cipitation at room temperature from an aqueous solution of $RuCl_3$ by pure H_2S and by further sulfidation in an H_2S flow at 400°C for 2 h. The catalyst was cooled to room temperature under the same atmosphere and flushed with an inert gas. X-ray diffraction was similar to that of RuS_2 reported in the JCPDS index, and elemental analysis indicated a stoichiometry S/Ru = 2.26. Its surface area determined by N_2 physisorption was 70 m^2g^{-1}.

The desulfurization of the catalyst was carried out in a dynamic microreactor which allowed us to measure the amount of H_2S removed under hydrogen by the use of a specific UV-photodetector (HNu Photoionization detector equipped with a 10.2-eV UV light source). The amount of H_2S evolved from the solid is simply quantified after calibrating the detector with a known concentration of hydrogen sulfide diluted in hydrogen. The sample was first flushed with a nitrogen flow and then contacted with an hydrogen flow of 40 cm^3 min^{-1} at room temperature. The temperature was then increased stepwise and the sample was left 3 h at each temperature of reduction. The degree of reduction α is defined as the ratio of the amount of H_2S evolved at a given temperature on the total sulfur content. The hydrogen chemisorbed during the reduction process was then desorbed by heating the sample up to 573 K under a nitrogen flow. Preliminary experiments have shown that 573 K was a sufficient temperature for cleaning the surface from adsorbed species. Hydrogen adsorption was then performed by flushing the solid with an hydrogen flow (40 cm^3 min^{-1}) for 1.5 h at room temperature. These experimental conditions are comparable to the one previously used for the determination of the H_2–D_2 exchange activity (9). The amount of adsorbed hydrogen was determined by thermodesorption of the solid at 530 K. Species leaving the catalyst surface were detected by a chromatograph equipped with a TCD detector. Preliminary experiments have shown that using moderate heating rates (~10 K/min) the obtained
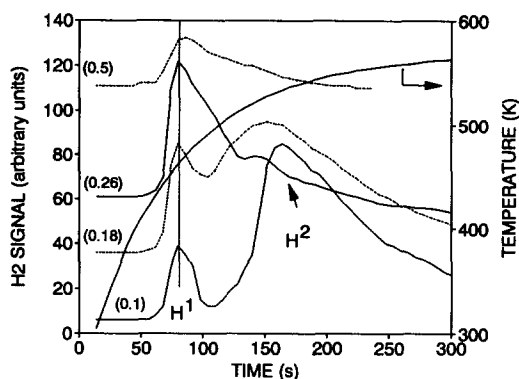

FIG. 1. Hydrogen thermodesorption profiles for various catalyst reduction states. The degree of reduction α is given in brackets.

thermodesorption profiles were extremely large, indicating the presence of several chemisorbed species. In order to improve the resolution of the various peaks related to the different kinds of adsorbed hydrogen, higher heating rates were used. For this purpose, the temperature of the catalyst was increased suddenly by introducing it in a furnace preheated to 573 K. A calculator-integrator (SP4290) allows simultaneously the storage of the H_2 signal coming from the detector and the measurement of the temperature of the catalyst bed.

Figure 1 shows the evolutions of the H_2 signal intensity as a function of time for various degrees of reduction of the catalyst (given in brackets) and the simultaneous variation of temperature. The obtained TPD profiles evidence the presence of at least two types of hydrogen species adsorbed on the surface of reduced ruthenium sulfide differentiated by their temperature of desorption. Moreover, the relative concentration of each species depends on the degree of reduction of the sample (Fig. 2). The hydrogen species leaving the surface at high temperature (H^2) reaches its maximum concentration for a degree of reduction α of about 0.1. Then, its amount decreases continuously with sulfur removal down to a low level for α = 0.4. In contrast, the evolution of the low temperature desorption peak re-

Hydrogen on Unsupported Ruthenium Sulfide: Thermodesorption and ^{1}H NMR Studies

The interaction of transition metal sulfides with hydrogen is a complex process. Understanding this process is important due to the very large number of industrial processes dealing with these systems. The main utilization of these catalysts concerns catalytic hydrotreating which involves hydrogenation reactions and C–S, C–N, and C–O bond cleavage reactions carried out in the presence of high partial pressures of hydrogen. The complexity of the interaction of hydrogen with metal sulfides is related to its double role, as reactant and as modifier of the concentration of active sites. As a matter of fact, the interaction of hydrogen with the surface of the catalyst provokes its partial reduction, leading to coordinatively unsaturated metal ions which are directly involved in the adsorptive and catalytic properties (*1*).

As molybdenum sulfide is the essential component of industrial hydrotreating catalysts, its interaction with hydrogen has been the subject of many investigations. The review of Moyes (*2*) and the recent paper of Hall and Komatsu (*3*) have shown that the amount of adsorbed hydrogen changes drastically from one study to another. In order to compare easily this large number of literature data the amount of adsorbed hydrogen is often expressed using the nomenclature H_xMoS_2. Using the same preparation procedure (decomposition of ammonium tetrathiomolybdate) the values of x vary between 0.012 and 0.37. This important variation of x has probably to be ascribed to different catalysts pretreatment prior to adsorption measurements, leading to different number of vacancies. This hypothesis has been demonstrated by Jalowiecki *et al.* (*4*), who

have reported that the activity and the hydrogen adsorption capacity of a molybdenum-based catalyst is greatly dependent on the sulfur-to-molybdenum ratio. Concerning the chemical nature of the adsorbed species, inelastic neutron scattering studies have evidenced that dissociated hydrogen resides on sulfur anions in the form of SH groups (*5*, *6*). This result has been recently confirmed by solid NMR spectroscopy (*3*). Although these techniques have never shown the presence of adsorbed hydride-type hydrogen, its presence on molybdenum or rhenium sulfides has been assumed for explaining the mechanisms of thiophene or hydrothiophene hydrodesulfurization and alkenes hydrogenation (*7*, *8*).

