

**Chemistry of Metals in Ionomers: Reactions of Rhodium-PSSA with CO, H<sub>2</sub>, and H<sub>2</sub>O**

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Rhodium(III) ions have been incorporated in ionic domains of sulfonated linear polystyrene (PSSA) to form PSSA-Rh<sup>III</sup> films. The Rh-containing domains can act as isolated chemical reactors, and their chemical interactions have been explored in this work by controlling the exposure of the rhodium sites to CO, H<sub>2</sub>, and H<sub>2</sub>O under mild conditions. Reaction with CO at low temperature, without either prior reduction by H<sub>2</sub> or complete dehydration of the PSSA-Rh<sup>III</sup> films, results in production of a Rh<sup>I</sup>(CO)<sub>2</sub> species. Partial or complete reduction of the films with H<sub>2</sub> preceded or followed by exposure to CO results in the formation of Rh<sup>I</sup>(CO)<sub>2</sub> and, under various conditions, linear and bridging PSSA-Rh<sup>0</sup> carbonyls and CO bound to small Rh(0) particles. The implications of the results for catalysis are discussed.

**Introduction**

Functionalized organic polymers have been used as supports for heterogenized homogeneous catalytic processes.<sup>1</sup> Transition-metal-containing complexes that are either active catalysts or potential catalytic precursors are usually bound to the support by covalent attachment.<sup>2</sup> There have been fewer reports of catalytic reactions involving transition-metal complexes incorporated into ion-exchange (polyelectrolyte) resins.<sup>3,4</sup> These resins are not thought to form ionic domains or to have the morphological properties of ionomers.

Ionomers are polymers that are functionalized with ionic groups attached at various points along the polymeric backbone. These usually are anionic groups such as carboxylate or sulfonate, and they may be joined directly to the backbone or attached by a short side chain. Ionomeric materials have come under intensive study in recent years because they have important materials applications.

Much of the interest in ionomers is associated with their tendency to form ionic domains in which anionic groups are microphase-separated from the hydrophobic portions of the polymer. Ionic domains are formed in sulfonated linear polystyrene or PSSA, when the degree of sulfonation exceeds a few percent of the available positions along the polystyrene backbone.<sup>5-7</sup> At such ionic group concentrations thermodynamics favors the separation of the ionic components (cations and anionic sites) and the backbone units into hydrophilic regions (the ionic domains) and hydrophobic regions. As a result, the ionic domains are largely surrounded by a medium of low dielectric constant formed by the polymer network, although in some cases the domains may be connected to one another by channels.<sup>8</sup> The domains are accessible to cationic species, including transition-metal-containing cations, by ion exchange.

Thus, an ionic domain contains anionic sites and metal ions and is a physically surrounded region, typically about 20-100 Å in diameter<sup>8</sup> and can be thought of as a small isolated chemical reactor. If the metal ions in the domains are transition-metal ions and can be treated to create active sites, the

domains would become isolated chemical reactors containing potential catalytic centers. The physical structure of the domains would contribute to their potential to function as reactors, because it would enable them to confine a reactant molecule in the proximity of an active site and other reactants. Any reactant molecules that diffuse into the domains could be confined for a residence time that would permit the sites and reactants to interact in the domain much as they would if they were surface sites and gaseous reactants from a gas at much higher pressure. The possibility thus exists that reactions can be catalyzed in ionomers under much milder external conditions than would be required otherwise. Moreover, in principle, the ionomers have other potential advantages as reactors since the anionic site concentration, and consequently the domain size and other properties, could be controlled. This would permit considerable flexibility in reactor design.

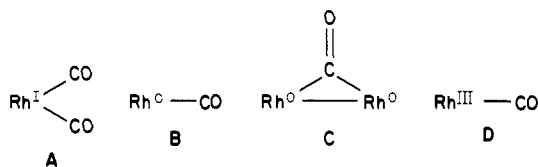
On the other hand, it is possible either that the ionic domains play no significant chemical role or that their role is very different. For example, they could simply change the rates of diffusion of gaseous molecules to the metal ion sites and thus have a minor quantitative effect on reaction rates without affecting the reactions qualitatively. Or, they could promote the growth of relatively large reduced metal particles by serving as nucleation centers throughout the polymer.

The reactions of CO on supported rhodium are quite important, and many infrared investigations of the structural features of rhodium carbonyls formed by chemisorption have been carried out. The first study of the infrared spectrum of CO chemisorbed on Al<sub>2</sub>O<sub>3</sub>-supported rhodium particles was reported by Yang and Garland<sup>9</sup> and has since been reinvestigated by Yates et al.<sup>10</sup> Recently, the effects of catalyst loading, oxidation state of rhodium,<sup>11</sup> rhodium site distribution,<sup>12,13</sup> and catalyst precursor<sup>14</sup> on the infrared spectra of CO adsorbed on Al<sub>2</sub>O<sub>3</sub>-supported rhodium particles have been studied. The results can be compared to those observed for chemisorption of CO on rhodium single crystals<sup>15</sup> and evaporated thin films<sup>16</sup> where the effect of the support is largely removed. While the nature of the underlying support and catalyst preparations may differ, infrared spectral studies suggest the formation of similar rhodium carbonyl species.

