

NMR Study of the Influence of Adsorbed Sulfur on Hydrogen Chemisorption on Supported Ruthenium Catalysts

S. BHATIA,* B. C. GERSTEIN,† AND T. S. KING*.¹

Departments of *Chemical Engineering and †Chemistry, Iowa State University and Ames Laboratory, Institute for Physical Research and Technology, Ames, Iowa 50011

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NMR of hydrogen chemisorbed on silica-supported ruthenium catalysts was used to study the dissociation of H₂S and its effect on subsequent hydrogen adsorption. A mixture of H₂S/He was used to sulfide the reduced catalyst. The hydrogen coverages resulting from the dissociation of H₂S as measured by NMR yielded estimates of sulfur coverages in good agreement with the results of X-ray fluorescence analysis of sulfur on the samples. The H₂S dissociation reaction was found to be enhanced on higher dispersion catalysts suggesting an important role for defect-like sites. At sulfur coverages greater than 0.25 sulfur atoms per surface ruthenium atom, no hydrogen from the dissociation of H₂S could be detected remaining on the surface. On the presulfided catalysts dosed to saturation with additional hydrogen, the NMR spectra revealed the presence of two species of hydrogen: a mobile species and a less mobile species. At sulfur coverages greater than 0.5 no detectable hydrogen could be adsorbed on the surface when exposed to 30 Torr of H₂. The ratio of weakly bound hydrogen to the strongly bound hydrogen at saturation coverage decreased with increasing sulfur coverage. The small change in the magnitude of the NMR lineshift of hydrogen-on-metal with sulfur coverage suggested that the adsorbed sulfur does not induce a strong electronic effect on the chemisorption of hydrogen. © 1992 Academic Press, Inc.

INTRODUCTION

Catalyst poisoning by sulfur is a severe problem commonly encountered in the commercial application of supported metal catalysts. The lifetime of supported metal catalysts may be greatly shortened and the catalytic performance can be altered by the presence of only trace amounts of sulfur contaminants in the feed resulting in irreversible adsorption of sulfur on metals. Because of the practical importance of sulfur poisoning, a considerable amount of information has been accumulated concerning the interaction of sulfur with the metal surfaces (1). Much of the attention has been focused on the nature of metal-sulfur bonding and mechanisms of sulfur adsorption on metal surfaces. The influence of sulfur adsorption on hydrogen-metal bonding has

also been reported in a number of studies (1-11).

The chemisorption of sulfur on metallic catalysts depends on the electronic properties of the catalyst. From a Pt single-crystal study by Barbier *et al.* (2), it was concluded that the sulfur adsorption takes place primarily on the high coordination sites of platinum crystallites (face atoms). Electron deficiency at defect-like edge, corner, and other low coordination sites is used to explain the reduced tendency of a metal for adsorbing an electron acceptor compound such as sulfur. This view is consistent with a study by Mellius *et al.* (3), who showed that corner and edge (low coordination) atoms are electron deficient. Somorjai and Blakely (4), however, suggest that sulfur present in small quantities will first block the kink sites (low coordination) that are of the highest binding energy on the heterogeneous surface.

¹ To whom correspondence should be addressed.

Keleman and Fischer (5) studied the interaction of H_2S with the Ru(001) single-crystal surface. They reported that H_2S dissociated over the entire sulfur coverage range at 350 K. Below the coverage of 0.67 the hydrogen recombined and desorbed leaving the adsorbed sulfur. Higher exposure of H_2S resulted in the dissociative adsorption of hydrogen sulfide with the simultaneous presence of both hydrogen and sulfur on the metal surface. It was suggested that the surface must be heated to 500 K for the chemisorbed hydrogen to begin desorbing. This temperature is considerably higher than that required for desorption of H_2 from the clean surface. It was suggested that the adsorbed sulfur acted as an inhibitor for the hydrogen recombination.

Fisher (6) investigated the adsorption of H_2S on Ru(110) and suggested that with increasing sulfur coverages, the dissociated hydrogen was gradually desorbed. He also provided ultraviolet photoemission spectroscopic evidence of SH species as intermediates in the dissociation of H_2S on Ru(110) at 80 K. In a separate study, Saleh *et al.* (7) suggested that hydrogen atoms close to (but not necessarily bonded to) sulfur atoms are slowly exchanged, whereas hydrogen atoms free from the influence of sulfur adatoms are readily replaced by deuterium.

The effects of sulfur coverage on the surface diffusion of hydrogen on Ru(001) have been studied by Brand *et al.* (8). They found that at both 270 and 300 K the surface mobility of hydrogen decreased rapidly with increasing sulfur coverage.

