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Sulfur Modifies the Chemisorption of Carbon Monoxide on Rhodium/Alumina Model Catalysts

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The effect of D_2S on the chemisorption of CO on supported rhodium is examined with tunneling spectroscopy. It is seen that for low concentrations, D_2S decreases the density of species with two CO molecules per Rh atom and increases the density of species with one CO molecule per Rh atom. At higher concentration D_2S decreases the density of all types of adsorbed CO.

I. INTRODUCTION

There is considerable interest in the effect of sulfur on supported metal catalysts because of industrial catalyst poisoning by sulfur compounds during the hydrogenation of coal and processing of petroleum raw materials (*1*). The nature of sulfur bonding to supported transition metals is not, in general, known. There are, however, model systems of small metal clusters which contain sulfur (*2*). These molecular systems can form the basis of understanding some of the reactions of sulfur compounds with supported metals (*3*).

There has been infrared work on the effect of sulfur on carbon monoxide adsorption. Recently Rewick and Wise (*4*) observed that, in the presence of hydrogen, H_2S would preferentially desorb β-CO (multisite attached) over δ-CO (single site attached) on alumina-supported Ni. In fact, under some conditions the amount of δ-CO would actually increase for small H_2S exposure. At large exposures it would decrease, but never as readily as β-CO. This type of measurement is exciting because it may lead to an understanding of selective catalyst poisoning.

We have chosen to study the effect of sulfur on carbon monoxide adsorption on alumina-supported Rh because: (i) the system of carbon monoxide on alumina-supported Rh has been extensively studied (*5, 6*) and is well understood, (ii) there are three different types of adsorbed CO species to observe, and (iii) the three types are agreed upon by both infrared and tunneling workers and can be distinguished from each other by either spectroscopy.

II. EXPERIMENTAL METHODS

The details of the preparation of inelastic electron tunneling spectroscopy tunnel junctions have been reported elsewhere (*7*). A brief description of the procedure follows:

Aluminum electrodes are deposited in high vacuum onto a glass slide. These thin aluminum films, usually 800 Å thick, are oxidized at 200°C in air to form the alumina insulating barrier necessary for tunneling. The oxidized electrodes are cleaned in an argon glow discharge prior to the deposition of rhodium. The rhodium is evaporated either in the presence of a CO plus D_2S gas mixture or in high vacuum, followed by exposure to the gas mixture. A gas mixture pressure of 1.3×10^{-3} Pa (10^{-5} Torr) is sufficient to dominate the residual gases present, typically 1.3×10^{-5} Pa (10^{-7} Torr) H_2O and H_2, and is maintained in the system for 700 sec to achieve a total exposure or order 1 Pa sec. Junctions are then

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completed by the evaporation of the top lead electrode. In this work all doped junctions were formed adjacent to undoped, control junctions to allow the subtraction of background structure. The differential spectrometer used has been described in the literature (*8*).

III. EXPERIMENTAL RESULTS AND DISCUSSION

With no added sulfur, CO chemisorbs in at least three different ways on alumina-supported rhodium particles (*6*). There are two different linear-bonded species (one CO per rhodium atom and two CO's per rhodium atom) and at least one multiply bonded species. The two linear-bonded species can be distinguished with tunneling spectroscopy by their different low-energy modes. Specifically, the one with one CO molecule per rhodium atom has a bending vibration at 58.1 meV while the one with two CO molecules per rhodium atom has a bending vibration at 51.6 meV[6] (multiply by 8.065 $\mathrm{cm}^{-1}/\mathrm{meV}$ to convert to cm^{-1}). The rhodium–carbon stretching vibrations for these linear species appear as broad overlapping bonds of low intensity centered at 73 and 70 meV, respectively.

The relative amounts of the different species can be changed. For example, in the limit of "ultradispersion" (*9*) all of the Rh atoms can adsorb two CO molecules. We can model an ultradispersed catalyst by simply evaporating a very small amount of Rh onto our oxidized Al (Typically $\frac{1}{4}$ monolayer average coverage as opposed to the one monolayer averaged coverage reported on previously (*6*)). Figure 1 shows the low-energy region for such a model catalyst. Note that for pure CO (0% D_2S) there is only one resolved peak, at 51.6 meV. This is the bending mode assigned to two CO molecules per Rh atom.

As sulfur is added, this peak decreases in intensity and a peak near 60 meV grows. This position is close to the 58.1-meV peak position for one CO molecule per Rh atom (*6*). It clearly suggests that the sulfur is displacing one of the CO molecules and leaving the other. The rhodium–carbon stretching modes are seen only as broad shoulders of low intensity in Fig. 1, and are thus difficult to interpret. An additional mode of low intensity near 42 meV appears after the rhodium is exposed to D_2S. It is tentatively assigned as a rhodium–sulfur vibration. Quantitative calibration of the observed d^2V/dI^2 spectra has not been attempted because of the difficulty (at present) of producing identical rhodium coverages.