The relation between the sulfur-to-metal ratio and the catalytic activity was also studied for other sulfides. We have recently reported that the H_2–D_2 exchange activity of a model ruthenium sulfide is drastically enhanced by sulfur removal (*9*). As ruthenium sulfide is one of the most active chalcogenide (13 times more active than molybdenum sulfide in the hydrodesulfurization of thiophene and 10 times in the hydrogenation of biphenyl), its activity could be related to a large adsorption capacity or to the presence of adsorbed hydrogen species different from those already detected on lamellar sulfides. To tackle this fundamental problem of hydrogen adsorption on ruthenium sulfide, we have taken the fully sulfided state as starting point and evaluated the influence of progressive desulfurization on the amount of adsorbed hydrogen. The nature of the adsorbed species was investigated using thermodesorption and ^{1}H NMR.
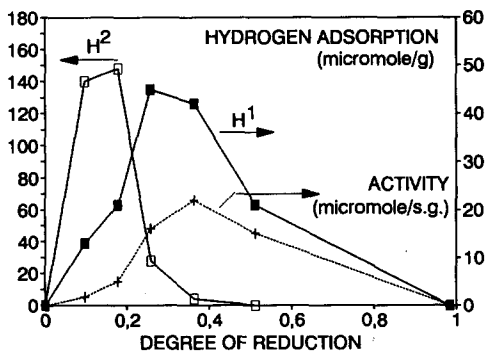
Ruthenium sulfide was prepared by pre-

FIG. 2. Amount of adsorbed H^1 and H^2 and H_2-D_2 exchange activity as a function of the degree of reduction of the catalyst.

lated to H^1 species follows a completely different trend, i.e., its amount increases with desulfurization, reaches a maximum for $\alpha = 0.3-0.4$, and then decreases above.

This different behavior of H^1 and H^2 toward sulfur removal suggests that different adsorbing sites are required for hydrogen chemisorption. As the concentration of H^2 decreases when the desulfurization of the solid increases, this type of hydrogen does not seem to be adsorbed on anionic vacancies but in interaction with sulfur anions as SH groups. This species is probably the one observed in Heise's INS work on ruthenium sulfide (10). By contrast, the amount of H^1 hydrogen increases with desulfurization up to $\alpha \sim 0.4$. At this stage of the reduction, the surface of the catalyst contains a very low concentration of sulfur anions. Consequently, these experimental data suggest that H^1 is adsorbed on coordinatively unsaturated ruthenium ions. The comparison of these adsorption results with those obtained previously for the H_2-D_2 exchange reaction (also reported in Fig. 2) and the 1-butene hydrogenation reaction (9, 11) evidences a striking similarity in their variations with α. This strongly favours the hypothesis that H^1 is the active species responsible for the hydrogenation reaction. For $\alpha > 0.5$, the diminution of H^1 adsorption can be ascribed to surface area collapsing and to the formation of a surface-poisoned ruthenium metal-

lic phase inactive for hydrogen activation, as already proposed for the exchange reaction (9, 12-14).

To obtain more information about the chemical nature of H^1 and H^2 two samples were studies by solid ^1H NMR spectroscopy. Sample 1 was poorly desulfurized and presented both kinds of adsorbed hydrogen ($\alpha \sim 0.15$), whereas sample 2 contained mostly type-1 hydrogen ($\alpha = 0.35$). Both magic-angle-spinning (MAS) spectra were recorded in sealed tubes on a Bruker MSL apparatus at 400 MHz at room temperature. A weak rotation speed (1 kHz) was enough to observe the signals (Fig. 3), the small widths of which characterize species moving during the time characteristic of the experiment (10^{-9} sec).

Figure 3 shows the results of the ^1H NMR. For both solids, the chemical shift relative to tetramethylsilane could be deduced with fair accuracy. Sample 1 exhibits two signals at -7.4 ppm and 5.1 ppm. The value of the later is consistent with an acidic character of the adsorbed species, in agreement with the hypothesis of the formation of superficial SH groups (15). The other signal, -7.4
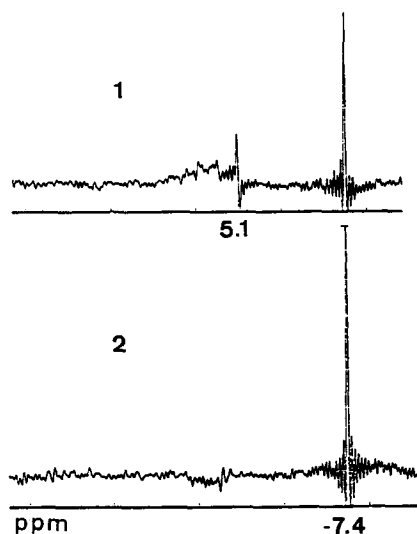

FIG. 3. Solid ^1H NMR of adsorbed hydrogen. The degree of reduction is 0.15 for sample 1 and 0.35 for sample 2.

ppm (upfield), can be most likely ascribed to a hydride-type species (*16–20*).

To sum up, the characterization of hydrogen adsorbed on partially desulfurized ruthenium sulfide has evidenced two different species: one leading to the formation of SH groups and the other with hydridic character being chemisorbed on coordinatively unsaturated ruthenium cations. The latter, related to the hydrogenating properties of the catalyst, probably explains the high activity of ruthenium sulfide.

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