Bartholomew *et al.* (1) investigated the effects of preadsorbed sulfur on hydrogen adsorption on nickel at room temperature. They reported a linear relationship between H_2 uptake and sulfur coverage, with an intercept at zero H_2 coverage corresponding to a ratio of $H_2S/Ni = 0.75$. This is in agreement with the adsorption stoichiometry reported by Oliphant *et al.* (9). Their work (9) on the Ni catalyst shows that removal of adsorbed sulfur by

hydrogen is slow even at high temperatures (~ 725 K).

Schwarz (10) studied the effect of sulfur on the adsorption-desorption kinetics of hydrogen on Ru(001). He found that no hydrogen could be adsorbed for coverages greater than or equal to 0.25. Increasing the sulfur surface coverage rapidly suppressed the amount of hydrogen that could be adsorbed by saturation exposure to hydrogen. Studies done by Kuo and Taturchuk (11) also showed that no hydrogen was adsorbed at temperatures between 300 and 473 K when the metal surface in the supported ruthenium catalysts was covered by more than 0.25 monolayer of sulfur. They used pulse oxygen chemisorption to measure the number of vacant ruthenium surface sites. According to previous studies (12-14), typical catalyst supports such as Al_2O_3 and SiO_2 adsorb relatively little sulfur.

In a previous study by Wu *et al.* (15), nuclear magnetic resonance (NMR) of hydrogen, or proton magnetic resonance (PMR), was successfully applied to measure the resonance linewidth and lineshift of hydrogen adsorbed on silica-supported ruthenium catalysts. PMR was used to determine the amount of hydrogen adsorbed directly onto the ruthenium surface in contrast to volumetric hydrogen uptake experiments, which measure the amount of hydrogen adsorbed on the support and on the metal. That study has shown that hydrogen can spill over to the silica support from the ruthenium crystallites.

In the present investigation, PMR was used to probe the nature of hydrogen adsorbed on the supported ruthenium surface. Both chemisorbed hydrogen resulting from the dissociation of hydrogen sulfide and from subsequent adsorption of hydrogen gas was studied. PMR offers a significant advantage: that of monitoring the hydrogen adsorbed from the dissociation of hydrogen sulfide and distinguishing between the reversibly adsorbed hydrogen and the irreversibly adsorbed hydrogen.

METHODS

Catalyst Preparation

The catalysts used in the present study were prepared by incipient wetness impregnation of an aqueous ruthenium solution with a dried, amorphous Cab-O-Sil HS5 (300 m²/g BET surface area) silica support. The impregnating solution was prepared by dissolving an appropriate amount of Ru(NO)(NO)₃ salt (ALPHA) in distilled water. The readily available RuCl₃ · nH₂O was not used as the metal salt in preparing the catalysts in this work because studies (16–19) have showed that the chlorine cannot be effectively removed from the surface of the ruthenium particles by hydrogen reduction at typical reduction temperatures (573–723 K). Approximately 2.2 ml of impregnating solution per gram of support was needed to bring about incipient wetness. The slurries obtained after impregnation were dried for 24 h at room temperature and 6 h in air at 383 K. Two sets of catalyst samples were prepared; one had 8 wt% loading and the other had 12 wt% metal loading.

Catalyst Reduction and Adsorption

A multiport Pyrex glass manifold (15) with a volume of 127.3 cm³ was used in preparing the NMR samples and measuring the dispersion of supported ruthenium catalysts by hydrogen chemisorption. Catalyst samples (50–70 mg) for NMR analysis were placed in 5-mm NMR tubes. Helium was allowed to fill the NMR tubes attached to the manifold and then the temperature of the furnace was raised to 423 K. Helium was replaced by hydrogen to maintain a pressure of about 760 Torr in the manifold. The furnace temperature was gradually raised to 723 K and the catalyst was reduced at this temperature for 2 h. Hydrogen was evacuated and replaced by fresh hydrogen every 30 min. Helium (99.999%) and hydrogen (99.8%) (Air Products) were used as received.

Hydrogen used for adsorption was purified by being passed through a catalytic hy-

drogen purifier (Engelhard Deoxo) in series with a gas purifier filled with Drierite and 5-Å molecular sieve (Alltech) to remove traces of oxygen and moisture. Hydrogen sulfide, diluted in helium with a concentration of 992 ppm (Matheson Gas Products) was used as received.

