

Hydrogenation and Hydroformylation with Supported Rhodium Catalysts. Effect of Adsorbed Sulfur

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(Received: March 24, 1987; In Final Form: June 11, 1987)

Freshly reduced Rh/SiO₂ samples have been exposed to a flow of hydrogen containing 10.9 ppm of H₂S and are then reduced again. The effects of increasing sulfur coverage of the Rh surface are studied for CO chemisorption, its IR spectrum, and the catalytic activity for ethylene hydroformylation and its hydrogenation. It is found that adsorbed sulfur selectively inhibits the chemisorption of bridging CO. The rate of ethylene hydrogenation is strongly suppressed by adsorbed sulfur, but the rate of hydroformylation is little affected at low sulfur coverage; in terms of surface sites counted by CO adsorption, the turnover frequency for hydroformylation to propionaldehyde actually increases. It is speculated that protruding corner atoms are most active in hydroformylation, while sulfur is preferentially chemisorbed on "hollow" sites.

I. Introduction

In recent years evidence has been obtained that the catalytic activity and selectivity of supported rhodium can be altered markedly by certain catalyst additives. With the hydrogenation of carbon monoxide as the test reaction and highly dispersed rhodium catalysts which had been prepared by decomposing a carbonyl, e.g., Rh₄(CO)₁₂, on silica or alumina supports, Ichikawa et al.^{1,2} could obtain a variety of product distributions depending on the "promoters" added to the catalyst. Whereas hydrocarbons were the predominant reaction products for unpromoted rhodium, the reaction was directed toward methanol for rhodium promoted with the oxides of Zn or Ca or Mg. Even more spectacular was the effect of additives such as Mn or Ti or Nb oxides; these increased the catalyst activity and induced the formation of higher oxygen containing molecules such as alcohols.³ For a Rh/SiO₂ catalyst promoted with the oxides of Mn and Mo van den Berg et al.⁴ obtained primary alcohols from C₁ to C₈ which followed a Schulz-Flory type of distribution; the total yield of oxygenates exceeded that of the hydrocarbons.

A number of concepts have been discussed⁵⁻⁸ about the nature of this "promoter effect" of metal ions added to the transition-metal catalyst. It is assumed either that they are located "below" the metal particles,^{9,12} serving as "chemical anchors", or that they form separate oxide particles, in which case the reaction mechanism is assumed to be of the bifunctional or of the dual-site type. A different concept assumes that the promoter oxide stabilizes positiveness¹⁰ of the catalytic metal (i.e., the rhodium); or it is assumed that the added metal ions are located "above" the metal particles, as is known to be the case for some "SMSI" systems.¹¹ In that latter model, some interaction of adsorbed carbon monoxide with coadsorbed Mn¹² or Zn¹³ ions has to be considered. Indeed, earlier work by Shriver et al.¹⁴ and Burwell et al.¹⁵ had shown that the interaction of Lewis acids with the oxygen end of a carbonyl can greatly enhance the rate of its insertion in a metal-alkyl bond. Moreover, the IR spectrum of Mn-promoted Rh/SiO₂ revealed a band at 1520 cm⁻¹,¹² suggesting an interaction of this type, as bands in the same region had been observed for those multimetal carbonyl complexes, for which X-ray diffraction had shown that the oxygen end of one CO ligand does interact with one metal atom.¹⁶

Recently, we have embarked in a program to elucidate these promoter effects. In Fischer-Tropsch type catalysis the adsorbed carbon monoxide molecules may undergo two types of reaction: (1) Dissociation to adsorbed C and O atoms. This step is known to be instrumental in the formation not only of hydrocarbon molecules but also of the alkyl groups of higher alcohols and aldehydes. C-O bond cleavage is not required, however, for the formation of methanol from CO + H₂ or for the hydroformylation of olefins. (2) Insertion of CO into a metal-alkyl (possibly also

metal-alkenyl) bond. This is a necessary condition for the formation of higher oxygenates from synthesis gas and for olefin hydroformylation, but it does not seem to play a role in the formation of hydrocarbons and alkyl groups.

The formation of aldehydes and higher alcohols from synthesis gas, therefore, requires the occurrence of two different reactions of adsorbed CO on the same catalyst. For research directed toward unraveling the above-mentioned "promoter effect", it is obviously more productive to use a test reaction which requires only one of these reaction steps. We, therefore, decided to use the hydroformylation of ethylene as our probe reaction. This reaction yields propanal and 1-propanol as the CO insertion products and ethane as the product of simple hydrogenation. In a previous paper we had shown that adding Zn to the Rh/SiO₂ catalyst reduced the selectivity and turnover frequency for hydrogenation to ethane but dramatically increased the selectivity for hydroformylation to propanal.

In order to discriminate between the various hypotheses for the promoter effect, we have now studied how chemisorption of sulfur modifies the catalytic properties of silica-supported rhodium. In this case we can reasonably exclude two of the possibilities mentioned above: sulfur will be chemisorbed on the Rh particles, not under them and not on the SiO₂; and it is highly unlikely that

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chemisorbed sulfur should chemically interact with the oxygen end of coadsorbed CO molecules.

