JOURNAL OF CATALYSIS 95, 249–259 (1985)

Characterization of Tungsten Sulfide Catalysts

KUMAR RAMANATHAN[1] AND S. W. WELLER[2]

Department of Chemical Engineering, State University of New York at Buffalo, Amherst, New York 14260

Received November 30, 1984; revised April 16, 1985

Unsupported tungsten sulfide catalysts of high surface area (60 m^2/g) were prepared by *in situ* decomposition of ammonium tetrathiotungstate (ATT) in flowing helium at 450°C. This catalyst (stoichiometry approx $WS_{2.2}$) was subjected to various pretreatments in both hydrogen and a mixture of 15% hydrogen sulfide in hydrogen at elevated temperatures (up to 450°C). Temperature-programmed reduction (TPR) in hydrogen showed two peaks, indicating the presence of two species of sulfur with different binding energies. Surface areas and pore-size distributions of the catalysts were found to be relatively unaffected by treatment in hydrogen at 450°C for 1 h, but treatment for 12 h caused the surface area to decrease from 60 to 35 m^2/g. Examination of catalyst samples under a scanning electron microscope showed that the large number of microcracks developed on decomposition of ATT were considerably reduced by a 12-h treatment in hydrogen at 450°C. Low-temperature oxygen chemisorption (LTOC) was measured on tungsten sulfide subjected to pretreatment in hydrogen for different times and temperatures. Samples with the greatest sulfur loss showed the highest LTOC, suggesting that oxygen chemisorbs at surface anion vacancies (coordinatively unsaturated tungsten ions). Appreciable LTOC was generated only upon removal of sulfur corresponding to the second peak. The ratio of surface area to LTOC for a sample treated for 12 h in hydrogen led to a value of 170 $Å^2/O_2$ molecule (85 $Å^2$/O atom). Catalyst activity for propylene hydrogenation at 100 and 150°C was measured using a pulsed-flow microcatalytic reactor. Activity was found to increase with increasing LTOC.

INTRODUCTION

Pioneering work on tungsten sulfide catalysts was carried out by Pier (*1*) and Donath (*2*) in West Germany and by Samoilov and Rubinshtein (*3–6*), Kalechits and Deryagina (*7*), and Pavlova *et al.* (*8*) in the USSR. Notable contributions since then have been made by Voorhoeve and coworkers (*9–12*), who studied both the unpromoted and Ni-promoted tungsten sulfide catalyst systems. On the basis of ESR measurements, they propose W^{3+} ions at surface anion vacancies as active sites for benzene hydrogenation.

The present work is concerned with unsupported tungsten sulfide catalysts. The objectives were several:

(1) to prepare, pretreat, and characterize tungsten sulfide without exposure to air;

(2) to determine the effect of pretreatment variables on BET area, pore volume, pore-size distributions, and morphology of tungsten sulfide catalysts; and

(3) to investigate correlations between low-temperature oxygen chemisorption (LTOC) and catalytic activity for olefin hydrogenation.

EXPERIMENTAL

Catalyst Preparation

Catalysts were prepared by the decomposition of ammonium tetrathiotungstate (ATT). This method gives tungsten sulfide of high surface area. Since one of the objectives of this work was to study the behavior of tungsten sulfide as a function of hydrogen treatment at elevated temperatures, the ammonium salt was decomposed in flowing He, and not in H_2, as was done in many previous studies (*3–8*).

ATT was prepared as follows: 40 g of am-

---

[1] Present address: Research Triangle Institute, Research Triangle Park, N.C. 27709.

[2] To whom all correspondence should be addressed.