After the catalyst was reduced, the sample was evacuated to 4×10^{-6} Torr with at 623 K for 10 h. The samples were then cooled to room temperature before being dosed with the hydrogen sulfide/helium mixture or hydrogen. Some samples were exposed to the H₂S/He mixture at various pressures and allowed to equilibrate for 4 h. In some cases the H₂S/He mixture was evacuated from the manifold, which was then refilled with the H₂S/He mixture at different pressures. The above dosing sequence was used to achieve higher coverages of sulfur on the metal. After evacuating the H₂S/He mixture from the manifold, some of the samples were then dosed with 30 Torr of hydrogen to saturate the surface with hydrogen. The extent of hydrogen adsorption on the sulfided ruthenium surface was then measured. The reversibly adsorbed hydrogen was removed from the metal surface by evacuating the samples to 10⁻⁵ Torr for 10 min, allowing subsequent measurements for the amount of the irreversibly adsorbed hydrogen (15).

The NMR tubes were sealed with a microtorch while the samples were immersed in a water bath. Sample weights were measured after the NMR tubes were sealed.

NMR Experiments

The home-built NMR spectrometer (20) used for this study operated at 220 MHz for proton resonance. A proton-free probe with a doubly wound coil (21) was used for all the NMR measurements. The details of the spectrometer's receiving system have been described elsewhere (22).

The spectrometer was capable of detecting 10¹⁷ protons with a linewidth of <20 kHz, while the number of hydrogen atoms adsorbed on ruthenium in a typical catalyst

sample was around 5×10^{18} . The resulting sensitivity is about 2% of a monolayer. The probe quality factor Q was set at 100 to optimize sensitivity versus ringdown time. The recycle time between 90° pulses was set between 0.2 and 0.4 s to selectively suppress the strong intensity of the peak corresponding to protons in the silanol group that have a relatively long spin-lattice time T_1 (on the order of seconds). The recycle rate given above avoids T_1 saturation of the peak corresponding to hydrogen adsorbed on ruthenium which has a spin lattice time constant of about 0.04 s. On each catalyst sample, 10,000 scans were acquired. NMR shifts are reported on the δ scale, with negative shifts being upfield. The reference is TMS. The PMR signals were recorded with a dwell time of 2 μ s and a spectral range of 250 kHz (1136 ppm). The receiver gain was kept the same for the water sample and for the catalyst samples. The T_1 measurements were made by inversion recovery pulse sequence ($180^\circ - \tau - 90^\circ$). The initial intensities at different delay times are exponential, which indicates that the receiver system is linear over the signal range extant in the present measurements. All NMR measurements were done at ambient temperatures (294 ± 1 K).

Volumetric H_2 Chemisorption Measurements

For each measurement about 1 g of catalyst was loaded in a glass cell attached to the glass manifold and was reduced at 723 K for 2 h under a static atmosphere of hydrogen. The hydrogen was evacuated and replenished every 30 min.

After reduction the manifold was evacuated to a final pressure of 4×10^{-6} Torr and the extra volume of the stopcock and the glass cell was measured using helium gas. After the helium was evacuated, hydrogen was admitted and the pressure was recorded. The adsorption of hydrogen on the catalyst was allowed to equilibrate for 4 h before the hydrogen pressure was recorded. More hydrogen was introduced in the manifold and allowed to equilibrate. The equi-

TABLE 1

The Ratio of Hydrogen Adsorbed to Total Ruthenium (H/Ru, by Chemisorption)

Ruthenium metal loading (wt%)	H Chemisorption		
	Total	Reversible	Strong
8	0.45	0.17	0.28
12	0.30	0.11	0.19

bration time for subsequent hydrogen adsorption was 1 h. To obtain the total isotherm, at least three sets of pressure readings were acquired. For the reversible isotherm, hydrogen was evacuated to 10^{-5} Torr for 10 min at room temperature before hydrogen was introduced again into the manifold and a new set of pressure readings recorded. The values for the ruthenium dispersion was calculated from the intercept at zero hydrogen pressure from the plots of the adsorption isotherms. The metal dispersion was taken to be the molar ratio of the strongly adsorbed hydrogen to the total amount of ruthenium in the catalyst, with an assumed stoichiometry of one hydrogen atom per surface Ru atom.

RESULTS

The results for the total hydrogen chemisorption and the strongly adsorbed H/Ru calculated from the difference between the total and the weakly adsorbed hydrogen are given in Table 1. The catalyst with 8% metal loading had a dispersion of 0.28 and that with 12% metal loading had a dispersion of 0.19.

