3654 *J. Am. Chem. Soc.* **1993,** *115,* 3654–3657

# Identification of New Hydrogen Species Adsorbed on Ruthenium Sulfide by Neutron Spectroscopy

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*Received October 13, 1992*

**Abstract:** Inelastic neutron scattering (INS) has been used to study the adsorption of hydrogen on a partially desulfurized ruthenium sulfide catalyst. Different hydrogen species have been evidenced by changing the experimental conditions (temperature and hydrogen coverage), by contrast to previous neutron studies which reported only SH groups. When $RuS_2$ is partially desulfurized, new vibrational peaks are found at 540 and 823 $cm^{-1}$. These peaks are assigned to the bending modes of two different RuH linear species. The hydridic groups, which are the active species in hydrogenation reactions, are more weakly adsorbed than the acidic groups; their relative proportion is derived from the INS spectra and discussed in relation with TPD measurements.

## Introduction

Hydrogen chemisorbed on large surface area materials is difficult to characterize by most of the vibrational techniques (e.g., infrared or Raman). Inelastic neutron scattering (INS) has proved to be a sensitive method to detect hydrogen because of the large incoherent cross section of this atom. With INS, all the local modes of hydrogen adsorbed on a given site can be observed because of the lack of selection rules. Further, the theory of neutron scattering is well known so that a measure of band intensities can provide hydrogen populations of the various surface sites.

Hydrogen activation is an important process for understanding the catalytic properties of various hydrogenating materials. If the nature of the adsorbed species is relatively well known for metal catalysts, the interaction of hydrogen with more complex systems like oxides and sulfides is still not completely elucidated. On such kind of solids it is generally assumed that hydrogen may be adsorbed either homolytically or heterolytically. Accordingly, hydrogen adsorption should form not only SH or OH bonds but also metal–hydrogen bonds.

Recently we have reported that the ability of ruthenium sulfide to adsorb hydrogen is extremely dependent on the sulfur-to-metal ratio.[1] Two different species have been detected by thermodesorption: one has been assigned to hydrogen adsorbed on surface sulfur anions while the other one could be retained on coordinatively unsaturated ruthenium cations. In agreement with this identification, $^1H$ NMR of the reduced samples has evidenced two signals located at 5.1 and −7.4 ppm, with respect to tetramethylsilane, respectively ascribed to SH groups and to hydride-type adsorbed species.[2] A very satisfactory relationship has been found between the concentration of hydridic species and the catalytic activity in hydrogenation reactions. These results appear different from previous INS studies performed on model molybdenum,[3,4] tungsten,[5] and ruthenium[6] disulfides which have reported only the presence of SH groups, indicating that hydrogen would reside only on sulfur anions. This discrepancy could arise from different catalyst pretreatments and consequently to various sulfur-to-metal ratios.

In this paper, we report new INS studies performed on partially desulfurized $RuS_2$. This technique provides information on both the geometry and energetics of the different hydrogen adsorption sites. Quantitative data, related to the relative amounts of adsorbed species, are discussed in relation to temperature-programmed desorption (TPD) results.

## Experimental Section

**Preparation of the Catalyst.** Unsupported ruthenium sulfide has been prepared by contacting an aqueous solution of ruthenium chloride with flowing $H_2S$. The resulting precipitate being amorphous, the solid was annealed during 2 h at 673 K in the presence of an $H_2S$ flow. The catalyst was cooled to room temperature under the same atmosphere and subsequently flushed with an oxygen-free inert gas. X-ray diffraction confirmed the presence of the expected pyrite phase, and elemental analysis indicated a sulfur-to-metal ratio equal to 2.25.[7]

**Catalyst Reduction.** The freshly prepared sulfide was first transferred into a flow reactor large enough to contain 30 g of ruthenium sulfide, and the system was flushed overnight at room temperature with a high flow (100 L/h) of dehydrated nitrogen in order to eliminate traces of oxygen. Nitrogen was then replaced by water-free hydrogen and the reactor was slowly (2 K/min) heated up to 513 K and kept at this temperature for 5 h before cooling down to room temperature. In agreement with previous results, the determination of the sulfur and hydrogen content of the reduced sample (by chemical analysis and isotopic titration, respectively) indicated a solid composition corresponding to $RuS_{1.88}H_{0.2}$. The hydrogen chemisorbed during this reducing procedure was removed by heating the sample up to 573 K under nitrogen flow.

