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Hydrogen Adsorption and Hydrogen–Deuterium Equilibration on Sulfided Ruthenium and Bulk Ruthenium Sulfide Catalysts

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The effect of presulfidization on hydrogen adsorption over ruthenium catalysts has been studied using volumetric adsorption and H_2–D_2 equilibration. On reduced ruthenium catalysts (101 kPa of H_2 at 673 K for 8 h) 10.2 μmol of H_2/m^2 of ruthenium (measured at 373 K) was irreversibly adsorbed, the activation energy for adsorption was negligible and the initial heat of adsorption was estimated to be between −109 and −126 kJ/mole H_2. On "mildly sulfided" ruthenium catalysts (101 of kPa 10% H_2S/H_2 at 673 K for 2 h, $S_a/Ru_{(s)} = 0.25$) both reversible and irreversible hydrogen adsorption were suppressed at temperatures below 473 K. Results of H_2–D_2 equilibration kinetics on these catalysts ($508 \leq T \leq 623$ K) revealed an activation energy of 71 ± 2 kJ/mole. On "extensively sulfided" ruthenium catalysts (101 kPa of 100% H_2S at 673 K for 2 h, i.e., crystalline RuS_2 at the surface) partial restoration of the H_2 adsorption capacity was observed (6.5 μmol/m^2 at 373 K). H_2–D_2 exchange rates at 573 K were ca. two orders of magnitude faster than those over mildly sulfided samples. The activation energy for hydrogen adsorption was 32 ± 2 kJ/mole (on RuS_2-like surfaces) and the heat of adsorption was calculated to be −269 kJ/mole H_2. It is suspected that this large heat of adsorption may result in higher hydrogen coverages at HDS reaction conditions. The above noted differences in hydrogen accommodation provide a unique means for understanding the selectivity toward hydrogenated products which extensively sulfided ruthenium catalysts possess.

INTRODUCTION

Recent studies from this laboratory (*1–13*) reveal that the activity and selectivity for thiophene HDS over supported ruthenium catalysts depend on presulfidization conditions. Mildly sulfided specimens, which retain between 0.1 and 0.25 monolayers of surface sulfur (i.e., presulfidization at 673 K in 101 kPa of 10% H_2S/H_2 for 2 h), yield only direct hydrogenolysis products including butane, butenes, and hydrogen sulfide. Extensively sulfided specimens, which possess RuS_2-like surfaces (i.e., presulfidization at 673 K in 101 kPa of 100% H_2S for 2 h), provide nearly equal quantities of the direct C_4 hydrogenolysis products as well as tetrahydrothiophene. While the definitive source(s) for this selectivity difference has not been identified, the relatively high specific activity of supported ruthenium crystallites, retaining partial monolayers of sulfur, compared to commercial $CoMo/Al_2O_3$ catalysts has been suggested to result from: (i) the multiatom ensemble demands of the HDS reaction combined with (ii) the inherent sulfur tolerance of small ruthenium crystallites. HDS over clean ruthenium ensembles is apparently quite facile with the strong accommodation of adsorbed sulfur being significantly reduced as crystallite dispersion is increased.

To further examine the nature and causes of the above noted selectivity trends, HREELS, TPD, and SIMS studies on Ru(0001) have been undertaken by Heise *et al.* (*8–10*) and Cocco *et al.* (*11, 12*) as well as D_2–C_4H_4S exchange studies by Kuo (*13*). While the above noted studies have focused on the interaction between thiophene and the surface, the role of the coreactant cannot be neglected. Hydrogen

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may affect the reaction mechanism either in a direct fashion via, e.g., α-assisted hydrogenolysis (*14*) or in an indirect fashion via its surface coverage. In the latter instance, the relative quantity, mobility, and energetics of adsorbed hydrogenous species may be expected to have a profound affect on both the activity and the selectivity of hydrogen addition reactions. Since thiophene hydrogenolysis/HDS involves hydrogen addition and sequential hydrogenation of intermediates such as tetrahydrothiophene, butadiene, or butene, the aim of this study is to examine the interaction of hydrogen with the catalyst. The goal of these efforts then is to discern whether the above noted activity and selectivity trends can be related to thiophene adsorption/reaction at the surface and/or to fundamental transitions in hydrogen accommodation following different presulfidization procedures.

EXPERIMENTAL

Gases

Hydrogen and helium used in this study (Linde prepurified grade, 99.99%) were further purified by passage through a Deoxo unit at 298 K, a copper turning trap at 500 K, and 5X molecular sieve at 77 K. Research grade deuterium (99.99%) was purchased from Air Products and used as received. Hydrogen sulfide obtained from Matheson (certified to be >99.5% pure), and a mixture of 10% H_2S/H_2 (Air Products custom mixture grade) was used without further purification.