What chemisorbed sulfur will do is block "Freundlich sites" (i.e., those adsorption sites which are used by metal atoms when a Rh crystal grows in its own vapor), thus isolating the surface Rh atoms from each other. It is also possible that a negative charge will be localized on the sulfur atoms, leaving adjacent Rh atoms as positive ions. Further, it is to be expected that at the reaction temperature of 180 °C and higher coverage of the rhodium surface with sulfur atoms, some surface reconstruction will occur, producing isolated Rh atoms or ions which are disconnected from the metal lattice and act as monatomic adsorption sites. In view of these considerations we decided to combine the catalytic tests with measurements of the infrared (IR) spectra of chemisorbed CO and with Auger electron spectroscopy (AES). We further used chemisorption of carbon monoxide to determine the percentage of the rhodium surface which was *not* covered with sulfur. The IR spectra were to provide information on (1) bridging CO or Rh_nCO (*n* = 2, 3), (2) linear CO or RhCO, (3) geminal CO or Rh(CO)₂, and (4) CO on positive Rh ions, or Rh⁺CO. For each of these the relative change due to sulfur adsorption has been monitored and correlated with the changes in catalytic activity, turnover frequency, and selectivity. The adsorption of sulfur was carried out by using a flow of highly diluted hydrogen sulfide in hydrogen at atmospheric pressure and 180 °C, followed by a flow of pure H₂ at 400 °C, in order to obtain fairly homogeneous distribution of the adsorbed sulfur over all Rh particles in the catalyst sample. After this treatment no sulfur is associated with silica.

II. Experimental Section

SiO₂-supported Rh catalysts (4 wt% loading Rh) were prepared by conventional impregnation of RhCl₃ (Johnson Mathey, 40.24% Rh) dissolved in methanol onto silica gel (Davison No. 62, mesh 60–80), pretreated by washing with 0.1 M HNO₃ and deionized water, drying at 120 °C, and calcination at 400 °C in air. Its surface area was 260–280 m²/g.

After removal of the solvent using a rotary evaporator, the impregnated catalysts were reduced by flowing H₂ (1 atm, 50 mL/min) at a temperature of 400 °C for 6 h using a temperature programmer. When desired, the reduced catalysts were subjected to controlled sulfurization: a sample of 0.6 g in a Pyrex glass tube was exposed to a flow of premixed gas of 10 ppm of H₂S in H₂ at 1 atm. At this stage the sulfur dosage was controlled by maintaining a constant flow rate of 150 mL/min and varying the contact time. After a flow time of 17 h the number of H₂S molecules entering the reactor is equal to the number of surface Rh atoms in the sample. Subsequently, the sample was reduced again with pure H₂ at 400 °C for 2 h to remove any weakly held sulfur and redistribute it over the sample. AES confirmed that after this treatment no sulfur is retained by the silica. After cooling to room temperature, the samples were exposed to lab air, rehomogenized mechanically, and distributed as follows: 0.3 g to be tested as catalyst for hydroformylation, 0.2 g to be used for measuring the chemisorption of carbon monoxide, and 0.1 g to be characterized by FTIR and AES. Each of these was then reduced in situ with pure H₂ at 400 °C for 2 h. As the amount of "dosed sulfur" is not necessarily equal to the quantity of "chemisorbed sulfur" after the above treatments, the latter parameter was derived from CO chemisorption and the S/Rh Auger peak ratio.

The measurements were carried out as follows:

1. *Hydroformylation of Ethylene.* A Pyrex glass reactor charged with 0.3 g of catalyst was used in the flow mode. A premixed gas containing C₂H₄, CO, and H₂ in volume ratios 1:1:1 was led over the catalyst at 30 mL/min and 180 °C. The gas was purified over MnO and a trap filled with Molecular Sieves 5A in order to remove oxygen and moisture. The effluent gas was analyzed for C₂H₄, C₂H₆, and the oxygenated products such as C₂H₅CHO and C₂H₇OH by FID GC (HP 5890A) by using a methyl-silicon gum phase capillary column (i.d. = 0.2 mm, 50 m, He carrier), temperature-programmed from –40 to +100 °C.^{4,25}

TABLE I: CO Chemisorption in Rh/SiO₂ Catalysts

dosed S, ML	[CO _{ad}], ^a mmol of CO/g of cat.	dispersion ^b (CO/Rh)	θ _s
0.0	0.112	0.287	0
0.014	0.109	0.281	0.021
0.07	0.104	0.266	0.073
0.14	0.084	0.216	0.247
0.14	0.082	0.210	0.268
0.28	0.062	0.159	0.446
0.28	0.063	0.161	0.439
0.42	0.039	0.0998	0.652
1.0	0.038	0.0981	0.658

^a[CO_{ad}] = total [CO] – [weakly adsorbed CO] (at 25 °C).