- (1) Chauvin, Y.; Commereuc, D.; Dawans, F. *Prog. Polym. Sci.* **1977**, *5*, 95.
- (2) Smith, T. W.; Wychich, D. *J. Phys. Chem.* **1980**, *84*, 1621.
- (3) Drago, R. S.; Nyberg, E. D.; A'mma, A. E.; Zombeck, A. *Inorg. Chem.* **1981**, *20*, 641.
- (4) Smith, R. T.; Ungar, R. K.; Baird, M. C. *Transition Met. Chem. (Weinheim, Ger.)* **1982**, *7*, 288.
- (5) Peiffer, D. G.; Weiss, R. A.; Lundberg, R. D. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1503.
- (6) Yarusso, D. J.; Cooper, S. L.; Knapp, G. S.; Georgopoulos, P. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 557.
- (7) Mattera, V. D., Jr.; Risen, W. M., Jr. *J. Polym. Sci., Polym. Phys. Ed.*, in press.
- (8) Gierke, T. D., paper presented at the Electrochemical Society Meeting, Atlanta, GA, 1977.

- (9) Yang, A. C.; Garland, C. W. *J. Phys. Chem.* **1957**, *61*, 1504.
- (10) Yates, J. T., Jr.; Duncan, T. M.; Worley, S. D.; Vaughan, R. W. *J. Chem. Phys.* **1979**, *70*, 1219.
- (11) Rice, C. A.; Worley, S. D.; Curtis, C. W.; Guin, J. A.; Tarrer, A. R. *J. Chem. Phys.* **1981**, *74*, 6487.
- (12) Cavanagh, R. R.; Yates, J. T. *J. Chem. Phys.* **1981**, *74*, 4150.
- (13) Yao, H. C.; Rothschild, W. G. *J. Chem. Phys.* **1978**, *68*, 4774.
- (14) Worley, S. D.; Rice, C. A.; Mattson, G. A.; Curtis, C. W.; Guin, J. A.; Tarrer, A. R. *J. Chem. Phys.* **1982**, *76*, 20.
- (15) Dubois, L. H.; Somorjai, G. A. *Surf. Sci.* **1980**, *91*, 514.
- (16) Garland, C. W.; Lord, R. C.; Troiano, P. F. *J. Phys. Chem.* **1965**, *69*, 1188.

At least four different rhodium carbonyl species on supported rhodium surfaces have been identified:

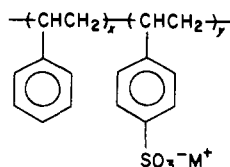


The appearance of two infrared bands of about equal intensity, whose frequencies (ca. 2100 and 2025  $\text{cm}^{-1}$ ) are independent of the CO coverage and are affected similarly by various treatments, has been attributed to an isolated *cis*-rhodium(I) dicarbonyl species (A), on the basis of comparison to the infrared spectra of compounds of the type  $[\text{Rh}(\text{CO})_2\text{X}]_2$  where X = Cl, Br, and I. The frequency of the linear rhodium(0) carbonyl species (B) is thought to be sensitive to the extent of CO coverage and rhodium particle size and structure but usually falls within the range of 2100–2000  $\text{cm}^{-1}$ . The observation of a band, often usually a broad-band structure, in the 1920–1780- $\text{cm}^{-1}$  region, generally is taken to reflect the presence of a bridging CO species (C). Species D, or a variant, has been suggested to account for observations in the 2120–2180- $\text{cm}^{-1}$  region under oxidizing conditions.

