1} for supported WO_3. Recourse to the differential form of Eq. (4),

$$\frac{d\alpha}{dt} = k_3 \exp(-k_2\alpha), \qquad (17)$$

where the rate of conversion, $d\alpha/dt$, represents the slopes of the curves in Fig. 6 at any given time, shows that for the supported WO_3, the following must occur: (i) the initial rate will be higher because of the larger k_3, and (ii) the later rate will be slower due to the larger k_2 in the exponential term. Thus the crossing of the curves in Fig. 6 is consistent with a single-rate law for both cases.

In order to be sure that differences in rates of sulfidation obtained in the microbalance reactor for bulk tungsten trioxide and in the fixed-bed metal reactor for supported trioxide were not due to the reactor used, a sulfiding run with supported tungsten was made in the microbalance reactor. The conditions were identical to those used for the bulk sulfiding run of Fig. 6. The sulfur content at the end of the run is shown in Fig. 6. Agreement with the curve predicted from the metal reactor runs is good, leading us to conclude that both reactors are equivalent for the purposes of sulfiding rate studies.

In comparing rate constants for the two cases, supported versus bulk oxide, one must keep in mind that very basic differences may exist in the structure and state of subdivision of the oxide phases. Actually, k_2 is only different by a factor of two for the supported oxide, whereas k_3 is 20-fold larger. The former implies that there is not a large difference in the physical structure of the oxide phases in the two cases. The latter implies a larger number of pores exposed per weight of oxide in the case of the supported oxide if it is assumed that the intrinsic reactivity per pore is identical, i.e., the same k_1, and the surface pore density is the same. This seems reasonable from the well-known fact that impregnation results in a dispersion of the oxide on the support *(13)* which leads to smaller particles. Lack of a definitive X-ray pattern for WO_3 on the supported sample supports this view. On a unit weight of oxide basis then, the supported WO_3 will have a larger surface area, in turn exposing more total pores, and hence should have a higher value of k_3. Our overall conclusion, therefore, is that the mechanism for sulfidation is essentially identical for supported and bulk tungsten trioxide, implying that the "pores" are indigenous to the tungsten phase itself and not to the silica–alumina phase.

The only example furnishing a comparative study on the sulfiding of bulk versus supported oxide concerns nickel oxide in pure H_2S (helium dilution used) at atmospheric pressure, where different mechanisms were claimed (*14*). Bulk NiO followed a parabolic law whereas NiO on silica–alumina obeyed a logarithmic law.

DISCUSSION

Relevant to the problem of competitive reduction versus sulfidation of WO_3 in the presence of both H_2 and H_2S, the question of ease of reduction in hydrogen arises. That reduction of oxide might be expected, comes from the fact that trungsten itself is reduced from the +6 valence state to the +4 state in going from WO_3 to WS_2. One might suppose, therefore, that the sulfidation of WO_3 would proceed through the following two-step mechanism:

$$WO_3 + H_2 \rightarrow WO_2 + H_2O, \tag{18}$$

$$WO_2 + 2H_2S \rightarrow WS_2 + 2H_2O, \tag{19}$$

that is, a simple reduction followed by a metathesis reaction. Such a sequence appears to be valid for bulk MoO_3, where only MoS_2 and MoO_2 phases were detected in incompletely sulfided samples (*15, 16*).

Our results on sulfiding WO_3 with H_2S/H_2 mixtures also indicate a two-step mechanism; however, instead of reduction to WO_2, only a partial reduction to beta-tungsten oxide, $W_{20}O_{58}$, occurs. Beta-tungsten oxide has been described as a defective structure containing random boundary paths formed from shear of adjacent octahedron blocks containing oxygen vacancies (*17*). This defective structure serves then as the precursor to the sulfiding which follows. Diffusion may be via dislocation lines, cracks, boundary paths or the like, which we encompass in the term "pores," but are actually crystalline defects. In view of this, and the magnitude of the experimental activation energy for sulfiding, we are probably not dealing with gaseous diffusion, but rather with ionic diffusion via defect paths in the beta-tungsten oxide phase. It seems reasonable, then, that conversion to the sulfide could exert compressional stress on neighboring pores as supposed in the logarithmic-law derivation, and thus, pore blockage could be explicable in terms of the defective beta-tungsten oxide structure. Possible support for the blockage of pores by WS_2, hindering further reaction with the unreacted oxide, may be inferred from the runs with gaseous HCl. These could explain the extreme slowing down of the reaction rate with time (conversion). If the sulfide formed at pore-mouths results in effective closing-off of pores, continued reaction must proceed via diffusion through bulk sulfide, a very slow process.