0021-9517/85 $3.00

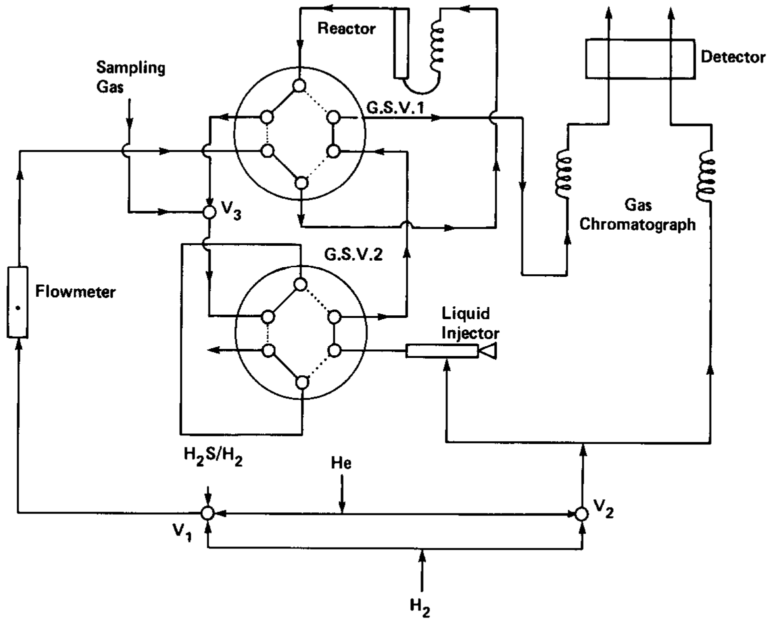

FIG. 1. Schematic diagram of the experimental setup.

monium metatungstate (99.9% pure, −80 mesh, purchased from CERAC, Inc.) was dissolved in 200 ml of distilled water. Twenty milliliters of ammonium hydroxide (Fisher Reagent ACS) was added to this solution. The resulting ammoniacal solution was transferred into a flask suspended in a water bath at 60°C. Hydrogen sulfide (CP grade, 99.5% purity, Union Carbide Corp., Linde Division) was bubbled through the solution for 4 h, after which the flow was shut off, and the inlet and outlet of the reaction vessel were sealed with clamps. The vessel was then removed from the water bath, lowered into an ice/water bath, and left to stand overnight. Large, orange–yellow, needle-like crystals precipitated from the solution. The mother liquid was decanted and the crystals were vacuum filtered to remove excess solution.

The ATT was flash-decomposed in flowing helium at 450°C to give tungsten sulfide of high surface area. The "flash-heating" was achieved by lowering the microreactor containing the ATT into a preheated furnace. The time taken to reach 450°C was typically 10 min.

Integrated Setup for Catalyst Testing

The experimental setup is schematically represented in Fig. 1. This was used for all measurements except surface area, pore-size distribution, and catalyst stoichiometry determination. The system consists of a fixed-bed microcatalytic reactor with an arrangement of valves and tubing that permitted *in situ* preparation, pretreatment, pulsed chemisorption, and activity testing of the catalyst. GSV 1 is a six-port gas-sampling valve that was used to switch the reactor between pretreatment and carrier gas streams, and GSV 2 is another six-port valve used for injecting pulses of chemisorbate or reactant.

Gases (supplied by the Linde Division of Union Carbide Corp. and used as received) were (a) hydrogen, prepurified grade, >99.99% purity; (b) helium, high purity grade, >99.995% purity; (c) hydrogen sulfide in hydrogen, 15% custom blend; (d) oxygen in helium, 1.5% custom blend (for chemisorption); and (e) propylene, CP grade, >99.0% purity.

A Varian 1420 dual-column gas chromatograph (GC) equipped with a thermal conductivity detector was used for pulsed chemisorption and activity measurements. The products of olefin hydrogenation were separated on a column packed with Durapak (*n*-octane on Porasil-C) and operated at room temperature. An empty column was used when oxygen was pulsed through the reactor. The signal from the GC was monitored by a Linear Instruments 252 integrating recorder.

Surface areas and pore-size distributions were determined by analysis of nitrogen adsorption/desorption isotherms at −195°C. These were obtained on a Quantasorb Analyzer manufactured by Quantachrome Instruments.

Catalyst stoichiometries after pretreatment were gravimetrically determined by calcining the sample to WO_3 in air at 550°C for 2 h. The tungsten content was calculated from the weight loss, assuming stoichiometric WO_3 as the product of calcination. Calcination to WO_3 is a standard analytical method for determination of tungsten content. The sulfur content was then determined by difference, with the assumption that the catalyst consisted only of sulfur and tungsten.

Catalyst Pretreatment

The term pretreatment refers to operations performed on the catalyst subsequent to preparation in helium, but prior to measurement of activity and/or chemisorption.

The reactor was cooled to room temperature in helium prior to introduction of the pretreatment gas. Valve V_1 (Fig. 1) was switched to the desired position and pretreatment gas flow was started at 35 to 40 cm^3/min. The reactor was then lowered into the furnace (previously cooled to room temperature) and heated to the pretreatment temperature.