^bDispersion (CO/Rh) = CO_{ad}/total Rh atoms in catalyst was obtained by dispersion = [CO_{ad}]/0.3887.

2. *CO Chemisorption.* Static CO chemisorption measurements were carried out in a conventional vacuum system. The catalysts were reduced in H₂ at 400 °C for 2 h, followed by purging with He (50 mL/min) for 20 min to remove adsorbed H₂. CO was then introduced at room temperature, its pressure being in the range of 50–200 Torr. The amount of strongly chemisorbed CO was obtained by subtracting the weakly adsorbed CO from the total adsorbed CO. For this purpose the system was evacuated at room temperature between two adsorption measurements. The quantity of weakly adsorbed CO, which is probably associated with the SiO₂, amounted to less than 1% of the total CO.

3. *FTIR Spectroscopy.* For IR observation, the samples were pressed into disk wafers (7-mm diameter, 9 mg) which were reduced at 400 °C in H₂ for 2 h in an IR cell. After cooling to room temperature, H₂ was replaced by He. The IR spectra were recorded with a Nicolet 60SX single-beam Fourier transform infrared spectrometer at a resolution of 1 cm⁻¹. Generally, 150 interferograms were accumulated to improve signal-to-noise ratios. CO was introduced at room temperature at 1 atm to the catalyst disk and then the cell was purged with He. Spectra of adsorbed CO were obtained by subtraction of the background spectrum of a catalyst wafer which had been reduced in H₂ but not exposed to CO.

4. *Auger Electron Spectroscopy.* For the AES analysis, a reduced sample was pressed in air on a copper gauze to eliminate electrostatic charging during the AES measurements. This sample wafer was mounted on the sample holder in the ultrahigh-vacuum chamber. AES spectra were obtained with a PHI scanning Auger microscope (Model 590) at a TV mode, using a 2-kV electron beam.

III. Results

1. *Adsorption of Sulfur.* The stoichiometric ratio of strongly chemisorbed CO to surface Rh depends on the crystal face and the formation of "geminal" carbonyl. This ratio is a priori unknown for supported rhodium, but for the purpose of recording the data it suffices to assume that a strongly chemisorbed molecule "counts" one exposed Rh atom. The lowering of CO chemisorption

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TABLE II: Total Conversion, Turnover Frequencies (TOF), and Selectivities over Sulfurized Rh/SiO₂^a

θ_s	total conv, %	TOF, min ⁻¹			selectivity, %		
		C ₂ H ₆	C ₂ H ₅ CHO	C ₃ H ₇ OH	C ₂ H ₆	C ₂ H ₅ CHO	C ₃ H ₇ OH
0	17.7	2.159	0.195	0.017	91.1	8.2	0.7
0.02	14.0	1.702	0.190	0.011	89.4	10.0	0.6
0.07	10.8	1.329	0.211	0.009	85.7	13.7	0.6
0.247	8.1	1.158	0.269	0.008	80.5	18.8	0.6
0.439	5.9	1.051	0.355	0.0064	74.4	25.1	0.5
0.652	3.2	0.908	0.310	0.008	73.8	25.3	0.8

^a Catalyst: 4.0 wt % Rh loading, 0.3 g. Reaction conditions: C₂H₄:CO:H₂ = 1:1:1; flow rate = 30 mL/min, 180 °C, 1 atm. TOF (min⁻¹ = rate (mmol/min × mmol of Rh)).

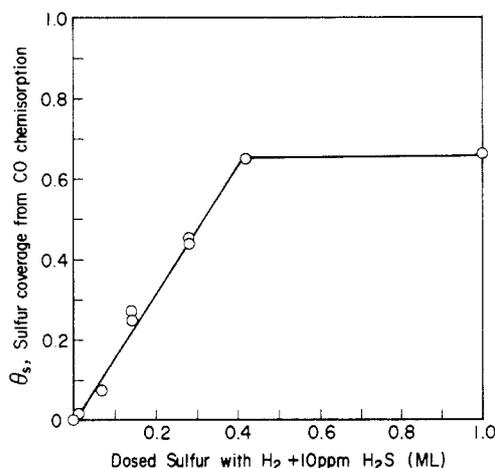


Figure 1. Relation between dosed sulfur on Rh/SiO₂ and sulfur coverage estimated by CO chemisorption. Rh/SiO₂ (4 wt %) treated with 10 ppm of H₂S in H₂ flow (150 mL/min) at 180 °C, followed with H₂ reduction at 400 °C for 2 h.