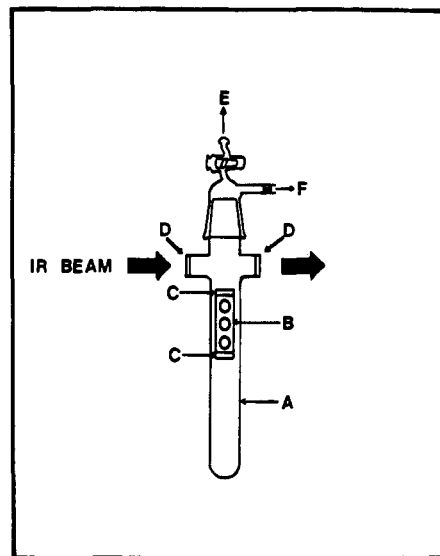
We have carried out reactions on metal-exchanged ionomers of several types to investigate their reactivities. One type is PSSA, mentioned above, which has the particular advantage that its members in the H-PSSA form are soluble and can be separated, in principle, from products formed. The other type is exemplified by perfluorosulfonic acid (PFSA), of NAFION,<sup>8</sup> which is not soluble but has the advantage that its backbone is very stable chemically. In this paper we report the infrared spectra due to CO chemisorption at rhodium sites prepared by the chemical modification of PSSA and of reactions of this system with  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{CO}_2$ . Although the thermal stability of PSSA is much lower than that of inorganic oxides (zeolites,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , etc.) with which these data will be compared, the reactions have been done in this ionomer under mild conditions leading to similar results. Our results show that rhodium particles can be formed in PSSA and that they and rhodium ions undergo reactions with CO under mild conditions to form rhodium carbonyls analogous to those observed on other supports. In other papers our related work on the reactions of PFSA and PSSA ionomers containing Pd,<sup>17</sup> Pt,<sup>18</sup> Rh, and Ru<sup>19</sup> and other metals will be reported.

### Experimental Section

The ionomer employed in this study is a sulfonated linear polystyrene, PSSA. Materials of this type have been prepared at various degrees of sulfonation and studied by R. D. Lundberg and co-workers at Exxon Research and Engineering Co.<sup>20</sup> That used in this work is designated PSSA (16.7) and was kindly provided by Dr. Lundberg. Its chemical composition is represented as



Here,  $y/(x + y)$  represents the mole fraction of sulfonate groups. The ionomer used had an average sulfonate composition of 16.7 mol



**Figure 1.** Reactor IR cell: A, Pyrex frame; B, film sample holder machined from PTFE stock; C, PTFE-coated magnets; D, KBr windows sealed to the cell dry; E, vacuum line connection; F, auxiliary gas attachment.

% and was chosen because the sulfonate groups aggregate at this composition to form ionic clusters dispersed throughout the nonpolar matrix.<sup>7</sup>

Transparent thin films of PSSA were prepared at ca. 25- $\mu\text{m}$  thickness, which is convenient for study by transmission infrared spectroscopy by dissolving the  $\text{H}^+$  form in tetrahydrofuran (THF) and then allowing the solvent to evaporate at 298 K. Rhodium ions were incorporated by an ion-exchange process in which the PSSA films were stirred in water/ethanol solutions (6:1 volume ratios) of rhodium(III) nitrate ( $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$  Alfa Products). The films, which became bright yellow upon ion exchange, were removed from solution, rinsed with distilled water, and allowed to air-dry prior to loading them in the reactor. Completion of ion exchange was demonstrated by observation of the features in the  $\nu(\text{SO}_3^-)$  and  $\nu(\text{O-H})$  vibrational regions of the infrared spectra.<sup>21</sup> Completely Rh-exchanged and dehydrated samples prepared in this manner were analyzed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY, and shown to contain 4.7 wt% rhodium (calculated 4.9).

The gases used in this work, carbon monoxide (99.99% CO, Matheson Corp.) and hydrogen (99.995%  $\text{H}_2$ , Airco, Inc.), were purified further by passing the gases through a series of liquid-nitrogen traps upon their addition to the reactor.

The primary reactor/infrared cell used is shown in Figure 1. It has a Pyrex body, with KBr windows affixed with a cyanoacrylate glue, and could be connected conveniently to a vacuum line or gas supply line. With this cell, the spectra were taken in situ of films subjected to various treatments. The geometric center of the circular PSSA films (diameter 1.5 cm) coincided with the center of the infrared beam in all experiments. The sample holder, all of whose parts were machined from a PTFE block, contained PTFE-coated magnets in each end so that the sample holder could be aligned in the infrared beam with an external magnet. The cell was heated and the temperature controlled by a Variac-regulated heating tape and monitored with a chromel-alumel thermocouple.

The infrared spectra in the 3800–400- $\text{cm}^{-1}$  region were recorded at 298 K with a Digilab 15B FT-IR spectrometer. Each trace represents the average of at least 100 scans recorded at 2- $\text{cm}^{-1}$  resolution.

Transmission electron microscopy (TEM) was used to investigate PSSA-Rh films after  $\text{H}_2$ -reduction treatment. Samples were prepared for TEM by embedding the films in Spurr's low-viscosity embedding medium (Electron Microscopy Sciences, Fort Washington, PA) and microtoming into sections. The samples, which were supported on Cu grids, were examined on a Philips Model 201 transmission electron microscope. When operated at 100 kV, in the bright-field mode at a calibrated magnification of 200 000 $\times$ , the instrument is capable of resolving features that are ca. 5 Å in diameter.