During pretreatment with hydrogen, the tail gas from the reactor was passed into an Erlenmeyer flask containing 200 ml of zinc acetate solution (concentration 10 g/liter) to absorb H_2S. The flask was connected to the vent on valve GSV 2 (Fig. 1). The contents of the flask were later titrated to determine the hydrogen sulfide evolution.

Experiments to measure oxygen chemisorption (LTOC) involved a helium purge for at least 15 min at the temperature of pretreatment before cooing to the temperature of chemisorption (−78°C). Purging for 1 h at pretreatment temperature did not significantly affect the subsequent value of LTOC. Purging was done in order to remove any adsorbed hydrogen sulfide that might block sites for chemisorption.

In experiments involving activity measurement, the reactor was cooled in the pretreatment gas to room temperature and reheated to reaction temperature (100 or 150°C) in hydrogen. In the case of pretreatment with 15% H_2S/H_2, the sample was purged with helium at the temperature of pretreatment and cooled in helium to prevent adsorption of H_2S on the catalyst surface during the cooling process.

Low-Temperature Oxygen Chemisorption (LTOC)

Oxygen chemisorption on the catalyst was measured at −78°C. The carrier gas (helium) flow rate was 20 cm^3/min. The first pulse of O_2/He (1.5% O_2 in He, 1.30 (STP) cm^3) was injected about 30 min after the reactor was immersed into the cold bath. Successive injections were made at 2-min intervals until three consecutive peaks of equal area emerged.

Activity Measurement

Catalyst activity for propylene hydrogenation was measured with injections of 2.26 (STP) cm^3. Hydrogen acted as both carrier gas and reactant for the pulse. The carrier gas (hydrogen) flow rate for activity measurement was 35 cm^3/min. Successive injec-

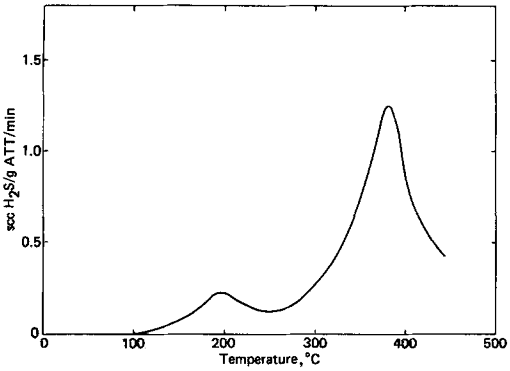

FIG. 2. TPR spectrum of tungsten sulfide prepared by flash-decomposition of ATT in He at 450°C.

tions were made at 9-min intervals until three consecutive pulses showed conversions within 2% of each other. This generally took six to eight injections. The normal procedure involved testing at 100°C and then at 150°C. However, in some cases, the catalyst was tested only at one of these temperatures.

RESULTS AND DISCUSSION

Effect of Hydrogen Treatment on Sulfur Removal

Tungsten sulfide prepared by the decomposition of ammonium tetrathiotungstate (ATT) contains excess nonstoichiometric sulfur (*1–8, 13*); the stoichiometry depends on details of the decomposition (heating rate, environment). No studies have been reported on sulfur removal by hydrogen from tungsten sulfide prepared from ATT in an inert atmosphere.

Our samples of tungsten sulfide, prepared by flash decomposition of ATT in flowing He, have a stoichiometry of $WS_{2.15-2.20}$. Figure 2 is a temperature-programmed reduction (TPR) spectrum: it shows the instantaneous rate of H_2S evolution versus temperature for a sample prepared *in situ*, cooled to room temperature in helium, and then heated in flowing hydrogen to 450°C at a rate of 15°C/min. All values are expressed as (STP) cm^3 H_2S/g ATT, since the weight of precursor salt was known accurately. The final catalyst weight was sometimes inaccurate because of the vigorous decomposition of ATT.

No H_2S evolution is observed until about 140°C, but two peaks then emerge (Fig. 2). The first is a small peak at about 200°C which is complete at 250°C. The total volume of H_2S evolved up to 250°C is 1 (STP) cm^3/g ATT, which corresponds to a loss of 0.016 atom S/atom W. The second peak, at a temperature of 380°C, is much larger. H_2S evolution corresponding to this peak (250 to 450°C) is 9.1 (STP) cm^3/g ATT or 0.15 atom S/atom W. The total sulfur loss during TPR to 450°C is, therefore, 0.17 atom S/atom W, 10% of which is evolved in the first peak. The existence of different types of sulfur bonding in sulfide catalysts has been postulated earlier in work by Samoilov and Rubinshtein (*3–5*) and Kalechits and Deryagina (*9*).

