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Hydrogenation and Hydrodesulfurization over Sulfided Ruthenium Catalysts

II. Impact of Surface Phase Behavior on Activity and Selectivity

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Thiophene hydrodesulfurization (HDS) has been studied over sulfided Ru/γ-Al_2O_3 and CoMo/γ-Al_2O_3 catalysts using a microreactor operated at 101 kPa and 548–623 K. The activity and selectivity of thiophene HDS over ruthenium catalysts depended on the presulfidization procedures, yet similar trends were not observed over CoMo/γ-Al_2O_3 catalysts. Ruthenium catalysts sulfided in 100% H_2S at 673 K possessed ca. sevenfold higher thiophene conversion rates than CoMo/Al_2O_3 when compared per square meter of active area. Thiophene HDS rates averaged over oxygen titratable sites were ca. twofold higher on Ru/Al_2O_3 catalysts than on CoMo/Al_2O_3 specimens when compared per oxygen titratable site. Mild presulfidization in 101 kPa of 10% H_2S/H_2 at $T \leq 673$ K or in 101 kPa of 100% H_2S at $T \leq 523$ K, provided surfaces (i) retaining partial monolayers of adsorbed sulfur as evidenced by microgravimetry, XPS, and pulse oxygen adsorption and (ii) catalyzing direct hydrogenolysis to C_4 products and H_2S. Extensive presulfidization in 101 kPa of $\geq$80% H_2S/H_2 at $T \geq 673$ K leads to sulfur incorporation into the bulk and formation of crystalline RuS_2 at the surface. The RuS_2-like surface produced approximately equal quantities of C_4 hydrogenolysis products and tetrahydrothiophene. $S_{(a)}/Ru_{(s)}$ ratios observed by microgravimetry, XPS, and pulse oxygen adsorption were found to depend on the presulfidization conditions. $S_{(a)}/Ru_{(s)}$ ratios could be reversibly altered by appropriate resulfidization/annealing procedures and were found to correlate well with thiophene HDS selectivity but not with the presence of RuS_2 in the bulk. The above-noted trends are believed to be the result of a phase transformation dictated by surface thermodynamic driving forces. Calculations and comparisons of thiophene selectivity versus presulfidization conditions indicate that Gibbs free energies of +7 kJ/mole are required to form RuS_2 at the surface compared to values of −59 kJ/mole in the bulk. The instability of the RuS_2 surface may be indicative of a generalized surface thermodynamic criterion applicable to other pyrite sulfides. RuS_2 surfaces were observed to chemisorb much larger quantities of reversibly and irreversibly bound hydrogen which may affect the competition between direct hydrogenation and direct hydrogenolysis pathways, thereby controlling the selectivity of thiophene conversion.

INTRODUCTION

As noted in previous reports (*1–5*), the demands which are expected to be placed on future hydrotreating schemes necessitates that fundamental examinations be undertaken to elucidate the manner by which this processing operation proceeds over various candidate materials. Since ruthenium sulfide has been shown to possess a relatively high specific activity compared to other transition metal sulfides (*6–8*), we have undertaken a detailed catalytic and characterization effort of this material aimed at determining the origin of its high specific activity.

The previous paper in this study (*1*) revealed that when ruthenium catalysts were exposed to H_2S/H_2 mixtures at concentrations and temperatures typical of reaction environments two distinct and apparently stable surface structures were obtained. If catalysts were exposed to ca. 10% H_2S/H_2 mixtures at temperatures below 673 K, less

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than one-half monolayer of strongly bound sulfur was retained by the catalyst surface, whereas, if catalysts were presulfided in >80% H_2S/H_2 at temperatures greater than 673 K, multilayers of sulfur were incorporated into the catalyst, with crystalline RuS_2 extending all the way to the surface so as to provide a unique set of catalytic properties compared to that provided by milder sulfidization treatments. Since both surface structures are *indefinitely stable under reaction conditions,* these states are of obvious catalytic interest.

In the previous paper (*1*) the characterization and performance of ruthenium catalysts which retained less than one-half monolayer of adsorbed sulfur were considered. The focus of this discussion, however, revolves around the physical and chemical characterization of ruthenium catalysts which incorporate multilayers of sulfur into the bulk. Since thermodynamic calculations indicate that sulfidization of ruthenium catalysts in as little as 30 ppm H_2S/H_2 should produce RuS_2 in the bulk, it is clear that at least one explanation for the aforementioned "sulfidization–activity regimes" may be attributed to the limitations provided by surface and bulk kinetic processes during sulfidization. While this rationalization may appear to provide a relatively straightforward explanation for these data, other presulfidization treatments at intermediary H_2S/H_2 ratios between 10 and 80% H_2S provide crystalline RuS_2 in the bulk (e.g., observed by X-ray diffraction (XRD)) yet possess specific activities and selectivities identical to those obtained over ruthenium surfaces which retain less than one-half monolayer of sulfur adatoms. This "apparent contradictory" behavior coupled with the observed reversibility between these two "sulfidization–selectivity" regimes is suggestive that additional influences including those provided by surface thermodynamic considerations may be important in determining the structure, stability, activity, and selectivity which these catalysts provide.

For the above-noted reasons, the motivations and goals of this study are to examine how the coupled influences of surface and bulk kinetics with surface and bulk thermodynamics control the formation, stability, and performance of sulfided ruthenium catalysts. These studies are accomplished by comparing the results of appropriate characterization techniques such as microgravimetry, X-ray photoelectron spectroscopy (XPS), XRD, chemisorptions of H_2 and O_2, and H_2–D_2 exchange reactions with thiophene selectivity to produce either C_4 hydrocarbons (i.e., direct hydrogenolysis) or tetrahydrothiophene (THT) (i.e., direct hydrogenation). Data provided in this paper for RuS_2 suggest that the surfaces of pyrite sulfides are inherently less stable than the bulk sulfide, but once stabilized at higher than expected H_2S/H_2 ratios, retain large quantities of surface hydrogen under reaction conditions, thereby enhancing catalytic selectivity toward hydrogenated products.

EXPERIMENTAL

1. Catalyst Materials

Supported catalysts in the form of 0.5, 3.7, and 8.4% $Ru/\gamma\text{-}Al_2O_3$ specimens were prepared by incipient wetness techniques followed by drying, calcination, and reduction prior to use (*9–11*). $\gamma\text{-}Al_2O_3$ supports with a BET surface area of 234 m^2/g were obtained from Harshaw. A commercial $CoMo/\gamma\text{-}Al_2O_3$ catalyst (American Cyanamid, HDS-1442A H-Coal, 331 m^2/g (BET), 14.78% MoO_3 and 3.46% CoO) was also studied for comparison purposes. The average ruthenium crystallite sizes and surface areas for the 0.5 and 3.7% Ru/Al_2O_3 specimens were determined by irreversible H_2 chemisorption using the previously noted procedures (*1*) and found to be 1.8 (0.98 m^2/g) and 2.5 nm (6.1 m^2/g), respectively. Controlled sintering of the 3.7% Ru/Al_2O_3 specimen was also used in this study to produce a catalyst with an average crystallite size of 3.8 nm and a surface area of 4.0 m^2/g.

The average crystallite size of the 8.4% Ru/Al_2O_3 catalyst was found to be ca. 15.0 nm by means of X-ray diffraction in conjunction with the analysis method of Debye and Scherre. The line broadening at half-maximum was corrected for instrumental broadening using Warren's equation (*12*), and the net broadening was used to calculate the average crystallite size.

Unsupported ruthenium sulfide catalysts were prepared by sulfidization of metallic ruthenium sponges discussed earlier (*1*) and/or direct precipitation of RuS_2 according to the procedures of Pecoraro and Chianelli (*6*). Formation of crystalline RuS_2 after precipitation, washing, and sulfidization was verified by X-ray diffraction. The precipitated material had a BET surface area of approximately 56 m^2/g.

2. *Chemical Reagents*

Purification of the various reactants and adsorption gases used during these studies has been discussed previously (*1, 5*). Tetrahydrothiophene obtained from Aldrich (>99%) was used without purification following gas chromatographic and mass spectrometric analyses.