A PMR spectrum of the 8% silica-supported ruthenium catalyst sample under a pressure of 30 Torr of hydrogen is shown in Fig. 1 (spectrum A). Two well-resolved resonance lines are observed in the spectrum. The peak with a maximum at 2 ppm near the reference is designated as the downfield peak, and the peak with a maximum at -55 ppm is called the upfield peak. The downfield peak is assigned to the termi-

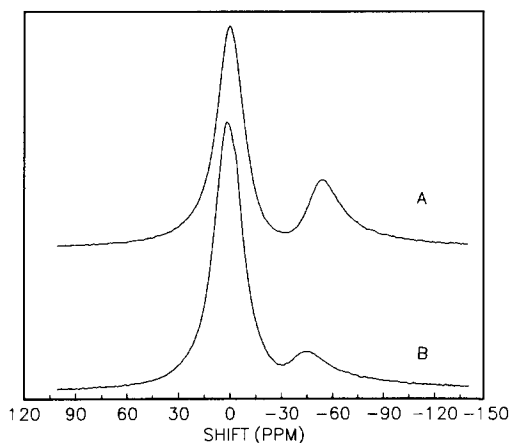


FIG. 1. ^1H NMR spectra of: (A) 30 Torr of hydrogen adsorbed on 8% Ru/SiO₂ catalyst and (B) 30 Torr of hydrogen adsorbed and evacuated to 10^{-6} Torr.

nal silanol protons (Si-OH) in the silica support (15). The upfield peak is assigned to the hydrogen adsorbed on the surface of the ruthenium. The magnitude of the shift is due to the influence of the metal's conduction band and is called the Knight shift (15, 21, 22).

The area under the upfield resonance line was obtained by integrating the spectrum from which the downfield peak had been subtracted. This area corresponds to the total hydrogen adsorbed on the ruthenium surface, whereas the volumetric uptake experiments measure the total hydrogen adsorbed on the supported catalyst including hydrogen that spills over from the metal to the support (15).

The upfield peak in spectrum B in Fig. 1 is due to the hydrogen strongly bound to the surface; i.e., it could not be desorbed at room temperature by evacuation to 10^{-5} Torr for 10 min. Previous work by Wu *et al.* (15) has shown that the quantitative PMR and the volumetric uptake results for strongly adsorbed hydrogen on the supported ruthenium catalyst show no significant difference. The hydrogen weakly adsorbed on the metal particles partially spills over to the silica support. Therefore the measurements of the total amount of hydro-

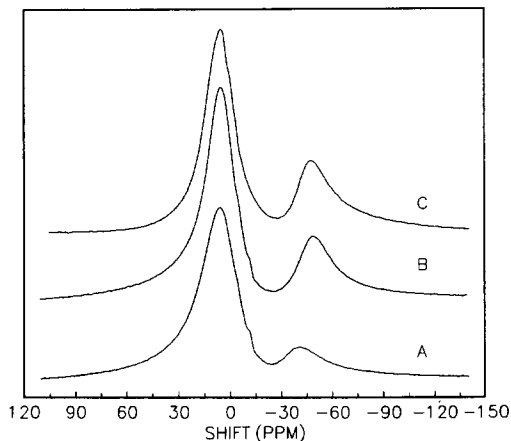


FIG. 2. ^1H NMR spectra of 8% Ru/SiO₂ (A) sequentially dosed with H₂S/He mixture, 760 Torr followed by 760 Torr, (B) 30 Torr of hydrogen dosed on the sulfided catalyst, (C) 30 Torr hydrogen dosed on the clean catalyst.

gen adsorbed on the catalyst differ for the volumetric chemisorption technique and the PMR method.

Figures 2 and 3 show the spectra of hydrogen adsorbed on the 8 and the 12% silica-supported ruthenium catalyst, respectively, for:

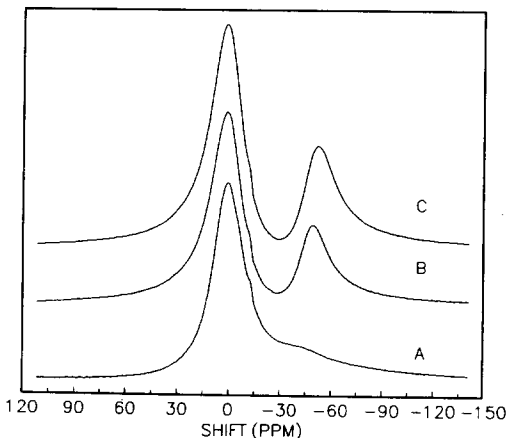


FIG. 3. ^1H NMR spectra of 12% Ru/SiO₂ (A) sequentially dosed with H₂S/He mixture, 760 Torr followed by 760 Torr, (B) 30 Torr of hydrogen dosed on the sulfided catalyst, (C) 30 Torr hydrogen dosed on the clean catalyst.