Catalysts

Both supported and unsupported ruthenium catalysts were used. Supported catalysts were prepared by vapor decomposition of ruthenium dodecarbonyl (*15, 16*). The catalyst support used was a Harshaw Al-3945 alumina powder with a BET surface area of 234 m^2/g. The unsupported catalyst, a pure ruthenium sponge (99.95%), was purchased from the Aesar group of Johnson Matthey, Inc. This catalyst had a BET surface area of 0.7 m^2/g.

A bulk ruthenium disulfide catalyst (i.e., RuS_2, laurite) was prepared using the precipitation method described by Pecoraro and Chianelli (*17*).

All the catalyst samples were pressed into pellets at 1.4×10^4 kPa, crushed, and sized between 20 and 40 mesh prior to adsorption and H_2–D_2 equilibration studies.

Apparatus

Hydrogen chemisorption measurements were performed using a conventional Pyrex volumetric adsorption apparatus (*15, 16*). A closed-loop recirculatory reaction system, adapted from the volumetric adsorption apparatus, was used for H_2–D_2 equilibration experiments. This reaction system had a total volume of 207 cm^3. Gas recirculation within the system was made possible by a double-action piston recirculation pump which was constructed in the laboratory (*18*). A portable gas sampling manifold was attached and consisted of a glass U-tube with six sampling ports isolated by high vacuum stopcocks (ACE Glass, Model 8194-90). Each sampling compartment had a volume of approximately 1.5 cm^3. The low ratio of sample volume to system volume (ca. 4.3%) was designed to minimize system perturbations caused by sample withdrawal. Equilibration products were analyzed using a calibrated Inficon IQ-200 quadrupole mass spectrometer in a separate vacuum system.

Catalyst Presulfidization

Catalyst samples were presulfided in ca. 50 cm^3/min (STP) of flowing hydrogen sulfide gas (100 or 10% H_2S/H_2) at 673 K for 2 h. In some instances, catalyst samples were presulfided in a closed-loop recirculatory fashion to allow direct determination of the sulfur uptake by the catalyst. In this procedure, a calibrated gas mixture of H_2S and H_2 was prepared in the system by mixing known quantities of hydrogen and hydrogen sulfide using the recirculation pump.

This mixture (ca. 60 kPa) was subsequently recirculated through a reduced catalyst sample at specified conditions. Control experiments were performed to verify the validity and accuracy of this procedure.

Hydrogen Adsorption

Hydrogen adsorption was measured on catalyst samples following procedures described in detail elsewhere (*15, 16*). A 2-h evacuation at 673 K was applied to all samples after reduction and/or presulfidization prior to hydrogen dosing. Hydrogen uptakes were determined from normal adsorption isotherms and also by means of a temperature jump procedure at 373 K (*15, 16*). Reversible adsorption was measured after the first adsorption isotherm and a 10-min evacuation at room temperature. The difference between the first adsorption isotherm and the reversible adsorption isotherm at 4 kPa is reported as the "irreversible uptake" at that temperature.

Hydrogen–Deuterium Equilibration Kinetics

In the study of H_2–D_2 equilibration, an equimolar mixture of hydrogen and deuterium was prepared in the glass reaction system. This mixture was dosed (ca. 20 kPa) and recirculated through the catalyst bed. Small volumes of the gas mixture were then withdrawn from the recycle system at regular intervals. The concentration of HD as a function of time was monitored over a period of ca. 40 min. Blank studies revealed that little or no contribution to the H_2–D_2 equilibration activity was provided by the empty reactor system. The pseudo-first-order rate constant for the equilibration reaction was calculated using the equation (*18, 19*)

$$k = -\ln(1-\eta) \times \frac{V}{At} \times \frac{2K_{\mathrm{eq}}^{1/2}}{2 + K_{\mathrm{eq}}^{1/2}}, \quad (1)$$

where K_{eq} is the equilibrium constant calculated at the temperature of the equilibration reaction, V is the volume of the reactor system, t is time, A is the active surface area of the catalyst, and η is the extent of reaction defined as

$$\eta = \frac{\text{the concentration of HD at time } (t)}{\text{the concentration of HD at equilibrium}}.$$

RESULTS

Effect of Presulfidization on Hydrogen Adsorption

Results of hydrogen adsorption on (i) reduced ruthenium (Catalyst A), (ii) sulfided ruthenium (Catalysts B and C), and (iii) bulk ruthenium sulfide (Catalysts D and E) at temperatures from 300 to 473 K are summarized in Table 1. As can be seen, the reversible and irreversible hydrogen uptakes at temperatures below 473 K on a 5% Ru/Al_2O_3 catalyst were suppressed following sulfidization (Catalyst B) in a flowing mixture of 10% H_2S/H_2 at 673 K for 2 h. A microgravimetric study of this catalyst revealed an atomic ratio of sulfur to surface ruthenium atoms ($S_a/Ru_{(s)}$) of ca. 0.3 (*1–3*).