3. *Catalyst Characterization*

Characterization equipment/procedures involving selective chemisorption, physical adsorption, and microgravimetry have been described earlier (*1–5*). XPS analyses conducted in conjunction with this study were performed on a Leybold–Heraeus LHS-10 spectrometer utilizing Mg$K\alpha$ X-rays. Further details of these procedures are provided by Cocco *et al.* (*13*). A specially designed *ex situ* reaction chamber had the capability of presulfiding the catalyst specimens from 298 to 773 K in gaseous mixtures from 1 to 10^{-7} Torr and then transferring these specimens into the XPS analysis chamber under vacuum. Subsequent sulfur-to-ruthenium atomic ratios have been calculated on the basis of the measured S $2p_{1/2-3/2}$ to Ru $3d_{5/2}$ peak areas ratios normalized by the respective X-ray cross sections. Additional normalizations with respect to appropriate inelastic electron escape depths have not been employed as such procedures presume knowledge of the specimen morphology.

X-ray diffraction studies were applied to supported and unsupported ruthenium catalysts after sulfidization treatments to determine bulk phase behavior (e.g., formation of bulk sulfides) and/or discern changes in the size of metallic ruthenium domains after sulfidization. XRD data were collected on a Phillips Model PW-1390 diffractometer using a Cu$K\alpha$ source operated at 35 kV and 30 mA. Measurements were made with a 1° divergent slit, a 0.1-mm receiving slit, and a curved crystal graphite monochromator. Glass sample holders were employed to eliminate the artifacts caused by adhesives and/or binders.

Unsupported catalyst specimens used in some cases during XPS studies were prepared from ruthenium sponge (Aesar, 99.99%) which was ground into a fine powder and pressed into a 1 × 0.1-cm pellet at a pressure of 1.4×10^5 kN/m^2.

4. *Kinetic Studies*

Details concerning the collection and analysis of kinetic data including system operating procedures, reactor modeling, chromatographic product analyses, and calculations of reactant conversions have been described in detail previously (*1, 5*).

Thiophene conversions were kept below 10% to ensure differential reactor behavior and to also allow easy distinction of primary from secondary reaction products in the limit of zero conversion. Procedures were also undertaken to verify that measured kinetic rates were not influenced by the effects of heat or mass transfer (*14, 15*). Conversions to tetrahydrothiophene were determined on the basis of the number of moles of tetrahydrothiophene in the product sampling loop divided by the number of moles of thiophene in the reactant sampling loop.

RESULTS

1. Sulfur Uptake versus Sulfidization Conditions: Definition

As noted in the previous paper (*1*), the larger van der Waals radius of sulfur compared to metallic ruthenium allows sulfur adatoms to saturate a ruthenium surface at a coverage of ca. one-half the monolayer density of ruthenium atoms. Therefore, the sulfidization regimes discussed in this study can be divided into two distinct regimes which involve (i) *mild presulfidization* treatments resulting in sulfur uptakes less than or equal to one-half the number of initial ruthenium surface atoms and (ii) *extensive presulfidization* treatments resulting in sulfur uptakes greater than one-half the number of initial surface ruthenium atoms. As shown earlier, appropriately chosen "mild presulfidization" conditions can be employed so that sulfur adatoms are restricted on and within the ruthenium surface, whereas incorporation of more than 0.5 monolayer of sulfur necessitates incorporation of sulfur below the plane of the surface. The above-noted presulfidization procedures may thus be classified as either "surface" or "bulk sulfidization," respectively, as noted below:

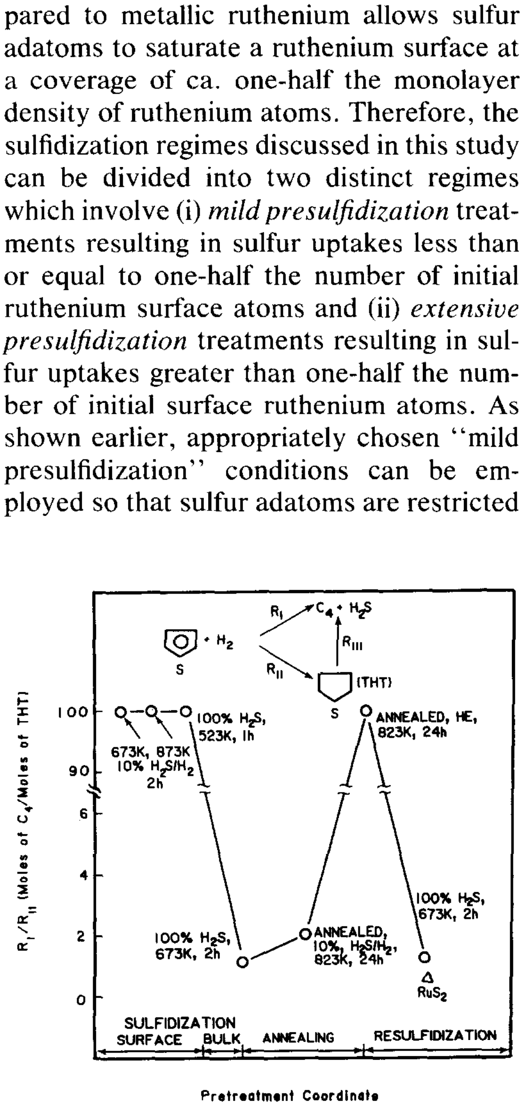

FIG. 1. Effects of pretreatment procedures on thiophene HDS selectivity over 3.7% Ru/Al$_2$O$_3$ (2.5-nm) and RuS$_2$ (56 m^2/g) catalysts; all specimens except RuS$_2$ were prereduced in H$_2$, 101 kPa, 673 K, 8 h, followed by the indicated sulfidization/annealing conditions at 101 kPa; selectivity is defined as the ratio of R_I (primary thiophene hydrogenoylsis) to R_{II} (primary thiophene hydrogenation) measured under the following conditions: P_{H_2} = 103.3 kPa, P_T = 10.3 kPa, P_{H_2S} = 1.04 kPa, 588 K.

"Surface sulfidization" resulting from "mild presulfidization" treatments applied to metallic ruthenium surfaces using (i) 50 cm^3/min (STP) of 1 to 10% H_2S in H_2 at 101 kPa for varying times (1–12 h, or longer) at temperatures below 673 K or (ii) 50 cm^3/min (STP) of 10 to 100% H_2S/H_2 at 101 kPa for varying times (1–12 h, or longer) at temperatures below 523 K (viz., $S_{(a)}/Ru_{(s)} \leq 0.5$);

"Bulk sulfidization" resulting from more "extensive presulfidization" treatments applied to metallic ruthenium surfaces using (i) 50 cm^3/min (STP) of 1 to 10% H_2S in H_2 at 101 kPa for varying times (1–12 h, or longer) at temperatures greater than 673 K or (ii) 50 cm^3/min (STP) of 10 to 100% H_2S/H_2 at 101 kPa for varying times (1–12 h, or longer) at temperatures above 523 K (viz., $S_{(a)}/Ru_{(s)} > 0.5$).

Since major differences in thiophene hydrodesulfurization (HDS) activity and selectivity were observed depending upon which of the above-noted presulfidization procedures was selected *as well as* the manner in which each treatment was performed, the goal of this investigation is to better understand the appropriate surface structures, surface thermodynamic constraints, and kinetic considerations which underlie these sulfidization steps and the catalytic trends which the resultant surfaces provide.

2. Thiophene Selectivity versus Presulfidization Conditions

A. A preliminary example. Figure 1 shows the reaction selectivity observed during thiophene HDS over 3.7% Ru/Al_2O_3 (d = 2.5 nm) catalysts following the indicated presulfidization procedures. R_I is the specific rate for direct hydrogenolysis (moles of C_4 products/$m^2 \cdot s$), R_{II} is the rate for primary hydrogenation to THT (moles of THT produced/$m^2 \cdot s$), and R_{III} is the rate for hydrogenolysis of THT (moles of C_4 products/$m^2 \cdot s$). The distribution of desulfurized-C_4 products as reported earlier (*1*) is in the following ranges: butane, 38.5–45.5%, and butenes, 54.5–61.5%, as determined at 588 K, $P_{H_2} = 104.03$ kPa, $P_T = 10.34$ kPa, and $P_{H_2S} = 1.04$ kPa. No butadiene was observed under any reaction conditions. In all cases examined, separate studies were conducted with THT to verify that the measured R_I/R_{II} ratio was not being obscured by a rapid removal of the THT intermediate. While the rate of pathway R_{III} was generally found to be about twice that of R_I during these studies, we believe this pathway did not appreciably influence our determination of the R_I/R_{II} ratio during differential reactor studies in the limit of zero conversion.