TABLE 2

Amount of Hydrogen Adsorbed on Ru/SiO₂ Catalysts as Indicated by the Ratio of Hydrogen to Surface Ruthenium (H/Ru_s)

Catalyst treatment	H/Ru _s by PMR	
	8% Ru catalyst	12% Ru catalyst
30 Torr of H ₂	1.54	1.47
H ₂ S/He dosed on the catalyst	0.47	0.58
30 Torr H ₂ dosed on the sulfided catalyst	0.99	1.26

(A) ruthenium catalyst dosed with the H₂S/He gas mixture; the area under the upfield peak gives the amount of ruthenium surface covered with hydrogen resulting from the dissociation of H₂S.

(B) 30 Torr of hydrogen adsorbed on the sulfided ruthenium catalyst; the area under the upfield peak gives the total hydrogen adsorbed on the sulfided ruthenium surface.

(C) 30 Torr of hydrogen adsorbed on the clean, unsulfided ruthenium catalyst; the area under the upfield peak gives the total hydrogen adsorbed on the clean ruthenium surface.

The amount of hydrogen per surface ruthenium (H/Ru_s) resulting from the dissociation of hydrogen sulfide, decreased when the ruthenium loading was increased from the 8% catalyst (H/Ru_s = 0.71) to the 12% catalyst (H/Ru_s = 0.58) for the same exposure of H₂S (Table 2). This indicates that more H₂S is dissociating on the 8% catalyst per surface ruthenium atom than on the 12% catalyst. When the catalyst was then exposed to pure hydrogen, more hydrogen per surface ruthenium was observed on the 12% ruthenium catalyst (H/Ru_s = 1.26) than on the 8% catalyst (H/Ru_s = 0.99). Under the same presulfiding conditions more sites were blocked by sulfur on the 8% Ru catalyst than on the 12% Ru catalyst.

To study the effect of presulfiding on subsequent hydrogen adsorption, three sets of

PMR experiments were performed on the 8% silica-supported ruthenium catalyst at various sulfur coverages. In the first set of experiments a catalyst sample was sulfided using sequential dosing of the H₂S/He mixture at different pressures to obtain different surface sulfur coverages. Figure 4 gives the spectra of hydrogen adsorbed from the dissociation of H₂S at various sulfur coverages. The area under the upfield peak gave the total hydrogen adsorbed on ruthenium surface from the dissociation of hydrogen sulfide. This gave an indirect measure of the sulfur surface coverage by taking the stoichiometry of two H atoms per S atom. Sulfur coverages were also determined independently by X-ray fluorescence analysis of the sulfided samples. The results from the two methods agree within experimental error (Table 3). For sulfur coverages greater than 0.32 no hydrogen-on-ruthenium peak was observed and the coverages were determined by X-ray fluorescence analysis only. In the second set of experiments to probe the effect of presulfiding, the sulfided catalyst samples were dosed with pure hydrogen and their PMR spectra were taken (see Fig. 5). The area under the upfield peak in this case gave the total hydrogen adsorbed on the sulfided ruthenium surface. In the third

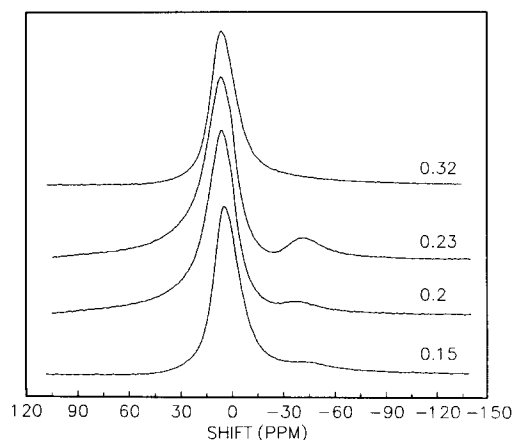


FIG. 4. ¹H NMR spectra of 8% Ru/SiO₂ catalyst sulfided with H₂S/He mixture to different sulfur coverages.

TABLE 3

Sulfur Coverages (Sulfur per Surface Ruthenium, S/Ru_s) on 8% Ru/SiO₂ Catalyst

X-Ray fluorescence	PMR
0.17	0.15
0.21	0.2
0.24	0.23

set of experiments, the sulfided catalyst samples were dosed with pure hydrogen and then evacuated to 10^{-6} Torr for 10 min. The spectra of the strongly adsorbed hydrogen remaining after evacuation are shown in Fig. 6. The area under the upfield peak in this case gave the amount of the strongly adsorbed hydrogen on the sulfided catalyst. The amount of weakly adsorbed hydrogen was obtained by subtracting the amount of strongly adsorbed hydrogen from the total hydrogen adsorbed; the two spectra could be so subtracted directly because there was no significant change in the position of the downfield peak.