Analysis of the shape of the TPR peaks by two methods (Smutek *et al.* (*15*) and Chan *et al.* (*16*)) gave values of apparent activation energies which were in good agreement. These were about 16 kcal/mole for peak 1 and 26 kcal/mole for peak 2.

Table 1 summarizes the effect of pretreatment on the physicochemical properties of tungsten sulfide catalysts. As might be expected, more severe conditions of reduction lead to greater sulfur losses. The catalyst composition is approximately stoichiometric WS_2 after 1 h in hydrogen at 450°C (No. 6). Twelve hours in hydrogen at 450°C results in a sulfur-deficient material, $WS_{1.81}$ (No. 7).

Effect of Pretreatment on BET Area, Pore-Size Distribution, and Morphology

(*a*) *BET area and pore volume*. The BET surface area of unsupported tungsten sulfide catalysts prepared from ATT varies considerably depending on the conditions of preparation (*13*). The temperature, gas environment, heating schedule, and time at temperature all play an important role in determining surface area. Much of the work

TABLE 1

Effect of Pretreatment on Physicochemical Properties of Tungsten Sulfide

No.	Gas[a]	Temp. (°C)	Time (min)	Atom S[b] / Atom W	LTOC[c] (STP) cm^3/g ATT	Atom O / Atom W	BET area (m^2/g cat.)	Å^2/O_2[d]	S/W
1	—	—	—	—	0	0	56.3	—	2.15
2	H_2	100	60	—	0	0	61.9	—	2.15
3	H_2	250	0	0.015	0	0	66.7	—	2.13
4	H_2	250	60	0.07	0	0	64.5	—	2.08
5	H_2	450	0	0.10	0.14	0.0044	61.3	1013	2.05
6	H_2	450	60	0.15	0.16	0.0050	58.1	980	2.00
7	H_2	450	12 h	0.34	0.57	0.0178	35.0	170	1.81
8	H_2S/H_2 (15%)	450	60	0	0	0	59.5	—	[e]

[a] All samples prepared by flash-heating ATT in flowing He at 450°C prior to pretreatment.

[b] Atom of sulfur removed per atom of tungsten in sample.

[c] Samples purged in He at temperature for 15 min and cooled to −78°C prior to LTOC. Pulses of 0.0195 (STP) cm^3 O_2 were injected until breakthrough.

[d] Area measured as m^2/g WS_x converted to m^2/g ATT before computing Å^2/O_2.

[e] Not measured.

done to date fails to report one or more of the above parameters.

Voorhoeve and Wolters (*9*) reported surface areas of 50 to 70 m^2/g for tungsten sulfide prepared under vacuum from ATT at temperatures of 330 to 400°C. They state that the decomposition was carried out at constant temperature. We assume that this corresponds to the flash-heating procedure used in our work.

Samoilov and Rubinshtein (*3*) obtained a catalyst of very low surface area (3 m^2/g) by decomposition of ATT in flowing hydrogen at 400°C. The heating schedule and time at temperature are not specified. The low area suggests that the heating was carried out at a very low rate. However, when this catalyst was heated to 400°C under vacuum, the surface area increased to 66 m^2/g. This increase was attributed to removal of excess sulfur present in the pores. Other workers, notably Pier (*1*), Donath (*2*), Kalechits and Deryagina (*7*), and Wright *et al.* (*20*) have reported surface areas ranging from 20 to 70 m^2/g for different methods of preparation.

Table 1 summarizes the effect of pretreatment on BET area and pore volume of the tungsten sulfide catalysts studied in the present work. The surface area remains essentially constant, at a value of 60 ± 5 m^2/g of final catalyst weight, for pretreatments of up to 1 h at 450°C in flowing hydrogen. This agrees with the values reported by Voorhoeve and Wolters (*9*) whose preparation method was closest to the one used in this work.

Loss of sulfur up to a value of 0.15 atom S/atom W (No. 6, Table 1) does not significantly affect the area of the catalyst. However, treatment in hydrogen for 12 h at 450°C, which results in a loss of 0.34 atom S/atom W, (No. 7) causes the area to decrease to 35 m^2/g. Treatment in 15% hydrogen sulfide in hydrogen at 450°C for 1 h does not have any significant effect on the surface area.