As shown in Fig. 1, little change in thiophene selectivity was observed following sulfidization in 10% H_2S/H_2 at 673 and 873 K for 2 h, or in 100% H_2S at 523 K for 1 h. In these instances the measured selectivity was greater than 100 toward the direct hydrogenolysis pathway. The value of 100 was estimated from the noise in the gas chromatogram at the appropriate retention time for tetrahydrothiophene, although no tetrahydrothiophene was detected. Following sulfidization in 100% H_2S at 673 K for 2 h, however, the specific activity for primary hydrogenation was increased to levels approximately equal to those for direct hydrogenolysis, resulting in a decrease in the R_I/R_{II} ratio to a value of 1.12. This selectivity ratio compared favorably to that observed over bulk ruthenium sulfide (RuS_2) as shown in Fig. 1. It was also found after annealing this sample in flowing helium at 823 K for 24 h that the selectivity could be converted back to its original value of greater than 100. Subsequent resulfidization of the sample in 100% H_2S at 673 K once again resulted in an R_I/R_{II} ratio close to one (i.e., 1.19), indicating that it was possible to move between these two selectivity regimes in a reversible fashion by appropriate annealing and/or resulfidization procedures.

Kinetic measurements following sulfidization in 10% H_2S/H_2 and in 100% H_2S at 673 K for 2 h were also performed over $CoMo/Al_2O_3$ catalysts. In contrast to the above findings over Ru/Al_2O_3 catalysts, no detectable THT was observed during our studies at atmospheric pressures.

The aforementioned results highlight the unique sulfidization–selectivity dependence provided by supported ruthenium catalysts with the remainder of this paper devoted to understanding the surface structures, surface compositions, and surface kinetics/thermodynamics responsible for the above-noted transitions in thiophene activity and selectivity.

B. Quantification of the effects caused by the temperature and the H_2S/H_2 ratio used during presulfidization. Table 1 provides specific activities and selectivities (measured at 588 K) over Ru/Al_2O_3 catalysts sulfided in 10% H_2S/H_2 and 100% H_2S at temperatures at or below 1023 K. It was found that (i) specific activities for direct thiophene hydrogenolysis over 0.5% Ru/Al_2O_3 catalysts appeared independent of presulfiding temperatures when 10% H_2S/H_2 was used and (ii) tetrahydrothiophene was not detected as a reaction product. A threefold increase in R_I was observed, however, as 3.7% Ru/Al_2O_3 catalysts were sulfided in 100% H_2S over the temperature range from 523 to 673 K as well as the appearance of tetrahydrothiophene in the product stream. The specific activity for thiophene hydrogenation to THT became comparable to R_I and measured selectivities decreased from greater than 100 to 1.12 comparing favorably to those measured over bulk ruthenium sulfide. Apparent activation energies for direct hydrogenolysis and hydrogenation were found to be 88 and 42 kJ/mole, respectively, and were independent of the

TABLE 1

Effects of Presulfiding Temperature on the Activities and Selectivities of Thiophene HDS[a]

Catalyst	Temp. (K)	Activity × 10^8 (moles/m^2 · s)		Selectivity R_I/R_{II}
		R_I	R_{II}	
0.5% Ru/Al_2O_3	673^b	2.33	0.014^c	>100
(0.98 m^2/g) (1.8 nm)	873^b	1.97	0.014^c	>100
	1023^b	2.20	0.014^c	>100
3.7% Ru/Al_2O_3	523^d	1.34	0.014^c	>100
(6.1 m^2/g) (2.5 nm)	573^d	1.87	0.37	5.05
	673^d	3.52	3.15	1.12
RuS_2 (56 m^2/g)	673^e	3.06	5.88	0.52
CoMo/Al_2O_3[f]	673^e	0.96	—	—

[a] P_{H_2} = 103.3 kPa, P_T = 10.3 kPa, and P_{H_2S} = 1.04 kPa; 588 K.

[b] Presulfidization in 10% H_2S/H_2, 101 kPa, 2 h.

[c] Estimated reaction rate from noise level in the chromatogram; therefore values for R_{II} represent upper limits.

[d] Presulfidization in 100% H_2S, 101 kPa, 2 h.

[e] Presulfidization in 10% H_2S/H_2, 101 kPa, 2 h.

[f] Assume 90% of the BET surface area (331 m^2/g) of the CoMo/Al_2O_3 catalysts was composed of "active surface area" (*1*).

above presulfiding conditions. Unlike the results obtained over ruthenium catalysts with partial monolayers of sulfur retained on the surface (*1*), the influence of crystallite size has been shown to provide only a minor influence on the observed selectivities and apparent activation energies (*5*).

Increasing thiophene hydrogenolysis activities with increasing presulfidization temperatures have also been observed by Morooka and Hamrin (*16*) using commercial CoMo/Al_2O_3 catalysts. Presulfidization in ca. 9% H_2S/H_2 at 723 K for 4 h provided a twofold increase in the thiophene HDS activity compared to that measured following sulfidization at 673 K, although only direct C_4 hydrogenolysis products were detected during their studies at 523–623 K and 101 kPa.

The specific activities of 3.7% Ru/Al_2O_3 sulfided in 100% H_2S at 673 K and CoMo/Al_2O_3 sulfided in 10% H_2S/H_2 at 673 K have also been compared in Table 1. It was found that 3.7% Ru/Al_2O_3 and CoMo/Al_2O_3 catalysts possessed relative activities of 0.067 and 0.0096 (μmole of thiophene converted per m^2 per second) at 588 K, respectively, assuming that 90% of the BET surface area of the CoMo/Al_2O_3 catalyst was composed of "active surface area" as mentioned earlier (*1*). Therefore, this comparison indicates that following the above-noted sulfidization conditions, 3.7% Ru/Al_2O_3 catalysts are about seven times more active than CoMo/Al_2O_3 specimens per "square meter of active surface area."

The effect of hydrogen sulfide concentration, used during presulfidization, on measured activities and selectivities is shown in Table 2 for a family 2.5-nm ruthenium crystallites presulfided at 673 K. These results indicate that both thiophene hydrogenation and direct hydrogenolysis are enhanced by increasing the H_2S/H_2 ratio from 50 to 100% H_2S with a greater than 100-fold increase in R_{II} being accompanied by a ca. 3-fold increase in R_I. Apparent activation energies for pathways R_I and R_{II} retained their previously noted values of 88 and 42 kJ/mole, respectively.

Global effects of the presulfidization temperature and the H_2S/H_2 ratio on thiophene selectivity over ruthenium catalysts are shown in Fig. 2. Two distinct regimes are observed as indicated by the "selectivity line" shown on this figure. One regime, with a R_I/R_{II} of ca. 1.0, is reminiscent of bulk sulfide-like behavior, whereas sulfid-

TABLE 2

Effects of H_2S Concentration Used during Presulfidization on Activities and Selectivities for Thiophene HDS[a]

Catalyst	% H_2S[b] in H_2	Activity × 10^8 (moles/m^2 · s)		Selectivity R_I/R_{II}
		R_I	R_{II}	
3.7% Ru/Al_2O_3	50	1.40	0.014^c	>100
(6.1 m^2/g) (2.5 nm)	75	1.54	0.26	5.92
	80	1.80	1.13	1.59
	90	1.98	1.23	1.60
	100	3.52	3.15	1.12

[a] P_{H_2} = 103.3 kPa, P_T = 10.3 kPa, and P_{H_2S} = 1.04 kPa; 588 K.

[b] Presulfidization at 101 kPa, 673 K, 2 h.

[c] Estimated reaction rate from noise level in the chromatogram; therefore values for R_{II} represent upper limits.

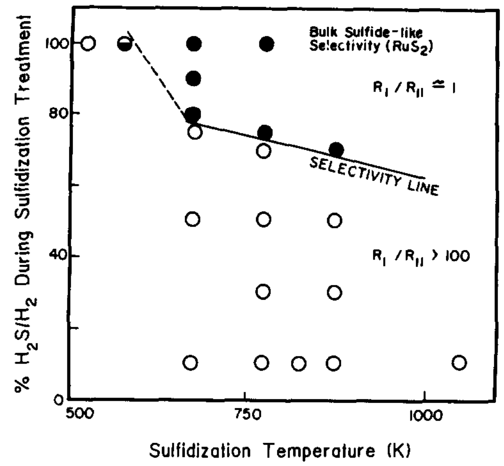

FIG. 2. Effects of the presulfidization temperature and the H_2S/H_2 ratio on thiophene HDS selectivity over 3.7% Ru/Al_2O_3 (2.5-nm) catalysts; all specimens were prereduced in H_2, 101 kPa, 673 K, 8 h, followed by the indicated sulfidization conditions at 101 kPa for 2 h; ● indicates RuS_2-like selectivity regime and ○ indicates surface sulfidization–selectivity regime; reaction conditions: P_{H_2} = 103.3 kPa, P_T = 10.3 kPa, P_{H_2S} = 1.04 kPa, 588 K.

ization conditions which yield an R_I/R_{II} ratio >100 appear to provide surface structures equivalent to those catalysts studied in the previous paper (*1*) where only 0.1 to 0.25 monolayer of sulfur is retained on the ruthenium surface.