In preliminary experiments with H_2S some characteristic hydrocarbon peaks were present in the spectra. To determine whether the source of the hydrogen in the hydrocarbons was the H_2S, we performed all subsequent experiments with D_2S. We never saw any CD stretching vibrations and concluded that the source of the hydrocarbon peaks was impurities. We have not observed any other modes possibly due to

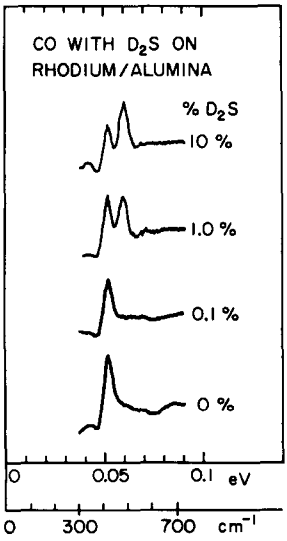

FIG. 1. The low-energy region of the model rhodium/alumina catalyst spectrum is shown for equal exposures to four mixtures of D_2S and CO. The rhodium is highly dispersed. With exposure to 100% CO one peak forms at 51.6 meV that is due to the absorption of two CO molecules per rhodium atom (*6*). With increasing D_2S exposure, a second peak near 60 meV also forms due to the absorption of only one CO molecule per rhodium atom (*6*).

deuterium from the D_2S. Either they are not present or are of low intensity. With a mass spectrometer, we saw a family of deuterium-containing fragments including D_2, HD, D_2O, and HDO in the gas phase. We do not know which are liberated from the junction and which are due to exchange on the walls and filaments in the chamber.

We also performed some experiments with D_2S or H_2S preadsorbition. We found that relatively low exposure ($\leq 3 \times 10^{-2}$ Pa sec) would totally poison the catalyst for CO adsorption. In contrast, a larger exposure (10^{-1} Pa sec) after CO adsorption would not totally desorb the CO. It would only decrease the peaks due to two CO molecules per Rh atom and the multiply bonded CO to roughly one-tenth of their original value. The peak due to one CO molecule per Rh atom remained the same or even increased. Its position remained near 58 meV. These experiments suggest that we are not observing sulfur-induced adsorption of CO but rather CO replacement by the D_2S.

We also prepared some junctions with no sulfur exposure, measured their spectra, and then heated the completed junctions in roughly 10^5 Pa (1 atm) of H_2S. At room temperature we observed a negligible effect for exposures as high at 10^8 Pa sec. At 110°C an exposure of roughly 10^7 Pa sec gave spectra comparable to those obtained by exposing uncompleted junctions (without the top lead electrode) to 10^{-1} Pa sec. Heating to 110°C without H_2S exposure does not give comparable spectra. Thus H_2S can diffuse through the top electrode, but the top electrode provides a significant barrier to this diffusion. The diffusion of a number of other substances through the top electrode has recently been studied by Jaklevic and Gaerttner (*10*). These experiments also suggest that we are observing CO replacement by D_2S and not sulfur-induced adsorption, because in this case only D_2S was present in the diffusion chamber.

Finally, we performed some experiments with very low CO exposures to determine if a species formed by adding just one CO molecule to a site that could absorb two CO molecules would resemble the species formed at CO saturation on the sites that could absorb only one CO molecule. Figure 2 shows the low-energy region for a model catalyst with roughly 1 monolayer averaged Rh coverage (not ultradispersed). At the lowest CO exposures a peak near 58 meV dominates. By 3 L (Langmuir) (1.3×10^{-4} Pa sec) exposure the spectrum resembles a saturation spectrum (*6*) with larger intensity in a 51.2-meV peak. Thus a peak at the position of one CO molecule per rhodium atom dominates for very low exposure while at higher exposures a peak at the position of two CO molecules per rhodium atom is larger. A reasonable interpretation is that at the low exposures (1 L) some rhodium atoms that could accommodate two CO molecules have only had a chance to chemisorb one. This implies that the

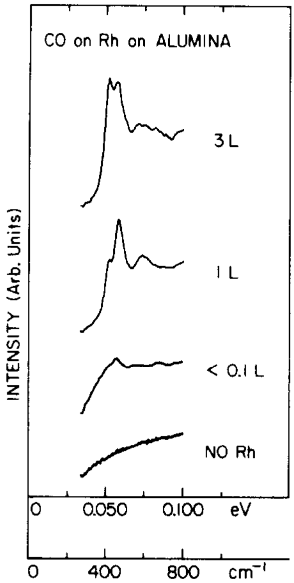

FIG. 2. The low-energy region of the model rhodium/alumina catalyst spectrum is shown for three different exposures to CO. The rhodium is not highly dispersed, but is in approx 30-Å-diameter particles. For CO exposures of a Langmiur or less, a peak near 58 meV, due to a single CO molecule per rhodium atom, dominates (*6*). For higher CO exposures, a peak at 51.6 meV due to two CO molecules per rhodium atom rapidly becomes the most intense (*6*).

species formed by adding just one CO molecule to a site that could adsorb two has a very similar bending vibrational frequency to that formed by adding one CO molecule to a site that can adsorb only one. The broad rhodium–carbon stretching mode for the single CO per rhodium atom species is seen at 73 meV in the 1 L exposure spectrum. The addition of the metal–carbon stretching mode due to the two CO's per rhodium atom species at 70 meV cannot be resolved in the 3 L exposure spectrum.

IV. SUMMARY

We have observed that:

(i) the species with one CO molecule per Rh atom is displaced less readily by sulfur than the species with two CO molecules per Rh atom or the multiply bonded species;

(ii) the species with two CO molecules per Rh atom will convert to a species with one CO molecule per Rh atom in the presence of sulfur. This new species is similar, but distinguishable from the species with one CO molecule per Rh atom that forms in the absence of sulfur;

(iii) hydrogen sulfide will diffuse through the top electrode to modify the adsorbed CO on Rh. The resulting spectrum is similar to that obtained by posttreatment with hydrogen sulfide before the top electrode is evaporated. However, higher exposures and temperatures are required.

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