A partial recovery of hydrogen adsorption capacity, however, was observed on a 3.7% Ru/Al_2O_3 catalyst after sulfidization (Catalyst C) at more severe conditions using 100% H_2S at 673 K for 2 h (i.e., $S_a/Ru_{(s)} = 5.0$ as determined by microgravimetry (*1–3*)). The amount of hydrogen irreversibly adsorbed at 300 and 373 K was 1.4 and 6.5 μmol/m^2, respectively, which corresponded to 14 and 64% of that adsorbed on the reduced metal. The increase in the hydrogen uptake with increasing adsorption temperature between 300 and 373 K indicated that hydrogen adsorption was activated. Therefore, the activation energy for adsorption on this surface was measured from $323 \le T \le 371$ K using kinetics procedures described elsewhere (*15, 16*). Results of these measurements are shown in Fig. 1. The apparent activation energy for hydrogen adsorption from $\theta_H = 0.3$–0.4 was found to be 32 ± 2 kJ/mole.

Adsorption of hydrogen on bulk RuS_2 was also investigated (Catalyst D). This

TABLE 1

Results of Hydrogen Adsorption on Sulfided Ruthenium and Bulk Ruthenium Sulfide Catalysts

Catalyst	Pretreatment	Irreversible hydrogen uptake (μmole/m^2)			Reversible hydrogen uptake at ca. 4 kPa (μmole/m^2) 300 K	$S_a/Ru_{(s)}$[a]
		300 K	373 K	473 K		
A. 3.7% Ru/Al_2O_3[b] (2.4 nm)	Reduced, 673 K, 101 kPa, 8 h	N.D.[c]	10.2	N.D.	4.7	0
B. 5.0% Ru/Al_2O_3[b] (3.5 nm)	Sulfided, 673 K, 10% H_2S/H_2, 101 kPa, 2 h	0.	0.	0.	0.	0.3
C. 3.7% Ru/Al_2O_3[b] (2.4 nm)	Sulfided, 673 K, 100% H_2S, 101 kPa, 2 h	1.4	6.5	N.D.	0.2	5.0
D. Bulk RuS_2[d] (39 m^2/g)[e]	Resulfided, 673 K 100% H_2S, 101 kPa, 2 h	0.8	5.3	N.D.	0.1	N.D.
E. Bulk RuS_2[d] (68 m^2/g)[e]	Resulfided, 673 K 10% H_2S/H_2, 101 kPa, 2 h	1.0	2.2	N.D.	0.2	N.D.

[a] Ratio of sulfur adatoms to surface ruthenium atoms determined by microgravimetry.

[b] Prepared from $Ru_3(CO)_{12}$ as described elsewhere (*15, 16*).

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

[d] Prepared by precipitation methods according to Pecoraro and Chianelli (*17*).

[e] Surface areas measured by nitrogen BET isotherms.

catalyst was resulfided in 100% H_2S at 673 K for 2 h before being dosed with hydrogen. Irreversible hydrogen uptakes were 0.8 and 5.3 μmol/m^2 at 300 and 373 K, respectively. These values are in good agreement with those measured on extensively sulfided ruthenium crystallites in which the RuS_2 phase was detected by XRD (*2, 3*). Considerably lower hydrogen uptakes (2.2 μmol/m^2 at 373 K), however, were measured on a RuS_2 sample after sulfidization in 10% H_2S/H_2 at 673 K for 2 h (Catalyst E).

Hydrogen Dissociation on Sulfided Ruthenium Surfaces

Since no hydrogen adsorption could be measured on mildly sulfided (10% H_2S/H_2, 673 K, 2 h) ruthenium surfaces at temperatures below 473 K, yet thiophene hydrodesulfurization readily took place on such surfaces at 573 K (*1–3*), it remained unclear as to what role hydrogen played on these sur-

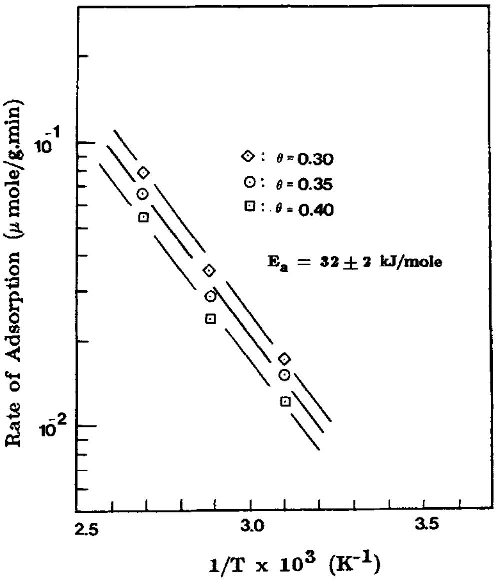

FIG. 1. Arrhenius plot for hydrogen adsorption over an extensively sulfided (100% H_2S, 673 K, 2 h) 3.7% Ru/Al_2O_3 catalyst (Catalyst C of Table 1); E_a, the activation energy for adsorption collected in the range from $323 \leq T \leq 371$ K.