by preadsorbed sulfur can then be expressed as a sulfur coverage θ_s , given by

$$\theta_s = \frac{n_{\text{Rh}} - n_{\text{Rh-S}}}{n_{\text{Rh}}} = 1 - D_s/D_0$$

where n_{Rh} and $n_{\text{Rh-S}}$ denote the numbers of CO molecules which are strongly chemisorbed on clean Rh or sulfur covered Rh, respectively, while D_s and D_0 are the dispersions of sulfur covered and pure Rh. Measured values of the dispersion and sulfur coverages are shown in Table I. In Figure 1 the sulfur coverage determined by CO adsorption is plotted versus the amount of sulfur dosed, calculated from the contact time of the H₂S/H₂ flow. It is found that initially θ_s rises linearly with a slope of 1.5, indicating that an adsorbed S atom blocks the surface for more than one CO molecule. When the coverage with sulfur has attained a value such that the amount of strongly chemisorbed CO has fallen to one-third of the original amount on the clean rhodium, further dosage of sulfur does not affect CO adsorption. As the heat of adsorption of sulfur is known to decrease with coverage, it is conceivable that a thermodynamic equilibrium for strongly adsorbed sulfur has been reached. If that is the case, all Rh particles in the sample will be covered equally with sulfur.

2. *Hydroformylation of C₂H₄*. Total conversions, turnover frequencies, and selectivities for different sulfur coverages are shown in Figure 2 and Table II. With increasing sulfur coverage θ_s , the total conversion decreases but the selectivity for hydroformylation increases. With increasing θ_s , the rate of hydrogenation displays a sharp nonlinear decrease as shown in Figure 2, while the rate of hydroformylation remains unchanged, within experimental error. By consequence, the turnover frequency (TOF) for hydroformylation increases and passes through a maximum as shown in Figure 3.

3. *FTIR*. Infrared spectra for samples with different sulfur coverage are shown in Figure 4. The measured IR adsorption depends on the wafer thickness, which was not exactly equal for different samples. All other factors being equal, a variation of 5–10% results from this trivial cause. The intensity of the

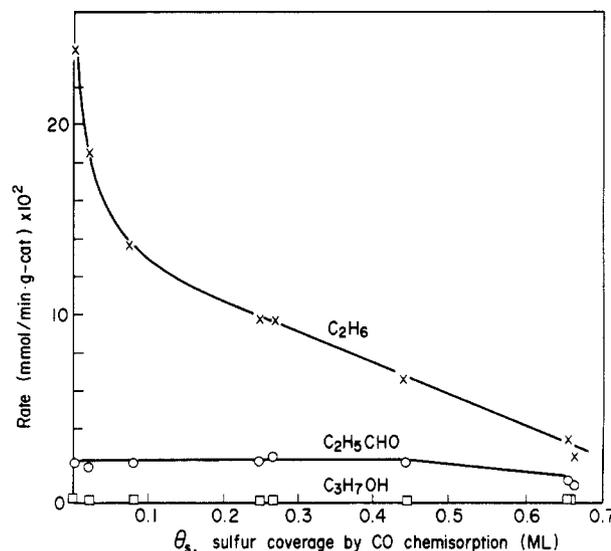


Figure 2. Rates of product formation in hydrogenation and hydroformylation of ethylene on Rh/SiO₂ against sulfur coverage estimated by CO chemisorption.

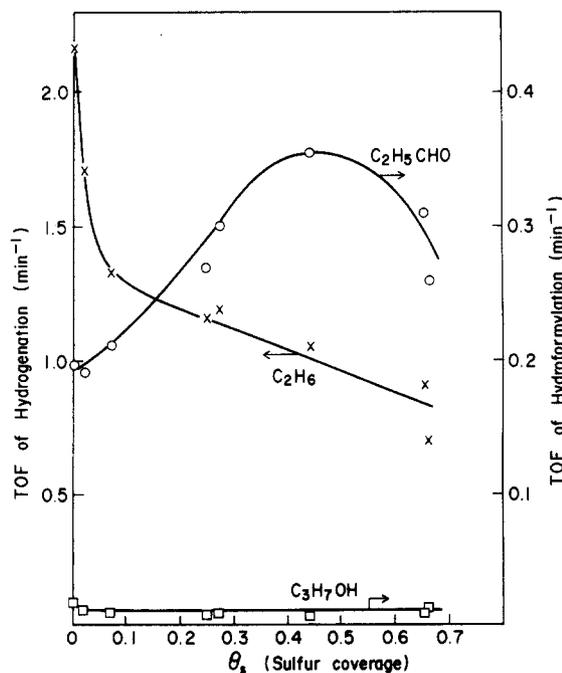


Figure 3. TOF of product formation by changing sulfur coverage on Rh/SiO₂.