The selectivity dependence shown in Fig. 2 provides an unexpected and interesting result since bulk thermodynamics predicts the formation of RuS_2 in only 30 ppm H_2S/H_2 at 673 K (*17*). While sulfur restriction on the surface can be easily rationalized at the lower sulfidization temperatures used in the previous study (*1*) by recognizing the importance of mass transfer limitations in the solid; the sulfidization conditions used in Fig. 2 (e.g., 1023 K, 2 h, 10% H_2S/H_2, 101 kPa, 2.5 nm) should be sufficient to overcome such limitations. However, the above-noted sulfidization conditions did not produce bulk sulfide-like selectivity! This result, combined with the observation that the "selectivity line" shown in Fig. 2 provided a sharp and reversible delineation between the two selectivity regimes, suggests that surface thermodynamic constraints in addition to kinetic artifacts may provide the source of the above-noted catalytic behavior.

In order to gain insight into the origin of this anomalous selectivity behavior, detailed catalyst characterization studies have been undertaken, and are reported below, to correlate the sulfidization surface structure of the catalyst with the observed selectivity.

3. *Catalyst Characterization following Sulfidization*

A. Microgravimetry. Figure 3 provides the weight gains experienced by prereduced 0.65 m^2/g ruthenium sponge catalysts sulfided under the indicated conditions. The weight gain, corrected for buoyancy effects, has been expressed as the number of sulfur atoms incorporated into/onto the catalyst divided by the number of surface ruthenium atoms prior to sul-

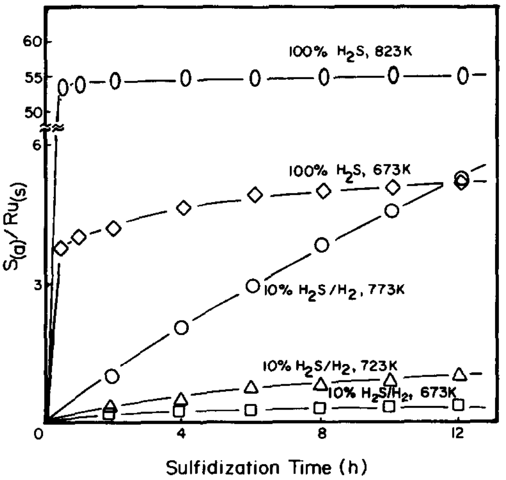

FIG. 3. Microgravimetric determination of Ru sponge (0.65 m^2/g) sulfidization; all specimens were prereduced in H_2, 101 kPa, 673 K, 8 h, followed by the indicated sulfidization conditions at 101 kPa; $S_{(a)}$, number of sulfur adatoms determined from sulfur uptakes after buoyancy corrections, and $Ru_{(s)}$, number of surface ruthenium atoms determined from H_2 chemisorption at 373 K (*9–11*) and/or N_2 BET.

fidization (viz., $S_{(a)}/Ru_{(s)}$). As noted earlier (*1*), mild presulfidization in 10% H_2S/H_2 at temperatures of 673 K provides sulfur to ruthenium ratios of ca. 0.3 with XPS and oxygen chemisorption studies indicating that these sulfur adatoms are confined to the ruthenium surface. Since these conditions provide a sufficient thermodynamic driving force to produce RuS_2 in the bulk, the lack of its formation must be attributed to limitations provided by surface and/or bulk kinetic phenomena under these conditions. Sulfidization in 10% H_2S/H_2 at temperatures of 723 and 773 K is sufficient to permit sulfur incorporation into the bulk as evidenced by $S_{(a)}/Ru_{(s)}$ ratios in excess of 0.5. These data are well fit by parabolic rate expressions suggesting that the rate of sulfur incorporation may be limited by solid-state diffusion and transport processes (*18*).

Sulfidization in 100% H_2S at 673 and 823 K provides a very different type of behavior from that observed in 10% H_2S/H_2. Significantly higher rates of sulfur incorporation are observed. These data are no longer fit by parabolic rate expressions suggesting that sulfidization may be limited by phase boundary reactions, nucleation phenomena, crystal growth, or some other process (*19*). The significantly higher sulfidization rates observed in 100% H_2S may also be related to the rate of mass transport of various species through a sulfide phase as opposed to metallic ruthenium. Support for this suggestion is provided by Fig. 4 where the rate of sulfidization is recorded versus the H_2S/H_2 ratio at 673 K. Comparison of these data to the critical H_2S/H_2 ratio required to cross the "selectivity line" in Fig. 2 (i.e., 80% H_2S/H_2 at 673 K) suggests that a significant increase in the sulfidization rate occurs under conditions nearly identical to those required to form RuS_2 at the surface as assessed by thiophene selectivity.

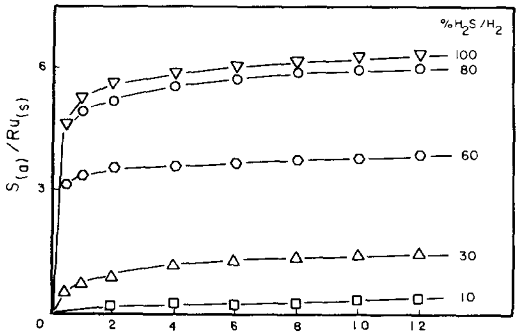

FIG. 4. Microgravimetric determination of the effects of the H_2S/H_2 ratio on 3.7% Ru/Al_2O_3 (2.5-nm) sulfidization at 673 K, 101 kPa; all specimens were prereduced in H_2, 101 kPa, 673 K, 8 h, followed by the indicated sulfidization conditions at 101 kPa; $S_{(a)}$, number of sulfur adatoms determined from sulfur uptakes after buoyancy corrections, and $Ru_{(s)}$, number of surface ruthenium atoms determined from H_2 chemisorption at 373 K (*9–11*) and/or N_2 BET.

TABLE 3

Microgravimetric Determination of Ruthenium Sponge Sulfidization Behavior[a]

Pretreatment	$S_{(a)}/Ru_{(s)}$	$\Delta S_{(a)}/Ru_{(s)}$
100% H_2S, 823 K, 14 h	56.2	
100% H_2S, 673 K, 14 h	56.2	0
10% H_2S/H_2, 673 K, 3 h	55.86	−0.34
2.5% H_2S/H_2, 673 K, 3 h	55.61	−0.25
10% H_2S/H_2, 673 K, 3 h	55.86	+0.25
He, 673 K, 14 h	55.33	−0.53

[a] The weight gain has been corrected for buoyancy effects.

The surface behavior of sulfided ruthenium catalysts was further investigated by examining the relative stability of these materials at 673 K in various H_2S/H_2 environments. As shown in Table 3, sulfidization in 100% H_2S at 823 K for 14 h produced a relatively large sulfur uptake which we assume to be in the form of a RuS_2-like skin as assessed by the thiophene selectivity observed following such treatments (see Fig. 2). This material was then cooled to 673 K in pure H_2S and held at this temperature for 14 h. This treatment apparently did not permit further sulfidization as no additional weight gains were recorded. The H_2S/H_2 ratio was then stepped down to 10 and 2.5% H_2S/H_2 followed by an increase back up to

10% H_2S/H_2 and finally annealing in helium at 673 K. Since reversible H_2S adsorption under these conditions is negligible, the weight changes shown in Table 3 have been attributed to sulfur removal/incorporation within the surface of the catalyst. It is interesting to note that the reversibility of these weight gains mimics the corresponding reversibility noted in thiophene selectivity (see Figs. 1 and 2) yet the total amount of sulfur removed/added is on the order of one monolayer.

B. X-ray photoelectron spectroscopy. Similar to the microgravimetric results discussed above, S/Ru atomic ratios determined by XPS were found to depend on both the sulfidization temperature and the H_2S/H_2 ratio (see Fig. 5). The data shown in Fig. 5 have been corrected for the appropriate X-ray cross sections and transmission factors within the photoelectron energy analyzer but not the respective photoelectron escape depths as such calculations presume knowledge of the specimen morphology. Further efforts along these lines (*13*) have shown, however, that the sulfur-to-ruthenium stoichiometry is close to the expected 2 : 1 value at the higher sulfidization temperatures in pure H_2S. This 2 : 1 (S : Ru) ratio compared favorably to that observed over a bulk RuS_2 sample when the appropriate photoelectron escape depths were included in the calculation (*13*). Despite the absence of these normalization factors, the data of Fig. 5 demonstrate the more corrosive behavior provided by pure H_2S environments with sulfur incorporation into the bulk occurring at lower temperatures in pure H_2S (i.e., >523 K) than in 10% H_2S/H_2 mixtures (i.e., >673 K).