TABLE 2

Hydrogen–Deuterium Equilibration Kinetics on Sulfided Ruthenium Sponges

Pretreatment	Equilibration reaction temperature	Pseudo-first-order rate constant (cm/sec)	Amount of sulfur removed during experiment[a] $S_a/Ru_{(s)}$
F. Reduced, 673 K flowing H_2, 101 kPa, 10 h	298 K	$>10^{-3}$	—
G. Sulfided, 673 K 10% H_2S/H_2, 101 kPa, 2 h	298 K	$<10^{-7}$	N.D.[b]
Sulfided, 673 K 10% H_2S/H_2 101 kPa, 2 h	573 K	$(2.1 \pm 0.1) \times 10^{-6}$	0.06 ± 0.01
H. Sulfided, 673 K 100% H_2S, 101 kPa, 2 h	573 K	$(5.2 \pm 0.2) \times 10^{-4}$	0.30 ± 0.02

[a] Determined by H_2S trapping experiments. See text for details.

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

faces. For this reason, H_2–D_2 equilibration reactions were employed to provide insight into the extent of hydrogen dissociation. Unsupported ruthenium sponge catalysts were used in this effort to avoid background activities provided by a support.

Results of equilibration kinetics measured on reduced and sulfided ruthenium sponges are listed in Table 2. As can be seen, hydrogen and deuterium equilibrated readily on the reduced sample at 298 K (Catalyst F). This activity, however, became immeasurably slow at 298 K after sulfidization in flowing 10% H_2S/H_2 at 673 K for 2 h (Catalyst G). When equilibration reactions were conducted using the same sample at an elevated temperature of 573 K (a typical temperature for thiophene HDS), a pseudo-first-order rate constant of ca. $(2.1 \pm 0.1) \times 10^{-6}$ cm/sec was measured. Since equilibration between H_2 and D_2 requires dissociative adsorption (*20*), the above results provide evidence for the existence of dissociated hydrogen intermediates on mildly sulfided ruthenium surfaces at 573 K.

The pseudo-first-order equilibration rate constant was also measured on an extensively sulfided (100% H_2S, 673 K, 2 h) ruthenium sponge sample at 573 K (Catalyst H). A ca. 100-fold increase in the rate constant was measured compared to that found on the mildly sulfided (10% H_2S/H_2) sample. These data parallel previous observations from irreversible hydrogen chemisorption studies and indicate that an extensively sulfided ruthenium (RuS_2-like) surface has a greater capacity for hydrogen adsorption *and* dissociation.

The H_2–D_2 equilibration kinetics on a mildly sulfided (10% H_2S/H_2, 673 K, 2 h) ruthenium sponge were measured over a temperature range from $508 \leq T \leq 623$ K (Catalyst G). Results from this study are presented in the form of an Arrhenius plot as shown in Fig. 2. An activation energy of 71 ± 2 kJ/mole was obtained.

Sulfur Stability

An additional effort was made to verify the stability of the sulfided ruthenium surfaces during equilibration reactions. In this instance, ruthenium sponge samples were

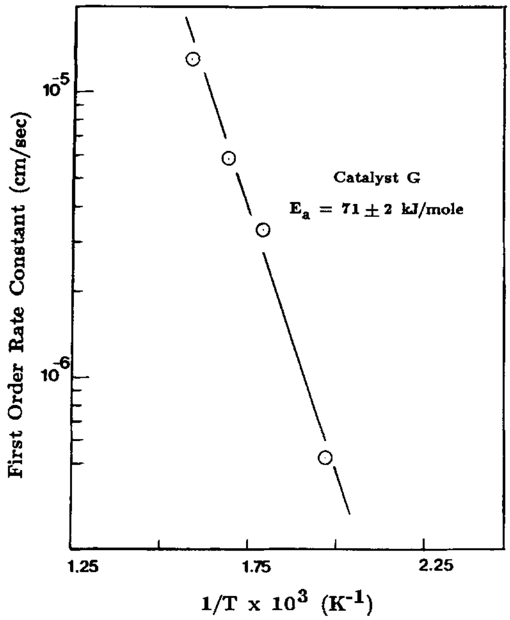

FIG. 2. Arrhenius plot for H_2–D_2 equilibration over a mildly sulfided (100% H_2S/H_2, 673 K, 2 h) ruthenium sponge (Catalyst G); E_a, the activation energy for adsorption collected in the range from $508 \leq T \leq 623$ K.