No hydrogen from the dissociation of hydrogen sulfide (indicated by the upfield peak) was observed on the 8% ruthenium catalyst for sulfur-to-surface ruthenium ra-

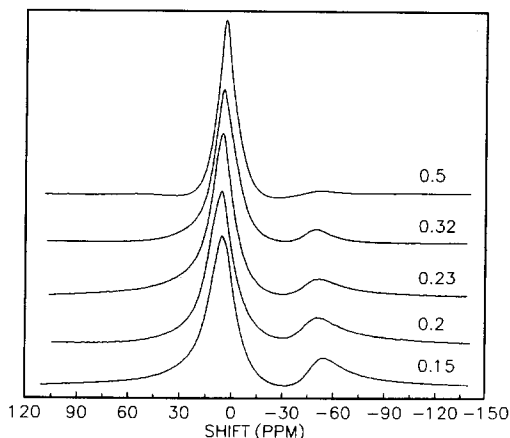


FIG. 5. ^1H NMR spectra of 8% Ru/SiO₂ catalyst sulfided and then dosed with 30 Torr of H₂.

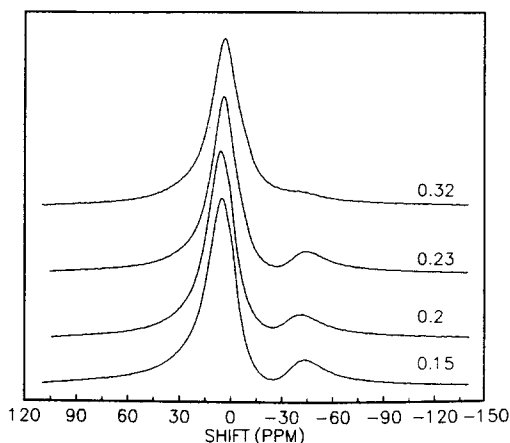


FIG. 6. ^1H NMR spectra of 8% Ru/SiO₂ catalyst sulfided, dosed with 30 Torr of H₂ and evacuated to 10^{-6} Torr.

tio (S/Ru_s) of 0.32 and higher. When the sulfided surface was exposed to 30 Torr of hydrogen, a peak corresponding to the hydrogen adsorbed on ruthenium appeared as seen from the spectrum in Fig. 5 for S/Ru_s = 0.32. Upon evacuation the intensity of this peak was only partially lowered, indicating the presence of the irreversibly adsorbed hydrogen. At sulfur coverages greater than 0.5, no hydrogen-on-ruthenium resonance was observed.

The amount of strongly and weakly adsorbed hydrogen resulting from exposure of the sulfided catalyst to pure hydrogen at 30 Torr at various sulfur coverages is given in Table 4. Figure 7 is a plot of the H/Ru ratio versus sulfur coverage for the total, the

TABLE 4

H/Ru Values for Both Total Ru and Surface Ru on the 8% Ruthenium Catalyst

Sulfur coverage	Total		Strong		Weak	
	H/Ru _t	H/Ru _s	H/Ru _t	H/Ru _s	H/Ru _t	H/Ru _s
0	0.43	1.53	0.28	1	0.15	0.53
0.15	0.31	1.11	0.21	0.73	0.10	0.37
0.2	0.26	0.94	0.19	0.69	0.07	0.24
0.23	0.21	0.77	0.18	0.67	0.03	0.11
0.32	0.15	0.53	0.13	0.48	0.01	0.05

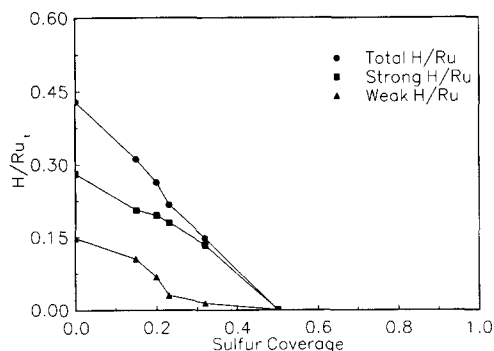


FIG. 7. Hydrogen to total ruthenium versus sulfur coverage. The amount of hydrogen was determined by ^1H NMR.

strongly bound, and the weakly bound hydrogen on the ruthenium surface. The ratio of weakly to strongly adsorbed H decreased with increasing sulfur coverage (Fig. 8).