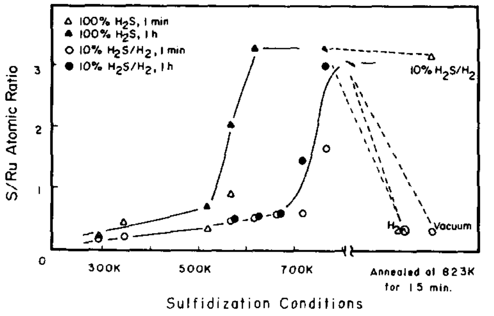

FIG. 5. Determination of sulfur to ruthenium atomic ratios from a ruthenium pellet (0.65 m^2/g) by XPS; all specimens were prereduced in H_2, 101 kPa, 673 K, 8 h, followed by the indicated sulfidization/annealing conditions at 101 kPa; S/Ru atomic ratios were calculated based on the measured S $2p_{1/2-3/2}$ to Ru $3d_{5/2}$ peak area ratios normalized by the respective X-ray cross sections and transmission factors (*13*).

Sulfidization in either environment at temperatures greater than the above-noted thresholds leads to sulfur incorporation into the bulk and a stationary S/Ru ratio indicative of a stable S : Ru stiochiometry within the sampling depth of this technique. Only a slight yet reproducible difference in the measured S : Ru atomic ratio was apparent depending on the sulfidization mixture employed (i.e., S : Ru = 3.15 in pure H_2S at 773 K, S : Ru = 2.85 in 10% H_2S/H_2 at 773 K). Additional efforts have shown that the magnitude of this small difference in going from 100% H_2S to 10% H_2S/H_2 is consistent with a surface depletion of ca. one monolayer of sulfur when averaged over the entire sampling depth of the photoelectrons detected (*13*). Thus, the magnitude of this sulfur loss is in general agreement with that observed by microgravimetry.

When specimens sulfided in pure H_2S were annealed in 10% H_2S/H_2 for 15 min at 823 K, the S/Ru atomic ratio was reduced to a value close to that obtained following sulfidization in 10% H_2S/H_2 (see Fig. 5). Other annealing treatments at 823 K under vacuum or pure H_2 provided more significant sulfur depletion with values close to those measured earlier for ruthenium substrates covered by partial monolayers of the adsorbate.

Based on the above-noted trends in (i) the sulfur uptake versus sulfidization conditions (XPS, microgravimetry), (ii) the reversibility of these trends as the H_2S/H_2 environment is changed (XPS, microgravimetry), and (iii) the corresponding reversibility trends observed during selectivity

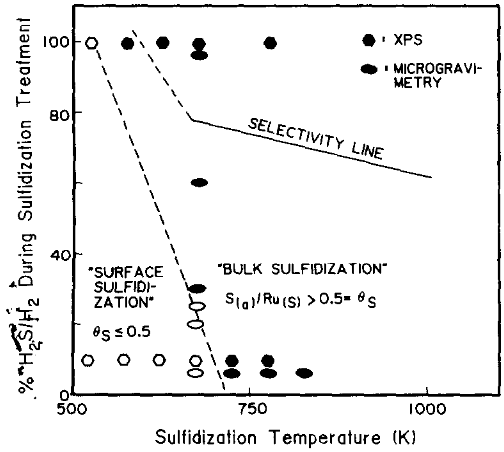

FIG. 6. Sulfidization–selectivity behavior of Ru sponge catalysts (0.65 m^2/g) determined by microgravimetry, XPS, and kinetic measurements (P_{H_2} = 103.3 kPa, P_T = 10.3 kPa, P_{H_2S} = 1.04 kPa, 588 K); all specimens were prereduced in H_2, 101 kPa, 673 K, 8 h, followed by the indicated sulfidization conditions at 101 kPa, 2 h. The dotted line separates the "surface sulfidization ($\theta_s \leq 0.5$)" regime from the "bulk sulfidization ($\theta_s > 0.5$) regime."

measurements, it appears that the catalytic selectivity can be altered through a sulfidization-induced relaxation/reconstruction of the surface which involves at most one monolayer of sulfur addition/removal. On the basis of comparison of the selectivity trends shown in Figs. 1 and 2 and the sulfur incorporation trends shown in Figs. 3–5, it is clear that the observed selectivity trends cannot be simply correlated to the amount of sulfur retained by the catalyst. This observation again suggests that differences in thiophene selectivity may be attributed to the presence of different sulfide phases at the surface depending on the sulfidization history of the catalyst.

For the purposes of subsequent discussions, the sulfidization data provided by XPS and microgravimetry have been divided into two distinct regimes depending on whether the $S_{(a)}/Ru_{(s)}$ ratio is greater than or less than 0.5. These data are shown in Fig. 6, with a dotted line separating the two regimes which have been termed "surface sulfidization" and "bulk sulfidization," respectively. The selectivity line (i.e., solid line) obtained from Fig. 2 has also been included for comparison purposes. Since bulk thermodynamic calculations indicate that crystalline RuS_2 should be formed under any of the conditions shown in Fig. 6, a dotted line has been used to divide those regions which we suspect are separated as a result of the influences provided by kinetic restrictions at the surface or in the bulk. Comparing the position of the "selectivity line" with the "surface-bulk sulfidization line" indicates that $S_{(a)}/Ru_{(s)}$ uptakes greater than 0.5 provide a set of necessary but not sufficient conditions to obtain RuS_2-like selectivity.

C. Oxygen chemisorption. Figure 7 shows the results of oxygen chemisorption performed over 3.7% Ru/Al_2O_3 catalysts following different pretreatments. An oxygen uptake of 14.9 μmole/g (measured at 298 K) was observed over ruthenium surfaces covered by partial monolayers of sulfur (sulfidization in 10% H_2S/H_2 at 673 K), compared to 7.6 μmole/g over RuS_2-like surfaces (sulfidization in 100% H_2S at 673 K). It was also found that helium annealing (823 K, 24 h) of the previous catalyst sample (presulfided in 100% H_2S) resulted in restoration of the oxygen uptake (14.3 μmole/g). Subsequent resulfidization in 100% H_2S at 673 K again decreased the ox-

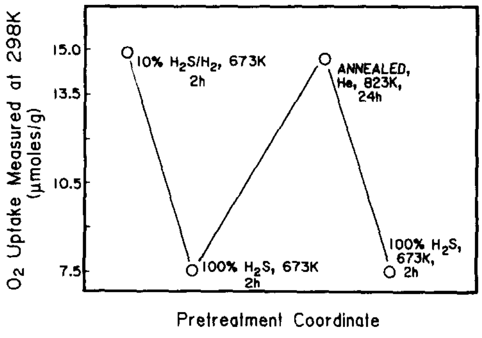

FIG. 7. Effects of pretreatment procedures on O_2 uptakes (measured at 298 K) over 3.7% Ru/Al_2O_3 (2.5-nm) catalysts. All specimens were prereduced in H_2, 101 kPa, 673 K, 8 h, followed by the indicated sulfidization/annealing conditions at 101 kPa.

ygen uptake to a value of 7.5 μmole/g. Therefore, oxygen chemisorption studies further demonstrated the above-noted reversible behavior observed over sulfided ruthenium catalysts.

The relative activities of Ru/Al_2O_3 and $CoMo/Al_2O_3$ have been compared in Table 1 on the basis of "square meters of active surface area." If these two systems are compared on the basis of oxygen titratable sites as described earlier (*1*), the relative activities of Ru/Al_2O_3 sulfided in 100% H_2S at 673 K and $CoMo/Al_2O_3$ sulfided in 10% H_2S/H_2 at 673 K are found to be 0.054 : 0.034 mole of thiophene converted per second per mole of oxygen titratable sites at 588 K, respectively. This comparison indicates that following the above-noted sulfidization conditions, Ru/Al_2O_3 catalysts are ca. 1.5 times more active than $CoMo/Al_2O_3$ specimens per oxygen titratable site.