- (17) Peluso, S.; Risen, W. M., Jr., to be submitted for publication.  
 (18) Noor-Chaudhuri, S.; Mattera, V. D., Jr.; Gonzalez, R. D.; Risen, W. M., Jr., to be submitted for publication.  
 (19) Barnes, D. M.; Mattera, V. D., Jr.; Gonzalez, R. D.; Risen, W. M., Jr., to be submitted for publication.  
 (20) Eisenberg, A., Ed. *Adv. Chem. Ser.* 1980, No. 187, 21.

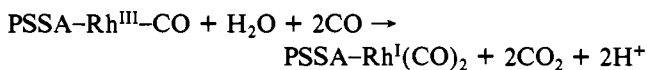
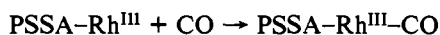
- (21) Mattera, V. D., Jr. Ph.D. Thesis, Brown University, 1984.

The PSSA-Rh films were treated in the cell described above. The reactions carried out are described in the Results section. The films or species are designated in the form PSSA-Rh<sup>A</sup>B, where *A* gives the oxidation state assigned and *B* designates the other chemical constituents.

## Results

The infrared spectra of the PSSA-Rh films were recorded first on the material as it was prepared and then after it had been subjected to various dehydration treatments of heating and evacuating the cell. The spectra of the hydrated PSSA-Rh<sup>III</sup> films contain broad bands at ca. 3300 and 1620 cm<sup>-1</sup> due to the  $\nu(\text{OH})$  and  $\delta(\text{HOH})$  modes of coordinated H<sub>2</sub>O, in addition to those of the ionomer. Complete ion exchange was accomplished, so no bands associated with vibrations of -SO<sub>3</sub>H moieties were found. Since water molecules form strong hydrogen-bonded networks with the sulfonate groups<sup>22</sup> and are expected to be associated with the highly charged Rh(III) centers, complete dehydration requires heating at elevated temperatures (ca. 443 K) under reduced pressure for times that depend on film thickness. Only partial dehydration of PSSA-Rh<sup>III</sup> films is obtained at  $P \approx 10^{-2}$  torr if the temperature is not raised above 398 K, even for a 7-day period, but it is not necessary to heat these materials above ca. 443 K to dehydrate them completely. Upon dehydration, the Rh(III) ions are coordinated by the sulfonate sites, as is evidenced by the 1265-cm<sup>-1</sup> band, which is assigned to the asymmetric stretching mode ( $\nu_a$ ) of the -SO<sub>3</sub><sup>-</sup> group.<sup>22</sup>

In order to investigate the reactions of PSSA-Rh<sup>III</sup> with CO under a variety of conditions and attempt to use several approaches to obtaining reduced Rh species in the PSSA ionomers, CO was added to partially dehydrated films. The addition of CO at 298 K (380 torr) to partially dehydrated PSSA-Rh<sup>III</sup> films gave rise to two weak infrared bands in the  $\nu(\text{CO})$  region. They appear at 2095 and 2023 cm<sup>-1</sup> and indicate the formation of a Rh<sup>I</sup>(CO)<sub>2</sub> species. The formation of this species will be discussed in more detail later. But, it is useful to note here that we postulate<sup>23</sup> that PSSA-Rh<sup>III</sup> is reduced to PSSA-Rh<sup>I</sup> in the presence of CO and H<sub>2</sub>O by the reactions



This postulate is based on an analogy with the reduction of Rh(III) by CO in solution.<sup>24</sup> Analogous reactions have also been postulated to occur on zeolite-supported rhodium under similar conditions.<sup>25</sup>

With further exposure to CO (up to 24 h), these bands increased slightly in intensity and new ones appeared at 2178 and 2148 cm<sup>-1</sup> characterized by relatively weak intensities. As also is discussed below, we assign these bands to  $\sigma$ -bound Rh<sup>III</sup>-CO and CO physically adsorbed on the PSSA-Rh<sup>III</sup> sites, which had not been reduced in the dominant water gas shift type reaction. When the reaction vessel containing CO as well as the sample was heated for 24 h at 368 K, the spectrum of the film was found to be as shown in Figure 2A. The principal features are the 2095- and 2023-cm<sup>-1</sup> band pair. The bands at 1942 and 1875 cm<sup>-1</sup> are due to the PSSA support,<sup>26</sup> and provided the rhodium clusters do not catalyze the