2068-cm⁻¹ band was found to vary by this amount only. Therefore, the spectra in Figure 4 have been normalized such that the intensity of the 2068-cm⁻¹ band is made equal for all spectra. Two strong bands at 2068 and 1912 cm⁻¹ for CO on sulfur-free Rh/SiO₂ are conventionally assigned to linearly bonded carbonyl and bridging carbonyl, respectively.¹⁹ In the absence of sulfur

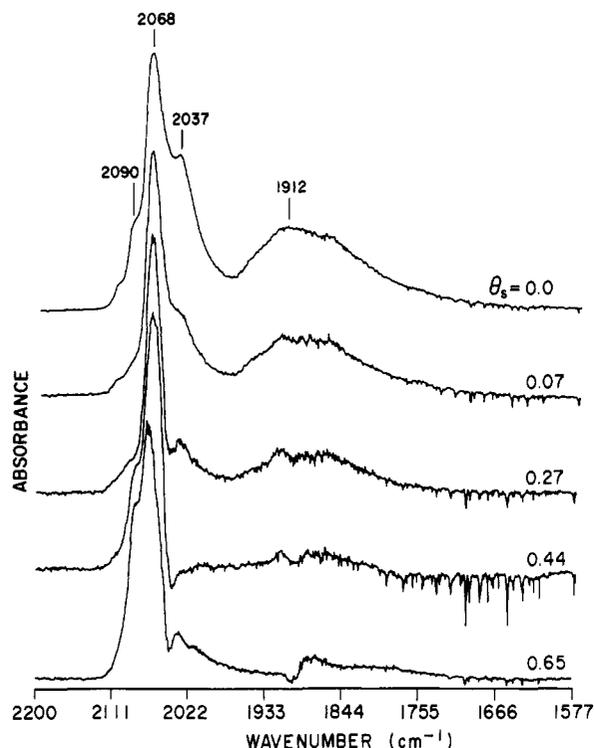


Figure 4. IR spectra of CO chemisorbed on Rh/SiO₂ as a function of sulfur coverage estimated from CO chemisorption.

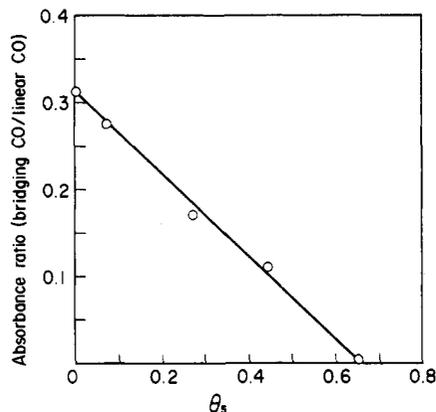


Figure 5. Change of IR absorbance ratio of bridging CO/linear CO ($\nu = 1912$ and 2068 cm⁻¹, respectively).

these bands have comparable intensities, but with increasing sulfur coverage the band attributed to bridging CO was preferentially suppressed and at high sulfur coverage a shoulder of a band at 2090 cm⁻¹ increases. The intensity ratio of bridging CO to linear CO is shown in Figure 5.

4. *Auger Electron Spectroscopy.* Rh and sulfur peaks observed of comparable intensity at high sulfur coverage. AES signals of C, Cl, and S detected with unsulfurized samples might be caused by contaminations picked up during sample transfer. After these background signals were subtracted, the S/Rh AES peak intensity ratio was found to be proportional to the coverage calculated from the sulfur dosage, confirming the internal consistency of our data. No sulfur was detected by AES on silica, which has been subjected to the same sulfurization treatment as the Rh/SiO₂ samples.

IV. Discussion

Sulfurization of Rh, as described in the Experimental Section, leads to the following results which justify some discussion: (1) decrease of CO chemisorption, (2) change in intensity ratio of IR bands attributed to linear and bridging CO, and (3) change in catalytic activity for hydrogenation and hydroformylation.

1. *CO Chemisorption.* Strong chemisorption of CO decreases linearly with increasing precoverage of the surface with sulfur until a saturation level is attained. This observation is in line with the

site blocking model. As might be expected, the stoichiometry of this relation deviates from the assumption—made for recording purposes only—that a surface Rh atom adsorbs either one CO molecule or one S atom. A number of causes can be recalled why the slope of the observed line in Figure 1 must be greater than 1. First, the atomic radius of a sulfide ion (1.84 Å) considerably exceeds that of a Rh atom (1.345 Å). A model calculation by B. Tatarchuk³³ assumes that 0.25 monolayer (ML) of sulfur on a Rh(111) face would fill every other threefold hollow site (i.e., every "Freundlich site") and reduce the CO adsorption on this face for steric reasons to half the value on pure Rh(111).

For particles which mainly exhibit (111) faces, the above value of 0.25 ML would conceivably represent saturation with strongly adsorbed sulfur in the absence of surface reconstruction. This model provides a reasonable explanation for the present observation that above a critical coverage no additional sulfur is adsorbed at 180 °C and $H_2S/H_2 = 10^{-5}$ or that weakly held sulfur is removed during the subsequent reduction at 400 °C. It is, however, also possible that, on particles which exhibit less densely packed crystal faces, surface reconstruction takes place, incipient to the formation of Rh₂S₃. It is well-known that sulfides such as Ni₂S₃ or MoS₂ are able to chemisorb hydrogen or olefins and catalyze hydrogenations and related reactions by virtue of the exposed transition-metal ions.¹⁸ The possibility that exposed Rh atoms or ions are present on a surface sulfide phase will have to be discussed below in the context of the infrared and the catalytic data.