Pore volumes (determined by adsorption of N_2 at a partial pressure of 0.98 at −195°C) are of the order of 0.05 cm^3/g, decreasing to 0.025 cm^3/g on heating for 12 h at 450°C in hydrogen. The average pore radius ($= 2V_p/S_{BET}$) is in the range of 15 to 20 Å. For the sintered catalyst, the average pore radius is also about 15 Å. These values agree well with the observations of Sa-

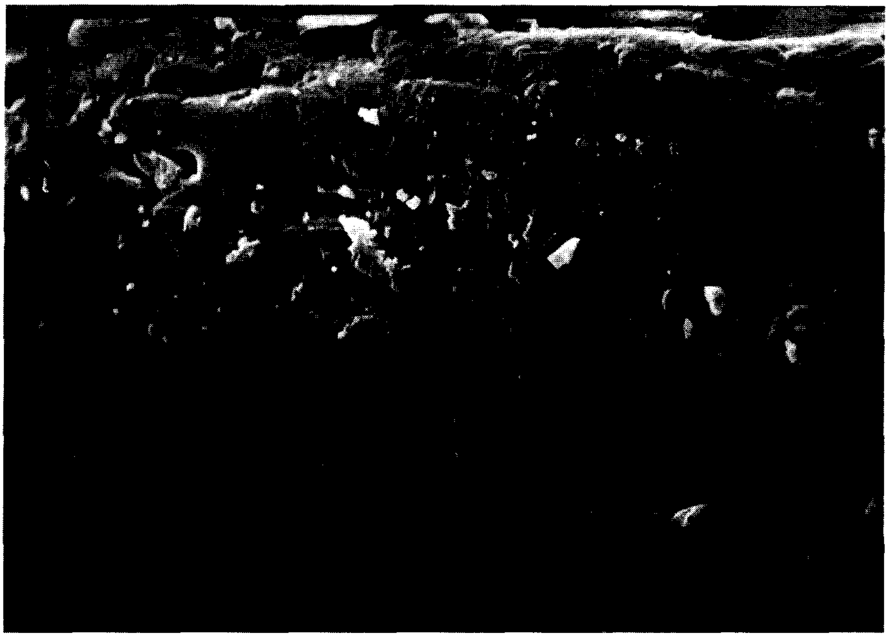

FIG. 3. Scanning electron micrograph of untreated ATT (2000×).

moilov and Rubinshtein (*3*) for catalysts of similar surface area.

Pore-size distributions were evaluated by analysis of the desorption isotherm of nitrogen at −195°C. The Kelvin equation and the adsorbed layer thickness as estimated from the Halsey equation (*21*) were used to compute pore radii. The radius of maximum pore volume lies at about 15 Å for almost all samples and is relatively independent of pretreatment.

(*b*) *Morphology*. Tungsten sulfide formed from the decomposition of ATT in helium at 450°C is pseudomorphous with the original (rhombic) ATT crystals. Particle sizes range from 200 to 1000 μm. Heating for 1 h in hydrogen at 450°C does not have any effect on gross particle size.

Figures 3 to 6 are scanning electron micrographs taken at high magnification (2000×) of the basal plane. Figure 3 is the untreated ATT; it shows quite a smooth surface, relatively free of cracks. When ATT is decomposed in helium at 450°C (Fig. 4), a large number of microcracks, ranging in width from 0.2 to 3 μm, develop on the surface. This is caused by the explosive escape of volatile matter during the decomposition process, giving rise to the high porosity and high surface area of the catalyst.

Treatment in hydrogen for 1 h at 450°C (Fig. 5) has no obvious effect on the morphology; the microcracks observed in Fig. 4 persist. After heating for 12 h in hydrogen at this temperature, however, a marked change takes place in the catalyst structure (Fig. 6). The microcracks almost disappear, leaving a smaller number of large cracks (2 to 4 μm) and a much smoother surface. This is consistent with our observations of lower surface area and decreased pore volume after this pretreatment. It appears also that the crystallites reorient themselves under these conditions.

There is evidence in the literature to support the theory of crystallite reorientation under severe pretreatment conditions. Wildervanck and Jellinek (*22*) observed a pronounced increase in crystallinity of molybdenum and tungsten sulfides, as evidenced by X-ray diffraction studies, on

FIG. 4. Scanning electron micrograph of tungsten sulfide (2000×).

heating the catalyst to 1000°C. Samoilov and Rubinshtein (*3*) noted that surface area and pore volume of tungsten sulfide heated in nitrogen to 1000°C decreased drastically, and attributed this to reorientation of crystallites into a hexagonal configuration. Bartovska *et al.* (*23*) explain their observation of anomalous reduction behavior of tung-

FIG. 5. Scanning electron micrograph of tungsten sulfide (2000×) prepared as in Fig. 2 and treated for 1 h in hydrogen at 450°C.