**Hydrogen Adsorption and Desorption.** Hydrogen adsorption measurements were performed by flushing the reduced and degassed catalyst with an hydrogen flow (2.4 L/h) at room temperature. The amount of adsorbed hydrogen has been determined by thermodesorption of the species retained by the solid after various contact times. Species leaving the catalyst surface were detected by a chromatograph equipped with a TCD detector. Preliminary experiments have shown that, when using moderate heating rates (10 K/min), the TPD profiles presented large and overlapping peaks indicating the presence of several adsorbed species. In order to improve peak resolution, higher heating rates were used. Thus, the temperature of the catalyst was suddenly increased up to 573 K by introducing the reactor into a furnace preheated at this temperature. A

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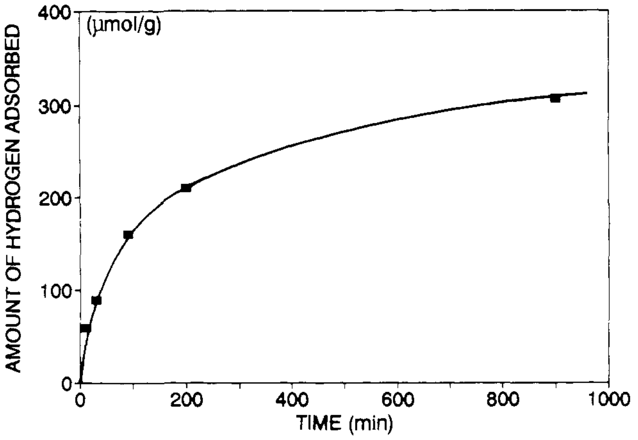

**Figure 1.** Quantity of hydrogen adsorbed on a partially desulfurized ruthenium sulfide as a function of time.

calculator-integrator coupled to the unit was used to store simultaneously the $H_2$ signal coming from the TCD detector and the temperature of the solid by using a thermocouple positioned into the catalyst bed. On this reduced sample it has been previously checked that no $H_2S$ was removed from the catalyst during hydrogen desorption, and various adsorption-desorption cycles could be done without changing the adsorptive properties of the catalyst.

**Neutron Spectrometer.** The neutron spectra were obtained at the ISIS spallation neutron source at the Rutherford Appleton Laboratory, U.K., using the spectrometer TFXA.[8] This spectrometer is a time-of-flight instrument with an inverse geometry and a time-focusing analyzer; it gives good counting rates and good energy transfer resolution ($\Delta E/E \approx 2\%$) over a wide range of energy transfers. The estimated absolute accuracy is ca. ±10 $cm^{-1}$.

For the neutron measurements the cell was placed in a cryostat, the evacuation and loading of the sample being performed out of the cryostat.

## Results

**Adsorption and TPD Measurements.** The evolution of the amount of adsorbed hydrogen as a function of time is reported in Figure 1. These data show that hydrogen adsorption proceeds via a slow process since more than 15 h on stream is required to reach the saturation equilibrium. The amount of surface sulfur and ruthenium ions has been calculated using a geometrical modelling of $RuS_2$ particles,[9] taking into account their average sizes determined by HREM (45–50 Å). The calculated values ($Ru \approx 1600$ μmol/g, $S \approx 3600$ μmol/g) would lead to an amount of adsorbed hydrogen of about 5200 μmol/g if all the surface Ru and S ions are saturated. The saturation equilibrium corresponds, in fact, to a coverage of surface atoms (S + Ru) of ≈6%. From the TPD profiles reported in Figure 2, it appears that at least two desorbing species are present on the surface of the catalyst. The species corresponding to the low-temperature peak ($H^1$) desorbs at about 450 K whatever the amount of adsorbed hydrogen, whereas the desorption temperature of the second species ($H^2$) shifts to lower temperatures as the coverage increases, suggesting a distinct mechanism of desorption.