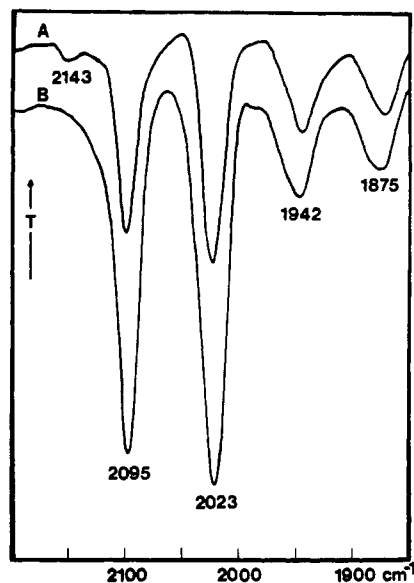


Figure 2. A: IR spectrum of a partially dehydrated PSSA-Rh<sup>III</sup> film that was exposed to CO at 298 K (380 torr) for 24 h followed by heating at 368 K for 24 h. B: IR spectrum of the PSSA-Rh<sup>I</sup>(CO)<sub>2</sub> film heated at 383 K for 48 h followed by evacuation of the CO from the reactor at 298 K for 22 h.

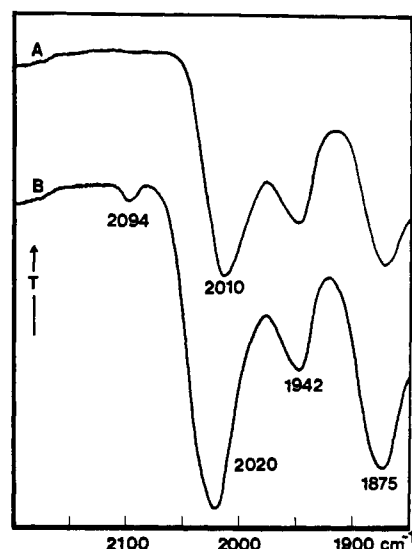


Figure 3. A: IR spectrum of the PSSA-Rh<sup>I</sup>(CO)<sub>2</sub> film that was exposed to H<sub>2</sub> at 408 K (380 torr) for 20 h. B: IR spectrum of the same film heated in H<sub>2</sub> at 418 K for 46 h followed by evacuation of the H<sub>2</sub> from the reactor at 298 K.

hydrogenation of the polymer, which would reduce the fraction of aromatic rings, the 1942-cm<sup>-1</sup> band has a constant absorbance and can serve as an internal standard.<sup>27</sup> The spectrum recorded after further heat treatment followed by evacuation of the free gas ( $\nu(\text{CO}) = 2143$  cm<sup>-1</sup>) from the reactor at 298 K is shown in Figure 2B. The 2095-cm<sup>-1</sup> band appears to be broadened to the high-frequency side and suggests the presence of a band at ca. 2125 cm<sup>-1</sup> assigned to a Rh<sup>III</sup>-CO species. At this stage in the reaction sequence the color of the film has changed from yellow to golden brown.

In an attempt to produce Rh(0) carbonyl species in the PSSA ionomer and characterize their reactivities, PSSA-Rh<sup>I</sup>(CO)<sub>2</sub> films were reacted with hydrogen. The spectrum

(22) Zundel, G. "Hydration and Intermolecular Interaction"; Academic Press: New York, 1969.

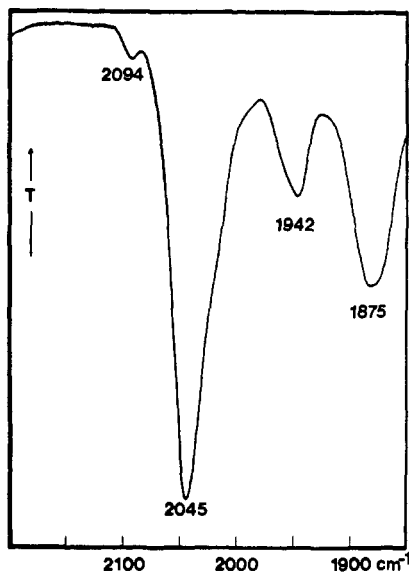
(23) Free CO<sub>2</sub> was observed in the gas cell, as appropriate, before gas evacuation.

(24) James, B. R.; Rempel, G. L. *Chem. Commun.* **1967**, 158.

(25) Primet, M.; Vedrine, J. C.; Naccache, C. *J. Mol. Catal.* **1978**, *4*, 411.

(26) Varsanyi, G. "Vibrational Spectra of Benzene Derivatives"; Academic Press: New York, 1969.

(27) The use of the aromatic band at 1942 cm<sup>-1</sup> as an internal standard was done only after confirming that the bands at 1493, 1450, and 1420 cm<sup>-1</sup> maintained a constant ratio, which would not be true if hydrogenation of these rings had occurred.