presulfided in 100% H_2S (Catalyst H) or 10% H_2S/H_2 at 673 K for 2 h (Catalyst G) in a recirculatory fashion. The sulfur uptake was determined following procedures described under Experimental. Hydrogen (ca. 20 kPa) was subsequently dosed and recirculated through the catalyst bed under reaction conditions identical to those used for H_2–D_2 equilibration (i.e., 573 K, 40 min). A portion of the recirculation loop was immersed in liquid nitrogen to condense out H_2S formed via the titration of surface sulfur. Trapped H_2S was then expanded and analyzed quantitatively. The amount of sulfur removed/trapped is reported in Table 2. As can be seen for all catalysts examined, only a small fraction of the incorporated sulfur was removed by hydrogen at 573 K and 20 kPa. These results indicate that significant loss of surface sulfur does not occur during H_2–D_2 equilibration.

DISCUSSION

Effect of Presulfidization on Hydrogen Adsorption

As shown in Table 1, sulfidization of ruthenium catalysts in 10% H_2S/H_2 at 673 K for 2 h (Catalyst B), which places ca. 0.25 monolayer of sulfur onto the ruthenium surface (*1–7*), suppresses both reversible and irreversible hydrogen adsorptions. These results are in general agreement with those observed over sulfur precovered Ru(0001) ($S_a/Ru_{(s)} = 0.25$) by Schwarz (*21*). He noted that no hydrogen was adsorbed on the (2 × 2) sulfur overlayer at 250 K and attributed this behavior to the blockage of hydrogen dissociation sites. The above noted reduction of hydrogen adsorption capacities by sulfur is also consistent with the results by Brand *et al.* (*22*) who studied the effects of surface sulfur coverage on the surface hydrogen mobility on Ru(0001) using laser-induced thermal desorption. They noted that at 300 K the hydrogen surface diffusion coefficient decreased by a factor of 30 as the surface sulfur coverage increased from 0 to 0.25 monolayer.

Extensive sulfidization in 100% H_2S at 673 K ($S_a/Ru_{(s)} = 5.0$, Catalyst C), however, provides partial restoration of the irreversible hydrogen uptake. Hou and Wise (*23*) observed a similar trend for hydrogen chemisorption over sulfided MoO_3/Al_2O_3 catalysts following different sulfidization conditions. They reported that the amount of hydrogen adsorbed increased with an increasing ratio of H_2S/H_2 used during presulfidization and thus the amount of sulfur incorporated into the catalyst.

Kuo and Tatarchuk (*2, 3*) used XRD to examine the structure of ruthenium crystallites following different sulfidization conditions. They found that the structure of ruthenium crystallites was not affected by mild sulfidization in 10% H_2S/H_2 at 673 K for 2 h; whereas, formation of the RuS_2 phase was detected when ruthenium crystallites were sulfided in a more severe environment using pure H_2S at 673 K for 2 h.

These results suggest that a change in catalyst structure brought about by the changing sulfidization conditions may be responsible for the observed differences in chemisorption.

It is also noted from Table 1 that 2.2 μmol of H_2/m^2 of ruthenium was irreversibly adsorbed at 373 K on a RuS_2 sample (Catalyst E) after sulfidization in 10% H_2S/H_2 at 673 K for 2 h compared to 6.5 μmol H_2/m^2 on the sample (Catalyst C) after sulfidization in 100% H_2S. This decrease in hydrogen uptake may be attributed to the depletion of surface sulfur and/or surface phase transformations which occur during resulfidization in hydrogen-rich environments. As noted earlier by Kuo and Tatarchuk (*2, 3, 7*), the magnitude of the weight change and the $S_a/Ru_{(s)}$ ratio determined by X-ray photoelectron spectroscopy both indicate the loss of about one monolayer of surface sulfur following the above noted treatments. Furthermore, results from incoherent inelastic neutron scattering (IINS) studies by Heise *et al.* (*24*) suggest that coordinatively unsaturated S–S anion pairs located on the surface of RuS_2 catalysts may be sites for hydrogen adsorption in the form of sulfhydryl groups (S–H). Removal of sulfur atoms from such S–S pairs may result in surface reconstruction dominated by strong metal–sulfur bonding (*2, 3*) with less accommodation of hydrogen than that provided by the RuS_2–pyrite surface.

Energetics of Hydrogen Adsorption/Desorption on Reduced and Sulfided Ruthenium Surfaces

On the basis of the above noted data, the adsorption/desorption energetics of hydrogen on (i) reduced, (ii) mildly sulfided, and (iii) extensively sulfided ruthenium catalysts are considered.