The concentration of both $H^1$ and $H^2$ species has been calculated by integrating the TPD peaks versus time. These results are reported in Table I. From these data it appears that the ratio $H^1/H^2$ increases with coverage since it varies from 0.1 at the beginning of adsorption to 0.5 after 210 min of contact time. For higher contact time (900 min), the overlap of the TPD peaks does not allow quantification of the amount of both species. However, this has been done by INS since surface species concentrations can be derived from the integrated intensities of the bands.

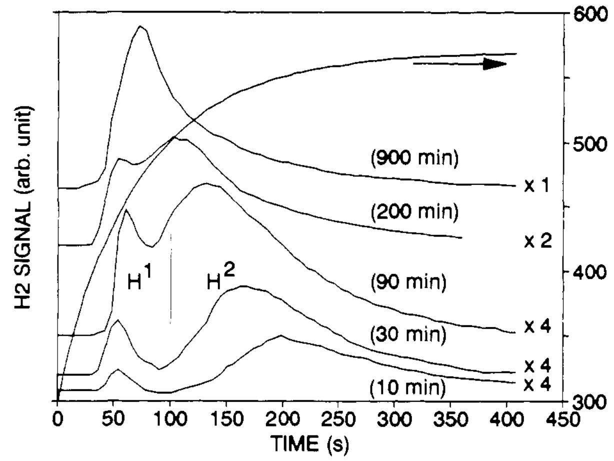

**Figure 2.** TPD profiles of hydrogen on partially desulfurized $RuS_2$ obtained after different contact times ranging from 10 to 900 min.

Table I. Amount of Adsorbed Hydrogen as a Function of Time

| time (min) | $[H^1]$ (μmol/g) | $[H^2]$ (μmol/g) | $[H^1]/[H^2]$ | $[H^t]$ (μmol/g) |
|---|---|---|---|---|
| 11 | 5 | 54 | 0.1 | 59 |
| 30 | 11 | 78 | 0.14 | 89 |
| 90 | 25 | 139 | 0.18 | 164 |
| 210 | 70 | 140 | 0.5 | 210 |
| 900 | | | | 306 |

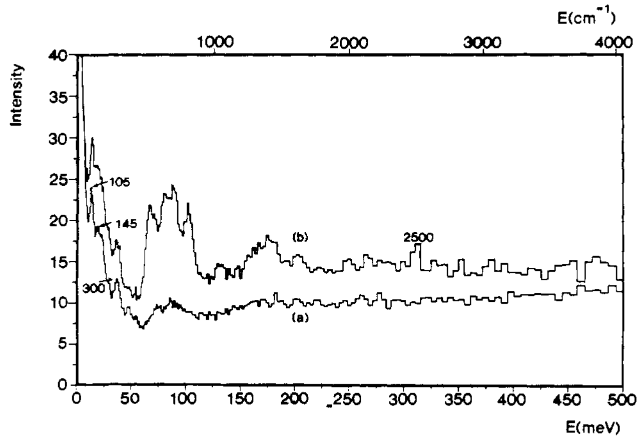

**Figure 3.** INS spectra of (a) degassed $RuS_2$, (b) hydrogen adsorbed at 25 K on partially desulfurized $RuS_2$ (the values within the figure are the transition frequencies in $cm^{-1}$).

**INS Measurements.** INS spectra of the degassed catalyst were first recorded at 295 and 25 K. Since the spectra were almost identical, they were added together to get better statistics. The resulting spectrum is shown in Figure 3a between 40 and 4000 $cm^{-1}$. The cell was then taken out of the cryostat, and hydrogen was slowly introduced at room temperature until a pressure of 0.5 bar was reached in the cell. The sample was left overnight to equilibrate. The cell was placed back in the cryostat and the INS spectrum, obtained while keeping the sample at 295 K, is shown in Figure 4 after subtraction of the bare catalyst contribution. In this figure the scattering observed at low-energy transfers, with a peak at 140 $cm^{-1}$, is partly due to gaseous hydrogen. Other peaks due to chemisorbed hydrogen are found at 540, 648, 719, and 821 $cm^{-1}$.