Measured data on supported metal particles cannot be interpreted in the same way as data obtained on single crystals. As mentioned, the CO/Rh_s ratio depends on the crystal face and on the mode of adsorption. For the geminal mode it is equal to 2. This mode is known to prevail for ultradisperse Rh, for which J. K. Vis reports an overall CO/Rh ratio of 1.9 .²¹ For macroscopic crystals other authors report data near CO/Rh = 0.5 . When a large fraction of the surface is covered with sulfur, the heat of adsorption for CO will be lowered, as most surface atoms have lost much of their original coordinative unsaturation, and this will, again, change the ratio between adsorbed CO and Rh atoms not covered with sulfur. Fortunately, a precise knowledge of this stoichiometry is not required in the context of the present paper. The facts of relevance to the following discussion are (1) there is a linear relation between adsorbed CO and dosed sulfur at low coverage and (2) above a critical coverage no additional sulfur deposition surviving reduction at 400 °C takes place.

2. *IR Spectra.* The IR data clearly show that the intensity ratio of bridging CO (at 1912 cm⁻¹) to linear CO (at 2068 cm⁻¹) is drastically decreased by covering the surface with sulfur. This result was expected on the basis of our earlier work with Rh-Zn-SiO₂¹³ and PdAg.³² It can be rationalized in a straightforward way by the conventional site blocking model; i.e., Freundlich sites are filled with sulfur and the remaining surface Rh atoms become isolated from each other. While the intensities change markedly, the band positions remain constant within experimental error. This observation lends justification to the "ensemble" or nearest-neighbor approximation, disregarding long-range electronic effects. If these were dominant, the positions of the main IR bands would be expected to change.

The bands at 2090 and 2037 cm⁻¹ might be ascribed to the symmetrical and antisymmetrical stretching mode of geminal carbonyl species.¹⁹ Various authors, accordingly, showed that these bands are very pronounced for highly dispersed rhodium.^{20,21} The

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intensity ratio of these bands is affected by other ligands and the actual oxidation state of the Rh ion as shown by Shannon et al.³⁴ The enhanced intensity of the 2090-cm⁻¹ band with respect to the 2037-cm⁻¹ band might indicate a positive charge, and the Rh ion carrying the CO ligands might also be coordinated with sulfur. Most authors assume that this "twin" complex consists of a positive Rh ion, presumably Rh⁺, carrying two CO ligands. Indeed, exposing a reduced Rh/Al₂O₃ catalyst to oxygen or air has been found to increase the band intensity, in particular of the high-frequency band, whereas the bands due to the linear and bridging CO are weakened or disappear. Vis et al.²¹ found that for an oxidized Rh/Al₂O₃ catalyst the dominant feature was a pair of bands of 2027 and 2097 cm⁻¹, assigned to twin CO. However, CO adsorption on positive metal ions is quite generally known to give rise to bands at higher frequency than CO on zerovalent metal atoms. Therefore, the high-frequency CO band might also be assigned to e.g. linear CO on Rh⁺ ions. Previously, Rice et al.²² had shown that oxidation of Rh leads to CO bands at 2028 and 2098 cm⁻¹, but the intensity ratio was different from that of the two bands of geminal CO on reduced Rh; with the oxidized catalyst the high-frequency band was more intense. Similar observations were recently made by Jen²³ in our lab; on one preoxidized Rh the high-frequency band at 2101 cm⁻¹ was almost 4 times more intense than the second band at 2027 cm⁻¹. We, therefore, conclude that the high-frequency band on the rhodium which is partially covered with sulfur shows that CO is adsorbed on positive Rh ions. Part of this CO may be present as geminal CO and part of it as linear CO.

In our spectra the intensity of the high-frequency band increases with increasing coverage of the surface with sulfur, indicating that electronegative sulfur atoms leave adjacent Rh atoms with a net positive charge. It is also conceivable that surface reconstruction takes place at 400 °C and the surface sulfide exposes isolated, protruding Rh⁺ ions which carry one or two CO ligands.

While the band at 2037 cm⁻¹ might be due to one vibrational mode of the geminal CO complex, it is also possible that a CO ligand bridging over three Rh atoms is present on clean Rh; the absence of this band for rhodium covered with 0.44 ML of sulfur would then be in agreement with the site blocking model.

3. Catalysis. As expected, partial precoverage of the Rh surface with sulfur has a dramatic poisoning effect on the rate of ethylene hydrogenation. Per gram of catalyst the rate decreases by an order of magnitude for the maximum sulfur coverage, which according to the CO chemisorption data corresponds to 2/3 of a monolayer. The first sulfur atoms adsorbed on the Rh surface are most efficient in impeding the hydrogenation activity: covering a small fraction of the surface and blocking it for 2% of the potential CO chemisorption result in a decrease of the hydrogenation activity by 21%. This further confirms that, with the procedure used in this work, the macroscopic distributions of sulfur over the rhodium particles in the catalyst bed was fairly uniform; also, at very low coverage with sulfur this poison is not concentrated on the front end of the catalyst bed, as might be feared on the basis of the high sticking coefficient of H₂S on metals. Such a macroscopic nonuniform distribution would result in a poisoning action proportional to overall coverage.