D. X-ray diffraction. Since the selectivity behavior observed in the previous sections has been attributed to the formation of a RuS_2-like surface (i.e., a crystalline solid), XRD has been employed to examine the formation of this phase. Recognizing that XRD is incapable of detecting the crystallographic orientation in the outermost atomic layer of a supported crystallite, it is nevertheless useful to determine whether or not the formation of RuS_2 in the bulk can be related to the structure and selectivity provided at the surface.

Figure 8 shows XRD patterns of 8.4% Ru/Al_2O_3 catalysts, with initial crystallite diameters of 15.0 nm, following sulfidization at the indicated conditions. Sulfidization in 101 kPa of 10% H_2S/H_2 at 673 and 873 K for 2 h resulted in $S_{(a)}/Ru_{(s)}$ uptakes of 0.25 and 6.0, respectively, yet did not lead to the formation of any detectable RuS_2. Comparison of these two sulfidization treatments with data shown in Fig. 2 also indicates that no detectable tetrahydrothiophene was produced over similarly presulfided catalysts. By contrast, catalysts sulfided in 101 kPa of 100% H_2S at 673 K for 2 h (i) retained only 4.5 monolayers of sulfur, (ii) possessed significant RuS_2 diffraction features, and (iii) produced significant levels of tetrahydrothiophene. In the above two instances, the appearance of RuS_2 diffraction features was clearly related to the earlier noted "RuS_2-like" selectivity and the production of tetrahydrothiophene.

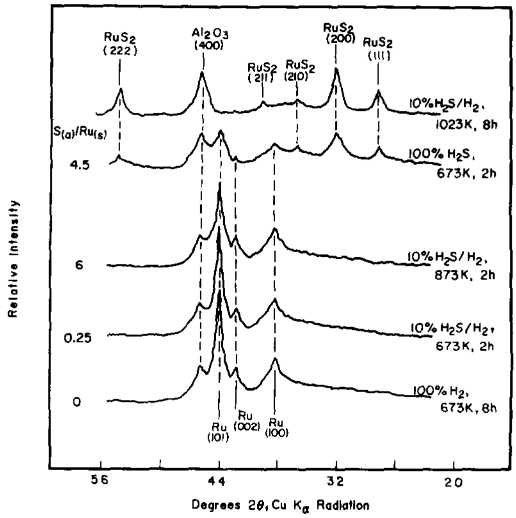

FIG. 8. XRD analyses of reduced and sulfided 8.4% Ru/Al_2O_3 catalysts (d = 15.0 nm); all specimens were prereduced in H_2, 101 kPa, 673 K, 8 h, followed by the indicated sulfidization conditions at 101 kPa.

In contrast to the above-noted trend, sulfidization in 101 kPa of 10% H_2S/H_2 at 1023 K for 8 h (i) removed all traces of metallic ruthenium, (ii) produced significant quantities of RuS_2, but (iii) did not produce any measurable quantities of tetrahydrothiophene. While the exact origin of this phenomenon cannot be inferred from XRD data alone, earlier noted XPS, microgravimetric, and selectivity studies have demonstrated the sensitivity of the reaction pathway to the sulfur concentration in the topmost atomic layer. Thus, it appears likely that the higher surface sulfur concentrations afforded by 100% H_2S treatments at 673 K readily permit nucleation of the bulk sulfide at the surface from the very onset of multilayer sulfur incorporation, whereas lower surface sulfur concentrations provided by, e.g., 10% H_2S/H_2 mixtures at 873 K, combined with the higher mobilities produced in the solid at these temperatures, necessitate saturation of the entire ruthenium crystallite with sulfur prior to nucleation of the sulfide. Driving forces for the formation of ruthenium sulfide *in the bulk* appear to be the H_2S/H_2 ratio and the temperature which in turn affects the kinetic contribution to, and nucleation of, ruthenium sulfide.

The formation of RuS_2 at the surface, with the concomitant production of tetrahydrothiophene, does not appear to be related to the presence of this phase in the bulk as evidenced by the data shown in Fig. 9. For comparison purposes, these data, which denote the detection of RuS_2 by XRD, have been placed on the same phase plane as that used earlier with a dotted line again being used to separate various regions which are believed to arise as the result of kinetic limitations. Comparison of the "XRD line" with the "selectivity line." demonstrates that RuS_2 formation in the bulk is not sufficient to provide a surface capable of producing tetrahydrothiophene. These data strongly suggest that the thermodynamic driving forces required to form RuS_2-like surfaces are different from those required to form RuS_2 in the bulk as discussed below.

TABLE 4

Gibbs Free Energy Changes for the Sulfidization of Ru/Al_2O_3[a]

		T (K)	% H_2S in H_2	ΔG^0 (kJ/mole)	Phase detected by XRD	Selectivity R_I/R_{II}
Sulfided metal	1.	673	10	−12.3	Ru^0	>100
	2.	823	10	−15.0	Ru^0	>100
	3.	1023	10	−18.7	RuS_2	>100
RuS_2-like	4.	673	80	7.7	$RuS_2 + Ru^0$	1.6
	5.	773	75	7.1	$RuS_2 + Ru^0$	1.2
	6.	873	70	6.2	$RuS_2 + Ru^0$	1.2

[a] Presulfided at 101 kPa for 2 h at indicated conditions.

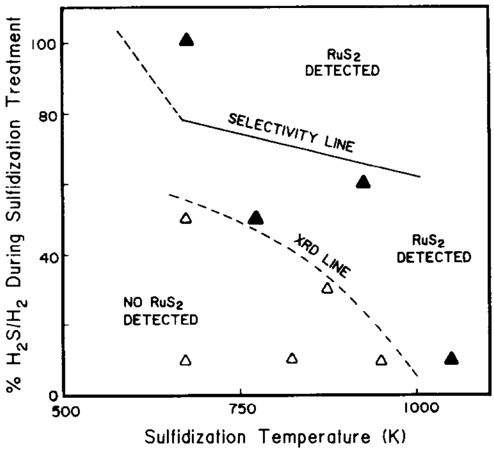

FIG. 9. Sulfidization–selectivity behavior of 8.4% Ru/Al_2O_3 catalysts (d = 15.0 nm) determined by XRD and kinetic measurements (P_{H_2} = 103.3 kPa, P_T = 10.3 kPa, P_{H_2S} = 1.04 kPa, 588 K); all specimens were prereduced in H_2, 101 kPa, 673 K, 8 h, followed by the indicated sulfidization conditions at 101 kPa, 2 h. ▲ indicates RuS_2 features detected by XRD and △ indicates the absence of RuS_2 features.

DISCUSSION

1. *Thermodynamic Requirements for the Formation of RuS_2 at the Surface*

Table 4 shows Gibbs free energy changes (i.e., ΔG^0) for the sulfidization of Ru/Al_2O_3 catalysts under various conditions calculated according to the equations

$$\tfrac{1}{2}\,\mathrm{Ru} + \mathrm{H_2S} \rightarrow \tfrac{1}{2}\,\mathrm{RuS_2} + \mathrm{H_2} \qquad (1)$$

$$\Delta G = \Delta G^0 - RT\ln(P_{H_2S}/P_{H_2}) \qquad (2)$$

since ΔG equals zero at equilibrium, the critical H_2S/H_2 ratio required to form RuS_2 in equilibrium with Ru as a function of temperature can be written as

$$\Delta G^0 = RT\ln(P_{H_2S}/P_{H_2}). \qquad (3)$$

The last three entries in Table 4 have been calculated using Eq. (3) and the critical H_2S/H_2 ratios and temperatures which are required to just cross the "selectivity line" shown in Fig. 2. Comparison of the ΔG^0 values in Table 4 with the free energies required to form RuS_2 in the bulk (i.e., ΔG^0 = −59 kJ/mole) suggests that surfaces possessing RuS_2-like selectivity are inherently less stable than the bulk compound. Formation of RuS_2-like surfaces appears to require at least +7 kJ/mole of free energy.

While the formation and detection of RuS_2 in the bulk of the specimens represented by entries 1 and 2 in Table 4 are certainly limited by kinetic phenomena, comparison of entry 3 with entries 4–6 demonstrates that the surface structure exposed for reaction can be quite different from the underlying material even when the underlying material is RuS_2. Additional electron microscopy studies using model supported Ru/Al_2O_3 catalysts (*13*) have demonstrated that the RuS_2 detected in entries 4–6 forms as an apparently contiguous skin on the outer surfaces of the ruthenium crystallites.