The sample was then cooled to 25 K; the raw data which were recorded at this temperature are shown in Figure 3b between 40 and 4000 $cm^{-1}$. It can be seen from Figure 3 that the signal due to hydrogen is large compared to the bare substrate. Further, the scattered intensity is weak in Figure 3a between 500 and 1000 $cm^{-1}$, which demonstrates that hydrogen was well-evacuated

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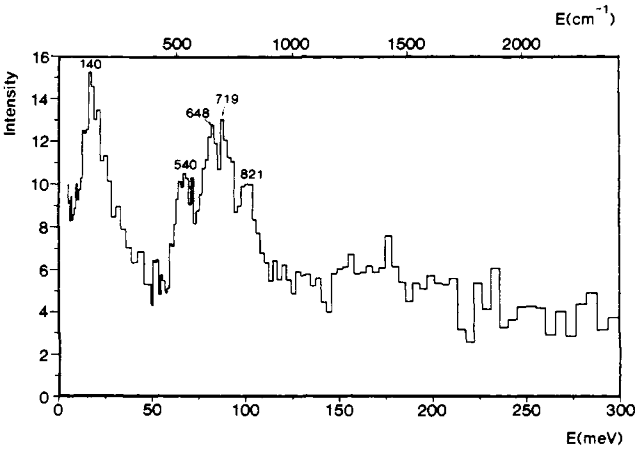

**Figure 4.** INS spectrum, obtained at 295 K, of hydrogen adsorbed on a partially desulfurized $RuS_2$ catalyst (the signal of the bare catalyst has been subtracted).

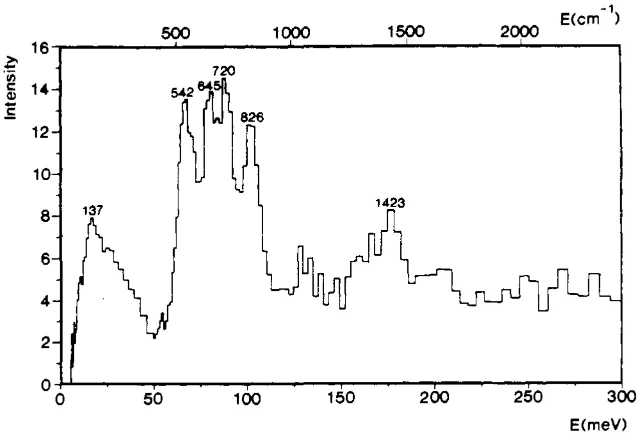

**Figure 5.** INS spectrum, obtained at 25 K, of hydrogen adsorbed on partially desulfurized $RuS_2$ (the background has been subtracted).

from the catalyst during the sample preparation. After background subtraction, the spectrum shown in Figure 5 is obtained. Compared with Figure 4, the intensity at low-energy transfers has been much reduced, which indicates that there is no more gaseous hydrogen in the beam. The intensity which is left in that range is assigned to physisorbed hydrogen and to hydrogen-coupled lattice vibrations. The intensities of all the other peaks have been increased, however, the frequencies are the same, within experimental precision. This increase of intensity could be due to a further occupation of the adsorption sites but also to an effect of the Debye–Waller factor.[10] Indeed, the theory of incoherent INS predicts that the intensity of a vibrational mode is multiplied by a Debye–Waller factor, $\exp(-Q^2\langle u^2\rangle)$, where $Q$ is the neutron momentum transfer and $\langle u^2\rangle$ the mean-square amplitude of the vibrating atom (hydrogen in our case). When the mean-square hydrogen amplitude decreases, the scattered intensity may therefore increase. Since the rate of adsorption is low, i.e., equilibrium reached after about 15 h, the Debye–Waller factor seems to be involved for explaining the variations of band intensities in our data. The peak at 1423 cm$^{-1}$ in Figure 5 is due to overtones and combinations of the bands situated between 500 and 850 cm$^{-1}$. This peak is clearly more resolved at 25 K than at 295 K.