The linewidth, full width at half maximum (fwhm), of the upfield resonance peak at different sulfur coverages and the linewidth of the upfield peak for the sulfided catalyst dosed to saturation with H_2 are given in Table 5. For the catalysts exposed only to H_2S the linewidth of the chemisorbed hydrogen decreased with increasing sulfur coverage. For the sulfided catalysts that were subsequently dosed with H_2 the linewidth went through a maximum at lower sulfur cover-

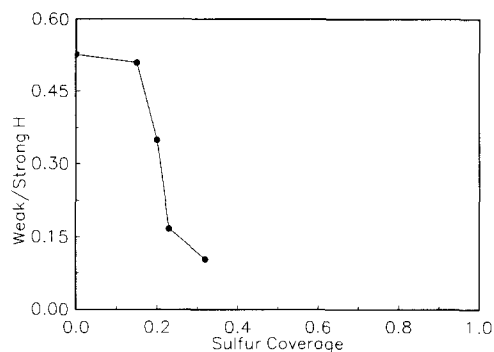


FIG. 8. The ration of weakly adsorbed to strongly adsorbed hydrogen on ruthenium versus sulfur coverage. The amount of hydrogen on the metal was determined by ^1H NMR.

TABLE 5
PMR Spectra Linewidth Data for the Hydrogen-on-Metal Peak

S/Ru _s	0	0.15	0.2	0.23	0.32
Exposure to H_2S only ^a					
Linewidth (KHz)		15	11	8	No peak
Exposure to H_2S then H_2 ^b					
Linewidth (KHz)		6.4	8.9	7.6	5.9
				4.2	

^a The catalyst was sulfided with the $\text{H}_2\text{S}/\text{He}$ gas mixture (992 ppm H_2S) at room temperature.

^b The catalyst was sulfided with the $\text{H}_2\text{S}/\text{He}$ gas mixture, evacuated, and then dosed with 30 Torr of hydrogen.

ages and then decreased at higher sulfur coverages.

The lineshift data for hydrogen-on-metal for the sulfided catalyst dosed to saturation with hydrogen is given in Table 6. There is no observable trend in the lineshift with sulfur coverage (S/Ru_s). The magnitude of the change in lineshift with sulfur coverage is not large, suggesting that the perturbation of the metal's density-of-states due to the presence of sulfur on the surface was minor.

The spin-lattice relaxation time, T_1 , of hydrogen-on-metal peak was measured for unsulfided and the sulfided catalysts under 30 Torr of hydrogen (Table 7). The relaxation times increased with increasing sulfur coverage suggesting that the presence of sulfur on the surface influences the relaxation process.

DISCUSSION

There are at least two broadly distinguishable types of adsorption sites on the metal

TABLE 6
PMR Spectra Lineshift Data for the Hydrogen-on-Metal Peak

S/Ru _s	Lineshift (ppm)
0	-55
0.15	-56
0.2	-52
0.23	-54
0.32	-51

TABLE 7

Spin-Lattice Relaxation Time, T_1	
Sulfur coverage, S/Ru _s ^a	T_1 (s)
0	0.039
0.2	0.049
0.23	0.054

^a All samples sulfided and dosed with 30 Torr of H₂.

surface: surface ruthenium atoms on low-index plane facets of the crystallite, much like those in ruthenium single crystals; and surface ruthenium atoms at edges and corners or at other defect structures, which are less fully coordinated. As the ruthenium dispersion increases, the fraction of edges and corners or other defect-like structures also increases. The dispersion of the 8% catalyst is higher than the dispersion of the 12% catalyst (28% versus 19%). Under similar dosing conditions, more hydrogen is adsorbed from the dissociation of hydrogen sulfide on the 8% catalyst than on the 12% catalyst. In this study H₂S dissociation appears to prefer surfaces with higher concentration of defect-like sites.

The linewidth, fwhm, of the hydrogen-on-metal peak (Table 5) broadened at lower sulfur coverages (the catalyst was sulfided and then dosed to saturation with H₂). The linewidth however narrowed considerably at higher sulfur coverages (S/Ru_s > 0.25). The narrowing of the linewidth could be due to the weakening of H-Ru interactions and higher mobility of adsorbed hydrogen and (or) increased internuclear distances between the adsorbed hydrogen species because of the presence of sulfur on the surface.