The effect of sulfur on the activity for hydroformylation contrasts markedly with that for simple hydrogenation of ethylene. Per unit mass of catalyst, the hydroformylation rate remains fairly constant, but when expressed per available site, as determined by CO chemisorption, the turnover frequency increases and passes through a maximum. As a result, the hydroformylation selectivity increases with increasing concentration of adsorbed sulfur. This promotion is, however, smaller than the corresponding effect found in our previous work¹³ with Zn and Fe ions.

Before we discuss this effect of adsorbed sulfur in terms of the molecular mechanism, a trivial effect has to be considered. The reaction order for hydroformylation is positive in hydrogen and ethylene but negative in carbon monoxide.²⁶ As hydrogenation

consumes hydrogen and ethylene, a strong hydrogenation function in the same reaction chamber must lower the rate of hydroformylation even if both reactions took place on completely different sites. Any suppression of the hydrogenation will thus result in an increase of the hydroformylation rate. This effect will, however, be small for conversions in the differential regime, where the partial pressures of the reactants change little. A rough estimate shows that under the experimental conditions of the present work only a small part of the observed increase in TOF for hydroformylation can be ascribed to this trivial cause. We, therefore, may conclude that the hydroformylation activity per exposed site is increased by covering part of the rhodium surface with sulfur.

Metallic rhodium is an excellent and selective hydrogenation catalyst, but on Rh complexes hydroformylation competes successfully with hydrogenation. The best known hydroformylation catalysts are mononuclear rhodium complexes, such as the Wilkinson catalyst HRh(CO)₁₂(PPh₃)₂. Clusters with several Rh atoms have also been used as active homogeneous catalysts in solution, but it was shown by Vidal et al.²⁷ that the active catalyst is formed by dissociation of the cluster to mononuclear complexes under the prevailing reaction conditions.

A possible cause for the spectacular difference between rhodium metal and mononuclear rhodium complexes, as regards their hydroformylation versus hydrogenation activity, is the different requirement of these reactions for vacant ligand positions.²⁴ We refer to the research by Siegel²⁹ and by Tanaka,¹⁸ who showed for a variety of reactions and catalysts that dramatic changes in selectivity are due to changes in the number of available ligand positions of a metal atom, either in a complex or at the surface of a metal sulfide. In the hydrogenation of an olefin the dissociative adsorption of dihydrogen requires two vacant sites, while at least one site must be available for the adsorption of the olefin molecule.²⁸ This necessity to find three positions forms no problem for reactions catalyzed by a metal surface; dihydrogen easily dissociates at any pair of vacant sites, and the H atoms can migrate to any hydrogen acceptor coadsorbed on the same surface. Even if each individual surface atom exposes only one free ligand position, such reactions requiring several free sites in different steps can be catalyzed by a metal surface. The situation is, of course, totally different for a mononuclear rhodium carbonyl, as all required adsorption sites have to be located on the same Rh atom. In particular, in an atmosphere of carbon monoxide the condition to find three vacant positions on the same rhodium atom is not easily met. Therefore, such a complex is a relatively poor hydrogenation catalyst. Its ability to catalyze hydroformylation suggests that for this reaction the requirement for vacant positions is lower than for hydrogenation. Moreover, the geometrical necessity to have room for all ligands is met easier for an isolated atom than for an atom in a crystal surface covered with adsorbed molecules. Only the corner atoms of metal crystals are accessible from various directions and in this respect most similar to the atoms in a mononuclear complex.^{18,24,28,29}

The simple geometric concept that atoms in well-defined crystal faces of rhodium will easily catalyze hydrogenation, while corner atoms catalyze hydroformylation in a manner comparable to complexes, could be sufficient to rationalize the present results. It is known that sulfur atoms will be most strongly adsorbed on sites where they contact more than one metal atom, for instance the Rh₄ squares on (100) or Rh₃ sites on (111) faces. Partially covering the surface of a rhodium particle with sulfur under equilibrium conditions will, therefore, preferentially fill these Freundlich sites, while edge and, in particular, corner atoms remain unpoisoned. This situation would result in an unchanged hydroformylation activity per unit mass of the catalyst and an increased TOF per surface atom "counted" by chemisorbed CO, as has indeed been found.

The possibility can also be mentioned that additional protruding rhodium atoms (or ions) are actually created by the chemisorption of sulfur. In previous work it was shown by Holscher and one of the present authors¹⁷ that strong chemisorption on metals leads to surface reconstruction or "corrosive chemisorption" at higher

(34) Shannon, R. D.; Védrine, J. C.; Naccache, C.; Lefèbvre, F. *J. Catal.* **1984**, *88*, 431.

coverages; i.e., some metal ions protrude above adsorbed anions. The well-known fact that sulfides of many metals are active catalysts for a variety of reactions is generally ascribed to these protruding ions. In recent work with supported rhenium catalysts we found³¹ that sulfur "poisoning" induces a remarkable activity for hydrogenation and double-bond shift, illustrating the catalytic action of surface sulfides.