A. Reduced ruthenium. It is generally believed that hydrogen adsorbs onto clean ruthenium with negligible activation energy (*20, 25*). Danielson *et al.* (*25*) report that hydrogen adsorbs readily (with an initial sticking coefficient of $S_0 = 0.4$) on Ru(0001) at 100 K. The activation energy for desorption of hydrogen from Ru(0001) has been measured by Schwarz (*21*) and also Feulner and Menzel (*26*) using TPD. Schwarz found a steady decrease of E_d from 109 to 46 kJ/mole H_2 as the surface coverage of hydrogen, θ_H, approached 0.8. Feulner and Menzel also observed this trend except higher E_d values were reported. In their investigation E_d decreased from 126 kJ/mole at zero coverage to 84 kJ/mole H_2 at saturation. From the above noted desorption data, the heat of adsorption (ΔH_a) at zero coverage can be estimated to be between -109 and -126 kJ/mole H_2. These data are in good agreement with the experimental work of Clark on silica-supported ruthenium (*27*) in which a value of $\Delta H_a = -109$ kJ/mole H_2 was measured. The above noted data are illustrated in Fig. 3a.

B. Mildly sulfided ruthenium. As noted earlier, at temperatures below 473 K neither reversible nor irreversible hydrogen adsorption was observed on a ruthenium sponge catalyst after sulfidization in 10% H_2S/H_2 at 673 K for 2 h. It is therefore impossible to gauge the activation energy for hydrogen adsorption on this surface by direct measurement of adsorption kinetics. Alternatively, hydrogen–deuterium equilibration kinetics were employed to provide an indirect assessment. Since equilibration between H_2 and D_2 takes place sequentially via dissociative adsorption, surface recombination, and desorption, the apparent kinetics for equilibration are representative of the rate limiting step in the above sequence. In this study, no reversible or irreversible hydrogen adsorptions were measured at 473 K suggesting that the activation barrier for adsorption was high. It was therefore assumed that the 71 ± 2 kJ/mole activation energy measured over mildly sulfided specimens between 508 and 623 K was representative of the dissociative adsorption process (see Fig. 3). Further attempts to estimate the heat of adsorption on this surface were not possible due to a lack of knowledge concerning the

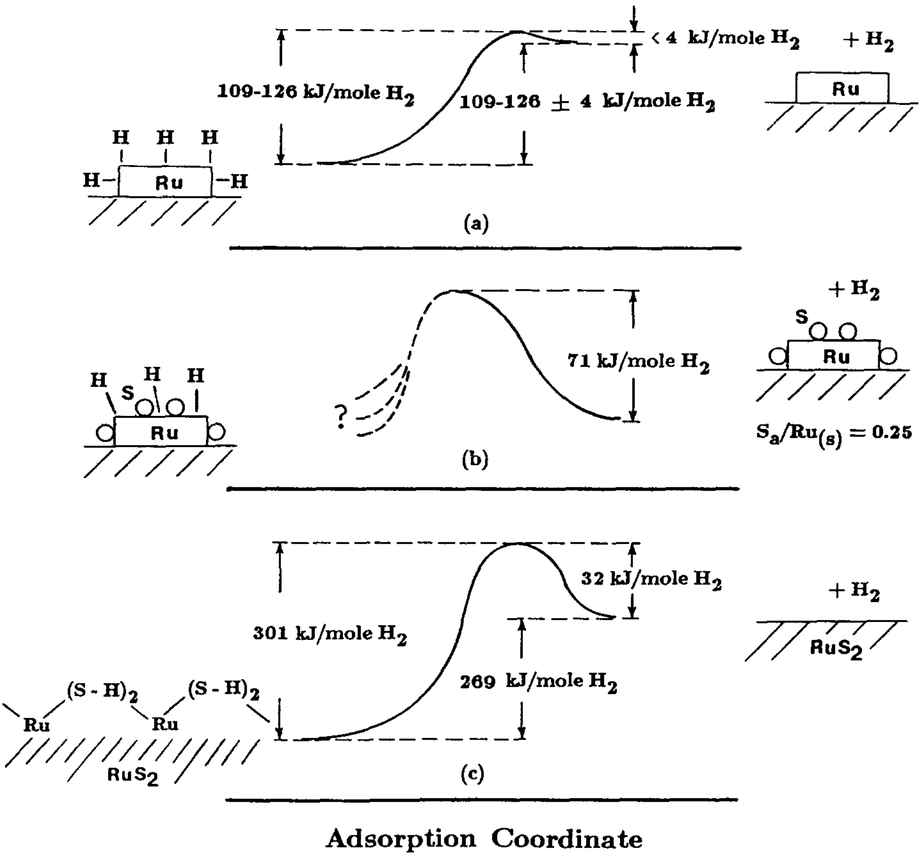

FIG. 3. Energetics of hydrogen adsorption on (a) reduced (H_2, 673 K, 8 h), (b) mildly sulfided (10% H_2S/H_2, 673 K, 2 h), and (c) extensively sulfided (100% H_2S, 673 K, 2 h) ruthenium catalysts.

adsorption site. However, it is likely that the activation energy for desorption is of the same magnitude as the activation energy for adsorption providing a relatively small heat of adsorption and rapid desorption of adsorbed hydrogen atoms once they are formed.