Brand *et al.* (8) have studied the effect of sulfur coverage on the surface diffusion of hydrogen on Ru(001) using laser-induced thermal desorption techniques. Their studies indicated that the hydrogen surface mobility decreased dramatically as a function of sulfur coverage. The broadening of the

linewidth at lower sulfur coverages is consistent with reduced mobility of the adsorbed hydrogen. The narrowing of linewidth of the upfield peak at higher sulfur coverages can be associated with an increase in the internuclear distances between the adsorbed hydrogen atoms.

The linewidth of the ¹H resonance corresponding to the hydrogen-on-metal peak after sulfiding with H₂S/He is larger at a given sulfur coverage than after subsequent deposition of H₂ (15 kHz ≥ fwhm ≥ 8 kHz compared to 9 kHz ≥ fwhm ≥ 4 kHz). Either the hydrogen adsorbed via the dissociation of H₂S is much less mobile or the ¹H internuclear distances are much smaller than for the hydrogen adsorbed on the sulfided catalyst at the same sulfur coverage.

Each Ru site has an area of about 8 Å² and the cross-sectional area of S⁻² is about the 10 Å². Sulfur atoms are too large to occupy adjacent sites that may be occupied by the smaller hydrogen atoms. The hydrogen atoms adsorbed between adsorbed sulfur atoms may be the less mobile species. It is likely that the increased broadening of the upfield peaks is due to restricted mobility. This observation is in agreement with the suggestion of Saleh *et al.* (7) that there are two types of hydrogen on the surface; one type closer to or associated with sulfur adatoms and the other free from the influence of sulfur.

At sulfur coverages of 0.32 we do not observe any upfield peak associated with hydrogen on the metal resulting from the dissociation of hydrogen sulfide. However, when the sulfided catalyst was subsequently dosed with additional hydrogen the presence of strongly adsorbed hydrogen was detected. It is probable that the hydrogen atoms on the surface, trapped between and around the sulfur atoms, are mobile enough to find another H atom at a recombination site, recombine and desorb from the surface rather than move further away from the S atoms into a stronger adsorption site. Hydrogen in the gas phase could adsorb onto the stronger adsorption sites, but under

these conditions the gas phase pressure of H_2 is too low making the rate for that adsorption process too slow to result in appreciable adsorption in the time frame of our experiments. Consequently, all the sites on the surface that could strongly bind hydrogen have not been occupied and so when the sulfided catalyst was subsequently dosed with additional hydrogen at 30 Torr, strongly adsorbed hydrogen was detected. However, at sulfur coverages greater than 0.5 there was no detectable hydrogen on the surface even when the sulfided catalyst was dosed with additional hydrogen at 30 Torr. This could be because all the sites for the dissociation of H_2 are blocked by the presence of sulfur or because there are no sites available for hydrogen to occupy.

Somorjai and Blakely (4) have suggested that sulfur preferentially blocks low coordination sites. In this study we have seen that H_2S preferentially dissociates on Ru surfaces with a higher density of defect-like sites, i.e., catalysts with a higher dispersion. Wu *et al.* (15) have reported that the ratio of weakly adsorbed hydrogen to strongly adsorbed hydrogen increased with Ru catalyst dispersion (or increasing fraction of defect-like sites). We found the ratio of weakly adsorbed hydrogen to strongly adsorbed hydrogen decreased with increasing sulfur coverage (Fig. 8). These results, taken together, suggest that sulfur reduces the weakly bound states of hydrogen relative to the strongly bound states on the supported ruthenium particle because it preferentially blocks edge, corner, and other defect-like sites.

CONCLUSIONS

There is evidence that H_2S preferentially dissociates on Ru surfaces with a higher fraction of defect-like sites. On the 8% Ru catalyst, dispersion 0.28 (versus the 12% catalyst, dispersion 0.19), more hydrogen was detected from the dissociation of H_2S and less hydrogen was observed from the subsequent adsorption of H_2 .

At sulfur coverages below 0.25 the disso-

ciative adsorption of H_2S produced both S and H atoms, which are present on the ruthenium surface. At higher sulfur coverages hydrogen resulting from the H_2S dissociation is no longer observed on the surface.

Two types of hydrogen, a highly mobile species and a less mobile species were detected on the sulfided metal dosed to saturation with hydrogen. The less mobile species is suggested to be closer to or associated with sulfur adatoms while the other highly mobile species is free from the influence of sulfur adatoms. However, no strong electronic effects due to presence of sulfur on the surface were observed.

The ratio of weakly adsorbed hydrogen to strongly adsorbed hydrogen at saturation coverages on the metal decreases with increasing sulfur coverage. The observation that sulfur selectively blocks weakly bound states of hydrogen may provide a means of probing the role of weakly and strongly bound hydrogen adstates on various hydrocarbon conversion reactions.

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