The one-half power dependence on H_2S concentration may be explained on the basis of adsorption of H_2S at the exterior surface of the basic oxide particles and pore diffusion into the interior. The rate of diffusion will be proportional to the concentration gradient of H_2S from the particle surface to the interior. Since diffusion is controlling, the concentration in the center of the particle is essentially zero. Thus, the diffusional flux will be proportional to the surface concentration. Moreover, the surface concentration can be assumed to be in equilibrium with the gas concentration and will be determined by the particular adsorption isotherm operating. Thus, the one-half power could stem from a Freundlich isotherm, i.e., surface coverage, θ, is related to H_2S partial pressure, p, according to,

$$\theta = K_f p^{1/n}, \tag{20}$$

where K_f and n are constants and n takes on the value of 2 in our case. This isotherm has recently received theoretical justification based on a varying heat of adsorption with increasing surface coverage (*18*). On the other hand, the one-half power could also arise from a Langmuir isotherm with dissociation (*19*),

$$\theta = \frac{(K_L p)^{1/2}}{1 + (K_L p)^{1/2}}, \tag{21}$$

where K_L is an adsorption coefficient. If in the range of our pressures, $(K_L p)^{1/2} \ll 1$, Eq. (21) reduces to Eq. (20). The Langmuir isotherm requires the H_2S molecule to dissociate into two entities, each one occupying a separate surface site. A half-order pressure dependence has been reported for adsorption of H_2S on a Ni/SiO_2 catalyst (*20*). On the other hand, the effect of pressure on the sulfidation of nickel powder was expressed by a simple first-power Langmuir isotherm (*21*).

Our conclusion that the sulfiding mechanism is essentially identical for supported and bulk oxide appears to be at variance with the results obtained for direct reduction. In the latter, the supported oxide was only reduced to $WO_{2.9}$ while the bulk oxide was reduced completely to W. Evidently the support exhibits a strong retarding influence on the reduction but not on the sulfidation. Equilibrium limitations may come into play here. Free energy changes at 900°F for sulfidation and reduction of bulk WO_3 are:

$$WO_3 + 2H_2S + H_2 = WS_2 + 3H_2O; \quad \Delta F^\circ = -30.5 \text{ kcal}; \quad (22)$$

$$WO_3 + 3H_2 = W + 3H_2O; \quad \Delta F^\circ = +6.5 \text{ kcal}. \quad (23)$$

It is apparent that sulfidation is quite favorable whereas reduction is not. Nevertheless, reduction is achieved in a flowing stream of hydrogen because the water is continuously removed, preventing equilibrium from becoming established. On the other hand, following the argument of Sontag *et al.* (*22*), who found a similar incomplete reduction of WO_3 on alumina, the hydrophilic character of the support may retain the water initially formed in the reduction at the surface, creating a stable local atmosphere containing a high pH_2O/pH_2 ratio. Since the ratio is exposed to this atmosphere, reduction is arrested, and higher temperatures are needed to achieve reduction by lowering the surface concentration of water. Although a similar situation could pertain to the sulfiding reaction, sufficiently high water concentrations cannot be maintained in this case to reach equilibrium limitation, and thus the sulfiding reaction is not arrested. The reasonableness of this proposition may be adduced from the following calculated equilibrium ratios at 900°F: $(pH_2O/pH_2)_{eq} = 0.24$ for reduction, and $(pH_2O/pH_2S)_{eq} = 61000$ for sulfidation with $pH_2S/pH_2 = 1:10$. It can be seen that equilibrium might be reached for reduction in the presence of a highly hydrophilic surface but is extremely improbable for sulfiding. Further support for the thermodynamic basis as the cause of nonreducibility of supported WO_3 derives from the reduction of bulk WO_3 in the presence of water (Fig. 1). Only 0.3% water in the hydrogen stream inhibited reduction beyond $WO_{2.9}$.

CONCLUSIONS

The salient findings of this study are: (i) Reduction of bulk WO_3 by hydrogen proceeds rapidly to $W_{20}O_{58}$ and then more slowly to W metal. (ii) Sulfidation of bulk WO_3 by hydrogen sulfide–hydrogen mixtures proceeds rapidly through formation of $W_{20}O_{58}$, followed by slower reaction to WS_2. (iii) Kinetics of sulfidation of supported WO_3 obeys a logarithmic law, which is interpreted in terms of a pore-blocking model. (iv) The sulfidation rate follows a one-half order dependency on H_2S partial pressure; zero order in H_2 partial pressure. (v) The activation energy for sulfidation is 36 kcal/mole in the temperature range 725–1100°F, which is ascribed to activated diffusion. (vi) The mechanism of sulfidation of bulk and supported WO_3 is similar.

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