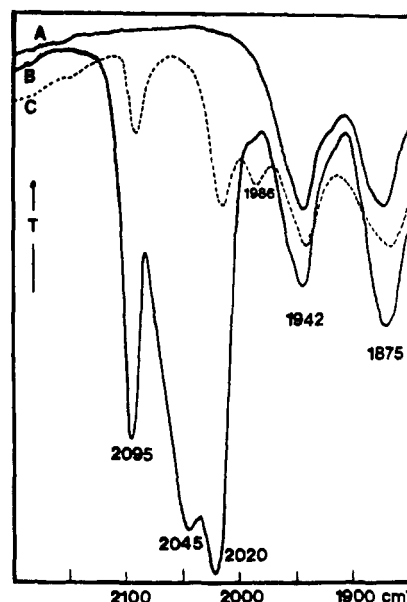


**Figure 4.** IR spectrum of the same film after reexposure to CO at 298 K (380 torr) for 12 h.

of the PSSA-Rh<sup>I</sup>(CO)<sub>2</sub> film after it was treated with H<sub>2</sub> at 408 K (380 torr) for 20 h is shown in Figure 3A. As can be seen by comparison with the spectrum in Figure 2B, the 2064-cm<sup>-1</sup> band was reduced in intensity by this treatment.

The shape of the broad band at 2020 cm<sup>-1</sup> in this spectrum makes it appear to arise from at least two types of Rh-CO species. The H<sub>2</sub> treatment also caused the intensity of the 1878-cm<sup>-1</sup> band, which is due to the formation of bridging carbonyls of zerovalent rhodium, to increase relative to that at 1942 cm<sup>-1</sup>. Thus, a reduction of Rh(I) to Rh(0) is postulated to have occurred. These results are similar to those of Smith et al.,<sup>28</sup> who observed bands at 2020 and 1850 cm<sup>-1</sup> upon addition of H<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub>-supported Rh<sup>I</sup>(CO)<sub>2</sub>, and are supported by the observation<sup>29</sup> that SiO<sub>2</sub>-supported Rh<sup>I</sup>(CO)<sub>2</sub> can be converted readily into Rh<sup>0</sup>-CO sites by the addition of H<sub>2</sub>. This also is supported by the observation of a shift in  $\nu_a(-SO_3^-)$  from 1265 to ca. 1220 cm<sup>-1</sup>, which is consistent with the re-formation of -SO<sub>3</sub><sup>-</sup>H<sup>+</sup> sites,<sup>21</sup> an important event in the sequence leading to super acid behavior in the presence of Rh(0) particles.

Further heating at 418 K with H<sub>2</sub> followed by evacuation of the cell at room temperature results in the disappearance of the pair of bands at 2094 and 2023 cm<sup>-1</sup> and leads to the decrease in frequency of the 2020-cm<sup>-1</sup> band to 2010 cm<sup>-1</sup> shown in Figure 3B. In the same spectrum it can be seen that all of the rhodium carbonyl bands have decreased in relative intensity. Reexposure of partially reduced films to CO at 298 K (380 torr) for 12 h results in a new feature at 2045 cm<sup>-1</sup> assigned to a linear CO species bound to rhodium particles probably of different size of structure than those which give rise to the 2020-cm<sup>-1</sup> band. The infrared spectrum shown in Figure 4 is of the film after it was heated to 408 K for 24 h and then evacuated at 298 K. Notice that the 2094-cm<sup>-1</sup> band and its counterpart at 2023 cm<sup>-1</sup>, which is superimposed on the low-frequency side of the principal band at 2045 cm<sup>-1</sup>, have reappeared. A feature at 1875 cm<sup>-1</sup> also reappears. The infrared spectrum of the film is nearly identical with that reported by Gates et al.<sup>30</sup> for a freshly prepared Rh<sub>6</sub>(CO)<sub>16</sub> phosphine-functionalized polystyrene membrane, which re-



**Figure 5.** A: IR spectrum of a freshly prepared PSSA-Rh<sup>III</sup> film that was first dehydrated at 438 K ( $1 \times 10^{-2}$  torr) for 24 h followed by exposure to H<sub>2</sub> at 438 K (380 torr) for 24 h. B: IR spectrum of the same film that was exposed to CO at 398 K (380 torr) for 48 h. C: IR spectrum of the film after simultaneous evaluation at  $1 \times 10^{-2}$  torr of CO and heating at 373 K for 6 h.

portedly contained rhodium particles approximately 40 Å in diameter.