The sample was then warmed up to room temperature and evacuated for 1 h. The cell was placed again in the cryostat, and the spectrum, obtained at 25 K after background subtraction, is shown in Figure 6. Compared with Figure 5, it appears that the heights of all peaks have been decreased to various extents. The

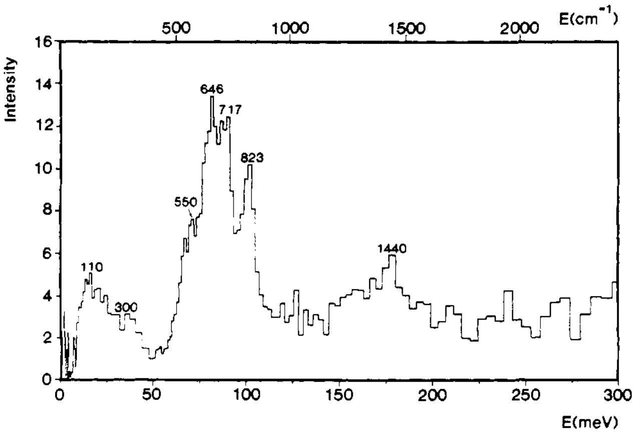

**Figure 6.** INS spectrum, obtained at 25 K after partial evacuation, of hydrogen adsorbed on partially desulfurized $RuS_2$ (the spectrum is background corrected).

intensity observed at low-energy transfers, with peaks at 110 and 300 cm$^{-1}$, now closely resembles the density of states of the bare substrate (Figure 3a), indicating that the scattering is due to hydrogen-coupled lattice vibrations.

## Discussion

In previous INS studies performed on sulfides, SH bending modes have been observed at 650 cm$^{-1}$ on $MoS_2$[3,4] and 694 cm$^{-1}$ on $WS_2$.[5] On $RuS_2$, two modes were measured at 600 and 710 cm$^{-1}$; they were assigned to two nondegenerate SH bending modes of a single state.[6] In our spectra we also have two peaks near 646 and 719 cm$^{-1}$ which are close in frequency to the previous results reported for SH bendings. These two peaks could be assigned to bending modes of two different SH species. However, by fitting the spectra with Gaussians, it is found that these two modes have similar intensities in Figures 4, 5, and 6. The previous assignment of these peaks to two nondegenerate bending modes of the same SH species is thus reasonable. In fact, the two peaks have the same INS intensity in our spectra, as it should be, whereas the peak at 710 cm$^{-1}$ was much stronger in ref 6. Nevertheless, the possibility of two different SH species cannot be discarded.

Compared to the work of Heise et al. on $RuS_2$,[6] two new peaks are observed at ≈540 and 823 cm$^{-1}$. These two frequencies are assigned to RuH bending modes since they are well out of the range usually observed for SH bendings. In transition metal hydrido carbonyls, metal–hydrogen bending modes have been observed in that range.[11] For example, in $H_2Os_3CO_{11}$, which contains one MHM bridge and one MH linear hydrogen, the MH bending mode of the terminal hydrogen is found at 800 cm$^{-1}$. By integrating the peaks in Figures 5 and 6, it is found that the peak at 540 cm$^{-1}$ is decreased by a factor of 2 upon evacuation and the peak at 823 cm$^{-1}$ by a factor of 1.2 only. These two peaks are therefore assigned to two different RuH linear species. A comparison between Figures 4 and 5 shows that the RuH bending modes increase more in intensity than the SH bending modes when the temperature decreases. This is an effect of the Debye-Waller factor which implies larger values of the hydrogen mean-square amplitudes, $\langle u^2\rangle$, for the RuH species.