The present results do not permit to discriminate between this geometric principle (corner atoms, protruding ions) and the "electronic" principle; i.e., the positively charged Rh atoms (or ions) might have a higher intrinsic activity for hydroformylation than zerovalent Rh atoms.

V. Conclusions

1. Exposing a freshly reduced Rh/SiO₂ catalyst to a stream of highly diluted hydrogen sulfide in hydrogen, followed by reduction in hydrogen at 400 °C, results in a macroscopically uniform distribution of the sulfur atoms over the rhodium particles in the catalyst bed. The ability of the catalyst to strongly chemisorb carbon monoxide decreases linearly with the amount of sulfur dosed, up to a critical coverage with sulfur. Further dosing of sulfur does not affect CO chemisorption.

2. Adsorbed sulfur selectively blocks the Rh surface for the bridging mode of chemisorbed CO.

3. Adsorbed sulfur appears to leave adjacent Rh with a net positive charge; CO adsorbed on these atoms displays a high-

frequency band in the IR region.

4. Low sulfur coverages, which reduce the capacity of chemisorbing CO by only a few percent, have a much stronger effect in reducing its ability to catalyze the hydrogenation of ethylene. This could indicate that the sites on the rhodium surface with highest hydrogenation activity also have the highest heat of adsorption for sulfur.

5. The turnover frequency for hydroformylation is increased by sulfur at low coverages. This is tentatively rationalized by assuming that Rh atoms in corner positions are most active in hydroformylation, while the adsorption of sulfur is strongest on Freundlich sites, consisting of metal atom ensembles. It is also possible that surface reconstruction of rhodium covered with sulfur leads to additional protruding Rh ions.

6. The promoting action of adsorbed sulfur is smaller than that of e.g. Zn ions reported previously. It is possible that in the latter case some chemical interaction between the metal ion and the oxygen end of coadsorbed CO enhances CO insertion into a metal-alkyl bond.

Acknowledgment. A donation toward equipment by the Shell Co. Foundation and a research grant by the Monsanto Co. are gratefully acknowledged.

Registry No. Rh, 7440-16-6; S, 7704-34-9; CO, 630-08-0; ethylene, 74-85-1.

Shock-Tube Study of Allene Pyrolysis

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(Received: March 30, 1987; In Final Form: June 4, 1987)*

The high-temperature pyrolysis of allene was studied by analyzing reflected shock zone gas with time-of-flight (TOF) mass spectrometry. A 4.3% C₃H₄-Ne mixture yielded a carbon atom density of about 2.0×10^{17} atoms cm⁻³ over the temperature and pressure range of 1300–2000 K and 0.2–0.5 atm. Product and reactant profiles were obtained during observation times of 750 μs. The mass balance with respect to observed carbon-containing compounds accounted for 84–100% of the total carbon atom input. The major products detected were C₂H₂, C₄H₂, CH₄, and C₆H₆, along with minor amounts of C₂H₄, C₂H₆, C₄H₄, and C₆H₂. Reasonable agreement is obtained between the experimental results and a mechanism consisting of 80 reactions which features the allene-propyne isomerization, initial decomposition via C₃H₄ + M = C₃H₃ + H + M, the thermochemical properties of the C₃H₃ isomers, and the role of C₃H₃ radicals in the formation of benzene. Experiments on 1,2-butadiene were performed to further elucidate the role of C₃H₃ and to understand how cyclic compounds may be formed from linear unsaturated hydrocarbons at high temperatures. Benzene yield is approximately the same from equivalent amounts of allene and 1,2-butadiene. The production of benzene observed correlates with reported soot yields in the order allene > 1,3-butadiene > acetylene.

Introduction

In studying soot formation during combustion processes, it is essential to understand the mechanisms of hydrocarbon pyrolyses. Among organic fuels, allene is an interesting compound that has attracted increased attention in recent years.^{1,2} Dissociation of allene was studied by Collin and Lossing³ in 1957 who derived bond dissociation energies for allene, propyne (methylacetylene), and 1,2-butadiene and the heat of formation of C₃H₃ radical. These values have been the subject of more recent work.^{4,5} Detailed investigations of allene pyrolysis have been conducted

by several groups.^{6–9} Levush et al.⁶ determined the product profiles from allene and propyne by using a flow system over the temperature range of 1173–1430 K. They also obtained first-order rate constants for the allene-propyne isomerization. The isomerization was faster than any decomposition process under the conditions of their study. Recent single-pulse shock-tube (SPST) studies of the isomerization support this contention.^{9–12} Walsh has proposed that isomerization occurs via the intermediate cyclopropene.^{13–15} Theoretical ab initio calculations made by Honjou

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