FIG. 6. Scanning electron micrograph of tungsten sulfide (2000×) prepared as in Fig. 2 and treated for 12 h in hydrogen at 450°C.

sten sulfide in the temperature range 500 to 800°C by using a similar argument.

Effect of Pretreatment on Low-Temperature Oxygen Chemisorption

The use of low-temperature oxygen chemisorption (LTOC) to characterize the active surface areas of chromia and molybdena catalysts has been reviewed recently (*14*). LTOC has been used as a measure of surface anion-vacancy concentration and as a positive correlator for catalytic activity. It is customary to use the ratio of LTOC and BET area on the unsupported oxide (or sulfide) as a conversion factor with which to multiply LTOC values on supported oxide (or sulfide) catalysts in order to deduce an apparent specific surface area of the active component in the supported catalyst (*17–19*). This methodology makes the assumption that the surfaces of the supported and unsupported catalysts behave identically towards LTOC. While this has not been proven, there is no evidence to indicate that such an assumption is unjustified. The value of area per chemisorbed O_2 molecule obtained is sensitive to details of preparation and pretreatment, and values varying over a tenfold range have been reported for molybdenum sulfide.

Table 1 summarizes the effect of pretreatment on LTOC of tungsten sulfide catalysts. In entries 1 and 2, corresponding to no removal of sulfur from the catalyst, no measurable LTOC is observed. Removal of sulfur corresponding to the first peak and slightly beyond (Nos. 3 and 4) also does not generate LTOC. Upon treatment in hydrogen at 450°C, which removes sulfur in the second peak, the catalyst begins to chemisorb oxygen. Comparison of entries 5 through 7 shows that higher levels of sulfur loss lead to larger values of LTOC. Entry 8 represents the effect of pretreating at 450°C for 1 h in a 15% H_2S/H_2 mixture. The final catalyst has a higher sulfur content than when pretreated similarly in hydrogen, and no measurable LTOC is observed.

The fact that increasing sulfur loss leads to increasing LTOC suggests that oxygen chemisorbs at surface anion vacancies (coordinatively unsaturated tungsten ions). This is not surprising in view of the work discussed earlier (*17–19*). Since removal of sulfur in the first peak of the TPR spectrum produces no LTOC, it is possible that this peak represents removal of elemental sulfur formed during the initial decomposition of ATT. Alternatively, since this peak is so small, it may be that a sufficient number of vacancies in the geometrical configuration necessary to chemisorb oxygen have not been generated.

The ratio of sulfur atoms removed to oxygen atoms chemisorbed varies with the extent of sulfur removal. After 1 h at 450°C in hydrogen, this ratio is about 30 (0.15/0.0050, No. 6). Twelve hours in hydrogen at 450°C decreases this value to about 19 (0.34/0.0178, No. 7). It appears that sulfur removed in the later stages of reduction leads to more sites capable of chemisorbing oxygen. The ratio of incremental sulfur loss to incremental oxygen chemisorption between Nos. 6 and 7 is about 15 (0.19/0.0128). Since much of the sulfur lost comes from the bulk, and oxygen chemisorption is a surface phenomenon, the high values for the ratios are not unreasonable.

The inverse site density, which constitutes a "calibration factor" for determination of active area on supported catalysts, drops from 1000 $Å^2/O_2$ after 1 h in hydrogen at 450°C to 170 $Å^2/O_2$ after 12 h at this temperature. Both the increase in LTOC and the decrease in surface area contribute to this decrease in "factor."

No data on LTOC on tungsten sulfide are available for comparison with those obtained in this work. Wright *et al.* (*20*) measured H_2S chemisorption at 400°C on tungsten sulfide prepared *in situ* from ATT at the same temperature in hydrogen. The catalyst was treated for 18 h in hydrogen in a static system prior to chemisorption measurements. This treatment is closest to entry No. 7 in Table 1. Their data yields a value of 190 $Å^2/H_2S$ which is close to the value of 170 $Å^2/O_2$ in entry No. 7. This agreement may be fortuitous, considering the differences in both preparation and pretreatment of the catalyst.