The difference spectrum between spectra of Figures 5 and 6 is shown in Figure 7; it corresponds to the species which have been eliminated during evacuation. It appears that the species which gives rise to the peak at 534 cm$^{-1}$ is more weakly adsorbed than the species which yields the peak at 830 cm$^{-1}$ (the band at 1050 cm$^{-1}$ in Figure 7 corresponds to the first overtone of the main peak at 534 cm$^{-1}$). It is also evident from Figure 7 that the number of SH groups has not been modified upon evacuation

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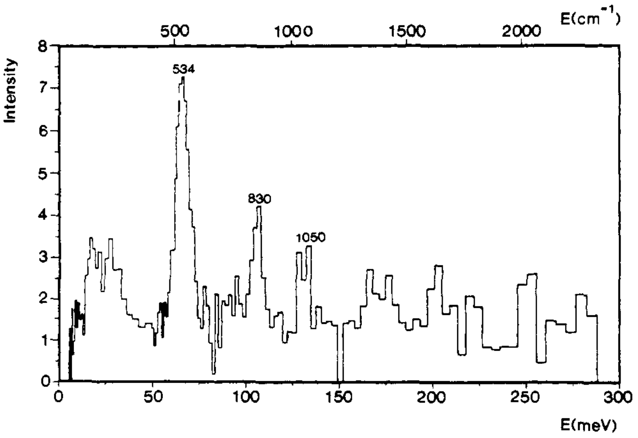

**Figure 7.** Difference spectrum between Figures 5 and 6.

since the difference spectrum is flat in the range 560–810 cm$^{-1}$. This is in agreement with TPD results which have indicated that no $H_2S$ is removed from the sample during hydrogen adsorption–desorption cycles at 300 K. Therefore, the SH species can be correlated to the high-temperature species measured by TPD (the $H^2$ band). For the RuH species, only one type was observed by TPD ($H^1$) and by NMR,[2] whereas two species are evidenced by INS. This technique is thus unique to reveal the presence of two RuH species which were not resolved by TPD. The environment of the two species must then be different to generate two different vibrational frequencies. From HREM examinations, the reduced solid can be considered as formed by a collection of homodispersed spheres having a mean diameter of 45–50 Å. From this low particle size, it is expected that the crystals may offer different crystallographic orientations leading to sites having various environments, in agreement with the observed INS features.

From the curve-fitting procedure, it is found that the ratio of RuH bands to SH bands is unity at 25 K (Figure 5). At 295 K, the ratio $H^1/H^2$ decreases to 0.8 (Figure 4) because the RuH vibrational bands are more strongly affected by the Debye-Waller factor. This ratio appears to be consistent with the value expected from TPD (Table I) for a larger contact time. By assuming that the particles have a cubic shape,[9] the surface Ru/S ratio of the partially desulfurized sample is ≈0.5, which is much smaller than the experimental $H^1/H^2$ obtained by INS. However, since only a small fraction of the surface is covered with hydrogen (≈6%), this high $H^1/H^2$ ratio remains consistent with the assumption of surface hydrogen species and the formation of bulk hydride does not need to be invoked. After partial evacuation of the sample, the ratio $H^1/H^2$ drops to 0.66 (Figure 6), which is in agreement with the lower stability of the hydride species.

The overtones and combinations of the four main peaks situated between 500 and 850 cm$^{-1}$ give intensity near 1430 cm$^{-1}$. Second-order processes appear in Figure 3b around 2220 cm$^{-1}$, overlapping a small peak at 2500 cm$^{-1}$ which can be assigned to SH stretching modes.[4] The RuH stretching modes, expected around 2000 cm$^{-1}$, are hidden by multiphonon features.

## Conclusion

INS spectra of hydrogen adsorbed on a partially reduced ruthenium sulfide have revealed the existence of several adsorbed species. In agreement with literature, two peaks near 646 and 719 cm$^{-1}$ are assigned to two nondegenerate SH bending modes of a single adsorbed state. Two other new bands respectively located at 540 and 823 cm$^{-1}$ are assigned to the bending modes of RuH linear species. Their different behavior toward a vacuum treatment suggests that they are adsorbed on distinct coordinatively unsaturated ruthenium atoms.

This work gives an experimental support to the often proposed hypothesis on the role of hydrogen adsorbed on coordinatively unsaturated sites in catalysis by sulfides.

**Acknowledgment.** We thank M. A. Adams for his assistance during the neutron measurements on TFXA, at ISIS, Rutherford Appleton Laboratory, U.K.