In order to investigate the nature of CO chemisorption on Rh surfaces in or on PSSA, which qualitatively may be quite similar to those of heterogeneous catalysts, PSSA-Rh<sup>III</sup> films were dehydrated at 438 K (ca.  $1 \times 10^{-2}$  torr) for 24 h and then treated with H<sub>2</sub> at 438 K (380 torr) for 24 h. The infrared spectrum shown in Figure 5A shows no indication of the formation of rhodium hydrides in the 2000-cm<sup>-1</sup> region. The only apparent change in the infrared spectrum is a shift in the  $\nu_a(SO_3^-)$  band from 1265 to ca. 1220 cm<sup>-1</sup>. These observations parallel those discussed earlier and suggest that the reduction of PSSA-Rh<sup>III</sup> occurs with the concomitant formation of Rh(I) and Rh(0) sites and leaves many of the SO<sub>3</sub><sup>-</sup> sites in the -SO<sub>3</sub>H form. The films have acquired a black color at this stage, and electron micrographs of them reveal the presence of rhodium particles. An electron micrograph of a typical film at this stage shows a rather uniform distribution of rhodium particles none of diameter greater than 10–20 Å. Care was exercised in the interpretation of images from particles smaller than 20 Å in diameter due mostly to phase-contrast effects.<sup>31,32</sup> To confirm spectroscopically that some of the Rh(III) had indeed reached the Rh(0) states, such films were reacted immediately with CO.

Following reactions of these films with H<sub>2</sub>, as described above, they were exposed to CO at 398 K (380 torr) for 45 h. The chemisorption of CO gave rise to the infrared spectrum shown in Figure 5B. The formation of *cis*-rhodium(I) dicarbonyl (2095 and 2023 cm<sup>-1</sup>), rhodium(0) carbonyl (2045 cm<sup>-1</sup>), and the carbonyl-bridged Rh(0) species (1875 cm<sup>-1</sup>) is observed. The absence of  $\nu(CO)$  bands above 2100 cm<sup>-1</sup> supports the deduction that there are no Rh(III) sites present after reduction. Mild thermal desorption was then carried out by evacuating the reactor at 373 K (ca.  $1 \times 10^{-2}$  torr). As shown in Figure 5C, the 2045- and 1875-cm<sup>-1</sup> bands disappear under this treatment while a new band at 1986 cm<sup>-1</sup> appears. By comparison of this result with those of other studies,<sup>15</sup> the

(28) Smith, A. K.; Hugues, F.; Theolier, A.; Basset, J. M.; Ugo, R.; Zanderighi, G. M.; Bilhou, J. L.; Bilhou-Bougnol, V.; Graydon, W. F. *Inorg. Chem.* **1979**, *18*, 3104.

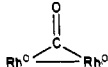
(29) Gonzalez, R. D., personal communication.

(30) Jarrell, M. S.; Gates, B. C.; Nicholson, E. D. *J. Am. Chem. Soc.* **1978**, *100*, 5727.

(31) Flynn, P. C.; Wanke, S. E.; Turner, P. S. *J. Catal.* **1974**, *33*, 233.

(32) Treacy, M. M. J.; Howie, A. J. *J. Catal.* **1980**, *63*, 265.

Table I. Summary of CO Species Observed on PSSA-Supported Rh<sup>a</sup>

$\nu, \text{cm}^{-1}$	assgnt	$\nu, \text{cm}^{-1}$	assgnt
2178	Rh <sup>III</sup> -CO	2045	Rh <sup>0</sup> <sub>x</sub> -CO
2148	Rh <sup>III</sup> -CO	2020	Rh <sup>0</sup> <sub>y</sub> -CO
2125	Rh <sup>III</sup> -CO	1986	Rh <sup>0</sup> <sub>z</sub> -CO
2095	} Rh <sup>I</sup> (CO) <sub>2</sub>	1870	
2023			

<sup>a</sup> x, y, and z indicate Rh particles of different size distributions and/or structures.

band at 1986 cm<sup>-1</sup> is assigned to a Rh<sup>0</sup>-CO species in which the CO is linearly bound to larger rhodium particles. Clearly, the bands of the Rh<sup>I</sup>(CO)<sub>2</sub> species have been diminished in intensity. The 2023-cm<sup>-1</sup> component of this vibration apparently is shifted to 2016 cm<sup>-1</sup>, but that is due to overlap with the 1986-cm<sup>-1</sup> band.

The infrared absorption bands of the PSSA support show that no significant changes in it occur during the reactions. For example, there is no sign of interaction of the PSSA arene rings with rhodium. Thus, the use of the intensity of the 1942-cm<sup>-1</sup> band as an internal standard for the qualitative comparison of relative Rh-CO band intensities is justified. Furthermore, during the reactions, although its domain-forming ability and the properties of the sulfonate groups are important for ligation, protonation, hydration, and charge balance. This is in contrast to the phosphine-functionalized polystyrene-supported rhodium catalysts<sup>30</sup> in which the oxidation of the phosphine ligands occurs in the presence of the rhodium particles.

The results indicate that films of PSSA-supported rhodium undergo CO chemisorption under mild reaction conditions. The spectral criteria for carbonyl absorptions as a function of the readily accessible oxidation states of rhodium have been established. The types of PSSA rhodium carbonyls observed here and their frequencies are listed in Table I.