Effect of Pretreatment on Propylene Hydrogenation Activity

Catalyst activities were measured using a pulsed-flow microcatalytic reactor technique. Propylene hydrogenation was chosen as a test reaction for a variety of reasons:

(1) The reaction proceeds to a measurable extent over the tungsten sulfide catalyst at temperatures below those corresponding to the two peaks in the TPR spectrum. This allows measurement of activity under mild conditions that does not destroy the effects of catalyst pretreatment.

(2) The catalyst reaches a steady level of activity after the injection of six to eight pulses.

(3) Propylene is a small molecule (4 Å). This minimizes pore diffusional effects on reaction rates with the small pore size present in our catalyst (15 to 20 Å).

The influence of nonstoichiometric sulfur content on hydrogenation activity of catalysts prepared from the tetrathiosalt has been the subject of some debate, and conflicting results have been reported in the literature (*5*, *8*).

Table 2 summarizes data for the effect of pretreatment on the propylene hydrogenation activity of tungsten sulfide catalysts. Activities are reported both in terms of conversions (X) after six to eight injections (when activity does not vary from pulse to pulse), and of apparent first-order rate constants (k_1^{app}). Since data from pulsed-flow microcatalytic reactors are not amenable to simple analysis except for first-order reactions, only qualitative trends in activity are considered here.

Removal of sulfur in the first peak in the TPR spectrum generated no measurable conversion (after the injection of six to eight pulses) at 100°C (Nos. 1 and 2). Con-

TABLE 2

Effect of Pretreatment on Propylene Hydrogenation Activity of Tungsten Sulfide

No.	Gas[a]	Temp. (°C)	Time (min)	X^b (100°C)	X^b (150°C)	$k_1^{\mathrm{app}\,c}$ (100°C)	$k_1^{\mathrm{app}\,c}$ (150°C)	S/W
1	H_2	100	60	0.00	—	0.00	—	2.15
2	H_2	250	0	<0.02	0.12	0.00	0.68	2.13
3	H_2	250	60	0.04	0.26	0.24	1.84	2.08
4	H_2	450	0	—	0.32	—	2.08	2.05
5	H_2	450	60	0.15	0.36	0.68	2.40	2.00
6	H_2	450	12 h	0.16	0.38	1.28	4.40	1.81
7	H_2S/H_2 (15%)	450	60	<0.02	0.13	0.00	0.84	—

[a] All samples prepared as in Table 1 prior to pretreatment.

[b] Measured as $X = C_3H_8/\Sigma C_3$ for a loop size of 2.26 (STP) cm^3 in a hydrogen flow of 30 (STP) cm^3/min.

[c] Units cm/s × 10^{-6}.

versions at 100°C were below 5% even for a catalyst treated in hydrogen at 250°C for 1 h. When sulfur corresponding to the second peak was removed, higher conversions were obtained at 100°C (Nos. 5 and 6).

Conversions at 150°C were large enough to be measurable in almost all cases. Activity at this temperature was hence chosen as a measure of the effect of pretreatment. Comparison of entries 2 through 6 shows that increasing sulfur removal increases conversion and apparent first-order rate constants at 150°C. While conversions in entries 5 and 6 are very close in spite of the large difference in sulfur content, the catalyst in No. 6 has sintered; consequently its activity per unit area is higher. This fact is more apparent on comparison of apparent first-order rate constants (which take into account the change in area of the catalyst); these increase consistently as sulfur is removed. Entry 7, in which the catalyst was pretreated in 15% H_2S/H_2 at 450°C for 1 h, shows activity very similar to a catalyst treated in hydrogen at 250°C (No. 2).

The observations in Table 2 support the hypothesis that anion vacancies (i.e., exposed surface tungsten ions) are the active sites for hydrogenation. They contradict the observations of Samoilov and Rubinshtein (*5*) that increasing sulfur content increases activity. Our results also do not agree with those of Pavlova *et al.* (*8*), who postulate that activity is independent of sulfur content. Differences in preparative technique, pretreatment, reactions, and conditions of reaction are all important in accounting for these divergent observations. The fact that the present experiments were conducted without exposure of pretreated catalysts to air may also be important.