C. Extensively sulfided ruthenium. In contrast to the mildly sulfided ruthenium surface, an extensively sulfided (100% H_2S, 673 K, 2 h) ruthenium catalyst adsorbed hydrogen at ambient temperatures and above, as shown in Table 1. It is also noted that the hydrogen uptake increased as the adsorption temperature was increased from 300 to 373 K and the apparent activation energy for hydrogen adsorption was measured to be ca. 32 ± 2 kJ/mole H_2 (Fig. 1). The above results indicate that hydrogen adsorption on an extensively sulfided ruthenium surface is less activated than that on a mildly sulfided ruthenium surface.

As mentioned earlier, studies of IINS indicate that hydrogen adsorption onto extensively sulfided ruthenium catalysts (RuS_2-like surfaces) occurs in the form of sulfhydryl groups (S–H). Therefore, attempts have been made to estimate the heat of adsorption (ΔH_a) on these surfaces according to the equation (*20*)

$$-\Delta H_a \text{ (per mole of } H_2) = 2D_{SH} - D_{HH},$$

where D_{SH} is the dissociation energy for the sulfur–hydrogen bond (351 kJ/mole) (*28*) and D_{HH} the dissociation energy for the hydrogen–hydrogen bond (433 kJ/mole) (*28*). It was found that a value of $-\Delta H_a$, as high as 269 kJ/mole H_2, was obtained for hydrogen adsorption on RuS_2-like surfaces compared to ca. 109–126 kJ/mole and ca. 0 kJ/mole on reduced and mildly sulfided ruthenium catalysts, respectively.

On the basis of the above discussions, schematic Lennard–Jones potential energy diagrams can be sketched for hydrogen adsorption on reduced, mildly sulfided, and extensively sulfided ruthenium catalysts, as shown in Fig. 3. As can be seen, a mild sulfidization (10% H_2S/H_2, 673 K, 2 h) which incorporates ca. 0.25 monolayer of sulfur onto the ruthenium surface imposes a high activation barrier for hydrogen adsorption. More severe sulfidization of ruthenium catalysts in 100% H_2S at 673 K for 2 h, however, results in the formation of crystalline RuS_2 on the surface which adsorbs hydrogen with moderate activation energy (32 ± 2 kJ/mole) but a somewhat larger calculated heat of adsorption (−269 kJ/mole).

Implications of Hydrogen Accommodation on Thiophene HDS

The above noted results of hydrogen adsorption and H_2–D_2 equilibration may provide one plausible explanation for the different thiophene HDS selectivities observed over mildly and extensively sulfided ruthenium catalysts. A larger negative heat of adsorption for hydrogen over RuS_2 surfaces may stabilize hydrogen on the surface, resulting in an increase of surface hydrogen at reaction conditions, thereby enhancing the relative rate of thiophene hydrogenation to tetrahydrothiophene compared to that of thiophene hydrogenolysis.

The absence of hydrogen chemisorption over mildly sulfided ruthenium catalysts appears perplexing since direct thiophene hydrogenolysis requires hydrogen incorporation into the molecule (*1–3*), yet this result can be rationalized by noting that a finite H_2–D_2 equilibration rate ($2.1 \pm 0.1 \times 10^{-6}$ cm/sec) is measured over these catalysts at 573 K. This result provides evidence for hydrogen dissociation and indicates that the instantaneous coverage of these species is apparently so small as to be immeasurable. It also suggests that loosely bound hydrogen atoms are mainly responsible for thiophene hydrogenolysis over mildly sulfided ruthenium catalysts. The observation of low hydrogen coverage is also consistent with earlier kinetic and modeling studies over mildly sulfided ruthenium catalysts where the rate limiting step was determined to involve reaction between adsorbed thiophene and hydrogen (*1*).

CONCLUSIONS/SUMMARY

Extensively sulfided catalysts possessing RuS_2-like surfaces are unique in that they strongly accommodate surface hydrogen during both adsorption and H_2–D_2 studies. This behavior is different than that provided by ruthenium surfaces retaining partial monolayers of adsorbed sulfur and may account for the high hydrogenation activity and selectivity which these catalysts possess.

(i) Ruthenium (10.2 μmol of H_2/m^2, measured at 373 K) was irreversibly adsorbed on reduced ruthenium catalysts. The activation energy for adsorption was negligible (<4 kJ/mole) and the initial heat of adsorption was between −109 and −126 kJ/mole H_2.