### Discussion

Numerous examples of reactions involving supported Rh, particularly heterogeneous catalysis over supported rhodium surfaces, have been reported. Typically, the catalysts were prepared on oxide supports (e.g., SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) by one of two different techniques. In one method, the support is impregnated with an aqueous solution of a rhodium salt, and the material is dehydrated and then reduced at high temperature. This produces a dispersed Rh catalyst with a distribution of metal particle sizes.

Novel rhodium-containing heterogeneous catalysts have also been prepared by the chemical modification of the ionic sites present in zeolites<sup>25,33,34</sup> and in work related to this study, in PFSA ionomer systems.<sup>19</sup> In contrast to the surface-modified oxides, these catalysts are prepared by ion exchanging a rhodium cationic species derived from a salt such as RhCl<sub>3</sub> or [Rh(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub>, dehydrating (or deamminating), and then reducing them in H<sub>2</sub>. Other studies<sup>28,30,35-38</sup> have focused

on the immobilization of homogeneous catalysts such as Rh<sub>6</sub>(CO)<sub>16</sub> onto insoluble supports, including phosphine-functionalized polystyrene in which the support plays the role of a ligand. With this method, metal cluster interactions can be reduced, thereby maintaining the metal in a state of atomic dispersion.

We have shown that ionomers represent a new class of potential catalytic supports into which transition-metal ions can be incorporated by a simple ion-exchange process. In addition, ionomers offer the possibility of forming atomically dispersed transition-metal particles at which new chemistry may be realized under mild reaction conditions. The results of the present study demonstrate that the ionic domains present in PSSA are accessible by cationic ion exchange and that this process leads to regions dispersed throughout the materials that contain active sites that can be made quite reactive to small gaseous molecules. Thus, when this material, PSSA-Rh<sup>III</sup>, is reduced by H<sub>2</sub>, Rh particles of 10 Å or smaller diameter are produced throughout the films. These react with CO to form rhodium carbonyls whose infrared spectra are similar to those observed on other supports. Furthermore, when incompletely dehydrated PSSA-Rh<sup>III</sup> films are exposed to CO, Rh<sup>III</sup>-CO and Rh<sup>I</sup>(CO)<sub>2</sub> species are formed through a sequence of reactions including the reduction of Rh(III) to Rh(I), by the water gas shift reaction and reaction of CO with the Rh species present.

The direct reduction of PSSA-Rh<sup>I</sup>(CO)<sub>2</sub> films with H<sub>2</sub> leads to the formation of Rh<sup>0</sup>-CO species and an overall decrease in the amount of Rh<sup>I</sup>(CO)<sub>2</sub>. The observation of an infrared band at 2020 cm<sup>-1</sup>, which is assigned to a linear Rh<sup>0</sup>-CO species, and of a band in the bridging CO region at 1870 cm<sup>-1</sup> is consistent with the initial formation of small rhodium particles. This is not unexpected since rhodium atoms, in contrast to the Rh(I) species, are not restricted by chemical bonding to a particular sulfonate site and aggregation is favored. Furthermore, since these reactions were carried out at temperatures above the PSSA glass transition temperature,<sup>21</sup> the potential for Rh particle growth is favored.

The infrared spectra of PSSA-supported rhodium suggest that the reaction products are similar to those formed on other supported rhodium systems. These results suggest that ionomer-supported transition metals may have potential materials applications as catalysts or may be useful catalytic models. Catalytic studies involving PSSA- and PFSA-supported rhodium are in progress.

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- (33) Primet, M. J. *Chem. Soc., Faraday Trans. I* **1978**, *74*, 2570.  
 (34) Gelin, P.; Ben Taarit, Y.; Naccache, C. *J. Catal.* **1979**, *59*, 357.  
 (35) Smith, G. C.; Chojnacki, T. P.; Dasgupta, S. R.; Iwatate, K.; Watters, K. L. *Inorg. Chem.* **1975**, *14*, 1419.  
 (36) Bilhou, J. L.; Bilhou-Bougnol, V.; Graydon, W. F.; Basset, J. M.; Smith, A. K.; Zanderighi, G. M.; Ugo, R. *J. Organomet. Chem.* **1978**, *153*, 73.

- (37) Watters, K. L.; Howe, R. F.; Chojnacki, T. P.; Fu, C. M.; Schneider, R. L.; Wong, N. B. *J. Catal.* **1980**, *66*, 424.  
 (38) Theier, A.; Smith, A. K.; Leconte, M.; Basset, J. M.; Zanderighi, G.; Psaro, R.; Ugo, R. *J. Organomet. Chem.* **1980**, *191*, 415.