Based on the above results and earlier noted trends in catalytic selectivity, etc., it appears that the Gibbs free energy for surface sulfide formation is considerably greater than that required for formation of RuS_2 in the bulk. This behavior appears to be contradictory to earlier reports (*20–22*) which suggest enhanced stabilities for "surface sulfides" based on the heats of adsorption of sulfur to clean metal surfaces. However, it must be remembered that in the case of the pyrite lattice, sulfur–sulfur bonds are required in addition to metal–sulfur bonds. Therefore, estimations of the free energy of formation for a "surface sulfide" based solely on the strength of sulfur accommodation to a clean metal surface (*20–22*) may not provide an accurate means to gauge the thermodynamic stability of a pyrite sulfide at an interface. In particular, the aforementioned estimation procedures may be especially misleading if the coordination numbers and bond strengths found at a "sulfur poisoned metal surface" differ significantly from those found in the bulk sulfide or at the reconstructed/relaxed surface of the bulk sulfide.

2. *Hydrogen Chemisorption and H_2–D_2 Exchange*

Table 5 provides data recently obtained in our laboratory (*9, 23*) showing hydrogen chemisorption uptakes and H_2–D_2 exchange rates obtained over sulfided Ru/

TABLE 5

Effects of Sulfidization on H_2 Chemisorption and H_2–D_2 Exchange over Ru/Al_2O_3 and Ruthenium Sponge Catalysts

Catalyst	Pretreatment	Irreversible H_2 uptakes (μmole/m^2)				Reversible H_2 uptakes (μmole/m^2)	H_2–D_2 first-order rate const. (cm/s)[a]
		77 K	300 K	373 K	473 K	300 K	
3.7% Ru/Al_2O_3 (6.1 m^2/g) (2.5 nm)	H_2, 673 K, 8 h	N.D.[b]	N.D.	10.2	N.D.	4.7	N.D.
3.7% Ru/Al_2O_3 (4.0 m^2/g) (3.8 nm)	10% H_2S/H_2, 673 K, 2 h	0 ± 0.02	0 ± 0.02	0 ± 0.02	0 ± 0.02	0 ± 0.02	N.D.
3.7% Ru/Al_2O_3 (6.1 m^2/g) (2.5 nm)	100% H_2S, 673 K, 2 h	N.D.	1.4	6.5	N.D.	0.2	N.D.
Ru sponge (0.7 m^2/g)	10% H_2S/H_2, 673 K, 2 h	0 ± 0.02	0 ± 0.02	0 ± 0.02	0 ± 0.02	0 ± 0.02	2.1×10^{-6}
Ru sponge (0.7 m^2/g)	100% H_2S, 673 K, 2 h	N.D.	0.5	1.9	N.D.	0.1	5.2×10^{-4}

[a] H_2–D_2 equilibration measured at 573 K according to the prodcedures of (*9, 23*).

[b] N.D. stands for not determined.

Al_2O_3 and ruthenium sponge catalysts, respectively. Irreversible and reversible hydrogen adsorption isotherms measured between 300 and 473 K indicate that ruthenium was all but poisoned after mild presulfidization in 10% H_2S/H_2 at or below 673 K or in 100% H_2S at temperatures below 523 K. These results are in general agreement with those observed by Schwarz (*24*) over Ru(0001) in the presence of sulfur. Following adsorption of H_2S on Ru(0001) at 350 K, no hydrogen could be adsorbed on the ordered (2 × 2) sulfur overlayer, and this behavior was attributed to the ability of sulfur to block hydrogen dissociation sites (*24*).

The absence of hydrogen chemisorption following mild presulfidization initially appears perplexing as the kinetic models discussed in the previous paper (*1*) find thiophene HDS to be limited by surface reaction between adsorbed thiophene and adsorbed hydrogen. This apparent dilemma can be rationalized by noting the H_2–D_2 exchange rates over these same catalysts. These data demonstrate a finite HD formation rate thus verifying the dissociation of molecular hydrogen but indicating that the instantaneous coverage of these species is apparently so small as to be immeasurable by conventional volumetric adsorption methods. These data indicate that hydrogen weakly interacts with the ruthenium surface following mild presulfidization and that loosely bound hydrogen atoms are mainly responsible for thiophene HDS in agreement with the kinetic studies of Massoth (*25*) and Owens and Amberg (*26*) over $CoMo/Al_2O_3$.

Sulfidization in 100% H_2S at temperatures greater than or equal to 673 K results in partial restoration of the irreversible hydrogen uptake. Similar results from neutron inelastic scattering (NIS) demonstrate that irreversible hydrogen adsorption onto bulk RuS_2 samples results in the formation of sulfhydral groups at 80 K as evidenced by hydrogen deformation modes at ca. 78 and 90 meV (*23, 27, 28*). In addition, H_2–D_2 exchange rates were found to be ca. 100 times faster over ruthenium sponge catalysts following these more extensive presulfidization treatments (see Table 5).

The above-noted hydrogen chemisorption and H_2–D_2 exchange studies provide one plausible explanation for the observed differences in thiophene selectivity following different pretreatments. Increased levels of adsorbed hydrogen on RuS_2-like surfaces may serve to enhance the relative rate of thiophene hydrogenation as compared to the relative rate of thiophene hydrogenolysis, thereby increasing the measured hydrogenation-to-hydrogenolysis ratio. Other possibilities exist, however, since hydrogenation may compete with hydrogenolysis on the surface. Indeed, recent studies in this laboratory using HREELS and TPD over sulfur precovered Ru(0001) (*29, 30*) demonstrate that thiophene decomposition to "metallocycle-like" C_4 intermediates can occur even at 120 K in the absence of hydrogen as the level of adsorbed sulfur is reduced. These data can therefore be used to rationalize the 23-fold higher specific activity which small ruthenium crystallites possess (ca. 1.8 nm) for direct hydrogenolysis based on the low levels of sulfur which these crystallites retain (*1*).

3. *Comparison of Catalytic and Characterization Studies*

Based on the above-noted microgravimetric, XPS, XRD, chemisorption, and selectivity measurements, the "sulfidization–selectivity" behavior provided by ruthenium catalysts after various presulfidization treatments is shown in Fig. 10. This behavior may be classified into four distinct regions.

Region I is produced following relatively mild presulfidization with less than or equal to 0.5 monolayer of sulfur restricted to the surface. While this surface must be considered metastable with respect to the predictions of bulk thermodynamics, *it has been shown to be stable for periods on the order of months under the indicated presulfidization and reaction conditions* (see Fig.

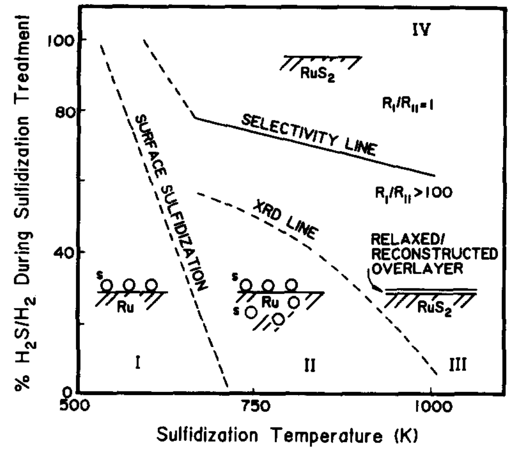

FIG. 10. Sulfidization–selectivity behavior of ruthenium catalysts determined by microgravimetry, XPS, XRD, and the kinetic measurements (P_{H_2} = 103.3 kPa, P_T = 10.3 kPa, P_{H_2S} = 1.04 kPa, 588 K); all specimens were prereduced in H_2, 101 kPa, 673 K, 8 h, followed by the appropriate sulfidization conditions at 101 kPa, 2 h.

10). This surface does not produce measurable quantities of tetrahydrothiophene.

Region II is produced following more extensive sulfidization than that for Region I, with the increased severity of the presulfidization being accomplished mainly through the use of elevated temperatures at H_2S/H_2 ratios below ca. 60% H_2S (see Fig. 10 for 2-h presulfidization treatments). Presulfidization under these conditions leads to sulfur incorporation below the surface (viz., into the bulk) yet crystalline RuS_2 is not produced during a given period of time most likely because the increased rate of solid state diffusion moderates the increased rate of sulfur incorporation to the extent that a given volume/region of ruthenium may have to become saturated or supersaturated with sulfur prior to nucleation of RuS_2. This region must be considered metastable with respect to the predictions of bulk thermodynamics, yet depending on the temperature, the background hydrogen pressure, and the size of the ruthenium domain; this region may persist for periods on the order of days. Because of the elevated temperatures and hydrogen pressures used in this presulfidization region, the sulfur concentration at the surface provides a surface similar in catalytic behavior and presumably structure to that found in Region I. The surface structure created in this presulfidization region does not produce measurable quantities of tetrahydrothiophene.