(ii) Mild presulfidization of ruthenium catalysts in 10% H_2S/H_2 at 673 K for 2 h, which placed ca. 0.25 monolayer of sulfur on the surface, suppressed both reversible and irreversible hydrogen adsorptions at temperatures below 473 K. Results of H_2–D_2 equilibration kinetics ($508 \leq T \leq 623$ K) revealed a high activation energy barrier for exchange, ca. 71 ± 2 kJ/mole. The activation energy for desorption may be of the same magnitude as that for adsorption providing little or no heat of adsorption and relatively low hydrogen coverages at typical HDS temperatures.

(iii) Partial recovery of the H_2 adsorption capacity (6.5 μmol/m^2 at 373 K) was observed following sulfidization in more severe conditions using 100% H_2S at 673 K for 2 h which resulted in the formation of crystalline RuS_2 on the surface. Complementary IINS data suggest that S–S anion pairs located on the surface of RuS_2 may be hydrogen adsorption sites in the form of sulfhydryl groups (S–H).

(iv) H_2–D_2 exchange rates at 573 K over extensively sulfided ruthenium sponges were found to be ca. two orders of magnitude greater than those over mildly sulfided samples. The activation energy for hydrogen adsorption was 32 ± 2 kJ/mole on RuS_2-like surfaces and the heat of adsorption was calculated to be -269 kJ/mole H_2. This large heat of adsorption likely results in an increase of surface hydrogen at HDS reaction conditions, thereby increasing the relative rate of thiophene hydrogenation compared to direct thiophene hydrogenolysis.

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REFERENCES

1. Kuo, Y. J., and Tatarchuk, B. J., *J. Catal.* **112,** 229 (1988).
2. Kuo, Y. J., and Tatarchuk, B. J., *J. Catal.* **112,** 250 (1988).
3. Kuo, Y. J., and Tatarchuk, B. J., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), p. 96. The Chemical Institute of Canada, Ottawa, 1988.
4. Kuo, Y. J., Lu, K., and Tatarchuk, B. J., Paper No. 18c, presented at the Symposium on Engineering Sciences and Fundamentals, Winter National Meeting of AIChE, New York, 1987.
5. Kuo, Y. J., Cocco, R. A., and Tatarchuk, B. J., presented at 193rd ACS National Meeting—Division of Colloid and Surface Chemistry, Los Angeles, 1988.
6. Kuo, Y. J., Heise, W. H., and Tatarchuk, B. J., *J. Catal.*, in press.
7. Cocco, R. A., Kuo, Y. J., and Tatarchuk, B. J., "Effects of Presulfidization on the Activity, Selectivity, and Morphology of Ruthenium Catalysts," in preparation.
8. Heise, W. H., and Tatarchuk, B. J., *Surf. Sci.*, in press.
9. Heise, W. H., and Tatarchuk, B. J., submitted for publication.
10. Heise, W. H., Ph.D. dissertation, Auburn University, 1988.
11. Cocco, R. A., and Tatarchuk, B. J., submitted for publication.
12. Cocco, R. A., and Tatarchuk, B. J., submitted for publication. Cocco, R. A., Papageorgopoulos, C., and Tatarchuk, B. J., submitted for publication.
13. Kuo, Y. J., Ph.D. dissertation, Auburn University, 1987.
14. Roberts, J. T., and Friend, C. M., *Surf. Sci.* **186,** 201 (1987).
15. Lu, K., and Tatarchuk, B. J., *J. Catal.* **106,** 166 (1987).
16. Lu, K., and Tatarchuk, B. J., *J. Catal.* **106,** 176 (1987).
17. Pecoraro, T. A., and Chianelli, R. R., *J. Catal.* **67,** 430 (1981).
18. Lu, K., Ph.D. dissertation, Auburn University, 1987.
19. Indovina, V., Cimino, A., and Valigi, M., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), p. 216. The Chemical Society, London, 1976.
20. Bond, G. C., "Catalysis by Metal." Academic Press, London, 1962.
21. Schwarz, J. A., *Surf. Sci.* **87,** 525 (1979).
22. Brand, J. L., Dechert, A. A., and George, S. M., *Surf. Sci.* **194,** 457 (1988).
23. Hou, P. Y., and Wise, H., *J. Catal.* **93,** 409 (1985).
24. Heise, W. H., Lu, K., Kuo, Y. J., Udovic, T. J., Rush, J. J., and Tatarchuk, B. J., *J. Phys. Chem.* **92,** 5184 (1988).
25. Danielson, L. R., Dresser, M. J., Donaldson, E. E., and Dickinson, J. T., *Surf. Sci.* **71,** 599 (1978).
26. Feulner, P., and Menzel, D., *Surf. Sci.* **154,** 465 (1985).
27. Clark, A., "The Chemisorptive Bond." Academic Press, New York, 1974.
28. Dean, J. A., "Lange's Handbook of Chemistry," 12th ed. McGraw-Hill, New York, 1979.