The fact that catalyst activity increases with increasing sulfur removal suggests that it should correlate well with LTOC. Since LTOC is immeasurably small for the initial (He-decomposed) samples, comparison is possible only for catalysts with lower sulfur content. Comparison of entries 5 through 7 in Table 1 with entries 4 through 6 in Table 2 shows that there does indeed appear to be a monotonic relationship between LTOC and catalyst activity.

CONCLUSIONS

(1) The TPR spectrum of tungsten sulfide prepared from ATT in helium at 450°C shows two peaks, indicating the presence of two kinds of sulfur atoms with different binding energies.

(2) Removal of sulfur corresponding to the second peak is necessary to generate

LTOC. The average valence state of tungsten in the bulk sample at this point is between +3 and +4. This may mean that the first H_2S peak originates from amorphous sulfur which is only mechanically bound to the catalyst. Higher sulfur loss leads to higher oxygen chemisorption, implying that oxygen chemisorbs at surface anion vacancies (coordinatively unsaturated tungsten ions).

(3) Sintering occurs at high degrees of sulfur removal. No sintering is observed for a change in stoichiometry from $WS_{2.15}$ to $WS_{2.0}$. For a catalyst with a stoichiometry of $WS_{1.81}$, the surface area drops from 60 to about 35 m^2/g.

(4) Propylene hydrogenation activity increases with increasing LTOC, suggesting that active sites are coordinatively unsaturated surface tungsten ions, with an average valence state (in the bulk sample) between +3 and +4.

REFERENCES

1. Pier, M., *Z. Elektrochem.* **53,** 291 (1949).
2. Donath, E. E., "Advances in Catalysis," Vol. 8, p. 239. Academic Press, New York, 1956.
3. Samoilov, S. M., and Rubinshtein, A. M., *Izv. Akad. Nauk SSR Otd. Khim. Nauk,* 1158 (1957).
4. Samoilov, S. M., and Rubinshtein, A. M., *Izv. Akad. Nauk SSSR Otd. Khim. Nauk,* 550 (1958).
5. Samoilov, S. M., and Rubinshtein, A. M., *Izv. Akad. Nauk SSSR Otd. Khim. Nauk,* 427 (1960).
6. Samoilov, S. M., *Izv. Akad. Nauk SSSR Otd. Khim. Nauk,* 1416 (1961).
7. Kalechits, I. V., and Deryagina, E. N., *Kinet. Katal.* **8** (3), 604 (1967).
8. Pavlova, K. A., Panteleeva, B. D., Deryagina, E. N., and Kalechits, I. V., *Kinet. Katal.* **6** (3), 493 (1965).
9. Voorhoeve, R. J. H., and Wolters, H. B. M., *Z. Anorg. Allg. Chem.* **376,** 165 (1970).
10. Voorhoeve, R. J. H., and Stuiver, J. C. M., *J. Catal.* **23,** 228 (1971).
11. Voorhoeve, R. J. H., *J. Catal.* **23,** 236 (1971).
12. Voorhoeve, R. J. H., and Stuiver, J. C. M., *J. Catal.* **23,** 243 (1971).
13. Weisser, O., and Landa, S., "Sulphide Catalysts, Their Properties and Applications." Pergamon, Oxford, 1973.
14. Weller, S. W., *Acc. Chem. Res.* **16,** 101 (1983).
15. Smutek, M., Cerny, S., Buzek, F., *in* "Advances in Catalysis" (D. D. Eley, M. Pines, and P. B. Weisz, Eds.), Vol. 24, p. 343. Academic Press, New York, 1975.
16. Chan, C. M., Aris, R., Weinberg, W. H., *Appl. Surf. Sci.* **1,** 360 (1978).
17. Tauster, S. J., Pecoraro, T. A., and Chianelli, R. R., *J. Catal.* **63,** 515 (1980).
18. Bodrero, T. A., and Bartholomew, C. H., *J. Catal.* **84,** 145 (1983).
19. Fierro, J. L. G., Tejuca, L. G., Agudo, A. C., and Weller, S. W., *J. Catal.* **89,** 111 (1984).
20. Wright, C. J., Fraser, D., Moyes, R. B., and Wells, P. B., *Appl. Catal.* **1,** 49 (1981).
21. Halsey, G. D., *J. Chem. Phys.* **16,** 931 (1948).
22. Wildervanck, J. C., and Jellinek, F., *Z. Anorg. Chem.* **328,** 309 (1964).
23. Bartovska, L., Cerny, C., and Kochanovska, A., *Collect. Czech. Chem. Commun.* **31,** 1439 (1966).