Region III is produced if a volume element in Region II becomes saturated with sulfur or if the surface of a material in Region IV is annealed in a hydrogen-rich environment at elevated temperatures. This region is characterized by crystalline RuS_2 in the bulk with a deficiency of sulfur at the surface causing a surface relaxation–reconstruction dictated by the strength of the metal–sulfur bond. This reconstruction provides a surface which is similar in catalytic activity, selectivity, and presumably structure to those encountered in Regions I and II and does not produce measurable quantities of tetrahydrothiophene.

Region IV is produced at higher H_2S/H_2 ratios and is believed to be characterized by an extension of crystalline RuS_2 to the very surface of the catalyst. This surface is characterized by a free energy of formation different from that found in the bulk and requires a temperature and H_2S/H_2 ratio providing at least +7 kJ/mole of free energy to be formed. The reduced stability of this surface compared to that found for the bulk sulfide (i.e., −59 kJ/mole) is believed to be related to the fact that pyrite lattices require metal–sulfur *as well as* sulfur–sulfur bonding. Based on H_2–D_2 exchange studies (*9, 23*), neutron inelastic scattering (*27, 28*), and hydrogen adsorption measurements (*23*), it appears likely that coordinatively unsaturated S–S anion pairs on the surfaces of these specimens provide numerous sites for hydrogen adsorption in the form of sulfhydral groups which assist thiophene hydrogenation to tetrahydrothiophene. Higher hydrogen pressures and elevated temperatures, however, can cause breakup of these S–S anion pairs, sulfur depletion from the surface via H_2S formation, and a surface reconstruction dominated by metal–sulfur bonding. While surfaces produced in Region IV require temperatures and H_2S/H_2 ratios equivalent to +7 kJ/mole, once these surface are produced they can be stabilized by kinetic means at lower temperatures and lower H_2S/H_2 ratios. Surfaces prepared in Region IV using 100% H_2S at 673 K have been observed to retain their affinity for producing tetrahydrothiophene for periods *on the order of months* at reaction temperatures of 600 K in 1% H_2S/H_2 backgrounds.

SUMMARY/CONCLUSIONS

1. The sulfidization–selectivity behavior of ruthenium catalysts after various presulfidization treatments can be classified into four distinct regions which can be reversibly altered by applying appropriate resulfidization/annealing treatments. Similar behavior is not observed over cobalt–molybdenum catalysts.

2. Ruthenium surfaces in Region I retained partial monolayers of sulfur adatoms and catalyzed direct hydrogenolysis of thiophene to C_4 products and H_2S in the absence of tetrahydrothiophene.

3. Ruthenium surfaces in Region II incorporated multilayers of sulfur into the bulk without the formation of crystalline RuS_2. These surfaces provided selectivities similar to those in Region I.

4. Ruthenium catalysts in Region III contained crystalline RuS_2 in the bulk with relaxed/reconstructed surfaces. These surfaces provided selectivities similar to those in Regions I and II.

5. Ruthenium catalysts in Region IV are characterized by an extension of crystalline RuS_2 to the very surface. These surfaces provided about equal quantities of C_4 products and THT.

6. Ruthenium catalysts in Region IV possessed ca. sevenfold higher thiophene conversion rates than $CoMo/Al_2O_3$ when compared per square meter of active area. Thiophene HDS rates averaged over oxygen titratable sites were ca. twofold higher on Ru/Al_2O_3 catalysts than on $CoMo/Al_2O_3$ specimens when compared per oxygen titratable site.

7. Calculations and comparisons of thiophene selectivity versus presulfidization parameters revealed that +7 kJ/mole of free energy is required to form RuS_2 at the surface versus −59 kJ/mole for formation in the bulk. The lack of stability of RuS_2 at the surface may be a generalized phenomenon applicable to other pyrite sulfides.

8. RuS_2-like surfaces (i.e., Region IV) chemisorb much larger quantities of hydrogen and possess much higher H_2–D_2 exchange rates than metallic ruthenium surfaces covered by partial monolayers of adsorbed sulfur (i.e., Region I). The higher levels of surface hydrogen found over RuS_2 may contribute to the higher hydrogenation rates and greater selectivities which these surfaces provide for tetrahydrothiophene production.

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REFERENCES

1. Kuo, Y. J., and Tatarchuk, B. J., *J. Catal.* **112,** 229 (1988).
2. Cocco, R. A., Toney, K. A., Kuo, Y. J., and Tatarchuk, B. J., Paper No. 88, presented at 190th National ACS Meeting, Division of Colloid and Surface Chemistry, Chicago, IL, Sept. 8, 1985.
3. Kuo, Y. J., Cocco, R. A., and Tatarchuk, B. J., Paper No. 34, presented at 191th ACS Meeting-Division of Petroleum Chemistry, New York, NY, April 13, 1986.
4. Cocco, R. A., Kuo, Y. J., and Tatarchuk, B. J., presented at the Symposium on Energy-Related Fundamental Research in Kinetics and Catalysis, Fall National Meeting of AIChE, Miami Beach, FL, Nov. 2–7, 1986.
5. Kuo, Y. J., Ph.D. dissertation, Auburn University, 1987.
6. Pecoraro, T. A., and Chianelli, R. R., *J. Catal.* **67,** 430 (1981).
7. Chianelli, R. R., *Catal. Rev. Sci. Eng.* **26,** 361 (1984).
8. Chianelli, R. R., Pecoraro, T. A., Halbert, T. R., Pan, W.-H., and Stiefel, E. I., *J. Catal.* **86,** 226 (1984).

9. Lu, K., Ph.D. dissertation, Auburn University, 1987.
10. Lu, K., and Tatarchuk, B. J., *J. Catal.* **106,** 166 (1987).
11. Lu, K., and Tatarchuk, B. J., *J. Catal.* **106,** 176 (1987).
12. Klug, H. P., and Alexander, L. E., "X-Ray Diffraction Procedures," 2nd ed. Wiley, New York, 1974.
13. Cocco, R. A., Kuo, Y. J., and Tatarchuk, B. J., submitted for publication.
14. Satterfield, C. N., "Mass Transfer in Heterogeneous Catalysis." MIT Press, Cambridge, MA, 1970.
15. Mears, D. E., *Ind. Eng. Chem. Process. Des. Dev.* **10**(4), 541 (1971).
16. Morooka, S., and Hamrin, C. E., Jr., *J. Chem. Eng. Sci.* **32,** 125 (1979).
17. Bartholomew, C. H., Agrawal, P. K., and Katzer, J. R., "Advances in Catalysis" (D. D. Eley, P. W. Selwood, and P. B. Weisz, Eds.), Vol. 31, p. 135. Academic Press, San Diego, 1982.
18. Meussner, R. A., and Berchenall, C. E., *Corrosion* **13,** 677 (1957). Moran, D. L., M.S. thesis, Auburn University, 1983.
19. Hauffe, K., "Oxidation of Metals." Plenum, New York, 1965.
20. Oliphant, J. L., Fowler, R. W., Pannell, R. B., and Bartholomew, C. H., *J. Catal.* **51,** 229 (1978).
21. McCarty, J. G., and Wise, H., *J. Chem. Phys.* **74**(10), 5877 (1981).
22. McCarty, J. G., and Wise, H., *J. Chem. Phys.* **72**(10), 6332 (1980).
23. Lu, K., Kuo, Y. J., and Tatarchuk, B. J., submitted for publication.
24. Schwarz, J. A., *Surf. Sci.* **87,** 525 (1979).
25. Massoth, F. E., *J. Catal.* **47,** 316 (1977).
26. Owens, P. J., and Amberg, C. H., *Adv. Chem. Ser.* **33,** 182 (1961).
27. Udovic, T. J., Rush, J. J., Heise, W. H., Lu, K., Kuo, Y. J., and Tatarchuk, B. J., presented at 191st National ACS Meeting, Division of Colloid and Surface Science, New York, NY, April 13, 1986.
28. Heise, W. H., Kuo, Y. J., Lu, K., Udovic, T. J., Rush, J. J., and Tatarchuk, B. J., *J. Phys. Chem.*, in press.
29. Heise, W. H., and Tatarchuk, B. J., presented at 193rd National ACS Meeting, Division of Colloid and Surface Chemistry, Denver, CO, April 5, 1987.
30. Heise, W. H., and Tatarchuk, B. J., submitted for publication.